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UTILIZATION OF HYDROGEN FOR SUSTAINABLE ENERGY AND FUELS

Edited by Marcel Van de Voorde

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Marcel Van de Voorde (Ed.)

Utilization of Hydrogen for Sustainable Energy and Fuels

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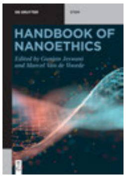

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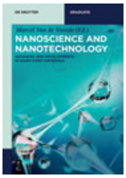

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Utilization of Hydrogen for Sustainable Energy and Fuels

Volume III

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Volume Editor
Professor Dr. Dr. h. c. mult. Marcel Van de Voorde
University of technology DELFT (NL)
Rue du Rhodania, 5,
BRISTOL – A, App. 31
3963 CRANS – MONTANA
Switzerland

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Hydrogen will play a decisive role in future attempts to solve the challenges in connection with global warming.
This requires enormous technological and political attempts.

Professor Gerhard ERTL,
Nobel Prize in Chemistry 2007

Hydrogen is often called the missing link of the energy transmission but equally important it is also a unique opportunity to create the necessary prosperity in our society!

Bart BIEBUYCK Executive Director
EU Research Programme FCHJU
(Fuel Cell and Hydrogen Joint Undertaking)

Series editor preface

The decarbonization of the energy system is critical to reach the European climate objectives for both 2030 and 2050. In this respect, the "European Green Deal" put forward the need to ensure a smart integration of renewable energy sources, energy efficiency, and other sustainable solutions such as carbon capture. The "European Green Deal" also recognized the production of hydrogen, hydrogen storage, hydrogen networks, and the utilization of hydrogen as one of the important technology options that can ensure that the EU industry remains at the technology forefront and delivers breakthrough technologies in key industrial sectors.

The book provides compiling reviews on these aspects from internationally recognized researchers, industrialists, and government agencies, and assembles top-class contributions. The topical scope of the book is broad, ranging from hydrogen production, storage of hydrogen, and the multiple applications but also the development of many new materials and new technologies and innovations will be necessarily developed in many fields of physics, chemistry, biology, and mechanical engineering. Common to all the books in the series is that they represent top-notch research and are highly application-oriented, innovative, and relevant for industry.

The titles of the volumes in the series *Hydrogen Technologies for Sustainable Economy* are:

- *Hydrogen Production and Energy Transition*
- *Hydrogen Storage for Sustainability*
- *Utilization of Hydrogen for Sustainable Energy and Fuels*

They fall in the topics of energy, environment, and new materials but mobile applications such as automobiles, air, and space transport are becoming very popular.

The book series appeals to a wide range of readers with backgrounds in physics, chemistry, biology, and engineering but also for those interested in renewables energy, environment, economy, and industrial safety. Students at universities to scientists at institutes and technologists in industrial companies may also have a great interest in this new hydrogen energy source.

Ever since hydrogen was introduced many years ago it will greatly change our lives for the next generations. Developments are planned for many areas, which will result in a new "hydrogen economy"; in short, hydrogen technology is a hot topic!

Marcel Van de Voorde,
November 2020

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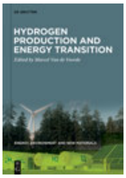
Hydrogen Technology – Innovations and Applications



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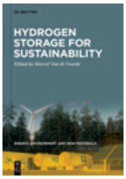

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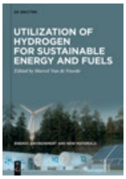

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About the series editor

Marcel Van de Voorde: Prof. Dr. Ing. ir. Dr. h. c., has many years' experience in European Research Organizations, including CERN- Geneva and the European Commission research. He was involved in research, research strategies and management. He is emer. professor at the University of Technology, Delft (NL), holds multiple visiting professorships and is doctor honoris causa. He has been a member of numerous Research Councils and Governing Boards: e.a. CSIC (F), CNR (I), CSIC (E), NIMS (JP), of science and art academies, of the Science Council of the French Senate and the National Assembly, in Paris, and Fellow of multiple scientific societies. He has been honored by the Belgian King and received an award for European merits in Luxemburg by the former President of the European Commission. He is author of multiple scientific and technical publications and books.

Thanks to my wife for the patience with me spending
many hours working on the book series through
the nights and over weekend.
The assistance of my son Marc-Philip related to the complex
and large computer files with many sophisticated scientific
figures is also greatly appreciated.

Marcel Van de Voorde

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List of contributors

Marcel Van de Voorde
University of technology DELFT (NL)
Rue du Rhodania, 5,
BRISTOL – A, App. 31
3963 CRANS – MONTANA
Switzerland
marcel@vdvoorde.eu

Paolo Ciambelli
University of Salerno
and
Narrando srl
Via Giovanni Paolo II, 132
84084 Fisciano
Italy
pciambelli@unisa.it

Louis Schlapbach
ETH & Empa, Zurich, Switzerland
louis.schlapbach@me.com

Alexander Wokaun
ETH Zurich
Switzerland
alexander.wokaun@chem.ethz.ch

Pierre Etienne Franc
Hydrogen Energy World Business Line,
Air Liquide
Hydrogen Council Secretary
Air Liquide, France, 75 quai d'Orsay Paris
France
Pierre-Etienne.Franc@airliquide.fr

Ad van Wijk
Department Process and Energy
Faculty of Mechanical, Maritime
and Materials Engineering.
TU Delft
Leeghwaterstraat 39
2628 CB Delft
The Netherlands
a.j.m.vanwijk@tudelft.nl

Andreas Züttel
Laboratory of Materials for Renewable Energy
(LMER)
Institute of Chemical Sciences
and Engineering (ISIC)
Basic Science Faculty (SB)
École polytechnique fédérale de Lausanne
(EPFL) Valais/Wallis
Energypolis
Rue de l'Industrie 17, CP 440
CH-1951 Sion
Switzerland
and
Empa Materials Science and Technology,
Dübendorf
Switzerland
andreas.zuettel@epfl.ch

Paula Abreu Marques
European Commission
Directorate General for Energy
DM24 4/138
B-1049 Brussels
Belgium
Paula.Abreu-Marques@ec.europa.eu

Ruud Kempener
Directorate General for Energy
European Commission
DM24 4/138
B-1049 Brussels
Belgium

Vaclav Bartuska
Ambassador-at-Large for Energy
Security
Ministry of Foreign Affairs
Loretanské nam. 5
118 00 Praha 1
Czech Republic
vaclav_bartuska@mzv.cz

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Tobias Christoph Brunner
Hynergy GmbH
Hauptstr. 8b
85630 Grasbrunn
Germany
brunner@hynergy.de

Gabriele Centi
University Messina
V.le F. Stagno D'Alcontres 31
98166 Messina
Italy
and
ERIC aisbl
Belgium
centi@unime.it

Siglinda Perathoner
University Messina
V.le F. Stagno D'Alcontres 31
98166 Messina
Italy
and
ERIC aisbl
Belgium

Paul E. Dodds
Institute for Sustainable Resources
University College London
Central House
14 Upper Woburn Place
London WC1H 0NN
UK
p.dodds@ucl.ac.uk

Daniel Scamman
Institute for Sustainable Resources
University College London
London, UK

Paul Ekins
Institute for Sustainable Resources
University College London
London, UK

Luigi Crema
Center on Sustainable Energy
Fondazione Bruno Kessler
Via Sommarive 18
I-38123 Trento
Italy
crema@fbk.eu

Matteo Testi
Center on Sustainable Energy
Fondazione Bruno Kessler
Via Sommarive 18
I-38123 Trento
Italy
testi@fbk.eu

Martina Trini
Center on Sustainable Energy
Fondazione Bruno Kessler
Via Sommarive 18
I-38123 Trento
Italy
mtrini@fbk.eu

Henning Zoz
Zoz GmbH
+49 (0) 2762 9756-0
Maltoz Straße
57482
Wenden
Germany
zoz@zoz.de

Tejas Bopardikar
Zoz GmbH
+49 (0) 2762 9756-0
Maltoz Straße
57482
Wenden
Germany
bopardikar@zoz.de

Luca Sementa
CNR-IPCF
Consiglio Nazionale delle Ricerche
via Giuseppe Moruzzi 1
I-56124 Pisa
Italy
luca.sementa@cnr.it

Fabio R. Negreiros
INFIQC, CONICET
Universidad Nacional de Córdoba
X5000HUA, Córdoba
Argentina
fabio.ribeiro@unc.edu.ar

Alessandro Fortunelli
CNR-ICCOM
Consiglio Nazionale delle Ricerche
via Giuseppe Moruzzi 1
I-56124 Pisa
Italy
alessandro.fortunelli@cnr.it

Michel Noussan
Future Energy Program
Fondazione Eni Enrico Mattei
Corso Magenta 63
20123 Milan
Italy
michel.noussan@feem.it

Massimo Prastaro
Eni s.p.a.
Retail Innovation and Alternative Fuels
Viale Giorgio Ribotta, 51
00144 Rome
Italy
Massimo.Prastaro@eni.com

Urs Cabalzar
Automotive Powertrain Technologies
Laboratory
Empa – Swiss Federal Laboratories for
Materials Science and Technology
Ueberlandstrasse 129
8600 Duebendorf
Switzerland
urs.cabalzar@h2energy.ch

Christian Bach
Automotive Powertrain Technologies
Laboratory
Empa – Swiss Federal Laboratories for
Materials Science and Technology
Ueberlandstrasse 129
8600 Duebendorf
Switzerland
Christian.Bach@empa.ch

Patrick Stadelmann
Automotive Powertrain Technologies
Laboratory
Empa – Swiss Federal Laboratories for
Materials Science and Technology
Ueberlandstrasse 129
8600 Duebendorf
Switzerland
patrick.stadelmann@h2energy.ch

Stefan Hiltbrand
Automotive Powertrain Technologies
Laboratory
Empa – Swiss Federal Laboratories for
Materials Science and Technology
Ueberlandstrasse 129
8600 Duebendorf
Switzerland
stefan.hi@sunrise.ch

Thomas von Unwerth
Institute for automotive Research
Faculty for Mechanical Engineering
Technical University Chemnitz
Reichenhainer Str. 70
09126 Chemnitz
Germany
thomas.von-unwerth@mb.tu-chemnitz.de

Jens Mitzel
German Aerospace Center (DLR)
Pfaffenwaldring 38-40
D-70569 Stuttgart
Germany
Jens.Mitzel@dlr.de

Andreas Friedrich
German Aerospace Center (DLR)
Pfaffenwaldring 38-40
D-70569 Stuttgart
Germany
and
Institute of Building Energetics, Thermal Engineering and Energy Storage (IGTE)
University of Stuttgart
Pfaffenwaldring 31
70569 Stuttgart
Germany
Andreas.Friedrich@dlr.de

Christophe Coutanceau
IC2MP, UMR CNRS-Université de Poitiers 7285
4 rue Michel Brunet 86073
Poitiers Cedex 9
France
christophe.coutanceau@univ-poitiers.fr

Marian Chatenet
LEPMI-Phelma Campus
UMR CNRS-Université de Savoie
UMR CNRS-Grenoble-INP-Université de Grenoble Alpes 5279
1130 rue de la piscine
38402 St Martin d'Hères Cedex
France

Deborah Jones
ICGM, UMR CNRS-Université de Montpellier
CC1502
Rue Eugène Bataillon
34095 Montpellier Cedex 5
France

Gael Maranzana
LEMTA, UMR CNRS Université de Lorraine 7563
2 avenue de la Forêt de Haye
BP 90161, 54505 Vandoeuvre-lès-Nancy Cedex
France

Ciro Caliendo
Department of Civil Engineering
University of Salerno
Via Giovanni Paolo II, 132
84084 Fisciano
Italy
ccaliendo@unisa.it

Paola Russo
Department of Chemical Engineering
Materials and Environment
Sapienza University of Rome
Via Eudossiana 18, 00184 Rome
Italy
paola.russo@uniroma1.it

Giuseppe Ricci
Chief Operating Officer Energy Evolution
at Eni S.p.A.
Rome, Italy
Giuseppe.Ricci@eni.com

Katsuhiko Hirose
HyWealth Co.
k.hirose@hywealth.co

Laura Prosperi
Energy Evolution – Green & Traditional Refinery
at Eni S.p.A.
Laura.Prosperi@eni.com

Maurizio Dessi
Energy Evolution – Power Generation & Marketing
at Eni S.p.A.
Maurizio.Dessi@eni.com

Marco Tripodi
Energy Evolution – Power Generation & Marketing
at Eni S.p.A

Laurent Allidières
Hydrogen Technologies Director – Air Liquide International Fellow
Air Liquide Hydrogen Energy World Business Line
2 rue de Clémencière
BP 15 – 38360 Sassenage
France
laurent.allidieres@airliquide.com

Marco Chiesa
Snam S.p.A.
Piazza Santa Barbara, 7
20097 San Donato Milanese MI
Italy
marco.chiesa@snam.it

Alessio Zolla
Snam S.p.A.
Piazza Santa Barbara, 7
20097 San Donato Milanese MI
Italy
alessio.zolla@snam.it

Paolo Ciambelli, Marcel Van de Voorde

Hydrogen: Presents Accomplishments and Far-Reaching Promises

Despite the realistic analysis of the waving trend of the enthusiasm for hydrogen in the last 50 years, starting from the oil crisis in the 1970s to announce the future of a hydrogen economy, today the driving force of the global warming issue and a favorable convergence of interests by different stakeholders support the role of hydrogen as zero-carbon fuel much strongly than before. After the Paris Agreement on climate in 2015, many countries produced national road maps and collaboration projects involving hydrogen in order to reduce greenhouse gas emissions and achieve deep decarbonization. Pioneering countries in investing huge financial resources are Japan and Germany. To reach this goal, it is expected that hydrogen could be produced from renewable sources, consumed with no pollution, and universally used, for example, in transportation, energy storage, residential and industrial applications, and high-grade heat production. In the last 2 years, IEA [1] and WEC [2] reports confirmed the "unprecedented momentum for hydrogen," the European Union (EU) has increased the financial support to research and innovation on hydrogen, and new investment plans are frequently announced, often at a gigawatt scale. At January 2021 Linde Company announced it will build, own and operate the world's largest (24 MW) Proton Exchange Membrane electrolyzer plant in Germany

The most concrete proof of this renewed interest is the publication by the EU Commission of two just published documents, inside the EU's Green Deal and its Covid recovery plan, which assign to hydrogen a fundamental role to contribute to reach a climate-neutral and zero-pollution economy in 2050 [3, 4]. Even more surprising was the China's President Xi Jinping announcement (September 2020) of pledge to achieve carbon neutrality before 2060, taking into account that China is the largest carbon emitter (28.6% share of global carbon emissions in 2018) and energy consumer.

The target of European Green Deal (55% reduction in emissions by 2030 with reference to 1990 and carbon neutral by 2050) is mostly based at medium term on electrolyzers (40 GW at 2030).

It is not an easy challenge, if one takes into account at least two main aspects: first, hydrogen today accounts for only a small fraction of the energy mix, while its contribution is expected to reach at least 15% in 30 years; second, more than 95% of 70 million tons of hydrogen yearly consumed for industrial purposes (mostly ammonia, methanol, and oil refining) is today still produced from fossil fuels (*grey* hydrogen from natural gas in Europe), giving a huge contribution to annual carbon dioxide release, close to 100 million tons. Therefore, the decarbonization goal requires a full change to *cleaner* hydrogen, especially *green* H_2 (water, wind, and sun related). There is a need to decrease the cost of renewable hydrogen, although there is a continuous

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improvement in this direction. Even more critical is the availability of all renewable energies necessary to produce all H_2. Therefore, storage, especially on a medium-to-long term is a critical issue to be considered. The only solution is to produce H_2 in remote areas where this can be cost-competitive, but here the problem is the transport from these regions. In terms of use, in the first phase, as indicated in the cited H_2 strategy, this can be just the substitution of *grey* H_2 with cleaner sources, but in the longer term (beyond about 2025) the issue is the development of new uses of H_2, from mobility to industrial uses, in competition with the direct use of renewable electrical energy. There is thus the need of a full change in the energy system in relatively short term, requiring an impressive effort for this system transformation, which can be realized only in a concerted effort which catalyzes the transformation.

With respect to the first aspect, the time to achieve the full change to *green* hydrogen, a realistic and objective analysis shows that in the short-to-medium term it will be necessary to resort to other forms of low-carbon hydrogen (*blue* hydrogen), to reduce emissions from actual hydrogen production, and to support the parallel and future growth of renewable hydrogen. Along this intermediate step, up to 90% of CO_2 emissions can be captured during the production of *grey* hydrogen and stored in adequate places, for example, empty gas fields. However, the cost of going over 90% increases significantly, while it is possible that at 2030 the cost of hydrogen from electrolyzers could be competitive with that from methane. Therefore, the necessity of this step caused, as expected, criticism by influential international associations, such as WWF, European Environmental Bureau, Friends of the Earth Europe, and also from part of the scientific community, fearing that maintaining the *blue* option at least until 2030 could compromise the EU action on climate. There are alternatives, however, which can be considered, even maintaining the use of fossil fuels as a primary source. In fact, a better and more economical alternative to achieve the same goal of decreasing H_2 production carbon footprint instead of producing CO_2 and then sequestrating and storing it (carbon capture and storage (CCS)) is to intrinsically decrease its production. By using electrically heated reactors for steam reforming of methane, it is possible to achieve a reduction in CO_2 emissions above 50–60%. Producing H_2 from cracking of biomethane is another better possibility with respect to the use of CCS.

Really, even if the priority of the EU is to develop *green* hydrogen, that is, hydrogen produced through the electrolysis of water powered by electricity stemming from renewable sources (wind and sun), it appears that it will be necessary to profit from intermediate opportunities for producing at least *blue* hydrogen, taking into account that they could be available in shorter time, contributing to progressively move toward the full change to the really *green* hydrogen. The European Clean Hydrogen Alliance, bringing together industry, national and local public authorities, civil society, and other stakeholders, aims at bringing together renewable and low-carbon hydrogen production by 2030.

It is obvious that to reach the final objective of decarbonization, a joint effort by the different stakeholders involved with different roles (industry, electricity, mobility, infrastructure building, government, research, and education) must be planned. This requires well-coordinated policies at national and European levels.

The publication of the EU Commission indicates three time steps and relevant actions, starting from now, to achieve the goal through an investment agenda for the EU:

- Boosting demand for and scaling up production
- Designing an enabling and supportive framework: support schemes, market rules, and infrastructure
- Promoting research and innovation in hydrogen technologies.

With respect to the financial aspect, the reference to the next-generation EU plan will strongly support these actions. A regulatory framework for the hydrogen market will be assessed.

Because of the complexity of the technology and the wish to achieve a breakthrough in the field, there is a great interest for a deep international collaboration between the United States, China, Canada, and EU countries, and some international organization between universities, research institutes, and industries. In addition, the EU, the International Energy Agency, and the countries themselves give hydrogen energy a top priority in their energy research and development plans.

Therefore, with respect to the invitation of the Commission to all stakeholders from their specific point of view as to how to help support the fundamental role of hydrogen in a decarbonized economy, we offer this series of books as a small contribution.

The series consists in three books treating, respectively, the three major areas of (i) processing technologies, (ii) storage technologies, and (iii) application technologies. The essential role of hydrogen for a sustainable development through decarbonization as fuel is analyzed and discussed in industry, in mobility (from cars to trains, to ships, to airplanes), for heating and cooling buildings, and in electricity demand and supply. Starting from the current, fossil-dependent, production processes, intermediate steps such as biomass and waste sources are presented, to arrive to updated progress in renewable hydrogen mostly based on water splitting and renewable energy. The second book deals with hydrogen storage. Together with an overview on technologies, most of the chapters are devoted to innovative materials for batteries and fuel cells, and others to stationary storage. The third book treats the whole range of applications in industry (power to gas to fuel, carbon dioxide conversion) and mobility (vehicles and refueling stations). One chapter is dedicated to a very critical issue: hydrogen safety and risk assessment, including the case of mobility.

A review is available with respect to new materials, components, designs for the installations and facilities for the future, as well as for the production, storage, and multiple applications. Without materials research, design, and development it would be impossible to think on the new hydrogen technology applications. However, it is necessary to really integrate all R&D developments in a single vision to achieve fast the transition. This book series contributes to give this unitary vision.

The pillars of the three books are “Role of Hydrogen Energy and Hydrogen Economy” reflected in the characteristics of the advanced technologies as well as their sustainability, that is, their implications on economy, society, including safety and public acceptability, and environment-friendly technologies. In addition, hydrogen technologies offer ways of handling some critical problems that current societies face, ways that could be preferable to other ways of coping with the problems.

We invited several authors from academy, research centers, companies, and authorities to write a chapter keeping in mind mostly two keywords: research and technology. Therefore, you will find different contents, from basic research to innovation, to realizations, to scenarios, to safety and regulation aspects.

All three books have an Introduction and are closed by Conclusions and recommendations. Their content typically includes chapters on the “State of Existing Technologies” and chapters on research and innovation in relevant fields from a theoretical, applied, innovative, and industrial point of view. Moreover, the current state of standardization and safety in the field of systems and devices for production, storage, transport, measurement, and use of hydrogen is analyzed in some chapters. The treatment of this aspect, a critical one for commercialization of hydrogen, is also required as an effect of cooperation of countries and continents on the roll out of hydrogen infrastructures, such as refueling stations or distribution networks.

Processing technologies

In this book, most of the potential *hydrogen processing technologies* have been described in detail: the improvements of actually operating systems toward completely new and flexible techniques. Therefore, from various chapters the itinerary from grey to blue to green hydrogen is covered. Attention has been given to the theoretical aspects, thermodynamics, process calculations, and modeling approaches and reports of multiple successful new pilot systems.

Storage technologies

This book focuses on new developments of *hydrogen storage technologies* with great attention to new advanced materials. Tools for the development of new materials focus on synthesis, kinetics, and thermodynamics and application of nanoscale hydrogen storage materials with status on existing technologies and perspectives. An impressive range of nanomaterials has been investigated: solid-state, metal, intermetallic, chemical, advanced carbon, and complex hydrides. Nanomaterials for hydrogen storage achieve an optimum compromise between having the hydrogen too weakly bonded to the storage material, resulting in a low storage capacity, and too strongly bonded to the storage material, requiring high temperatures to release hydrogen. For the storage of electric energy, nanostructured materials for positive and negative electrodes are used for advanced next-generation batteries.

Application technologies

This book presents the current state of hydrogen economy with the focus on applications in the automotive technology and industry, aiming to reply to some key questions: Where are we in the implementation of hydrogen economy? What are the perspectives? Which are the directions to develop this field? This book provides compiling reviews on these aspects from internationally recognized researchers, industrialists, and government agencies.

The mobile applications such as automobiles, air, and space transport are becoming very popular with a wide number of different types of fuel and electrolysis cells well described in the book.

Large attention is being given to materials science and technologies with focus on the development of new materials for specific applications, as well as structured and functional materials, including research and innovations on electrolytes. Functional materials are key for advances in energy research in preparation of energy carriers from renewables, energy storage, and efficient energy conversion. Nanostructured materials offer high potentials, provided that they are tailored to exactly the right size of the nanometer scale. Catalysts for efficient energy conversion are a crucial enabling factor, but there is a need to avoid the use of critical raw materials such as noble metal catalysts in fuel cells.

Hydrogen is a chemical widely used in various applications including ammonia and methanol production, oil refining, and energy. Hydrogen is widely regarded as an ideal energy storage medium, due to the ease with which electric power can convert water into its hydrogen and oxygen components through electrolysis and can be converted back to electrical power using a fuel cell. Power to gas is the conversion of electricity to a gaseous fuel such as hydrogen to be injected in methane distribution network. Via underground storage, hydrogen is stored in caverns, salt domes, and depleted oil and gas fields.

Challenges and requirements for car industry are discussed presenting a status on existing technologies, particularly hybrid systems. Specific attention is devoted to mobility application discussing efficiency, technological development, and demonstration projects for fuel cell vehicles such as cars, heavy-duty vehicles, trains, and ships. Strictly related to mobility is the relation between vehicles and refuel stations, discussed in some chapters. One more critical aspect connected to automotive mobility is the safety analysis, risk assessment for both infrastructures and transport of persons or dangerous goods.

The state of the art and development of portable applications is also presented. Some chapters gave an overview of the research and development of new components for hydrogen designs, and of newly developed monitoring and control equipment to assure reliable and efficient operation.

Because of the great interest in “Hydrogen Technology” worldwide, the authors participating are university professors, research managers, industrialists, and government agencies from industrialized countries: China, Japan, the United States, Australia, Africa, South America, and many European countries. Focus is given to modernization of existing technologies to completely new developments.

Developments are planned in many areas, which will result in a new “Hydrogen Economy” in the next decades given from the progresses in “Hydrogen Technology.” Breakthroughs are expected, and efforts are planned so that the new “Hydrogen Technology,” which has been impossible in the past, will finally become a reality.

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Forewords

Louis Schlapbach

Foreword

Overcoming the initiated climate crisis is the greatest challenge of humanity. Human activities like power generation and mobility, industrial processing, and building, and maintenance of infrastructure need to become carbon neutral, that is, to transform into a sustainable energy economy with a closed carbon cycle. Our attitude in handling of energy and materials must change from "just consume" to using renewable sources in a circular economy. Hydrogen is a key component in the sustainable handling of energy, materials and chemicals, and processing.

Is the production of the three new volumes *Hydrogen Production and Energy Transition*:

i) Synthesis and Processing
ii) Storage and Transport
iii) Hydrogen Applications

timely? Yes, it is, as "Climate change is now detectable from any single day of weather at global scale" [1], and as the crucial function of hydrogen in all major low carbon energy technologies is well established, innovative solutions are needed leading us to a *Hydrogen Based Low Carbon Society*. The global acceptance that we are approaching directs us to serious challenges relative to our handling of energy and environment and thus of climate. All three subfields of the book series have gained a lot of international priority in science, technology, economics, and politics.

Over the *last decennies*, it was shown that on a lab scale, hydrogen-based steps are able to make significant contributions to almost all non-nuclear energy technologies for main use in buildings, for mobility of persons and transport of goods including air and space, for industrial manufacturing and processing, as well as for communication and handling of big data. Hydrogen technology and economy covers *production* by traditional steam methane reforming and coal gasification and water splitting by electrolysis, *transport and storage* by high-pressure pipelines and tanks for gaseous hydrogen, by cryotechniques for liquid molecular hydrogen, and solid-state storage by reversible hydride formation, and finally the *use and applications* in thermal, mechanical, chemical, electrical, and electrochemical processes. Apart from space technology, *wave-like ups and downs of enthusiasm and budgets for research, development, and innovation (R&D&I)* characterized the chances for a major techno-economic breakthrough.

There are clear signs for a *turning point*: For those who want to set up climate-friendly energy technologies, closed hydrogen cycle and closed carbon cycle are central topics based on renewables. Concerning hydrogen, we approach asymptotically what Jules Verne was dreaming about in his "L'Ile mystérieuse" stating that "water will be the coal (fuel) of the future."

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After the Kyoto Protocol, 187 countries signed and ratified the Paris 2015 Climate Agreement COP21 for limiting greenhouse gas emissions. A Global Hydrogen Council was founded in 2017 in Davos by Toyota, Air Liquide, and Linde. IEAs 2019 statement by Director Fatih Birol, “Hydrogen is today enjoying unprecedented momentum; the world should not miss this unique chance to make hydrogen an important part of our clean and secure energy future,” supports the turning point. The European Academies Science Advisory Council EASAC published in September 2020 its strong Hydrogen and Synthetic Fuel support paper on the implementation of the EU Hydrogen Strategy on production and use of renewable hydrogen. Japan acts as a pioneering country in science, technology, and politics on hydrogen [Japanese Hydrogen Gamble, NATURE 591, 25 March 2021]: Tokyo Olympics 2020 (postponed to 2021) runs a hydrogen-based mobility system. JR East tests hydrogen FC trains. Fukushima Hydrogen Energy Research Field will soon operate a 10,000 kW hydrogen production facility. Many public R&D&I laboratories in PRC China focus their work on innovation in energy-efficient technologies for enhancing resource recycling and energy efficiency [2]. Reduced promotion of battery-electric cars in favor of methanol and hydrogen-powered cars is a crucial example. Hydrogen fuel cell pioneering car manufacturers in Japan and South Korea not only entered the car market (Toyota’s Mirai and Hyundai’s Nexo) but also have advanced plans for extensions to buses and trucks as hydrogen fuel cell electric vehicles including a 1,000 vehicle fleet in Switzerland. In Europe, Germany set a goal with the recent decision to push hydrogen-powered mobility. Fast recharging is a main advantage compared to battery-powered electric vehicles. Cost reductions by almost two orders of magnitude have been realized. Already in 2018, Germany started the commercial service of its Cordia iLint hydrogen fuel cell trains over 100 km rail. Hydrogen technology for marine applications based on H-fuel cells with metal hydrides or methanol reformers as providers of hydrogen are a hot navy topic [3]. The potential to transform nonmilitary transport of goods by open sea navigation – still exempted from Paris COP15 agreement – from today’s polluting heavy oil to sustainable hydrogen-based powering corresponds to around 4% of global CO_2 emissions. We are used to transport goods over very large distances, for example, coal from Australia to Japan or crude oil from South America to everywhere. Why do we not (yet) transport solar power in the form of synthetic liquid hydrocarbons from Australia or other parts of the southern hemisphere to consumers further north, with the additional advantage of seasonal storage?

Near-future energy scenarios will – in addition to the naturally used solar power – rely on decreasing amounts of fossil fuels (decarbonization) and classic fission-type nuclear energy and on rapid raising of different types of renewables (solar radiation, hydropower, wind power, biomass conversion, etc.) and some geothermal energy. The relative importance of the different contributing technologies is not yet fixed. However, it is clear that after the energy production and conversion, storage, especially seasonal storage to bridge the lower solar radiation of the winter period, will be the great challenge. In view of today's low-cost solar and wind power, the old idea to use fission-based nuclear heat for the coproduction of electricity and hydrogen is reconsidered "to provide an outlet for the nuclear power that is now sold at a loss" [4].

Hydrogen (H) is a present of nature: with only one proton (zero neutrons) and one electron per hydrogen atom with strong (13.5 eV) binding energy, hydrogen has the highest energy per weight or mass of all chemical energy carriers. It is a carbon-free synthetic fuel; when burnt with oxygen, water vapor is produced and no CO_2. Nature has quasi-nonlimited amounts of hydrogen chemically bound in water (H_2O). Hydrogen atoms are not stable, so they combine to molecular H_2. The challenge is that molecular hydrogen (H_2) is a gas at room temperature. Cryogenic temperatures allow liquefaction, and additional very high pressure leads to solidification. For compact applications around room temperature densification of H_2 gas, for example, compression by up to three orders of magnitude is needed. Important, still challenging options are the transformation of pure hydrogen into a hydrogen-rich synthetic fuel, a hydrocarbon or ammonia, preferentially in the liquid state.

The extraordinary potential of hydrogen is first of all a strong driver for R&D&I for energy technologies but secondly for materials science and as a crucial chemical for semiconductor industry, metallurgy, and petroleum refinement. The following short list of selected recent achievements illustrates the progress and topicality of the themes.

The publication "How the energy transition will reshape geopolitics; path to a low-carbon economy will create rivalries, winners and losers" by Goldthau et al. [5] elaborates *societal impact by hydrogen energy and climate politics*. Grolms [6] analyzed economic challenges of the realization of a sustainable hydrogen economy.

The handling of *safety and risks* of new energy technologies requires reliable sensing. Based on nanostructured sensing devices, sensitive and fast response detectors were developed to handle hydrogen as a highly flammable, colorless, and odorless gas [7, 8].

Promising R&D&I work aims at larger scale synthesis of hydrogen by water splitting and at the production of synthetic liquid hydrocarbon fuels, both using solar, thermal, or photonic energy. Photo- or photoelectrochemical water splitting, solar thermal CO_2 reduction, and CO_2 hydrogenation reactions are steps in the direction of solar fuels. Hydrogen is always involved in an intermediate step. Laboratories like the Joint Center for Artificial Photosynthesis, an US-DOE Innovation Hub established in 2010 or GREEN at the National Institute for Materials Science in Tsukuba, Japan, started early as pioneers. Pham et al. [9] reviewed solar water splitting heterogeneous interfaces. Various hydrogenation reactions of CO_2 based on intermediate H_2 storage are well described by Bhanage and Arai [10].

The European H2020 project "From sun to liquid-fuels from concentrated sunlight" with a leading team at ETH Zurich is developing a solar thermochemical technology for synthetic hydrocarbon at large scale and competitive costs. Solar radiation is concentrated by an array of heliostats and efficiently absorbed in a solar reactor that thermochemically splits H_2O and CO_2 and converts via hydrogen to syngas, which is subsequently processed in a Fischer–Tropsch process into hydrocarbon fuels. Solar-to-syngas energy conversion efficiencies exceeding 30% can potentially be realized, thanks to favorable thermodynamics at high temperature and utilization of the full solar spectrum [11]. Such solar-based carbon-neutral fuels – produced in more than lab-scale quantities – will make aviation and maritime transport sustainable.

Hydrogen-dominated materials remain a hot topic in materials science and technology. First of all, we refer to reversibly formed solid hydrides of metallic elements and compounds and their surfaces for hydrogen gas storage, as electrodes for rechargeable batteries, and as sources of atomic hydrogen, for example, in catalytic reactions [12]. An example is *superconductivity* of materials transporting electricity with zero resistivity and expulsing magnetic fields. At low temperature and very high pressure, pure molecular hydrogen gas transforms first into liquid (21 K) and then solid molecular hydrogen; under still higher pressure a transition to atomic metallic hydrogen, supposed to be superconducting, is expected (see, e.g., Dias et al. [13] and references therein). Rather than using pure hydrogen, it was demonstrated recently that the incorporation of hydrogen atoms into suitable solids (hydrogen compounds) induces superconductivity. Newest results report superconductivity in lanthanum hydride at 250 K under high pressure [14, 15].

Research will open more and attractive solutions, technology development will make it economically feasible, and the society will make its choice, hopefully respecting needs of mankind and nature.

The well-advanced hydrogen technologies continue to offer great challenges for materials science and technology and are promising fields for young scientists and engineers with entrepreneurial spirit, for this and coming generations. And, on a medium term, it will be profitable for investors.

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Alexander Wokaun

Foreword

Why does hydrogen play such an eminent role as an energy carrier? From a chemist's point of view, the answer is clear and unambiguous: it offers the best ratio of chemical binding energy to weight. Hydrogen consists of one electron, involved in chemical bonds, and one nucleon, the proton. By comparison, lithium features 1 binding electron per 7 nucleons,[1] and sodium contains 1 binding electron per 23 nucleons.

Consequently, dihydrogen offers the highest value of stored energy *per weight*: its heat of combustion (lower heating value) amounts to 120 MJ/kg, and rises to 142 MJ/kg with condensation of the produced water (higher heating value). This value is unsurpassed by any other chemicals.

Besides, hydrogen offers many advantages: As we shall discuss, it may be produced by a variety of routes, is useful and required for a plethora of applications, and can be converted to other forms of energy by clean and efficient routes. Of course, there are also some disadvantages: For hydrogen as a light gas, the energy stored *per volume* is low (11 MJ/m^3), as compared to methane (36 MJ/m^3). For energy storage, hydrogen must therefore be compressed or liquefied, and pipeline transport needs to move larger volumes. As a reactive gas, hydrogen requires safe handling with adequate precautions. Fortunately, appropriate technical solutions are available to overcome these difficulties, such that society and industry can take advantage of hydrogen's eminent properties.

Henry Cavendish discovered the element of hydrogen in 1766. Soon thereafter in the eighteenth century, the light gas hydrogen was already used for lifting gas balloons, and its use for aerial transportation continued until the twentieth century. Unfortunately, this early career found an undeserved end with the accident of the "Hindenburg" zeppelin, although later it was established that the disastrous fire was due to burning of the aircraft's skin, not of the hydrogen. The rising chemical industry continued to use hydrogen as a clean reducing agent, albeit in small quantities in the nineteenth century.

Hydrogen in the chemical industry

The volume of hydrogen required and used increased drastically at the beginning of the twentieth century, mainly for two applications. The first is the chemical synthesis of nitrogen fertilizers for agriculture, when the need of the growing world population

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[1] Naturally occurring lithium is a mixture of two isotopes: ^{7}Li with an abundance of 92.5% and ^{6}Li with an abundance of 7.5%.

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could no longer be covered from mineral or organic sources. Catalyzed ammonia synthesis ($N_2 + 3H_2 \rightarrow 2NH_3$) fixes nitrogen from air. This is accomplished by the famous Haber–Bosch process. The technical chemist Fritz Haber laid the foundations by establishing the reaction conditions of high pressure and moderate temperature, and chemical engineer Carl Bosch realized the reactors for large-scale production. The decisive role of the catalyst was elucidated by Nobel prize winner Gerhard Ertl, and search for advanced catalysts is still ongoing to afford ammonia synthesis at milder reaction conditions of temperature and pressure.

Part of the ammonia is subsequently oxidized to yield nitric acid. Without the availability of ammonium nitrate, the so-called green agricultural revolution and the associated crop yield increases would definitely not have been possible. Today, the production of hydrogen for ammonia synthesis accounts for more than 2% of the global energy needs.

The second large application of hydrogen is oil refining. Two of the associated processes rely on hydrogen, that is, the removal of sulfur from crude oil by hydrotreating, and the conversion of heavy (large) molecular weight fractions to lighter compounds by hydrocracking (breaking of carbon–carbon bonds with hydrogen). The amount of hydrogen used for these purposes matches the global volumes of transportation fuels (gasoline, diesel, and kerosene); hence, refineries handle very large volumes of hydrogen which is often transported in pipeline networks.

In the early days of the Haber–Bosch ammonia synthesis, hydrogen was obtained as a side product of the chlorine–alkali electrolysis ($2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH$), with chlorine as the main product. As the demand for hydrogen increased and natural gas became available, the steam reforming of the latter became the predominant source. In fact, the steam reforming of methane (overall reaction[2] $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$) is still the highest volume and least expensive production route of hydrogen, amounting for 48% of global use, followed by hydrogen from coal and oil. Together, these fossil sources still account for 96% of the hydrogen produced, which is termed *brown hydrogen* in the literature.

Clearly, the production of hydrogen as an energy carrier in a future sustainable energy system cannot be based on fossil fuels, and hence we shall return to the production based on renewable energies, after briefly discussing another use of hydrogen.

Space applications

Hydrogen played a pivotal role in NASA's Apollo and Apollo-Soyuz space projects. The carrier rockets used in the launches between 1961 and 1975 were propelled by

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[2] The overall reaction consists of steam reforming ($CH_4 + H_2O \rightarrow CO + 3H_2$) and water gas shift ($CO + H_2O \rightarrow CO_2 + H_2$).

hydrogen. For example, the fuel of Saturn II rocket consisted of an astounding quantity of 1,000,000 L of hydrogen, and 331,000 L of oxygen, both in liquefied form. Today, heavy-duty carriers like the Ariane rocket series use a combination of solid-state propellant boosters and hydrogen/oxygen engines, and carry more than 100 tons of fuel.

Interestingly, the Apollo mission already featured another use of hydrogen: Electricity on board of the lunar command module was provided by fuel cells, and similarly the supply of the International Space Station is furnished by alkaline fuel cells (cf. section on transportation).

Hydrogen production by renewable energy

Solar energy, wind, and hydropower are the renewable energies used for the production of so-called *green hydrogen*. There are three basic routes to achieve this aim.

The first avenue harnesses renewable electricity and uses the latter in electrolysis to produce hydrogen and oxygen. The invention of electrolysis by Nicholson and Carlisle dates back to 1800. In the past three decades, tremendous advances have been achieved with respect to efficiency, power density, and cost reduction. There are three main variants, the choice among which depends on the application:

- alkaline electrolysis is the industrial benchmark, usually the least expensive option for applications requiring semicontinuous hydrogen production;
- high-temperature electrolysis is related to solid oxide fuel cells (see below[3]); it uses steam as the reactant, and the efficiency is increased by the possibility to use waste heat as secondary input;
- polymer–electrolyte membrane electrolyzers excel by high current densities and fast switching times, and are therefore well matched to photovoltaic or wind energy sources with their inherently varying power; rapid start-up is possible as a lengthy warm-up phase of high-temperature electrolyzers is not required.

At this point, it is appropriate to mention briefly another variant nicknamed *blue hydrogen*. The latter is again produced using (nearly) CO_2-free electricity, but this time generated either by nuclear power or by coal/gas-fired power plants where CO_2 is removed from the flue gases by carbon capture and sequestration.

The second pathway uses concentrated solar power. The latter may again either be used to provide renewable electricity, or for the direct production of hydrogen using thermochemical cycles. A variety of cycles has been tested, and at present, the most promising candidates appear to be based on perovskite-type materials. In the high-temperature step, lattice oxygen is released from these materials, while in the subsequent low-temperature step the desired reduction of reactants takes place:

The now oxygen-deficient perovskite is exposed to water vapor or water/CO_2 mixtures, whereby either hydrogen or synthesis gas (H_2/CO mixtures) are produced.

The third route is termed "photocatalytic water splitting." A suitable semiconducting material, or a sandwich of two judiciously chosen semiconductors, is doped with cocatalysts on either side, and exposed to sunlight. If the band gaps of materials and their surface chemical composition are adequately positioned in energy, hydrogen and oxygen gases are produced directly on opposite sides of the device, without the intermediacy of electricity generation. With respect to maturity, photocatalysis is still investigated at the laboratory scale, and hence considerably less advanced with respect to technological readiness, as compared to the abovementioned photovoltaics/electrolysis combination. Yet, a community of researchers considers photocatalysis as an option with highest long-term potential. In general, it mimics the photosynthesis process of nature in which water and CO_2 are reduced; this is why one research team designated its realization as an "artificial leave."

Energy storage using hydrogen

Decarbonization of electricity generation is a high-level target in the European Union and worldwide. As the potential for an increase in hydroelectric power generation is limited on the continent, further substantial increases in photovoltaic generation and wind energy are elements of many national strategies.

The intermittent generation due to these sources poses a well-recognized problem. While in summer, the peak of insolation may coincide with the maximum demand for air conditioning in warmer countries, photovoltaic electricity is not available in the later evening and night hours. The partially complementary profile of wind energy cannot yet be fully exploited due to a lack of high-voltage north–south transmission lines. Consequently, there is a need to store electricity on a daily, weekly, and seasonal timescale.

Demand side measures (shifting consumption to match available power) and sectoral transfer to transportation are valid, but only partial responses that will likely not be sufficient. Batteries provide storage of up to megawatt-hours of electricity over timescales of hours or days. *Chemical* energy storage potentially offers large volume solutions of up to terawatt-hour quantities, operated during periods when an excess of renewable power in the grid cannot be absorbed otherwise, with the option of storing the produced chemicals over timescales of months and seasons.

Conversion of the electrical energy to chemical energy stored *in the form of hydrogen* is the most efficient solution for long-term storage; this process is termed "power to gas" in the literature. Electrolyzers with efficiencies exceeding 70% are available for this purpose, and are being installed at increasing power ratings and decreasing cost.

For *longer term* storage of the produced hydrogen, three strategies may be followed. Hydrogen could be injected directly into the natural gas grid with its inherently large storage capabilities. While the hydrogen content of the transported gas is presently limited to 2%, most pipelines could be safely operated with up to 10% hydrogen if regulations were adapted. Where direct injection is not feasible, conversion of hydrogen to methane is an option (cf. section on synthesis). Third, tests are ongoing to realize dedicated hydrogen storage caverns, for example, by repurposing salt caverns previously used as natural gas reservoirs.

Transport applications

The decarbonization of the transportation sector is likely the most recalcitrant problem on the pathway to an energy system with “zero” CO_2 emissions. The difficulty of replacing the standard fossil fuels by CO_2-free fuels increases in the order from motorbikes, passenger cars, heavy-duty vehicles, to ships and airplanes.

A wave of vibrant interest in hydrogen fuel cells for transportation started around 1990. In the fuel cell process, the reverse of electrolysis, hydrogen and oxygen (air) react electrochemically to produce electricity on board, which is then used to power an electric motor propelling the vehicle. As early as 1839 and 1845, respectively, Christian F. Schoenbein and William R. Grove had invented the principle of the fuel cell, but the technology was for long considered as too expensive for cars, and only used for space and military applications.[3]

Tremendous progress in increasing the fuel cell power per weight and volume, in decreasing the amount of required platinum, and in driving down the cost gave rise to the expectation that fuel cell passenger cars would be on the road by 2005. However, several challenges (mainly lifetime and cost) need to be addressed, and the development took until 2015 when the first fuel cell cars were sold to the general public.

In the meantime, another form of electric propulsion had made headways, that is, the direct use of electricity in battery electric vehicles. This was made possible by advances in lithium ion battery technology – increasing the energy and power per weight, providing adequate safety, and decreasing the cost per stored kilowatt-hour to an unprecedented level. As of present, battery electric vehicles are on the market with ranges around 300 km, and premium models with ranges above 500 km.

The consequence was a heated debate about the pros and cons of fuel cell and battery technologies, at times resembling a war of faith, with various countries and automotive companies taking different bets on the winning option. On the scientific

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[3] Polymer electrolyte fuel cells are predominantly used for transportation, as they are capable of rapid start-up and fast power-level changes. High-temperature solid oxide fuel cells, usually fueled with reformed natural gas, are suited for stationary combined heat and power applications.

level, this was accompanied by careful life cycle analyses, emphasizing the importance of the source of electricity (for both), the materials used in the manufacturing of batteries or fuel cells, the weight increase of the car due to aggregates, the “refueling” time, the storage of the fuel on board, and the available utilities in summer and winter.

Today, a consensus is slowly arriving that there is not an either/or decision between the two options but that the two technologies complement each other for defined purposes. For (lighter) vehicles mainly used in short-distance driving, battery electric vehicles offer unbeatable advantages due to the efficiency of charge/discharge cycles, albeit at the price of longer charging time. On the other hand, for heavy vehicles with longer driving distances per day, and the need for fast refueling, propulsion by fuel cells is the preferred option. Heavy-duty trucks and buses are prime candidates to be equipped with fuel cell aggregates. Delivery truck and bus fleets offer the advantage that they often depart from a central location, where the refueling infrastructure can be built up close by and thereby profit from predictable turnover. Several companies are investing in the development of fuel cell trucks. Particularly noteworthy is the concept of a Swiss consortium that focuses on the parallel buildup of fuel cell truck fleets and hydrogen fueling stations located close to their home base.

Synthesis of transportation fuels and base chemicals

Two issues need to be addressed in the context of using hydrogen for transportation. First, the buildup of a hydrogen refueling infrastructure covering a country’s complete area is expensive, while a well-organized distribution network for liquid fuels already exists. Second, fueling by hydrogen for the most energy-demanding applications, such as large airplanes for long-distance flights, appears close to impossible, as here the high energy density of liquid fuels is irreplaceable.

The synthesis of liquid fuels starting from hydrogen and CO_2 offers a solution for aircraft and other heaviest duty applications. The simplest liquid fuel that can be produced by catalyzed synthesis is methanol. The advantages of methanol have been recognized early in the discussion around hydrogen, such that even the term “methanol economy” had been proposed. Methanol is a an important intermediate in chemical industry – today being produced from fossil sources in very large volumes, and used for a variety of applications, including the methanol-to-gasoline process. The latter might become an option for producing gasoline from renewables.

A further option for production of a liquid fuel is Fischer–Tropsch synthesis. The basic technology was developed early in the twentieth century and is used to produce diesel-like hydrocarbon fuels from coal. Researchers improved the catalysts that promote the formation of carbon–carbon bonds and yield long-chain saturated hydrocarbons from synthesis gas ($CO + 2\,H_2$). With suitable modifications, the Fischer–Tropsch-type catalysts can be adapted to synthesize liquid hydrocarbons from hydrogen and CO_2, a subject that received renewed and increasing interest from the late 1980s onward.

For all of these options, the question about the source of CO_2 remains to be answered. In the first option, CO_2 is separated from the flue gases of fossil power plants, incinerators, cement plants, or steel production (carbon capture, storage, and use). The carbon moiety is thereby still of fossil origin but the emissions of the plant are “reused,” and the fossil transportation fuel is thereby replaced. The purist option is the extraction of CO_2 from the ambient air (direct air capture), a cycle being closer to CO_2 neutral, except for the energy expended for the capture. It offers the advantage that the synthesis plant can be erected wherever renewable hydrogen is available, not requiring the proximity of a flue gas separation facility.

Another potential source of carbon is biomass. The combustion of biomass for power generation, combined with CO_2 separation from the flue gases, has been proposed as a “negative emission” technology (biomass energy carbon capture and sequestration). If, instead of storing the separated CO_2 underground, the latter is used for the synthesis of liquids, the overall cycle ending with combustion of the synfuel becomes CO_2 neutral, as the biogenic carbon had before been extracted from the atmosphere by photosynthesis.

At this point, we should mention another option, the synthesis of *methane* from H_2 and CO_2, which is also termed “power to gas” in a broader sense. It is legitimate to ask when this technology can make a meaningful contribution while, at the same time, hydrogen is produced in large volumes from fossil methane in today’s chemical industry. The answer requires careful argumentation: The target is the storage of “excess” renewable electricity. If the large volume of hydrogen, produced by electrolysis from this electricity, cannot be used in short time nor fed into the gas grid, then the production of CH_4 offers a valuable solution. A prime application of the so-produced biogenic methane is the fueling of natural gas cars, thereby reducing their tailpipe emissions close to zero. Further, European directives target a content of 10% of renewable gas in the natural gas grid, and the methanation of CO_2 will be needed to achieve this value.

An attractive option for “power to methane” is a combination with the fermentation of biogas. The raw fermentation gas contains roughly equal amounts of CH_4 and CO_2, and conventionally the latter must be separated and released to the atmosphere before the biogas can be injected into the grid. If instead, the CO_2 in the raw biogas stream is converted to methane using renewable hydrogen, the overall yield can be increased (technically by ~60%) while the separation step becomes superfluous.

Widening the scope of syntheses from H_2 and CO_2, we focus on the feedstock for chemical industry. Presently, the base organic chemicals used in industry – olefins, aromatic compounds, and others –are almost exclusively derived from fossil fuels, mainly from natural gas and oil. The point has often been made that rather than burning oil for heating and transportation, one should save oil reserves as a resource for chemical industry as the chemical feedstock is difficult to replace. However, for a system targeting “zero” carbon emissions, other sources for feedstock are required. Biomass (“naturally regrowing raw materials”) can offer a partial replacement of the fossil base, provided that competition with food production can be avoided. For a larger volume, the synthesis of base chemicals and intermediates from H_2 and CO_2 provides a sustainable solution. The production of methanol, mentioned above, is a first option. Further, a plethora of small molecules exists that can be synthesized from the CO_2 building block, and suitable routes have been developed and are available. In this way, renewable hydrogen opens a viable path to decarbonize the chemical industry.

Role of hydrogen in energy systems integration

Sector coupling is key to achieving the goals of the energy strategies of many European countries, to reach their emission targets. The concept implies that the sectors of energy provision, industry, services, households, and transportation are no longer advanced separately but are considered as a connected entity and controlled together to reach a global optimum with minimum emissions.

Examples of system integration have been amply discussed and have meanwhile become accepted concepts. For example, individual houses become prosumers that import and export electricity. The electricity grid and transportation may be coupled such that excess renewable electricity is used for charging electric vehicles, while the latter vehicles feed electricity stored in their batteries to the grid in periods of high demand (vehicle to grid). “Smart grids” implement demand side management by load shifting.

The operational control of such a “smart” sector-coupling network has been termed “energy hub.” As one of key characteristics, these energy hubs, typically at the community or city quarter level, share a network of grids where not only electricity but also heat, cooling fluids, and gases circulate and can be exchanged. In such multienergy carrier grids, *hydrogen* will undoubtedly have to play an important role.

The future role of hydrogen

Technology development often proceeds in “waves,” a concept proposed by Cesare Marchetti in other context. Reviewing the discussion of the preceding sections, one could discern the following phases that each implied a surge in the importance and use of hydrogen:

- the first wave started with the massive need for hydrogen in the chemical industry, for fertilizer production, and refining;
- the second wave involved the highly visible use of hydrogen in space missions;
- the third wave, in the 1990s, was characterized by widespread enthusiasm for hydrogen in transportation and energy industries, such that hydrogen was considered *the* unique energy carrier of the future, and scientist formulated the vision of *the hydrogen society*.

Today, we are in the middle of a fourth, more realistic, yet more powerful phase that will engender a massively increased production and use of hydrogen. We no longer suppose a single solution and one unique predominant energy carrier, but realize that interconnected grids of electricity, heat, hydrogen, and other gases are required to achieve system integration and the needed coupling of sectors of our society and economy.

Conclusions and recommendations

- Hydrogen is an indispensable energy carrier in the future energy system.As was demonstrated in the previous sections, hydrogen is urgently needed for energy storage, in transportation, as well as for the synthesis of renewable liquid fuels and feedstock for the chemical industry.
- European and global targets for energy efficiency, renewable energy shares, and decarbonization, and the associated climate protection goals, cannot be reached without hydrogen.
- For large-scale penetration, hydrogen technologies must become competitive in the energy markets. Therefore, research and development should focus on innovations that drive down costs. At the same time, governments need to agree on an adequate price for CO_2 emissions. Several measures (CO_2 tax and emission trading systems) have been discussed elsewhere.
- In order to reach competitiveness, initial support is required to mature the associated technologies. In particular, the entire chain from academic research via industrial development to pilot and demonstration should be financially encouraged by science policy.
- Hydrogen must become an integral part of teaching at institutions of higher education, in particular, at the universities of technologies. These institutions should also offer courses of continued education for practicing engineers and industrial leaders. Researchers are to be encouraged to reach out in communication to governments, to industry, to insurance companies, and to the public, to enter into a dialogue in the spirit of partnership, and to inform stakeholders about the advantages and

unique properties of hydrogen, including the safety aspects. The financial support of such a dialogue process must be considered an integral part of public funding.
- Implementations at industrial scale are required to demonstrate to societal public the safe handling of hydrogen, according to the established standards.
- Capacity markets are an adequate measure to valuate hydrogen as a storage medium for intermittent renewable electricity (photovoltaics and wind energy).
- In transportation, strategies should aim for a concomitant build-up of hydrogen supply infrastructure and hydrogen demand, in order to avoid expensive upfront investments.
- The various variants of power-to-X technologies should be further advanced to increase the efficiencies of each step subsequent to hydrogen production. Innovative combined approaches such as coelectrolysis and coproduction of H_2 and CO are to be pursued.
- Power to methane is a powerful option to store hydrogen by injection of CH_4 into the national gas grids. This technology is required, in addition to biogas, in order to meet the European targets of renewable shares in the circulating and dispensed gas.
- In particular for air transportation, the synthesis of liquid fuels based on renewables should become a high-level target for research and development. Without the availability of these synthetic fuels, the decarbonization goals of transportation cannot be reached.
- The sectors of the economy must be coupled by implementing “smart” energy systems, including multi-energy carrier grids.
- Chemical industry should prepare for a change from fossil to renewable resource base. This constitutes a major challenge in view of the very large associated mass flows.
- Europe’s energy strategies and its decision to establish a CO_2-neutral energy system by 2050 make it a prime mover to advance and demonstrate hydrogen technologies. The determinedness of Europe with respect to these goals provides a strategic advantage compared to the United States and China, countries that have partially other priorities. In view of Japan’s strategy of direct governmental financial support to industry, the European Union should act to secure its competitive advantage and thereby open up sustainable energy markets of the next decades.

In summary, hydrogen is thus truly indispensable to reach Europe’s high-level goals. It has a vital role to play on our ambitious climb toward a sustainable energy system. It offers the unique advantages of high energy per weight, long-term storability, pollution-free convertibility to other forms of energy, and flexibility in application. The quantity of hydrogen to be employed in society and the global energy system is only limited by the available renewable energy used for its generation, as the only other resource required for its production is water. Within a future-oriented, multipronged energy system, our societies should be strongly encouraged to exploit this unique potential of hydrogen as one truly renewable energy carrier.

Further Reading

For scholarly quotations on the individual aspects and technologies, the reader is kindly referred to the respective chapters where a large number of technical references are given. Here we restrict ourselves to a very few general references and compendia.

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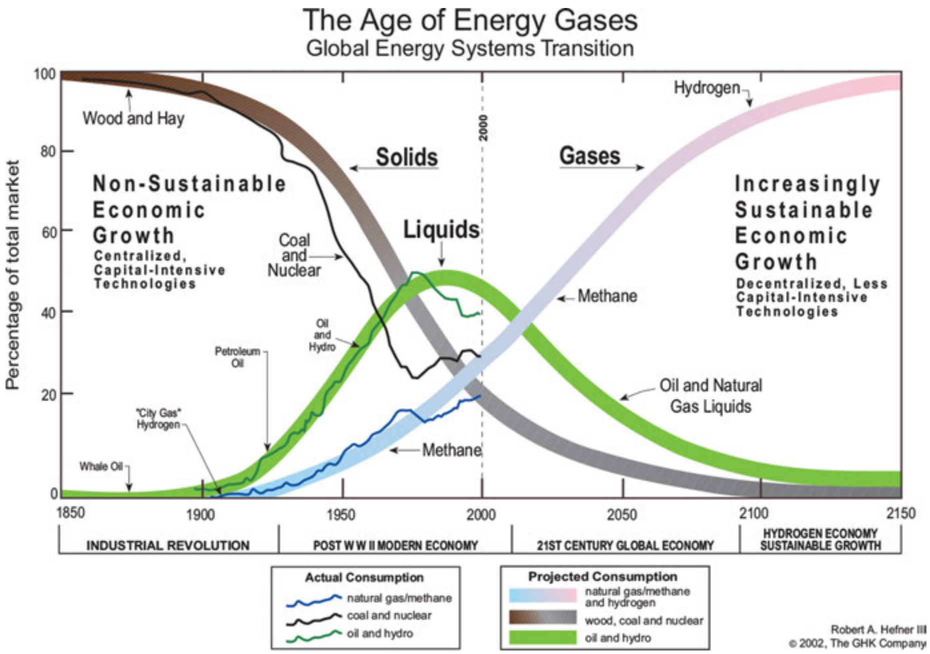
Extended Introductions

Pierre Etienne Franc

Hydrogen: why the times to scale have come

Hydrogen technologies have been around for centuries. In the early decades of the eighteenth century, many engineers developed their first engines to use this magic molecule. However, the human history of energy utilization has – to now – chosen different routes to heat, move, and industrialize.

A well-known graph shows, in a simplified way, that the history of our relationship with energy seems like the one of a quest to reduce its carbon content (even though it never was a conscious move). Each step of civilization seems to mean one level of carbon less, toward pure hydrogen-based solutions. Each step involves a further reach in technological knowledge to meet higher energy needs. We started our quest with wood, and then shifted to coal. The discovery of oil brought a fuel with far better energy density, boosting the transport revolution. Natural gas came next – getting us closer to hydrogen – but this shift to gas sources required us to master new storage, transportation, and distribution techniques. At the same time, each step has enabled a further sophistication of the materials and feedstocks used, shifting the use of fossil resources from a pure energy source to a far broader source of materials for building, equipment, and everyday life provisions for our needs.



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But the hydrogen economy, the hydrogen society, has not yet arrived. This long awaited next step into a hydrogen-driven energy model, where only electrons and hydrogen become the vectors of energy generation, storage, transport, and distribution, is not here yet.

The key technologies needed to achieve such a hydrogen-based system are known, mastered. They still have their complexities and challenges, which are broadly discussed in this book and some are significant. But the issue of taking that next step is not technology related. It all depends on our goals.

Why can't we say this time, therefore, that hydrogen is no longer the future, but the present? What has fundamentally changed to build conviction from the key hydrogen players and supporters?

As noted, technologies have a major impact to progress in all key fields – power electronics, materials chemistry, thermodynamics, silicon technologies, miniaturization technologies, and digital – all enable performance improvements in the production, storage, distribution, and use in fuel cells of hydrogen-based solutions. Many solutions that exist today to store and transport high pressure or liquid hydrogen safely and competitively (heavy storage, supercritical transportation, leakage detection and leak preservation, safety measures, and control systems), to boost electrolysis performance (footprint, capex, usage of raw and precious materials in the catalyst and electrodes), and to capture carbon – all fields of global technological progress that enable the use of hydrogen in places, at densities and for public uses – could not have been considered when Cavendish, Rivaz, and other key scientists of the time first discovered hydrogen's properties.

In a way, hydrogen technologies take a full benefit of everything being developed around them, including the huge electrification wave currently under development in the automotive world.

But more significantly, to reach the scale necessary to make a change, hydrogen technologies needed to serve a proper goal, one which outweighs all challenges and enables whole sectors to grasp it properly. This required three following steps:

1. Designing a shared vision against a major challenge.
2. Developing concrete and tangible proofs of the viability of hydrogen-based solutions.
3. Developing a concerted, coordinated multilateral ambition.

This is what has been achieved over the past decade.

The vision

The vision, at present, results from the widely accepted challenge of fighting climate change. Whatever the economic options are considered, our world will not continue its current course of growth and energy use without significant life-threatening harm to our societies. Either through different growth models or a change in economic wealth patterns and goals, we need to shift to low-carbon energy sources, as renewable as possible, and this has to happen now. And it does. The share of renewable power in primary production continues to grow; new energy capacity additions are now higher from renewable sources than from fossil ones, and the levelized cost of electricity (LCOE) of those new sources of energy are in many places competitive with fossil base sources. Primary generation of renewable sources is on its way, but its transport, distribution, and use in downstream consuming sectors (transport, industry, district heating) are now the key challenges. Many analyses of future energy systems have now clearly demonstrated that hydrogen is an essential vector to enable a below 2 °C scenario.

A key vector to store and transport vast amounts of renewable intermittent energy in places or times where they are in surplus to places and times where they are in need.

A key vector to enable the continued use, for several decades, of fossil fuels that are as clean as possible, by using only the hydrogen part and sequestering the carbon through carbon capture and use or sequestration technologies.

A key vector to decarbonize transport, alongside battery electric solutions, especially for large and intensive mobility needs.

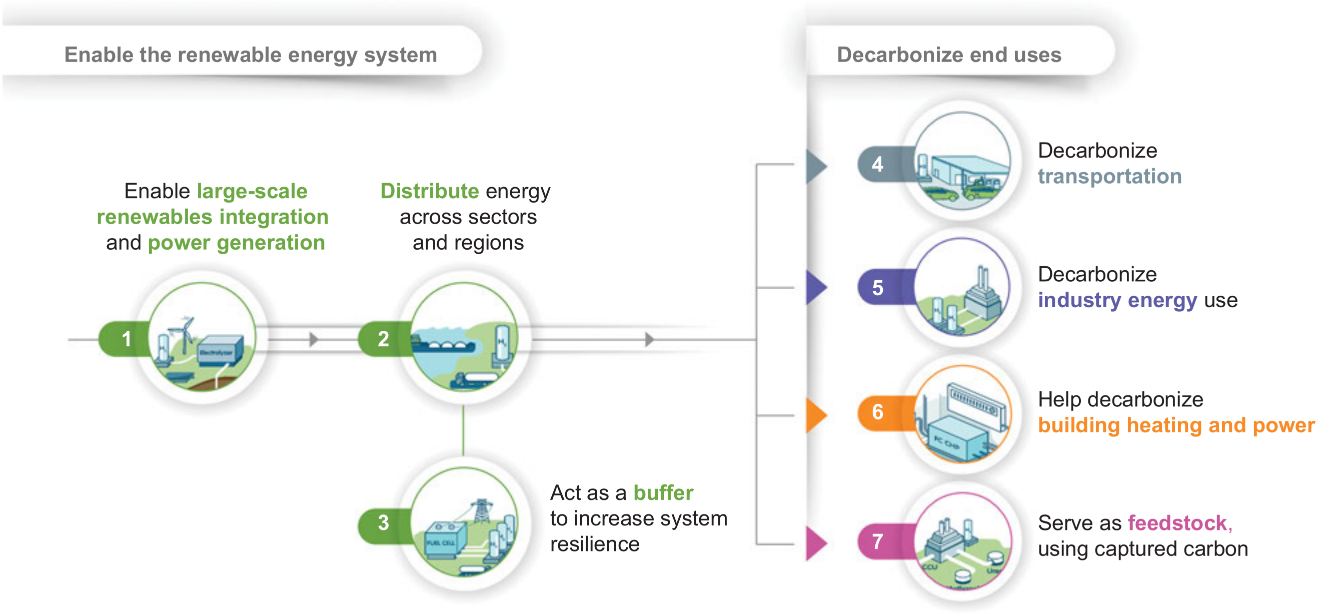
A key vector to decarbonize the use of feedstocks (by synthesis of gases) or fuels in high-energy-intensive industries.

A key vector (in some geographies) to develop highly efficient low-carbon stationary heat and power generation solutions for district heating needs.

These views have led several different organizations to converge on the view proposed by the Hydrogen Council, that hydrogen could represent up to 18% of final energy demand by 2050 and help achieve 20% of the CO_2 reduction target of the planet.

In other words, hydrogen is now increasingly seen as an unavoidable part of any future clean energy system. This vision, proposed by the coalition of CEOs on the Hydrogen Council, followed initial views pushed by leading countries on the matter – Germany, California, Japan. Recently, strong measures have also been adopted by South Korea, China, Australia, the European Union, and several Middle East countries. The International Energy Agency (IEA), the ETC, the International Renewable Energy Agency (IRENA) and Bloomberg, to name the most prominent consultants/commentators on the energy field, have all acknowledged the need to boost the deployment of hydrogen technologies if we are serious about energy transition.

The 7 roles of hydrogen in the energy transition



Hydrogen by 2050:
a quantified vision of its key role in the energy transition

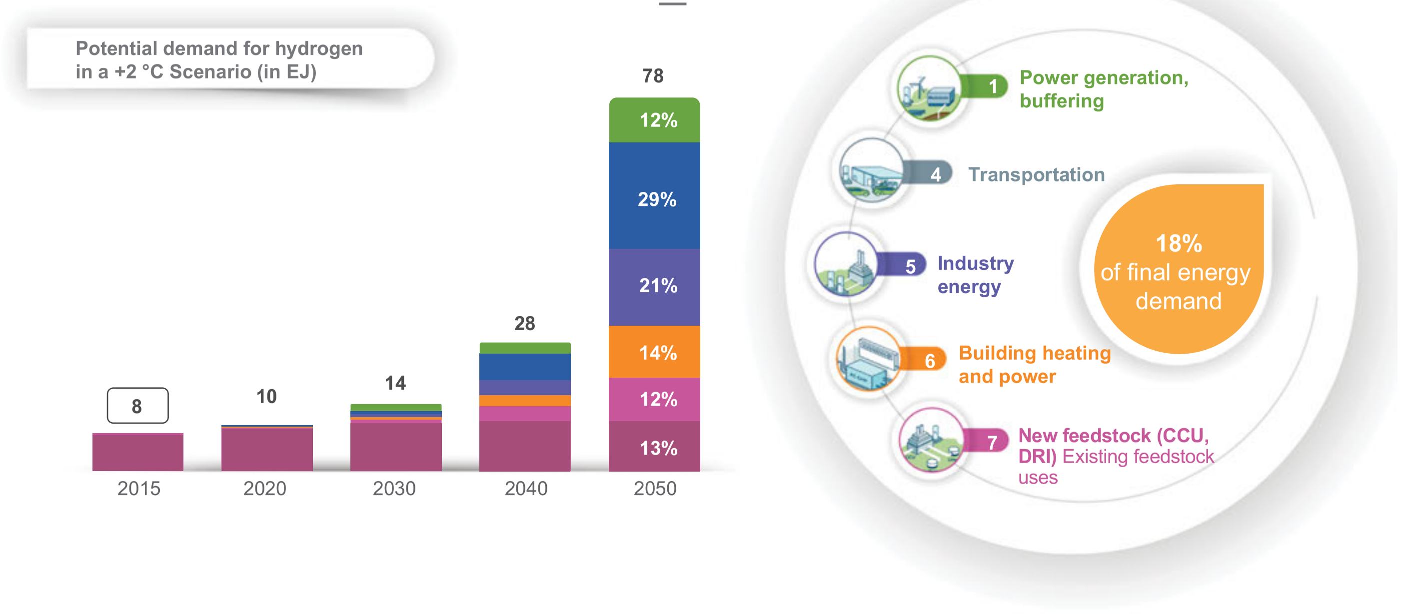
This has also been possible because not only technologies but also implementations have progressed significantly over the decade. Back in 2010, a couple of hundred cars from several original equipment manufacturers (OEMs) were nicely demonstrating that it is possible to drive a hydrogen car. Stations were tested here and there, but nobody was seriously thinking yet that electrolysis could become a key node in the future energy system of the world. Ten large demonstration projects for buses were started in several cities. First forklift applications were considered in the United States.

Now, technology deployment is catching up in all fields, and series have started to reach scale. The year 2020 saw more than 20,000 vehicles on the road, more than 500 stations up and running, several thousand trucks and buses, 30,000 forklifts in use every hour of the year, several GW of electrolysis capacity under construction and tens of GW of projects in development. The first large-scale trials for the use of hydrogen in power plants, in steel-making processes and of the first-liquid hydrogen carriers have been launched. The whole vision of a hydrogen-enabled energy system is being backed by a significant wave of deployments, experimentations, and tangible operations.

Finally, this has also worked because not only have we seen a vision been built and the first tangible operational demonstrations being developed but also there is a clear alignment of views on the remaining key hurdles that the industry, jointly with policy makers, has to clear to make this real.

First **safety**. Hydrogen, as any energy carrier, is dangerous. It needs to be handled with proper care and correct operating procedures. This includes stringent equipment, process, and behavioral rules that will have to pervade throughout the general public – so in a far broader and more public space than was the case when it was confined to industry-related topics. The more the technology spreads in its potential and use, the more players – large and small – will touch it, and the more chances we face for handling and safety issues. For this to be addressed properly, **regulations have to be developed and harmonized between countries and a**

Tomorrow's use for the energy transition will unlock ten times bigger market



Hydrogen: a significant role in global recovery plans

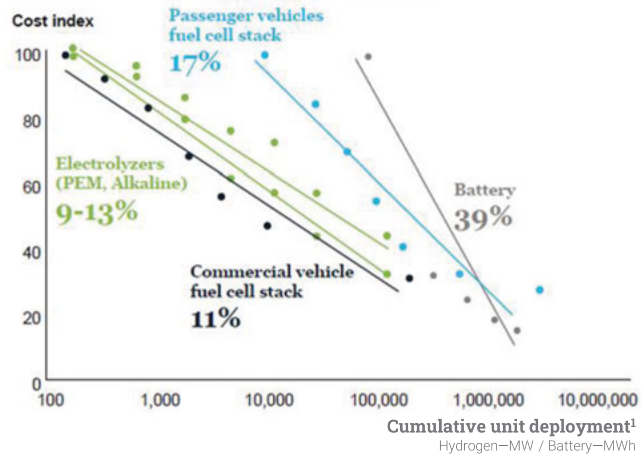
very stringent program of training and education of all energy related players and OEMs will have to be developed. This is by far the most critical of the challenges ahead and it has to be tackled rapidly as many SMEs and new actors are entering the field. Education and normalization is to be developed to help them properly capture the challenges of this molecule in their activities and to benefit from competent resources to grasp those safely. But it is no different an issue than that which arose with the growth of oil-based activity, then gas, and now battery and electric uses. We are starting a new wave, developing uses of hydrogen technologies in much larger spaces for far more numerous applications, and we need to prepare the population for it.

Second – **low-carbon shift**. Hydrogen technologies have to provide for a low-carbon hydrogen source. If not, the hydrogen revolution will not happen, as it will not serve our common goal with respect to using clean energy vectors. Clean hydrogen technologies exist, but they are, by definition, more expensive today than fossil-based methods. In total, 95% or more of hydrogen produced today is based on natural gas, coal, or oil with an associated 10–20 kg CO_2 produced/kg of hydrogen. The end game is to provide a kg of hydrogen at the point of use for less than 1 kg CO_2. This is a huge technical and economic challenge. It is also the place where hydrogen reconciles all players, as it is the ultimate high-energy molecule if we are able to supply it without associated carbon. Developing the right methodology and goals for low-carbon hydrogen production, to be shared between geographies with agreed metrics and measurement methods, with a tracking system enabling hydrogen to be traded with its CO_2 footprint and thus to contribute to decarbonizing energy in each geography is a key topic. Second, new disruptive technologies for low carbon or zero-carbon hydrogen production are still likely to emerge in coming decades and we shall see many future developments which could further accelerate the shift to hydrogen systems. In that context and in the light of the above, **European 2021–2027 Research & Development program needs to continue to support Hydrogen technologies and be further strengthened, next to the need for broad deployment support schemes**. Last, low-carbon hydrogen requires a low-carbon supply chain, and thus requires strong investment upstream with renewable sources, or with low-carbon energy sources to optimize the energy cycles and the capex cost of those solutions. Similarly downstream, as the book will show, because often only 10% of the hydrogen value chain relates to production, while up to 80% relates to the conditioning, transport, and distribution side where emissions and energy spending happen as well. Optimization of the supply chain solutions – on site, gas pipes re-purposing, liquid solutions, other hydrogen rich vectors as transportation means – will all have to be revisited over the coming decade to develop the best techno-economic compromise to enable safe, reliable, and competitive low-carbon pathways to hydrogen at the point of use.

Third, **cost**. Hydrogen production through fossil means is relatively mature today, with a landed cost of ~ 1.5 €/kg (50 €/MWh). But the whole value chain goes from production, in a clean way, to the transition of all downstream processes to enable the use of hydrogen at the point of use. The gap to competitiveness with longstanding and mature incumbent technologies is significant. In each part of the value chain, efforts still have to be made to halve the cost of hydrogen-related technologies. In certain applications, this will still not be enough to make hydrogen competitive with incumbent fossil solutions, but in others, it will. The Hydrogen Council developed a strong fact-based

Technology achievements

Manufacturing scale up will drive down costs



1. Battery 2010-20, fuel cells and electrolyzer 2020-30

1. Durability of systems
2. Volume reduction (increase W/L ratio)
3. Rare metals content reduction
4. Steady operation in extreme temperature conditions
5. System costs
6. Mass manufacturing capabilities
7. Supply chain development
8. Effective operations experience
9. System capacity scale up (from kW to MW)

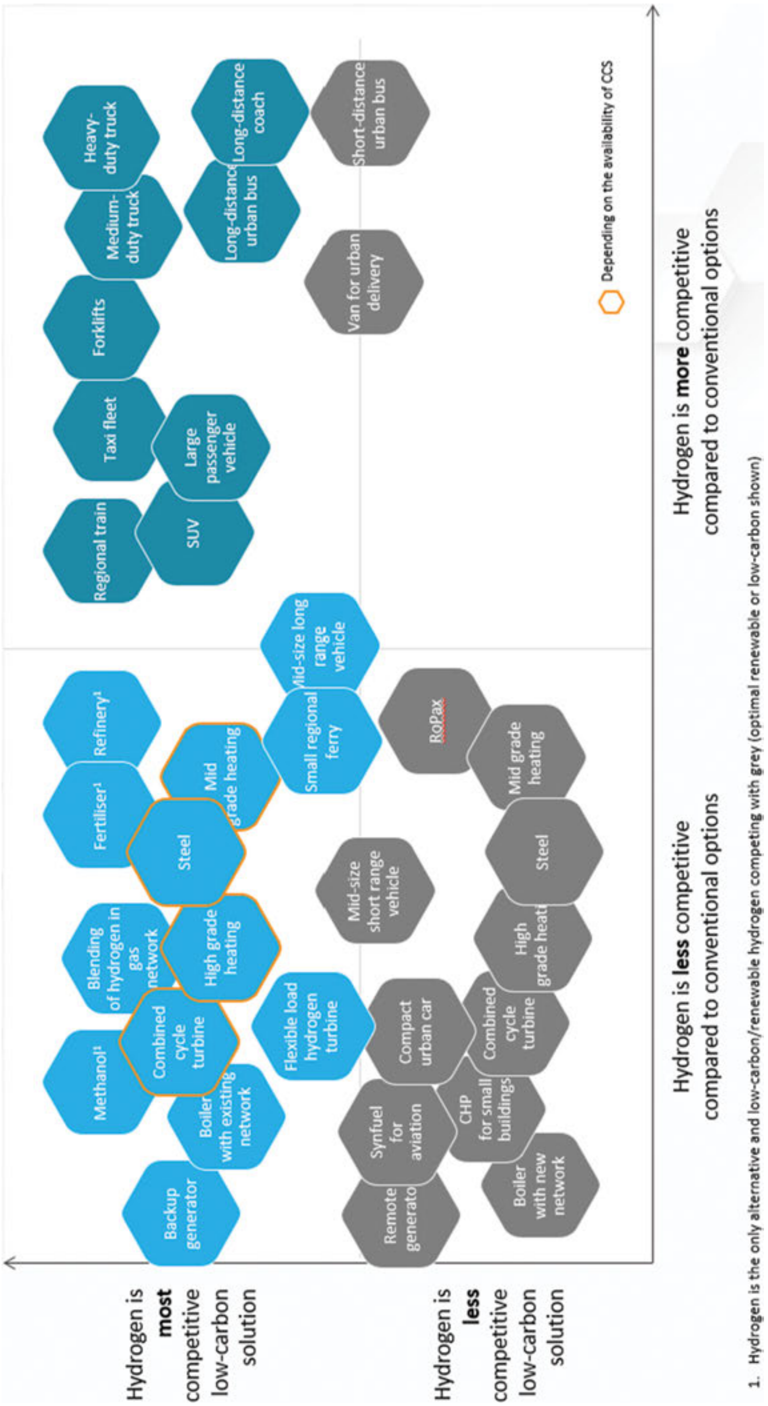
analysis of 33 applications enabling hydrogen to cover 60% of world emitting sources. Of those, half can achieve competitiveness in the coming decade if the proper cost roadmaps are put in place.

Those call for further progress in technologies, but primarily for scale deployments. This is especially the case for fuel cell technologies, electrolysis, and network development for hydrogen distribution. It is, however, widely acknowledged by all players that a pathway to cost competitiveness exists for most key transport applications, many heavy heat-intensive processes, and several district heating applications.

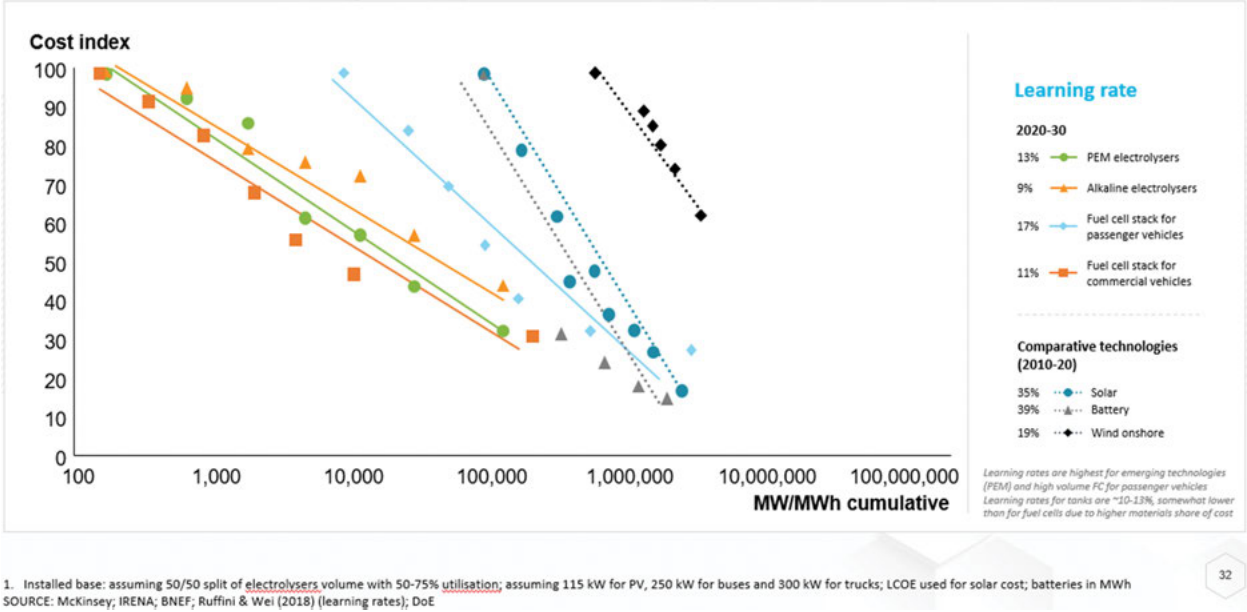
Last but not least, this will not work without a paradigm change in the way industry and policy makers' act and play. To date, the world has benefited from the dynamics of a very competitive environment, in which the economics of scale and the role of the free market has driven a fierce struggle to cost- and value-based solutions to the point that the satisfaction of individual needs comes with only a marginal cost to volume-based production. Digitalization, massive marketing efforts, and supply demand elasticity of production tools have enabled this. But, we are reaching the point of no return in terms of resource absorption, saturation of needs, deterioration of environment, livestock, and resources. The marginal cost of "things" brings with it the risk of the whole planet's destruction! The next phase will require a paradigm shift to a more resilient and clean energy growth environment, for which hydrogen is one of the essential tools. It means more cooperation to reach scale, by sharing risks between industry players, strong alignment of development and deployment strategies between industry verticals, and a very stringent and sustainable regulatory and financial support scheme from the policy makers to ensure that efforts made will be valued over time. This also calls for different approaches to performance metrics from the financial markets and new accounting standards, to enable large industry players to commit significant amounts of investment to collaborative schemes, with adjusted returns at start. This would acknowledge the cost of developing competitive solutions using so many disruptive yet critical technologies as hydrogen to scale. What is a stake is a first, not only in the diversity of fields touched, but also in its criticality for the planet.

In this context, it is of paramount importance that a comprehensive review of the current state of hydrogen technologies is put forward as proposed in this book, which would also help design properly the key expected pillars of the future European Research Program for the years to come. This will both explain to the public where we stand and what is ahead of us, and also enable opinion leaders, policy makers, investors, and industry leaders to see the amount of progress achieved already toward the successful realization of a clean – and hydrogen-based – energy system.

For the European citizen, we have here a chance to prepare Europe early enough, not only to master and use the future key clean energy vector for its energy needs (it being coming from fossil or renewable sources) but also by making such moves early enough to also provide a new source of technologies, growth, and jobs



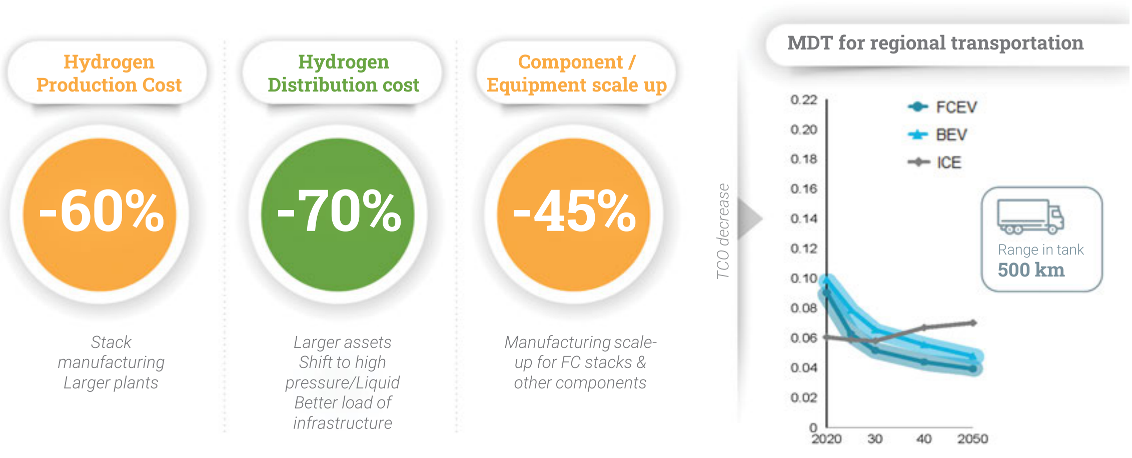
1. Hydrogen is the only alternative and low-carbon/renewable hydrogen competing with grey (optimal renewable or low-carbon shown)



Learning rates are highest for emerging technologies (PEM) and high volume FC for passenger vehicles
Learning rates for tanks are ~10-13%, somewhat lower than for fuel cells due to higher materials share of cost

1. Installed base: assuming 50/50 split of electrolysers volume with 50-75% utilisation; assuming 115 kW for PV, 250 kW for buses and 300 kW for trucks; LCOE used for solar cost; batteries in MWh
SOURCE: McKinsey; IRENA; BNEF; Ruffini & Wei (2018) (learning rates); DoE

Scale-up will drive cost down across the value chain



Hydrogen Production Cost

-60%

Stack manufacturing
Larger plants

Hydrogen Distribution cost

-70%

Larger assets
Shift to high pressure/Liquid
Better load of infrastructure

Component / Equipment scale up

-45%

Manufacturing scale-up for FC stacks & other components

TCO decrease

MDT for regional transportation

for the continent. Energy policies for Europe need to match the famous tryptich of sovereignty, competitiveness, and sustainability. Hydrogen, by proposing a versatile source of energy as feed, will enable Europe further to build energy independence, as a way to use all possible sources of energy, including locally produced with its strong renewable resources. It creates a further element of network integration and interconnection between southern and northern parts of Europe, as possible feed for a clean hydrogen production and the central and continental Europe as a strong energy consumer. Last, starting early, the phases of deployments should help master the key technologies and reach competitiveness earlier than other geographies.

As we said in a book done on the matter,[1] hydrogen also provides Europe with another way to provide guidance to the world with a better policy for sustainability and climate change, and therefore provides a strong alignment with Europe's political agenda in the global geopolitics.

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[1] Hydrogen, La transition énergétique en marche, PE Franc / P. Mateo, Preface from Pascal Lamy.

Ad van Wijk

Hydrogen key to a carbon-free energy system

Abstract: Hydrogen has a key role to play as a carbon-free energy carrier alongside electricity. Hydrogen can be transported worldwide by ship and pipeline and can be stored underground in large volumes. This makes it possible to deliver cheap renewable energy, especially solar and wind, cost efficiently at the right time and place to the customers. Next to this systemic role, hydrogen is important to decarbonize energy use in hard to abate sectors in industry, mobility, electricity balancing, and heating.

Future hydrogen systems will have similar characteristics as present day natural gas systems. Large-scale multi-GW renewable hydrogen production plants at good resources sites will produce a minimum of 1 million tonnes hydrogen. Hydrogen infrastructure can be realized by re-using the gas infrastructure, pipelines, and salt cavern storage, without major adaptations. As a transition, hydrogen produced from fossil fuels at the resource sites with Carbon Capture and Storage directly in the field below, can bring low-carbon hydrogen volume in the system. Such an approach can establish a fast, cheap, and reliable transition to a sustainable energy system, whereby hydrogen will fully replace natural gas, coal, and oil.

The conversion technology used today is based on combusting technologies: boilers, furnaces, engines, and turbines. These combustion technologies can be easily and are fast adapted to combust hydrogen. In future, however, combustion technologies will be replaced by electrochemical conversion technologies including heat pump technologies. These technologies offer the promise to be cheaper, more-efficient with no harmful emissions to the air, land, or water.

A smart symbiosis between electricity and hydrogen as zero-carbon energy carriers with electrochemical and heat pump technologies, will establish a clean, cost-effective, reliable, fair, and circular energy system.

1 The role of hydrogen in a carbon-free energy system

Hydrogen today (2020) is produced from natural gas and coal, emitting CO_2 to the air. The use of hydrogen today is especially as a feedstock in the chemical and petrochemical industry. However, in a future zero greenhouse gas emissions, reliable, affordable, and fair energy system, hydrogen needs to play a more important role. Hydrogen is, like electricity, a carbon-free energy carrier, with a high mass energy density. The role of hydrogen in a future sustainable energy system is therefore to transport and store large volumes of energy and to decarbonize energy use in hard-to-abate energy sectors.

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1.1 Worldwide energy and hydrogen consumption

1.1.1 At present, hydrogen is mainly used as feedstock, representing 2% of primary energy consumption

About 90% of the world's primary energy consumption in 2016, amounting to 556 EJ or 155,000 TWh, is fossil energy: oil, gas, and coal. This fossil energy is transported around the world by ship or pipeline, and then converted into a useful energy carrier, electricity, gasoline/diesel, or a gas. The conversion to a useful energy carrier is often associated with energy losses. For example, the efficiency of a modern gas-fired power plant is about 60%, which implies that 40% of the energy is lost as heat. These useful energy carriers are then distributed and used in houses, cars, factories, and so on.

Energy is used in many parts of our modern life: For heating and cooling houses and buildings; for electricity production to power equipment, appliances, and lighting; for transport by vehicles, ships, or planes; and for industry where processes require high temperature of heat and steam. Moreover, fossil energy is also a feedstock, from which chemical products such as plastics or fertilizers can be made. The final energy consumption represents the energy use by companies, houses, cars and is the primary energy consumption minus conversion losses in power plants, refineries, and so on.

A distribution of 2014 global final energy consumption [1] is given in the Fig. 1.

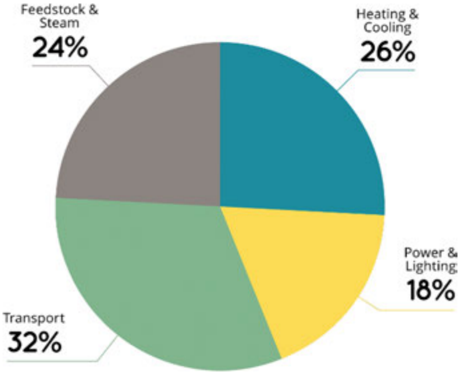


Fig. 1: Final energy consumption worldwide [1].

At present, hydrogen is mainly produced from natural gas and coal and primarily used as a feedstock to produce chemical products, ammonia (the main component of fertilizers), and methanol. And hydrogen is used in refineries to desulfurize oil and in the production of gasoline and diesel. The primary energy input by gas and coal is about 3.200 TWh, representing roughly 2% of worldwide primary energy consumption. Figure 2 presents the energy balance for worldwide hydrogen production and consumption [2]. At present almost all of the hydrogen is produced and used at or nearby chemical and petrochemical sites.

1.2 Solar and wind potential

1.2.1 In 1 h time the earth receives from the sun more energy than total worldwide energy demand

The question is whether all the world's fossil energy use can be replaced by renewable energy. From all renewable resources, solar and wind have by far the largest potential, therefore the question could be rephrased, "is it possible to generate worldwide energy use, by solar energy systems and wind turbines. The answer is simple: that is no problem. The potential of solar and wind energy is very large [1]."

If worldwide energy demand, 155,000 TWh, had to be produced with solar PV systems only, it would require a surface area covering about 10% of Australia (see Fig. 3) or 8% of the Sahara Desert [1]. The Sahara Desert is about 9.2 million km^2 in size, which is more than twice the area covered by the European Union.

The global wind energy potential is also very high. In a scenario where the entire worldwide energy demand that would be produced with wind turbines would only require an area of 1.5% of the Pacific Ocean, see Fig. 3. It should be noted that surface, however, is used to a limited extent, with one large floating wind turbine at every kilometer.

So there is more than enough space to produce all the necessary energy for the whole world with solar and wind. This is even the case with an increasing global population and rising prosperity level.

1.3 Development solar and wind levelized cost of electricity

1.3.1 At good resource locations, solar LCOE will be about 1 $ct/kWh and wind LCOE about 2 $ct/kWh before 2030

The development of electricity production cost by solar and wind energy, expressed in the LCOE, Levelized Cost of Electricity, has seen a steep decrease over the past 10 years. In the past couple of years, LCOE for onshore wind and solar PV at the best resource locations, are even below low cost electricity generation by fossil fuels, as showed in Fig. 4 [3]. Recent Tenders for 2 GW Solar PV in Abu Dhabi and 1 GW solar PV in Portugal has resulted in prices respectively of USD 1.35 cents/kWh [4] and Euro 1.12 cents/kWh [5]. Also wind onshore tenders have shown prices between USD 2 and 3 cents/kWh, for example in Mexico [6].

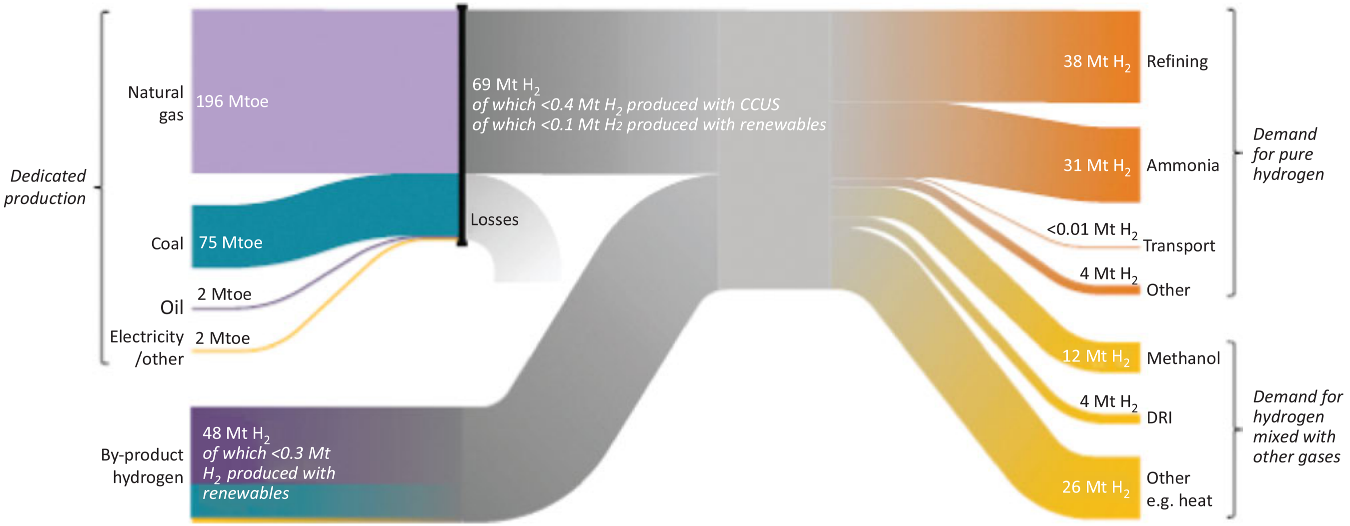


Fig. 2: Energy balance for worldwide hydrogen production and consumption 2018 [2].

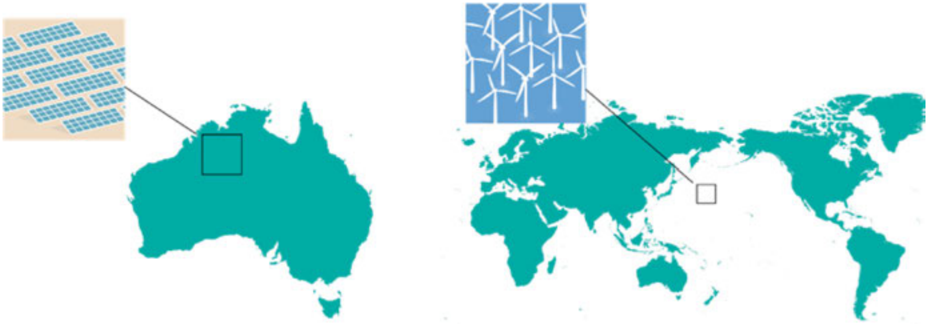


Fig. 3: Surface needed to meet global primary energy demand (155.000 TWh) by solar (10% of Australia) or wind (1.5% of Pacific Ocean) [1].

The expectations are that prices could drop to USD 1 cent/kWh and even below for solar PV and for wind onshore below USD 2 cent/kWh before 2030. Also, offshore wind and concentrating solar power will show price reductions to about USD 2–3 cents/kWh.

1.4 Why hydrogen?

1.4.1 Hydrogen is needed for long distance transport and large-scale storage of renewable energy and to decarbonize hard-to-abate end-use sectors

Low electricity production cost for solar and wind are at locations that are, in most cases, far from the energy demand, in desert areas, at remote windy sites or at sea. The new challenge is therefore "How do we bring this cheap solar and wind energy at the right time at the right place." Converting renewable electricity into hydrogen makes it possible to transport hydrogen over long distances by pipeline or ship and to store hydrogen at large-scale underground at salt caverns and maybe in some empty gas fields. Hydrogen transport and storage is thereby much cheaper than electricity transport and storage, if possible at all.

Next to this transport and storage function, hydrogen can be used to decarbonize energy use in hard-to-abate sectors. Hydrogen can be used as a renewable feedstock, in the chemical, synthetic fuel, and steel production sectors. Also for high and low temperature heating, hydrogen can replace natural gas, oil, or coal more easily than electricity. Hydrogen can replace rather easy natural gas in boilers, furnaces, engines, and gas turbines with some adaptations. In mobility, hydrogen and/or ammonia can replace gasoline and diesel, even up to 100%, in existing combustion engines. However, fuel cell-electric drive trains will replace combustion drive trains in future, especially in heavy transport such as trucks, busses, ships, planes and also in future

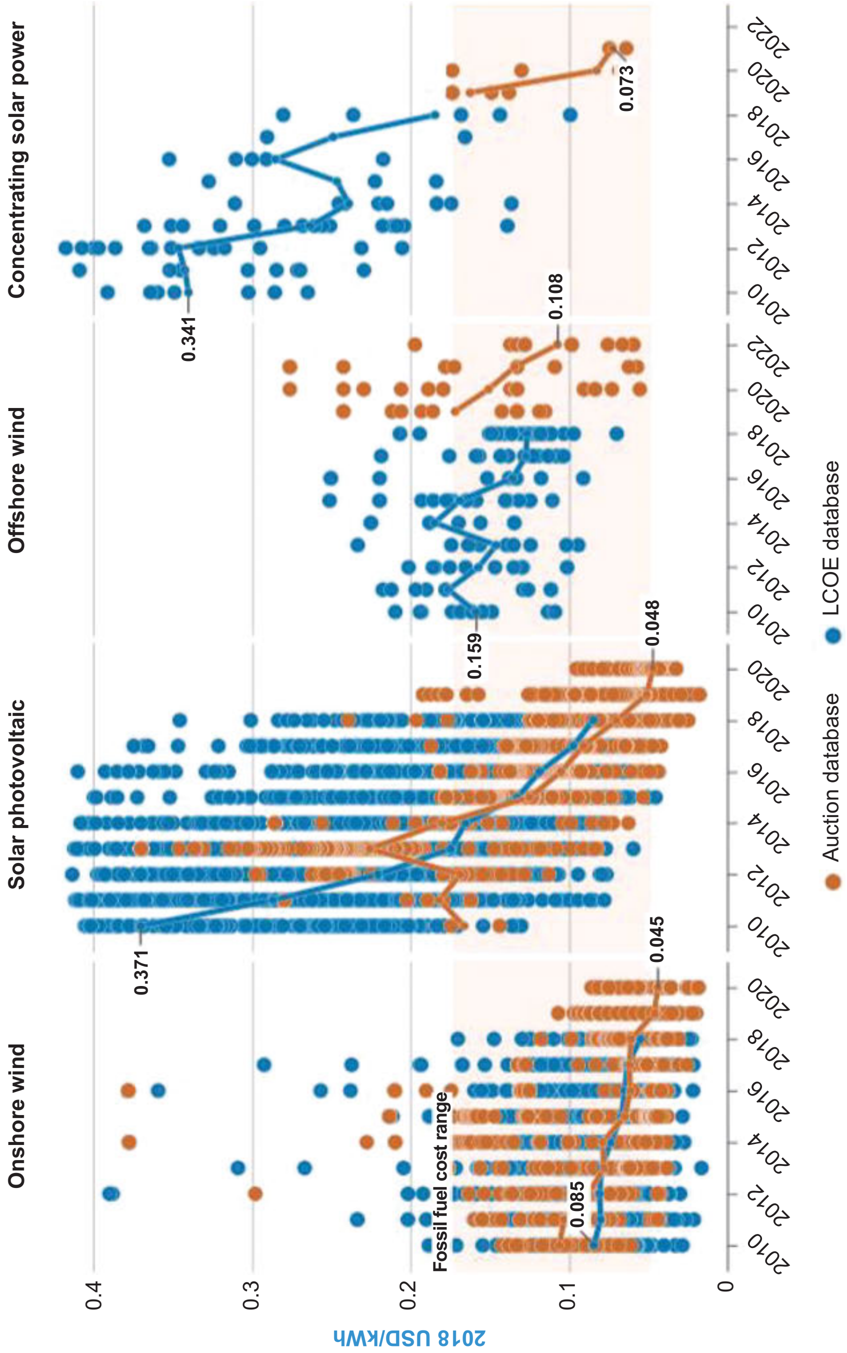


Fig. 4: The LCOE for projects and global weighted average values for CSP, solar PV, onshore and offshore wind 2010–2020 [3].

drones. Also in electricity generation, especially for electricity balancing, hydrogen and/or ammonia can replace natural gas rather easily.

The Hydrogen Council showed these different functions for hydrogen in a carbon-free energy system, in Fig. 5 [7].

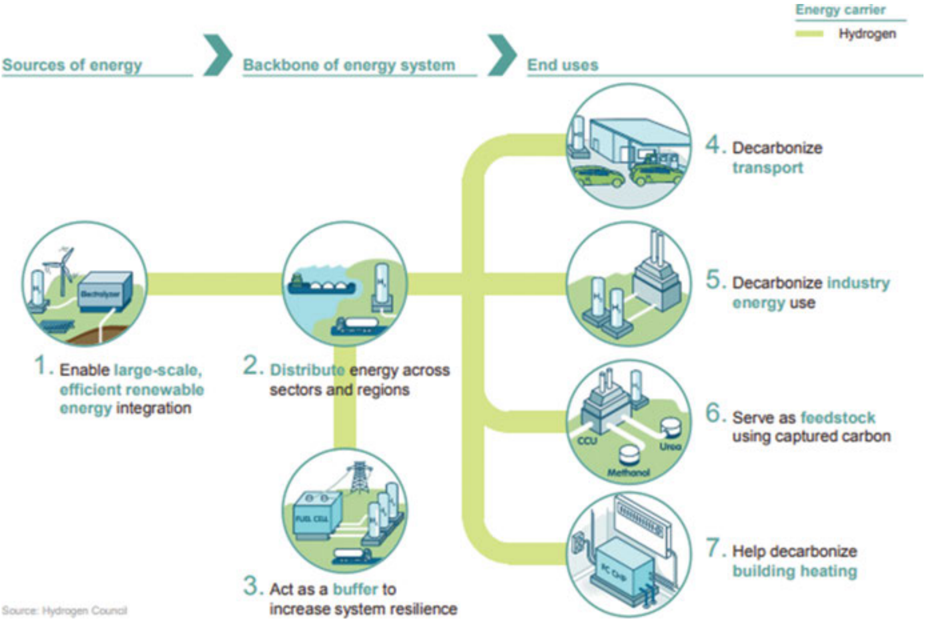


Fig. 5: Hydrogen has seven roles in energy transport, storage, and in decarbonizing major sectors of the economy [7].

1.5 Hydrogen characteristics

1.5.1 Hydrogen has a high energy density by mass, but a low energy density by volume

Hydrogen is the first element in the periodic table of elements and therefore the lightest element. In Tab. 1 a selection of the energy and physical properties is given for both hydrogen and methane.

Some general observations about hydrogen characterizations are the following [16]:

- Hydrogen is non-toxic and non-poisonous;
  - it will not cause ill effects if inhaled with ambient air,
  - it will not contaminate groundwater; hydrogen has a very low solubility in water,
  - it is not a pollutant when released in the air or in water.

Tab. 1: Properties for hydrogen and methane. (HHV = higher heating value, LHV = lower heating value).

Property	Unit	Hydrogen	Methane
Density (gaseous) [8]	kg/m^3 (25 °C, 1 bar)	0.0813	0.657
Density (liquid) [8]	kg/m^3	71.14 (−253 °C, 1 bar)	422.6 (−162 °C, 1 bar)
Boiling point	°C at 1 bar	−252.76	−161.6 [9]
Mass energy density	MJ/kg (HHV) MJ/kg (LHV)	141.8 [10] 120.0	55.5 [11] 50.0
Volume energy density (25 C, 1 bar) [12]	MJ/m^3 (HHV) MJ/m^3 (LHV)	11.54 9.76	36.46 32.85
Auto-ignition Temp.	°C	500	580
Flammability limits [13, 14]	% in air by volume	4%–75%	5%–15%
Ignition energy [15]	MJ	0.02	0.28
Buoyancy [13]	Relative to Air	14 × lighter	2 × lighter (natural gas)
Rising speed in air [13]	m/s	20	3.3 (natural gas)

- Hydrogen is odorless, colorless, and tasteless, which makes it undetectable by human senses;
- Hydrogen is extremely flammable. However, this is mitigated by the fact that hydrogen rapidly rises and often disperses before ignition.
- Hydrogen has a high energy density by mass, but a low energy density by volume compared to other fuels.

2 Hydrogen production technologies; state of the art and “color”

Hydrogen, like electricity, is not an energy source but an energy carrier; it can be produced from fossil fuels and also from renewable energy sources. At present, hydrogen is mainly produced from gas via steam methane reforming or from coal by coal gasification. However, hydrogen can also be produced from water, by using electricity to split the water molecule into hydrogen and oxygen. And this process could be reversed, producing electricity and water via a chemical reaction between hydrogen with oxygen (from the air). Finally, hydrogen can be produced from biomass and biogenic waste, which can even result in negative CO_2 emissions.

In the end, it is the energy resource direct or indirect (for electricity production) that determines whether or not “renewable” or **“green”** hydrogen is produced. Using biogas, biomass, or biogenic waste as a resource, also “renewable” or “green” hydrogen is produced, although CO_2 will be produced too. This CO_2 is renewable or green CO_2 and could be released to the air, having a net zero CO_2 balance. However, this “green” CO_2 could be captured and used as a green feedstock or even stored underground.

2.1 Hydrogen production from fossil hydrocarbons

2.1.1 Steam methane reforming

Methane (CH_4), the main component of natural gas, is a molecule with one carbon atom and four hydrogen atoms. Steam methane reforming (SMR) is worldwide the most used process to produce hydrogen from natural gas. Steam methane reforming is an endothermic process that requires temperature between 750–900 °C, a pressure above 30 bar and a catalyst, see Fig. 6. Steam (H_2O) reacts with methane (CH_4) to form hydrogen (H_2) and carbon dioxide (CO_2), described by the following reactions [17]:

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$

$$CO + H_2O \rightarrow H_2 + CO_2$$

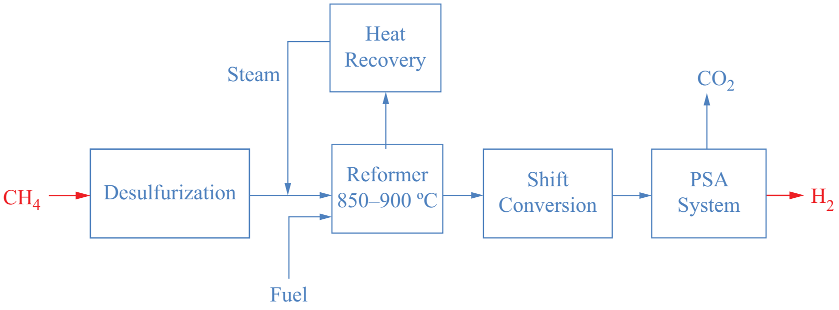


Fig. 6: Flow diagram of the steam methane reforming process [17].

2.1.2 Coal gasification/partial oxidation

Coal and oil or heavy hydrocarbons (C_nH_m) consisting of molecules with a multiple amount of carbon and hydrogen atoms. Due to the lower hydrogen-to-carbon ratios of these heavy hydrocarbons compared to methane, a larger portion of the hydrogen produced comes from steam. Partial oxidation or coal gasification is worldwide used to produce hydrogen from coal [17]. Coal gasification is an endothermic process, which requires temperatures between 1.100 and 1.400 °C and pure oxygen, see Fig. 7. The process is described by the following reactions:

$$C_nH_m + \tfrac{1}{2}nH_2O + \tfrac{1}{4}nO_2 \rightarrow (\tfrac{1}{2}n + \tfrac{1}{2}m)H_2 + nCO$$

$$nCO + nH_2O \rightarrow nH_2 + nCO_2$$

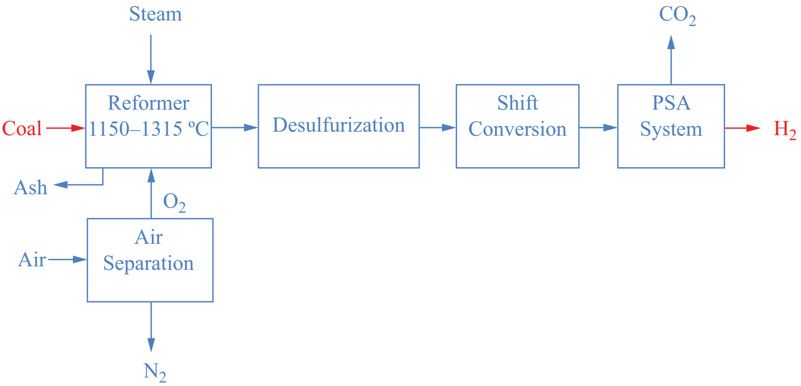


Fig. 7: Flow diagram of the partial oxidation or coal gasification process [17].

2.1.3 Pyrolysis

Pyrolysis is a process in which the only source of hydrogen is the hydrocarbon itself, which undergoes thermal decomposition through the following general reaction [18]:

$$C_nH_m + \text{heat} \rightarrow \tfrac{1}{2}\,mH_2 + nC$$

Through pyrolysis, natural gas can be decomposed into hydrogen and carbon. Catalytic thermal decomposition is the most common pyrolysis technology for this. BASF is actively involved in developing this technology and expects a first commercial plant around 2025 [19]. Introduced from the bottom of a vertical reactor, the natural gas is pre-heated in exchanging with carbon particulates on their way out by gravity, then heated at above 800 °C by electric induction in the middle of the vertical reactor, while hydrogen escapes from the top. The carbon atoms resulting from the split coagulate and then go down to the bottom of the reactor.

Natural gas is only a feedstock in this pyrolysis process. All energy for the process comes as electricity. The minimum energy required, 38 kJ/mol H_2, is much less than for water splitting via electrolysis, 285 kJ/mol H_2 [20]. In practice, the ratio is less advantageous depending on the pyrolysis technology and the losses that result from the high temperatures needed, but methane splitting still requires four to five times less electricity than electrolysis.

In this process, no CO_2 is formed, but only solid carbon, which can be used as a feedstock for all kind of products or as a soil enhancer is formed. When the electricity input for this process is from renewable resources, the hydrogen is produced without CO_2 emissions to the air. The produced hydrogen is called "**turquoise**" hydrogen.

2.1.4 Underground coal gasification

Coal gasification is also possible underground in a coal seam. In the Underground or in situ Coal Gasification process, injection wells are drilled into an unmined coal seam, and either air or oxygen is injected into the seam along with water. The coal face is ignited, and the high temperatures (about 1,200 °C) from the combustion and limited oxygen causes nearby coal to partially oxidize into hydrogen, carbon monoxide (CO), carbon dioxide (CO_2), and minimal amounts of methane (CH_4) and hydrogen sulfide (H_2S). These products flow to the surface through one or more production wells located ahead of the combustion zone. As the face is burned and an area depleted, the operation is moved to follow the seam. The CO_2 can be captured also and injected in the coal seam. Figure 8 illustrates the general process of underground coal gasification [21].

Underground coal gasification is associated with many risks and environmental concerns. There are several projects in operation, but large-scale applications need to deal with many technological, environmental, and safety challenges.

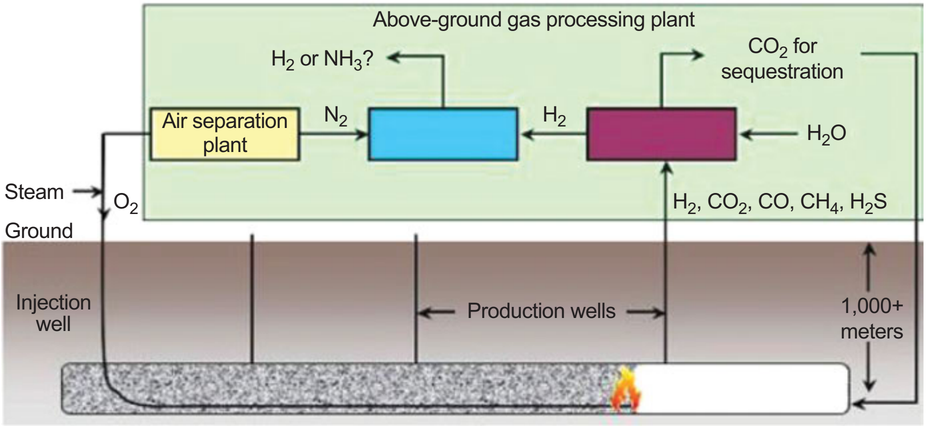


Fig. 8: Schematic illustration of underground coal gasification process [21].

2.2 Hydrogen production from biogenic resources

Traditionally wet biogenic residues (manure, food processing waste, sludge, etc.) produce biogas, consisting mainly of CH_4 and CO_2, via a digestion process. With a small-scale SMR plant and gas separation with membrane technology, the biogas can be converted to pure H_2 and CO_2.

Solid biogenic residues (waste wood, straw, sawdust, etc.) can be converted into a syngas, consisting mainly of H_2, CO, and CO_2, and solid char, by a gasification technology. Through a water shift process, the syngas can be fully converted into H_2 and CO_2 whereby the char is also a valuable product as feedstock or soil enhancer. There are a number of biomass gasification pilot plants operational; however, many of these gasification processes suffer with problems of tar.

Many new technologies to process biogenic residues into a bio-syngas, such as super critical water Gasification, Plasma Gasification and Microbial electrolysis cells, are in development [22]. The first two will be discussed, because for both, a first production plant is under construction.

2.2.1 Super critical water gasification

New technologies such as Super Critical Water Gasification can produce from wet biogenic residues a syngas, consisting of H_2, CH_4, and CO_2.

Supercritical water (SCW) exists at pressures higher than 221 bar and temperatures above 374 °C. By treatment of biomass in supercritical water (and in the absence of added oxidants) organics are converted into fuel gases and are easily separated from the water phase by cooling to ambient temperature, see Fig. 9. The produced high-pressure (HP) gas is rich in hydrogen. A typical overall reaction for glucose can be written as follows [23]:

$$2C_6H_{12}O_6 + 7H_2O \rightarrow 15H_2 + 2CH_4 + CO + 9CO_2$$

The Super Critical Water Gasification process consists of a number of unit operation as feed pumping and pressurizing, heat exchanging reactor, gas-liquid separators, and if desired, product upgrading. The reactor operating temperature is typically between 600 and 650 °C; the operating pressure is around 300 bar. A residence time of up to 2 min is required to achieve complete carbon conversion, depending on the feedstock. Heat exchange between the inlet and outlet streams from the reactor is essential for the process to achieve high thermal efficiency. The two-phase product stream is separated in a high-pressure gas-liquid separator ($T = 25–300$ °C), in which a significant part of the CO_2 remains dissolved in the water phase.

In Alkmaar, the Netherlands, a first super critical water gasification plant is under construction. This plant will be operational in 2023, producing 500.000 m^3 bio-syngas/year [24].

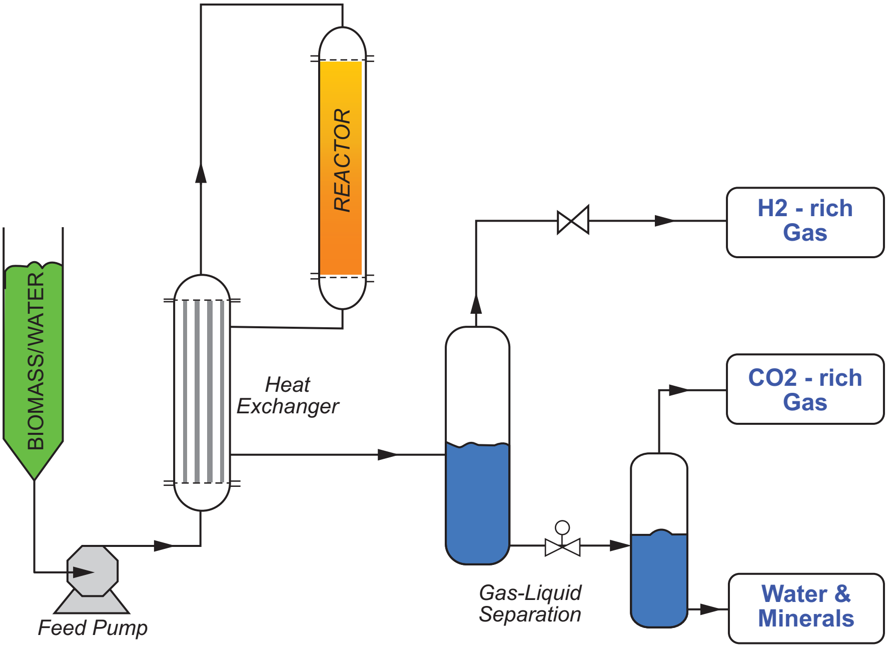


Fig. 9: Super critical water gasification process [23].

2.2.2 Plasma gasification

New technologies such as Plasma Gasification can produce from solid biogenic residues a syngas, consisting of H_2, CO, and CO_2.

A Plasma Enhanced Gasification (SPEG) system, developed by a start-up company SG-H2 energy, is a thermal catalytic conversion (oxygen blown, fixed-bed, counter-current gasification enhanced by plasma) process utilizing plasma arc torches. These plasma arc torches have been used at commercial scale for decades to increase the temperatures of oxygen blown fixed bed gasifier in order to optimize the efficiency of producing syngas and hydrogen from difficult to handle feedstocks such as waste, recycled mixed plastics, and tires.

In the SPEG at very high temperatures of 4,000 °C in a partially oxygen-deprived reactor, there is no combustion but complete molecular dissociation of all hydrocarbon organic compounds and their partial oxidation/conversion into bio-syngas. The resulting bio-syngas consists of H_2 and CO, is free of tar, heavy metals, and other long chain hydrocarbons (CxHy). Through a water-shift reaction, pure H_2 and CO_2 will be produced [25].

A first project will be realized in Lancaster, California. The facility shall utilize 120 tons/day of Refuse Derived Fuel (RDF) including plastic and recycled mixed paper as feedstock for a Plasma Enhanced and Oxygen fired Gasifier to produce green H_2 rich gas which shall be further enhanced and conditioned to 11 tons of 99.99% pure Green H_2/day. This plant is expected to be operational in 2023 [26].

2.3 Hydrogen production from water

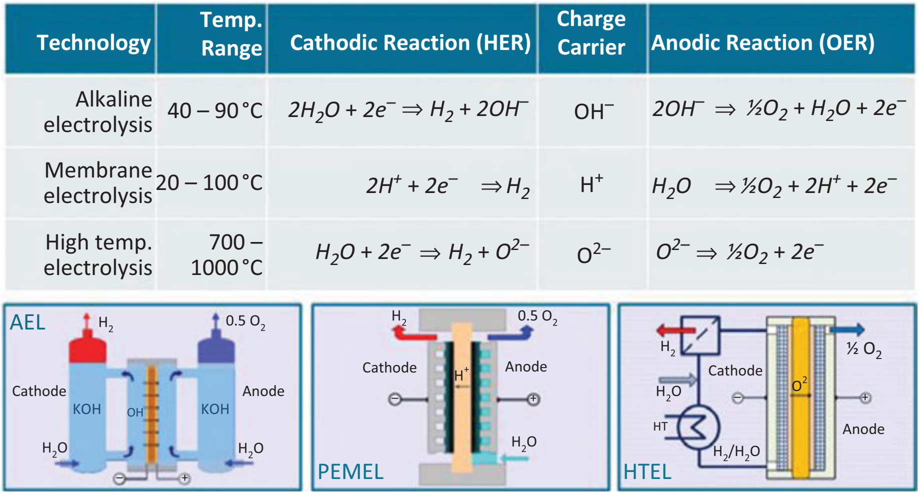
Hydrogen can be produced from water. Several processes exist to split the water molecule into hydrogen and oxygen: electrolysis, photolysis or photo-electrochemical conversion, thermochemical water splitting. Water electrolysis is the most common and mature technology. Other water splitting processes are still in a research phase [27].

2.3.1 Water electrolysis

Hydrogen can be made from water (H_2O) in a process called electrolysis, which is a chemical reaction in which a substance is decomposed into components under the influence of an electric current. In water electrolysis, the water molecule (H_2O) is split into hydrogen (H_2) and oxygen (O_2), depicted by the following overall reaction:

$$\text{Electrolyzer: } 2H_2O + 2e^- \rightarrow 2H_2 + O_2$$

There are different kinds of water electrolysis technologies such as alkaline, membrane and high temperature electrolysis. An overview of the chemical reactions and process characteristics are given in Fig. 10.



Technology	Temp. Range	Cathodic Reaction (HER)	Charge Carrier	Anodic Reaction (OER)
Alkaline electrolysis	40 – 90 °C	$2H_2O + 2e^- \Rightarrow H_2 + 2OH^-$	OH^-	$2OH^- \Rightarrow ½O_2 + H_2O + 2e^-$
Membrane electrolysis	20 – 100 °C	$2H^+ + 2e^- \Rightarrow H_2$	H^+	$H_2O \Rightarrow ½O_2 + 2H^+ + 2e^-$
High temp. electrolysis	700 – 1000 °C	$H_2O + 2e^- \Rightarrow H_2 + O^{2-}$	O^{2-}	$O^{2-} \Rightarrow ½O_2 + 2e^-$

Fig. 10: Schematic view, cathodic and anodic reactions for alkaline, membrane and high temperature electrolysis [67].

Alkaline electrolyzers are considered a mature technology, currently used to produce chlorine, but now adapted for hydrogen production. Polymer electrolyte membrane (PEM) and high temperature solid oxide electrolyzer (SOEC) electrolyzers are going through a steep learning curve. Alkaline, PEM, and SOEC electrolyzers can be used for water electrolysis to produce hydrogen. All electrolyzer technologies consist of electrolyzer cells that are combined to build an electrolyzer stack. To build a GW scale electrolyzer, a number of electrolyzer stacks need to be placed in parallel. Electrolyzer technologies are expected to achieve remarkable technology improvements in the next decade. Amongst others, higher efficiencies, less degradation, higher availability, larger cell sizes, higher operating pressure, less critical material use together with overall reduced material use, will reduce hydrogen production cost by electrolyzers.

However, next to these technology improvements, especially installed capacity volume and plant size will bring down the electrolyzer cost. An electrolyzer plant has a similar technology structure as a solar power plant. Both electrolyzers and solar plants are built by producing cells, assembling a number of cells to a solar-module/electrolyzer-stack and installing a number of modules/stacks to realize the required plant capacity. Although different, a comparable cost reduction process similar to solar power plants can be foreseen for electrolyzer plant. Automated production of the electrolyzer cell components, cells and stacks will bring down the cost for the electrolyzer stacks and building GW scale electrolyzer plants will reduce the balance of plant costs/kW. The balance of plant costs are the costs for compressors, gas cleaning, demineralized water production, transformers, and the installation cost. A substantial electrolyzer market volume together with realizing GW-scale electrolyzers, are essential drivers for significant cost reductions [2, 28].

2.3.2 Photo-electrochemical water splitting

Hydrogen can also be produced by a photo-electrochemical (PEC) process, whereby sunlight is used to split a water molecule into hydrogen and oxygen. In a photo-electrochemical water splitting process, photons are first absorbed by the photo-electrode producing electrons and holes, which are then separated and participated in the hydrogen evolution reaction on cathode and the oxygen evolution reaction on anode, see Fig. 11 [29].

This technology is still in a research phase. Many universities and research labs around the world perform research into photo-electrochemical water splitting. Over the past years, considerable efficiency improvements have been reported. In July 2020, the Australian National University claims to have set a record efficiency of 17.6% [30]. However, improving solar fuel water splitting efficiency facing tremendous challenges, due to the energy loss related to fast recombination of the photo-generated charge carriers, electrode degradation, as well as limited light harvesting.

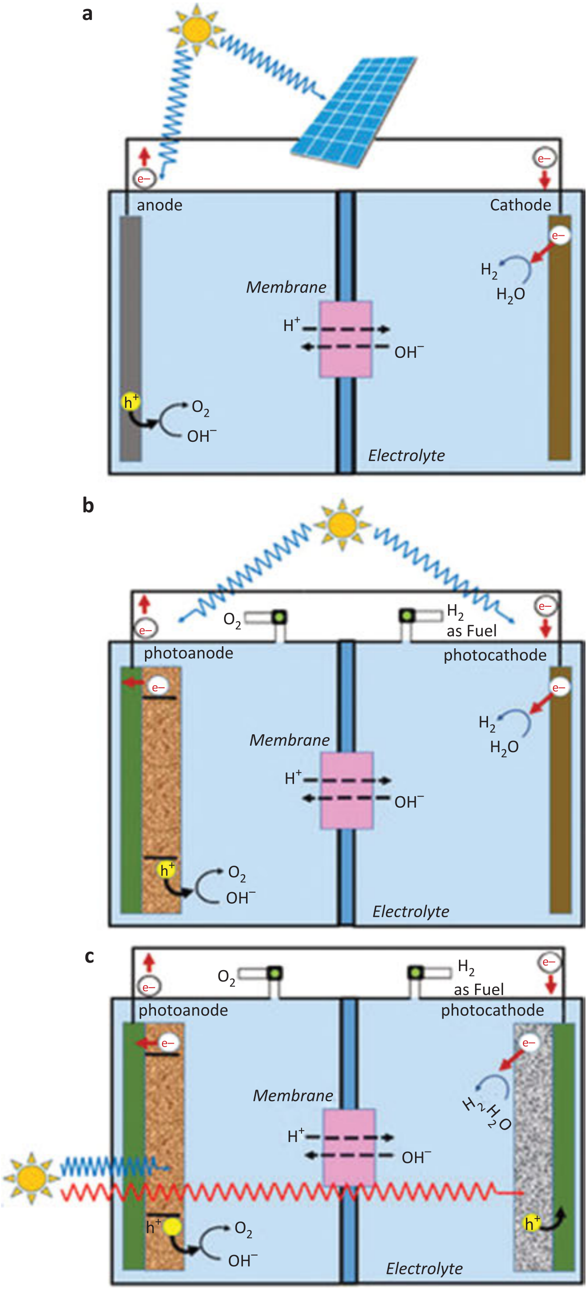


Fig. 11: General illustration of photo-electrochemical water splitting (PEC). (a) A single photo-electrode PEC configuration powered by a photovoltaic (PV) cell to allow water reduction at the cathode. (b) A two photoelectrodes PEC configuration connected in parallel. (c) A two photoelectrodes connected in series [29].

Next to this, also cost reduction of PEC will be challenging, because scarce and precious materials are used today.

2.4 The “color” of hydrogen

Hydrogen is a carbon-free energy carrier. However, the energy source together with the production process, additional input energy and flue gas treatment processes determines whether or not direct or indirect CO_2 emissions to the air will take place. An overview of the described hydrogen production technologies with their present (2020) maturity level, main output products and the related CO_2 emission to the air, expressed in a “color” are summarized in Tab. 2. It is humorous to describe a colorless gas with a color, but the color of hydrogen indicates the amount of CO_2 emissions to the air. However, it is not a precise definition of the amount of CO_2 emissions to the air, it only gives an impression.

The general opinion is that renewable or green hydrogen, without CO_2 emissions to the air can only be produced by water electrolysis using renewable electricity, whereby renewable electricity is most often seen as only solar and wind electricity. From this table, it is obvious that using biogenic waste could produce also renewable or green hydrogen. When the CO_2 from these processes is captured and used or stored, hydrogen from biogenic waste could even have negative CO_2 emissions to the air. And even hydrogen production from natural gas could have zero CO_2 emissions to the air, with pyrolysis process, whereby the used electricity is from renewable resources.

Tab. 2: Hydrogen production processes, their maturity status, main output molecules, and their “color.”

Source	Process/Technology	Maturity	Main Output	Color of Hydrogen
Natural gas	Steam methane reforming	Mature	$H_2 + CO_2$	**Grey** or **blue**, depending on the CCS technology 50–90% of CO_2 can be captured and stored. With ATR higher CO_2 emission reductions with lower cost are possible
	Auto-thermal reforming	Mature	$H_2 + CO_2$	
	Thermal pyrolysis	First plant 2025	$H_2 + C$	**Turquoise**, CO_2 emissions Depend on the source for electricity production

Tab. 2 (continued)

Source	Process/Technology	Maturity	Main Output	Color of Hydrogen
Coal	Partial oxidation/ gasification Underground coal gasification	Mature Projects exist	$H_2 + CO_2 + C$ $H_2 + CO_2$	**Brown** or **blue**, depending on the CCS technology 50–90% of CO_2 can be captured and stored.
Solid Biomass, Biogenic waste	Gasification plasma gasification	Near Maturity First Plant 2023	$H_2 + CO_2 + C$ $H_2 + CO_2$	**Green** Negative CO_2 emissions possible
Wet Biomass, Biogenic waste	Super critical water gasification Microbial electrolysis cell	First Plant 2023 Laboratory	$H_2 + CH_4 + CO_2$ $H_2 + CH_4$	**Green** Negative CO_2 emissions possible
Electricity + Water	Electrolysis Alkaline PEM SOEC	Mature Near Maturity Pilot Plants	$H_2 + O_2$ $H_2 + O_2$ $H_2 + O_2$	All shades of **grey** to **green** depending on the source for electricity production
Sunlight + Water	Photo-electrochemical	Laboratory	$H_2 + O_2$	**Green**

3 Hydrogen system cost

Energy system cost is most important, not energy system efficiency

Hydrogen system cost is the cost to produce hydrogen plus the cost for transport and storage to deliver the produced hydrogen to the right place and the right time. Therefore, the cost for hydrogen production, transport, and storage will be discussed. And finally a system cost comparison is made, between the cost of roof-top solar electricity and desert solar electricity that is converted into hydrogen transported and stored and converted to electricity again. It shows that in a sustainable energy system cost and not system efficiency needs to be the determining factor.

3.1 Hydrogen production cost

3.1.1 Hydrogen production cost from natural gas and solar PV are comparable by equal energy cost

Many studies have made hydrogen production cost analysis, amongst which are the IEA, Bloomberg-NEF, DNV-GL, the Hydrogen Council and many others. In general, for all mature hydrogen production technologies, the energy cost is the most important factor in the hydrogen production cost. The IEA analyzed the production cost of hydrogen from natural gas in several parts of the world, see Fig. 12. The hydrogen production are the lowest in regions with low gas prices, the Middle East, the Russian Federation, and North America and highest in gas importing countries such as Japan, Korea, China, and India. Gas prices vary between 3 and 11 dollar/million Btu (0,010–0,038 dollar per kWh) with fuel costs the largest cost component accounting for between 45% and 75%. The hydrogen production cost by SMR from natural gas varies between 0.9 to 1.8 dollar/kg H_2.

The hydrogen production cost by SMR with carbon capture and storage (CCS) is also calculated by the IEA. The results show that CCS adds about 1 dollar/kg hydrogen to the hydrogen production cost. If a carbon tax is added to the hydrogen production cost from natural gas by SMR, every 10 dollar/ ton CO_2 price adds about 0.1 dollar/kg to the hydrogen price.

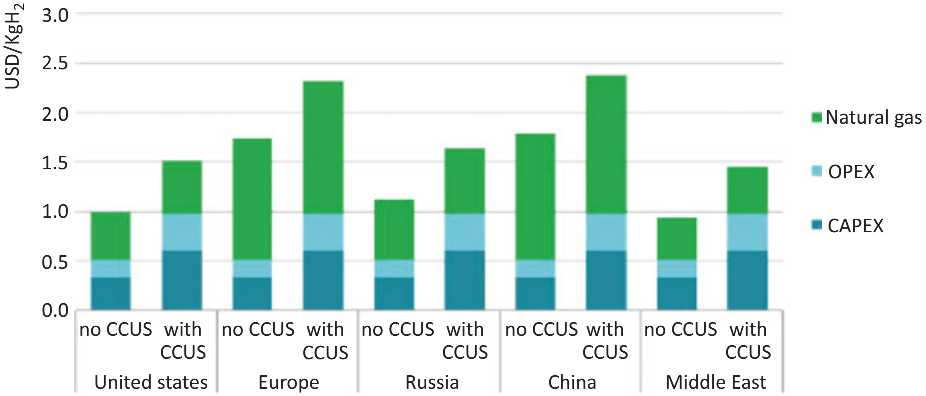


Fig. 12: Hydrogen production cost using natural gas in different regions in 2018 [2].

Hydrogen can also be produced by water electrolysis with electricity as energy input. Also in water electrolysis, the energy (electricity) cost is the most important factor in the hydrogen production cost. The IEA has analyzed the hydrogen cost as a function of full load hours for different electrolyzer investment cost and electricity cost, see Fig. 13. It shows clearly that the electricity cost is the most determined factor in the hydrogen production cost. As a rule of thumb every 10 dollar/MWh (0.01 dollar/kWh) with an electrolyzer efficiency of 80% HHV (67% LHV) adds 0.5 dollar/kg H_2 Of course the electrolyzer Capex and Opex cost at low full load hours, which is the case for solar PV contributes also to the hydrogen production cost. As an example the hydrogen production cost from solar PV electricity cost of 0.01 dollar/kWh, electrolyzer Capex of 250 dollar/kW and 2.000 full load hours are about 1 dollar/kg H_2 The electricity cost is 50% of the total hydrogen production cost.

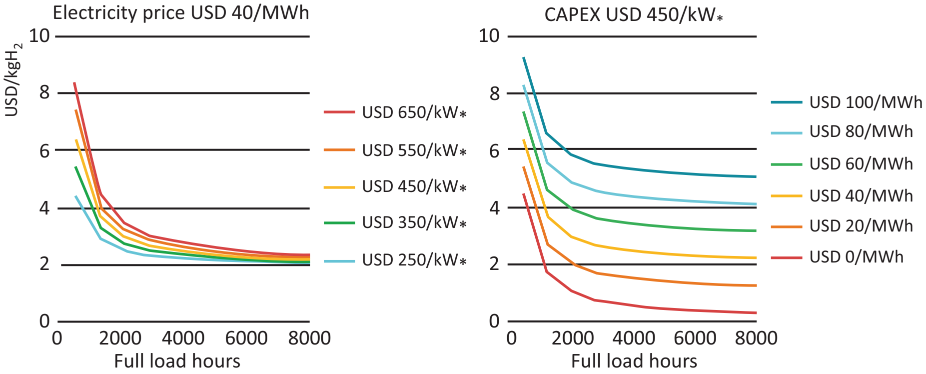


Fig. 13: Levelized cost of hydrogen production as a function of full load hours for different electrolyzer investment costs (left) and electricity cost (right) [2].

If a comparison is made between hydrogen production from natural gas and hydrogen production from solar PV electricity, a similar cost structure is seen. Natural gas cost of 3 million BTU (0.01 dollar/kWh) contributes about 0.5 dollar/kg hydrogen, which is the same for electricity cost of 0.01 dollar/kWh. SMR CAPEX cost, estimated by IEA, are between 500 and 900 dollar/kW and with 8.000 full load hours it contributes also about 0.5 dollar/kg H_2. This equals the CAPEX cost of 250 dollar/kW for electrolyzers with 2.000 full load hours, which is the case for solar PV.

In the Hydrogen Europe report “Green Hydrogen for a European Green Deal; a 2×40 GW Initiative” the hydrogen production cost are analyzed when 2 × 40 GW electrolyzer capacity will be realized in the European Union, North Africa and Ukraine, in the period up to 2030. When this market will be created, the electrolyzer industry will be committed to the Capex, Opex, and efficiency developments for electrolyzer plants as presented in Tab. 3. The Capex and electricity cost are presented as a range. The low Capex and electricity cost will be realized at the “off grid” multi GW solar and wind hydrogen plants at good renewable energy resources sites. The high Capex and electricity cost will be realized at multi MW scale electrolyzer connected to solar/wind farms and the electricity grid, located near the hydrogen demand.

It can be concluded that renewable, green hydrogen production can compete with grey hydrogen production from natural gas in 2030 [31].

Tab. 3: Green Hydrogen production cost development [31].

Hydrogen Production by Electrolyzers*	Capex (€/kW)	OPEX %/yr Capex	System Efficiency (HHV**)	Electricity (4.000–5.000 hr) (€/MWh)	Hydrogen (€/kg)
2020–2025	300–600	1.5%	75–80%	25–50	1.5–3.0
2025–2030	250–500	1%	80–82%	15–30	**1.0–2.0**
Up to 2050	<200	<1%	>82%	10–30	0.7–1.5

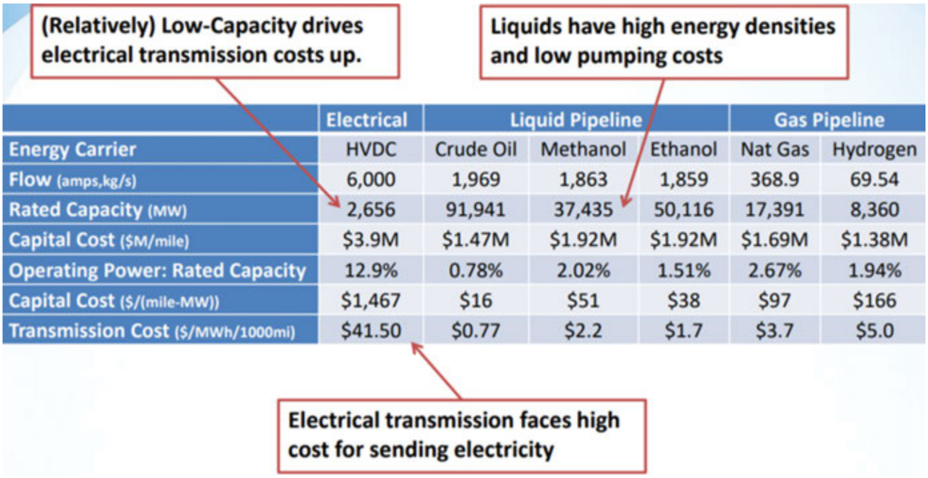
* Hydrogen production cost for hydrogen delivered at 30 bar pressure and 99.99% purity.
** HHV = higher heating value.

3.2 Hydrogen transport cost by pipeline

3.2.1 Hydrogen transport cost by pipeline 10 times cheaper than electricity transport cost by cable

Hydrogen transport by pipeline over distances of a couple of 1,000 km is a cost-effective way to transport energy. In comparison with electricity transport over these distances, hydrogen transport is a factor of 10 cheaper. In a study for the US-DOE, the cost for energy transport of natural gas, hydrogen, oil, methanol, ethanol, and electricity have been compared [32]. The results are shown in Fig. 14. As can be seen, the capacity of an HVDC transport is much lower than for liquid or gaseous molecule transport through a pipeline. Also energy losses at electricity transport are considerable due to the resistance in the cable. For molecule transport, there are no molecule losses, although due to the pressure drop over the pipeline compression energy is needed. Hydrogen cost could be further reduced by increasing the hydrogen flow speed in the pipeline, which is possible because hydrogen is lighter than natural gas, and therefore turbulence effects will occur at higher flow speeds. In the study for US-DOE, the flow speed for hydrogen is kept the same as for natural gas.

In the paper “Hydrogen, the bridge between Africa and Europe” [33] hydrogen transport cost calculations have been carried out for a very large-scale hydrogen transport by pipeline, comparable to the size of the “Nordstream” natural gas transport pipeline, a “South-Nordstream” hydrogen pipeline from Egypt, via Greece to Italy, which is 2,500 km. The capacity is similar to the actual Nordstream, with 66 GW capacity, consisting of 2 pipelines of 48 inches each, would imply total investments of € 16.5 billion. The cost figures are derived from the Nordstream project [34] and a study for US DOE. With a load factor of 4,500 h/year, an amount of 300 TWh or 7.6-million-tonnes H_2/year can be transported. Given the assumptions, as shown in Tab. 4, the levelized cost for hydrogen transport by pipeline, is 0.005 €/kWh or 0.2 €/kg H_2.



(Relatively) Low-Capacity drives electrical transmission costs up.

Liquids have high energy densities and low pumping costs

	Electrical	Liquid Pipeline			Gas Pipeline	
Energy Carrier	HVDC	Crude Oil	Methanol	Ethanol	Nat Gas	Hydrogen
Flow (amps,kg/s)	6,000	1,969	1,863	1,859	368.9	69.54
Rated Capacity (MW)	2,656	91,941	37,435	50,116	17,391	8,360
Capital Cost ($M/mile)	$3.9M	$1.47M	$1.92M	$1.92M	$1.69M	$1.38M
Operating Power: Rated Capacity	12.9%	0.78%	2.02%	1.51%	2.67%	1.94%
Capital Cost ($/(mile-MW))	$1,467	$16	$51	$38	$97	$166
Transmission Cost ($/MWh/1000mi)	$41.50	$0.77	$2.2	$1.7	$3.7	$5.0

Electrical transmission faces high cost for sending electricity

Fig. 14: Transmission cost comparison between electricity transport cables, liquids, and gases through pipelines [32].

Tab. 4: The energy transport volumes and levelized cost of hydrogen transport for a “South-Nordstream,” connecting the good solar and wind resources in Egypt and Greece to the European gas grid in Italy [33].

South-Nordstream: Egypt-Greece-Italy **Levelized Cost of Hydrogen Transport by Pipeline**		
Assumptions		
Pipeline diameter	inch	48
Number of pipelines		2
Pipeline pressure	bar	100
Pipeline flow speed	m/s	30
Pipeline Capacity	**GW**	**2*33 = 66**
Pipeline Length	km	2,500
Specific Investment Cost	€/10GW/km	1,000,000
Capex (Total investment cost)	billion €	16.5
O&M cost (including compressor energy)	% Capex/yr	1
WACC (Weighted Average Cost of Capital)	%	7
Lifetime	yr	40
Load factor pipeline	hr/yr	4,500

Tab. 4 (continued)

South-Nordstream: Egypt-Greece-Italy
Levelized Cost of Hydrogen Transport by Pipeline

Calculations		
Energy Transport	**TWh/yr**	**300**
	Tonnes H_2/yr	**7.6 million**
Levelized cost of hydrogen transport	**€/kWh**	**0.005**
	€/kg	**0.2**

3.3 Hydrogen storage cost

3.3.1 Hydrogen storage in salt caverns has a large potential and is at least 100 times cheaper than battery storage

Although there are many technologies to store hydrogen [35], see Fig. 15, for a large-scale hydrogen storage, especially compressed hydrogen storage in salt caverns is the most economic today.

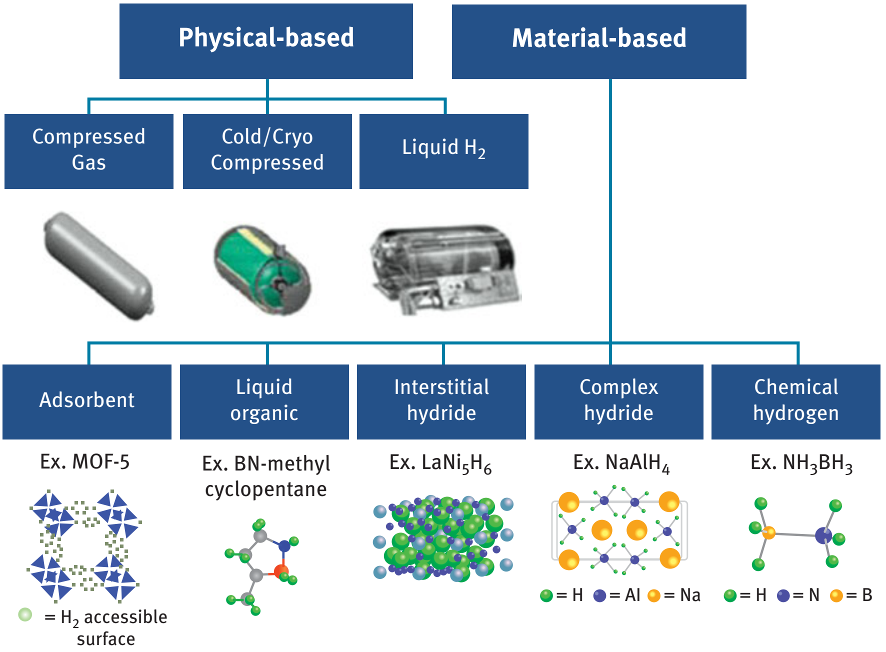


Fig. 15: How is hydrogen stored? [35].

Salt caverns can be used to store hydrogen in the same way as that they can store natural gas. In the United Kingdom, a salt cavern has been in use for hydrogen storage already for many decades. Also in the United States, salt caverns have been used to store hydrogen for many years.

In a typical salt cavern, hydrogen can be stored at a pressure up to 200 bar. The storage capacity of a salt cavern is up to 6,000 tonnes hydrogen (236.6 GWh HHV) [36].

The total installation costs, including piping, compressors, and gas treatment, are about € 100 million [37]. For comparison, if this amount of energy would be stored in batteries, with costs of 100 €/kWh, the total investment cost would be about € 24 billion.

The need for cheap hydrogen storage will grow exponentially over time. Salt caverns can provide this cheap hydrogen storage solution. Europe has still many empty salt caverns available for a large-scale hydrogen storage, but dedicated salt caverns for hydrogen storage capacity can be developed in the different salt formations in Europe. Potentially, hydrogen can be stored in empty gas fields that meet specific requirements to store hydrogen. However, this needs more research.

In a recent study by Jülich research center [38], the potential for hydrogen storage capacity in salt caverns, which are especially leached for hydrogen storage, was investigated. There is a huge potential for hydrogen storage in salt caverns all over Europe, see Fig. 16. Total onshore salt cavern storage capacity is 23,200 TWh of which 7,300 TWh could be developed taking into account a maximum distance to the shore of 50 km, called the constrained storage capacity. This maximum limit is set for the brine disposal. The offshore storage capacity is even larger than the onshore capacity, 61,800 TWh. It should be noted that the salt cavern storage capacity potentials are even larger than total final energy consumption in Europe. Although not studied so far, a substantial potential for hydrogen storage in salt caverns is available at many other places in the world too.

3.4 Energy system cost comparison shows the importance of hydrogen

3.4.1 Roof-top solar electricity cost in North West Europe comparable with desert solar electricity-hydrogen-electricity cost and delivered at any time needed

The debate today in comparing energy systems is about comparing the system energy efficiency. Converting electricity to hydrogen and back to electricity again, results of course in considerable energy losses, compared to direct use of electricity. That is true, of course, but is not the right way to make renewable energy system comparisons. Energy system comparison needs to be done on system costs and not

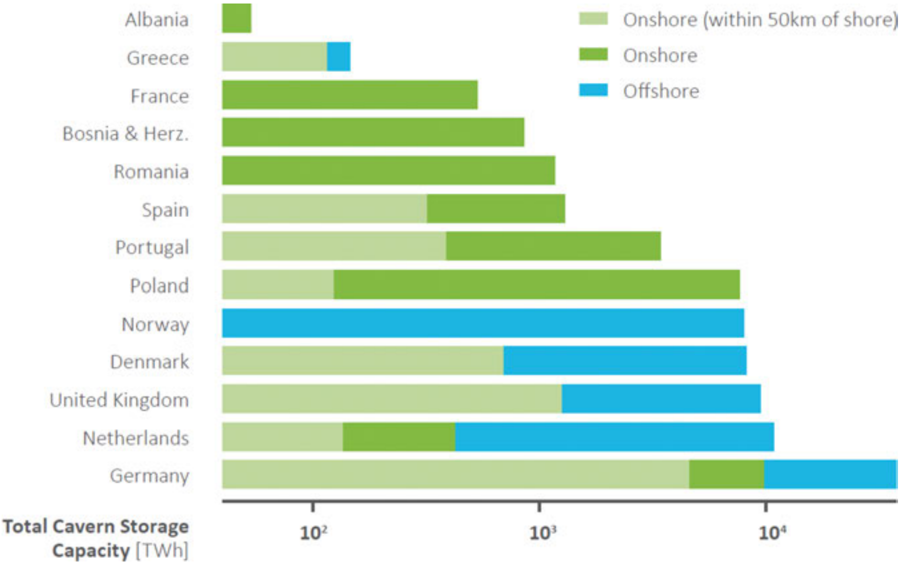


Fig. 16: The potential hydrogen storage capacity in salt caverns in Europe [38].

on system efficiency, because geographical difference in yield from solar and wind in addition to transport and storage cost have to be taken into account.

Today, in 2020, at the good resource sites, solar and wind electricity is even cheaper than electricity generated using fossil fuels. However, these good resources sites are mainly in areas far away from the demand that leaves the question how this cheap green energy can be delivered to the energy user at the right place and time. This requires transport and storage of energy. Transport of electricity is possible via electricity cables, but that is roughly 10 times more expensive than transporting the same amount of energy as hydrogen by pipeline as shown in chapter(3.2) Equally, storage of electricity in batteries or by pumping up water is more than 100 times as expensive than storing hydrogen in underground salt caverns, as shown in the chapter (3.3).

For longer distances, beyond the feasible range of cables or pipelines, energy will have to be transported by train, truck, or ship. The only feasible pathway is by converting electricity into hydrogen for transport. Like natural gas, hydrogen can be liquefied, which requires temperatures of –253 °C, only 20 ° above the absolute zero. Hydrogen can also be combined with nitrogen from air to produce ammonia, the main component of fertilizer, which is already liquid at –33 °C, so cheaper and easier to transport than liquid hydrogen.

Now when comes to calculating, which is cheaper? Is it cheaper to generate electricity from solar or wind far away from demand and to bring it to the user via electricity cables and when necessary, store this electricity in batteries? Or is a conversion to hydrogen and transport by pipeline and hydrogen storage in salt caverns and (if necessary) conversion back to electricity cheaper, despite the energy losses and extra conversion cost? Or is higher cost solar or wind electricity generation closer to the user, but with lower transport costs, a cheaper solution?

An example for a simplified comparison is given in Fig. 17. It is a comparison between a solar cell system on the roof of a house in North-Western Europe and a solar cell system in a desert. Both systems must supply 100 kWh electricity to the house. The assumption is that desert electricity can be produced at a cost of 1 Euro cent/kWh. Because the yield at the roof of a house in North-Western Europe is a factor 2 to 3 lower and the costs of a small system are a factor 2.5 to 3 higher than for a large system in the desert, the solar panels on the house produce electricity at a cost of 5–9 Euro cents/kWh. So, 100 kWh electricity from the solar panels on the roof costs 5–9 Euro.

The solar power from the desert, on the other hand, is converted via electrolysis into hydrogen, liquefied, and transported in a ship; put in a pipeline and converted into electricity at home with a fuel cell. Electrolysis in the desert requires not only solar electricity but also water. By pipeline, sea water can be transported to these solar hydrogen production plants, reverse osmosis converts the sea water into demineralized water, the feedstock for hydrogen production. Even with distances over 1,000 km, these demineralized water cost, are only a couple of percent of total hydrogen production cost.

Despite all the extra costs and losses, 100 kWh of solar power from the desert costs about the same as that from the solar panels on the roof. The major advantage of the desert electricity, however, is the availability at any time, summer and winter and day and night [1].

It is also interesting to note that a factor of 2.5 more electricity must be produced in the desert given the conversion losses, but the number of solar panels placed on the roof or in the desert is approximately the same. After all, the same solar panel in the desert produces 2–3 times as much as on the roof in North-West Europe.

This simple example shows that a sustainable energy system is about total system cost and not about system efficiency. And it clearly shows the merit of hydrogen in a sustainable energy system, namely for cheap transport and storage of low cost solar and wind electricity.

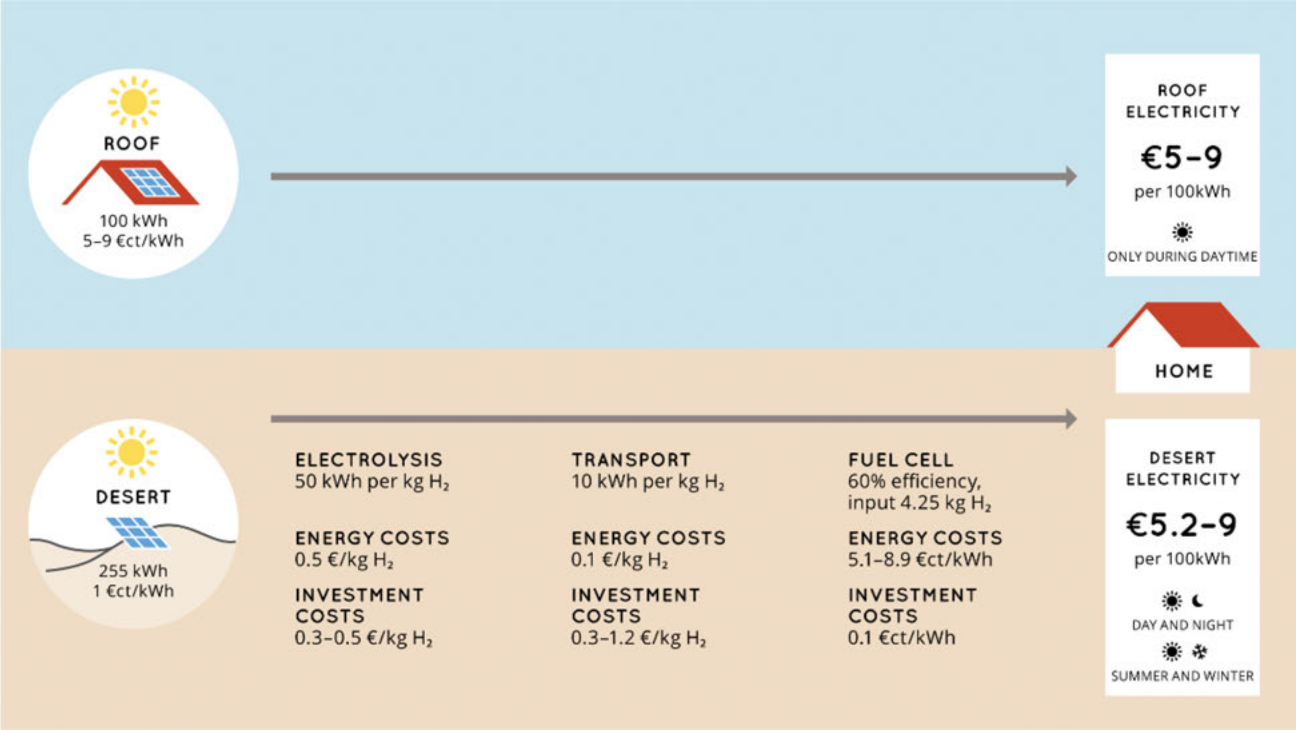


Fig. 17: Solar energy from rooftop in North-West Europe compared to solar energy from the desert [1].

4 Present natural gas, electricity, and hydrogen systems

The present natural gas system is characterized by a large-scale production from gas fields far from demand, whereby the gas is transport by transport pipelines or by ship over large distances. A gas transport and distribution pipeline system transport and distributes gas to the consumers. At present, electricity is produced in power plants mainly fueled by gas, oil, or coal. The fossil fuels are transported from production locations all over the world to these power plants. An electricity transport and distribution system will transport and distribute the electricity to the consumers. The hydrogen system at present is hydrogen produced from fossil fuels at the demand site (captive production). Gas or coal is transported to the hydrogen plants, whereby the hydrogen is produced and consumed at the same location. Only a limited, privately owned hydrogen pipeline infrastructure exists between some chemical and petro-chemical sites.

Present natural gas system lay out

Energy systems can be characterized by their production, infrastructure, storage, distribution, and demand structure. The natural gas system is characterized in general by a large-scale production from gas fields far from demand, large capacity pipeline transport over 1,000 km, central and a large-scale storage and meshed gas distribution grid that distributes the gas to millions of customers. In many regions in the world such a natural gas infrastructure and system exists and will be even expanded in the near future. A schematic view of the natural gas system and infrastructure is given in Fig. 18. The gas system includes the following:

- Gas production facilities at gas fields on- and off-shore plus import via pipeline and ship,
- Gas processing facilities to bring the gas quality on the right specifications,
- Large-scale storage facilities to balance supply and demand on daily to seasonal time scales,
- Transport pipelines with compressors to transport gas at high pressure to large consumers and to city gate stations,
- City gate stations where the gas pressure is reduced and brought on specification for distribution to local customers.
- Local gas distribution pipelines at medium and low pressure that distribute the gas to local customers.
- Local biogas production that is brought on the required gas quality specifications before it is fed into the local distribution pipelines.

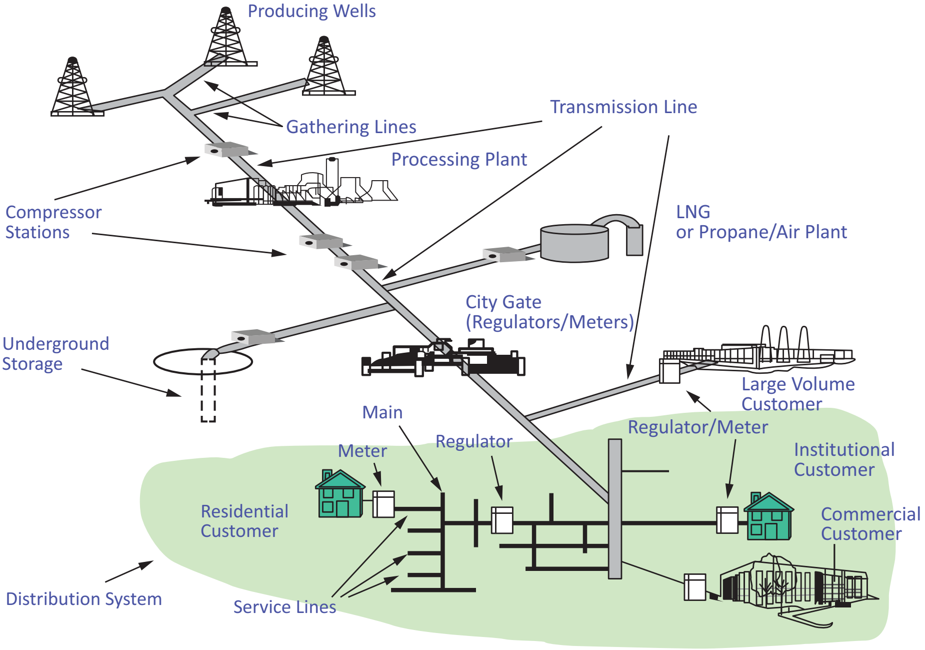


Fig. 18: A schematic view of a natural gas system [39]. Not included are local biogas/bio-methane production feeding at the distribution system.

4.1 Present gas, electricity, and hydrogen systems – Europe as an example

4.1.1 Energy production

Gas production in Europe is concentrated in Norway, the United Kingdom and the Netherlands, especially at the North Sea, many gas production locations are present. In the Northern Netherlands onshore, one of the largest gas fields in the world is located. In 2011 about 50 bcm (roughly 500 TWh HHV) was produced from this field; however, production will be stopped at the end of 2022 [40], due to the little earthquakes caused by the gas exploration. Norway has considerable gas production and reserves and to a lesser extent also the United Kingdom. In particular, Russia and Algeria are exporting gas to Europe by pipelines, see Fig. 19 and via liquefied natural gas (LNG), gas is imported by ship from all over the world.

At present, electricity production in Europe is still dominated by fossil fuel and nuclear power plants. The largest power plant in Europe is the Bełchatów lignite fired power plant in Poland with a capacity of 5.102 MW and an annual power production of 27–28 TWh [41]. The fuel for power plants is transported by pipeline or ship to the plant locations that are located in general within distances of up to a couple of 100 km from the demand centers.

At present, hydrogen is to a large extend used as a feedstock in the chemical and petrochemical industry. The production locations are at or near the demand. Production of hydrogen in Europe is mainly from natural gas by SMR plants. A typical large-scale SMR plant produces 150.000 m^3 H_2/h or about 100.000 tonnes H_2 (3.9 TWh HHV)/year.

4.1.2 Energy transport infrastructure

The European transport grid for natural gas is approximately 200,000 km long with a distribution grid that is a multiple of that. The transport grid has major connections to the large gas production fields, to Norway, Russia, and Algeria, see Fig. 19. As an example, there is a gas transport infrastructure available between North Africa and Europe, transporting gas from Algeria and Libya to Europe via Italy and Spain, see Fig. 19. The gas transport volume through these pipelines between North Africa and Europe is over 63.5 bcm (billion cubic meter)/year, which equals a capacity of more than 60 GW [42].

Next to the intercontinental gas pipeline infrastructure in Europe, 36 LNG terminals were operational – 7 under construction and 21 in the planning phase [43]. This makes it possible to import large quantities of LNG from all over the world.

The transport capacity by the natural gas grid is a multiple of the transport capacity in the electricity grid. In general, the capacity of one large gas transport pipeline is about 10–20 GW, while a large electricity transport cable has a capacity of about 1–2 GW. Also the electricity transport grid has no large capacity interconnections between countries, to the North Sea, Russia, or North Africa. As an example, Spain has only two transport cable connections of 700 MW each with Morocco.

Present hydrogen production in Europe is mainly by reforming natural gas. The gas pipeline infrastructure transports natural gas to the hydrogen SMR plants that are located at or nearby the demand for hydrogen in refineries and ammonia plants. There is no major hydrogen pipeline infrastructure, only some privately owned small hydrogen pipeline infrastructure between chemical clusters. The present hydrogen system is therefore called a “captive” production and consumption system.

4.1.3 Energy storage

Natural gas demand in Europe, especially in Northern Europe, shows a strong seasonal variation, in wintertime, the gas demand is 2–3 times higher than in summertime. However, natural gas production is constant throughout the year. Therefore, a

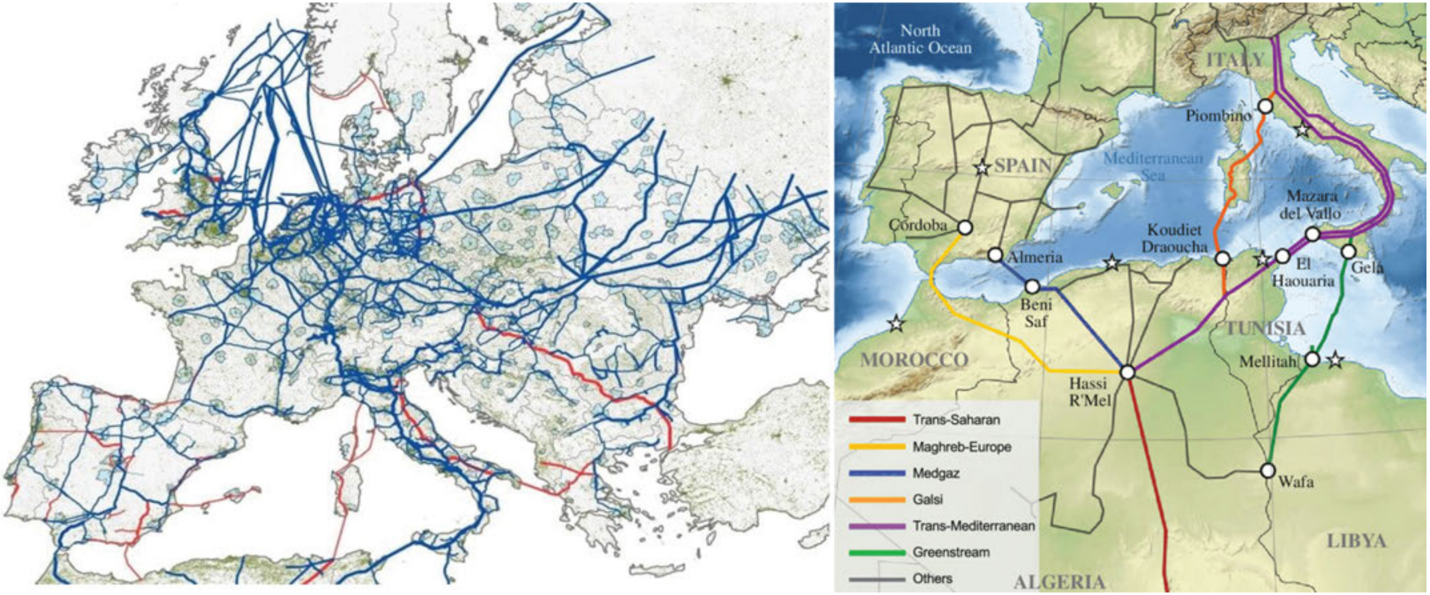


Fig. 19: Gas transport infrastructure in Europe (left) [68] and Gas transport infrastructure from North Africa to Europe (right) [69].

large-scale seasonal storage of natural gas is necessary. Natural gas is stored in empty gas fields, porous rock formations, and salt caverns. The overall storage capacity in operation within the EU28 amount to 89.2 bcm (871 TWh). The largest storage capacities for gas are in Germany, in total 21.8 bcm (213 TWh). Half of this storage is in salt caverns, amounting to 10.9 bcm (106.5 TWh) [42]. Germany has by far the largest gas storage capacity in salt caverns in Europe, but they are in use in several other countries too, see Fig. 20.

Salt caverns today are "left overs" from salt production. A typical salt cavern has a height of 300 meter and a diameter of 60–70 meter. A number of these salt caverns are in use for natural gas storage and in some other oil, compressed air, or other products are stored. As an example, the salt caverns in use in the Netherlands for gas storage can store about 50 million (500 GWh HHV) cubic meter gas each.

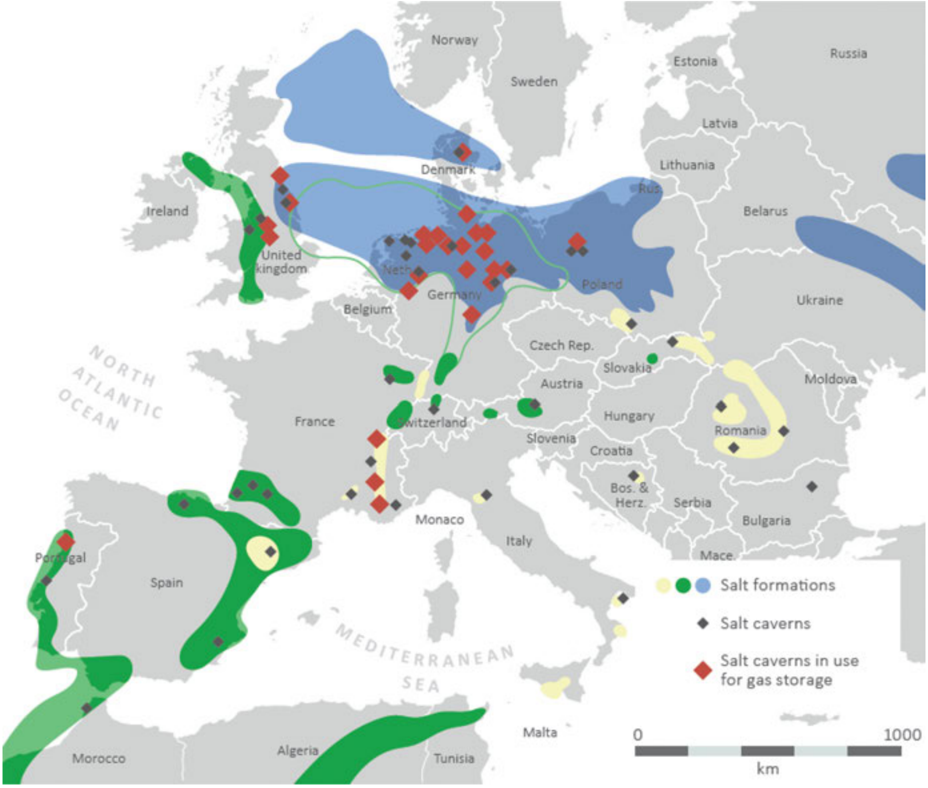


Fig. 20: Salt formations with salt caverns throughout Europe. The red diamonds are salt caverns in use for natural gas storage [44].

Total gas consumption in the EU28 in 2017 was 493 bcm (4,813 TWh) [45]. This total gas consumption includes 2,782 TWh as final gas consumption, with the remainder used as feedstock and for electricity production. The storage capacity is therefore 18% of total gas consumption in Europe. This storage capacity is especially necessary to balance large scale, seasonal, weekly, and daily gas demand fluctuations especially for space heating and to a lesser extent for electricity production.

Total electricity generation in the EU-27 in 2017 was 2,815 TWh [46]. Balancing electricity supply and demand is mainly done ramping up or down power output of power plants, and in most cases, gas fired power plants. That means that electricity balancing is done by gas storage. There is some storage in the electricity system via pumped hydro power. Total installed pumped hydro power in 2017 in the EU-28 had a capacity of 47.4 GW and generated 30.1 TWh. The electricity production from pumped hydro power storage was 1% of total [47].

In an all renewable electricity system, batteries could be an alternative for balancing supply and demand, on a daily or weekly basis. However seasonal storage will be a challenge due to the losses over time. Battery cost has decreased sharply over the past decade and will decrease further in future. Tesla and PG&E have announced (August 2020) to build the largest in the world battery storage system in California, with a storage capacity of 0.73 GWh and a rated power of 182.5 MW, with an option to expand to 1.2 GWh storage capacity [48].

Hydrogen storage facilities at present are limited, because hydrogen production follows the demand, and is mainly base load. The natural gas system and storage facilities deliver the flexibility, although in the United Kingdom since 1972 a salt cavern is in use for hydrogen storage.

4.1.4 Comparing present gas, electricity, and hydrogen system characteristics

The gas system is an order of magnitude larger then the electricity system both in volume as in capacity. The hydrogen system is at present even not an energy system, because there is no public and a large-scale infrastructure and can be characterized as part of the natural gas system. Gas is thereby providing the necessary flexibility for the electricity system as well as for the hydrogen system. The following scale observations can be made:

- Gas production at gas fields have a larger size in production volume and are located further from demand sites than power plants. In general, the dimensions in production volume and distance are about a factor 10 larger in the gas system compared to the electricity system.
- Gas can be transported over long distances and with large volumes by pipeline (continental to intercontinental) or ship (worldwide). Electricity can only be transported via cables (regional to continental). In general, the dimensions in transport

pipeline/cable length and capacity are a factor 10 larger in the gas system compared to the electricity system.
- Gas supply and demand balancing is via large-scale gas storage. Electricity production and demand balancing needs to be done at every moment by ramping up and down power plants. There is some storage in the electricity system via pumped hydro power, but in fact the gas system delivers the flexibility in the electricity system.
- Gas is supplied by pipeline to hydrogen production plants, located at or near the hydrogen demand. There is only a limited privately owned hydrogen pipeline infrastructure. The gas systems provide the necessary flexibility for hydrogen production.

In Tab. 5 system characteristics for present gas, electricity, and hydrogen systems are presented.

Tab. 5: System characteristics for present gas, electricity, and hydrogen systems.

	Gas System	**Electricity System**	**Present Hydrogen System**
Production volume per location	10–1,000 TWh/yr Gas field	1–30 TWh/yr Power Plant	0.1–4 TWh/yr SMR plant
Distance between production location and demand centers	Up to 4,000 km Pipeline Worldwide Shipment	Up to 1,000 km Cable	“Captive” production only for demand on location
Capacity Transport Pipeline/Cable	10–35 GW Pipeline	1–4 GW Cable (HVDC)	Some small Pipeline infrastructure on and between industrial sites
Infrastructure ownership	Public and Private (e.g. at North Sea, intercontinental)	Mainly Public	Private
Storage Capacity	200–500 GWh Salt cavern Gas Empty Gas field storage capacity factor 10 larger then salt caverns	5–25 GWh Pumped hydro power storage Largest battery storage system announced 0.73 GWh	100–250 GWh Salt cavern H_2 A couple of salt caverns are in use for H_2 storage

5 Future renewable hydrogen system

Future renewable hydrogen system will look like the present natural gas system

In 2050, a zero-carbon energy system needs to be realized in Europe. Hydrogen as an energy carrier and for decarbonizing hard-to-abate sector will contribute substantial to fulfil this goal. It requires a tremendous expansion of large-scale renewable hydrogen production, mainly from solar and wind resources. For an intermediate period, to reduce greenhouse gas emissions substantially in the coming decades, natural gas needs to be converted to hydrogen with CCS or by producing only solid carbon. This makes it possible that the natural gas infrastructure and storage facilities, can be converted to hydrogen quickly and cost effectively. And remarkable enough the gas transport infrastructure fits geographically well with a future hydrogen infrastructure that needs to connect the large-scale renewable hydrogen production to the demand. Also dedicated hydrogen storage in salt caverns can be realized at the hydrogen production sites, because salt formations are at or nearby these locations.

5.1 Future large-scale renewable and low-carbon hydrogen production characteristics

Hydrogen production will be located at the energy resource locations

In future, hydrogen can re-use the gas infrastructure, pipelines, and salt cavern storage without major adaptations. This can contribute to a fast, cheap, and reliable transition to a sustainable energy system, whereby hydrogen will fully replace natural gas. Hydrogen production will have to be at or near the resources, both large and small scale, and will connect to the hydrogen infrastructure only. So the system characteristics for hydrogen production will be as follows:

- Large-scale low-carbon hydrogen production at the gas or coal field locations for an intermediate time period. The CO_2 emissions will be captured and stored in the same field. Typical production sizes will be comparable with production size of gas or coal field minus the conversion losses. Production volume at gas fields could therefore be as large as 10 million tonnes (394 TWh HHV).
- Large-scale hydrogen production at the good solar and wind resource areas. At least with a production volume of 1 million tonnes (39.4 TWh) hydrogen. Such an amount of hydrogen can be produced from 25 GW solar PV or from 10 GW offshore wind.
- Small-scale hydrogen production from biogenic waste streams at the collection points. The bio-synthetic will be converted to H_2 and CO_2. Hydrogen will be fed into the hydrogen grid and CO_2 will be transported by pipeline or truck to the chemical industry or greenhouses.

- Small-scale hydrogen production from local renewable electricity production to alleviate electricity grid capacity constraints. The hydrogen will be fed into the hydrogen grid.

5.1.1 Blue and turquoise hydrogen production at gas fields to create hydrogen volume

The natural gas infrastructure needs to be fully converted to a hydrogen infrastructure. However, at the moment, natural gas is flowing through these pipelines. The natural gas is transported and distributed to millions of customers, where it is combusted to produce electricity, high, or low temperature heat. With the flue gasses from these combustion processes (gas turbines, furnaces, motors or boilers), the CO_2 is also released to the air.

At large power plants, chemical plants or refineries, the CO_2 emissions could be captured from the flue gasses and stored in empty gas fields or aquifers, at reasonable cost. However, this is not the case at the millions of space heating boilers in houses and buildings. So the question is how could all these millions of natural gas consumers realize, cost-effective and fast, a zero greenhouse gas emission energy system for heating/cooling, electricity, and mobility.

Reducing CO_2 emissions is possible by switching to electricity use, but this requires major investments in upgrading and expanding the capacity of the electricity grid. Next to this, the end-use equipment has to be replaced by new technology, such as heat pumps and electric engines. Especially installing heat pump technology for space heating requires massive insulation and installing low temperature heat radiator systems. In new buildings and houses, this can be easily implemented and is a good solution, but in existing buildings this is challenging.

Another solution is to provide all customers with a zero-carbon gas, hydrogen, whereby the gas infrastructure could be re-used to transport and distribute the hydrogen to the customers. To convert the natural gas infrastructure into a hydrogen infrastructure can be realized fast and cost-effective. However, all end-use equipment needs to be retrofitted or replaced too, which is a major operation.

To convert from gas to hydrogen implies that sufficient volumes of hydrogen needs to be produced to supply all customers connected to the hydrogen infrastructure, because natural gas cannot be transported and distributed anymore by these pipelines. The way out is to convert natural gas at the gas field immediately into hydrogen. This could be with auto-thermal reforming (ATR) plants with CCS, capturing the CO_2 and store the CO_2 in the gas field. Or large-scale pyrolysis plants, reforming natural gas by using renewable electricity could be installed, with only carbon as other output. The capacity of these plants needs to be much larger than present day SMR plants. At a large gas field, typically 10 million tonnes of low-carbon H_2/year or more can be produced.

5.1.2 Space requirement for a large-scale renewable hydrogen production

Renewable hydrogen production at low cost is possible at good solar and wind resources sites. These good solar and wind resources sites are in many cases at remote areas, far from the demand. This will result in large transport distances, whereby converting to hydrogen will be cost-effective because of lower transport and storage cost. Electrolyzers need to be an integral part of the design and engineering of these large-scale renewable hydrogen production sites. Instead of a transformer station, that converts the produced electricity to HVDC electricity for transport by a HVDC cable, an electrolyzer plant, that converts the produced electricity to compressed hydrogen for transport by a pipeline, is realized.

However, in order to fully utilize the advantage of lower transport costs, a much larger amount of hydrogen energy must be produced than with electricity production. A 1 or 2 GW wind or solar farm is for electricity production a sufficient size, because an HVDC cable has a capacity of 1 to 2 GW. But for hydrogen production, a wind or solar park needs to be sized, based on a hydrogen transport pipeline capacity, between 10–20 GW. If a transport pipeline has a capacity of 10 GW and the capacity factor of such a pipeline is about 4,000 full load hours, a volume of 40 TWh a year will be transported. This is roughly equivalent to 1 million tonnes of hydrogen.

Production of 1 million tonnes hydrogen needs space, space for the electricity production by solar or wind, for the electrolyzers, compressors, cabling, and pipelines, access roads, and so on. Table 6 gives an overview of the required area that is needed to produce about 1 million tonnes of hydrogen.

As can be seen, for solar an area of less than 500 km^2 is needed, more or less fully occupied with installations and equipment. Especially the solar PV or concentrated solar power (CSP) electricity production requires by far most of the space. An alkaline electrolyzer has a larger footprint than a PEM electrolyzer, however the space requirements for an alkaline electrolyzer, 10 ha/GW [2] are modest compared to space requirements for solar electricity production.

For onshore and offshore wind, the physical space that a wind turbine needs is not much. In a wind farm, however, the turbines need to be spaced well apart from each other, due to the wake effects and turbulence caused by wind turbines. A rule of thumb is a spacing of seven times the rotor diameter. Therefore, the total area that is needed to realize a wind farm is much larger than the physical area needed. It is estimated that based on realized wind farms onshore about 6 MW/km^2 and offshore about 8 MW/km^2 can be realized. It implies that the physical area size is only 1–2% of total wind farm area size. So it is possible to use the land or sea for agricultural purposes or even to place large solar PV farms in between the wind turbines.

The estimated space requirements does not necessarily mean it has to be a contiguous area of 500–2,000 km^2. It could be smaller areas, not too far from each other, producing and transporting hydrogen through a smaller pipeline feeding into a large hydrogen transport pipeline. Such a large hydrogen pipeline from the renewable

Tab. 6: Space requirements for multi-GW solar and wind hydrogen production plants.

	Capacity Factor (Full load hours)	**Installed Capacity (GW)**	**Hydrogen Production* (million ton)**	**Specific Space Requirement (km^2/GW)**	**Space Requirement (km^2)**
Solar PV (South Europe)	1,800	30 GW	1.10	16,5 [49, 50]	500
Solar PV (North Africa)	2,100	25 GW	1.07	16,5 [49, 50]	420
Solar CSP	4,000	12,5 GW	1.02	30 [51]	375
Wind Onshore	4,000	12,5	1.02	3 (physical space) [52] 170 (wind farm space)	38 2,125
Wind Offshore	6,000	9 GW	1.10	2 (physical space) [53] 125 (wind farm space)	18 1,125

* Electrolyzer system efficiency 80% HHV

production site preferably goes to a large-scale hydrogen storage system; salt caverns or suitable empty gas fields. These large-scale hydrogen storage systems must ensure that intermittent hydrogen production is converted into a basic load hydrogen flow. This constant hydrogen flow can then be transported from the storage to the hydrogen demand areas. Close to demand, a large-scale hydrogen storage in salt domes can then balance the supply and demand.

The development of such large-scale sites for renewable hydrogen production requires the government to designate these areas. The government will have to select such areas on the basis of a number of criteria. Zoning plans will have to be drawn up for these areas, an environmental impact analysis will have to be carried out, infrastructure such as roads and communication will have to be constructed and TSOs will have to construct the large-scale hydrogen transport and storage infrastructure and the necessary electricity infrastructure.

5.1.3 Combining multi-GW hydrogen production from renewables and natural gas

Combining hydrogen production from renewables and natural gas makes it possible to convert the natural gas infrastructure sooner and faster into a hydrogen infrastructure. Besides much larger volumes of renewable and low-carbon hydrogen can be produced at lower cost, which makes a faster and more cost-effective decarbonizing of energy use possible. Two examples of such a large-scale combination are the North Sea and Algeria.

5.1.3.1 North sea

Major gas exploration in Europe is at the North Sea and further North in the Norwegian and Southern Barents Sea. The gas from this North Sea gas fields is transported to the shore by pipelines, see Fig. 21. At the North Sea and further North also good wind resources are available. And at the North Sea, salt formations are present in the underground, located above the gas fields.

A large-scale hydrogen production system could be developed at the North Sea combining hydrogen production from natural gas and offshore wind. Offshore natural gas can be converted to hydrogen with carbon capture and storage of the carbon in an empty gas field or in the same gas production field, thereby contributing to enhanced gas recovery. At the same time large-scale offshore wind-hydrogen farms will be developed in the neighborhood of these gas fields and gas transport pipelines. The offshore wind electricity will be converted at sea at the wind farm into hydrogen. Gas transport pipelines will be converted to hydrogen transport pipelines, which make it possible that both hydrogen production from natural gas, combined with hydrogen produced by offshore wind farms can be transported to land. In the offshore salt formations dedicated salt caverns could be realized for hydrogen storage, which makes it possible that hydrogen supply can balance production and demand fluctuations.

The North Sea has an area size of 575,000 km^2 and above the North Sea the Norwegian Sea has an area size of 1,383,000 km^2. In 2017, North Sea gas production was 190 bcm [54] or about 1.900 TWh, with Norway by far the largest gas producer at the North Sea. If all this gas would be converted to hydrogen, about 1.400 TWh or 36 million tonnes hydrogen would be produced at the North Sea.

It is possible to install far offshore at the North Sea about 300 GW offshore wind, producing 1.800 TWh electricity, converted in 1.400 TWh or 36 Mton hydrogen. The physical area covered by the wind turbines will be only 600 km^2, representing only 0.1% of the total North Sea area size. But the wind farms total area size will be 37,500 km^2, representing 6.5% of total North Sea. As can be concluded, future offshore wind-hydrogen could replace total natural gas production.

A fast and cost-effective transition from natural gas to hydrogen is possible as follows. At first (some of) the natural gas pipelines will be converted to hydrogen, fed by natural gas converted to hydrogen at sea, whereby gradually more offshore wind-hydrogen will be fed in. In the end, offshore wind-hydrogen has taken over all hydrogen produced from natural gas.

5.1.3.2 Algeria

The Hassi R'Mel gas field in Algeria is the 18th largest gas field in the World, in production since 1961. The yearly production volume is around 100 bcm (about 1.000 TWh) [56]/year, with an estimated gas in the field of about 3.000 bcm. The underground reservoir size is 70 by 50 km, 3,500 km^2 Roughly 30% of the gas production is for national consumption, and 70% for export via pipelines and LNG. This gas field is directly

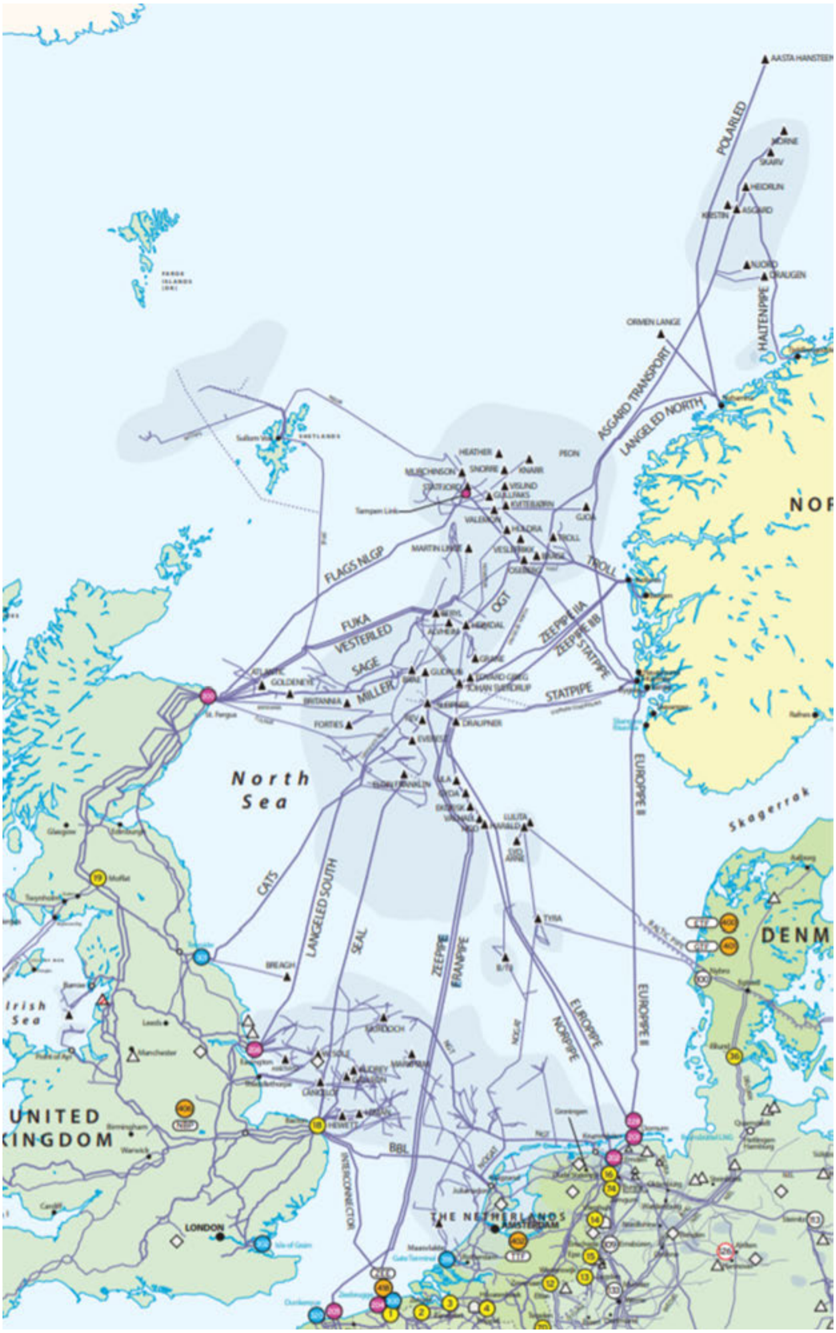


Fig. 21: North Sea map with gas fields and pipelines [55].

connected by transport pipelines to Italy and Spain, see Fig. 22. When all gas production would be converted into hydrogen by ATR, with CCS roughly 750 TWh or 19 million tonnes hydrogen will be produced.

At and around this gas field site in Algeria, there are excellent solar but also wind resources. To produce a similar amount of 19 million tonnes hydrogen by solar PV alone would require 450 GW solar PV with an estimated area size of 7,500 km^2. If combined with wind, this area could even produce more than 22.5 million tonnes hydrogen (885 TWh). The land area of Algeria is 2,382,000 km^2, so only 0.3% of total land area will be used. For comparison, the land area of the EU27 is 4,422,773 km^2.

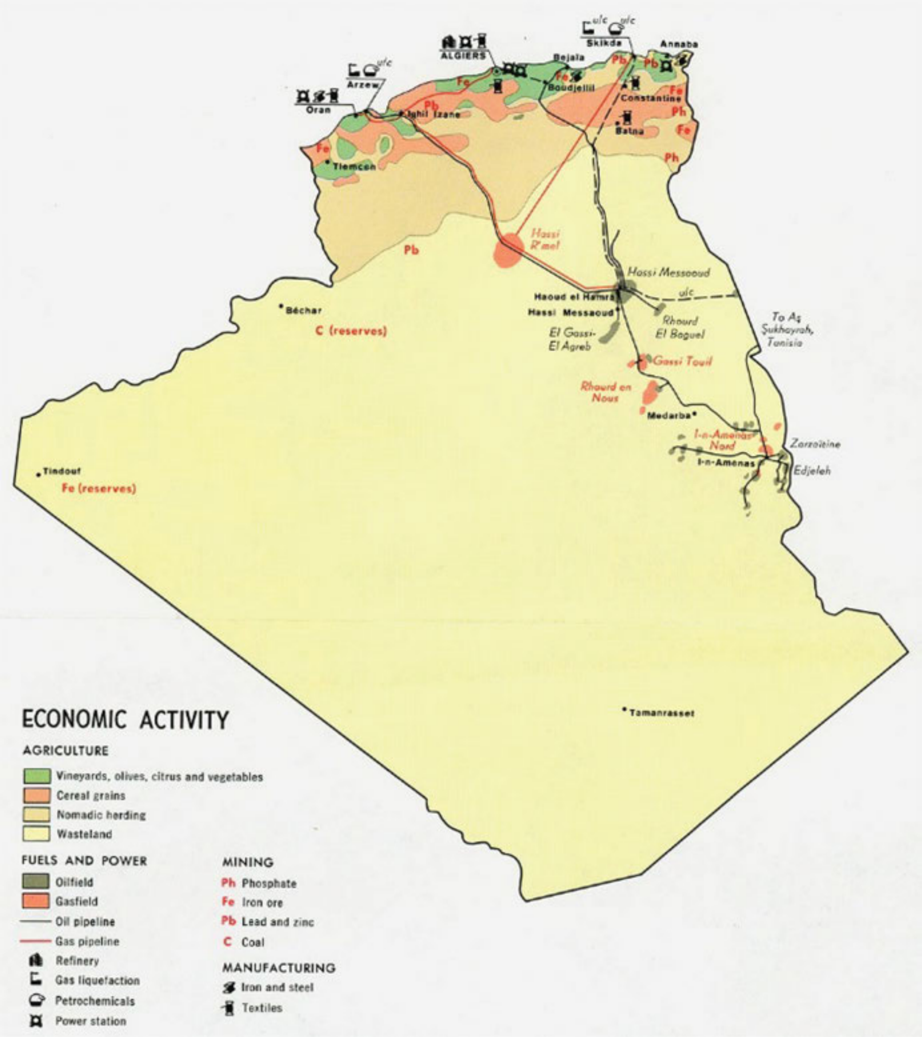


Fig. 22: Map of Algeria with energy, mining, and agriculture activities [56].

Near this site also salt formations are present, it is likely that dedicated salt caverns could be realized, which makes it possible to supply baseload hydrogen for export to among others Europe.

5.2 Total space required to produce 220 Mton renewable hydrogen in 2050

Large-scale renewable hydrogen production can be realized at the same locations as large-scale natural gas production with new production in Greece, Spain, and Portugal

In the paper “Hydrogen, the bridge between Africa and Europe” [33] a 2050 scenario for the EU28 has been presented. The EU final energy demand, including feedstock and international transport, is estimated to be 12.000 TWh in 2050, with 50% supplied by electricity and the other 50% supplied by hydrogen. Energy production is only by renewables, mainly solar and wind.

In this scenario in the EU28 5.000 TWh, renewable electricity is produced for direct consumption. Next to this, about 70 Mton hydrogen needs to be produced in the EU28, which needs a renewable electricity input of 3.400 TWh. About 150 Mton hydrogen, requiring 7.400 TWh renewable electricity, needs to be imported into the EU28, which is assumed to come through pipeline from North Africa, (the Middle East), Norway, and Ukraine.

An estimate of the total space required is made to produce 70 Mton hydrogen in the EU28 and 150 Mton renewable hydrogen in neighboring countries. Three simple criteria used to select areas where at least 1 million tonnes low-cost renewable hydrogen can be produced. These criteria are as follows:

- excellent renewable energy resources,
- low population density,
- Sufficient space available to produce at least 1 million tonnes hydrogen.

In the European Union, a large amount of hydrogen production will be from offshore wind at the North Sea, Baltic Sea, Black Sea, and the Mediterranean Sea. At the Mediterranean Sea also floating solar can be installed to produce hydrogen. Especially in Greece, offshore wind can be combined with floating solar. In Spain, Portugal, and Italy a large-scale Solar PV on land, especially in Spain combined with onshore wind, is foreseen to produce hydrogen. Some countries in Central Europe do not contribute to large scale, low cost renewable hydrogen supply, because renewable energy resources are not good enough in those countries. This does not necessarily mean that smaller scale hydrogen production for local consumption is not possible, and it could be certainly competitive with importing hydrogen. An indication of the land and sea use that is necessary for hydrogen production is given in Tab. 7.

Five North African countries have a land area size larger then the EU28, less inhabitants, better solar energy resources and in certain areas even very good wind resources. Especially Algeria has a large area size, excellent solar and wind conditions, a gas industry with gas infrastructure, and is in principle promptly situated to become a major renewable hydrogen exporting country. However, other North African countries can also become important renewable hydrogen exporting countries.

Furthermore, Ukraine and Norway have the potential to become renewable hydrogen exporting countries. Especially the Ukraine could become an exporting country of both green hydrogen and green CO_2 whereby the CO_2 can be used as a renewable feedstock for chemical products and synthetic fuels.

Tab. 7: Total space required in EU28 to produce 70 Mton renewable hydrogen, and in North Africa, Ukraine and Norway to produce 150 Mton renewable hydrogen.

	EU28				**North Africa**				**Other Europe Norway + Ukraine**			
Area size land (km^2)	4.467.000				5.762.200 Algeria, Egypt, Libya, Morocco, Tunisia				988.800			
Area size sea (km^2)	3.934.400 North Sea, Baltic Sea, Mediterranean Sea, Black Sea, Irish Sea				–				575.000 North Sea			
	GW	**Mton H_2**	**Size km^2**	**%**	**GW**	**Mton H_2**	**Size km^2**	**%**	**GW**	**Mton H_2**	**Size km^2**	**%**
Solar PV	440	16,1	7.260	0,16	2.350	100,2	38.775	0,67	40	1,5	660	0,05
Onshore wind	120	9,7	17.190	0,46	300	36,5	37.500	0,65	12	1,0	2.040	0,15
Offshore wind	365	44,5	43.125	1,10	–	–	–		90	11,0	11.250	1,96
		70,3				136,5				13,5		

The multi-GW renewable hydrogen production areas, producing at least 1 million tonnes hydrogen each, require substantial space. However, the percentage space required compared to total area size are rather small, around 1%. The only exception is offshore wind at the North Sea. Installed offshore wind-hydrogen capacity at the North Sea is estimated to be 250 GW, requiring 31.250 km^2 of space, which is 5,4% of total surface of the North Sea.

When looking at the locations where multi-GW renewable hydrogen production is concentrated, it is at Sea, especially the North Sea and in the South of Europe, but not much in Central Europe. And, of course, in North Africa, Norway, and the Ukraine and so outside the EU. This shows a remarkable similarity with gas production, also at the North Sea in North Africa and Russia and not much in Central Europe. Renewable hydrogen production also shows a large potential in Southern European countries, especially Greece and Spain because they have both solar and wind. These countries can become the new hydrogen rich exporting countries in Europe.

5.3 Hydrogen infrastructure and storage

5.3.1 Natural gas infrastructure could be re-used for hydrogen transport and fits geographically well

5.3.1.1 Salt formations are present at large-scale renewable hydrogen production sites

Most of existing gas infrastructure, pipelines but even parts of LNG terminals, can be re-used for hydrogen transport, which is a major advantage over electricity, where major additional investments are required to connect future offshore wind generation from north-western Europe and solar generation from southern Europe to the load centers.

Surprisingly enough the geographical lay out of the gas infrastructure fits also on the large-scale hydrogen production locations, in the North Sea, North Africa, and Ukraine. Especially in the South of Europe, new hydrogen transport infrastructure will be necessary to connect large-scale hydrogen production in Greece, Spain, and Portugal to the demand in North-West Europe, see Fig. 23 for an impression of a hydrogen backbone throughout Europe, connecting North Sea and North Africa [33].

By re-using gas infrastructure for hydrogen transport, so-called hydrogen backbones can be realized, fast, and cost-effective. These hydrogen backbones will connect areas of low-cost hydrogen production in and outside Europe, with large-scale storage and demand centers elsewhere. The European gas infrastructure can, with few exceptions, be used to transport 100% hydrogen. Gas transmission pipelines can accommodate pure hydrogen, but compressors and flow meters need to be adjusted or replaced. And most natural gas distribution pipelines, typically made from PVC or PE, can accommodate 100% hydrogen as well [57–59]. Germany and the Netherlands have already planned to convert part of their natural gas transmission system into a dedicated hydrogen backbone. And at 17 July 2020, 11 European gas TSO’s launched their plan to develop an integrated European hydrogen backbone, see Fig. 24 [59].

Hydrogen storage can be realized in salt caverns, such as natural gas. The salt caverns for gas storage are located throughout Europe, but concentrated in Germany. These salt caverns are mainly in use to balance base load gas supply with the gas demand. With renewable hydrogen production, there is no base load supply. Therefore, salt cavern storage needs to be realized near large-scale renewable hydrogen

Fig. 23: Natural gas infrastructure in Europe (blue and red lines) and first outline for a hydrogen backbone infrastructure (orange lines). The main part of the hydrogen backbone infrastructure consists of re-used natural gas transport pipelines with new or retrofitted compressors. A new pipeline from the solar and wind resource areas in Greece needs to be realized as well as transport pipelines along the south coast of Portugal and Spain [33].

production locations to balance fluctuating hydrogen production into baseload supply. Salt formations, however, are present at these large-scale renewable hydrogen production sites, for example, not only at the North Sea and Algeria but also in Morocco, Egypt, Spain, and Portugal. So dedicated salt cavern hydrogen storage could be created at these large production locations, see Fig. 20. And a large potential for salt cavern storage in Europe exists, see Fig. 16

5.4 Future hydrogen system lay out

A future hydrogen system will look a lot like the present natural gas system. The lay-out of such a future hydrogen system will consist of the following, see Fig. 25.

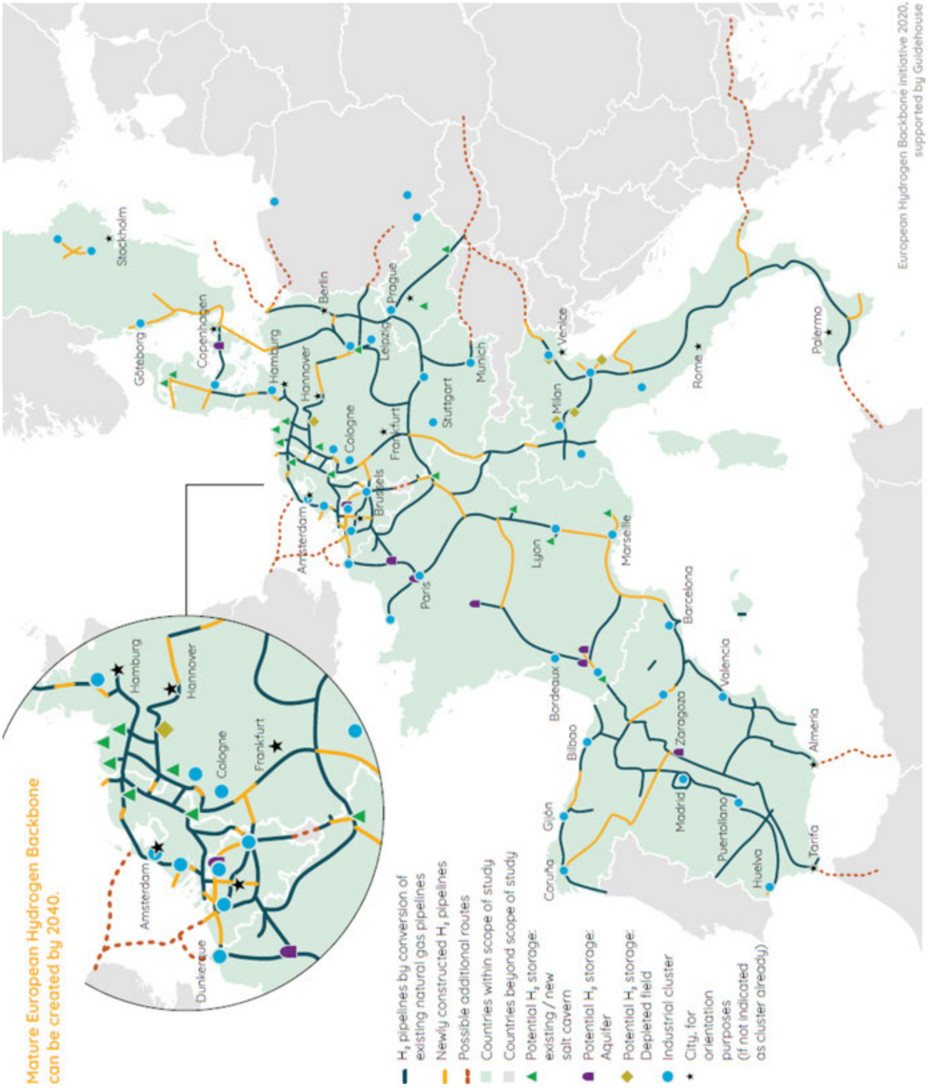


Fig. 24: European hydrogen backbone as proposed by 11 gas TSOs [59].

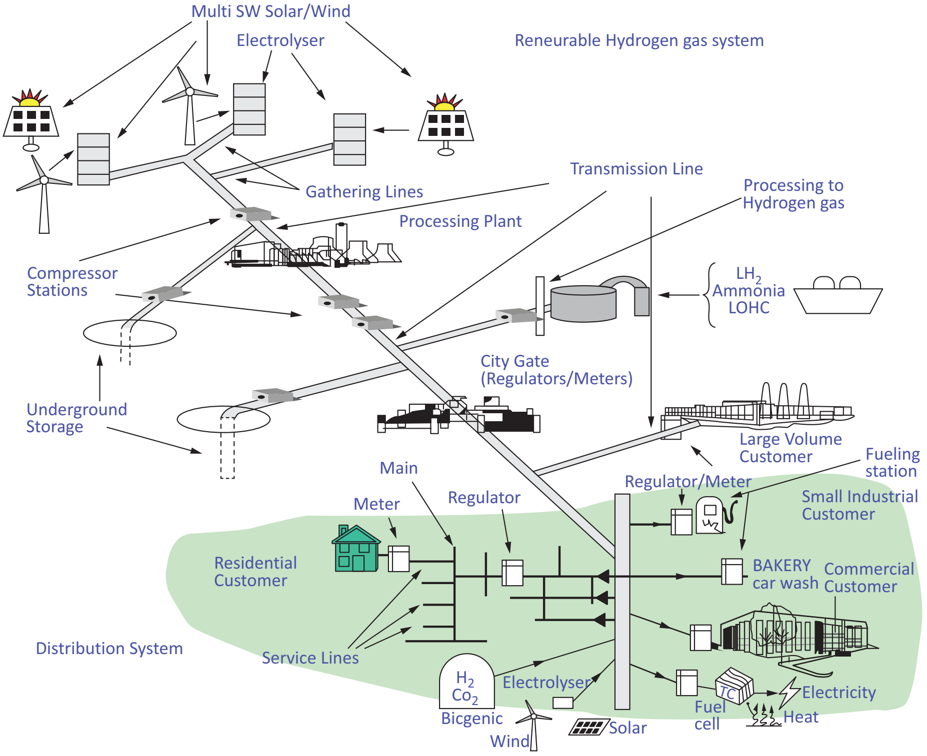


Fig. 25: A schematic lay out of a future renewable hydrogen gas system.

- Large-scale renewable hydrogen production sites will be connected with gathering lines to underground storage facilities to balance production fluctuations and hydrogen processing plants to bring it on specification.
- In an intermediate period large-scale low-carbon hydrogen production from fossil fuels at the resource sites with carbon capture and storage directly in the gas or coal field can provide hydrogen volume in the system. Gathering lines will transport the hydrogen to hydrogen processing plants to bring it on specifications.
- Intercontinental and continental transport pipelines will transport the hydrogen to the demand centers.
- At Ports, hydrogen can be imported via LH2, Ammonia or LOHC by ship and temporarily stored in tanks.
- Hydrogen is then transported to large volume, base load, customers (e.g. chemical industry, steel plants, synthetic fuel production plants) and to underground storage facilities to balance daily to seasonal demand fluctuations.
- Now hydrogen is transported to city gate stations, whereby pressure levels are reduced to medium pressure levels, connecting medium volume customers, industries (e.g. food processing, paper, special chemicals, data centers) large

commercial sites (e.g. distribution centers, campus sites, offices and stores) and hydrogen fueling stations.
- At medium pressure, local and regional hydrogen production from biogenic waste streams brought on specification can be fed in the hydrogen grid.
- At medium pressure, also local and regional hydrogen production from renewable electricity to alleviate electricity grid capacity constraints can be fed into the hydrogen grid.
- Finally hydrogen is distributed at low pressure levels to residential customers (e.g. houses, small shops, offices, schools).

6 Electricity and hydrogen symbiosis to fulfil end-use energy demand

Present combustion technology today will shift to electrochemical conversion and heat pump technology in future

A global sustainable energy system can be constructed with pre-dominantly solar and wind as energy source, converted into electricity via solar panels and wind turbines. Where possible, useful and cost-effective, the electricity produced is directly used. However, lowest cost solar and wind electricity can also be produced far away from the demand, requiring conversion to hydrogen for cheap transport and storage. The lower electricity production cost and cheaper transport and storage cost will compensate for extra energy conversion losses and costs.

6.1 Hydrogen as a feedstock

Hydrogen as a feedstock to produce chemical products is a direct use of hydrogen. Present hydrogen feedstock use is especially for ammonia and methanol production and in refineries to desulfurize oil and to produce gasoline, diesel, and other oil-refinery products. Renewable synthetic fuels, such as synthetic kerosene or synthetic diesel can be produced by using green H_2 and green CO produced by gasification of solid biogenic waste, using the Fischer–Tropsch synthesis process. The Fischer–Tropsch process is a catalytic chemical reaction in which carbon monoxide (CO) and hydrogen (H_2) in the syngas are converted into hydrocarbons of various molecular weights according to the following equation [60]:

$$\text{Fischer–Tropsch: } (2n+1)\ H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O$$

In future, hydrogen as a feedstock can also be used for direct reduction of iron ore, thereby replacing carbon monoxide produced from coal. The reduction process is given by the following equation.

$$\text{DRI: FeO} + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{O}$$

There are several steel plants that have started crude steel pilot production plants using hydrogen as a reducing agent. Three Swedish companies, steel manufacturer SSAB, mining company LKAB, and energy company Vattenfall are exploring the use of hydrogen in steel production processes. This joint endeavor is known as HYBRIT, short for Hydrogen Breakthrough Ironmaking Technology [61]. A schematic view of the HYBRIT production process, compared to the blast furnace process, is given in Fig. 26.

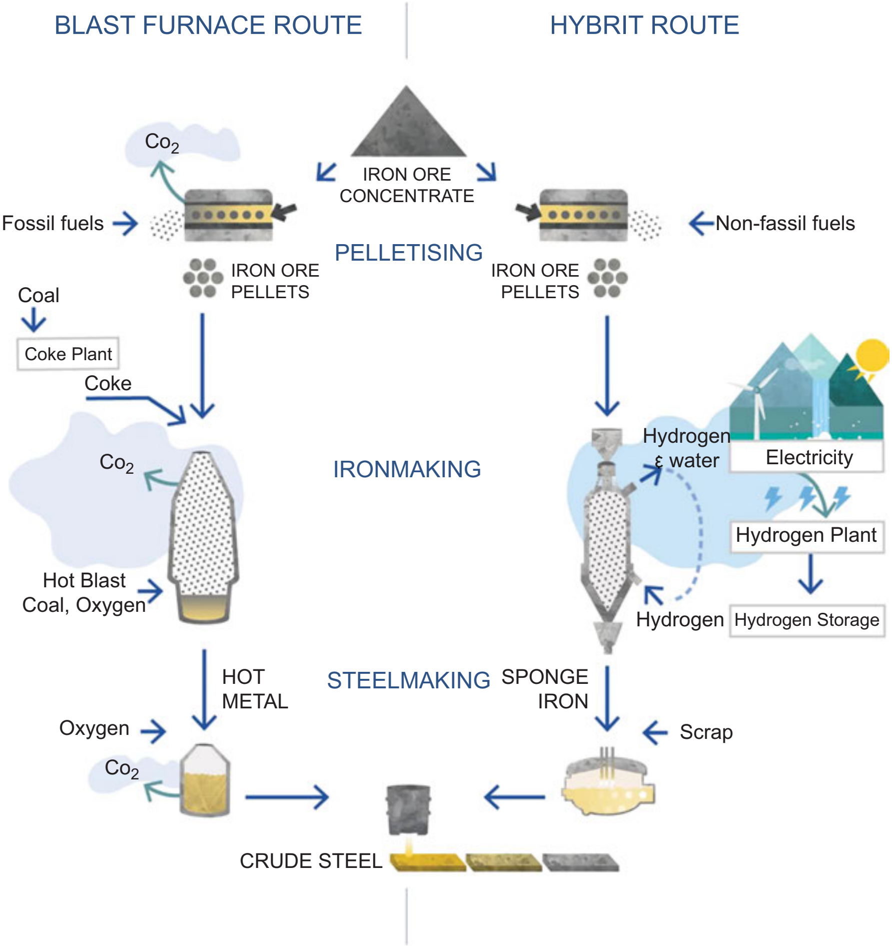


Fig. 26: HYBRIT production compared to traditional blast furnace methods [61].

6.2 Hydrogen as an energy carrier

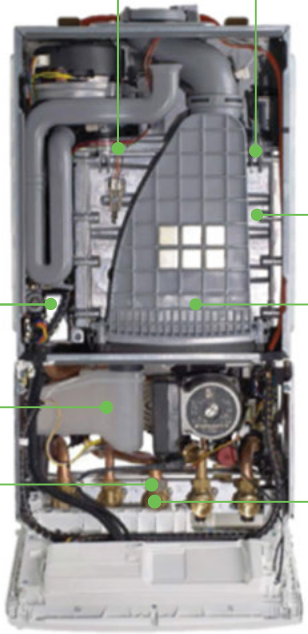
Hydrogen can be used as an energy carrier which can be converted in high or low temperature heat, in electricity or mechanical power. Today, the conversion process to convert hydrogen in heat, electricity or mechanical power is via combustion in a boiler, furnace, engine, or turbine. These combustion technologies are mature technologies when combusting natural gas, but in development for combusting hydrogen. However, it is not very difficult to adapt or retrofit these combustion technologies for combusting hydrogen. Although the different appliances need to be re-engineered, the essential difference is only the burner.

Hydrogen boilers for heating houses and buildings have come on the market in the United Kingdom and the Netherlands already. Even boilers have been developed that are hydrogen ready, which means that they can combust natural gas but in future hydrogen as well. Worcester Bosch in the United Kingdom has released such a hydrogen-ready boiler in February 2020 [62], see Fig. 27.

Gas turbines are versatile and can be used in several different modes in critical industries such as power generation, oil and gas, process plants, aviation, as well as in smaller related industries. At present hydrogen mixed with natural gas can be burned in gas turbines, with some simple adaptations. All gas turbines manufacturers have a technology roadmap to bring gas turbines on the market or to retrofit existing gas turbines to 100% hydrogen fueled. In January 2019, the gas turbine industry strongly committed to develop gas turbines operating with 100% hydrogen till 2030 [63].

Airbus has revealed new zero-emission concept aircrafts in September 2020. The AirbusZEROe blended Wing Body Concept is the most futuristic concept, see Fig. 28. In the blended-wing body configuration, two hybrid hydrogen turbofan gas turbine engines provide thrust. The modified gas-turbine engines run on hydrogen, rather than jet fuel, through combustion. The liquid hydrogen storage tanks are stored underneath the wings. Airbus wants to bring these hydrogen planes on the market in 2035 [64].

Hydrogen can be blended in diesel engines. Especially for heavy duty and heavy transport blending, hydrogen in a diesel engine, can reduce CO_2, fine dust, and NOx emissions. New Holland in cooperation with Jos Scholman land and water works company, has developed a H_2 Dual Fuel tractors, whereby hydrogen can be blended up to 80%, see Fig. 29. The H_2 Dual Power hydrogen set is a modification that can be added to a normal tractor, whereby the hydrogen is injected in the air inlet of the diesel engine. On the roof of the tractor, five hydrogen tanks are placed, that carry 11.5 kg H_2 at a pressure of 350 bar [65]. The first H_2 Dual Power tractors are deliver to Jos Scholman in October 2020.



Flashback Prevention

Hydrogen has a higher flame speed than natural gas. One of the key technical advances in hydrogen boilers are burners which can hold a stable hydrogen flame against its high speed.

Gas-Air Ratio Control

Hydrogen has very similar energy-flow properties to natural gas, so the new components will be very similar.

Condensate

Hydrogen produces significantly more condensate than natural gas. This has little consequence but must be considered in heat cell design.

Materials Compatibility

At the low pressures used in domestic boilers, most materials currently used for natural gas will also be suitable for hydrogen.

Flame Detection

Hydrogen flames are invisible and create no electrical signal, but we can detect it by it’s ultra-violet (uv) emissions.

Conversion

In order to minimise the impact of conversion on end-users and installers, boilers will be developed to be quickly and easily re-configured for hydrogen on conversion day.

Performance

Hydrogen appliances will perform very similarly to natural gas boilers in terms of output, efficiency and emissions. The products of combustion are very clean.

Gas-Tightness

Hydrogen has a small molecule size and is a very seeking gas. However, energy leakage rates are very similar to natural gas and there is unlikely to be a need for significant re-engineering.

Fig. 27: Worcester Bosch, technical application of their hydrogen-ready boiler [62].

6.3 The future is electrochemical conversion instead of combustion

In a transitional period, hydrogen can be used by combustion in a boiler, furnace, engine, or turbine, to produce heat, electricity, or mechanical power. However, in future electrochemical conversion via fuel cells will become more important.

Fig. 28: The AirbusZEROe concept with hydrogen gas turbines and liquid hydrogen storage tanks [64].

Fig. 29: H_2 Dual Fuel tractor, hydrogen can be blended in the diesel engine up to 80% [65].

The fuel cell reaction is the reverse of the electrolyzer reaction: A chemical reaction between hydrogen and oxygen will produce electricity, water, and also heat:

$$\text{Fuelcell}: 2H_2 + O_2 \rightarrow 2H_2O + 2e^-$$

When fuel cells will be produced in mass production, the cost will come down drastically. Mass production of cells and stacks will bring down Capex cost to $ 30–40/kW, according to studies by US-DOE, see Fig. 30 [66]. These Capex cost are much cheaper, with higher conversion efficiencies, than Capex cost of present combustion technologies, such as engines or turbines. Therefore fuel cell technology will be at least cost competitive, but in most cases, cheaper than present day combustion technology.

Fuel cells that produce electricity and heat will be used in houses and buildings. The volume and temperature level of the heat can be brought to the desired level by using heat pumps. And the electricity from the fuel cells supplements the electricity from solar panels on the roof.

Electricity from batteries can directly power an electric engine for light cars, ships, and airplanes that travel short distances. For heavier vehicles, ships, trains, and airplanes with longer ranges, an onboard fuel cell converts hydrogen into electricity, which drives the electric motor. Much more energy can be carried on board

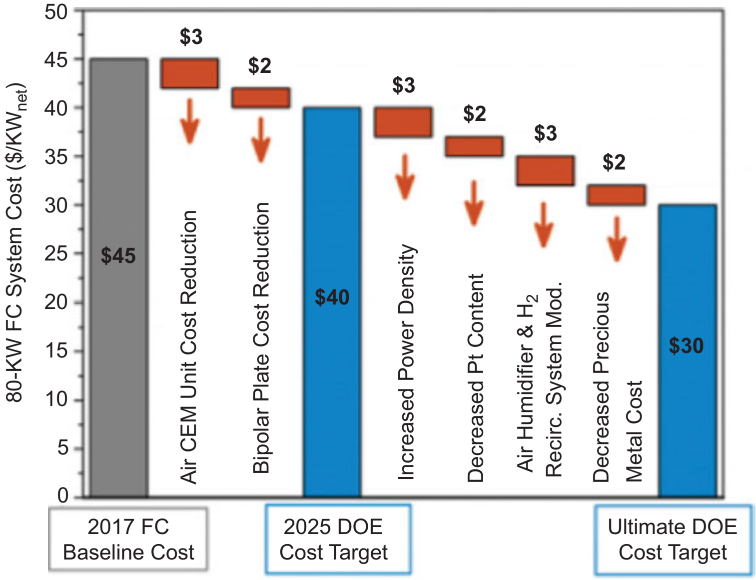


Fig. 30: Prospective cost reduction measures of automotive FC system needed to reach 2025 and ultimate DOE cost targets [66].

by hydrogen (gaseous, liquid, or packaged as e.g. ammonia) then by electricity in batteries.

And fuel cells will be the electricity balancing plants of the future, producing electricity at moments that renewable sources cannot meet the demand. These fuel cell systems can be placed very de-centralized in villages, neighborhoods and at office sites, because there are no emissions to the air and no noise production. Decentralized fuel cell systems can produce electricity (and heat) locally, eventually avoiding electricity grid expansions.

6.4 The hydrogen cycle

In the end electrochemical conversion using electrolyzers and fuel cells will fully replace combustion technologies. Electricity and hydrogen will be the carbon-free symbiotic energy carriers, which can be electrochemically converted into each other by electrolyzers and fuel cells. Hydrogen will be produced by electrolysis of water. Besides hydrogen, oxygen and heat is produced. At multi-GW renewable hydrogen plants, the oxygen will be released to the air.

The hydrogen can be transported and stored in large quantities worldwide by ship or up to distances of 3,000–4,000 km by pipeline. At the demand centers, hydrogen and oxygen from the air can be converted by fuels into electricity, heat, and water. The water that is released is very clean, demineralized water. With the addition of salt and some minerals, it is very clean and safe drinking water.

In this cyclic process, there is no water and oxygen used. On the hydrogen production site (electrolyzer), water is used and oxygen released. But on the use side (fuel cell), the same amount of oxygen is used and water is produced. It is a perfect balance, a circular process, called **"The Hydrogen Cycle,"** see Fig. 31.

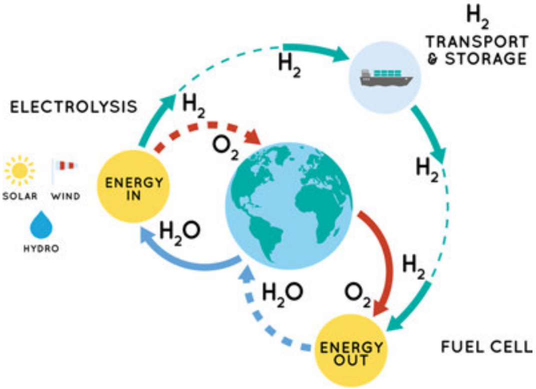


Fig. 31: THE HYDROGEN CYCLE; Electricity and water electrochemical conversion into hydrogen, oxygen and heat by electrolysis – Transport and storage of hydrogen – Hydrogen and oxygen electrochemical conversion into electricity and heat [1].

7 Conclusions

7.1 Why hydrogen?

Hydrogen has a key role to play as a carbon-free energy carrier alongside electricity. Hydrogen can be transported worldwide by ship and pipeline and can be stored underground in large volumes. This makes it possible to deliver cheap renewable energy, especially solar and wind, cost efficiently at the right time and place to customers. Next to this systemic role, hydrogen is important to decarbonize energy use in hard-to-abate sectors in industry, mobility, electricity balancing, and heating.

7.2 How to produce hydrogen?

Present day hydrogen use is only as feedstock in industry, representing 2% of global primary energy use. Hydrogen is mainly produced from fossil fuels, also called "hydrocarbons," especially from natural gas and coal, whereby CO_2 emissions are released to the air, called "grey" hydrogen. However, up to 90% of the CO_2 emissions can be captured and stored underground, the produced hydrogen is then called "blue." New technology makes it even possible to produce hydrogen and solid carbon from fossil fuels, so without CO_2 emissions and is called "turquoise" hydrogen.

However, hydrogen can also be produced from renewable resources, such as biogenic waste. With new technologies, pure H_2 and CO_2 can be produced, instead of methane. Both hydrogen and CO_2 are called "green" and if the CO_2 is used as a feedstock or captured and stored, even negative CO_2 emissions could be realized.

Hydrogen can be produced from hydrocarbons, but also by splitting water. The energy input for splitting water can be electricity, heat, or in future even direct sunlight. At present, water electrolysis is the most commonly used process. Only when the electricity is from renewable resources, the produced hydrogen is called "green."

7.3 Hydrogen production and system cost

Hydrogen production cost is mainly determined by the energy cost. Grey hydrogen production cost from natural gas with a gas price of 3 dollars/MBtu (=0,01 dollar/kWh) is below 1 dollar/kg hydrogen. But green hydrogen production cost from water using solar PV electricity at a cost of 0,01 dollar/kWh is also below 1 dollar/kg H_2 (Capex electrolyzer 250 $/kW with 2.000 full load hours). So green hydrogen production cost from solar PV can compete with grey hydrogen production cost at equal energy prices. With higher full load hours, which is the case with onshore and offshore wind, electricity prices can be even higher than natural gas prices to be competitive. In future, renewable hydrogen can even compete with low gas prices.

Multi-GW solar and wind electricity production costs at the good resources sites are between 2–5 times cheaper than solar and wind production cost at moderate resource sites. Hydrogen transport cost by pipeline is about a factor of 10 cheaper than electricity transport cost by cable. And hydrogen storage cost underground in salt caverns is at least a factor 100 cheaper than electricity storage cost by pumped hydro or batteries. In comparing renewable energy system cost, the following can be concluded:

- The further away from the energy demand and with an increasing share of sustainable electricity, conversion to hydrogen with transport and storage of hydrogen and conversion back to electricity becomes more attractive than electricity transport and storage with direct use.
- Green hydrogen production cost in areas/countries with moderate renewable resources will compete with green hydrogen import cost (including production, transport, and storage cost) from good renewable resources sites.
- In the end even renewable electricity production cost in areas/countries with moderate renewable resources will compete with renewable electricity production cost from imported hydrogen, produced by renewable electricity from good renewable resources sites.

In a renewable energy system, it is about comparing system cost and not about comparing system efficiency.

7.4 Future hydrogen system characteristics

Future hydrogen systems will have similar characteristics as present day natural gas systems. Large-scale Multi-GW renewable hydrogen production plants, producing more than 1 million tonnes (=40 TWh) H_2/year at good resources sites needs to be developed. Hydrogen production cost will be below 1 dollar/kg H_2 around 2030 and will become competitive with present day gas prices around 2040. Hydrogen infrastructure can be realized by re-using the gas infrastructure, pipelines, and salt cavern storage, without major adaptations. As a transition, hydrogen produced from fossil fuels at the resource sites (gas or coal field) with Carbon Capture and storage directly in the field below, can bring low-carbon hydrogen volume in the system. Such an approach can establish a fast, cheap, and reliable transition to a sustainable energy system, whereby hydrogen will fully replace natural gas, coal, and oil.

7.5 Hydrogen production space requirements

To build a fully renewable hydrogen production system, producing 70 Mton hydrogen in the European Union, including the United Kingdom and 150 Mton in neighboring countries in North Africa, Ukraine, and Norway, requires on average 1% of land and sea space. There will be hydrogen-exporting countries in the South of Europe, the United Kingdom, Norway, and in North Africa. Especially North-West and Central European, countries will need to import cheap renewable hydrogen. There will be a need for innovative spatial planning policies to designate areas for large-scale, more than 1 million tonnes hydrogen production.

7.6 Hydrogen demand and end-use technology development

Present day hydrogen use is only as a feedstock in the chemical and petro-chemical industry. In future hydrogen will be used as a feedstock too in new areas such as steel and synthetic fuels production. And hydrogen as an energy source will be used for mobility, high to low temperature heating, and for electricity balancing.

The conversion technology used today is based on combusting technologies: boilers, furnaces, engines, and turbines. These combustion technologies can be easily and fast adapted to combust hydrogen. It is possible to fully replace fossil fuels in all combustion technologies by hydrogen, but in a first phase, dual fuel combustion technologies will enter the market.

In future, however, combustion technologies will be replaced by electrochemical conversion technologies together with heat pump technologies. These technologies offer the promise to be cheaper, more-efficient with no harmful emissions to the air, land, or water. A smart symbiosis between electricity and hydrogen as zero-carbon energy carriers with electrochemical and heat pump technologies, will establish a clean, cost-effective, reliable, fair, and circular energy system. In such an energy system, the hydrogen cycle is the ultimate circular mass and energy cycle.

8 Recommendations

Hydrogen is a zero-carbon energy carrier which makes it possible to cost efficiently transport and store large volumes of cheap renewable energy from production to demand worldwide. This systematic role of hydrogen is key to realize a clean, affordable, reliable, and fair renewable energy system worldwide. The following crucial developments need to be implemented to establish the role of hydrogen as the zero-carbon energy carrier worldwide.

1. Develop a hydrogen system with similar characteristics as the present natural gas system, whereby hydrogen can be transported worldwide by ship and pipeline, with large-scale storage facilities and a large-scale hydrogen production (more than 1 million tonnes hydrogen/year/production location). The scale and dimensions of such a hydrogen system are in general about a factor of 10 larger than the electricity system.
2. Stimulate both large-scale (more than 1 million tonnes hydrogen/year) low-carbon hydrogen and renewable hydrogen production at the resource sites. Over time renewable hydrogen will replace low-carbon hydrogen production, because it is cheaper.
3. The EU does not have the good renewable resources and enough space and therefore will not be self-supporting in cheap renewable energy production. It needs to develop unique and long-lasting mutual cooperation on political, societal, and economic level between the EU and neighboring regions, especially North Africa to be able to import cheap renewable hydrogen.
4. Large-scale renewable hydrogen production requires substantial space, more than 1 million tonnes hydrogen production by solar and/or wind requires at least 500 km^2. It is therefore necessary to implement spatial planning policies to designate areas for large-scale low cost (>1 million tones hydrogen/year) renewable hydrogen production.
5. To stimulate renewable and low-carbon hydrogen production, develop CO_2 emission reduction mechanisms, such as Energy Trading Systems or subsidy/grant systems based on energy system cost and not on energy production cost alone.

6. Convert the existing natural gas pipeline infrastructure as soon as possibly into a hydrogen pipeline infrastructure or realize a new dedicated pipeline hydrogen infrastructure as soon as possible.
7. Develop import and export facilities for hydrogen and hydrogen products such as ammonia or hydrogen bound to other elements by ship. Stimulate ports and shipping companies to build up terminals, logistics and supply chains for hydrogen and hydrogen products.
8. Develop large-scale hydrogen storage near the production (in order to level out fluctuating renewable hydrogen production) and near the demand (in order to deal with demand fluctuations).
9. Hydrogen will take over the role of fossil fuels, oil, gas, and coal as the energy commodity that can be transported worldwide. A worldwide hydrogen market will emerge, with worldwide price setting and international price competition. It is important to develop hydrogen trade markets as soon as possible.
10. Combustion technologies produce NOx, particulates, and other emissions to the air. Electrochemical conversion technology including heat pump technology does not have these emissions. Therefore, it is not only stimulating replacement of fossil fuels by hydrogen in present day combustion technology but also stimulating electrochemical conversion technology.

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Paula Abreu Marques, Ruud Kempener

The European hydrogen strategy

Summary: On July 8, 2020, the European Commission (EU) presented “A hydrogen strategy for a climate-neutral Europe.” The strategy was published alongside the Energy System Integration strategy, which examined the pathways toward climate neutrality by 2050. This article discusses the background for the hydrogen strategy, the drivers for the publication of the strategy, and the rationale for the proposed actions that have been considered by the hydrogen strategy.

1 Introduction

Energy has always been at the core of Europe’s cooperation efforts to secure peace, economic growth, jobs, and a rising standard of living. The creation of a common energy market, equal and secure access, competitive prices, and rational use of our natural energy resources have been guiding principles over the last 60 years [1].

The current Commission continues to put energy high on the agenda, with “A European Green Deal” as its top priority [2]. This strategy, published in December 2019, takes the Commission’s vision of a climate neutrality by 2050 as the starting point, and argues that a transition of both the energy system and economic activities are needed to ensure the EU’s economic, societal, and environmental objectives.

The decarbonization of the energy system is critical to reach the European climate objectives for both 2030 and 2050. In this respect, the “European Green Deal” put forward the need to ensure a smart integration of renewable energy sources, energy efficiency, and other sustainable solutions, such as smart grids, energy storage, carbon capture, utilization and storage as well as the production of hydrogen and hydrogen networks, to ensure decarbonization at the lowest possible cost. The “European Green Deal” also recognized hydrogen as one of the technology options that can ensure that the EU industry remains at the technology forefront, and delivers breakthrough technologies in key industrial sectors.

Following the launch of the “European Green Deal,” the European Commission delivered its dedicated strategy on Energy System Integration [3] and Hydrogen [4] in July 2020. Both strategies delivered a concrete set of actions to deliver on the objectives outlined in the “European Green Deal.”

The Energy System Integration strategy provided an overall vision on how to accelerate the transition toward a more integrated energy system. The strategy includes six pillars where coordinated measures are needed to address existing barriers for energy system integration. The role of hydrogen is identified in three out of the six pillars.

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First, renewable and low-carbon hydrogen provides the opportunity to decarbonize a number of end-use applications where the direct use of renewables or electrification might not be feasible or has higher costs. In this respect, low-carbon hydrogen is defined as encompassing fossil-based hydrogen with carbon capture and electricity-based hydrogen, with significantly reduced full life-cycle greenhouse gas emissions compared to existing hydrogen production. Furthermore, the strategy identifies that renewable hydrogen produced through electricity using renewable electricity can play a particularly important "nodal" role in an integrated energy system, by providing flexibility by offloading grids in times of abundant supply, and by providing long-term storage and energy buffering options.

Second, the Energy System Integration strategy identified new actions to ensure that energy markets are fit for new decarbonization options, including issues around the creation of open and competitive markets for hydrogen.

Third, the Energy System Integration strategy foresees activities to ensure a more integrated energy infrastructure. This includes a more holistic view of both electricity and gas infrastructure, as well as CO_2-dedicated infrastructure for those hydrogen projects relying on carbon capture and storage.

Alongside the Energy System Integration strategy, the Commission also published a dedicated strategy on hydrogen [4]. This strategy elaborated in more detail on the opportunities and necessary measures to scale up the production and uptake of hydrogen, but also linked the opportunities of hydrogen in the context of recovery from the COVID-19 crisis that struck Europe in March 2020.

The Hydrogen Strategy not only builds upon the Strategy for Energy System Integration [3] but also looked in more detail at the actions that would be needed to build a dynamic hydrogen ecosystem in Europe, create new opportunities for the European industry as well as Europe's role in the emerging international market for hydrogen. The strategy also provided a roadmap for hydrogen production and consumption in Europe, and set out the Commission's priority to develop renewable hydrogen as the most compatible option with the EU's climate neutrality and zero pollution goals in the long term and as the most coherent option with an integrated energy system.

The next four sections discuss the four key topics of the European hydrogen strategy. The first topic is the key application areas for hydrogen, and its role in the future energy mix. The second topic discusses the different policy options that are under consideration to promote the production and demand of hydrogen, including the need for market rules and infrastructure. The third topic discusses the role of research and innovation, and the different activities proposed under the European hydrogen strategy. The fourth topic discusses the international role of hydrogen.

2 The role of hydrogen in the energy system

The European energy system is more diverse, more secure, more efficient and cleaner than it has ever been. The level of interconnections between European Member States is stronger than in any other world region, and new digitalization solutions are already allowing energy trade deals to take place at an hourly basis across Europe. Energy consumers have a wider range of choices to satisfy their energy demand, and decentralized renewable energy production is increasingly empowering citizens and communities to play an active role in the energy transition.

This energy system provides a solid starting point to achieve Europe's ambitions to become the first climate neutral economy, and has significantly evolved since the 1990s (see Fig. 32). However, the scale and pace of transition is such that simply replacing traditional energy carriers with greener alternatives will not be cost-effective or even possible at all. The data clearly show that to achieve climate neutrality, the change of pace needs to be significantly different and the energy consumption will radically change across different end-use sectors. Furthermore, a more distributed, digitalized, and decarbonized energy system will require fundamental changes in the way we develop and manage our energy system, some of which are already becoming visible today.

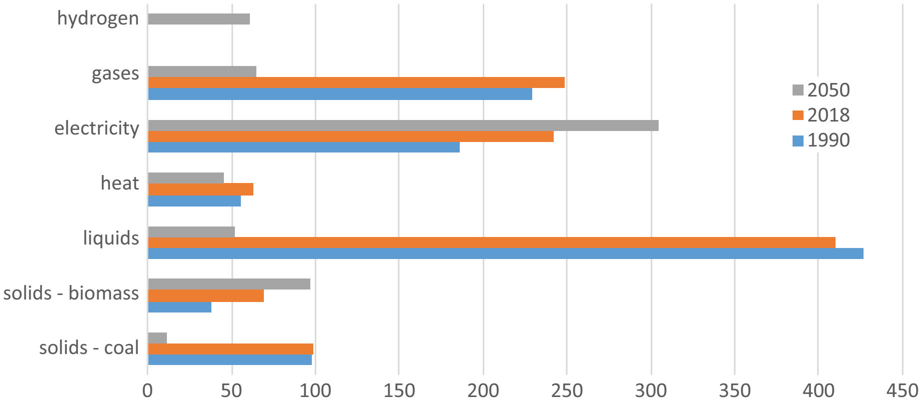

Fig. 32: Historical and future energy mix within the European Union [5, 6].

In the 2018 analysis, "A Clean Planet for All" [7], the Commission analyzed eight scenarios to examine different levels of greenhouse gas emission reductions for 2050. It also included two specific scenarios, called Hydrogen and Power-to-X that looked at promoting hydrogen as a pathway toward climate neutrality [6]. These specific scenarios showed that the high level of hydrogen consumption, especially through hydrogen consumption in residential and services sector and if hydrogen would be used for the production of e-fuels, increases the need for more renewable and low-carbon electricity production.

Furthermore, the scenarios showed that when combining all gaseous fuels (natural gas, biogas, e-gas, and hydrogen), different patterns emerged. In the scenarios that promote strong energy efficiency measures and electrification, gaseous fuels are roughly halved compared to today. Conversely, large-scale end-uses of hydrogen or the use of e-gases would result in a total consumption of gaseous fuels that could even exceed expected gaseous consumption in 2030. Finally, the share of hydrogen and e-gases increases with the ambition levels for greenhouse gas emission reductions.

At the same time, the analyses showed that irrespective of the technology pathway or ambition levels, the share of hydrogen in the energy mix will substantially increase compared to today's levels. Furthermore, all scenarios found significant growth of hydrogen consumption in the transport sector and industrial applications, as well as a role of hydrogen as a storage option in the power sector. The analyses show that solar and wind power are expected to increase to 36% and 65% of electricity production in 2030 and 2050, respectively [8]. Short- and medium-term flexibility will be needed in the day-ahead, intraday, and balancing markets by demand response, batteries, and other technologies. By transforming electricity into hydrogen when electricity is abundant and cheap, and seizing production when electricity is scarce and prices are high, hydrogen production can provide flexibility at all time scales [9]. Hydrogen can also be stored seasonally as a backup to produce electricity when needed providing security of supply for our future energy system.

These findings of these analyses on the long-term energy mix to achieve a climate neutral economy were re-affirmed by the analyses done for the 2030 Climate Target Plan [8]. The analysis shows that increased energy efficiency as well as the rapid uptake of renewable power continues to be strong driving forces to reduce greenhouse gas emissions in the period up to 2030. However, at the same time, it recognizes that to allow industry to truly decarbonize after 2030, zero or very low-carbon technologies and business concepts, including system integration, access to sustainable resources and increased circularity, medium and high heat electrification, hydrogen and carbon capture, utilization and storage, will need to be developed and tested at scale in this decade.

The analysis underpinning the 2030 Climate Plan shows that from a cost-optimization perspective, the role of hydrogen remains relatively limited with 12–13 GW of electrolyzers needed by 2030, compared to the 1.5 GW of electrolyzers projected in the baseline scenario. However, to achieve the climate neutrality objectives, all policy scenarios foresee a rapid ramp up of installed electrolyzer capacity between 40 and 70 GW by 2035 and between 528 and 581 GW in 2050 [8].

Other analyses have similar results, although the overall scale of hydrogen consumption differs substantially across the different scenarios. An overview of 11 different climate-neutral scenarios show that the majority of studies foresee the use of hydrogen in the transport sector and in industrial applications, with smaller amounts of hydrogen used to support the electricity sector. Only 3 out of the 11 scenarios foresee a significant role of hydrogen in the buildings sector. The level of hydrogen consumption highly depends on assumptions about the overall energy consumption in 2050. The scenarios with the lowest energy demand have also the lowest hydrogen demand in 2050, although the share of hydrogen in the energy mix could still reach 5% to 20% [10].

At the same time, current hydrogen production in Europe amounts to only 325 TWh, primarily produced by natural gas or as by-product, and used as feedstock in the chemical industry [11]. Hydrogen production through electrolyzers accounts for less than 4% of current hydrogen consumption. Hydrogen is not being used to decarbonize energy consumption yet, because it is a more expensive decarbonization option compared to the direct use of renewables or through electrification with renewable power and thus requires significant changes in industrial processes or vehicle technology.

Whilst around 280 companies are active in the production and supply chain of electrolyzers and more than 1 GW of electrolyzer projects are in the pipeline, total European production capacity for electrolyzers is currently below 1 GW/year [12]. Increasing production would require a sustainable industrial ecosystem, which would include strengthening a skilled workforce, industrializing key components, and scaling-up technologies for creating new businesses opportunities across the full supply chain.

Based on this analysis, the European Hydrogen Strategy identified industrial applications in existing demand centers such as large refineries, steel plants, and chemical complexes a key application area for scaling up renewable hydrogen production. In this respect, several demonstration projects have already come online or are in final stages of development. Existing projects include a 6 MW renewable hydrogen electrolyzers at a steel plant in Austria, a 10 MW renewable hydrogen electrolyzer to be completed close to a refinery in Germany, and a 20 MW renewable hydrogen electrolyzer for the production of methanol in the Netherlands [13]. In addition, specific transport applications, such as heavy duty transport applications, could be fueled through hydrogen refueling stations supplied by local renewable hydrogen production. Already, more than 125 hydrogen refueling stations exist within the EU with 87 located in Germany, whilst there are around 66 fuel cell busses and 300 fuel cell commercial vehicles on the road [14].

In a second phase, the European hydrogen strategy foresees industrial demand to gradually include new applications, including steel-making, trucks, rail and some maritime transport applications, and other transport modes. In the steel sector, several producers have already put demonstration projects in place to use hydrogen for the production of sponge iron, and the first large-scale projects for the production of green ammonia have been announced in Spain. Furthermore, several European truck manufacturers have announced the production of fuel cell trucks and an Italian shipbuilder has announced the delivery of the first fuel cell ships.

In this phase, renewable hydrogen will start playing a role in balancing a renewables-based electricity system by transforming electricity into hydrogen when renewable electricity is abundant and cheap and by providing flexibility. Several projects, including a 1.2 MW electrolyzer in Denmark, have already demonstrated the possibilities for renewable hydrogen in this perspective. Furthermore, the European

Commission supports under its Union cohesion policy innovative small- and medium-size enterprises and the creation of new firms, growth start-ups and accelerators to promote the development and actual use of hydrogen innovative solutions across the value chain, including through the Hydrogen Valleys partnership launched in 2019.

3 Policy support for hydrogen

To facilitate this phased development, the European hydrogen strategy also introduces a number of policies to support the deployment of hydrogen. These policy instruments can be broken down into four categories: 1) financial instruments; 2) terminology, certification, and targets; and 3) market and infrastructure regulation.

First, the European hydrogen strategy does not expect the production of both low-carbon hydrogen and renewable hydrogen to be cost-competitive with fossil-based hydrogen. As such, the hydrogen strategies identify a number of financial instruments as well as political decisions that could be considered to support the production of renewable and low-carbon hydrogen. As such, the European Commission has already analyzed the investment needs in the EU Member States [15], and has proposed a flagship project under its Recovery and Resilience Facility to support the production of renewables and renewable hydrogen within its Member States. Furthermore, the European Commission is developing its financing instruments under the newly agreed budgets for the period from 2021 to 2027, including support for the development of infrastructure as well as leveraging private sector investments through grants and loans.

Second, the strategy proposes to develop a comprehensive terminology and European-wide criteria for the certification of renewable and low-carbon hydrogen. Such a certification scheme would also have to be compatible with certification of other renewable and low-carbon fuels that could be used by end-consumers. Such certification could draw from the existing requirements for renewable fuels and fuels of non-biological origin that exist under the Renewable Energy Directive to support renewables targets in the transport sector [16] as well as industry initiatives to track life-cycle greenhouse gas emissions for the production of renewable and low-carbon hydrogen from "well-to-gate."

At the same time, the strategy also considers different instruments to promote the production of renewable and low-carbon hydrogen, including through the revision of the EU Emissions Trading Scheme and the possible introduction of carbon contracts for difference. Finally, the strategy is also considering direct market based support schemes and quotas specifically for renewable hydrogen. Such measures are currently considered for the impact assessments for the revision of the existing renewable energy directive [16].

Third, the strategy proposes to examine the need for new regulation for hydrogen. This may include new regulation to ensure the interoperability of markets for pure hydrogen, common quality standards (e.g. for purity and thresholds for contaminants), or cross-border operation rules. At the same time, the rules for operating and financing hydrogen infrastructure will have to be examined as well as the process for ensuring the full integration of hydrogen infrastructure in the infrastructure planning for electricity, gas, heat in addition to transport infrastructures.

4 Research and innovation

Europe has a long history of research and innovation in hydrogen, culminating in the integrated European strategy on hydrogen in 2003, which led to the establishment of the Hydrogen and Fuel Cells Technology Platform in 2003, the Fuel Cells and Hydrogen Joint Undertaking (FCH JU) in 2008, and its successors in 2014 and 2019.

Since its launch in 2008, the FCH JU has been a public–private partnership supporting research, technological development, and demonstration activities in fuel cell and hydrogen energy technologies in Europe. It has supported more than 260 projects, for over 900 million euros from public money (matched on an equal basis by the industry), in the areas of transport, green hydrogen production, heat and electricity production, critical raw materials, and energy storage [17].

The FCH JU has succeeded to establish a European leadership for technologies such as electrolyzers, and the latest projects aim at demonstrating multi-MW installations, several projects on micro-CHP, medium size fuel cells, and MW-scale fuel cells, including projects on hydrogen injection in the gas grid.

To ensure a full hydrogen supply chain to serve the European economy, further research and innovation efforts are required, spanning a variety of technologies and maturity levels. This is the case for upscaling to larger size electrolyzers in the range of the GWs that, together with mass manufacturing capabilities, is needed to serve sustainable industrial areas as well as ports and airports at scale. Projects such as the Port of Rotterdam MULTIPLHY illustrate the leadership and dynamism in Europe: it will become the world’s first commercial-scale solid oxide electrolyzer at a bio-refinery, producing 960 tonnes of renewable hydrogen by the end of 2024 [18].

Infrastructure also needs further development in order to distribute, store, and dispense hydrogen at large volumes and possibly over long distances. A particular question is the possibilities to repurpose large parts of the existing gas infrastructure for the use of pure hydrogen flows, with already some positive experiences in the Netherlands [19]. In the area of hydrogen storage, the Hestor research project in Poland [20] is investigating the storage of hydrogen generated from renewables in salt caverns and use it as a fuel for gas turbines during peak demand periods, in refineries and for transport purposes.

At the same time, the development of low-carbon industrial clusters equipped with highly efficient CO_2 capture and compression solutions, such as the H-vision project [21] in the port of Rotterdam that aims to capture CO_2 stored in depleted gas fields deep below the North Sea seabed, would be necessary to support a transitional low-carbon hydrogen role in the path toward renewable hydrogen.

Solutions at lower technology readiness level need also to be incentivized and developed such as, hydrogen production from marine algae, from direct solar water splitting, or from pyrolysis processes with solid carbon as side product, while paying due attention to sustainability requirements. Further research is needed to support policy making, in particular to enable improved and harmonized (safety) standards and monitoring.

At the same time, continued research and innovation is needed to create a full ecosystem around hydrogen. Reliable methodologies have to be developed for assessing the environmental impacts of hydrogen technologies and their associated value chains, including their full life-cycle greenhouse gas emissions and sustainability. Importantly, critical raw material reduction, substitution and recycling needs a thorough assessment in the light of their future expected increasing deployment, with due account being paid to ensuring security of supply and high levels of sustainability in Europe.

To address all these challenges, the Commission has proposed the continuation of the FCH JU under Horizon Europe as an institutionalized Clean Hydrogen Partnership, expected to have a stronger focus on renewable hydrogen production, transmission, distribution, and storage, alongside the focus on fuel cell end-use technologies. The partnership will engage Member States efforts and collaborate with other proposed partnerships under Horizon Europe, and focusing specifically on the decarbonization of end-use sectors (e.g. on clean steel, circular and climate neutral industries, zero-emission transport) [4].

Beyond the partnership, the Commission will mobilize a wide range of support instruments, including capacity building initiatives, to cover the entire innovation cycle and to foster cooperation and synergies between relevant hydrogen research programs. The cooperation with research and innovation efforts of Member States in the context of the Strategic Energy Technologies (SET) Plan priorities [22] will also be ensured. Synergies with other instruments such as the Innovation Fund or Structural Funds will be sought in order to bridge the valley-of-death through first-of-a-kind demonstration projects. The first call for the Emissions Trading Scheme (ETS) Innovation Fund closed in October 2020, with its example list of projects including more than 20 different hydrogen projects.

5 International cooperation

International cooperation among countries started as early as 1977, when the first collaborative frameworks on hydrogen were established under the International Energy Agency. In 2003, the International Partnership for Hydrogen and Fuel Cells in the Economy (IPHE) was established as an additional international research cooperation, with close cooperation between the United States, Japan, and the EU, addressing different segments of the hydrogen value chain.

The 2015 Paris Agreement and the national governments, determination to move toward climate neutrality in 2050 are regaining the momentum for hydrogen at an international level. Besides governments of both energy exporting and energy importing countries, today's coalition in favor of clean hydrogen includes a variety of stakeholders, including from industry and transport sectors that increasingly are aligning their businesses toward climate neutrality in 2050. The rapid decline of the costs of renewable power, electrolyzers, and fuel cells contribute to repositioning the role of renewable hydrogen at European and global level.

The foundation of the Hydrogen Council – an industry initiative launched under the World Economic Forum – and the First Hydrogen Energy Ministerial Meeting, hosted by Japan in 2018 all added to the political attention for hydrogen. This was followed by hydrogen-focused G20 Ministerial Meeting on Energy Transition in 2019, the launch of a Hydrogen Initiative under the Clean Energy Ministerial, and the establishment of a collaborative framework on green hydrogen under the International Renewable Energy Agency in 2020.

As a consequence, international cooperation on hydrogen is rapidly moving beyond research activities to discussions on hydrogen policies, the setting of international standards for hydrogen, as well as cross-border cooperation on hydrogen. The European hydrogen strategy foresees three areas of actions in this respect.

First, the European hydrogen strategy foresees increased cooperation with its with neighboring countries and regions. This increased cooperation could range from research and innovation to regulatory policy, direct investments and trade, and focus on compatible policy frameworks for the energy transition, and associated infrastructure in addition to the opportunities for trade.

Second, the European hydrogen strategy foresees increased cooperation with other third countries on the setting of international standards, the development of the required infrastructure and setting up common definitions and methodologies to define overall emissions from each unit of hydrogen produced and carried to final use. The development of global standards for hydrogen will be facilitated by cooperation under G20, as well as with the International Energy Agency (IEA), the International Renewable Energy Agency (IRENA), and the Clean Energy Ministerial (CEM) initiatives.

Third, the European hydrogen strategy also foresees opportunities in the creation of a global market of hydrogen, including providing support to the energy transition and climate commitments by third countries. These activities include raising awareness of clean hydrogen opportunities amongst public and private sectors, capacity building to effectively address regulatory barriers, transfer of knowledge, and identification of business opportunities for market ready clean hydrogen solutions, for instance, for industrial uses, transport applications, or as energy storage.

6 Conclusions

The article shows that both the internal European situation as well as the international setting is rapidly changing, and that the European hydrogen strategy has to be placed within this specific context. The simultaneous publication of both the Energy System Integration strategy and the Hydrogen strategy provides the right framework within which to examine the different decarbonization options and their contributions to a transition toward a climate-neutral economy. At the same time, the European Green Deal as Europe's economic growth strategy as well as the need for a post-COVID recovery plan provides an unique opportunity to scale up investments in the development and deployment of renewable and low-carbon hydrogen. The article shows that it is important to separate out three objectives. First, renewable and low-carbon hydrogen can contribute to the objective of increased greenhouse gas emission reductions as well as economic recovery in the short term. Second, renewable hydrogen can support the creation of a competitive industrial ecosystem and contribute to economic development in the medium-term, including strengthening EU's position globally. Third, renewable hydrogen can become an indispensable part of a decarbonized energy system to support the climate neutral economy in the long term. None of these policy objectives can be met in isolation, and that is why it is so important that the hydrogen strategy brings together the different policy instruments to ensure a coherent approach.

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Andreas Züttel

Introduction to the hydrogen books

Abstract: Hydrogen produced from renewable energy represents the most important chemical energy carrier storing renewable energy. It can be produced by water splitting with electricity or thermal energy. The storage of hydrogen, that is, the reduction of the volume, is the challenge of the direct application of hydrogen as an energy carrier. While the density of hydrogen molecules is limited to the density of liquid hydrogen, hydrogen atoms bond to other elements exhibit densities up to greater than twice the density of liquid hydrogen, for example, metal hydrides. The storage of hydrogen at elevated densities requires a sophisticated storage system, which makes the storage more expensive and technically challenging. Hydrogen in hydrocarbons is stored by well-established technology and significantly less expensive than pure hydrogen storage.

1 The post fossil era

It is 200 years after the steam engine has formed the basis for the industrialization and the energy for the engines was found in fossil fuels. Before the only engines available were wind turbines used in the Netherlands to pump water and to run the mills and hydropower moving the hammer for the black smith all based on renewable energy. After the Second World War, the western world heavily industrialized, the mobility increased, and the houses became much more comfortable. With the analysis and modeling of the depletion of oil fields by M. King Hubbert [1], it was realized that the global reserves on fossil fuels are limited. His model was validated by the oil crisis in 1973 and the report "Global 2000" by the Club of Rome [2]. The climate change due to the combustion of fossil fuels and release of CO_2 was first estimated by Svante Arrhenius in 1896 [3]. However, only a hundred years later it became generally accepted that the increase of the average temperature correlates with the increase of CO_2 in the atmosphere [4] and that the climate change is going to have a severe impact on the environment [5]. The limited resources, the climate change together with the growing population and the economic dependence on the energy consumption are the main driving forces for the global energy turnaround. The goal is to limit the increase of the CO_2 concentration in the atmosphere and introduce closed materials cycle for energy as well as closed cycles for all materials in order to provide more energy and materials with less impact on the environment. However, the growth of photovoltaic (PV) and wind power in Germany in the last ten years from 5 to 40 and 20 to 40 GW_p of installed peak power [6], respectively, demonstrated that within a decade the installed peak power of renewable

https://doi.org/10.1515/9783110596274-007

energy can exceed the average electric power consumption (61 GW annual average in Germany).

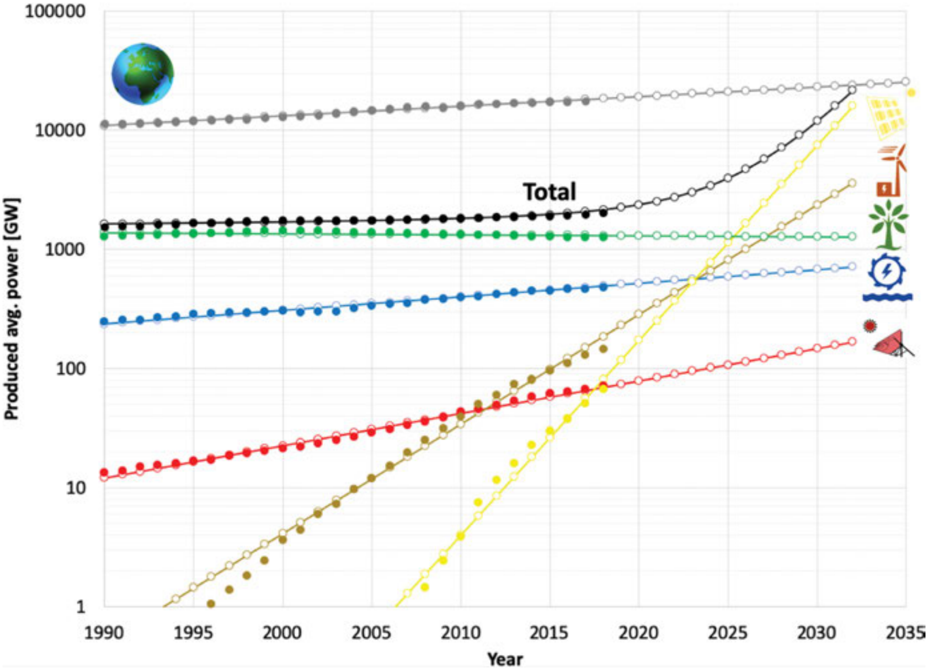

Fig. 33: Global produced power from renewable energy converters (hydroelectric power in blue, solar thermal in red, wind power in green and PVs in yellow) and extrapolation assuming the exponential growth continues [7]. The sum "Total" grows more than exponential with >58%/year [8].

The global installed peak power for PV is growing exponentially since 20 years, with a growth rate of approximately an order of magnitude every five years (+58%/year). The growth rate of wind power is smaller. The installed peak power of PV bypassed the one of wind two years ago. Extrapolating the exponential growth of renewable energy production (Fig. 33) leads to 18 TWp (the current average global energy demand is estimated to be 18 TW) in the year 2025. In order to cover the world energy demand hypothetically by renewable energy, the peak power needs to be approximately two to ten times larger than the average power and will be reached in an additional five years of continuous growth, that is around 2030. However, the growth is slowing down as can be seen in the figure for the recent years the fitted line is above the actual installed power for PV, wind, and solar thermal.

The intermittent character of solar and wind power requires to store a significant amount of the annually produced energy because of the seasons. Close to the equator are no seasons observed and no seasonal storage is needed, however, if the energy is produced and converted it has to be transported and distributed. Therefore, the main challenge is no more to produce electricity from renewable energy but to store the energy in a usable form, which is to technically realize the conversion of renewable energy into an energy carrier and to build up the necessary storage capacities as well as the energy distribution network.

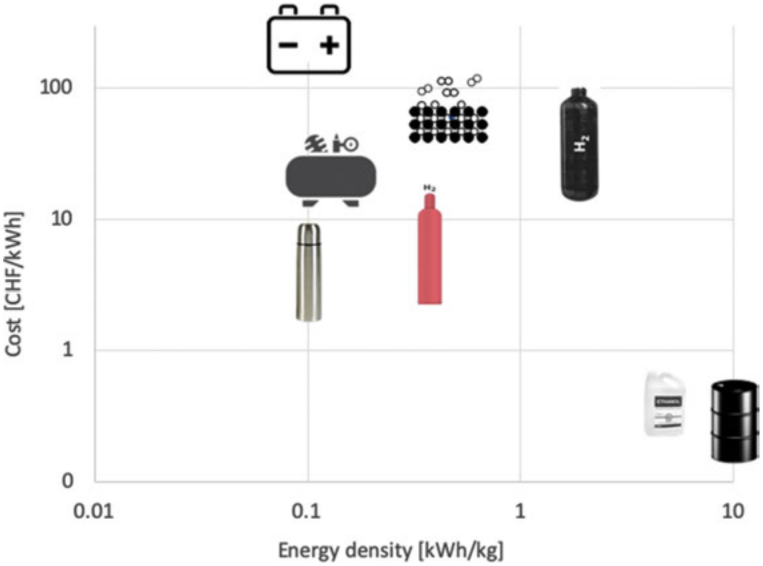

Fig. 34: Cost of energy storage versus gravimetric energy density.

Currently Europe and the United States have a focus on electrifying the residential energy demand and the mobility with storage of electricity in batteries, while in Asia, for example, Japan and Korea develop a hydrogen economy especially for mobility. From Fig. 34, it is obvious that battery storage is the most expensive and exhibits the lowest energy density. As a consequence, the battery electric cars become heavier and more expensive with a much smaller range. The consequences and efficiency of the energy system for the transport by electric car is a debated topic and still not proven, if it will lead overall to a reduction of the CO_2 emission.

Hydrogen can be produced by electrolysis from renewable energy and water and is the direct product from water splitting. Nature closes the hydrogen cycle because water precipitates from the atmosphere in contrast to CO_2 that remains diluted in the atmosphere.

2 Hydrogen as an energy carrier

Hydrogen can be produced from renewable energy and with the highest energy density of all combustibles and an abundant material source, that is water, represents the most appealing energy carrier for renewables. Furthermore, energy storage in batteries [9]

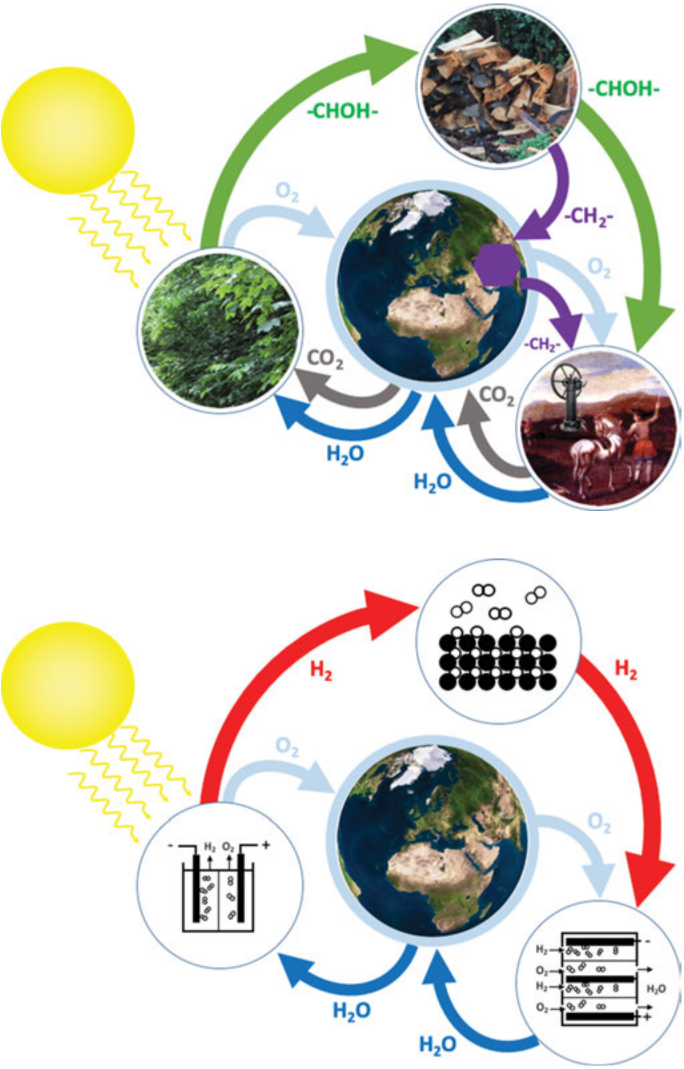

Fig. 35: Natural carbohydrate cycle on the left where the plants do photosynthesis i.e. synthesize carbohydrates from CO_2 and water, the biomass spontaneously decomposes into hydrocarbons or degrades or digested to CO_2 and H_2O. The hydrogen cycle on the right starting with electrolysis of water with renewable (solar) energy, followed by hydrogen storage and finally the combustion of hydrogen in a fuel cell.

costs 200 US$/kWh, in hydrogen 5 US$/kWh and in a hydroelectric power station 0.05 US$/kW [10], therefore, hydrogen offers a cheap way to store energy and is a mobile energy carrier. The hydrogen cycle consists of three sectors: hydrogen production, hydrogen storage, and hydrogen combustion. Nature closes the hydrogen cycle by precipitation of the evaporated water.

The main challenge of the realization of the hydrogen cycle is the efficient and cost-effective production of hydrogen from renewable energy and the dense hydrogen storage. Hydrogen can be produced from any hydrogen containing compound, however, the most sustainable process is water splitting with renewable energy. Hydrogen production from renewable electricity by electrolysis is the most efficient method known for the conversion of renewable energy to an energy carrier. Electrolyzers work with current densities of 0.2–3 A/cm^2 that corresponds to 3–60 kW/m^2 and, therefore, the production of 1 kg H_2/hour requires approximately 1 m^2 of electrode surface. An electrolyzer with a nominal power of 1 MW (380 V) consists of 200 cells in series with 1 m^2 of geometrical electrode surface each. Beside electrolysis, hydrogen can be produced by thermal water splitting, oxidation with water (e.g. steam reforming of methane) and photo-electrochemical water splitting. The main cost of hydrogen production is the electricity cost, the investment today is around 1500$/kW that corresponds to less than 1 cts./kWh, if the electrolyzer lasts for more than 20 years.

Hydrogen exhibits the highest gravimetric energy density (heating value) of all combustibles but, due to its physical properties, takes a very large volume. The goal of hydrogen storage is to reduce the volume as much as possible with adding as little weight as possible. The maximum hydrogen density is found in metal hydrides with 150 kg/m^3, more than twice the density of liquid hydrogen (70.8 kg/m^3) and hydrogen at atmospheric pressure and room temperature exhibits a density of only 0.089 kg/m^3. The ratio of the factor of volume reduction to the factor of weight increase (Tab. 8) allows to qualify the storage beside the efficiency and the cost of the material.

Liquid hydrogen has a volume factor of 877, that is, in a volume of liquid hydrogen, there is 877 times more hydrogen than in the same volume at standard conditions ($p = 10^5$ Pa at $T = 298$ K). Compressed hydrogen gas (Fig. 36), liquid hydrogen, and physisorbed hydrogen are described by the Van der Waals interaction, while hydrides and hydrogen containing compounds are chemical bonds between the hydrogen and the other elements. Hydrides exhibit a volume factor of >1500 and are, therefore, the densest form of hydrogen beside hydrocarbons with 1504. Complex hydrides exhibit the highest ratio f_V/f_m, that is, allows to reduce the volume the most with adding the lowest amount of mass and are, therefore, an ideal hydrogen storage media.

Hydrogen is a very versatile fuel and is used as a rocket fuel for propulsion, in catalytic combustions for heat or in fuel cells to produce electricity and heat.

Tab. 8: Hydrogen storage materials with the storage parameters mass, volume, volume factor, mass factor, and ratio volume to mass ratio.

	[mass%]	[kg/m^3]	f_V	f_m	f_V/f_m
Compressed hydrogen 200 bar	1	13.9	172	100	2
Compressed hydrogen 350 bar	5	21.7	269	20	13
Compressed hydrogen 700 bar	5	34.1	422	20	21
Liquid hydrogen at 21 K	20	70.8	877	5	175
Physisorption 77 K	7	7.0	87	14	6
Metal hydrides	1.4	150.0	1858	71	26
Complex hydrides	18	140.0	1734	6	312
Carbohydrate	7	46.7	578	14	40
Hydrocarbon	15	121.4	1504	7	226

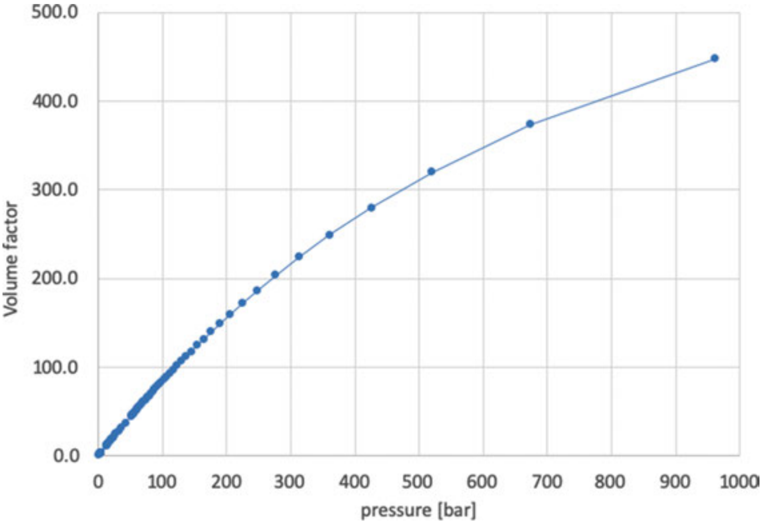

Fig. 36: Volume factor (factor of standard volume at pressure p) of compressed hydrogen gas versus pressure.

2.1 Synthetic fuels

Synthetic fuels are beside pure hydrogen compounds of hydrogen, nitrogen, or carbon and oxygen, preferably liquid at room temperature or at least condense to liquid at ambient temperature and reasonable pressure. Synthetic fuels have the great advantages that they are easier to store, that is, less material dependent than hydrogen, and they exhibit a high gravimetric and volumetric energy density. The combustion products of synthetic fuels with oxygen (O_2) are preferably gaseous, for example, H_2O vapor, CO_2, and N_2. The synthesis of the fuels starts directly or indirectly from hydrogen providing the element and also the energy and nitrogen (N_2) or carbon dioxide (CO_2). The concentration of nitrogen in air is close to 80% while the concentration of CO_2 is increasing but currently only 0.04%, therefore, the CO_2 capture is approximately 32 times more energy demanding than capture of N_2.

The synthesis of ammonia (NH_3) is a well-established industrial process and the mechanism has been investigated in great detail [11]. Ammonia is stored in liquid form at 20 °C below 10 bar of gas pressure and exhibits a density of 607 kg/m^3 with a higher heating value of 6.25 kWh/kg similar to methanol. The stem-methane-reforming-fed Haber–Bosch synthesis is more or less at its technical limit and demands 7.8 kWh/kg NH_3 depending on the source of energy. The theoretical electric input required to produce hydrogen by the electrolysis of water is 7 kWh/kg ammonia [12]. Carbon dioxide reduction allows to produce a large variety of hydrocarbons, carbon hydrates, alcohols, and ethers. The capture of CO_2 from air requires theoretically 0.12 kWh/kg CO_2 at 400 ppm and 4 times less energy at 12 Vol.% CO_2 concentration in the exhaust of a combustion process. The CO_2 reduction is an exothermic reaction with a negative entropy change, therefore, the equilibrium is at low temperature on the product side and at higher temperature moves toward the reactants. This makes the catalyst crucial for a high yield of the reaction. More than 70% of the energy in the hydrogen is conserved in the hydrocarbon product.

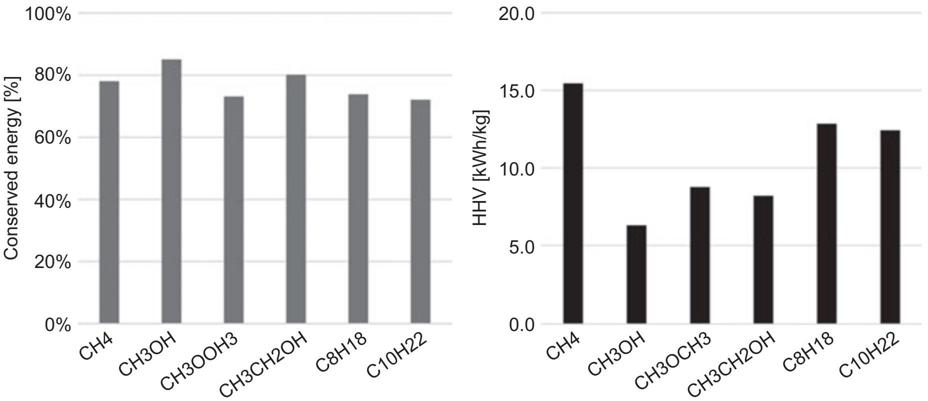

Fig. 37: Energy transferred in the CO_2 reduction reaction from H_2 to the product (left) and higher heating value of the products (right).

While the Sabatier reaction, that is reduction of CO_2 to methane, is selective and reaches a very high yield with Ruthenium catalysts, all the other products are formed with less selectivity and lower yield. The Fischer–Tropsch synthesis, where the CO_2 is first reduced to CO bound on the surface of the catalyst and subsequently a random number of CO form a chain before the intermediate is completely reduced and the product desorbs. This reaction represents a feasible process in large-scale refineries where the desired product is extracted and all other compounds are recycled. The synthesis plant Pearl GTL facility in Qatar [13] produces 140,000 barrels oil/day (8 GW) and has cost 18 B$. This unique example shows that on large scale the synthesis of hydrocarbons (Fischer–Tropsch Synthesis) requires an investment of close to 2300 $/kW. Therefore, synthetic oil is just slightly more expensive than hydrogen, and the cost of the final product is mainly determined by the cost of the electricity.

The production of hydrogen from renewable energy only requires electrolysis and the storage is the main challenge depending on the application. The storage of hydrogen in synthetic hydrocarbons is an interesting alternative that requires a more sophisticated process to produce the hydrocarbon but allows the storage of the product in simple barrels. Furthermore, the combustion of the hydrocarbons delivers energy from the oxidation of hydrogen as well as the carbon, that is, the host material; therefore, hydrocarbons exhibit an energy density greater than 10 kWh/kg.

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Václav Bartuška

Geopolitics of hydrogen

Abstract: Successful implementation of hydrogen strategy by the EU needs to solve two geopolitical constrains: *Technology* (nowadays mostly invented in the United States and built in China) and *Raw materials* (avoiding new dependencies on unstable/unfriendly countries). The impact of Europe's energy transition on present oil and gas exporters is another angle the EU has to take into account.

Introduction

What a difference a single year can make. Twelve months ago, a book published in the EU to promote hydrogen energy would probably not include a chapter on geopolitical risks. Nowadays, no serious publication can ignore the security implications of our energy transition. Increasing dependency on technologies invented in the United States and built in China, shrinking European industrial capacities, growing need of imported raw materials – the year 2020 did not create any of these risks, they have been with us for quite some time. COVID-19 forces us to see them.

Our direction has not changed. The European Union is doubling down on renewables and new technologies, including hydrogen. Post-Covid recovery offers unique opportunity to build whole new industries, rather than repair faltering ones. What has changed is our broader view of security. At the height of the pandemics, European governments learned the hard way that our continent stopped making many basic things. We have spent weeks and months waiting for deliveries of medical material (both elementary and hi-tech) from other parts of the world. Much of the needed equipment did not arrive in time, because the producing countries blocked/postponed export to us.

We need to decrease our present dependencies, not to create new ones. That is why the next two parts are called *Technology* and *Raw Materials*. We also have to understand that our energy transition threatens the livelihood of present oil and gas exporters. We are not going to abandon our effort because of them, but we have to think how to mitigate the new perils. The final part is called *Losers* for a reason.

Technology

In September 2017, as Hurricane Irma neared Florida and the authorities ordered mass evacuation, Elon Musk made a gesture: He increased the range of some models of Tesla cars in Florida for a week. “That's due to Tesla using an unforeseen feature of

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their over-the-air software update system," the article innocently reported in Electrek magazine [1]. The anecdote did not make headlines – mass media, as usual, showed pictures of torn roofs, bent palms, and flooded streets. They missed *the* story of Hurricane Irma.

Yet, we should pay close attention. For in that moment, we got a glimpse of not-so-distant future. Or, as they found out in Florida, the future has already arrived.

Here is a serious warning for Europe: we are introducing technologies, whose authors (and source codes) are beyond the EU borders. Our data, our privacy, even the functioning of our machines and industries increasingly depends on outside players. They may be friendly today. They also may turn against us in the next crisis. Thus the broader context of energy transition is positioning Europe in the world of new technologies.

In the past thirty years, personal computer, internet, and mobile communication transformed our industries and our workplaces beyond recognition; they also changed us in the process, while giving immense amount of profit and control to a handful of companies. None of the Googles and Facebooks of today is a European company – and we are only slowly coming to realize how powerful these firms became.

Next decades will bring widespread use of artificial intelligence, big data, and quantum computing. Owners of these technologies could dwarf the giants of today. For Europe to succeed, the less vulnerable we will be the better.

The connection between new energy systems and advanced software is not always visible at first sight. A case in point is the wind energy. Intermittent by its nature: The wind blows when it wants to. We have no way of predicting whether a particular wind turbine will produce electricity an hour from now, hence the need for back up sources. Yet this is not the whole picture. Over the years, with amassed data about weather patterns from around the globe, our predictions have become more and more precise: There is only limited amount of cloud configurations and pressure differences in the atmosphere, while our computing power is becoming limitless. The truly important question remaining is whether the computers running wind farms in Europe's coastal waters will have our know-how, or depend on outside knowledge.

The greatest opportunity for hydrogen comes in the area of energy storage. This is the weakest point of the whole energy transition so far: We can harvest a lot of Sun's energy – the problem is how to keep it from day to night, let alone from summer to winter. The same applies to wind energy – apart from pumped-water hydropower, we lack means to stockpile the excessive electricity made on weekends or during nights. Hydrogen could be the answer.

These systems will be based on technologies often not yet developed: From new processes to produce hydrogen to novel ways of storage, we need *European* know-how. It will not be easy to get there: The Commission's Hydrogen Strategy [2] is a good start when it comes to investment and government policies; however, we also need to scale up our scientific capacities. Our best universities are lagging behind their US counterparts. We are only slowly creating an European response to the American network of US National laboratories [3]. We need many more CERNs to become truly competitive. The list of present Nobel laureates in physics is mostly an American affair – especially in the “Affiliation at the time of the award” column [4]. It may sound strange from a security guy, but the major recommendation to our Governments and the Union as whole is to significantly increase funding for science and research – not only in the area of hydrogen or broadly energy transition.

In recent years, we started to talk about EU’s *strategic sovereignty*: It is about guns and intel and foreign policy, but increasingly also about science and research capabilities. Since many conflicts in this world originate from struggle for resources, here is a great opportunity for European science – not to allow the energy transition to fall into the trap of new dependencies on outside resources.

Raw materials

Discussing raw materials may seem unnecessary in a book about hydrogen energy. After all, hydrogen is the most common element in the universe. Yet harvesting its potential here on the Earth’s demands the use of other elements, many rather scarce.

One area where hydrogen may play very important role is energy storage. Here are the limitations of other technologies already visible. A good example is the presently most common batteries of the Lithium-ion sort (Li-ion). Lithium is not a problem; there are many deposits in different parts of the world. Crucial component for Li-ion batteries is cobalt – and here lies a trio of issues: War, child labor, and China.

In 2019, more than 70% of global cobalt production came from Democratic Republic of Congo (DRC) [5]. A country tormented recently by two conflicts, dubbed *Africa’s First World War* (1996–1997) and *Great African War* (1998–2003). The latter claimed 5.4 million lives, the biggest bloodshed since WW2. Diamonds, gold, and cobalt were the main spoils of war. The slogan “No blood for oil” is a great one, yet switching to present electric cars (using Li-ion batteries) makes these words hollow.

Child labor is another aspect of cobalt production we do not want to hear about. One third of DRC cobalt is mined by children [6]. A recent lawsuit filed by human rights’ non-profit accuses five major computer and Internet companies (Tesla, Apple, Alphabet, Dell, and Microsoft) of being complicit in death/crippling of 14 children in cobalt mines of Congo [7].

The final problem with cobalt is dominance by a single country: In 2019, half of global production was refined in China [8]. Increasing our dependency on the “systemic rival” (term used in recent EU strategy document [9]) is not a smart thing to do.

This is even more true in case of the rare earth metals, vital elements for much of modern technologies. Here, the Middle Kingdom simply calls the shots: “As of 2019, China still produced roughly 85 percent of the world’s rare earth oxides and approximately 90 percent of rare earth metals, alloys, and permanent magnets,” sums up the report from US think-tank CSIS [10].

We are only at the beginning of the road to fully use hydrogen. We can still make the right choices – and the crucial ones will be how to avoid technologies and processes that would tie us to things we can not live with. I believe in European energy transition, but do not want one based on child labor.

Here is a suggestion to the hydrogen community: Avoid, whenever possible, raw materials linked to human suffering. Sure, money is important and costs are fundamental, but momentum for the whole energy transition is not economy-based. If money was our highest objective, we would keep burning coal for another century. Leaving fossil fuels is based on the fundamental willingness of Europeans to suffer a bit of discomfort today for the benefit of future generations. People feel good about it. Should they find out that their feel-good technologies are based on massive abuse of human rights elsewhere, they might turn against the whole project. You can neither put a price tag on climate change nor on child labor.

Beyond morality, there is also a hard security angle. To put it very bluntly, one of the reasons we are undertaking journey away from CO_2 is to get rid of our reliance on oil and gas producers. We are leaving Persian Gulf. It would make no sense to leave the Gulf for Congo. And even less sense to leave Riyad for Beijing.

Losers

When I tell students at the College of Europe that our energy transition will bring huge economic loss to many countries, their first reaction is disbelief. European Union is *Angelus pacis*, the biggest peace project in history – surely no harm can come from our good intentions?

Yes, it can. Not deliberately, of course; but that does not make it any less real. And the sooner we realize this, the better.

When deciding to leave oil and gas behind, one of the key factors were costs– in normal times, the EU spends roughly 400 billion euros/year on imports of fossil fuels [11]. Moving to domestic and renewables sources will save us a lot of money. By the same token, these 400 billion euros/year will be sorely missed by those who supply us with oil and gas today. What should they do? Our usual response is to tell them “diversify your economy, get rid of dependency on oil and gas.” It’s a great advice – if you are in Berlin or Lisbon or Prague. However, it ignores the size of the problem. The TOP 20 oil and gas economies are [12] as follows:

- Iraq
- Libya
- Venezuela
- Algeria
- Brunei
- South Sudan
- Kuwait
- Azerbaijan
- Qatar
- Nigeria
- Saudi Arabia
- Oman
- Russia
- Kazakhstan
- Iran
- Colombia
- Norway
- United Arab Emirates
- Bahrain
- Bolivia

From Iraq to Saudi Arabia, these countries have more than 85% of state income from oil/gas; the rest a bit less (e.g. Russia “only” 75%), but still more than half. Telling them to diversify their economy away from oil is easy; we should be more concerned what happens to those who fail to do so (because of laziness, incompetence, or civil war). Most of these states unfortunately are not like Norway with its stable democracy, clean politics, and ability to save today’s income for future generations.

Throughout history, severe decline in living standards often resulted in economic collapse, which in turn led to collapse of the state. The European Union is surrounded by countries which view *Green Deal* as a major security threat. From Algeria and Libya to Middle East and post-Soviet space (Azerbaijan, Kazakhstan, Russia), these are all our neighbors; their problems can quickly become ours. Looking at a global scale, there is a certain irony here: From the above-mentioned TOP 20, China has in its proximity a single country (Brunei), while the United States has three (Venezuela, Colombia, Bolivia). It is Europe who has a real problem – yet does not want to acknowledge it.

The present pandemics provide an unexpected insight: The global demand for oil dropped 30% in spring of 2020 and the overall yearly contraction will be around 10%. Such decrease was expected by the greenest scenarios in fifteen years; it is here already (albeit probably not permanently). The negative rate event (–40 dollars/barrel, Cushing, Oklahoma on April 20, 2020) was one-off, limited to a single location and a specific type of contract [13]. Nevertheless, the slowdown of global economy and subsequent diminished need for oil is here to stay for at least a couple of years. We can study in real time what the plunging income from oil will do to oil-dependent economies. And what steps will be needed to keep Europe prosperous and safe. Most likely, they will include hard security (both as detergent against failing states and to protect our borders), as well as more emboldened diplomacy.

A year ago, we thought we have time to think about those security consequences later: It seemed that "peak oil" is decades away and threat to oil/gas exporters from our policies is a long-term one. With global economic trouble due to COVID-19 comes a realization that trouble for oil economies is here – and might not go away.

Coda

Our endeavor to drastically alter energy landscape is one of the biggest projects ever of the European Union. Its success is far from guaranteed: We will need technologies not yet existing and processes not yet developed, with costs not yet fully known. It is in moments like this that I like to quote Václav Havel: "Hope, in this deep and powerful sense, is not the same as joy that things are going well, or willingness to invest in enterprises that are obviously headed for early success, but rather an ability to work for something because it is good, not just because it stands a chance to succeed." [14].

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Volume III: Utilization of hydrogen for sustainable energy and fuels

Gabriele Centi, Siglinda Perathoner

1 Applications of hydrogen technologies and their role for a sustainable future

1.1 Introduction

Hydrogen technologies still maintain a strong momentum for their role in decarbonizing economy. Hydrogen plays multiple roles. It can be used as a feedstock, a fuel, or an energy carrier and storage, although this is still a critical aspect. Furthermore, hydrogen has many possible applications across industry, transport, power, and buildings sectors. Although H_2 uses avoid to emit CO_2 and has almost zero impact on air pollution, H_2 production (and transport, storage, etc.) is different, and even for greener methods such electrolysis, the effective impact on greenhouse gas (GHG) emissions largely depends on how green is the electrically energy used for the continuous production. The term “continuous” is the crucial one, because, for example, in energy-intensive industries (like steel manufacture) a continuous supply of hydrogen is required, while clean energy sources such as wind and photovoltaic are intermittent. If electrical energy is provided from the grid, on the average only about one third derives currently from non-fossil sources.

Thus, in analyzing the role of hydrogen, care is necessary to consider all the pros and cons, and that hydrogen is one element, but not the only one, to construct a sustainable energy future and economy. Nevertheless, hydrogen technologies will undoubtfully be part of the solutions to decarbonize society, including industrial processes and economic sectors where reducing carbon emissions is both urgent and hard to achieve. However, often its use is not so straight in these sectors. There is a growing effort worldwide to realize a hydrogen economy, although there is still a large debate and interests whether in the short term gray or blue H_2 should be introduced, or rather go directly to green H_2 solution.

This introductory chapter aims to present a status of the ongoing discussion and trends in application of hydrogen technology and their role for a sustainable future. It is a viewpoint, rather than a state of the art, specific aspects being analyzed in the following chapters. For this reason, reference is made to personal papers together with selected literature references as examples to sustain discussion, even if this does not imply that these references are the only valuable in the area.

1.1.1 Gray, blue, and green hydrogen

Gray hydrogen is produced using cleaner, but still fossil fuels based sources such as natural gas; blue hydrogen is generated using non-renewable energy sources, for

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example, nuclear, while green hydrogen meets low-carbon thresholds and is generated using renewable energy sources such as solar or wind. Blue hydrogen includes also that still produced from natural gas but avoiding theoretically CO_2 emissions by using carbon capture and storage (CCS) technology. So the question is whether to pass progressively first from a bit cleaner productions of H_2 (gray hydrogen from natural gas), then blue hydrogen (but avoiding the use of nuclear energy for the great societal opposition but also for the costs of the new nuclear plants that are largely above those declared, and the still unsolved problem of nuclear waste) and finally to green hydrogen.

Demand for H_2 in 2019 was about 70 Mt, while forecasts for 2020–21 were strongly influenced by the Covid-19 crisis which has largely affected the clean energy progress [1]. A decrease in H_2 demand between 10% and 20% is estimated and a negative impact also on low-carbon production projects, mostly for oil refining and chemical production. This hydrogen currently is produced from natural gas and coal, and the associated CO_2 emissions are significant. Low-carbon hydrogen production was 0.36 Mt in 2019, thus about 0.5% of the total. The projected production capacity of green H_2 (according to International Energy Agency (IEA) estimations [2]) is 1.45 Mt in 2023, thus an almost 400% increase in just a few years, even remaining at the level of few percentage of the overall H_2 consumption.

In the area of "low-carbon hydrogen" the following two points show the present main production routes typically considered, as mentioned in the IEA report on hydrogen [2]:

(i) coupling conventional technologies with CCS (sometimes using the alternative CCUS acronym, where U indicates utilization, presented as a more sustainable alternative, although the solution presented as utilization is often enhanced oil recovery, which has not these characteristics), for example, blue hydrogen;
(ii) generating hydrogen through water electrolysis, that is, green hydrogen.

In addition, shifting from the use of oil (heavy) fractions or coal to natural gas is still considered an important technology pathway for near-term hydrogen production, although in many countries (e.g., the United States) already over 90% of production derives from natural gas reforming in large central plants.

The number of projects combining conventional technologies with CCS is on the rise. At the end of 2019, 6 projects, with a total annual production of 350 kt of H_2, were in operation, and more than 20 new projects have been announced [2].

Some numbers are necessary to understand better the advantages or not of these solutions. On the average emissions of CO_2 deriving from H_2 production are about 100, 80, and 55 kg CO_2/GJ, from coal, oil fractions, and natural gas, respectively. However, if the impact related to production and distribution of these fossil fuels is also accounted, even higher CO_2 equivalent emissions should be considered. Especially for natural gas, having methane up to 100 times higher (depending on the timescale considered) global warming potential than CO_2, its fugitive emissions due to production/transport are critical. Klemun and Trancik from MIT reported recently [3] that CH_4 emissions from the power sector would need to be reduced by 30–90% from today's levels by 2030 in order to meet a CO_2 equivalent climate policy target while continuing to rely on natural gas as clean fuels.

If production of H_2 from fossil fuels is combined with CCS, the increase of energy (and thus CO_2 emissions) related to CO_2 capture and storage should be first accounted. On the average, for coal the CO_2 equivalent emissions increase to about 170 kg CO_2/GJ, which thus reduce to about 70 and 35 kg CO_2/GJ, if a capture rate of 60% and 80% is considered. This may appear not very high but increasing the capture rate also increases largely the costs and issues related to storage. In addition, besides the several environmental concerns related to storage of large amounts of CO_2, most of the storage are far from the place where H_2 is produced for the local utilization. Additional costs and CO_2 equivalent emissions for transporting carbon dioxide at long distance should be added. Thus, today the increase of costs related to CCS in relation to the relatively low benefits in terms of effective impact on CO_2 reduction, and, in addition, the many environmental concerns present in storing CO_2 make the coal + CCS solution not attractive. In terms of numbers, the situation is better for natural gas + CCS situation, with about 30 and 15 kg CO_2/GJ for a capture rate of 60% and 80%, respectively. Thus, on average 45% and 70% reduction of CO_2 emissions, but if the impact of methane losses related to production and transport are also considered, these values decrease significantly. Thus limited reduction of carbon footprint in front to relatively high costs for this solution. Reliable effective costs for CCS are difficult to find, and often effective costs are larger than estimations. Even specific recent studies, such as that by the Hydrogen Council [4], report indications to total costs for H_2 to become competitive for various applications, rather than precise indications on CCS added costs. Nazira et al. [5], in evaluating recently gas switching reforming as a cost-effective technology for natural gas reforming with inherent CO_2 capture, concluded with CO_2 avoidance cost of 15 $/ton. This is an estimated cost, and in practice it will be higher, and will depend on case to case, but reasonably in the 30–50 $/ton of effective CO_2 reduction (thus considering also that the CCS technology has energy costs). With these costs, it may be questioned whether it is realistic to make the large investments necessary to pass through blue (or even before from coal to natural gas and then natural gas + CCS, i.e., blue H_2) or it is better to directly pass to green H_2. This is still an unsolved question in roadmaps such as that recently presented in EU [6] or dedicated studies [2, 4, 7].

We do not consider the use of fossil fuels to produce H_2, with sequestration of the produced CO_2, a sustainable solution. The CSS is a costly and energy-intensive operation. It is thus not a long-term solution and expected technological and cost reduction for better solutions (green H_2) is faster than the time to recover the cost for the investment necessary to have this intermediate transition. We could expect that by year 2030 green H_2 technologies will be ready for large-scale use, while their implementation would be shifted to around 2045, if an intermediate technology step is introduced.

In addition, CO_2 sequestration causes many environmental issues and hazards still largely not well understood. There are many CO_2 equivalent emissions related to production, storage, and transport of fossil fuels, not only their use. And finally, to produce H_2 from fossil fuels is an energy-intensive operation. These intermediate technologies, even if readily available on a large scale, cannot be considered as a low-carbon production of H_2 that meet criteria for sustainable H_2 economy, even in a short- and medium-term option. While creating a realistic trajectory for novel technologies introduction is always necessary, a significant risk is that to invest on this technology (use of conventional H_2 production from fossil fuels combined with CCUS) would delay, rather than make faster, the transition.

The main justification for the need of an intermediate transition rather than to pass directly to a cleaner next generation technology of production of H_2, such as by electrolyzers, is economics. However, IEA [7] estimated costs for fossil-based hydrogen with CCS to be around 2 €/kg, while that of renewable hydrogen (such as from electrolyzers) in the 2.5–5.5 €/kg range (assuming natural gas prices of 22 €/MWh, electricity prices between 35 and 87 €/MWh, and capacity costs of 600 €/kW). However, costs for renewable hydrogen are rapidly decreasing. For example, electrolyzer costs have been reduced by 60% in the last ten years and are expected to decrease further. Other technologies for direct production of H_2 (by photocatalysis or photoelectrocatalysis, from waste sources, etc.) are also fast growing. There is thus not the effective need to have an intermediate step of maintaining current technologies based on fossil fuels but combined with CCS. It may be eventually a solution for the existing processes but not for the forecast expansion of the market.

1.1.2 Transport and storage of hydrogen

An important aspect to discuss in the scenario for future H_2 is the role of injecting hydrogen into the gas grid. This is another point that is indicated that could significantly boost low-carbon hydrogen demand. In fact, injecting hydrogen into the gas distribution grid is often pushed as a valuable option for increasing low-carbon hydrogen demand for domestic and industrial heating, which is considered, together with transport, the other main sector where H_2 could contribute to decarbonization. Blending hydrogen up to 20% on a volumetric basis into the gas grid requires minimal or potentially no modifications to grid infrastructure or to domestic end-user appliances. Various projects have demonstrated the technical feasibility of this approach for domestic use, although aspects related to the larger volatility of H_2 with respect to methane and thus the losses from the grid were not fully considered. Injecting hydrogen into the gas transmission grid (rather than the distribution grid) is more challenging due to material incompatibilities at high pressures and a lower hydrogen concentration tolerance in the blending that industrial users can accept. Some pilot experiments showed the feasibility of blending hydrogen up to 10%.

As a hydrogen delivery method, blending can defray the cost of building dedicated hydrogen pipelines or other costly delivery infrastructure during the early market development phase. However, there are intrinsic limits in adding H_2 to methane and thus this is again a transition technology rather than a longer-term vision. There are, in addition, many critical issues, for which still not fully convincing indications exist. Among these [8] are: i) the safety aspects, the probability of ignition and the severity of explosion of the pipeline systems being higher, ii) leakage, H_2 being more mobile than methane in many polymer materials including the plastic pipes and elastomeric seals used in natural gas distribution systems, iii) durability of the steel of pipelines, being susceptible to hydrogen-induced brittle cracking and iv) integrity of the transmission pipelines subjected to hydrogen-induced cracking.

Thus, again it may be questioned whether there is the need of this transition technology (whose main impact is to justify further the use of natural gas) or rather maybe better to pass directly to cleaner methods. There is an analogous recent question about the possibility to use biomethane, produced from anaerobic digestion of wastes, to produce H_2 by catalytic decomposition. One kg biomethane would produce 0.75 kg carbon and 0.25 kg H_2. The carbon remains on the catalyst and should be periodically removed, although this is not a so-simple process. In addition, each kg biomethane deriving from biogas produces about 1.5 kg CO_2 (considering that typically biogas is formed by 65% methane and 35% CO_2, but there is a ratio of about 2.75 in molecular weights). Thus, this also does not appear as a rational strategy for the future of H_2. Nevertheless, this is one of the four necessary actions identified by IEA [7] to boost hydrogen on the path toward its clean widespread use. Thus, a more open discussion with a longer term vision pushing to overcome the use of fossil fuels is necessary. In agreement the EU Hydrogen Strategy for a Climate-Neutral Europe [6] stresses caution in relation to the blending of hydrogen into the natural gas network. The International Renewable Energy Agency remarked that “a strategic use of natural gas infrastructure in the energy transition can benefit large, established energy companies,” to evidence that it is part of the strategies to preserve the use of fossil fuels rather than to develop an hydrogen future.

Hydrogen storage particularly necessary for the transport at long distance is another critical question, but surprising not considered with the necessary attention in recent roadmaps and evaluation studies [2, 4, 6, 7]. Related to this is the use of H_2 to produce what is called “e-fuels” (or electrofuels), that is, liquid fuels produced using H_2 and other reactants (CO_2, N_2, etc.), which can be directly used in many applications or used as hydrogen-transport energy vectors. Among the different benefits of hydrogen-based e-fuels, the following may be indicated [7]:

- Easier storage than for hydrogen
- Easier integration with existing logistic infrastructure (e.g., use in gas pipelines, tankers, refueling infrastructure)
- Ability to enter new markets (e.g., aviation, shipping, freight, building heating, and petrochemical feedstocks)

There are at the same time disadvantages: further costly processing is needed, a climate-neutral CO_2 source is needed, and further efficiency losses occur. One of the hidden questions is the worry that these solutions with straightforward integration stifles efforts to introduce enabling changes for radical solutions, as necessary for use of H_2 in several cases. On the other hand, there is an undoubting question that a 100% economy based on renewable energy sources in substitution of fossil fuels cannot be enabled without having fuels (and chemicals) that are the equivalent of liquid fuels in terms of easy transport to long distance, energy density, and easiness of storage. H_2 cannot meet this requirement and it is necessary to integrate its direct use with other solutions where H_2 is the intermediate to produce other fuels or chemicals that can be directly used. In some cases, these compounds could be simply necessary to transport/store H_2 (chemical energy vectors), but in various other cases, these products are those which allow to enlarge the solutions to substitute the fossil fuels use. As initially commented, H_2 is a part, but not the only solution, for the transformation to an almost fossil fuel-free society. A more balanced debate to analyze this context would be certainly necessary.

Note also that it is usual to consider that H_2 as molecule is necessary to produce fuels/chemicals, for example, to produce methanol from CO_2. This is the current technology which foresee to produce H_2 by (photo)electrolysis from water and then use the hydrogen molecule for the further step of catalytic conversion of CO_2 to methanol (two step process). The actual alternative is to use the hydrogen equivalents (H^+/e^-) which are produced in the (photo)electrolysis process to convert directly CO_2 to methanol (one step process). In this way, the question that additional costs (also energetic) are needed to convert further H_2 is largely overcome.

To transport/store H_2 in a liquid form, with reversible generation of H_2 at the end of the transport/storage, different possibilities exist. The storage and thus transport over long distances is the major hurdle to overcome. Liquid organic hydrogen carriers (LOHC) have been developed to solve this issue, and they are already commercially implemented for niche applications in Japan (Chiyoda's SPERA Hydrogen Technology), but the energy density by weight is low (<8 wt% in terms of gravimetric H_2 content), the product needs to be transported back, and there is a small but not negligible irreversible transformation. All these aspects make this solution costly and not fully effective. An alternative solution, commercialized by HySiLabs and based on the generation of a Si-hydride, has been also proposed, but is suffering from similar limitations as LOHC. H_2 storage is about 8 wt% only also in this case.

Formic acid (HCOOH) is another possibility. Among its virtues are: a hydrogen carrier; its low toxicity, nonflammability, and biodegradability; and being a liquid at ambient temperature. However, the energy density by weight is low, around 4 wt %, and requires capturing CO_2 and transport back at the end of the process. Furthermore, only relatively costly catalysts have been developed for formic acid production and decomposition.

Therefore, it is important to have a carbon-free energy vector, liquid at room temperature and with high energy density, which should avoid the need to create a closed loop for its use. Ammonia has these characteristics. The H_2 content by weight is about 18%, thus over twice with respect to that of the other mentioned H_2 carriers, and about 4–5 times higher than formic acid. By catalytic decomposition, it generates H_2 and N_2, with nitrogen as the clean waste product that can be released into the atmosphere. Ammonia is currently produced catalytically from N_2 and H_2 in very large amounts worldwide (over 150 Mt/y) with hydrogen deriving from fossil sources (methane, typically). Both high temperature and high pressure are currently needed to overcome the catalytic barrier for breaking of the N_2 triple bond and have good kinetics, while the equilibrium formation of NH_3 requires low temperatures of operation. The consequence is that the process is highly unfavorable from a thermodynamic perspective with large entropy generation. A cleaner decarbonized route is to produce H_2 from electrolysis and then produce ammonia using an advanced catalytic approach operating at lower pressure to be compatible to those of maximum pressure operations for electrolyzers. The ammonia synthesis process itself by operating in current industrial conditions would consume 40–50% of the electric power generated by renewable energy sources, and thereby electric power available for H_2 production is quite limited. Thus, a sustainable, low-carbon process for ammonia production would require developing innovative catalysts able to operate effectively at low temperatures/pressures [9], overcoming also the issue of strong inhibition of current catalysts at low temperature of operations, due to the formation of stable species between the catalyst (Fe) and dissociated N_2 molecule. The further step is the direct (photo)electrocatalytic production of ammonia from N_2 and H_2O over earth-abundant materials [10]. This solution could produce potentially ammonia at competitive costs with respect to H_2 but enabling a simpler transport/storage and a larger spectrum of uses. However, still significant improvements in the technology and electrocatalysts are necessary, but this could be achieved by an intensified R&D. Thus, the objection that further transformation of H_2 adds costs is in principle not true; the current limit is the technology gap to reach the needed performances. This is a general current indication. There is a technological gap to move to new generation technologies based on renewable energy sources to produce fuels and chemicals, which is the main currently limiting factor of the energy transition.

Several chemicals and fuels can be also produced in a first step via H_2 as intermediate, but in the future directly from CO_2 and H_2O, offering in addition the possibility to use waste CO_2 sources. In many biorefineries and bioenergy plants, CO_2 is a relevant waste product, which can be valorized in a first step through conversion with H_2 and in a longer-term perspective via direct photoelectrocatalytic conversion with H_2 equivalents (H^+/e^-) as the intermediate (so-called artificial leaf devices) [11]. Biorefineries and bioenergy plants produce large amounts of CO_2 from anaerobic (biogas) and fermentation processes (e.g., 1 ton CO_2 per ton bioethanol is produced), and thus the possibility to use these emissions to produce fuels/chemicals using sun light is a major current frontier. Many commodities can in principle be produced in this way, extending the limited possibilities form the use only of H_2.

1.1.3 Green hydrogen production routes

The period 2019–2020 recorded a very large increase in electrolysis units becoming operational, even if low-carbon production capacity remained relatively constant. Still major issues are present in hydrogen production and use, such as:
- scale-up and cost reduction;
- development of effective technologies to replace high-carbon processes with those based on green hydrogen use, minimizing investment costs for the transformation;
- reliable use of H_2 in fuel cell vehicles (which include long-term costs, storage and transport, infrastructure for distribution), notwithstanding the fuel cell electric vehicle market almost doubling in the last 2 years (2019–2020), and
- iv) expansion of hydrogen use to new applications [2].

A large expansion of green hydrogen production is expected in the 2020–2030 decade according to the various roadmaps and position papers [2, 4, 6, 7, 9]. The “A hydrogen strategy for a climate-neutral Europe” [6] indicates in the very short term (2020–2024) and medium term (2025–2030) for EU only the installation of at least 6 (short term) and 40 GW (medium term) of renewable hydrogen electrolyzers and the production of up to 1 and 10 Mt of renewable hydrogen, for short and medium term respectively. Thus, an impressive expansion of the production. The IEA analysis [2], similarly, expects a growth for low-carbon hydrogen from 0.46 Mt/year in 2020 to 7.92 Mt/year, thus lower than what indicated for only EU, but equally impressive, being an increase of almost 17 times in a decade.

The difference in the numbers is related to the fact that in EU strategy, besides to be more optimistic, it is considered that “other forms of low-carbon hydrogen are needed, primarily to rapidly reduce emissions from existing hydrogen production and support the parallel and future uptake of renewable hydrogen.” Thus, production of H_2 from fossil fuels having reduced CO_2 emissions with respect to those of actual gray H_2 (therefore cleaner technologies and in a medium term combined with CCS) is considered necessary (although indicated only in indirect terms) in the short and medium term, justified to facilitate the transition and obtain immediately some benefits. Given that a CCS plan should have at least 15–20 years amortization time and requires large investments also in infrastructure to transport CO_2 (in EU the sites for storage are limited), likely this will retard rather than accelerate the transition to green H_2. Wood Mackenzie (an investment consulting society) [12] reported that green hydrogen projects doubled in the last half year and on March 2020, already about 8.2 GW of novel electrolyzer capacity are planned. The effect of Covid-19 [1], as mentioned, will impact these projects, and probably only in part they will be realized. Nevertheless, it is of no doubt that the outlook for hydrogen is getting more and more attractive, and larger integrated energy, industrial, and financial players are following this strategy of "net-zero" carbon policy, with projects spanning multiple segments and being integrated across various sectors of the economy.

Hydrogen from electrolyzers will be thus an important element for decarbonization, but the EU strategy [6] indicates that the share of hydrogen in Europe's energy mix is projected to grow from the current less than 2% (including the use of hydrogen as feedstock to 13–14% on the average by 2050 [13]). Thus, hydrogen deriving from electrolyzers will remain an important component, but still covering a minor fraction of the energy mix.

An important element to create a hydrogen eco-system is cost of production. The EU strategy document [6] indicates estimated costs (based on elaboration of IEA data [2]) with the year 2020 as reference for fossil-based hydrogen of around 1.5 €/kg (highly dependent on natural gas prices), for fossil-based hydrogen around 2 €/kg (thus around 30% increase in costs) with CCS, while costs for green hydrogen from electrolyzers are estimated to be about 2.5–5.5 €/kg. Thus, the estimation indicates that only by applying carbon prices in the range of 55–90 €/t_{CO2} lower carbon footprints routes for H_2 would become attractive, and in the current perspective, fossil-based hydrogen with CCS will be competitive. The issue is whether these cost estimates are reliable, especially in a longer term strategy, and what is the degree of possible cost reduction by electrolyzers. IRENA estimated [7] that electrolyzer (alkaline) CAPEX (capital expenditure; fixed costs) will decrease from 840 to 200 US$/kW, but other relevant elements for cost are the cost of the renewable electricity to be used in the process and the number of operating hours (load factor) on a yearly basis. IRENA [7] thus estimated that the levelized hydrogen costs from a 2018 year range of 2.7–5.0 US$/kg H_2 for wind electrical energy and 3.4–6.4 US$/kg H_2 for photovoltaic electrical energy will decrease to 0.9–1.2 and 1.2–2.6 US$/kg H_2 for wind and photovoltaic, respectively, in the year 2050. However, this estimation does not consider the still large possible improvements in photovoltaic technology (still quite large, if we consider only the possible improvement in efficiency), differently from the eolic case where further improvements are limited. Based on thse indications, may be thus reasonable to consider that the target of average 1.5 US$/kg H_2 could be reached earlier, around 2035.

On the other hand, the cost for fossil fuel + CCS solution is not expected to decrease below the 30% additional cost, and thus will largely depend on cost of fossil fuels. Long-term forecast in this field is very difficult. However, an important element to consider is that the cost of fossil fuels is not really related to their production costs, but to the market demand and on a factor that is not often considered; for example, the producers of fossil fuels have an economy largely based on the economic return they have from marketing fossil fuels. The current economy structure in these countries will not allow to significantly decrease these incomes, and thus even if the market will contract, it may be estimated that the cost of fossil fuels will increase in the medium term.

Thus, revising from these perspective the current estimations, it may be indicated that a green technology from electrolyzers would become competitive around 2030–2035 and would be preferable to fossil fuels + CCS combination, on the basis of cost for effective amount of CO_2 emissions saved. These considerations further support previous indications that it is preferable to directly invest in green H_2 technologies, rather than dilute the effort with an intermediate production of H_2 from fossil fuels combined with CCS.

The status of electrolyzers is summarized in various reports, among which the recent one may be the EU report "Current status of Chemical Energy Storage Technologies" [14]. Alkaline electrolyzers are currently the preferable technology, particularly in the case of stationary hydrogen generation in an industrial environment. A main issue is when they should operate under dynamic or discontinuous conditions, which will be necessary, for example, for coupling with dynamic energy sources such as wind or solar. Electricity consumption is expected to slowly decrease from current 50 kWh/kg (year 2020) to 48 kWh/kg in year 2030, reflecting the advanced nature of this technology. However, CAPEX costs will decrease in the next decade by about one third (from 600 to 400 €/kW) and also operational and maintenance (O&M) costs of about 40%. Density of current is also expected to increase from 0.7 to 0.8 A/cm^2.

PEM electrolyzers have the advantage of operational flexibility and thus better coupling with intermittent renewable energy sources which can deliver H_2 under pressure with high overload capability. The current issues are related to material degradation and high capital cost. In the next decade (2020–2030) it is expected that electricity consumption will decrease from 55 to 50 kWh/kg, current density increase from 2.2 to 2.5 A/cm^2, CAPEX costs decrease from 900 to 500 €/kW and also O&M nearly halves. Substitution of the use of noble metals is another relevant target to achieve.

Solid oxide electrolyzers, which operate at temperatures of 500–850 °C, are at a much earlier stage of development, and there are still significant problems of reliability. They are more efficient, with electricity consumption expected to decrease in the 2020–2030 period from 40 to 37 kWh/kg, but CAPEX and O&M are currently about 3–5 times higher than other electrolyzers, even with significant progresses expected in the next decade. However, still it is expected that it will remain on the average 2 times higher. Commercial developments are thus mainly focused on alkaline and PEM electrolyzer technologies.

The point that is remarked in the cited EU report [14] is that production and direct use of hydrogen (indicated respectively as power to hydrogen, and hydrogen to power technology) can account only for a part of the complex panorama of energy transition (indicated with a yellow area in Fig. 1.1). Some industry applications can also be feasible with direct use of green H_2, but due to the need of continuous and often large-scale operations, they cannot be effective without a reliable distribution and storage of H_2 that to be effective requires having chemical energy storage technologies (highlighted with blue area in Fig. 1.1). Chemical uses and conversion options, indicated with a green area in Fig. 1.1, require transformation of H_2 to products that are better suited for these uses. These are defined with the generic indication power to X, where X could be G, for example, a gas such as methane, or L, for example, a liquid such as methanol. These technologies could be direct (one stage) or two-stage via intermediate H_2 formation in a separate unit, but directly integrated on-site for further utilization. As commented earlier, the future challenge, which can largely decrease the costs, is to make reliable the direct power-to-X technologies, which include also artificial photosynthesis devices.

In a short term, however, production of H_2 by electrolyzers and then use of H_2 to produce chemicals or fuels (hydrogen to X) is the feasible solution, which adds value to hydrogen rather than add costs, as commented earlier. The cited EU report [14] provides an updated status of these technologies. Current focus is on how to combine hydrogen with other molecules to produce ammonia, methanol, formic acid, or other hydrocarbons (electrofuels, or e-fuels). However, the range of application is broader, and may include other relevant chemicals, for example, light olefins or aromatics [15] which are the building blocks for petrochemistry.

Hydrogen to methane (power to gas) is one of the solutions explored to store excess renewable energy with several demonstration plants built to investigate this possibility. Today attention, however, is moved to power-to-liquid technologies, with methanol being one of the preferred liquid fuels. There are a range of possibilities also to prepare more valuable e-fuels, in particular for aviation and shipping transport.

The level of development of the conversion pathways varies, with the processes aimed at obtaining liquid and gaseous synthetic fuels having the lowest development level. The reduction of the cost of all these technologies is a common issue. However, the results demonstrate that chemical energy storage technologies are a necessary component for the integration of renewable electricity and decarbonize various end-use sectors. Thus, going beyond hydrogen production and its direct use, integrating hydrogen with downstream technologies to produce fuels and chemicals from H_2 and other molecules (CO_2, N_2) should be a part of the roadmap for hydrogen's future.

Note that H_2 should be not considered only as a molecule produced separately (even if in an integrated process) but also as the H_2 equivalent, that is, protons/electrons that are the first element produced in many photo-processes where solar light is directly used in the technology, or in co-electrolysis processes, where water oxidation occurs in parallel to CO_2 or N_2 electrocatalytic reduction. The direct use of these "H_2 equivalents" could save energy (about 30%) related to produce from them H_2 and then activate H_2 for its reaction with the other molecules that are typically of low reactivity (CO_2, N_2). In addition, it could save CAPEX costs, and when coupled with direct use of solar energy (the general area of photoelectrochemical devices) could also reduce the costs for producing renewable electrical energy. Thus, the future is in this direction, even if many scientific and technological issues must be solved before application. Today, solar to chemical conversions of 5–10% and in the future of >15% are possible, making promising the development in this area if enough investments will be made.

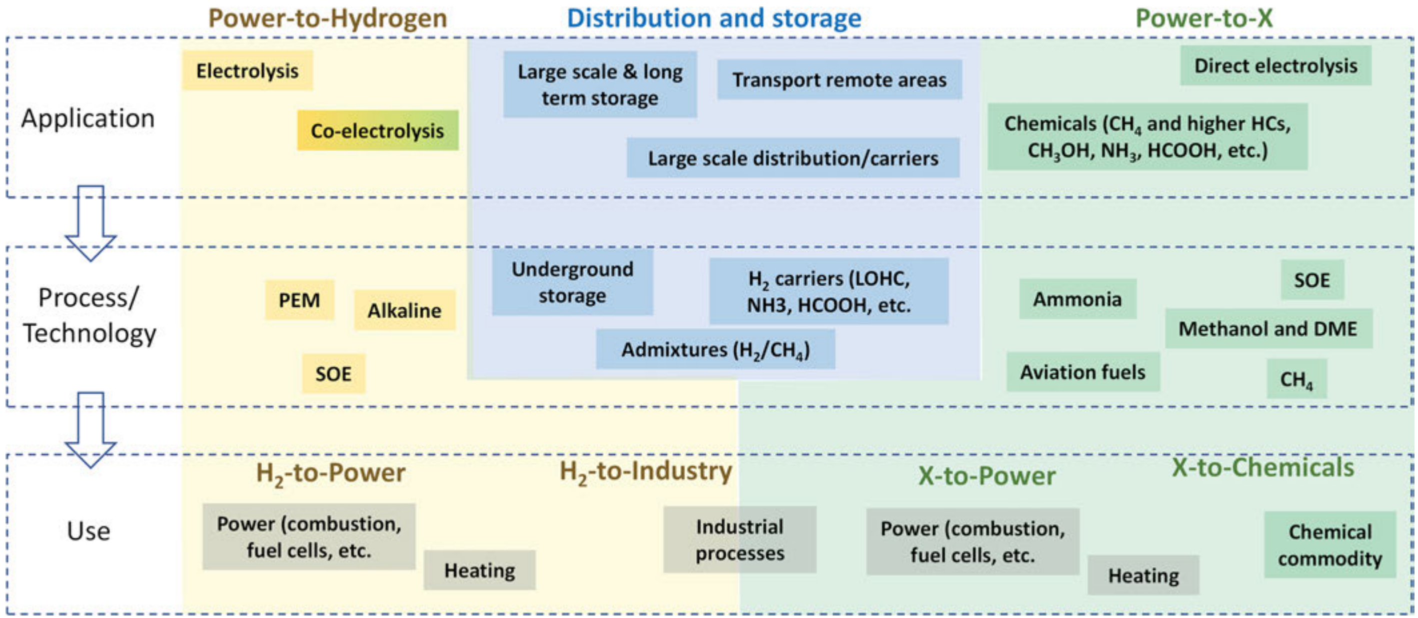

Fig. 1.1: Scheme of possible pathways and conversion steps for sectors coupling through hydrogen Elaborated from "Current status of Chemical Energy Storage Technologies" report [14].

A final relevant remark is that in this scenario, often the possibility to produce H_2 from waste resources is not considered, while a relevant possibility, also taking into account that it can be actually produced at competitive costs and with a carbon-neutral or even slightly negative impact can be an important element toward a circular economy [16].

1.1.4 Future of hydrogen in roadmaps

Many roadmaps have been reported recently to define these aspects and the role of hydrogen to reach carbon neutrality. Among these, the EU roadmap “A hydrogen strategy for a climate-neutral Europe” [6], very recently presented (July 2020), is one of the relevant ones with being hydrogen an important pillar for the EU European Green Deal, a roadmap with a related large investment plan for transforming the EU into a modern, resource-efficient, and competitive low-carbon economy, with net-zero GHG emissions by 2050. Another relevant recent roadmap is that prepared by the IEA for the G20 meeting in 2019 in Japan [7]. This landmark report analyzed the situation for hydrogen technologies and their role to achieve a clean, secure, and affordable energy future and how its potential could be realized.

There are three key indicators to monitor progresses for green hydrogen:

1. the degree of replacing conventional H_2 with green hydrogen in existing industrial applications;
2. the market expansion, for example, the demand in new sectors where the use of H_2 allows meeting requirements of sustainability and avoiding other costs such as carbon taxes;
3. the rate of increase of demo (or larger scale) units for cross-cutting technologies to produce green H_2 (such as electrolyzers) or to use it (such as fuel cells).

These and other position papers or documents [1, 2, 4, 6, 7, 13, 14] converge in defining hydrogen as part of the solution to achieve the necessary societal decarbonization. However, these documents remark that to enable hydrogen’s key building-block role it is necessary to support research and innovation in the end-use of hydrogen. Realizing this objective requires investing in hydrogen’s further transformation to products directly usable in these key sectors (hydrogen-derived commodities and fuels) and to realize an efficient long-distance transport (hydrogen chemical storage). Building a coherent framework for future hydrogen is a key necessary action, but a right balance among all the possibilities has still to be achieved having a longer-term perspective, with the necessary more in-depth reflection whether some transition technologies are necessary and worth of the large investment necessary. In addition, emerging technologies must be better considered in the future scenario, notwithstanding the difficulties in understanding their effective potential impact. An example is given by the direct production of green H_2 by photo- or photoelectrochemical methods, including their possibility for direct (one step) production of higher added value fuels and commodities.

A cost perspective is a key factor. However, it is necessary to have a clear view of the technology's advances (and their impact on cost reduction) and of the dynamics of costs at a worldwide scale. Otherwise, the reliability of these estimations may be questioned. Nevertheless, it is relevant to have a view of the current state of the art, which was analyzed in detail recently by the Hydrogen Council [4]. Their report indicates that hydrogen is "already surprisingly competitive as a low-carbon option" by analyzing 35 hydrogen applications in transport, buildings, industry heat, and industry feedstocks, overall responsible for about 60% of the world's energy- and process-related emissions. Figure 1.2 summarizes the hydrogen applications in relation to their overall impact on CO_2 global emissions.

Other applications for hydrogen include the mobility sector (container ships, tankers, tractors, motorbikes, tractors, off-road applications, and fuel cell airplanes) and other sectors (auxiliary power units, large-scale CHP for industry, mining equipment, metals processing (non-DRI steel), etc.), but those listed in Fig. 1.2 were the main considered. Figure 1.3 reports the competitiveness of hydrogen applications versus low-carbon and conventional alternatives as indicated in the report [4].

A series of considerations can be made from data summarized in Fig. 1.3, even if some of the indications of the reports may be questioned. Limited to only some specific sectors of transport, H_2 is identified as the more competitive option (compared to conventional) and the most competitive low-carbon solution (thus in the top right part, highlighted with a yellow background, of Fig. 1.3). There are a good range of options that meet the criteria for being the most competitive low-carbon solution, although still not (fully) competitive from an economic perspective to the alternatives. Some of these fields of H_2 use (top left part), however, are preferable (as low-carbon solution) only when in combination with CCS. Among this group of the most competitive low-carbon solutions, those for industry feedstocks are preferable. Several areas, including for transportation, on the contrary, belong to those neither advantageous as low-carbon solution nor from an economic perspective. Thus, care should be made in considering generically the use of H_2 for mobility as the solution.

Another relevant information in this "Path to hydrogen competitiveness" report [4] regards the estimated breakeven hydrogen costs at which hydrogen application becomes competitive in 2030 against low-carbon alternative in a given segment (the four categories indicated in Fig. 1.2). Four main regions (China, the United States, EU, and Japan/Korea) were analyzed. It can be noted that in several segments, transportation and distribution add significant costs.

Hydrogen can unlock approximately 8% of the global energy demand with a hydrogen production cost of USD 2.50 per kg, while a cost of USD 1.80 per kg would unlock as much as roughly 15% of global energy demand by 2030. Thus, a target of H_2 production cost in <1.5 USD per kg (in 2030) should be the objective for hydrogen to account >15% of final energy demand. Note, however, that these cost estimates

Transportation (T)
1. Compact vehicle for urban transportation
2. Mid-size vehicle with long range
3. Lightweight truck/van for urban distribution
4. Mid-size vehicle with short range
5. Medium-duty truck for regional haul
6. Passenger train for regional transport
7. SUV for family usage
8. Heavy-duty truck for long-haul transportation
9. Regional ferry
10. Forklifts
11. Large passenger vehicle for commercial usage
12. Bus for short-distance urban transportation
13. Large ferries
14. Large passenger vehicles for commercial usage
15. Bus for long-range urban transportation
16. Coaches for long-distance transportation
17. Synfuels for aviation

Heat and power for building (HPB)
1. Fuel cell-based CHP (Combined heating and power) for old hospital
2. Hydrogen boilers (new buildings)
3. Hydrogen boilers (old hospitals)
4. Hydrogen boilers (old flats)
5. Hybrid heat pump and boiler
6. Blending H_2 in natural gas boilers
7. Fuel-cell based CHP (new houses)
8. Fuel-cell-based CHP (old flat)

Heat and power for building (HPI)
1. Fuel cell-based backup generator
2. Simple cycle H_2 turbine
3. H_2 furnace for high-grade heat
4. Combined cycle H_2 turbine
5. Fuel-cell remote generator
6. Hydrogen furnace for medium-grade heat

Industry feedstocks (I)
1. Low-carbon NH_3
2. Refining
3. Low-carbon steel H_2 direct reduced iron (DRI)
4. Methanol (for CCU, carbon capture utilization)

Fig. 1.2: Overview of hydrogen applications lumped in four main sectors with their overall impact on CO_2 global emissions. Elaborated from “Path to hydrogen competitiveness” report [4].

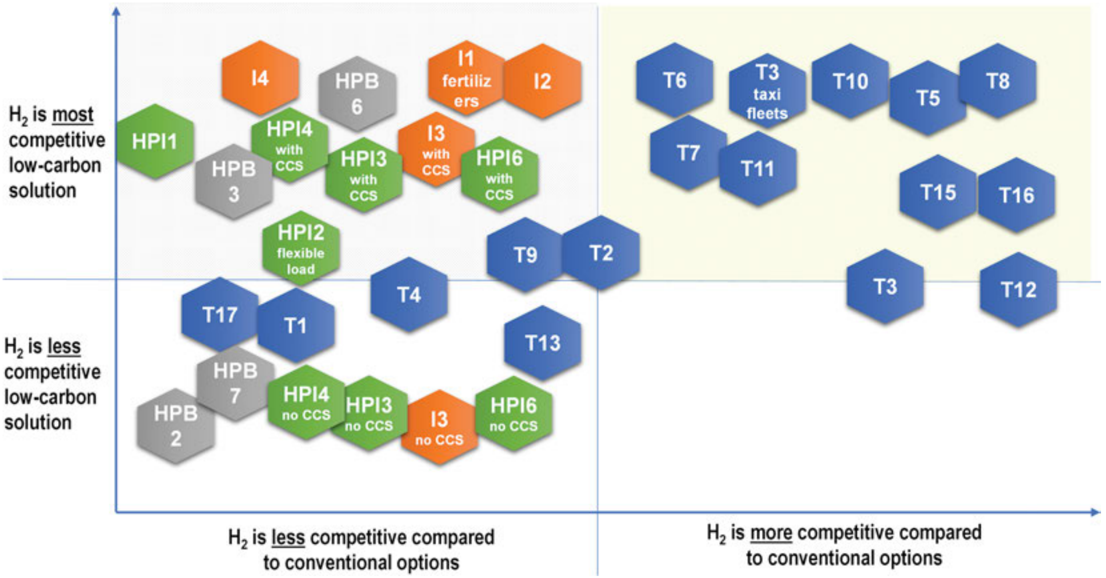

Fig. 1.3: Competitiveness of hydrogen applications versus low-carbon and conventional alternatives. See Fig. 1.2 for codes and meaning of the different colors. Elaborated from “Path to hydrogen competitiveness” report [4].

consider the need of CCS as a feasible and accessible option to include in costs, and that, on the other hand, no carbon taxes will be applied and conventional fuels such as natural gas and coal will remain abundant and with a low cost. This estimation, as discussed before, may be questionable. It should be better considered that i) the fast developments in producing green H_2 (with related impact on costs), ii) fossil fuel costs will likely increase (as discussed before), and iii) incentives will likely be introduced in avoiding rather than sequestrating CO_2. Thus, these factors may change the estimations presented in Fig. 1.4. In addition, other technological developments pushed from the energy transitions should also be better considered, for example, the fast development of electrically heated boilers/furnaces and industrial reactors rather than the use of H_2 to heat these process units. Therefore some of the options for heat and power for industry indicated in Fig. 1.4 should be reconsidered.

1.1.5 Conclusions

This introductory chapter has the aim to present a critical analysis of the applications of hydrogen technologies and their role for a sustainable future, particularly from the perspective of the various recent roadmaps and position papers published, due to the growing relevance of hydrogen in regional strategies and development plans all around the world. While in general there is an undoubtfully role of hydrogen in the transition to a low-carbon future, but also in increasing competitiveness and innovation, some aspects of the strategy defined in these documents should be questioned. In particular, the following aspects were highlighted:

- the need of investing in the intermediate blue hydrogen (production from fossil fuels combined with CCS),
- the possibility that cleaner and more economic novel technologies (based on the direct use of solar energy) could become feasible in a shorter-term than expected (when sufficient investments in R&D will be made),
- the need to broaden the approach to include more extensively the transformation of H_2 to other fuels and commodities that integrate straighter in the industrial production and energy infrastructure,
- the necessity of a better integration of technologies for H_2 conversion to liquids for long-distance transport (hydrogen vectors) to enable a worldwide trading economy on hydrogen, and
- a broader view with revised considerations in terms of both economics perspectives (particularly on costs of fossil fuels) and capability of technology development (with related impact not only in terms of cost reduction, but especially of opening new directions) in defining future cost-competitiveness, and thus inherently the area when investments in R&D is necessary.

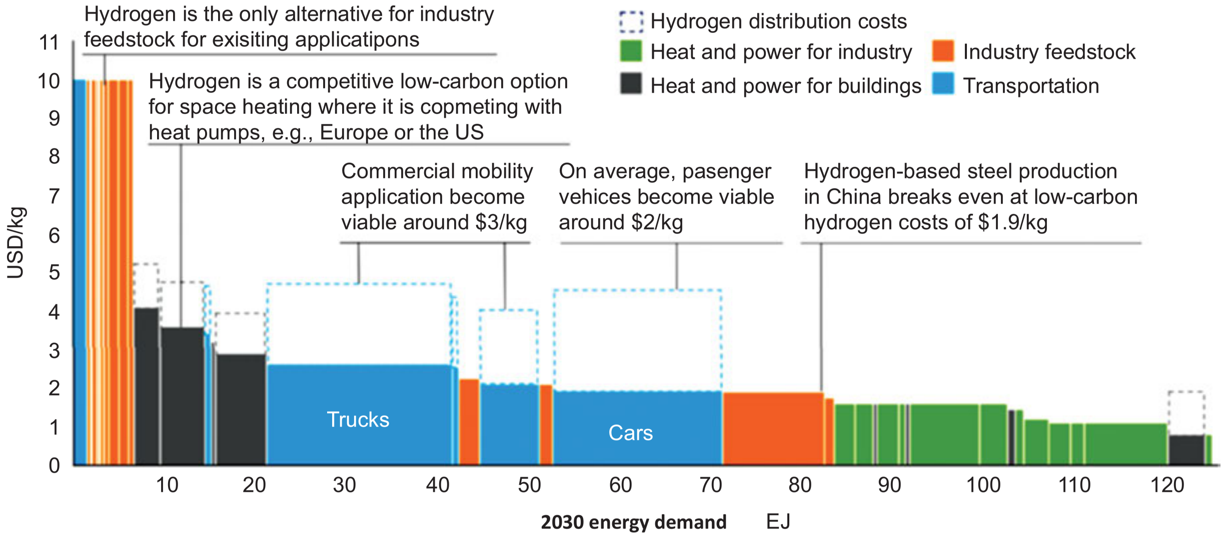

Fig. 1.4: Breakeven hydrogen costs at which hydrogen application becomes competitive in 2030 against low-carbon alternative in a given segment. Elaborated from “Path to hydrogen competitiveness” report [4].

We hope that this discussion could give “food for thought” to analyze from a broader perspective the other technical contributions presented in this volume and in the other two volumes on this “Hydrogen Technologies for Sustainable Economy” series. This is expected to be a massive area of investment in R&D all around the world, and especially in regions such as EU making decarbonization and substitution of fossil fuels a priority. For this reason, together with a detailed analysis of the status and perspectives from a technological view, it is necessary also to have a longer term vision able to prioritize the different options and determine those that can have a better ratio between investment costs and effective contribution to targets. We hope that this chapter could provide some indication or at least elements for a discussion in this direction.

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Tobias Christoph Brunner

2 Perspectives of hydrogen in trucks

Abstract: Given the per vehicle effect, zero-emission long-haul trucks would be a meaningful starting point for decarbonizing mobility, since a limited refueling or charging infrastructure along main transit routes could power a significant fleet of zero-emission trucks. Three options of technologies are regarded the most promising candidates to power zero-emission trucks: electric trucks with catenary overhead line system, battery electric trucks with high-capacity onboard batteries and fuel cell hybrid electric trucks with moderate batteries as well as a fuel cell and hydrogen storage systems to generate electric power onboard the vehicle. All three candidate technologies come with different requirements on fueling infrastructure, with a different carbon footprint balance as well as at different cost. Hydrogen trucks using “green hydrogen” may eventually become a leading technology approach, since they promise the best compromise between carbon footprint reduction, cost of technology, and infrastructure.

2.1 Perspectives of hydrogen trucks

Diesel trucks represent less than 10% of the overall world’s vehicle population, but are responsible for almost 40% of the greenhouse gas emission [1]. For a long time, this relation had been ignored by regulators all over the world, since the market of good transportation is extremely competitive. Since 2019, significant changes can be observed driven by the societal awareness of climate change as well as the regulators’ efforts to stay on track with the target to limit global warming to 1.5 °C. Regulatory frameworks in many of the world’s key truck markets enforce stricter rules on greenhouse gas emissions. In 2020, the California Air Resources Board has set in power the Advanced Clean Truck Directive that requires 50% of all diesel trucks in the state to convert to zero-emission technologies until 2035, while in 2045 California will only allow zero-emission trucks on its roads [2]. In Europe, the EU Council and Parliament have passed the “Regulation setting CO_2 emission performance standards for new heavy-duty vehicles” [3], which prescribes cutting down carbon dioxide emissions from new trucks on average by 15% from 2025 and by 30% from 2030 onward, compared with 2019 levels. In the strongly regulated market of China, a one-million fuel cell vehicle target has been set for 2035 with up to 50% involving trucks [4].

Given the regulatory shift toward zero emission, many truck manufacturers have revised their internal technology strategies recently; some are still working on their new strategic frameworks. The world’s largest truck manufacturer Daimler has made

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the decision to focus on battery as well as hydrogen fuel cell trucks [5]. Moreover, a joint venture between Daimler and Volvo, the world's largest and third-largest truck manufacturers, respectively, has been set up to accelerate the development of fuel cell technology for long-haul heavy-duty trucks. Other European manufacturers follow, such as Traton, number seven in the world's truck manufacturers' ranking, cooperating with Hino in Japan to roll out fuel cell trucks [6]. In China, the world's largest fuel cell R&D and manufacturing joint venture, United Fuel Cell System R&D (Beijing) Co. Ltd. around Toyota, has been established. The world's second and fourth largest truck manufacturers, FAW and Dongfeng from China, respectively, are key partners and shareholders of the newly formed joint venture [7].

The reasons why truck manufacturers have decided to put their focus on hydrogen powertrains, mainly fuel cell powertrains, are evident:

- Hydrogen fuel cell and battery electric powertrains with or without catenary line access are the only zero-emission tailpipe technologies; natural gas and even hydrogen internal combustion engine drives are currently not recognized as zero emission in key markets.
- Overhead line applications seem to be far out given the infrastructure challenge of building an overhead catenary line system covering thousands of kilometers, while the pantograph adds significant additional weight and cost to the truck.
- Compared to battery electric trucks, hydrogen fuel cell trucks allow a similar range as diesel trucks as well as a quick refueling option, which complies best to today's business models in transportation.

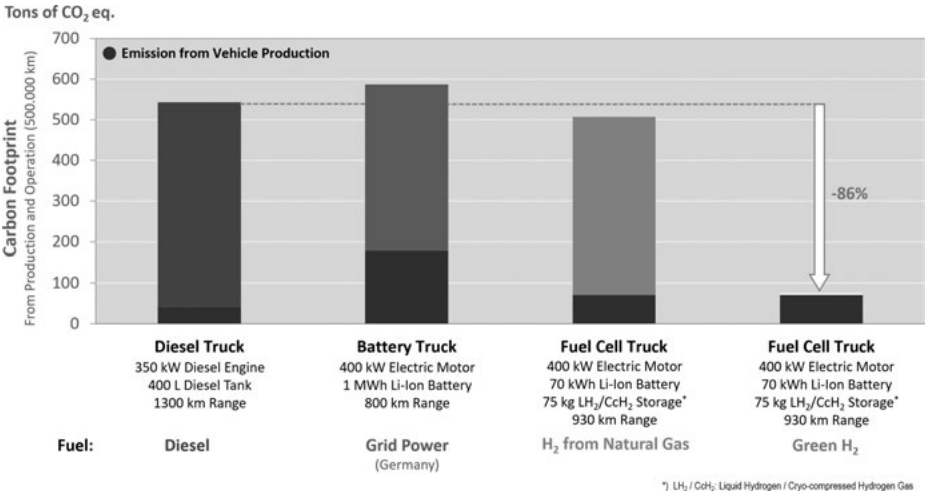

Fig. 2.1: Carbon footprint of different truck technologies including vehicle production and 500,000 km mileage [8].

- Given an expected significant drop in fuel cell technology cost while battery cost reductions starting to slow down, projected total costs of ownership 2030 and later speak for long-haul fuel cell trucks.

A key argument for fuel cell trucks that does currently not get high attention, but may become the origin of future societal dispute and eventually affect future regulatory frameworks, is the lifecycle carbon footprint advantage of fuel cell trucks using green hydrogen. The carbon footprint of a battery truck with 1 MWh Li-ion battery as derived from Sternberg et al. [9], featuring a range of around 800 km on a single charge, produced and operated in Germany, would lead to a significant carbon footprint from vehicle production and operation. Such truck would need to be operated more than 500,000 km to only meet the total carbon footprint of a modern diesel truck. While a fuel cell truck driven with hydrogen from steam methane reforming would not show a significant advantage either, filling a fuel cell truck with green hydrogen could reduce the overall carbon footprint of the truck from the first year of operation.

2.2 The source of green hydrogen for zero-emission hydrogen trucks

Green hydrogen for hydrogen trucks may be only partially produced in Europe, since the costs of renewable energy in many areas are too high to electrolyze water to hydrogen in a cost-effective way. Since today Europe imports a significant amount of fuel feedstocks as oil and gas, a substitution of those fossil fuels by green Power-to-X fuels is subject to various studies. To fuel hydrogen trucks, gaseous hydrogen transfer by pipeline and shipping of liquefied/liquid hydrogen (LH_2) from overseas have been identified as the two most promising pathways to provide hydrogen fuel to hydrogen stations. Other carriers with hydrogen bound in chemical or organic liquids need to be dehydrogenated in the destination country. Dehydrogenation in Europe leads to additional cost and increases carbon footprint, which makes carriers less favorable for direct hydrogen fuel as recent studies from the Hydrogen Council [10] or Fraunhofer ISE [11] suggest.

The green LH_2 pathways as projected in Fig. 2.2 for 2030+ derived from [10, 11] would result in the cost of 3–4 €/kg for green LH_2 at the import terminal arriving from the Kingdom of Saudi Arabia (KSA) or Morocco, where it could be electrolyzed and liquefied with low-cost renewable energy from wind and solar power. Distributing such LH_2 to LH_2-based hydrogen stations would enable compressed gaseous hydrogen (CGH_2) the cost of hydrogen at the pump can be even lower if 4.5 and 5.5 €/kg in a range of 500 km around the import terminal; the cost of hydrogen at the pump can be even lower if LH_2 at the station would be pumped into the truck directly or compressed to cryogenic gas (CcH_2, cryo-compressed hydrogen) before being filled in the truck. In

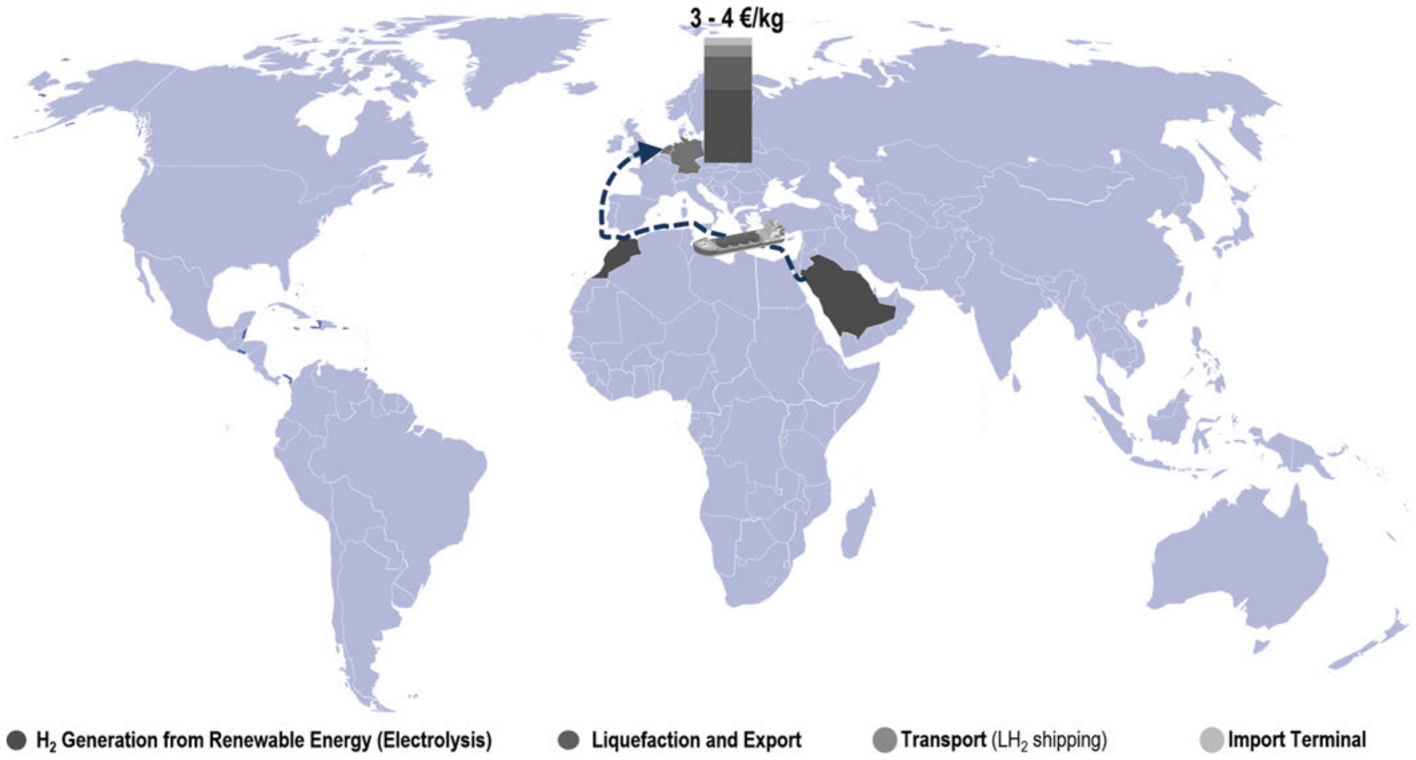

Fig. 2.2: Green liquid hydrogen (LH_2) import pathway from KSA to Europe [10].

the years until 2030, when the import pathway is still on the way to be implemented, large LH_2 carrier ships built, and green electrolyzer and liquefiers installed overseas, first liquefaction units could be implemented in areas with abundant wind and solar power in Europe as well to power first fleets of long-haul heavy-duty trucks in selected transit corridors.

2.3 Design requirements for long-haul hydrogen trucks

The majority of truck manufacturers put their focus on fuel cell powertrains. A few others prefer to bridge the time to a hydrogen economy with hydrogen internal combustion engines, ideally converted from diesel engines. A difference in consumption of 20% to 40% between a fuel cell–powered electric truck and a hydrogen internal combustion engine–driven truck with or without hybrid electric powertrain design is likely to be expected in favor of the fuel cell. Long-haul fuel cell electric heavy-duty hydrogen trucks will require fuel cells with a continuous nominal power between 200 and 300 kW and additional batteries of 75 kWh up to more than 100 kWh to provide continuous power for high-load operation during steep climbing events when it is challenging to provide enough cooling power to the fuel cell.

To match an acceptable convenience similar to a diesel truck, a hydrogen truck would need to reach a driving range of minimum 600–800 km, preferable above 800 km per fill. With a projected consumption of 8 kg/100 km for a fuel cell electric long-haul heavy-duty truck, around 70–80 kg usable capacity should be installed onboard the tractor, 20–40% more on a hydrogen internal combustion engine–driven truck. In existing platforms that will likely be used for integrating hydrogen powertrains until 2030, such capacities can best be stored behind the truck cabin or mounted along both sides of the vehicle frame.

The new European length directive on the maximum length of lorries [12] will give truck manufacturers an additional freedom to extend the length of trucks up to 900 mm. Originally meant to design more efficient tractors with improved aerodynamics, this regulation can also be used to package more hydrogen storage behind the cabin allowing vessel diameters of 500–900 mm in some cases. With a package diameter of 600 mm, a usable capacity of 75 kg could be integrated in four 70 MPa CGH_2 storage vessels (70 MPa). With CcH_2 storage [13], up to 79 kg could be stored in a three-vessel package. With 35 MPa CGH_2 storage technology, less than 45 kg usable capacity could be reached in the full package and would not comply with the minimum range target of long-haul heavy-duty logistics.

A frame-mounted hydrogen storage integration with package space of 700 mm times 2,650 mm at each side of the frame would limit the onboard capacity to less

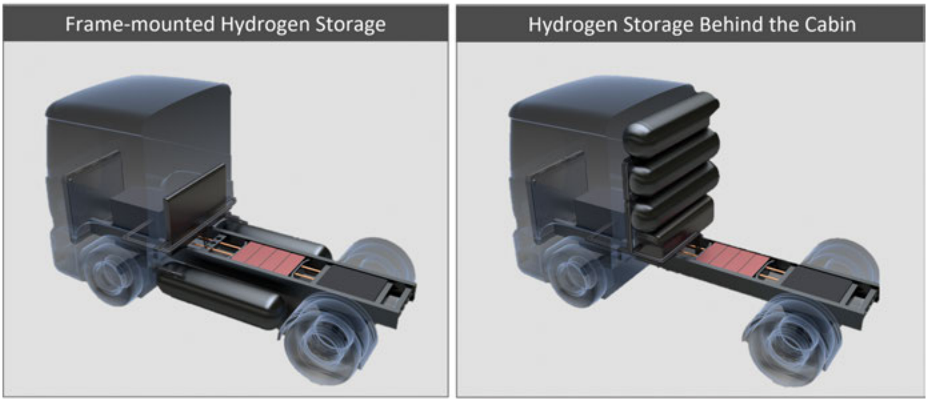

Fig. 2.3: Mounting options for hydrogen storage vessels in a hydrogen tractor.

than 60 kg with CGH_2 70 MPa and less than 40 kg with CGH_2 35 MPa. LH_2 onboard storage would match the target of 75 kg closely. With CcH_2 storage technology, the 80 kg barrier may be exceeded even in a frame-mounted hydrogen storage package.

2.4 Design requirements for a hydrogen truck refueling infrastructure

Direct filling of gaseous hydrogen, LH_2, or CcH_2 so far seems to be the only viable baseline for a long-haul hydrogen truck infrastructure. The daily demand of a future truck station may pose significant challenges on the supply logistics. A large hydrogen truck station may require 8,000 kg of hydrogen per day to fill a hundred trucks and more. Such stations either require a pipeline connecting the station to a continuous gaseous hydrogen supply or truck-in of liquid hydrogen in insulated LH_2 trailers. A pipeline connection to each hydrogen station will hardly be a short-term option and certainly come with a larger station space, energy, and carbon footprint than a station with trucked-in green LH_2. Besides these advantages, LH_2-based stations can supply CGH_2, LH_2, or CcH_2 and, thus, offer a flexible solution to support any type of onboard truck storage.

2.5 Summary

Hydrogen trucks offer a significant opportunity to accelerate the decarbonization of transportation in Europe. A smart combination of battery as well as hydrogen trucks complementing distribution and long-haul applications may pave the way to a zero-emission truck logistics in Europe. Green hydrogen plays a key role, since it could contribute to reduce carbon intensity of trucking fast and in a significant manner. The supply of green hydrogen will eventually decide about the future of hydrogen trucks. A combination of green hydrogen generation in Europe as an integrated part of a European renewable energy system and intercontinental import to Europe from countries with low-cost abundant renewable energy seems the only practical way to fully replace diesel and natural gas in trucking until 2050. The time to act is now. So do most truck manufacturers in Europe who have started to develop hydrogen truck powertrains and first hydrogen truck vehicle platforms with a target to roll out long-haul hydrogen heavy-duty trucks starting from 2025 onward.

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Katsuhiko Hirose

3 Hydrogen for transport

3.1 Background and history of chasing fuel cell and hydrogen for transport

Transport is consuming about 20+% of world energy and thus it is responsible for emitting 20+% of greenhouse gas (GHG, 23% in 2010 in IPCC report [1]). This is expected to grow further by economic growth and by increase of people's travel (see Fig. 3.1 [2]). In the early days of fuel cell development, hydrogen was important since hydrogen was alternative fuel to replace oil before the "End of Oil". Hydrogens role was to replace oil rather than reducing carbon emissions so that hydrogen from other than oil such as natural gas was promised too, thus it was considered as the one of the solutions for future mobility fuel. In California, FCEV(Fuel Cell Electric Vehicle) is developed to solve the local emission since local emissions from automobiles were so serious there.

These two main purposes (oil alternate and emission free) propelled the development of hydrogen FCEV in the beginning of the twenty-first century. Then, more and more climate change issue initiated more serious discussions and led to be seeking actions and solutions. The total de-carbonization of the society has been discussed seriously and target date of carbon neutrality is 2050 not far away from now. Hydrogen's potential to decarbonize the society in total has been re-recognized. Hydrogen has very important role for decarbonization from power generation to heating and industrial activities. Hydrogen's use for transport has extended beyond the road transport to the total transport sector [3].

Hydrogen technologies in transport are widespread both in scale and in maturity. Some applications like forklift and bus are already significantly important for commercial use. The passenger vehicles are changing phase from remonstration (tens of hundreds) to commercial phase (hundreds of thousands) the other hand heavy duty tracks are still early demonstration phase. Other surface transport such as train and ship is also in the demonstration phase. Hydrogen in aviation is at a very early stage. Aviation was once seriously considered because of the high energy density per weight. The first airplane powered by hydrogen was the Russian TU155 jet flown by liquid hydrogen on April 15, 1988. However, in the last few years hydrogen aviation has become very hot again. EU study [4] promised the future of hydrogen in aviation, coincident to the announcements by big aerospace giants such as Boeing and Airbus [5]. On the other hand space hydrogen has become very common and is commercialized because no alternative technology has been found for rocket propulsion fuel where the hydrogen's advantage of high gravimetric energy density cannot be overtaken by any other way.

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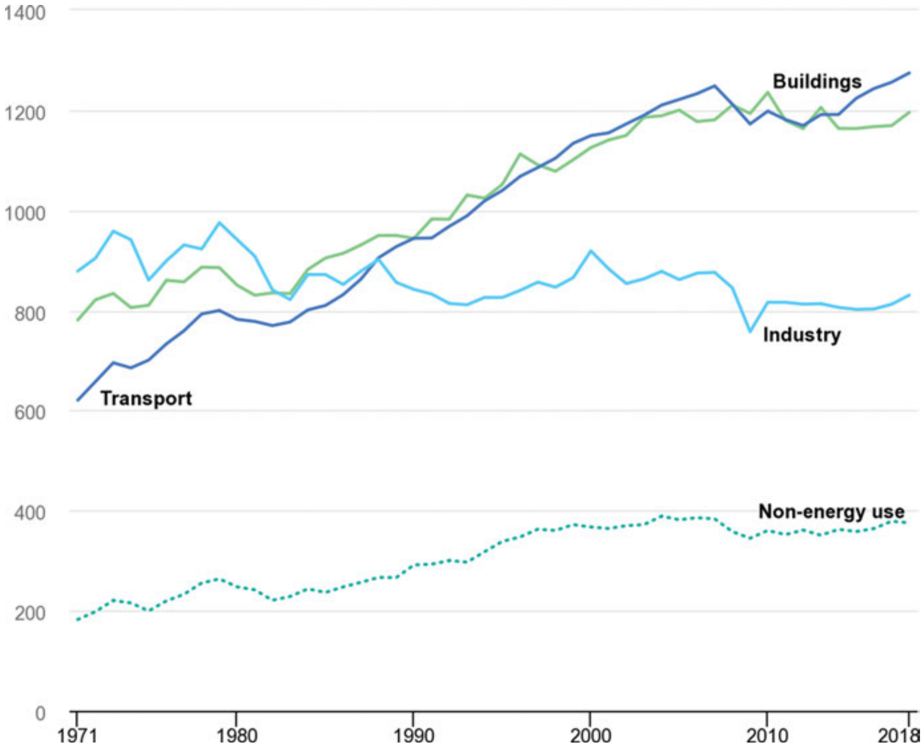


Fig. 3.1: Energy consumption by sectors except power generation (IEA), total final consumption by source, OECD, 1971–2018, IEA, Paris [2].

In this chapter I will try to summarize history, developments, and vision for all the transport except space application for which you may find a better book. Please allow me to describe more for FCEV passenger vehicles than others. Figure 3.2 shows the potential area of hydrogen and battery according to the expert report of Hydrogen Council [3]. Vehicles with daily short travel, and relatively small vehicle is suit able for Battery EV and other areas especially large long-range vehicles is suitable for hydrogen. At the time of this report (2016–17) aviation and shipping were still uncertain for decarbonization fuel. But it is changing now.

Figure 3.3 shows the GHG emission responsibility within the transport. Large passenger vehicles, trucks, and buses as well as ships and aviation are blamed to be the largest emitter. Therefore, introduction of hydrogen is more effective for GHG reduction than the introduction of BEV. Even BEV is spot lighted easily because of large number and visibility. Figure 3.4 shows the roadmap of hydrogen-related technologies that are the combination of technological progress, maturity, and economic priorities.

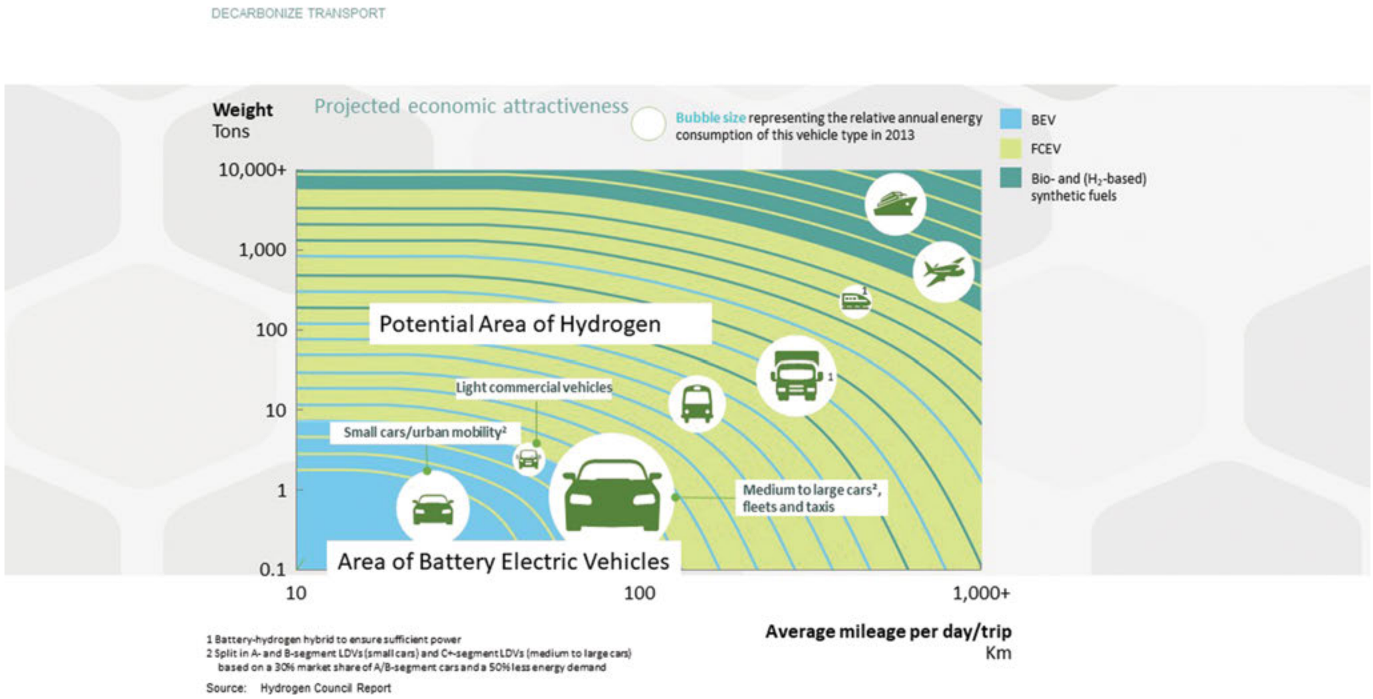
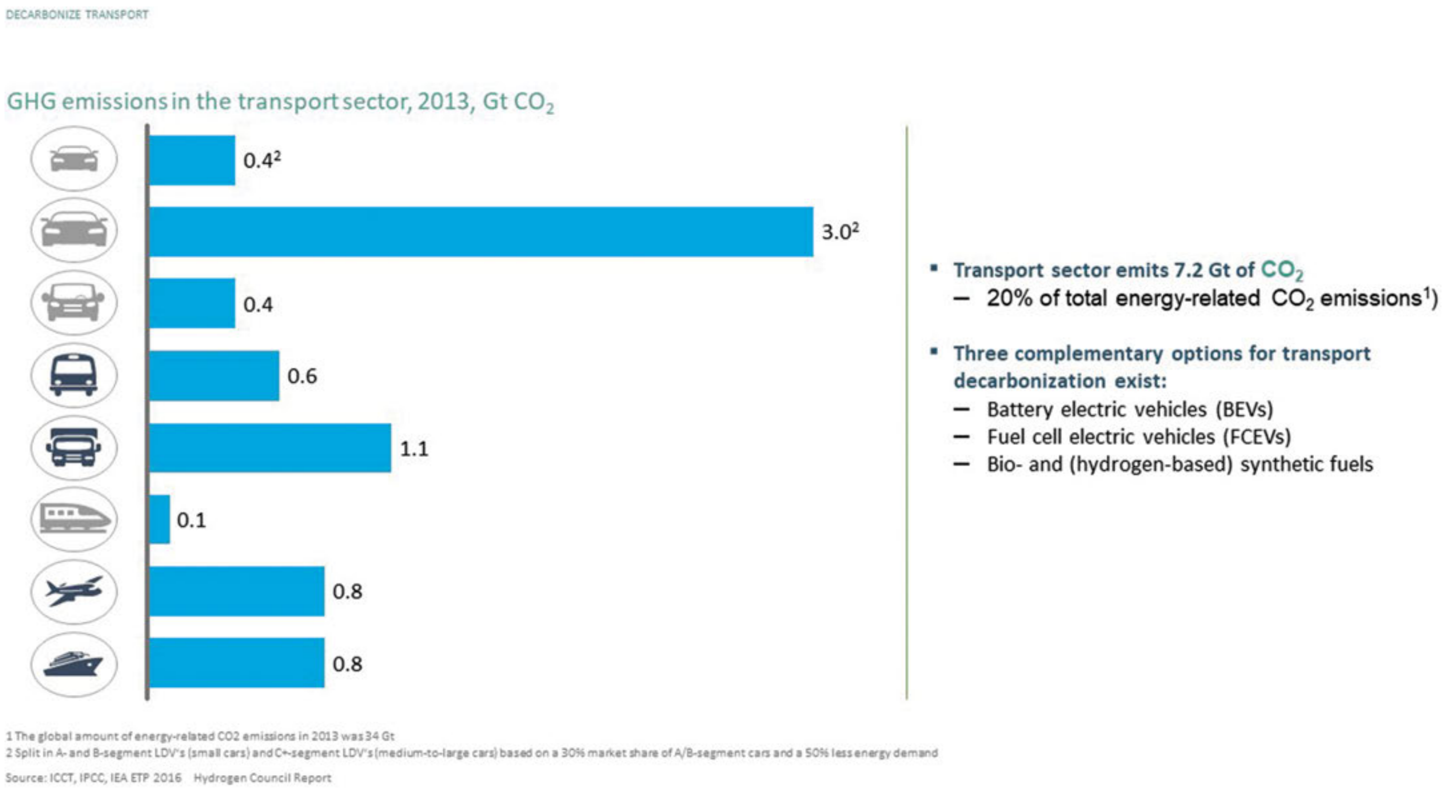


Fig. 3.2: Hydrogen and battery potential in transport (source: Hydrogen Council Report).



DECARBONIZE TRANSPORT

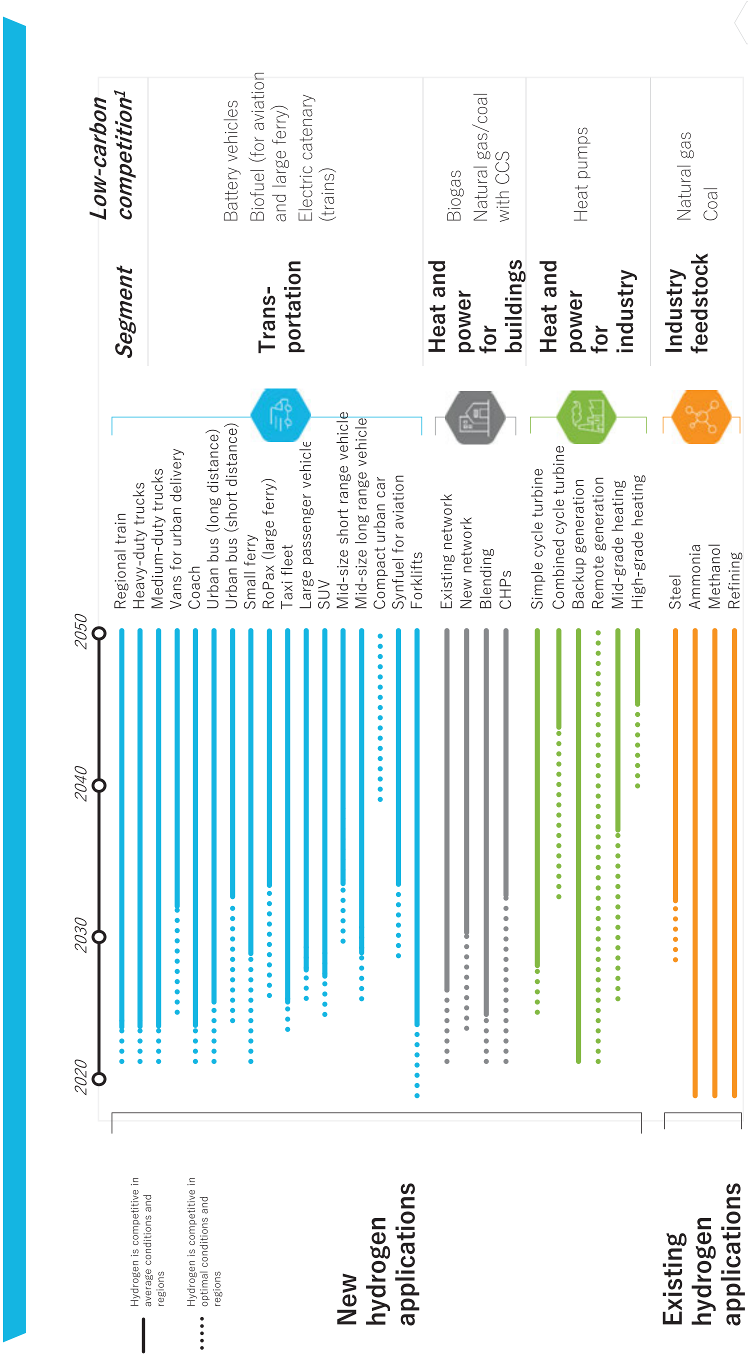
GHG emissions in the transport sector, 2013, Gt CO_2

- **Transport sector emits 7.2 Gt of CO_2**
  - 20% of total energy-related CO_2 emissions[1])
- **Three complementary options for transport decarbonization exist:**
  - Battery electric vehicles (BEVs)
  - Fuel cell electric vehicles (FCEVs)
  - Bio- and (hydrogen-based) synthetic fuels

1 The global amount of energy-related CO2 emissions in 2013 was 34 Gt
2 Split in A- and B-segment LDV's (small cars) and C+-segment LDV's (medium-to-large cars) based on a 30% market share of A/B-segment cars and a 50% less energy demand

Source: ICCT, IPCC, IEA ETP 2016 Hydrogen Council Report

Fig. 3.3: GHG emission within transport (source: Hydrogen Council Report).



1. In some cases hydrogen may be the only realistic alternative, e.g. for long-range heavy-duty transport and industrial zones without access to CCS

Fig. 3.4: Roadmap of hydrogen applications (source: Hydrogen Council Report).

3.2 Hydrogen as fuel for transport

3.2.1 Hydrogen as fuel for transport

Before describing the role of hydrogen in transport in detail, it is important to understand how the fuel is chosen for transport as fuel. Fuel is chosen by the user, but its choice reflects the history and geographical conditions as well as economic condition (cheapness). However, even economic reason is not just cost of energy in thermal value ($/MJ). Choice of fuel and priority of choosing condition are made with the wider aspects such as follows:

1. Cost of operation (fuel cost, maintenance cost, necessary resource)
2. Ease of use (refueling, storage both onboard and infrastructure)
3. Ease of use for purpose of transport (individual, commercial, fleet and other uses)
4. Infrastructure (investment, early balance, business margin)
5. Convenience, cruising range, refueling time
6. Safety (in use, in transport, in delivery)
7. Greenness (emissions both source and onboard)
8. Other aspects for society (energy security, geographical stability)

Priorities of aforementioned choices also vary by the user, such as private passenger or taxi driver/operator use; such as long-distance driving or city delivery purpose. Basically, private car users may be very keen for convenience as they can compromise the price for comfort and performance but may not accept inconvenience in general. Commercial user tends to be keen for total cost of ownership and reliability.

In addition to the above conditions, technology maturity is also important, which gives the user to choose from a wide variety; in immature stage vehicle brands and sizes are limited. Majority of users/customers are very conservative and postpone the change till the regulations force them or market moves significantly. Alternative fuel vehicles shall meet above condition and adopted widely by the users to be able to contribute the energy transition.

3.2.2 Is hydrogen a stupid choice for energy/fuel?

Frequent criticism for hydrogen as a fuel for transport is low efficiency. If energy starts from electrons several conversions accumulate the loss, resulting in the total efficiency at the end being quite low in comparison with the direct use of electricity. For the case of hydrogen when the energy comes from the renewable electricity such as solar or wind. You need electrolysis to produce hydrogen which efficiency is about 70–80 % and when it is used in the electric machine you need to generate the electricity which loses another 40–50% of thermal energy. This is correct if you measure the value of hydrogen in caloric value. However, when it measures economical values this efficiency loss is not the main issue. Economical value can be measured by how much consumer (end user) can pay for this fuel. In case of fuel for FCEV customers may pay a competitive price to replace oil/gasoline. Oil is most expensive per MJ as fuel for the vehicles. Fig. 3.5 shows the relationship of thermal energy value and economic (societal) values (money). Electrolysis will lose the thermal values but obtaining the economic value as a chemical product. When it is used as fuel for FCEV, system efficiency of FCEV can add more advantage for its economic value since with proton-exchange membrane (PEM) fuel cell (FC), vehicles can be driven more km than combustion engine which is around 2-2.5 times more km. In addition, some advantages of not emitting CO_2, not emitting harmful emissions, will further enhance the additional value. This is easily understandable as users will pay the same dollars/kilometer of mobility rather than the caloric value, and price of mobility can be varied with competitive alternative. The fare of taxi is much more expensive than the fare of bus for the same kilometer mobility, but customers pay for extra conveniences and other comfort, etc. In addition, the potential of hydrogen value can be further enhanced when combined more with city design with the desired specifications for the advanced mobility/transport in future.

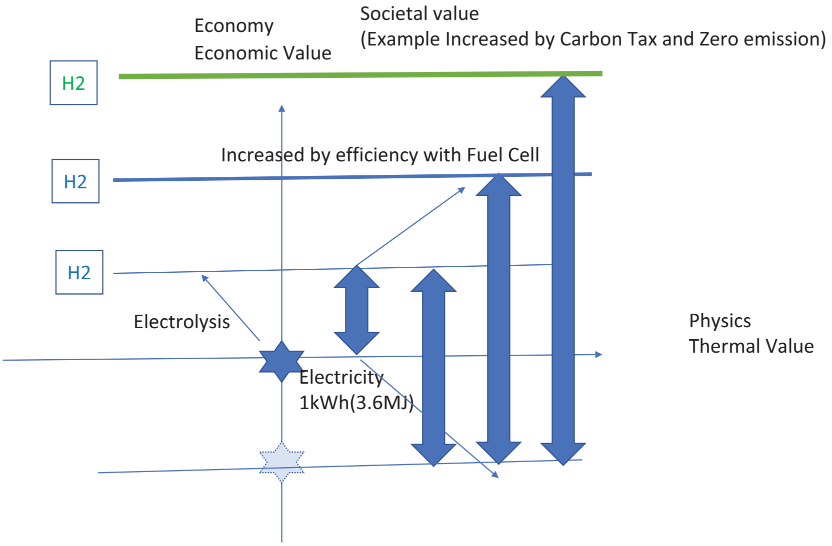


Fig. 3.5: Value of hydrogen in the society.

Conclusion against the criticism for the use of hydrogen is “Hydrogen has a way to use more valuable than the direct use of electrons.” Hydrogen will enhance or at least be competitive to enhance the society than the direct use of electrons. Therefore, hydrogen is being selected for the fuel and energy vector for the future society.

3.2.3 Cost of hydrogen

When hydrogen is used as alternative fuel, cost in operation is very important. Total cost of ownership (cost of operation) consists of capital expenditure (Capex) and operating expenses, so the associated technology is also important. Total cost of ownership is used to compare the potential of technologies and application.

Figure 3.6 shows the number in dollars when the cost of hydrogen becomes breakeven for each application. Breakeven varies by the replacing fuel and deploying technologies. Some applications are feasible with higher hydrogen cost where no other solution can be found. And for transport heavy-duty truck application is feasible with around 3 \$/kg but passenger vehicles need around 2 \$/kg. However, this will vary with additional tax and regulations. Figure 3.7 is overlapping the expected cost of renewable hydrogen onto the previous figure. Break-even hydrogen price (cost of production + predicted delivery) at pomp is very attractive for trains, heavy-duty/medium-duty trucks and long-range passenger vehicles in comparison with BEVs. This is true even with higher hydrogen cost around 4–6 \$/kg. Small passenger vehicles are difficult to reach the break-even because of the CAPEX increase of vehicle itself.

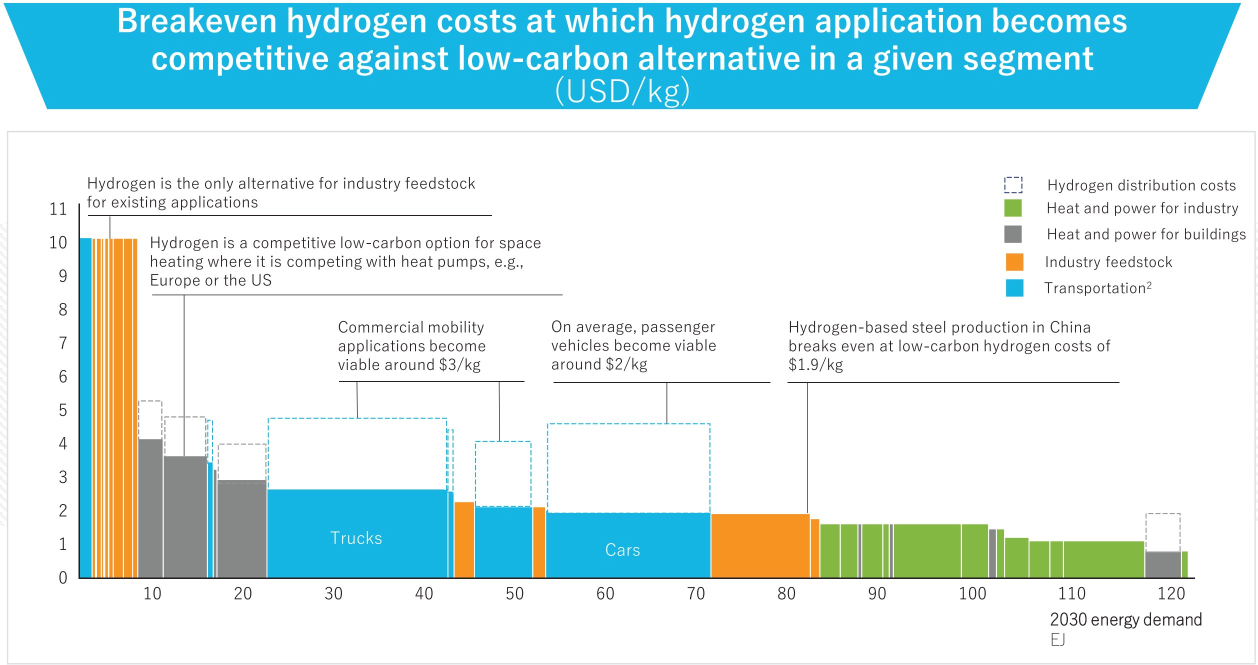
Figure 3.8 shows the TCO (total cost of ownership) comparison progress by vehicle sizes. Larger vehicles may obtain advantages over BEVs quickly; again, small vehicles may be a bit difficult to be cheaper than BEVs.

3.3 Brief history of FCEV development and regulation

3.3.1 Brief history of FCEVs

3.3.1.1 1990s' chase of low emission vehicles and alternative fuels

After the several decades of automobiles with combustion engines, people gradually recognize to blame the role of automobile for local air pollution. In California very stringent emission regulation called "musky low" were implemented which almost killed combustion engines. It also triggered many low emission technologies as well as combustion engine modifications for the passenger vehicles applications. The three-way catalyst development achieved the emission target with combustion engines, but later a more strict regulation called ZEV (zero-emission vehicle) regulation was implemented. This ZEV regulation requires original equipment manufacturer (OEM) to provide a certain ratio of passenger vehicle sold to be driven emission free and later all the vehicles shall be emission-free. This regulation forced OEM to initiate the development of BEVs and FCEVs. OEMs need to sell required a percentage of ZEV into their products. Later several OEMs started selling some EV models such as GM's EV1 and



Breakeven hydrogen costs at which hydrogen application becomes competitive against low-carbon alternative in a given segment (USD/kg)

1. Regions assessed are the US, China, Japan/Korea, and Europe
2. Transportation segments breakeven calculated as weighted average

SOURCE: McKinsey; IHS; expert interviews; DoE; IEA

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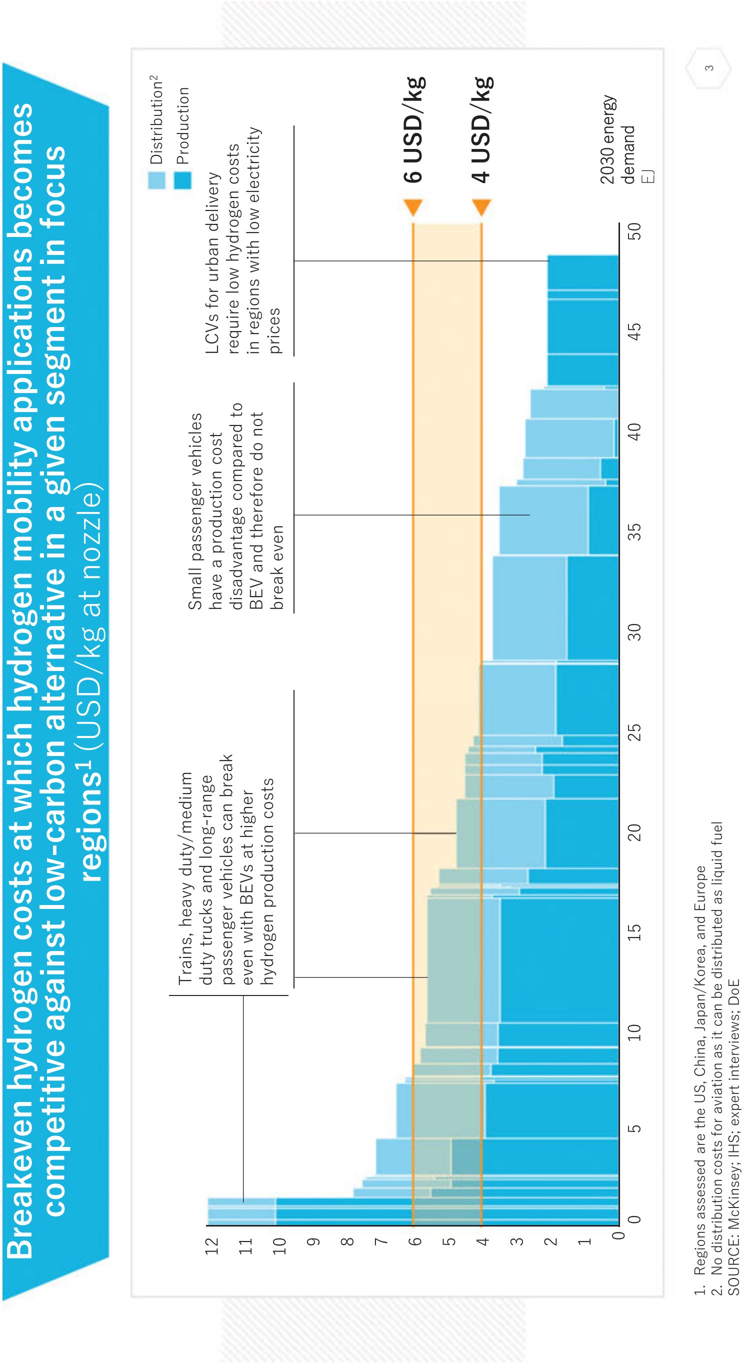
Fig. 3.6: Breakeven cost of hydrogen in the applications (source: Hydrogen Council).



Breakeven hydrogen costs at which hydrogen mobility applications becomes competitive against low-carbon alternative in a given segment in focus regions[1] (USD/kg at nozzle)

Trains, heavy duty/medium duty trucks and long-range passenger vehicles can break even with BEVs at higher hydrogen production costs

Small passenger vehicles have a production cost disadvantage compared to BEV and therefore do not break even

LCVs for urban delivery require low hydrogen costs in regions with low electricity prices

1. Regions assessed are the US, China, Japan/Korea, and Europe
2. No distribution costs for aviation as it can be distributed as liquid fuel
SOURCE: McKinsey; IHS; expert interviews; DoE

Fig. 3.7: Competitiveness of hydrogen cost in the transport (source: Hydrogen Council).

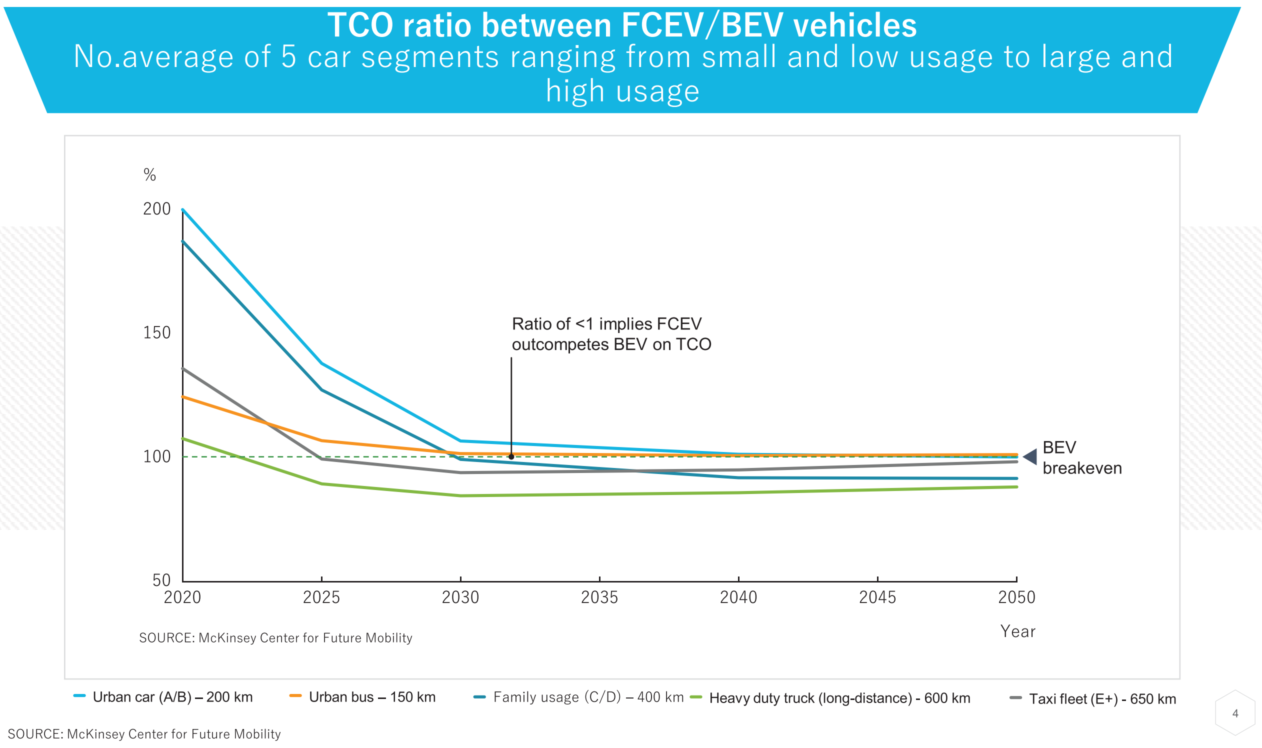


Fig. 3.8: TCO comparison of several road vehicles (source: Hydrogen Council).

Toyota's RAV4EV. However, BEVs sales were suffered to the normal costumers who care about the lack of practical cruising range, inconvenience of charging time and lack of charging spots/infrastructure of BEVs. Fuel cell vehicles are considered as a better alternative for the drivers, and so several OEMs accelerated the FC developments. However, early FCs were powered by methanol or petrol or natural gas. One of the early FC vehicles is DAIMLER NECAR1 as shown in Fig. 3.9. Early FC systems were very large and almost occupied the whole cargo space of the vehicle. These fuels were internally reformulated into the hydrogen gas and then fed to the FC unit so that they emitted CO_2 in exhaust. This reformulated type FCV has a big disadvantage, It need longer starting up time from cold stop, reforming reactor needs half an hour for heating up thus customer need to wait quite long time before the day drive. OEMs decided to use pure hydrogen and avoided this starting up time and efficiency issue. However, the infrastructure became more difficult than originally planned to use alcohol or natural gas.

Fig. 3.9: First drivable fuel cell vehicle NECAR 1 from Daimler (source: Daimler).

3.3.1.2 2000–2015 demonstration and infrastructure preparation

In 2002 Toyota and Honda announced the introduction of hydrogen-powered FC vehicles and inaugurated a demonstration program with several road-going vehicles in both the United States and Japan. Later, GM and Daimler joined the demonstration. Toyota in 2009 "FCHV adv and Hyundai "ix35 FCV" in 2013 brought homologated (type approved) FCVs into the market. For this phase hydrogen storage had been simplified into 70 MPa compressed tank with carbon fiber–reinforced composite structure (see later part).

Besides the development of vehicles, infrastructure developments were also initiated (see Tab. 3.1). It is important to co-develop and build up vehicle technologies and infrastructure technologies synchronously. First, in the United States, California CAFCP (California Fuel Cell Partnership), in Japan JHFC (Japan Hydrogen & Fuel Cell Demonstration Project), later in Europe, in several regions such as Germany, Denmark, and Norway, similar government industry programs have been established.

Figure 3.10 shows prototype FCVs in JHFC around 2002. Figure 3.11 shows the one of the demonstrations HRS (hydrogen refueling stations) in German CEP (Clean Energy Partnership).

Fig. 3.10: Top left to right and bottom left to right Honda FCX, Toyota FCHV, Mercedes Benz F-Cell, and General Motors Equinox Fuel Cell. GM model is latter compressed gas models (source: IHFC HP [6]).

Fig. 3.11: CEP early hydrogen station at Berlin (source: CEP HP [7]).

3.3.1.3 2014: start of commercialization of FCV and start of hydrogen refueling network

After the long period of demonstration, in 2014 the first mass-produced FCEV “Mirai” was announced and launched by Toyota. “Mirai” is the E-segment sedan with a range of 500–600 km (differentiated by driving cycle for Japan and the United States). Car price was about 7 million yen (65 k$). Toyota claimed a practical range of 500 km and less than 5 min charging time. Mirai was introduced to the United States and European market in the next year. Honda Clarity followed later in 2016. In 2018 Hyundai brought SUV-type FCV “NEXO” into the market in both the United States and Europe as well as Korea. Daimler also launched Mercedes GLC F-Cell in 2018.

Fig. 3.12: First commercialized FCEV TOYOTA Mirai and Honda Clarity (source: Toyota, Honda).

3.3.1.4 Infrastructure movement

Synchronized with the introduction of commercial vehicle products, infrastructure of hydrogen refueling network was initiated in Japan, California, and Europe.

Tab. 3.1: Infrastructure programs past and now (August 2020).

Area	Demonstration	Status	HRS number
Japan	**JHFC 2002–2010** Japan Hydrogen and Fuel Cell Demonstration Project	JHyM Japan H2Mobility [8]	133 stations in operation target 200
California/United States	**CAFCP 2002-** California Fuel Cell Partnership [9]	Continues Fund expanded to private entities	42 stations in operation [10]
Germany/Europe	**CEP 2002 ~** Clean Energy Partnership [7]	Infra part H2MOBILITY	85 stations in operation [11]

In Japan following the government-supported JHFC (Japan Hydrogen and Fuel Cell Demonstration Project) project, government and industry (energy, industrial gas companies and OEMs) agreed and started to construct 100 HRS in major metropolitan cities of Tokyo, Nagoya, Osaka, and Fukuoka. Later industry created the hydrogen network company "JHyM" [8]. JHyM is currently targeting 200 stations till 2025. In California industry and the government of California jointly created CAFCP [9]. It supported the demonstration program and is also planning an optimum station network. CAFCP efforts make minimum but optimum network to support world's largest FCV population with only 42 stations currently. Actual operations and buildings are being done by the private entities. In Germany the demonstration program CEP continues while independent network company H2Mobility is building the network; each station is operated under the individual energy companies.

JHFC, JHyM, and H2Mobility are funded by both government and industries, Unique but interesting funding mechanism is US LCFS (Low Carbon Fuel Standard) [12] credit. Energy companies need to meet LCFS regulation. Building the hydrogen refueling station receives some credit to be exchangeable with this LCFS fulfillment. With this market mechanism it can accelerate the HRS construction and reduce government incentives. Similar system is implemented at British Columbia in Canada near Vancouver and the system is actually assisting building several HRS.

3.3.2 Expansion of hydrogen-powered transport

3.3.2.1 Bus and commercial vehicle

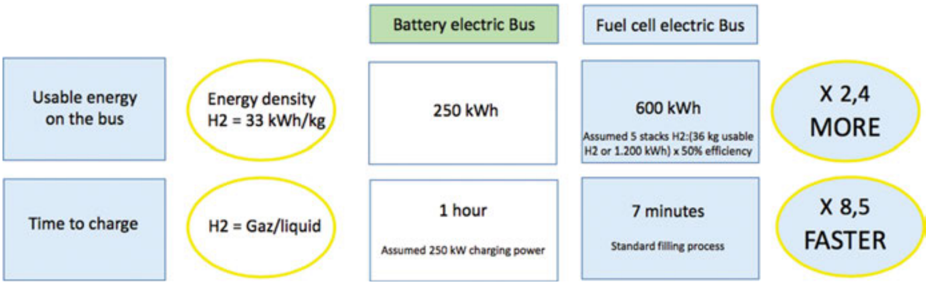
Prior to the passenger vehicle, several bus demonstration projects were carried out in the United States, Japan, and Europe. These Bus demonstration projects helped technical developments of hydrogen refueling system and logistics.

Fig. 3.13: FC prototype bus Mercedes-Benz (left) 2013; Toyota (right) 2006.

Bus is the ideal application for FCs, however if the FC unit is developed for only for bus application, number of FC unit is difficult to reach the competitive cost to the diesel competitor. Early FC bus developments also faced the cost of electrification of bus unit same as FC number of units is difficult to reach the competitive cost. Recent move for zero-emission operation accelerated the electrification of bus mainly for BEVs. As a result, electric bus power train has become competitive finally and this is pushing hydrogen FCVs again.

Fig. 3.14: Toyota Sora 2018 and Van Holl Equi. City18 FC (source: Toyota and Van Hool).

In 2018 Toyota launched FC Bus SORA (Fig. 3.14) into the market and announced 100+ buses for Tokyo Olympic game transport. European cities are requesting a very high number of ZEV buses to fulfill their local environmental target and global CO_2 emission target. Several bus companies such as Van Hool and Caetano announced the introduction of FC bus in their product lines. Van Hool claims the FC bus has 2.4 times more energy storage and is 8.5 times quicker to charge than the BEV (see Fig. 3.15 [13]).



		Battery electric Bus	Fuel cell electric Bus	
Usable energy on the bus	Energy density H2 = 33 kWh/kg	250 kWh	600 kWh Assumed 5 stacks H2:(36 kg usable H2 or 1.200 kWh) x 50% efficiency	X 2,4 MORE
Time to charge	H2 = Gaz/liquid	1 hour Assumed 250 kW charging power	7 minutes Standard filling process	X 8,5 FASTER

Fig. 3.15: BUS operation FC versus BEV (source: Van Hool).

3.3.2.2 New movements to extend to larger and heavy-duty commercial truck applications

In 2018, China announced an FCEV roadmap with more bus and truck deployment targets. This is a surprise for those who believed BEVs won the transport for China, but the Chinese government recognized the importance of BEV and FCEV technologies to improve their local and global environment. This coincided with the announcement of a heavy-duty truck demonstration in US port by Toyota [14] in 2015 and 2018 and Nikola Motor's FC powered heavy-duty truck in 2016 [15].

In 2019-2020 many heavy-duty truck manufactures announced their introduction plan of hydrogen (see Fig. 3.16 and 3.17) [16].

Fig. 3.16: Heavy-duty truck from Toyota 2016 (left) and Hyundai (right) (source: Toyota, Hyundai).

Fig. 3.17: Nikola One 2016 and Nikola Badger Pick-up 2020 (source: Nikola Motor).

3.3.2.3 Expansion of hydrogen in transport toward land, sea, and air transport

3.3.2.3.1 Train

The first hydrogen FC train Alstom "Coradia iLint" FC train went into demonstration in Germany (Fig. 3.18) in 2017 and it successfully completed its trial run in real service after 180,000 km [17]. Alstom claims the range of iLint is 1,000 km, up

Fig. 3.18: Alstom Hydrogen Train Coradia iLint (source: Alstom).

to 140 km/h cruising speed and importantly they claimed the TCO to be competitive to the diesel engine version and much cheaper than electrification. They also announced receiving an order for 27 trains from the German local train operator and they will be in operation in 2022 around Frankfurt. There are several announcements of train developments in the UK and other areas recently. Hydrogen FC train is a good decarbonized solution for non-electrified line in Europe.

3.3.2.3.2 Sea, ships

Energy Observer announced first round the world trip project with hydrogen in 2017 [18]. It already sailed more than 10,000 NM in the sea. They produce hydrogen onboard and use for the vessel.

Several other plans and concept are announced such as ferry in Nordic and Port of Rotterdam.

There are also several aggressive projects announced such as hydrogen cruiseship and big container carrier with hydrogen and sail.

3.3.2.3.3 AIR aviation

After a long absence of aviation with hydrogen, hydrogen airplane HY4 flew in September 2016. HY4 is developed by German DLR and consortium [19]. HY4 is the FC battery hybrid airplane. With 5 kg of 35 MPa compressed hydrogen and 80 kW motor, HY4 can fly around 750–1,500 km range (depend on the speed).

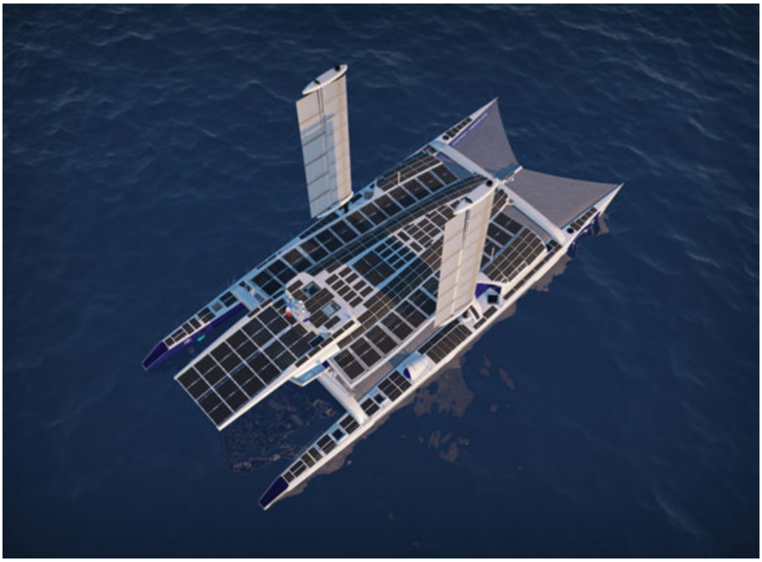


Fig. 3.19: Energy observer hydrogen ship (source: Energy Observer).

Fig. 3.20: German HY4 4-seater airplane (source: HY4.org).

3.3.2.3.4 Commercial airplane is coming

Airbus and Boeing both announced the development of hydrogen-powered commercial aircraft.

Airbus announced the target of hydrogen commercial aircraft is 2035. See Fig. 3.21 [5].

Fig. 3.21: Air bus zero-emission aviation including hydrogen (source: Airbus).

Hydrogen is a bulky gas, but it has 3 times higher gravimetric energy density than the conventional jet fuel. This benefit is also attractive for air taxi and other aviation mobilities and there are several eVTOL developments ongoing (Fig. 3.22).

Fig. 3.22: eVTOL from Alaka'i Technologies (source: Alaka'i's Technologies).

3.3.2.3.5 Hydrogen in future vision

In the coming decarbonized world hydrogen is no longer the alternative fuel to replace fossil fuel. Together with the renewable energy and part of circular economy, hydrogen will be the important vector of society. Transport is also a part of society and is strongly combined with logistic and mobility. Toyota announced a woven city concept where mobility and society are strongly combined.

Fig. 3.23: Toyota Woven City concept where mobility/energy and society are combined. Similar concept is shown for Saudi Arabia's new city called NEOM where primary energy is provided nearby solar and wind. Hydrogen is produced from those renewable energy. City's mobility is the combination of hydrogen and electricity.

3.4 Technologies

3.4.1 Main engines

Use of hydrogen for transport is either combustion in the engine or electrochemical process with fuel cell. In the case of combustion engine, modification is limited and relatively easy. However,combusting hydrogen in the engine cannot improve the efficiency drastically and need large quantity of hydrogen needed to store on board. Storing hydrogen on board in large amount is always issue. And combustion cannot avoid emission such as NOx so system need need expensive after treatment.

In the case of hydrogen to feed to FC and generate electricity, you can expect more increase of efficiency and hydrogen use can be reduced and thus onboard storage can be easier. However, for using FC, vehicles needed to be electrified. This was the difficult part of vehicle development but recently electrification of vehicle is getting very popular so that same component can be shared with hybrid electric vehicle sand BEVs. This is still the issue for large ship and heavy-duty trucks where electrification has not been developed yet.

3.4.1.1 Fuel cell

Historically several FC systems had been developed but finally for road transport (passenger and heavy duty), PEM-type FC is the mainstream. This is because of the compactness and short start-up time as well as cost potential. For large ships and other larger applications, other types can be possible but these are still early days of development.

FC produces electricity through the electrochemical process, hydrogen split into protons and electrons by the Platinum base catalyst and through the membrane protons meet the oxygen to form the water while generating the electric current. This process has much higher efficiency than combustion. Electricity propels the vehicles' motor and normally the system is hybridized to optimize the energy flow and uses a regenerative brake. Emission is only water or water vapor.

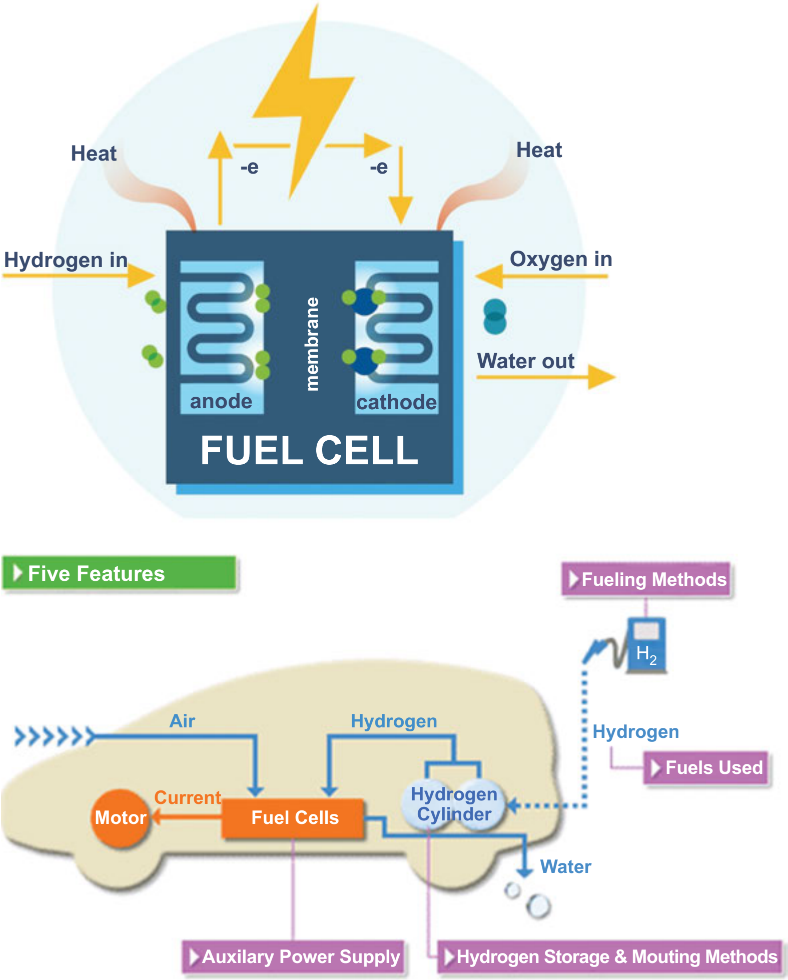
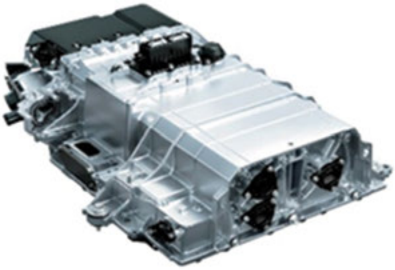


Fig. 3.24: Schematic diagram of fuel cell and fuel cell system for vehicle.

Fig. 3.25: Real installation of FC system in the vehicle (Toyota Mirai) (source: Toyota).

Tab. 3.2: Fuel cell vehicle and FC power unit.

Toyota Mirai 2014 Range 500 km(Actual) 		113 kW
Honda Clarity 2015 Range 589 km 		103 kW

Tab. 3.2 (continued)

Hyundai NEXO 2018 Range 756 km 		90 kW
Daimler GLC FC 2018 Range 478 km 		90 kW

3.4.1.2 Combustion engines

3.4.1.2.1 Hydrogen combustion engine

Use of hydrogen in combustion engine has been tested in many projects and institutes, mainly universities such as Tokyo City University[1] whose famous one is Prof. Takagi's work. Large scale on road demonstration was carried out by BMW project, vehicle was Hydrogen 7 and certain number of vehicle are tested in Europe and US around 2005–2008. Hydrogen 7 is the bi-fuel hydrogen/petrol car and it is possible to change from petrol to hydrogen or opposite during the drive. It stores the hydrogen in liquid phase (−253 °C). A complex cryo-storage tank is installed in the extended body. However, the efficiency of combustion engine is very low (though slightly better than the conventional with quicker combustion of hydrogen's flame). The actual cruising range of Hydrogen seven fueled by hydrogen is very limited, no other follower comes out to the road.

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[1] Furuhama, Shouichi (1978). *International Journal of Hydrogen Energy Volume 3, Issue 1, 1978, Pages 61–81.* https://www.ammoniaenergy.org/articles/man-ammonia-engine-update/

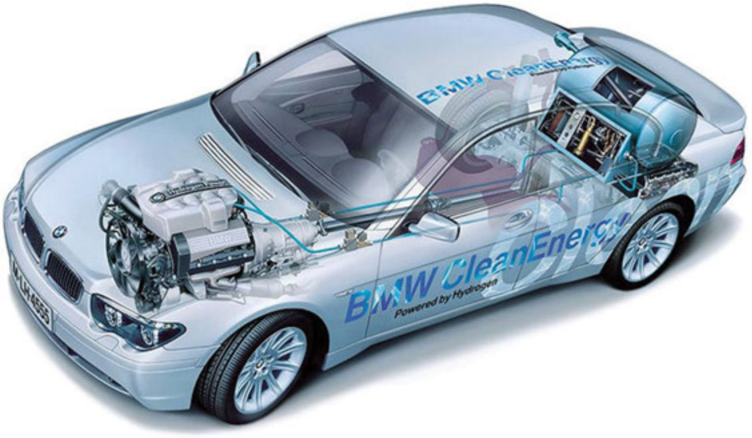


Fig. 3.26: Hydrogen-powered combustion engine vehicle BMW Hydrogen 7 (source: BMW).

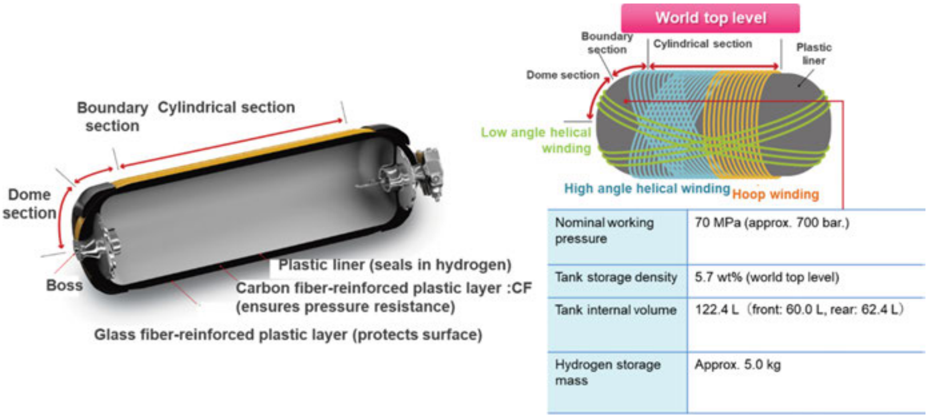
3.4.2 Hydrogen storage

3.4.2.1 High-pressure compressed storage, phase in commercial

Hydrogen is compressed and kept in composite tank. There are several types of composite tanks but mainly carbon fiber is reinforced. For bus and forklift 35 MPa and passenger and heavy truck application is 70 MPa. Bus application uses either 35 MPa or 70 Mpa; currently two types of tank are in production. One is aluminum internal tank (called type 3) and plastic internal tank (type 4). Both has pros and cons but there is a tendency to select type 4 because of its cost potential and lightness. For forklift application, 35 MPa tank (type two = carbon reinforced steel tank) is in use. Latest 70 MPa tank reaches 5.7 wt% level of gravimetric performance and so currently the light weight and enough capacity as well as easy to use requirement. So that all most all FCEV use high pressure tank hydrogen storage currently. And fore seeable future this will continue. Since infrastructure development necessary for other storage system.

3.4.2.2 Cryo-storage: phase in small production in the past and new progress

Hydrogen can be liquid phase and high density (0.07 kg/m^3) in very low temperature (−253 °C in ambient pressure). This is attractive store for both transport and mobility; however, hydrogen tank needs to be kept in very cold cryo-condition and needs to feed gas when it is in use.



Nominal working pressure	70 MPa (approx. 700 bar.)
Tank storage density	5.7 wt% (world top level)
Tank internal volume	122.4 L (front: 60.0 L, rear: 62.4 L)
Hydrogen storage mass	Approx. 5.0 kg

Fig. 3.27: Carbon fiber-reinforced high pressure tank (TOYOTA Mirai 2014).

The first hydrogen car Hydrogen 7 uses liquid hydrogen as fuel. Hydrogen is stored in a cryo-storage tank. The tank is maintained at −253 °C with a passive cooling system together with double wall insulation. Tank is highly thermally insulated by a vacuum multilayer insulation system and hydrogen is cooled by its own evaporation heat. As a result, the tank maintains several days of liquid hydrogen in real use but needs a longer parking time to release hydrogen. There are several issues with cryo-storage. Despite a relatively large amount of hydrogen storage capacity there is no other follower to develop. In the real usage long actual charging time and evaporative loss during parking showed the difficulty for passenger application. After the hydrogen 7 the passenger application moved to use compressed gas storage.

Recently, potential large capacity for bigger application such as long haul truck and bus application, attract this cryo-storage again. For the large ship and the train application, cryo-storage are also in serious investigation.

This is enhanced due to the increase of liquid hydrogen delivery for logistics for hydrogen refueling stations.

3.4.2.3 Another hydrogen storage/tank system

3.4.2.3.1 Metal hydride tank: phase in prototype

Hydrogen can be stored inside the metal, hydrogen atoms penetrate the metal lattice and form broad connection with the metal material. This storage, hydrogen contents are relatively low (1-3%) but very high volumetric capacity (bringing compactness). Several prototypes are made and being tested in several demonstrations. Despite of its big expectations, low gravimetric capacity and high cost of absorbing metal is limited for the actual implementation.

3.4.2.3.2 LOHC (liquid organic hydrogen carrier): phase in proto small demonstration

Some organic chemicals can combine hydrogen chemically and developed to be a carrier for logistic of hydrogen. Physical characteristics of this material are similar to current liquid fuels such as gasoline/diesel and easy to share the similar engineering (tank, tanker, and pipeline). This is called LOHC (liquid organic hydrogen carrier), hydrogen is provided through the on-board reactor to split LOHC into hydrogen and carrier material. Carrier material is collected and reuse.

Benefit of LOHC is easy to transport and is handled like the current oil usage except return cycle. Obstacle of LOHC is necessity of return cycle and heat is necessary to split hydrogen from LOHC.

Several prototypes are proposed and tested but currently no commercialized products are in use yet.

3.4.2.3.3 Ammonia and methanol as fuel for FCV

Ammonia and methanol are the chemicals having high contents of hydrogen and are the candidates of hydrogen carrier for transport and storage. To use them onboard can be an attractive option and several attempts have been done. Methanol and ammonia both have potential to be fed into the direct FC but because of the low output density currently they could not reach the serious developments phase yet. Ammonia's direct use for combustion engine is still under investigation.[2]

3.5 Conclusion and future actions hydrogen in the transport

Hydrogen is considered as an important fuel for road, train, sea, and air transport. In addition, hydrogen will play not only an alternative fuel. Hydrogen will play more role than the fuel for the transport. Hydrogen can be stored and transportable frozen renewable energy. And it will help to use renewable energy more flexibly. Sometimes Hydrogen VS Battery argument exist in the media. However, electrons and hydrogen are going to be a strong partner or supplemental to build the future sustainable low carbon society.

Fossil fuel is very convenient and easy to use but hydrogen and electricity need new infrastructure and new technologies. But hydrogen can be made anywhere and any-energy from, even from the waist or the abandoned source. It is unlike fossil fuel geographical restrictions is very limited. Local efforts to produce hydrogen and use it will enhance the local economy and create more jobs. This will reduce the friction between the south and north or between the countries of having and not having. Even hydrogen vehicles can be a bit expensive for everybody in the beginning.

However used or secondhand cars can be cheap but still working well and will no longer consume fossil fuel. It will be refueled by the local energy. This will liberate many countries which suffer from the expensive oil to import and consume precious money. With hydrogen and renewable energy, then they can use their own energy thus they can leave their money left for the investment for their own development.

Even in the developed countries new movement of using hydrogen can help the society moves more robust and sustainable way. Figure 3.28 shows the new concept of hydrogen bus to help the society with its large energy storage to provide electricity to the local community together with the movable battery. Vehicle can be an emergency base for the local community in case of disaster/emergency. Transport machine may have more functionsthan just providing the mobility in future together with hydrogen [20].

Fig. 3.28: Toyota and Honda's charging station concept for emergency energy system.

3.5.2 Actions necessary

De-carbonization cannot be done by individuals efforts. Mobilities or transport will play an important role but more ideas necessary to accelerate the implementation of these technologies. Key is how society enhances the individuals choices into more environmentally friendly direction. We need steady policies and good incentives, both monetary and non-monetary, for the users.

Hydrogen in transport leads the peaceful (friction less), robust (safe at disaster), clean (emission free), low carbon and freedom energy system into our society thus it will help us to live happier and healthy sustainable world in near future.

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[10] CAFCP Station Map, “https://cafcp.org/stationmap,”.

[11] H2 Station in Europe, “https://h2.live/en,”.

[12] LCFS, “https://ww2.arb.ca.gov/our-work/programs/low-carbon-fuel-standard,”.

[13] Van Hool, “https://www.sustainable-bus.com/news/van-hool-launch-new-a330-fc-and-exqui-fuel-cell-future/,”.

[14] Toyota Truck, “https://www.sustainable-bus.com/news/van-hool-launch-new-a330-fc-and-exqui-fuel-cell-future/,”.

[15] Nikola One, “https://nikolamotor.com/press_releases/nikola-one-truck-revealed-tonight-700-p-m-mst-32,”.

[16] Hyundai Truck, “https://news.hyundaimotorgroup.com/MediaCenter/Library/green-hydrogen-allows-hyundai-hydrogen-mobility-and-hydrospider-to-connect-electricity-with-mobility-sectors-in-switzerland,”.

[17] Alstom, “https://www.alstom.com/our-solutions/rolling-stock/coradia-ilint-worlds-1st-hydrogen-powered-train,”.

[18] Energy Observer, “https://www.energy-observer.org/,”.

[19] HY4, “http://hy4.org/,”.

Laurent Allidières

4 Introduction to hydrogen energy: from applications to technical solutions

4.1 Introduction

Hydrogen can be used as a clean energy vector in fuel cell vehicles contributing largely to the energy transition to a carbon-neutral world. It can be produced from renewable energy sources – such as wind and solar – using water electrolysis, or from natural gas with steam methane reforming using carbon capture utilization and sequestration (CCUS) technologies to obtain “low-carbon hydrogen.”

Yet, developing clean transportation means starting with the bias to have it powered by hydrogen (or electricity, or synfuel) is not the correct way to approach the problem. As in any product development process, functional requirements should prevail over a techno push approach.

Let us imagine that you have developed an awesome box. As great as it is, if it is not adapted to the functional needs of storing eggs (“the box shall have compartments in the shape of an egg” as the functional requirement), you will never be able to safely transport said eggs!

It is the same for hydrogen. It has great properties, such as one of the highest energy densities achievable on the Earth,[1] but with its low density at ambient pressure and temperature (0.089 g/L at 1.013 bar and 273 K) and its low temperature (20.4 K, 1.013 bar abs) when liquefied, it will add challenges to the storage and might disqualify the molecule from some specific applications.

This is why functional specifications are key. Very simple requirements such as “the refilling time shall be the same for a hydrogen vehicle as a gasoline vehicle” can lead to decades of discussion and norm developments around fast filling protocols of hydrogen storage tanks.[2]

This chapter will try to provide tips to engineering teams on how to preselect a hydrogen-based fuel storage system, from the supply chain to the storage and fuel cell integration. Detailed studies will still need to be done anyhow to end up with a final approved design, but these general rules of thumb might – in some cases – save engineering teams from a lot of useless detailed studies to try to compare apples to apples different hydrogen storage ways, where actually some could be eliminated quite easily.

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[1] 120 MJ/kg not taking into account antimatter (89,875,517,874 MJ/kg) or fissile materials: https://en.wikipedia.org/wiki/Energy_density.

[2] For instance SAE J2601 Fueling Protocols for Light Duty Gaseous Hydrogen Surface Vehicle https://www.sae.org/standards/content/j2601_202005/.

https://doi.org/10.1515/9783110596274-012

4.2 How to bring hydrogen to your system?

First, let us have a quick reminder on hydrogen production and the main different possibilities to deliver it to a customer:

Contrary to conventional fuels, there is currently no existing pre-established hydrogen infrastructure allowing deploying hydrogen energy solutions in any part of the world at almost a flat cost, particularly when we consider the very fast growth of hydrogen energy needs as well as the large volumes engaged.

In the current fast hydrogen energy market takeoff, volumes cannot anymore be taken on extra capacity available on industrial customer plants. Therefore, a hydrogen-based zero-emission vehicle project is also – in most cases – a supply chain project requiring investments to bring the molecule to the user. Therefore, it will be important to bring in the discussion hydrogen suppliers at an early phase of the project in order to check whether delivering hydrogen where the vehicles will be deployed is economically feasible, and if synergies this other users can be found, even if everything is technically possible, industrial gas suppliers having already succeeded in getting hydrogen all the way to the arctic ice floe.[3]

Scaling up is of prime importance when producing and distributing hydrogen. A rough order of magnitude gives a factor of around two in hydrogen cost reduction when the production is multiplied by ten.[4]

Therefore, hydrogen suppliers will try as much as possible to develop basins of consumption, privileging some geographies for early fuel cell deployments, allowing to bundle different projects and reach economies of scale for producing and distributing.

Early discussions about the geographies of the deployments will allow optimizing the costs upfront.

Once a basin is selected, it becomes interesting – on a pure supply chain point of view (therefore excluding hydrogen production cost), without considering the customer functional specifications which could privilege a technical solution versus another – to compare the different routes on an economic and CO_2 emission points of view. Such studies are very dependent on the energy cost and carbon footprint,[5] but the tendency of the table hereunder is quite reproducible in any part of the world:

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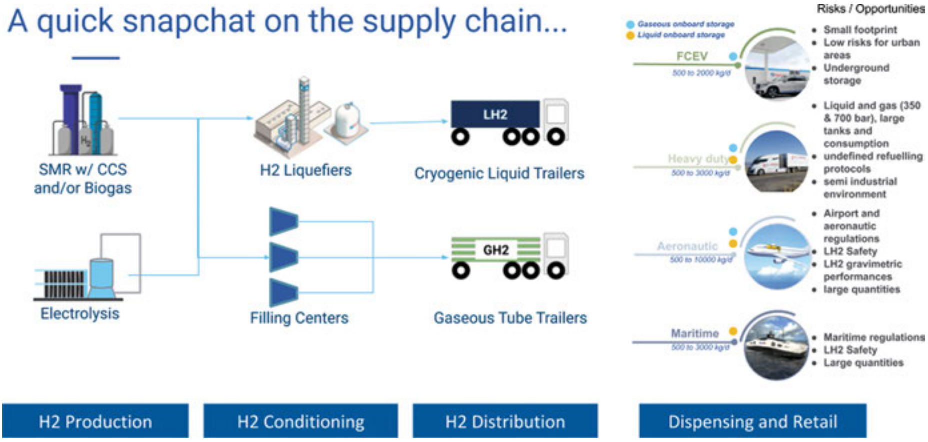
[3] Polarpac project: https://advancedtech.airliquide.com/sites/abt_at/files/2017/01/10/cryoscope_no22-f.pdf.

[4] More information about impact on scaling up hydrogen systems on costs can be found here: https://hydrogencouncil.com/wp-content/uploads/2017/11/Hydrogen-scaling-up-Hydrogen-Council.pdf.

[5] In the example shown, the data includes supply chain and HRS costs (molecule cost is 0), 30 tons per day liquefier/filling centers and 50 €/MWh electricity cost, EU Energy mix CO_2 emissions.



A quick snapchat on the supply chain...

Risks / Opportunities

- Small footprint
- Low risks for urban areas
- Underground storage
- Liquid and gas (350 & 700 bar), large tanks and consumption
- undefined refuelling protocols
- semi industrial environment
- Airport and aeronautic regulations
- LH2 Safety
- LH2 gravimetric performances
- large quantities
- Maritime regulations
- LH2 Safety
- Large quantities

H2 Production | H2 Conditioning | H2 Distribution | Dispensing and Retail

Fig. 4.1: Typical hydrogen supply chain (source: Air Liquide).

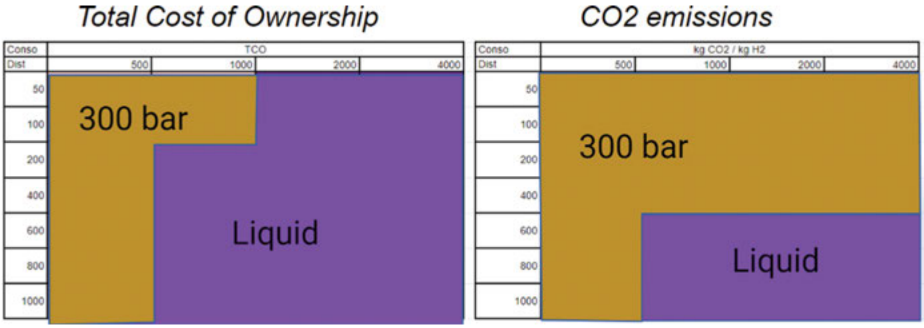


Fig. 4.2: Compared cost (left) and CO_2 footprint (right) of gaseous and liquid supply chain (source: Air Liquide).

The tables herein consider in a column the HRS[6] capacity (kg/day) versus the single trip distance from the hydrogen source.

Comparing different gaseous supply chain modes (particularly with regard to pressure) and thanks to the recent development in composite cylinders, 300 bar pressure looks the most promising.

In terms of costs, we see that the liquid supply chain becomes more competitive than gas for capacities higher than 500 kg/day, unless the distance of the HRS from the source is short.

In terms of CO_2 emission, the liquid hydrogen supply chain efficiency (the payload for a truck transporting liquid hydrogen being 4 times higher than for one

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[6] Hydrogen Refueling Station.

carrying gaseous hydrogen at 300 bar) offsets the CO_2 emissions of the liquefaction process for large stations (>500 kg/day) located 600 km away from the source. In case renewable electricity is used to liquefy hydrogen, then the liquid hydrogen supply chain always emits less CO_2 than its gaseous counterpart.

This table does not consider on-site production as it only compares supply chains, from the output of the hydrogen production plant to the 700 bar HRS dispenser. Indeed, the interest of on site systems very much depends on the size considered for the basin of production, and the possibility to deliver hydrogen by road from the production plant to the customer (can be difficult if the production is too far from the HRS or it the consumption requires too many daily deliveries).

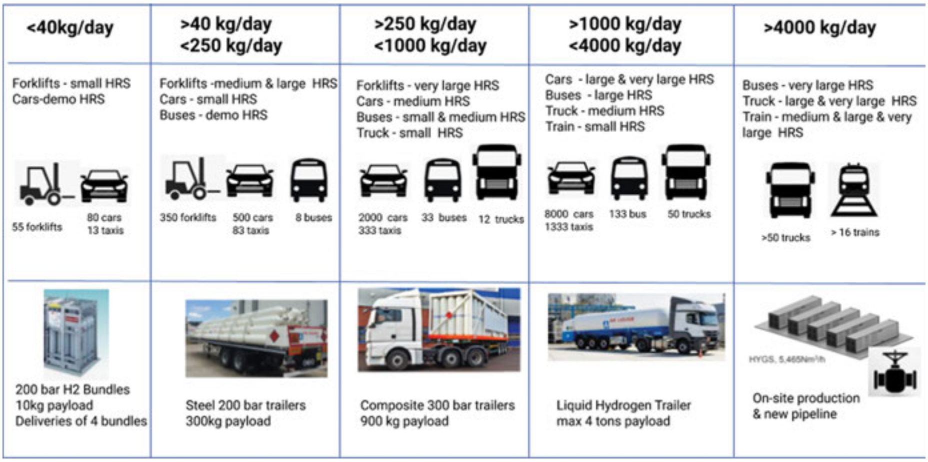
Table 4.1 tries to illustrate this, comparing centralized on-site production by SMR and further transport of gas versus on-site production by SMR: when we have small consumption basins, with limited size centralized production, the economy of scale done in the centralized production plant does not compensate the cost of filling and transporting hydrogen to the HRS. Therefore on-site production is economically interesting in these situations.

The larger is the basin, the more economies of scale are made on hydrogen production, and the longer can be the distance between the source and the station to offset the high cost of on-site hydrogen production.

Tab. 4.1: Competitiveness of on-site production compared to centralized production: size of basin (tpd) up to which an on-site system is competitive for a given HRS capacity and distance from source.

One-way distance from source (km) ↓	**HRS H_2 consumption (kg/day)[7]**			
	500	**1,000**	**2,000**	**4,000**
50	<2	<2	2	20
100	<2	<2	2	20
200	<2	<2	5	20
400	<2	2	20	>50
600	<2	2	20	>50
800	2	20	>50	>50
1,000	5	20	>50	>50

Figure 4.3 displays another very schematic optimization of the hydrogen delivery mode:



<40kg/day	>40 kg/day <250 kg/day	>250 kg/day <1000 kg/day	>1000 kg/day <4000 kg/day	>4000 kg/day
Forklifts - small HRS Cars-demo HRS	Forklifts -medium & large HRS Cars - small HRS Buses - demo HRS	Forklifts - very large HRS Cars - medium HRS Buses - small & medium HRS Truck - small HRS	Cars - large & very large HRS Buses - large HRS Truck - medium HRS Train - small HRS	Buses - very large HRS Truck - large & very large HRS Train - medium & large & very large HRS
55 forklifts 80 cars 13 taxis	350 forklifts 500 cars 83 taxis 8 buses	2000 cars 333 taxis 33 buses 12 trucks	8000 cars 1333 taxis 133 bus 50 trucks	>50 trucks > 16 trains
200 bar H2 Bundles 10kg payload Deliveries of 4 bundles	Steel 200 bar trailers 300kg payload	Composite 300 bar trailers 900 kg payload	Liquid Hydrogen Trailer max 4 tons payload	HYGS, 5.465Nm³/h On-site production & new pipeline

Fig. 4.3: Supply chain optimization versus HRS capacity (source: Air Liquide).

This example is to be taken as a starting point. Liquid hydrogen might not be available everywhere, but it will be the hydrogen supplier responsibility to run such models for any customer requiring it. This will allow to optimize the overall molecule cost, adding in the comparison (in most of cases) CO_2 reduction mechanisms (with certificates, low-carbon or renewable electricity, biogas, and/or CCUS usage[8]).

The study would also need to assess the opportunity to install on-site production systems if it makes sense, as discussed earlier in this chapter.

4.3 Hydrogen specificities compared to other molecules

As mentioned in the introduction, hydrogen has the highest gravimetric energy content amongst non-fissile elements while being able to release its energy electrochemically (therefore not being limited by classical Carnot efficient limits) with water as the only by-product.

Besides these evidences, it is always comfortable to reason by deviations from known products when designing a system. Usually, the comparison is made with CNG/LNG[9]: both are gaseous at ambient temperatures, liquid under cryogenic

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[7] Based on 37€/MWh natural gas cost, only comparing centralized versus on-site SMR production.

[8] https://www.airliquide.com/magazine/cryocap-co2-cold-capture-system-unlike-any-other-in-the-world.

[9] Compressed/liquid natural gas.

temperatures, flammable, and lighter than air. However designing a GH_2/LH_2 system comparably to a CNG/LNG one could lead to dramatic consequences, Tab. 4.2 explaining why:

Tab. 4.2: Comparison of physical properties of water, LCH_4, and LH_2.

	Water	**LCH_4**	**LH_2**	**Consequences on LH_2 system design**
Boiling temperature @1.013 bar abs (°C)	100	−162	−253	– Long-distance pipes are a challenge. LH_2 temperature is below air liquefaction temperature ⇒ **LH_2 lines/ tanks need to be vacuum insulated**. – **Risk of oxygen enrichment** at the LH_2/air interface – **All impurities are solid in liquid hydrogen** ⇒ LH_2 is ultra-pure
Gas to liquid density ratio	6×10^{-4}	4×10^{-3}	2×10^{-2}	– Gaseous H_2 bubbles in liquid hydrogen do not behave like boiling water: they are **easily entrained by the liquid**. – For the same heat input in a pipe, the gaseous fraction of H_2 is more important than CH_4 ⇒ **higher risk of gaseous plugs in piping**
Latent heat of vaporization ratio between 1 and 6 bara		1.26	0.78	– LH_2 at is easier to vaporize at high, rather than at low, pressure (contrary to LCH_4) ⇒ **privilege transport at low pressure**
Density ratio between 1 and 6 bara		0.90	0.82	– Saturated LH_2 at high pressure is less dense than at low pressure ⇒ privilege transport at low pressure ⇒ **privilege volumetric pumping from low pressure**
Hydrostatic height for 1 bar overpressure (m)	10	24	140	– No pump head can be achieved by installing a pump below a storage as classically done with CH_4 or water – LH_2 pumps will cavitate ⇒ **privilege liquid transfer by pressure difference or design very specific pumps**
Critical pressure (bara)	220	46	13	– Above 13 bar, no more liquid phase ⇒ **stay below 13 bar**

Tab. 4.2 (continued)

	Water	LCH_4	LH_2	Consequences on LH_2 system design
Embrittlement		No	Yes, from ~ 150 K to ~ 350 K	– Even if H_2 embrittlement does not occur at LH_2 temperatures, the system has to be designed to withstand the phenomenon, as cool-down sequence, and some parts of the system temperatures could be in the critical zone
Purity			As per NF ISO14687[10]	– In Europe, H_2 quality needs to be guaranteed by a proper quality control plan, based on a risk analysis to be done according to EN17124 – In the United States, gas quality control is based on analysis

This quite self-explicit table should convince us that designing hydrogen systems require specific competences and the effort to acquire this hydrogen expertise should not be underestimated.

4.4 Storage technologies, pros and cons

4.4.1 Introduction

If we focus on commercially available physical based systems, hydrogen needs to be either compressed or liquefied to be stored. As an intermediate solution, hydrogen can also be stored under pressure in cryogenic conditions, also called cryo-compressed hydrogen or cCH_2.
The following discussion will focus exclusively on commercially available storages, either compressed (CGH_2) or liquefied (LH_2).

Even if hydrogen is an extremely dense way to store energy, we should not forget that the molecule has to be confined. The major difficulty is then to find an optimal

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[10] NF ISO 14687 2019: Hydrogen fuel quality – Product specification, in Europe H_2 quality needs to be guaranteed according to EN 17124 2018 Hydrogen fuel – Product specification and quality assurance – Proton exchange membrane (PEM) fuel cell applications for road vehicles.

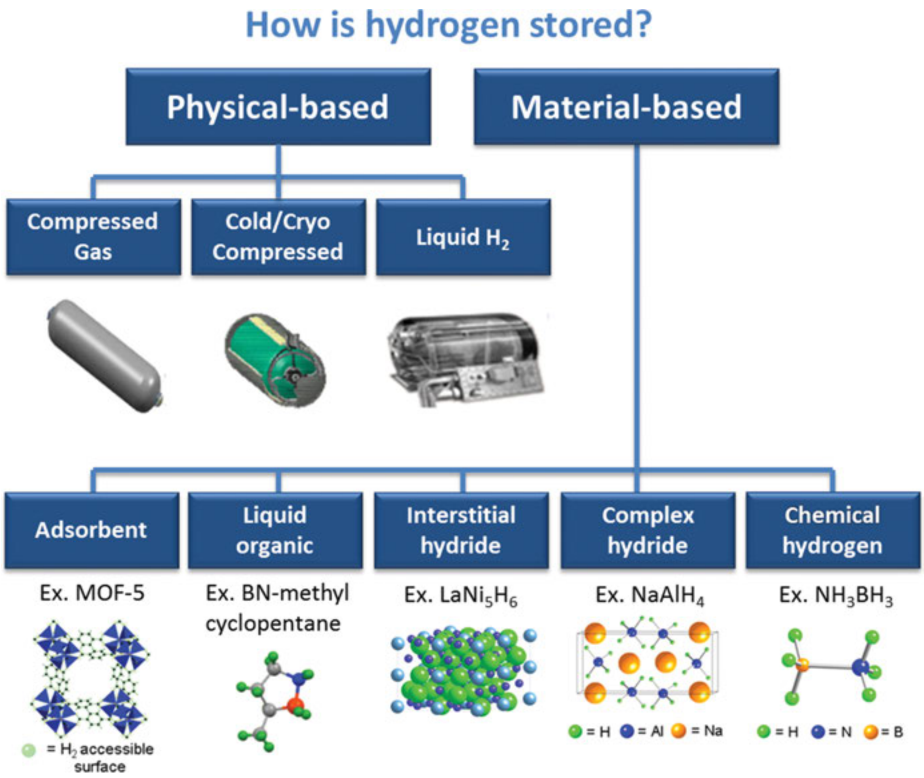

Fig. 4.4: There are different ways to store hydrogen (source: Air Liquide).

package besides the physical state of hydrogen to store it, and yet, get a reasonable system level energy density.[11]

4.4.2 Compressed hydrogen

Hydrogen can be compressed and commercially stored in cylinders up to 1,000 bar in storages types described by Fig. 4.5.

Each storage type has its pros and cons, which are summarized in Tab. 4.3:

These storages need to be integrated in packages (bundles, containers, or trailers) in order to transport a significant amount of gas in a single unit.

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[11] In a lot of literature studies comparing energy densities of hydrogen storing components, the weight and volume (and cost) of the envelope containing the storage media is excluded, as well as the system to remove the hydrogen (heater in case of hydrides). This can give false hopes to some readers.

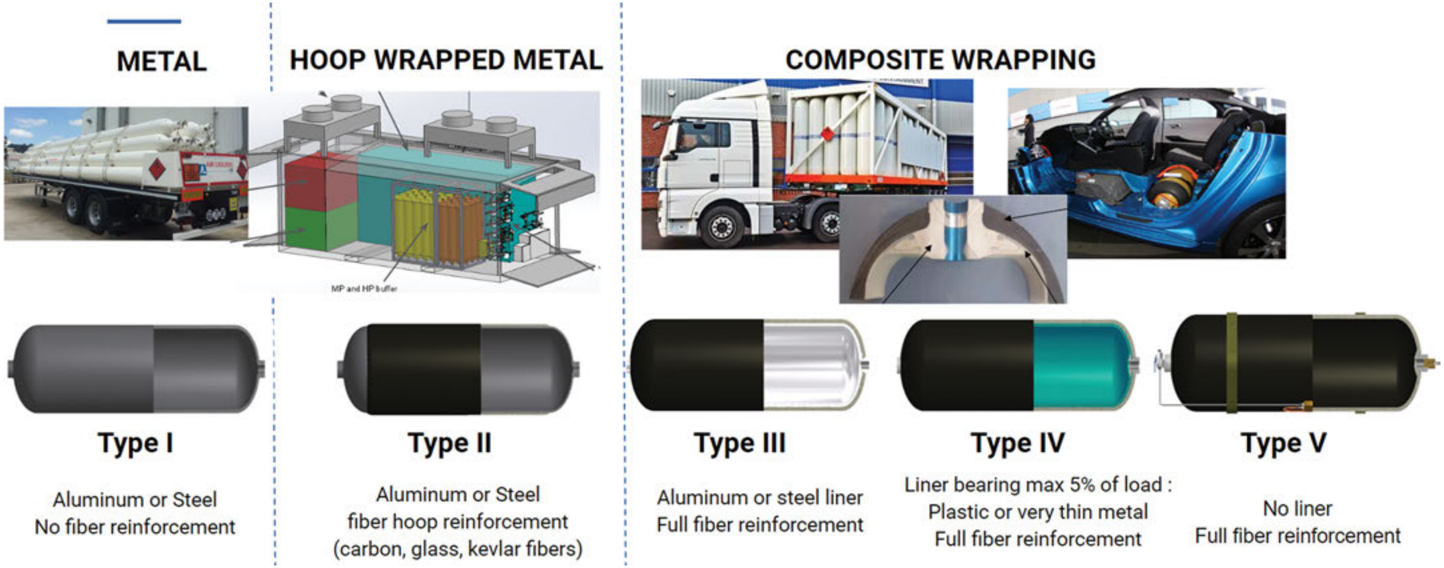

Fig. 4.5: Types of hydrogen storages.

Tab. 4.3: Comparison of different storage types.

Vessel type	Gravimetric efficiency	Max pressure (bar)	Cost per kg H_2	Fire resistance	Cycle resistance	Material compatibility	Blistering	Permeation
I	~1%	1,000	*	**	**	H_2 embrittlement		0
II	~1.5%	1,000	**	**	**	H_2 embrittlement		0
III	~4–5%	500	***	**	*	H_2 embrittlement – stress corrosion of some aluminum liners		0
IV	~4–5%	1,000	***	**	***		liner blistering	~0.5–2 $cm^3/L/h$
V	~4–5%	700	***	***	***			~0.5–2 $cm^3/L/h$

Designing and developing these packages are very different exercises depending on the type of storage: Historical Type I- and II-based trailers are limited by the weight limitations in road transportation regulations. New storage technologies relying on carbon fibers (types III and V) allow for a significant increase in hydrogen payload, resulting in limitation by the trailer volume. In addition to this, each type of storage gas has a different fire resistance behavior, requiring specific mitigation measures.

Pressure optimization is a complex question when considering the supply chain, as the more pressure there is, the more gas is transported. However, the hydrogen compressibility factor deviates from 1 at high pressure (1.4 at 700 bar), and storage costs are very much a function of the pressure, while not all storage technologies are allowed in every country (some of them also have pressure limitations).

4.4.3 Liquid storages

Storing liquid hydrogen at around 20 K requires a double-wall vacuum-insulated storage capable of keeping the liquid cold. In the literature, those storages are often compared to super thermos capable of keeping coffee hot for months, which is not really true as they are optimized to store a liquid 14 times less dense than water: they would break if filled with coffee.

These vessels are quite complex pieces of engineering. They work at lower pressure than the critical pressure of the fluid (13 bar abs for hydrogen), which means that comfortable[12] shape pressure vessels to better fit the required package are possible. However, in this case, one should not forget that these storages are double-wall tanks with a vacuum interspace. Hence, the outer vessel has to withstand 1 bar outer pressure (actually, 2 bar according to some regulations), which makes anti-buckling analysis and design extremely challenging (therefore not recommended). This is why, even if they are working at close to atmospheric pressures, liquid hydrogen cryogenic storages never deviate from spherical or cylindrical shapes.[13]

4.5 Onboard storage orders of magnitudes to help selections

When designing a vehicle, the first question to ask is: how much autonomy do we need? In most cases, the autonomy will be directly proportional to the MWh of the

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[12] Other than cylindrical or spherical shapes.

[13] With the notable exception of this project: *Aline Léon*, Hydrogen Technology: Mobile and Portable Applications, Springer Science & Business Media, p. 331.

energy stored, providing that we consider that the energy storage mass is negligible compared to the vehicle mass. This has been historically the case with conventional liquid fuel, but this paradigm is changing with new clean energy vectors such as electricity and hydrogen, where the package weight is significant compared to the fuel weight. Adding fuel adds weight to the vehicle, increases its specific consumption, and does not increase the autonomy by the amount of fuel added.

Taking the simplified example of a genset producing electricity, Fig. 4.6 provides a comparison between the mass packages of a hydrogen-based system compared to fuel-based ones, considering a 2,000 kWe electrical output, typically used in the maritime or rail industry for instance.

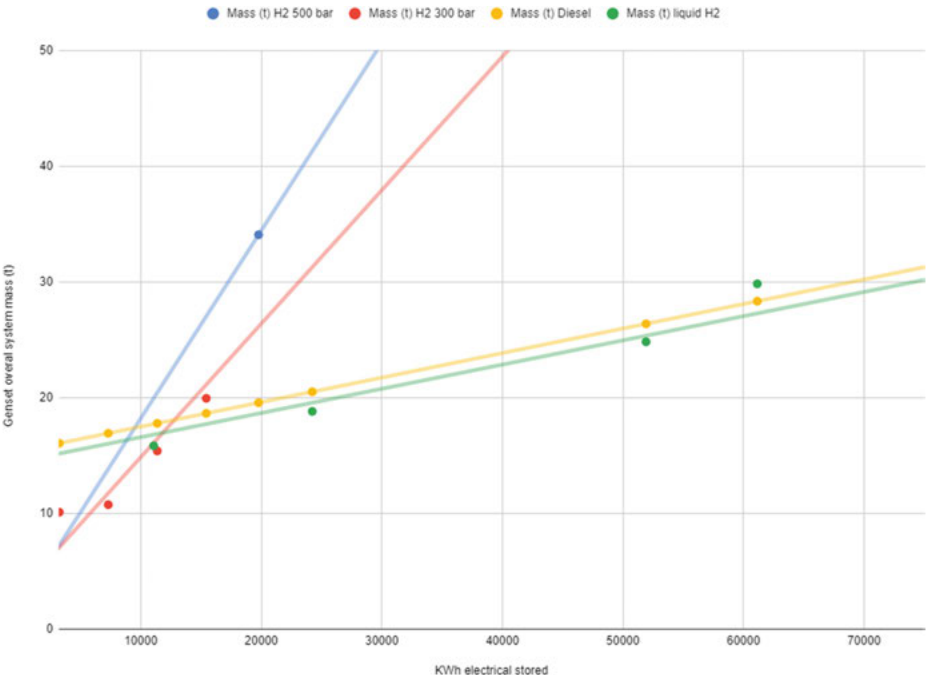

Fig. 4.6: Mass comparison for a 2,000 kWe electrical output system based on diesel (yellow), liquid hydrogen (green), 300 bar (red) and 500 bar (blue) gaseous hydrogen.

This graph shows that starting from 12 MWhe (about 600 kg of hydrogen), a liquid hydrogen system is lighter than a 300 bar gaseous one. The total weight of a liquid hydrogen system is, in this case, comparable to the weight of a diesel-based genset. Interestingly, a 500 bar system is heavier than a 300 bar one, with volume as its only advantage.

The weight difference between liquid hydrogen- and diesel-fueled gensets is narrowing with increased electrical power, with a breakeven at 2,500 kW.

In terms of system volume, whatever stored energy and electrical output, a liquid hydrogen system is 8 times the volume of an equivalent diesel system; a 500 bar system 17 times, and a 300 bar system 24 times.

Note that this example is oriented toward heavy-duty applications starting from 500 kW, and shall not be extrapolated below this power level.

Using the same approach for lower-power applications such as trucks, the threshold between gaseous storage and liquid is closer from 100 kg embarked (2 MWhe stored).

Other criteria can be used to select liquid versus gas, such as the refueling time. Indeed, in order to ease the operation as much as possible, and to use the same procedure for conventional- and hydrogen-powered vehicles alongside, it is often required to have similar fueling times.

Refueling a liquid hydrogen system typically occurs without any major challenge, at a flow rate of 60 kg/min[14] by pressure difference from a sourced trailer (or even higher with a centrifugal pump). This is not possible with gaseous hydrogen, as such high-flow compressors cannot be integrated in refueling stations. The flow is also triggered by pressure difference between a high source pressure and the vehicle tank, requiring large amounts of high-pressure storages on the refueling station side, not considering the necessity of back-to-back refuelings. It is usually considered that a maximum filling flow is in the range of 10–12 kg/min for heavy-duty applications, and a 10 min refueling time.

When the storage size is not compatible with fast refueling, or when liquid hydrogen is not available, swapping containerized storages is an option. This has already been carefully studied in the past, even for light-duty application (300 bar Peugeot TaxiPac in 2001[15] or 300/700 bar HyChain Scooters, wheelchairs, cargo bikes in 2005[16]) but mostly abandoned due to the hydrogen storage weight to be manipulated, and the complexity of the docking system.

Yet, the interest of swapping hydrogen storages (liquid or gas) has resurfaced in recent years for heavy-duty applications such as river ships. The following chapter will analyze the pros and cons of this technical solution compared to classical onboard storage.

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[14] Equating to charging a battery electric vehicle with a 65 MW electrical power!

[15] http://www.conceptcars-peugeot.com/peugeot-taxi-pac/.

[16] http://ieahydrogen.org/Activities/National-Projects-(1)/France/HYCHAIN_PAULMIER_Tech-Days05_051205_DR.aspx.

4.6 Onboard storage or storage swap?

As mentioned earlier, heavy-duty applications will require large quantities of hydrogen, difficult to transfer quickly to onboard storage (i.e., when about more than 200 kg is required). Moreover, refueling stations are quite capex-intensive systems, and hydrogen infrastructure is not present everywhere.

When the package shape is not a priority (trains, boats can easily integrate container-type hydrogen storages), and when refilling might occur in different areas (cruise ships), then swapping empty containers against full ones – instead of refueling onboard storage systems – might be an interesting technical solution.

Containers would be brought to the user by a dedicated logistic chain, and hydrogen suppliers would manage the refilling in their own filling centers.

Moreover, hydrogen is already widely transported by road in ISO40′ type packages (see Fig. 4.5); therefore, the difficulty will not be technical. However, designing an onboard storage in the form of a container will still bring on the table some challenges that should not be underestimated:

1. The gravimetric efficiency will be lower than onboard storages due to the chassis' weight.
2. The containers will anyhow be customized for the application. They will not only have to meet rules for transporting dangerous goods by road (ADR in Europe), rail (RID in Europe), and/or river (ADN in Europe), but also specific rules regarding hydrogen usage as a fuel (with some of these rules currently not existing yet). A specific example of difference would be in the G-forces to be applied on the package in case of a crash, the necessity to have automatic shut off valves on cylinders, or even pressure cycle tests during cylinder homologation, and others.
3. Containers will have to be invested in by the user or the hydrogen supply company, and a detailed supply chain study should be done beforehand in order to dimension the proper rolling stock, assuring continuity of service in any circumstances (including maintenance periods). Indeed; the ratio between the total number of containers to be invested and containers actually connected to the H_2 consumer can be higher than 2.
4. In case the containers are invested in by the user, and filled by the hydrogen supplier, the container design will have to be approved by the hydrogen supplier in order to guarantee safety of operations and people during refilling.
5. Handling means will have to be properly designed, particularly typical trailer cranes used to deliver industrial gases in bundles that cannot lift containers of this type.
6. Operators will have to manage a temporary connection under pressure (10–20 bar) for each container swap.

Onboard container-shaped hydrogen storage actually brings the design team a lot of constraints and difficulties, for limited system performance. The advantages brought by containers are eventually very often offset by its constraints.

In most cases, the actual reason for selecting containerized solutions are linked to the large amount of hydrogen that needs to be stored in gaseous form as a prerequisite, which relates to the issues presented in the introduction: trying to push technologies and specific technical solutions instead of focusing on functional specifications.

Focusing on functional requirements, when large quantities of hydrogen are needed (more than 200 kg for heavy-duty applications) and with fast fueling being a must, the actual solution for onboard storage will most likely be liquid hydrogen, leading to its own specific constraints (see following chapter).

4.7 How to fill onboard liquid hydrogen storages?

If we go back to the physical properties of liquid hydrogen (Fig. 4.2), one might easily realize the difficulty of transferring cryogenic hydrogen from one recipient to another.

Here are the usual methods to transfer fluids:

1. **Difference of hydrostatic height**: Hydrogen being 14 times lighter than water, a liquid hydrogen column does not create much head for fluid transfer. This method is never used.
2. **Increasing head with a transfer pump**: Liquid hydrogen low density and temperature require multistage pump designs with excellent insulation and low required NSPH.[17] LNG transfer centrifugal pumps are certainly not adapted for this service. This method of delivery – providing that the pump is efficient enough – does not add internal energy to the source tank. Sourced liquid hydrogen saturated pressure and temperature do not increase. This method of delivery is preferred when large source tanks are used, allowing to fuel multiple systems from a single tank.
3. **Increasing head by increasing the source manometric pressure**: It consists in adding total energy to the source of LH_2, increasing its pressure and transfilling by pressure difference the product. This mode allows fluid transfills without using rotatory equipment. Liquid is evaporated from the source tank (therefore lost) and then reinjected by natural convection in order to pressurize it. Globally the internal energy of the source tanks increases from one filling to another, meaning that the saturated pressure of the liquid increases, to the detriment of doing multiple fillings with one source tank. This method is to be preferred

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[17] Net Positive Suction Head: The Required NPSH ($NPSH_R$): the head value at the suction side (e.g., the inlet of a pump) required to keep the fluid from cavitating (provided by the manufacturer), source https://en.wikipedia.org/wiki/Net_positive_suction_head.

when full drops of liquid are made from delivery trailers or containers to the destination tanks (i.e., destination tanks larger than delivery tank).

4. **Using a source tank with saturated pressure higher than the system tank pressure:** In this case, the flow is controlled by throttling a regulation valve on the filling line. The main drawback of this method is that isenthalpic expansion through the regulating valve will flash saturated liquid (e.g., 2.5% mass flashed gas phase for 500 mbar pressure loss). The issue won't be much about the amount of liquid lost, but rather the volume fraction of gas created (53% in the previous case), inducing large pressure drops in the lines. Therefore, this method is not recommended unless very low pressure drops are considered in the refilling lines.

Although most of the projects currently designed rely on solution #3, transfer pumps are being qualified for liquid hydrogen service in order to ease operations and upscale systems. These pumps can ensure large transfer flows without increasing the temperature of the liquid.

Another issue is the temperature of liquid hydrogen (20 K), well below the air condensation point. Lines are typically double wall vacuum insulated to avoid air condensation and creation of oxygen-rich fluids pouring on possibly flammable surfaces (such as bitumen) or blocking loading arm mechanisms because of iced air.

Last but not least, interfaces need to be developed to ensure safe and user-friendly transfill of liquid for the user. These interfaces shall not only guarantee low-pressure drop for efficient transfill, and that no liquid is spilled during the transfer, but also have proper insulation, limited weight for easy handling, and the possibility of handling safely the emergency release ("breakaway function").

4.8 Other considerations to take into consideration

When integrating a hydrogen storage system into any vehicle, a specific attention should be paid to:

- **Fire**: Gaseous storage systems are made of multiple cylinders interconnected by valves and fittings, which can leak. If these leaks catch fire, flames can possibly impinge on surrounding vessels without triggering the fire pressure release system (local fire).
- **Maritime environment**: In the past, some composite pressure vessels (particularly type II with carbon steel liner) have been subject to corrosion at the carbon steel/liner interface.
- In all cases: Properly designing the ventilation system for hydrogen compartments.
- **Material compatibility**, and specifically hydrogen compatibility with steel, stress corrosion of some aluminum alloys (water in liquid form can brittle liners of type

III cylinders with AL6061 liners and reduce their lifetime by a factor of up to 40[18]) and the possibility of type IV liner blistering by diffusion of hydrogen in the polymer structure.
- **Cycle** count: Some composite tanks will require a cycle count.
- **Residual pressure:** Low pressure (<10–20 bar) can blister type IV liners. It is then essential to keep the system above the recommended minimum pressure by installing residual pressure valves.
- **Visual inspection**: Vessels are usually visually inspected at each filling, following ADR regulation. In case of swapped containers, there will be a need to have at least a feasible visual inspection without too much challenge.
- **Gas purity**: Hydrogen suppliers need to guarantee the gas purity as per EN17124:2018[19] harmonized with Directive 2014/94/EU of The European Parliament and of The Council of 22 October 2014 on the deployment of alternative fuels infrastructure. The method described in EN17124 allows quality assurance by doing a risk analysis on the entire supply chain. Recent analysis showed that the gas packages are also a source of contaminants, particularly water (5 ppm) from inappropriate reconditioning of gas packages after maintenance.
- Liquid hydrogen tanks **operating pressure**: The operating pressure range needs to be wide enough to ensure correct dormancy time of the vessels while keeping the safety valve set below critical pressure (around 13 bar). The operating pressure range shall not overlap with the boil-off valve and safety valves operating pressures (also considering uncertainties in setpoints, reclosing pressures, etc.).
- **Liquid hydrogen release** from storage.
- **Cold embrittlement** of ambient temperature designed equipment, such as process equipment by failure of the liquid hydrogen vaporizer or structural equipment in case of spillage.
- **Thermodynamic equilibrium** of LH_2 storages: when pressurized by pressure build-up coils, warm gas is injected in the gaseous phase of the liquid hydrogen tank. In case of subsequent ballottement, this gas can be recondensed by mixing with cold liquid and the pressure can suddenly collapse, causing eventually fuel cell shutoff.

This list is non exhaustive, and a risk-based design approach will be necessary to identify all the potential sources of danger and mitigate/eliminate them.

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[18] https://www.eiga.eu/publications/eiga-documents/doc-7218-water-corrosion-of-composite-cylinders-with-aa-6061-liners/.

[19] EN 17124:2018 Hydrogen fuel – Product specification and quality assurance – Proton exchange membrane (PEM) fuel cell applications for road vehicles. This document specifies the quality characteristics of hydrogen fuel and the corresponding quality assurance in order to ensure uniformity of the hydrogen product as dispensed for utilization in proton exchange membrane (PEM) fuel cell road vehicle systems.

4.9 Some hints on how to properly integrate a storage with a fuel cell

4.9.1 Key parameter #1: safety

Safety is a must. Safety levels need to be maintained during all operational phases of the system, considering the possible presence of an operator or even some public. The main characteristics of hydrogen (e.g., flammability) need to be under control, but safety management and scenarios can differ depending on the type of storage:

For gaseous storage, one will pay attention to:

- First, the risk associated with pressure. Be extremely cautious regarding the approval of the pressure vessel according to the enforced standards.
- As mentioned earlier, fire impingement on composite pressure vessels can really be problematic and aggravate very quickly the consequences of a somehow minor safety scenario. Multiple solutions exist to mitigate the consequences of an ignited leakage, from intumescent paints to fire protection plates or active tank depressurization systems.
- More classical fire engulfment scenarios (vehicle or tire fire for instance) are somehow easier to deal with than localized fire. Installing temperature triggered pressure relief valves on cylinders allows for safe depressurization of the cylinders before the fire can reduce their mechanical properties. With this regard, linerless type V cylinders with thermoplastic resins are promising as they would leak before bursting without further protection.

Liquid hydrogen storages have the advantage of being operated at low pressure (<13 bar) and are made out of two envelopes. Of course, there are safety scenarios associated with these tanks that should not be underestimated:

- The main safety scenario is the rupture of a pipe, leading to possible spillage. Safety shutoff valves located in the vacuum interspace as close as possible from the inner vessel will reduce the possible consequences.
- The risks associated with low temperature need to be considered, particularly cold embrittlement of carbon steel structural parts that could come in contact with liquid hydrogen, or process parts downstream the hydrogen vaporizer that could be submitted to low temperatures in case of a vaporizer malfunction. Liquid hydrogen temperature being lower than air liquefaction temperature, liquid air can be created, enriched in oxygen (50% O_2, 50% N_2).
- Vacuum loss in the interspace (associated or not with a fire) needs to be considered when designing the safety valve. In case of loss of vacuum, air can be cryo-pumped at the surface of the inner tank to form solid oxygen. The tank manufacturer will have to take this into consideration and select noncombustible material for the interspace (tank support, insulation, etc.).

4.9.2 Key parameters #2: flow, pressure, and temperature

In a gaseous hydrogen storage system, the pressure is already built in the storage and needs only to be reduced to the fuel cell pressure, typically in two stages. In a liquid hydrogen system, the pressure needs to be built in the tank, usually by taking liquid in the bottom of the tank, vaporizing and re-injecting it using natural convection from the top of the tank. Hydrogen is then further reduced in pressure in the fuel cell.

Temperature and flow are very much lined up with pressure in the systems we are looking at, hence the amalgam of the three parameters in a single discussion.

We will see here that the pressure management of both systems has nothing to do with each other. Let us take a closer look.

4.9.2.1 Gaseous hydrogen storage systems pressure issues

In order to compensate the temperature rise during filling that is linked to the adiabatic pressure increase in the tank, and to fill a specified mass of hydrogen in the storage, a maximum filling pressure, so-called developed pressure (i.e., max manometric pressure at maximum temperature of typically 85 °C) can go up to 875 bar for a 700 bar system and up to 438 bar for a 350 bar system. All components will therefore need to have this rated pressure as a minimum.

During the phase of emptying of the cylinders, two phenomena with opposite effects occur:

- First, the cylinder will undergo an isentropic pressure decrease. As composite cylinders are quite insulant, the hydrogen temperature getting out of the tank can drop below the minimum operating temperature (typically –40 °C) if the consumption is too high and the ambient temperature cold enough. An first order calculation gives in the range of –50 °C minimum hydrogen outlet temperature for a 700 bar tank emptied in one hour. This cooling can damage the tank liner, resulting in a leakage during the next filling. This is why emptying scenarios of hydrogen tanks have to be carefully studied in order to avoid this situation.
- Contrary to natural gas, at ambient conditions hydrogen temperature will increase when submitted to an isenthalpic pressure decrease (i.e., pressure reduction in a valve). This increase can be in the range of 10 °C, not compensating for the isentropic temperature decrease explained earlier. There are typically no severe consequences of such limited temperature increase, making hydrogen a little bit easier to handle than natural gas.

As mentioned earlier, the pressure in the storage needs to be release from up to maximum 875 bar and minimum 20 bar down to less than 1 bar, depending on the fuel cell, with flow rates ranging from idle to maximum power (ratio 1:10).

This means a significant constraint on the mechanical characteristics of the pressure reducer system with flow rangeability coefficients in a range of about 500:1, leading to extreme engineering challenges, not considering the validation requirements of typical applicable regulations such as EC79.[20]

Pressure reducers can fail, in which case it will become important to be able to release the pressure in the low pressure circuit thanks to appropriate safety valves.

Last but not least, pressure reducer valves are not intended to act as shut-off valves, which should be installed wherever a need for circuit isolation is required (for either functional or safety requirements). These high-pressure valves need to be qualified for pressure and opening/closing cycles that are either required by regulation and/or by the system operating mode. Opening/closing cycles under pressure difference are usually the most complex tests to pass.

4.9.2.2 Liquid hydrogen storage systems' pressure issues

Pressure is controlled in a liquid hydrogen tank by adding energy to the system, either by vaporizing liquid taken in the bottom of the tank and injecting warm gas from the top, or by activating a heating element in the tank. The more flow is withdrawn from the tank, the more energy needs to be injected to vaporize the amount of liquid taken to keep the pressure constant. This ability to keep a constant pressure in the tank at maximum rated fuel cell power will be the design point of the tank pressure control system. In case of a pressure build-up system using gravity or natural convection, the design will have to be validated at minimum tank level.

As mentioned earlier, for easier system management, liquid hydrogen storage will be kept below hydrogen critical pressure, 13 bar abs.

This does not mean that hydrogen pressure will rise up to 13 bar abs in normal operating conditions, and 13 bar is the maximum pressure at which the secondary safety valve of a liquid hydrogen storage tank will be fully opened. If we consider that the boil-off valve, primary safety valve and secondary safety valve need to operate without overlap, taking into account the different uncertainties in safety valve design (defined in standards[21]), the maximum pressure that a liquid hydrogen tank is submitted to during normal operation is usually in the range of 8 barg before the boil-off valve opens.

In order to increase dormancy time (time to reach opening pressure of the boil-off valve from operating pressure, without any product consumption), the maximum

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[20] Regulation (EC) No 79/2009 of the European Parliament and of the Council of 14 January 2009 on type-approval of hydrogen-powered motor vehicles, and amending Directive 2007/46/EC (Text with EEA relevance).

[21] Such as ISO 4126-1:2013 Safety devices for protection against excessive pressure – Part 1: Safety valves.

operating pressure should even be reduced well below this 8 barg limit as latent heat of evaporation decreases by 30% from 1 barg and 8 barg.

We do not want to release liquid hydrogen through the safety valves. Liquid hydrogen density being a decreasing function of saturated pressure, we need to consider the dilatation of liquid hydrogen with increasing saturated pressure. In other words, the lower the safety valve operating pressure is, the higher the maximum allowable filling level will be. A numerical approach shows that if we were to fill a tank with 1.5 barg saturated pressure liquid hydrogen, and in case the safety valve pressure is 10 barg, then the maximum filling level will be as low as 75%. But, if we manage to lower the safety valve setpoint to 6 barg, the maximum tank filling level would be 85%.

Hence, reducing liquid hydrogen tanks operating pressure will not only make the tank cheaper (thinner), but will also increase the hydrogen payload as well as its dormancy time and boil-off rate.

One last consideration about liquid hydrogen systems is that a cryogenic storage consists of a liquid phase, usually in equilibrium with the gaseous phase. If that balance is broken (let us say that, for some reason, the gas temperature increases), then the overall system is not in equilibrium anymore. This is basically what happens when liquid hydrogen storages are pressurized (by injection of warm gas in the gaseous phase) or when they are in stand-by. The tank temperature stratifies, the gas temperature increases above the liquid temperature at equilibrium while its overall pressure rises. An immediate consequence of such a phenomenon on a mobile system is that it will recover its overall thermodynamic equilibrium at the first movement of the liquid, mixing with the gas. This will lead to a brutal pressure drop (as the warm gas gets condensed by cold liquid), possibly leading to a system shutdown on low pressure. Liquid hydrogen tank designers for mobile applications will therefore aim at keeping the tank in thermodynamic equilibrium at all times, by diverse means.

4.9.2.3 Key parameter #3: purity

Although some of the existing norms[22] on fuel cell purity specifically limit their domains of application to road vehicles, they are widely used to specify product purity at the fuel cell inlet.

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[22] SAE J2719 Hydrogen Fuel Quality for Fuel Cell Vehicles / EN 17124:2018 – Hydrogen fuel – Product specification and quality assurance – Proton exchange membrane (PEM) fuel cell applications for road vehicles / ISO 14687 Hydrogen fuel quality – Product specification.

In Europe, EN 17124:2008 is harmonized with the Alternative Fuel Directive 2014/94/EU, hence is mandatory in countries having transferred the directive in their national regulations[23] (see Chapter 8).

One major difference between the European approach and the rest of the world's is that EN17124 can guarantee a product quality based on a risk acceptance matrix (defining risk criticality function of the probability and gravity of the feared event) all along the supply chain, not always requiring complete gas analysis of all components listed in the specification.

The most critical impurities (most frequent and most problematic) are typically carbon monoxide and water.[24]

Carbon monoxide is often considered as a "canary specy" in hydrogen, as it is usually the first impurity to breakthrough from typical ambient purification system such as hydrogen PSA, downstream SMR, ATR, or POX units.[25] Although the carbon monoxide specification is 0.2 ppm, keeping it typically below 10 ppm in the PSA product limits the chances of having other impurities (such as CH_4, H_2O and N_2 above the specification threshold of EN, ISO and SAE standards) in the gas. The step between 10 and 0.2 ppm is then achieved with proprietary systems dedicated to hydrogen energy applications at centralized filling centers or even at hydrogen refueling station sites in case they are directly connected to a pipeline.[26]

The functional specifications limiting the amount of water in the gas is mostly to avoid entraining a water particulate (ice) at high velocity in the gas during cold filling at −40 °C, which could damage hydrogen storage valve seats for instance. Saturated water pressure at filling condition and minimum temperature has a determined maximum water concentration in the gas of 5 ppm. Liquid water entrained in the gas (and specifically some dissolved ions) could also damage fuel cells.

Surprisingly, water specifications are quite hard to guarantee, as actual water concentration in high-pressure storages is difficult to measure (a storage would need to be depressurized to get a reliable value).

As in most of the cases, the final hydrogen purification is achieved with a molecular sieve type of adsorbents (either PSA downstream SMR/POX/ATR or drier downstream electrolysis plant). The main source of gas pollution with water (but also

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[23] "Arrêté du 8 décembre 2017 relatif aux caractéristiques de l'hydrogène en tant que source d'énergie pour le transport" in France.

[24] Very interesting considerations on the effects of the different impurities on fuel cell stacks are available in Annex A of EN17124:2018 – Hydrogen fuel – Product specification and quality assurance – Proton exchange membrane (PEM) fuel cell applications for road vehicles.

[25] Pressure Swing Adsorption, Steam Methane Reformer, AutoThermal Reactor, Partial Oxidation Reactor. See https://www.engineering-airliquide.com/fr/technology-handbook.

[26] Example of a hydrogen refueling station connected to a pipeline: https://www.fuelcellbuses.eu/wiki/demos-europe-hydrogen-refuelling-stations/rotterdam.

with O_2/N_2 with the notable exception of low suction pressure compressors) is coming from air or water introduction in the pipeline during maintenance operations.

Therefore, filling, purging, and maintenance procedures will need to be strictly enforced in order to make sure that no water or air is present in the gas.

At 20 K – where all impurities but helium are solid – liquid hydrogen is intrinsically ultra-pure, well below the specification threshold. However, the main risk is that impurities will keep accumulating in the storage over time and reach a point where it needs to be heated up and purged to evacuate water, nitrogen, oxygen, and ice particles from the tank. This operation needs to be done strictly according to procedures, as explosive atmospheres can be created in the tank when oxygen liquefies in the hydrogen-rich gas.

4.10 Conclusions

This chapter tried to summarize the challenges of building a supply chain adapted to specific functional requirements of hydrogen powered systems, mostly targeting heavy-duty applications, to provide hints in the process of choosing an onboard storage technology, and to explain the major challenges in integrating a fuel cell system with a hydrogen storage system.

Even if this is not an exhaustive handbook for hydrogen energy supply chain and usage design, it does represent a snapchat at a given time of the status of the technology, as major large (potentially breakthrough) developments are undergoing.

The most important conclusion of this chapter is that hydrogen supply chains and system designs need to be handled professionally in a single approach to make sense economically and to remain as safe as it has historically been in the industry for the past hundred years[27] and more.

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[27] Of course, some will always refer to the Hindenburg accident as a counterexample from back in 1937!

Luigi Crema, Matteo Testi, Martina Trini

5 High-temperature electrolysis: efficient and versatile solution for multiple applications

Abstract: The European Commission is considering electrolysis as a high priority for the development of a hydrogen-integrated European energy system, and a cornerstone in the European Hydrogen Strategy [1], where it is planned to deploy electrolyzers en masse on the market: 6 GW within 2024 and another 40 GW within 2030. Several technologies will be competing here, the highest maturity being occupied by water electrolysis such as alkaline electrolysis (AEL) and proton-conductive membrane electrolysis (PEMEL). A considerable slice of the market is being shared by steam electrolysis, which is rapidly maturing, scaling up and looking to be competitive in the short term against the low-temperature technologies, particularly in target sectors.

Steam electrolysis, also known as high-temperature electrolysis, comprises several technologies, some more advanced in development, others still at the research level. They are a central part of the European Partnership of Hydrogen, receiving a large contribution within the Fuel Cells and Hydrogen Joint Undertaking (FCH JU) in Horizon 2020. They will be part of the program of the next European Partnership on Hydrogen, Clean Hydrogen for Europe, and should reach the same maturity level as AEL and PEMEL.

Among other technologies proton-conductive ceramic electrolyzers (PCCEL) are well worth mentioning and are analyzed in this chapter. This technology holds high potential, meeting the challenge of operating at lower temperatures than solid oxide electrolyzers (SOEL) and integrating additional functions such as purification, filtration, separation, and/or compression of hydrogen.

Both SOEL and PCCEL are technologies able to operate at medium-high temperatures, their advantages being management of the conversion process, capacity to capture external waste heat for the production of steam, and their cell structure making limited use of critical raw materials. The most mature technology is solid oxide cells, already available as demo technologies, and soon to be scaled up to reach market maturity and commercial application in several sectors, as presented in Section 5.2. A second technology, proton-conductive ceramic (PCC) cells, is still at the research stage and

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needing to consolidate the cell layout, specific geometry, materials utilized, and optimal working conditions.

Major studies on SOEL started to appear back in the 1970s [2–5]. However, interest in the technology rose in the 1980s, prompting many research projects. Among these studies one should note the investigations performed by Westinghouse [6–7], the research by Barbi and Mari [8–12], and the HOTTELLY project described by Dönitz et al. [13–16].

The discovery of PCC is attributed to Professor Hirosyasu Iwahara in the late 1970s; investigation of these materials for electrolysis applications started right from the beginning of the 1980s [17]. In the following years, PCCEL acquired increasing interest and more details on materials and applications of this technology will be presented in what follows. This chapter will present an analysis of the basic principles of high-temperature electrolysis and related technologies, with a specific focus on SOEL and PCCEL cells and structures, including the main materials, as well as an overview of the main applications they can support with their different technology configurations and systems, and the future prospects for development as breakthrough applications.

5.1 High-temperature electrolysis technology

5.1.1 Basic principles

5.1.1.1 Steam electrolysis process

High-temperature electrolysis occurs in electrochemical devices that operate at high temperature (usually between 800 and 1,000 °C) and are known as solid oxide electrolysis cells (SOECs) [18]. The materials used for these cells guarantee good physical and electrochemical performance by the cell at high temperatures. However, operating at such high temperatures causes fast degradation of materials and requires steady state operation limiting, hence repeated starting and stopping of the system. In this regard, there is mounting interest in lowering the operating temperature of SOECs, without affecting cell performance.

In parallel, novel (semi)automatic manufacturing lines are better able to control tolerances at the interconnections and interfaces, thus limiting the thermal stresses and structural problems that affect cells at high temperature gradients. Solid oxide cells (SOCs) are particularly attractive as electrochemical devices since they can operate both as fuel cells and as electrolyzers depending on the need. Solid oxide fuel cells (SOFCs) have several modes of operation that have been deeply and intensively studied while the possibility of operating these cells in reversible mode as electrolyzers has been investigated since the 1980s when both steam [4, 14–16, 19–52] and carbon dioxide [4, 52] electrolysis were experimented with. More recently, PCC cells have gained interest where the electrolysis process is concerned. PCC cells operate in the same temperature range as SOCs, although they present some differences in the working principle and in the materials utilized. These differences will be highlighted in the following sections where PCCs will be explained separately.

A generic SOC is composed of three main components: a porous fuel electrode (cathode) where hydrogen is reduced, a solid electrolyte that guarantees the conduction of oxygen anions in SOECs or hydrogen cations in PCCs, and a porous oxygen electrode (anode) where oxygen is oxidized. The materials used for the cells become conductive at elevated temperature (in most architectures above 650 °C). Therefore, once the cell has reached the desired temperature and electricity is supplied while feeding the cell with steam (or other fuels) and air/oxygen, electrochemical reactions start to occur, and the cell starts working. Two semi-reactions occur at the two electrodes. These reactions are different for SOE and PCC cells. The main difference between the two technologies is that oxygen anions are transported through the electrolyte of SOEs while hydrogen cations are transferred through the electrolyte of PCC cells. The semi-reactions occurring at the fuel and air/oxygen electrode of both an SOE and a PCC fed with steam are reported in eqs. (5.1) and (5.2), and eqs. (5.3) and (5.4), respectively:

$$\text{Oxidation reaction at the anode (SOEC)} \qquad O^{2-} \rightarrow O_2 + 2e^- \tag{5.1}$$

$$\text{Reduction reaction at the cathode (SOEC)} \qquad H_2O + 2e^- \rightarrow H_2 + O^{2-} \tag{5.2}$$

$$\text{Oxidation reaction at the anode(PCC)} \qquad H_2O \rightarrow {}^{1}\!/_{2}O_2 + 2H^+ + 2e^- \tag{5.3}$$

$$\text{Reduction reaction at the cathode (PCC)} \qquad 2H^+ + 2e^- \rightarrow H_2 \tag{5.4}$$

The semi-reactions in eqs. (5.1–5.4) consider only electrolysis of steam. However, one of the main advantages of SOECs and PCCs lies in their high fuel flexibility that allows proper cell operation with a variety of fuels such as hydrocarbons, biogas, and synthetic gases. With a focus on PCCs, it is worth mentioning that this technology enables pure hydrogen to be produced without development of water at the fuel electrode. This fact also allows one to avoid the fuel circulation, from outlet to inlet, necessary for SOECs where the high steam content at the cell inlet could cause severe cell degradation.

5.1.1.2 Co-electrolysis process

In addition to the electrolysis process summarized in eqs. (5.1)–(5.4), SOECs allow one to perform the simultaneous electrolysis of H_2O and CO_2 (known as co-electrolysis). The overall splitting reactions occurring in the cell for both H_2O and CO_2 electrolysis are reported in eqs. (5.5) and (5.6), respectively. While the overall reaction of steam and CO_2 co-electrolysis is expressed in eq. (5.7):

$$H_2O \rightarrow H_2 + {}^1\!/_2\, O_2 \tag{5.5}$$

$$CO_2 \rightarrow CO + {}^1\!/_2\, O_2 \tag{5.6}$$

$$CO_2 + H_2O \rightarrow H_2 + CO + O_2(xx) \tag{5.7}$$

As with other electrochemical devices, the reaction can occur only inside the cell when the voltage between the two electrodes exceeds the minimum theoretical value (i.e., the reversible voltage), which is equal to 1.23 and 1.33 V for H_2O and CO_2 electrolysis, respectively. Co-electrolysis may be more complicated than the two separate electrolysis reactions (eqs.(5.5) and eqs. (5.6)) since the water–gas shift (WGS) reaction in eq. (5.8) needs also to be considered, occurring as it does simultaneously with the reactions reported in eqs. (5.5) and (5.6). Hence, the reactors and feed flows need to be properly designed to guarantee production of hydrogen and carbon monoxide:

$$H_2O + CO \rightleftharpoons CO_2 + H_2 \tag{5.8}$$

However, the WGS reaction does not impair the efficiency of the co-electrolysis process, which in general shows a higher efficiency than the two reactions occurring separately. Such increased efficiency can be attributed to the lower energy consumption required for co-electrolysis than for single CO_2 electrolysis [4, 53–56]. In this regard, a typical steam electrolysis operation, involving a 25-cell stack of 100 cm^{-2} each operating at 1.3 V at a flow of 20 Nm L/min cm^2, would lead to a current density of –1.4 A/cm^2, a 50% conversion rate, and a 1.5 Nm^3/h hydrogen production rate. This results in a stack operating temperature of around 800 °C [57]. On the other hand, a similar co-electrolysis system (25-cell stacks of 100 cm^2 each) might be considered to operate at 1.35 V at the same flow of 20 NmL/min cm^2 leading to 1.5 A/cm^2 current density and a 60% conversion rate, while the operating temperature would be around 810 °C (slightly exothermic) [57]. Moreover, co-electrolysis requires only one reactor to produce the synthesis gas resulting from simultaneous electrolysis of H_2O and CO_2.

From a thermodynamic point of view, the electrical voltage equilibrium, also called electromotive force (Efm), of the cell is given by the following relation:

$$-\Delta G = nF\,\mathrm{Efm}$$

where ΔG is the Gibbs-free energy of the reaction, n is the number of electron exchanges in the reaction, and F is the Faraday constant ($F = 96{,}485$ A s/mol). Considering the reactions expressed in eqs. (5.1), (5.2), and (5.5) and standard conditions ($T = 25$ °C and $p = 1$ atm), two electrons participate in the reaction and the Gibbs-free energy is equal to −273 kJ/mol H_2. The resulting Efm is 1.23 V, which can be used in the Nernst equation to calculate the cell voltage as expressed in the following relation:

$$E = E_0 - \frac{RT}{nF} ln\left(\frac{pH_2O}{\sqrt{pO_2}}\right)$$

More details on the deviation of the cell voltage from the theoretical voltage are described below.

In general, the performance of an electrolysis cell is evaluated by measuring the current and the voltage of the cell during operations. The data are then reported in a graph having the current density on the *x*-axis and the voltage on the *y*-axis, these curves being known as IV curves. For a given value of current density and temperature value, the cell needs to operate at higher voltage than the theoretical voltage. This is due to losses in the electrochemical process and the excess voltage necessary to guarantee cell operation, which is usually called overpotential. The three main sources of overpotential are: i) activation overpotential that accounts for the transfer kinetics of electric charges in the electrochemical reaction; ii) concentration polarization that accounts for the obstacles to mass transport; iii) ohmic overpotential that accounts for the electrolytic resistance. The higher the overpotential necessary to operate the cell, the lower the cell performance. Moreover, the slope of an IV curve gives an indication of the overall cell resistance and therefore of the cell performance. By recording IV curves at different times during the cell operation, it is possible to observe the decline in cell performance over time. This method is also used to evaluate performance when the cell is fed with different gases and different operating conditions are tested. Additionally, electrochemical impedance spectroscopy is another technique commonly adopted to evaluate cell performance. The degradation rate of Ni-based SOECs is reported to be between 0 and 6 mV for 1,000 h of operation between –0.25 and –0.75 A/cm^2 at 850 °C for a fuel composition of 45% CO_2, 45% H_2O, and 10% H_2 [53, 55, 58].

For steam electrolysis, an increase in the current density results in a higher hydrogen flow rate at the cell outlet. A 45-cell stack with a compact SOFC architecture was tested in electrolysis mode at –1.8 and –2 A/cm^2 resulting in the production of 245, 250 gH_2 per hour, respectively [59]. However, it must be considered that, usually, an increase in current density leads to an acceleration of cell degradation due partly to material deterioration. Additionally, when operating an SOEC in co-electrolysis mode to produce syngas, the different current density applied may influence the conversion rate and the composition of the syngas at the outlet.

Figure 5.1 illustrates the working principle of a SOC for both fuel cells and electrolyzer operation. The figure highlights the transport of the species involved in the reactions and the sites where the reactions take place.

5.1.2 Materials and architectures

Some advantages have been mentioned for both SOE and PCC cell technologies as regards H_2O and CO_2 electrolysis as well as co-electrolysis. However, these technologies present some problems preventing the technology from achieving complete maturity and highlighting the need for further innovation and development of both SOE and PCC cells. One of the main issues here is internal degradation and structural

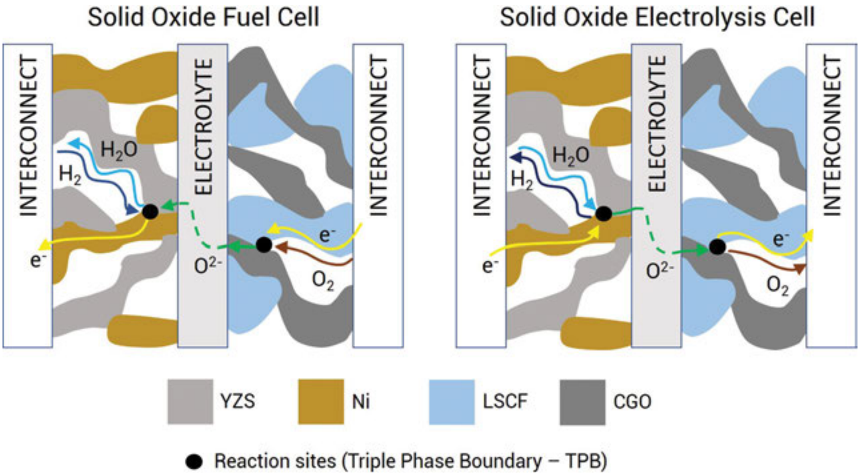

Fig. 5.1: On the left-hand side: working principle of a solid oxide fuel cell. On the right-hand side: working principle of a SOEC. The gray phases are the ones responsible for oxygen ions conduction (YSZ at the fuel electrode side and CGO at the oxygen electrode side), the ochre phase represents the electronic conducting phase at the fuel electrode side (generally Ni) while the light blue is the electronic conducting phase at the oxygen electrode side (usually LSCF). The pores are white. The fluxes of the species involved in the reactions are represented by arrows: light blue for steam, dark blue for hydrogen, red for oxygen, yellow for electrons, and green for oxygen ions. The reaction sites where the three phases meet each other are indicated by black dots.

stability of materials working and cycling at high temperatures that also affect cell durability. In this regard, many studies are continuously seeking to develop and improve the cell component materials. In this section, the state-of-the-art materials mostly used for the three main components of SOECs and PCCs (anode, cathode, and electrolyte) will be presented. The section will also summarize the main studies performed on such materials to improve cell performance and durability. For what concerns cell architectures, two main structures have been studied since the 1980s when the first studies on SOECs started. After an initial interest in tubular cells [4, 13–16, 50, 52, 61, 62] where the cell support is given by a layer inside the oxygen electrode tube, the attention shifted toward planar geometries of SOECs that yield better performance and lower production costs [61]. However, tubular cells have recently gained interest again [63–65], including the micro scale [61, 66–71]. Planar cells offer the possibility of investigating different architectures depending on the support: cathode-supported cells are in wide circulation thanks to the good performance and mechanical stability observed [72]. Electrolyte-supported cells [73, 74], and anode supported cells [75] yield lower performance causing interest in these architectures to wane. Usually, the thickness of the support layer is in the order of a few hundred micrometers while the thickness of the other layers in the cell can vary from a few micrometers for the electrolyte to a few dozen micrometers for the electrodes.

Finally, metal-supported cells are acquiring interest and showing promising potential for both SOECs [76] and PCCs [77]. Here below we give a summary of the main materials used for the electrodes and electrolyte of SOECs, with a separate focus on PCC electrolyte materials.

5.1.2.1 Oxygen electrode

The anode of an SOEC is responsible for both electronic and ionic conductivity and is exposed to highly oxidizing conditions. Hence, noble metals would be particularly suitable to withstand the severe operating conditions and ensure conductivity requirements at the same time; however, use of these materials implies an increase in cost. Therefore, to avoid using noble metals, electronic/ionic composite and mixed ionic and electronic conductors (MIEC) have gained interest as oxygen electrodes for SOECs. The evolution reactions occur differently at the two electrodes: the electrochemical active sites of electronic/ionic conductors are the triple phase boundaries (TPBs) while in MIECs oxygen evolves on part of the gas-exposed surface [78]. Usually, MIECs are perovskite oxides with a broadly $ABO_{3-\delta}$ composition where, generally, A is a large trivalent lanthanide ion that can be partially substituted by divalent alkali earth ions to increase both electronic and ionic conductivity, while B is generally occupied by one or more small tri- or tetravalent transition metal ions of the 3d-block. The most commonly used material for the SOEC anode is a composite of lanthanum strontium manganite (LSM) and zirconia (ZrO_2) doped with yttria (Y_2O_3) called yttria-stabilized zirconia (YSZ) [79]. LSM has been shown to have a high performance when used as oxygen electrodes for SOEC as reported and an area-specific resistance (ASR) of the cell between 0.15 and 2.7 Ω/cm^2 for similar operating conditions [61, 74, 80–88]. However, recent studies have reported a higher oxygen electrode performance when substituting LSM with other materials such as lanthanum cobaltite (LC) [82], strontium-doped lanthanum cobaltite (LSC) [81, 82, 88–92], strontium-doped lanthanum ferrite (LSF) [88, 90, 93–99], strontium-doped lanthanum ferrite partial substituted with cobalt (LSCF) that displayed lower polarization resistance than occurs in cells where LSM is used as the oxygen electrode [91, 93, 94, 96, 97, 100–108] (the electronic conductivity of LSCF is in the range of 200–300 S/cm while the ionic conductivity is 0.001–0.1 S/cm [109]), strontium-doped lanthanum ferrite partially substituted with copper [93, 110] or strontium-doped barium ferrite partially substituted with cobalt (BSCF) [90, 111–113] and even neodymium [114–116], lanthanum [117], praseodym [117, 118], nickelates or strontium-doped lanthanum nickelate partially substituted with cobalt [119]. Recently, Park et al. [120] tested three different oxygen electrodes: LSCF, $Sr(Ti_{0.3}Fe_{0.7})O_3$, and $Sr(Ti_{0.3}Fe_{0.63}Co_{0.07})O_3$. Additionally, in particular for CO_2 electrolysis, double perovskite $AA'B_2O_{5+\delta}$ of $A_2BB'O_{6-\delta}$ were also considered as SOEC electrodes yielding particular interest for $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFM) that showed promising performance during the testing campaign (0.26 Ω/cm^2 at OCV, 0.88 A/cm^2 at 1.3 V, and high stability) [121]. Another double perovskite material is $PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$ that achieved good stability for 120 h and a low degradation rate [122, 123]. Moreover, Ruddlesden–Popper phase materials are being investigated and research is focusing on $A_{n+1}Ni_nO_{3n+1}$, $A_{n+1}Co_nO_{3n+1}$, and $A_{n+1}Cu_nO_{3n+1}$ [124, 125]. Several tests have been performed in both fuel cell and electrolysis mode for the different materials investigated. Better performance at the OCV was observed with an LSCF-gadolinium-doped ceria oxide (CGO) or an LSC-CGO oxygen electrode that revealed an ASR of 0.19 and 0.15 Ω/cm^2, respectively [126]. These values were lower than the 0.27 Ω/cm^2 recorded for an LSM-YSZ anode [126]. It must be mentioned that both cells with LSCF-CGO and LSC-CGO oxygen electrodes also possess a CGO barrier layer limiting gas diffusion at the oxygen electrode side. It is also to be noted that an apparent increase in cell performance can be attributed to feeding air instead of pure oxygen at the anode. However, this improvement may simply be due to the increase in oxygen partial pressure at the anode side due to the production of oxygen in electrolysis mode [126–130]. At an intermediate temperature, $Ba_{1-x}SrxCo_{1-y}Fe_yO_{3-\delta}$ (BSCF) is used at the anode side of SOFCs and is usually blended with an ionic conductor (e.g., Sm_2O_3-doped ceria – SDC) to increase both ionic and electronic conductivity of the electrode and reduce the ASR down to 0.105 Ω/cm^2 [131].

5.1.2.2 Fuel electrode

Research into the materials of the SOEC fuel electrode is crucial if we are to ensure high performance and cell durability since the cathode is responsible for electron, oxygen ion, and gas conductivity. Among the many materials investigated, the most common are porous cermet of YSZ and metallic nickel [79], such electrodes being usually referred to as Ni/YSZ electrodes. As with oxygen electrodes, electrochemical reactions occur at the TPBs in fuel electrodes, these active sites being defined as the boundaries where the three networks of interest (i.e., Ni, YSZ, and pores) meet to form the percolating pathways for the species transported (i.e., electrons, oxide ions, and gas, respectively) [132–134]. One of the main issues with these electrodes is the rapid oxidation of Ni when exposed to pure H_2O and/or a CO_2 atmosphere. Hence, recirculation of a small part of cell off-gases may be a useful way of reducing material degradation. On the other hand, Pt electrodes have also been studied as an alternative to Ni, since Pt allows one to operate cells under conditions that would otherwise expose Ni to rapid oxidation. Several studies have been conducted evaluating performance in terms of ASR for cells with various different architectures. It was observed that, when using the same fuel, electrolyte-supported bottom cells with Ni/YSZ electrodes showed an ASR of 0.35 Ω/cm^2 [73, 74] while 0.9 Ω/cm^2 was observed at 800 °C for a fuel composition of 50% H_2O – 50% H_2 for a fuel electrode-supported cell with a Ni/YSZ thickness of 500 µm [93]. Moreover, Ni/YSZ|YSZ half-cells were tested under the same operating conditions (800 °C, 50% H_2O – 50% H_2)

achieving 0.29 Ω/cm^2 of ASR [135]. The good performance obtained for H_2O electrolysis was matched for CO_2 electrolysis.

Studies on different materials have been performed to improve fuel electrode performance. Thus, nickel nanoparticles dispersed in a SDC matrix [136–139] have been investigated but showed lower performance than Ni/YSZ electrodes (0.51 Ω/cm^2 of cell resistance [137]). Other materials studied as SOEC fuel electrodes include strontium ferrite-molybdenum (SFM) that gave a cell polarization resistance of 0.26 Ω/cm^2 at 900 °C [140], lanthanum-doped strontium vanadate (LSV) that displayed an electrode polarization resistance between 0.45 and 0.54 Ω/cm^2 in hydrogen [141], titanate/ceria composites [110], while perovskite materials such as lanthanum strontium chromium (LSCM) [142–154] have presented particular interest. Most of these electrodes showed good results, in particular, lanthanum strontium titanate (LST)-ceria electrodes yielded a better performance than Ni/YSZ cermets [93] though an initial performance decrease was observed when increasing the H_2O/H_2 ratio at the inlet side. Recently, Wang et al. [155] found promising results when testing $La_{0.6}Sr_{0.4}Fe_{1-x}O_{3-\delta}$-$Gd_{0.1}Ce_{0.9}O_{2-\delta}$ ($LSFM_x$-GDC) with different values of x (0, 0.05, 0.10, and 0.15) as the fuel electrode for direct CO_2 electrolysis. For what concerns the perovskite-related oxides used as cathodes for SOECs in CO_2 electrolysis, several methods of improving their electrocatalytic activity are worth mentioning: infiltration, doping, and exsolution are the most common. Some of the materials studied are LSCM-CGO loaded with $Ce_{0.9}Mn_{0.1}O_{2-\delta}$ [156], $La_{0.3}Sr_{0.7}Ti_{0.3}Fe_{0.7}O_{3-\delta}$ loaded with CeO_2 nanoparticles that achieved a current density of 3.65 A/cm^2 and a decrease in the polarization resistance in the range 0.82–0.13 Ω/cm^2 when the cell was operating between 750 and 850 °C [157], and $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ doped with CGO that increased the operating current density up to 0.466 A/cm^2 at 1.6 V and 800 °C [158].

5.1.2.3 Electrolyte

The electrolyte of an SOEC ensures transport of oxygen ions from the fuel electrode to the oxygen electrode. The state-of-the-art electrolyte material commonly used in SOECs is a dense ionic conductor of YSZ 8 mol%, which, in addition to good ionic conductivity (0.1 S/cm at 1,000 °C), guarantees adequate thermal and chemical stability at the customary cell operating temperature. Additionally, others such as scandia-stabilized zirconia (ScSZ) [159, 160], ceria-based electrolytes with a fluorite structure [81, 161], and lanthanum gallate (LSGM) with a perovskite structure [162, 163] have been intensely studied in the last decade to replace YSZ electrolytes and increase cell performance. Such studies showed that the choice of electrolyte material also influences the electrode performance. For instance, positive results were obtained when using a SDC electrolyte [159]. However, ceria has high electronic conductivity under highly reducing conditions and hence its use in SOEC electrolytes increases the risk of short-circuiting [81] making this material unsuitable for the purpose. With particular reference to CO_2 electrolysis, the use of Sr- and Mg-doped $LaGaO_3$ ($La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ – LSGM) [18, 164, 165] is worth mentioning, as is doped bismuth oxide that shows good ionic conductivity at intermediate temperatures [164].

Besides steam and CO_2 electrolysis, SOECs are also used for fuel production. For this purpose, a low cell operating temperature may be opportune, though temperature reduction also causes a decrease in YSZ conductivity. Thus, other materials have been investigated for this specific purpose and for operation at lower temperatures. Studies on doped lanthanum gallate showed that when using this material as an electrolyte the cathode will be subjected to $LaNiO_3$ formation [166–170] and fractures due to the thermal expansion coefficient (TEC) mismatch between electrolyte and electrode. Major changes on the cathode side were found to be necessary to guarantee good cell performance.

5.1.2.4 Materials for PCC cells

PCCs materials are presented below in a separate paragraph. Although the structure of a PCC is similar to that of an SOEC (anode, cathode and electrolyte), there are some differences in the materials used. The electrolyte of a PCC guarantees the conduction of hydrogen cations from the anode to the cathode while, in an SOEC, the electrolyte needs to have high conductivity to oxygen ions. For what concerns the electrodes, the first materials that gained interest for this function were platinum based while several combinations were investigated for PCC electrolytes: strontium cerate [17, 171–179], doped strontium zirconate [175, 180–182], and doped strontium cerate partially substituted with zirconia [182]. Recent studies have investigated other solutions for PCC electrolytes including doped barium cerate [181, 183–185], doped barium cerate partially substituted with zirconia and also with cobalt [126] or zinc [187–189] addition. A few studies showed that doped strontium cerate can guarantee stable hydrogen production at the cost of high electrolyte resistance [177]. Hence substitution of ceria with zirconia was investigated and resulted in higher production rates with increased current efficiency at a higher water content [175, 182]. Likewise, doped barium cerates are acquiring interest because of their high proton conductivity so their use as PCC electrolytes is being thoroughly studied [190–193]. However, research studies have been carried out to improve the stability of these materials at high temperatures by using CO_2 and steam [194–197]. Recently, increasing interest has focused on materials based on $BaCe_{1-x}Zr_xO_3$. In particular, Huan et al. [198] studied $BaCe_{0.5}Zr_{0.3}Y_{0.2}O_{3-\delta}$ (BCZY53) that yielded a good performance overall in the short term, though instability was observed in a high-steam atmosphere [199, 200]. Additionally, Yb doping was also considered for $BaCe_{1-x}Zr_xO_3$-based electrolytes ($BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\delta}$ – BCZYYb) that achieved good stability under mild testing conditions even in the long term [201–203]. However, stability issues were discovered under adverse conditions [204] leading to the introduction of a $La_2Ce_2O_7$ (LCO) protective layer on the air electrode side [204, 205]. Recently, some studies have tried using non-platinum-based materials for both electrodes to reduce the costs. The anode is usually a perovskite such as strontium-doped lanthanum cobaltite [177], strontium-doped lanthanum ferrite partially substituted with cobalt [180, 206], strontium-doped lanthanum manganite partially substituted with chromium [188, 189], samaria-doped strontium cobaltite [182, 207], while the cathodes PCC uses for steam electrolysis are generally Ni based, similarly to SOECs [177, 182, 188, 189, 207–209].

5.1.3 Stacks and balance of plant (BoP)

Extensive testing of cells has been performed at the stack level to study behavior and performance in real operative conditions. For instance, the Idaho National Laboratory together with Ceramatec Inc. has performed a lot of tests for high-temperature steam electrolysis and co-electrolysis testing different sized devices up to 60-cell stacks [210]. As a rule, degradation of the cells tested as part of a stack is observed to occur faster than in the case of single cell testing. The main cause of the difference in degradation may be chromium deposition as it evaporates from the interconnects [211]. Moreover, the thermal imbalance inside the stack may markedly affect degradation [210, 212]. Again, each stack component degrades by itself (interconnect oxidation, deposition of impurities, and contact losses) and this could adversely affect the overall degradation [97, 212–215]. Besides these considerations, Topsoe Fuel Cell [102, 216–218] and Ceramatec [97] tested an SOEC stack that showed similar degradation to that observed for single cell [219] testing when operating below 1 A/cm^2. Another point to be considered is that lower flow rates were fed to the stack than the rate used for single cell testing. This difference in flow rates may partly increase the gas conversion rate [216]. The same study showed that the electrode performance of the single repeating units (SRU) composing the stack were comparable with that of a single cell test [216]. In this regard, Topsoe Fuel Cell proved that the use of chromium-based interconnects together with their glass sealing did not adversely affect the stack performance at 850 °C, and the stack could operate without marked degradation up to −0.75 A/cm^2 [102, 216, 218]. It is worth mentioning that a Strategic Research and Innovation Agenda (SRIA) has recently been published by Hydrogen Europe and Hydrogen Europe research. The document reports the state-of-art and the targets expected until 2030 for several parameters. For instance, at a systems scale, a reduction in electricity consumption from 40 kWh/kg in 2020 to 37 kWh/kg in 2030 and a reduction in heat demand from 9.9 to 8 kWh/kg over the decade 2020–2030 [220]. Additionally, a decrease in both capital cost and operational and maintenance costs down to 1500 €/(kg/day) and 75 €/(kg/day)/year by 2030, respectively [220]. For what concerns the stack, a reduction in degradation is expected, reaching 0.5%/1,000 h by 2030, together with an increase in the current density of up to 1.5 A/cm^2 (2030) [220]. Finally, roundtrip electrical efficiency is expected to increase from 46% in 2020 to 59% in 2030 [220].

Figure 5.2 shows a typical large stack module generally used for stationary applications.

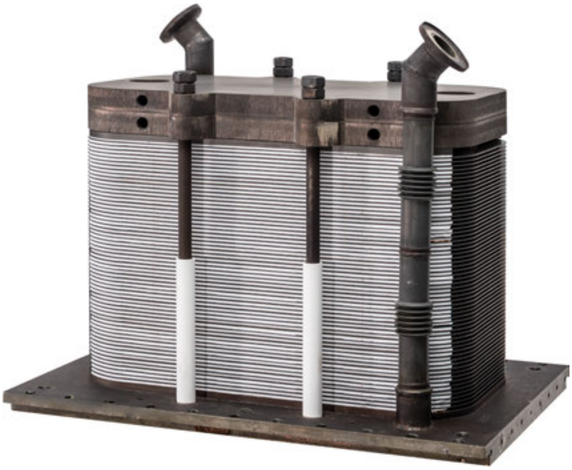

Fig. 5.2: A generic large stack module used for stationary applications.

The layout of an SOEC-based plant may assume different configurations depending on differences in user (exclusively electrolysis, reversible operation, co-electrolysis, etc.). Figure 5.3 reports a classic layout for a pure electrolysis plant.

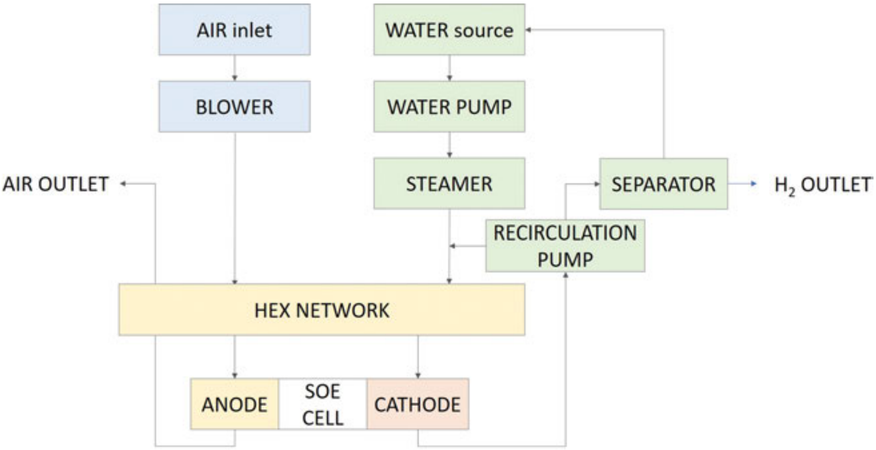

Fig. 5.3: Generic logic architecture schema of SOEC system.

The BoP (balance of plant) is crucial for the whole SOE system: it is responsible for heat management that includes heating up, operation at high temperatures, and recovery of the thermal content of outlet gases. Generally, SOEC operation achieves thermal equilibrium (thermoneutral mode) when the electrical energy input equals the enthalpy of reaction. In this case, the gas outlet temperature equals the steam inlet temperature, and the electrical-to-hydrogen conversion efficiency is 100%. In the thermoneutral mode, the entropy necessary for the water splitting equals the heat generated by the reaction in the cell. In the exothermal mode, by contrast, the electric energy input exceeds the enthalpy reaction, corresponding to an electrical efficiency lower than 100%. This is due to the thermal losses that are intrinsic to cell operation. Finally, in endothermal mode the electric energy input is lower than the enthalpy reaction leading to a cell voltage below thermoneutral (<1.3 V). Thus, heat must be supplied to the system to avoid temperature fluctuations. This mode means an electrical-to-hydrogen conversion efficiency on the part of the HTE cell above 100%.

Again, ceramic cells are extremely fragile, and this makes pressure management a critical issue for SOE plants. Pressure inside the stack pipes should be kept as constant as possible to reduce the absolute pressure fluctuation at both the anode and the cathode side (approximately 50–100 mbar with respect to atmosphere), by monitoring the differential pressure between them so as to avoid dangerous cracking of solid electrolytes (around 15–25 mbar) [221]. For this reason, the BoP of an SOE has dedicated active management systems (control loops and proportional valves to tune the pressure drop along the line) and a proper interface system (i.e., buffer volumes) to control the pressure by decoupling the SOE plant and the downstream process.

BoP includes several auxiliary components (pumps, heat exchangers, compressor, heaters, electricity converter, and hydrogen separator) enabling an SOE cell stack to operate correctly and efficiently; these will be described in the course of this section.

A pump is used to adjust the feed water pressure to the system. This is particularly indicated when the water is separated from the outlet flow and stored in a tank of its own to reduce the amount of demineralized water required. Regarding the quality of the water, tap water can be used as a raw material, purified by several technologies (such as reverse osmosis, ion exchange bed) to achieve water conductivity between 2 and 0.2 mS/cm [222, 223]. The steamer/evaporator is responsible for complete evaporation of the water flow in the system. Consequently, most of the heat consumed by the system can be set down to steamer/evaporator operation (the enthalpy of water evaporation is 0.63 kWh/kg, approximately 60% of the heat supplied to produce steam in a state of overheating at 600 °C). For this reason, some systems include a three-stage evaporator, composed of: an economizer, an evaporator, and a super heater. Note, too, that generation of heat involves a marked increase in volume and a quick change in the heat transfer coefficient – a point to be borne in mind when designing a steamer/evaporator so as to avoid a pronounced fluctuation in the flow rate and pressure that can damage the SOE stack [224]. Moreover, in SOE voltage fluctuations may be observed, caused by instable vaporization of water in the steam generator. This is a well-known issue in SOEC operation. Such voltage fluctuations increase with increasing current density [225]. Heat exchangers (recuperators) are part of a general heat exchanger network (HEN), which can include various different distribution and configuration options maximizing heat exchange and minimizing heat loss. The HEN configuration depends on the specific use of the SOE system (electrolysis, CO-electrolysis, reversible operation, etc.), which also bears greatly on the final layout and sizing of the individual heat exchanger. Identification of a successful HEN is one of the main engineering concerns when designing an SOE system. This goal has led in recent years to development of several innovative approaches to increase the efficiency and performance of the system. In particular, the use of multi-object optimization algorithms has a major role in identifying "best candidate" layouts. To achieve this, several simulations are performed against a validated steady-state case with specific boundary conditions and a proper optimization function.

An electric heater can be used to provide any additional heat needed to ensure the stack has the right inlet stream during the heating up procedure and transients. During this transition, the electrical heaters are generally switched off to avoid loss of electrical efficiency in the SOE system. In any case, it is a good practice to include these devices in the system layout and thus forestall possible emergency situations and deviations from nominal operation.

On the anode side, many different configurations can be realized depending on the specific SOE plant [226]. A simple SOE system for water electrolysis includes an oxygen circuit on the anodic line that has the role of levelling the stack temperature and removing the oxygen produced via a proper pressure regulator. Outlet O_2 from the SOE stack is used to preheat the inlet gas and thus enhance the efficiency of the overall system. The anodic contribution to heat management is limited due to a low mass flow rate [227]. Such an approach improves the efficiency of the whole SOE plant but only for low current density. In other applications, such as reversible system or co-electrolyzer systems, the SOE plant uses air instead of pure oxygen recirculation. This layout guarantees the air flow even other operative modes as well (reversible fuel cells, for instance) and contributes to increasing the system efficiency at system-level by improved heat management, particularly for high current application. Regarding the cathode side, a small amount of the hydrogen produced needs to be recirculated on the inlet side to prevent nickel oxidation. Generally, the cathode side needs a hydrogen concentration of 10% in volume [228]. This can be provided via recirculation of the stack's downstream output if no other reducing gas is available. Unfortunately, the literature on this topic is still quite scanty. Moreover, SOE plants are equipped with a proper hydrogen inlet directly in the steam flow. Such hydrogen stream is often extracted from the outlet hydrogen flow after compression. Such a configuration enables the SOE plant to work autonomously, but it needs a hydrogen buffer (or a connection with the H_2 storage) to solve the transient and the hot idling modes [228]. The separator is a simple expansion volume, located next to a condenser, with the purpose of removing as much water as possible from the gas phase. The condensation water is separated off by gravity, while saturated hydrogen is collected from the top of the component. Pressure control in the separator is quite important. Particularly in big systems, water is directly drained by using a level control and an on/off valve. In this case, the big empty volume of the separator can smooth the draining of water. Otherwise, for small systems, one may apply a water trap regulated automatically by a floating valve. This solution has the advantage of not affecting the pressure in the cathode line.

Finally, the downstream processes generally include both separation/purification and compression. Separation/purification is designed to reduce contaminants in the hydrogen supply in compliance with the user's requirements. Compression increases the hydrogen production of the SOE system at the operating pressure. Here, a hydrogen recirculation line is generally installed to supply hydrogen in the steam inlet flow. This practice ensures one has a reducing atmosphere on the cathode side. Many different processes and techniques are currently used for this purpose.

5.2 High-temperature electrolysis applications

5.2.1 SOC end uses: an introduction

SOCs are being used or are showing potential in many applications, covering most of the hydrogen value chain, either in electrolysis or fuel cell modes or with reversible operation, from hydrogen production to transport, handling and distribution, and including a number of end uses in industrial or residential settings, or in the mobility sector, or again for infrastructure used in some specific sectors (e.g., maritime).

In this section, the various segments of the value chain and the most promising applications of SOC technology will be analyzed.

Among the main driving factors for SOCs are:

- The fact of being a flexible technology connecting production to utilization in a flexible way via reversible systems. Thus, SOC solutions may enable the flexibility to have power or methane-rich mixtures such as feeding energy, while they can produce in a flexible way hydrogen and/or power as their output.
- High cycle efficiency, integrating waste heat as a valuable energy input, able to leverage overall cycle efficiency to 100% or more (thermal power given for free).
- Their ability to work in a co-electrolysis mode, synthesizing complex molecules at a high cell temperature. This involves ammonia, syngas (e.g., usually a mix of CO, CO_2, and H_2 mostly) and focuses on synthetic fuel synthesis processes (e.g., bio-methane, methanol from CO_2 and H_2).

5.2.2 Key industrial initiatives

The application of SOCs is spreading on an industrial level for both fuel cells and electrolyzers. Since SOFC technology has a higher maturity level than “reverse mode electrolysis” in SOEC technology, several commercial SOFC products can now be found, while integration of SOECs in energy systems has recently made approaches to the market in a series of upscaled demos at the MW size. Many SOEC-based systems have been developed and demonstrated as part of international projects with a number of specific applications designed to prove their feasibility on an industrial level. This section gives an overview of the main projects involving SOEC-based demonstrators.

One of the most important European-funded projects has been GrInHy (Green Industrial Hydrogen). GrInHy was funded by the Fuel Cells and Hydrogen Joint Undertaking under call 2015 and inside the specific topic FCH-02.4-2015. It developed between 2016 and 2019. The project was coordinated by Salzgitter Mannesmann Forschung with the objective of developing the largest, at that time, reversible SOEL 120 kW_{el}). The system seeks to derive electricity from hydrogen or natural gas when renewables cannot satisfy the energy demand. During the three years of the project, a flexible and dynamic prototype was designed, manufactured, and operated to demonstrate its potential. Sunfire GmbH technology was used to develop the SOC part of the system. Green hydrogen production was tested as part of the GrInHy project by using high-temperature electrolysis for Salzgitter AG’s hydrogen-based and low carbon steel making concept. It was demonstrated that this part of the project is able to reduce total emissions by more than 95%. In this sense, the main energy advantage of the system lies in recovering the wasted heat from industrial processes at iron-and-steel works. In this way, industrial steam can be used directly for hydrogen production while meeting the quality required for steel annealing processes. The GrInHy prototype operated until mid-2020 when it gave place to the prototype GrInHy2.0, destined to have five times the capacity of the GrInHy prototype. GrInHy2.0, funded by FCH JU in 2019, aims to scale the GrInHy electrolyzer up to 720 kW_{el} and produce 18 kg/h of hydrogen with an electrical efficiency of the electrolyzer up to $84\%_{el,LHV}$. The system will operate for more than 13,000 h while the SOEC stack will be tested in operation for more than 20,000 h [229, 230].

ENGIE is coordinating the MultiPLHY project (producing renewable hydrogen on a large scale to decarbonize a biorefinery), the aim being to build a 2.6 MW, $60kg_{H2}$/h capacity electrolyzer based on high-temperature technology at the Neste biorefinery in Rotterdam. Neste owns a patented technology for renewable hydrogen production and direct water and CO_2 conversion into raw materials for petrochemical products. The technology is supported by Neste’s equity investment in Sunfire, which is a key player in the field of high-temperature electrolyzers producing hydrogen and/or syngas production units. The two companies are working together to test renewable hydrogen production at Neste’s refinery, using the electrolysis technology developed at Sunfire since 2010. Validation of this project will represent a crucial step in the commercialization of Sunfire products. Sunfire, as an international key player in the current SOEC framework, is also involved in the E-CO2MET project in which Total SA is a participant. E-CO2MET represents the first step toward industrialization of synthetic methanol production from renewables and industrial concentrated CO_2 production the part of Total Raffinerie Mitteldeutschland GmbH [220, 231].

Recently the proof of concept of a 10 kW pressurized SOEC prototype was designed and validated by Sunfire as part of the HELMETH project (integrated High-Temperature Electrolysis and Methanation for Effective Power Gas Conversion) that was financed by FCH JU between 2014 and 2017. The main advantage of such a system is the use of steam available from industrial processes between 5 bar(g) and 30 bar(g), thus avoiding the expensive step of compressing hydrogen. At the end of the project, the pressurized SOEC electrolyzer was coupled with a methanation plant; in this configuration the steam produced to cool the methanation exothermic reaction can be fed directly to the SOEC, saving the electricity needed for water evaporation [232].

5.2.3 Transport, handling, distribution

The flexibility of SOCs in terms of both variable generation and reversible mode caters for novel applications that are arousing interest in the sector of distributed hydrogen generation combined with infrastructures for hydrogen refueling stations (HRS) as well as multifuel stations.

In this connection, two European projects should be mentioned: CH2P (cogeneration of hydrogen and power using solid oxide–based systems fed by methane-rich gas) and SWITCH (smart ways for in-situ totally integrated and continuous generation of hydrogen). The CH2P project was funded in 2017 as part of H2020-EU [233]. The project aims to achieve an innovative energy system for the cogeneration of hydrogen (H_2), heat, and power, using SOFC technology. SOFC stacks are fueled with methane-rich gases or mixtures. The system generates both hydrogen and electricity more efficiently and with less environmental impact than do conventional technologies. The CH2P system can have three operating modes:

1. Hydrogen and electricity production, in different fractions, at HRSs. The system can reach 100% hydrogen and power capacity, or operate at partial load of either hydrogen or power capacity;
2. Net electricity consumption. In this case, electric energy is supplied to the system, which produces hydrogen only, using the reforming reaction;
3. Hydrogen generation without need of additional water. This operating mode is particularly suitable for regions where water is scarce and the system layout configures an off-grid solution.

The CH2P plant is the result of a complex integration of different sub-components: natural gas sulfur removal, a fuel pre-reforming reactor, a steam generator with heat recovery system, SOFC stacks, a WGS reactor for full conversion of residual carbon monoxide to carbon dioxide, H_2 separation by water knockout system, a compressor and a pressure-swing adsorption unit. The high purity hydrogen flow produced complies with ISO 14687-3:2014. The CH2P system will support fuel demand in novel refueling stations, producing H_2 for vehicles and electricity for both the refueling station needs (self-consumption and recharging of vehicles) and for business applications (grid balancing, energy selling) with a high degree of cogeneration flexibility. Moreover, it will present an innovative cost model for hydrogen production. Design of the CH2P system was based on a systematic and multi objective optimization approach. Results from numerical simulations as well as from experimental validation show that the plant could attain a weighted efficiency (i.e., considering the overall working hours per period per day) of over 75%, taking all generated fractions into account.

The SWITCH project, funded in call H2020-JTI-FCH-2019-1 in 2019, is extending the functionalities of CH2P, including reversible operation. As mentioned in other parts of this chapter, SOCs are efficient ways of converting the electricity produced from intermittent renewables into green hydrogen. At the same time, they can be used in reverse mode to enable the use of other sources (e.g., methane, bio-methane, and ammonia), combining variable energy production with continuous and guaranteed hydrogen production for specific end uses. SWITCH focuses on developing this particular solution and achieving mostly green and always safe production of hydrogen, heat, and power. The core of the system is a reversible solid oxide module based on anode supported cells, integrated with an advanced fuel processing unit able to manage steam generation and methane reforming reactions at high efficiency. In addition, the system is equipped with a purification unit to guarantee highly pure hydrogen in compliance with the main industrial and automotive standards. SWITCH focuses on demonstrating a 25 kW (SOFC)/75 kW (SOEC) system operating in a major industrial environment for at least 5,000 h. Part of the activities will address the issues of cost competitiveness and environmental impact, the target being to achieve a hydrogen price lower than 5 €/kg. The basic solution will be designed to be up scalable to bigger sizes and thus extending to target applications in different sectors such as industrial, residential and grid services. The system modularity, the low transient times, an integrated gas treatment unit, and different modules combined in between SOFC and SOE mode will provide a solution able to combine different sources and flexible production of hydrogen, heat, and power with the specific uses envisaged.

Figure 5.4a and b shows the two operating modes of the SWITCH system while Fig. 5.4c illustrates the inputs and outputs to the SWITCH system for the SOFC operation.

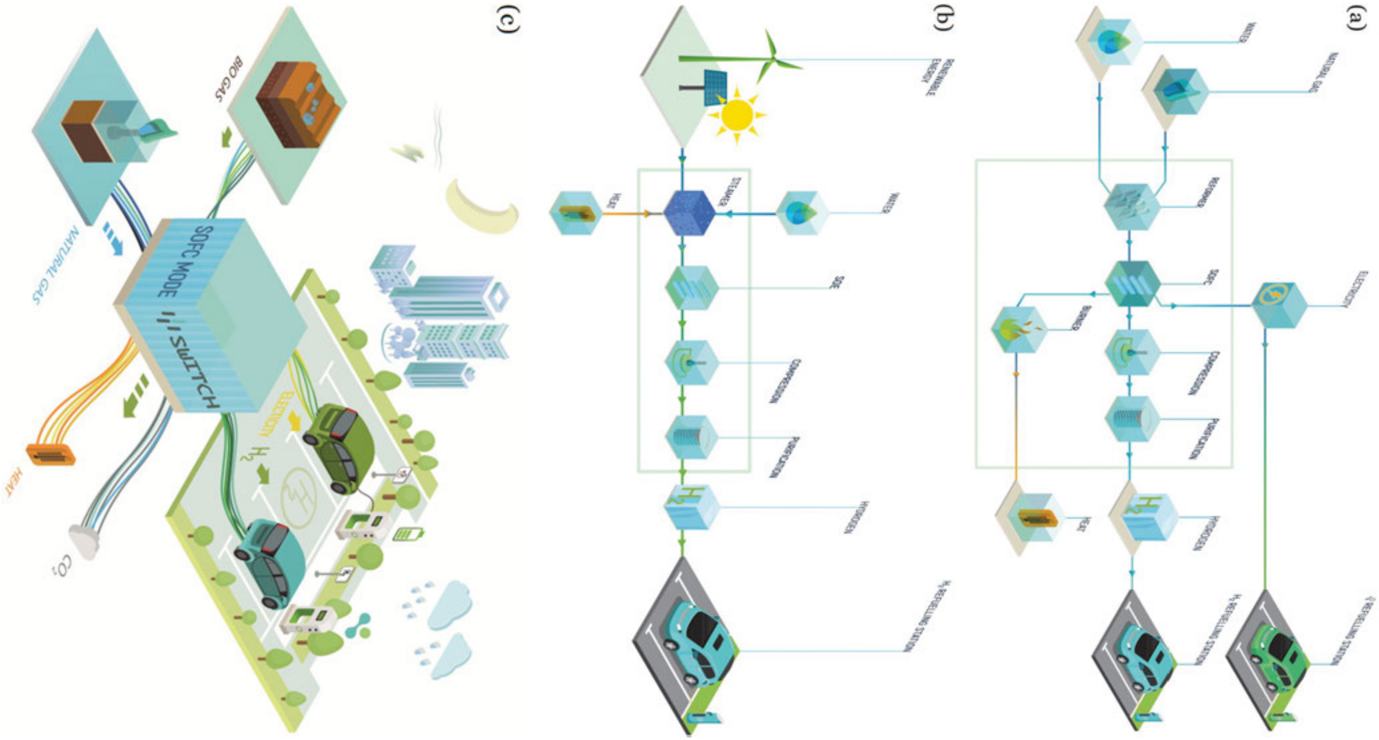

Fig. 5.4: (a) SOE operation of the SWITCH module: water, heat, and electricity are provided to the steamer for producing the steam to feed the SOE cell for the production of hydrogen. The hydrogen needs to be compressed and purified before reaching the hydrogen refueling station. (b) SOFC operation of the SWITCH module: water and natural gas are supplied to the reformer to produce the synthesis gas for the SOFC. The exhausted from the SOFC are fed to the burner for heat production while the excess hydrogen and the electricity is used in the hydrogen refueling station. c) illustration of the SWITCH module operating in SOFC mode with relative outputs.

5.2.4 Mobility

In the mobility sector SOCs are not an obvious solution to apply and nowadays the range of applications where they are integrated and tested is limited (specifically, where the application requires steady-state operation by SOCs).

Until the beginning of the twenty-first century, SOCs were not considered at all for mobility applications, while today they are being introduced in several demo projects that may pave the way for massive future utilization, given the fact that the technology is capable of meeting a number of open challenges.

Several driving elements are thus causing the use of SOCs to extend to mobility applications, as reported by Boldrin et al. [235]. Some of the key factors identified as drivers for an SOC breakthrough into the mobility sector are lifetime and degradation, fuel flexibility, efficiency and power density.

SOFCs are reported to be utilized in various mobility sectors such as: maritime, heavy duty vehicles such as trucks, and buses. This is particularly the case when the specific mobility service utilization requires prolonged constant operation, thus reducing the transients, the starting and stopping, and the need to activate the system by means of considerable thermal mass in between.

Among the various schemes to use hydrogen in the mobility sector, one should mention the development – at Delphi, 2010 – of a 3 kW SOFC working as an APU in gasoline fueled trucks [234]. This system was able to increase by 50% the efficiency of electricity generation dedicated to onboard services and alongside the overnight standby. In this scheme, the SOFC was in the end oversized to overcome to the presence of sulfur at 750 °C, which is otherwise difficult to remove. Another venture involved AVL, installing an SOFC system in a Volvo truck and achieving similar results [235].

It is worth mentioning that SOCs are playing a greater role in maritime applications, where they are widely used for auxiliary power. One major scheme was started by Wärtsilä (now Convion Oy): it installed a 20 kW SOFC system directly fed by methanol in a car carrier ship [236]. Again, Thyssen Krupp and Sunfire have developed a bigger SOC system, size 50 kW, powered by diesel for a freighter [235].

Considering the sector of all-terrain vehicles, Atrex Energy (formerly Accumentrics) has utilized a 1 kW tubular SOFC system on an all-terrain vehicle. Unlike planar cells (sealed at the edges), the tubular cells need to be sealed at the end of the tube. Testing was performed off-road using compressed natural gas for over 100 miles and demonstrated that the fuel saving reduced fuel consumption down to one third of standard powered vehicles. The cell was used as part of the system without need of a reformer.

Among the various SOC applications one should mention the increasing interest in using SOFCs in unmanned airborne vehicles [236]. Another major solution reviewed by Boldrin et al. [235] is the use of metal-supported SOFCs. The main advantages of these cells are that they are more resistant to cycling and thermal cycles and they are able to reach 50% of electric efficiency. One of the main stakeholders in this technology is Ceres Power [237], which is receiving attention from Nissan and Weichei for application mainly as range extender solutions in vans and buses, respectively. The latter had a deal to develop a scaled plant in China for the manufacture of cells [235].

5.2.5 Electrolysis

Many applications of SOC have already been mentioned in this chapter. This section focuses on the use of carbon for hydrogen production. Several studies have been performed on this topic. For instance, the feasibility of solid oxide natural gas-assisted steam electrolyzer (NGASE) was studied by Martinez-Frias et al. [238]. The reactions occurring in an NGASE involve the natural gas and oxygen produced in electrolysis. This oxygen flow can totally ($CH_4 \rightarrow CO_2 + H_2O$) or partially ($CH_4 \rightarrow CO + H_2$) oxidize the natural gas flow. The process reduces the electrochemical potential across the electrolyzer and minimizes the electricity consumption. Both CO and CO_2 are crucial for this application since the catalytic activity of the materials can be reduced when they are present. Wang et al. [239] studied Cu_3 and Pd composites for the anode of NGASE. It was observed that, while the Cu_3 composites showed low catalytic activity in the presence of CO and CH_4, the catalytic conductivity of Pd was improved, although CH_4 oxidation was lower than the theoretical value. One more interesting application of solid oxide membranes for hydrogen production from steam was investigated by Pati et al. [240]. The authors used solid carbon reductant in a liquid metal anode to reduce the energy required for hydrogen production. Another study on hydrogen production from carbon was performed by Lee et al. [241] on YSZ cells with platinum electrodes; the system developed used electricity cogeneration during galvanostatic operation and produced carbon-free hydrogen from steam and carbon.

5.2.6 Co-electrolysis

As already mentioned, one of the main advantages of SOECs lies in the fuel flexibility, and, in this regard, the co-electrolysis of steam and CO_2 is considered of high interest. Co-electrolysis has aroused particular interest in the last decade or so for converting the CO_2 produced by energy plants into sustainable hydrocarbon fuels [242–249]. By doing so it is possible to reduce the CO_2 emission and facilitate energy storage and conversion as well as integrating renewable energies into the electric grid. Steam and CO_2 used in co-electrolysis can be captured from power plants and/or industrial processes and fed together on the cathode side of the cell where syngas is then produced.

The use of SOECs for co-electrolysis could become widespread, producing a range of fuels such as diesel. In the specific case of diesel production, the co-electrolysis process needs to be combined with Fischer–Tropsch synthesis. Interestingly, the price of diesel produced via co-electrolysis proved comparable with the diesel produced from fossil fuels. On the other hand, hydrogen production from steam electrolysis proves cheaper [126]. One should note here that the fuel price, when produced by co-electrolysis, is closely affected by the electricity price. However, more theoretical and experimental studies are needed to guarantee the economic feasibility of fuel production from co-electrolysis. More generally, integration of SOEC systems with major sources of energy such as renewable energy sources (e.g., wind, solar, and geothermal), fossil fuels, and waste energy from industrial processes is clearly one of the best ways of harnessing the potential of this technology. Of course, government support for the integration of these energy sources in the electric grid will play a key role in developments to the overall energy scenario.

The increasing interest in co-electrolysis has led to development of several international projects to better investigate the potential of this technology in various frameworks. The European project SOPHIA (Solar-Integrated Pressurized High-Temperature Electrolysis) ran from 2014 to 2017, developing a solar powered high-temperature electrolysis 3 kW-scale prototype operating at 15 bar by co-electrolysis. Market analysis of this system showed that the availability of solar power here represents the limiting factor [250].

The European project ECo (Efficient Co-Electrolyzer for Efficient Renewable Energy Storage) was funded by FCH JU between 2016 and 2019 and focused on developing and validating a high efficiency process. The process was designed to use the co-electrolysis of steam and CO_2 to convert the electricity excess from renewables into hydrocarbons that can then be distributed or stored, depending on the need. During design of the co-electrolysis system to produce hydrocarbons, particular attention was paid to integrating the reactor into the whole system, including renewables that give fluctuating energy inputs. The final test of the system was performed under real operating conditions in order to validate the results obtained on a large scale [251].

5.2.7 Reversible systems using SOCs

It has been mentioned that SOCs can be operated as SOFCs or as SOECs. When the same cell is alternately operated as a fuel cell and as an electrolyzer it is usually called a reversible SOC (rSOC). This working mode has been gaining interest thanks to its high operation flexibility that makes it suitable for use with fluctuating renewable energy sources (RES). rSOCs can operate as electrolyzers when there is over production from RES. Hydrogen produced during periods of RES abundancy can be stored in dedicated systems until RES fail to meet the energy demand, at which time the stored hydrogen is used for energy production. Again, rSOCs can potentially be used in many different fields such as the chemical, polysilicon, metallurgical or glass industries. Interest in rSOCs technology has also risen for remote power generation using natural gas, for the realization of combined heat and power plants to distribute the power generated as backup power, and also for trigeneration of power, hydrogen or syngas, and heat.

At an industrial level, the reversibility of SOC was tested when Sunfire collaborated with Boing in 2015 [252]. The prototype developed as part of that collaboration was composed of two modules of Sunfire rSOC, each module being characterized by a power consumption of 80 kWDC (approximately 100 kWAC) when operating in SOEC mode and a power production of 25 kWDC (approximately 20 kWAC) when operating as SOFC. The whole system developed was extremely complex and several additional components were considered during the design and engineering of the plant: a compressor on the air inlet side, a compressor for recycled hydrogen, a hydrogen storage system, an air filter and dryer, heat exchangers, a furnace to host the stacks, a steam generator, and several mass flow controllers. Careful design of all components is crucial to guarantee proper interaction between them and correct operation of the whole system. This fact makes realization of such a system and similar plants particularly challenging.

Among the European projects funded by FCH JU on the topic of rSOCs, W2G (Waste2Grid) was approved between 2018 and 2019. The main objective of the project was the preliminary investigation of long-term techno-economic feasibility on the part of W2G plants. The project was highly multidisciplinary as expertise in several different fields was necessary: rSOC, waste identification, gasification and syngas cleaning, grid operation, and energy/process system engineering. The working principle of W2G plants is particularly suitable for the decarbonization goals foreseen by the European Commission. In these plants, the syngas can be fed into the rSOC system operating in fuel cell mode for power generation and the net power produced is delivered to the electrical grid. On the other hand, when there is an overproduction of RES the syngas produced is used to synthesize methane [253].

5.3 Future perspectives

5.3.1 Introduction

Although high-temperature cells are currently scaling up, particularly true for SOCs, there are still several technological and application challenges that need to be addressed, as mentioned in the previous sections.

Research and innovation can still do a lot to remove some of these barriers and bring new prospects for the future of the high-temperature cell industry.

This chapter summarizes the future perspective for high-temperature electrolysis cells in some of the most promising directions foreseen. The paragraph is organized in two main sections:

- The future from a technological point with a focus on the evolution of middle temperature and PCC cell technology;
- The future for cutting-edge applications of high-temperature electrolysis cells.

5.3.2 Technology perspectives

5.3.2.1 Middle-temperature solid oxide electrolysis cells

As already mentioned, the use of YSZ electrolytes in high-temperature SOCs demands that the cell operates above 800 °C to ensure good ionic conductivity. Such a high-temperature compromises the long-term stability of the individual cell and increases sealing related issues at stack level. Moreover, it is not easy to find high-temperature heating sources to guarantee adequate SOEC operation and performance. Hence, more and more research studies are focusing on intermediate-temperature SOECs (IT-SOEC) that can operate in the temperature range between 500 and 700 °C [254, 255]. The possibility of operating at lower temperature brings several advantages to SOEC technology. Intermediate temperature operation not only improves durability, reduces materials issues and increases the nanostructure stability, but also offers a wider choice of heating sources than high-temperature SOECs as well as reduced BoP costs and improved system efficiency. The materials used for IT-SOEC electrolytes permit high oxygen ion conductivity at cell operating temperature. For instance, doped ceria is particularly suitable for operation at intermediate temperature since it shows an ion conductivity of 10^{-2} S/cm at 600 °C. However, one of the main drawbacks of using doped ceria as an IT-SOEC electrolyte is its high propensity to reduce Ce^{4+} to Ce^{3+} during operation [256]. A reaction of the kind significantly degrades the cell microstructure, causing a consequent reduction in the cell's electrochemical performance. In this regard, the study by Eguchi et al. [81] highlighted that the slower hydrogen evolution rate in IT-SOECs using doped ceria as the electrolyte is due to the reduction reactions occurring in the doped ceria. Consequently, the prevention of ceria leakage forms one of the main challenges for IT-SOEC development, prompting a number of research studies to seek a solution to this specific issue. Some studies have focused on developing blocking layers to prevent ceria leakage [257, 258]. However, introducing these layers in the cell architecture increases the complexity of the cell fabrication process and decreases the overall ionic conductivity of the cell. Luo et al. [259] suggested a Ba-rich electron blocking layer to prevent ceria reduction. Testing of cells with the Ba-rich layer showed good results compared to the state-of-the-art IT-SOEC, achieving a current density of 0.86 A/cm^2 at 1.3 V (700 °C). One additional advantage of cells with the Ba-rich layer is the possibility of producing the cell by a one-step co-firing approach [259].

As with high-temperature SOEC, the efficiency of IT-SOEC is affected by steam concentration. In this regard, Wang et al. [155] performed a study to highlight the relationship between electrochemical performance and steam concentration in IT-SOECs. The authors observed 98% system efficiency when operating at 650 °C with 0.5 A/cm^2 of current density [68].

Lastly, the operation of SOECs at intermediate temperature shows several advantages over high-temperature SOEC. The main points can be summarized as:

- reduction of cell manufacturing costs [260] (for instance, colloidal drop coating can be used for electrolyte deposition in bilayer electrolyte SOFCs [261]);
- reduction of material costs [260] (on a systems scale, the materials of the BoP would not have to withstand high temperature and hence the cost would be lower. On the cell scale, Sr- and Mg-doped lanthanum gallate can be substituted by low-cost materials that guarantee good electronic conductivity and mechanical strength [162–264]. For instance, $Sr_{0.8}La_{0.2}TiO_3$ was tested [265]);
- wider choice of materials (in particular, an operating temperature as low as 350 °C allows one to use stainless steel interconnects) [260];
- mitigation of stability issues [260].

5.3.2.2 Proton-conducting ceramic cells – PCC

As previously mentioned, the main difference between SOE and PCC cells lies in the species that are conducted through the electrolyte: oxygen cations and hydrogen protons, respectively. This leads to the cells having different working principles. In SOECs, the hydrogen is produced on the same side where the steam is fed and, therefore, drying the hydrogen outlet flow is required to remove humidity. By contrast, PCC cells produce dry pure hydrogen directly on the fuel electrode side. An additional advantage with PCC cells is the possibility of performing electrochemical compression by increasing the operating pressure of the fuel electrode and, thus, producing compressed hydrogen. This operation allows one to simplify the system and increase its efficiency [266]. Among the other advantages of PCC cells is the fact that these cells can operate at a lower temperature than SOECs. In this regard, PCC's high ionic conductivity and low activation energy enables it to operate in the temperature range between 600 and 700 °C [267]. Such a reduction in the operating temperature reduces the overall cost of the system allowing the use of cheaper materials for both the BoP and the interconnects [142]. The low operating temperature of PCC cells compared to SOECs also limits cell degradation, preserving performance [260, 268–270]. Moreover, for what concerns the co-electrolysis process, at low temperatures the thermodynamics shifts toward production of a CH_4-rich gas and thereby increase the volumetric energy storage density.

It has already been mentioned that PCC cells are gaining interest in the field of high-temperature electrolysis. The versatility of these cells makes them suitable for several applications other than mere hydrogen production, in some of the key sectors for hydrogen handling, purification, separation, filtration, and compression.

Iwahara et al. [176] used PCC membranes as solid electrolytes for electrochemical dehumidification. For this specific application, the target gas enters the cell and undergoes the electrolysis process that reduces the water content of the gas from inlet to outlet. This process also enables small amounts of water to be effectively removed from the inlet gas. In particular, it was observed that, by using a $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ electrolyte and porous Pt as electrodes, dehumidification could be performed successfully even on Ar containing only a small amount of water ($PH_2O = 45$ Pa) arriving at $PH_2O = 6.7$ Pa by applying a current density of 150 mA/cm^2 [176]. One more application investigated for PCCs is the electrochemical reduction of CO_2. The experiment performed by Xei et al. [207] consisted in feeding H_2O into the air electrode and CO_2 into the hydrogen electrode separately, and resulted in the following reaction scheme:

$$\begin{aligned}
&\text{Air electrode:} && 2H_2O \rightarrow 4H^+ + O_2 + 4e^- \\
& && H_2 \rightarrow 2H^+ + 2e^- \\
&\text{Hydrogen electrode:} && 2H^+ + 2e^- + CO_2 \rightarrow CO + H_2O \\
& && 8H^+ + 8e^- + CO_2 \rightarrow CH_4 + 2H_2O
\end{aligned}$$

The process developed by Xei et al. [207] showed a conversion rate of 65%. This value is much higher than the 37% characteristic of the reverse WGS reaction and the 11.5% obtained with SOECs [271]. The final gas composition obtained was 61% CO, 8% H_2, 1.2% CH_4, and 29% of unreacted CO_2.

One more application of PCC consists in the reduction of NO, one of the most harmful compounds emitted from internal combustion engines. In this connection one should mention the study performed by Kobayashi et al. [272] where PCCs were used to reduce NO. This specific application required the use of electrolyte materials that could operate in the acidic NO atmosphere. Kobayashi et al. [272] used PCCs with a $SrZr_{0.9}Yb_{0.1}O_{3-\delta}$ electrolyte NO reduction. The reactions that occur to reduce NO under electrolysis conditions are:

$$2NO(g) + 4H^+ + 4e^- \rightarrow N_2(g) + 2H_2O(g)$$

$$2NO(g) + 2H^+ + 2e^- \rightarrow N_2O(g) + H_2O(g)$$

$$NO(g) + 5H^+ + 5e^- \rightarrow NH_3(g) + H_2O(g)$$

The main products of the reduction reactions were N_2O and N_2 at low current densities, and N_2 and NH_3 at high current densities. The results showed that 100% removal could be achieved for current densities higher than 1.2 mA/cm^2 at 450 °C [273]. The use of PCCs for NO reduction allows one to use gases where O_2 is present, as happens in the exhaust gases of engines. By contrast, SOEC cannot reduce NO in atmosphere containing O_2 [274]. The results obtained for NO reduction lead one to assume that PCC electrolyzers may be used for the electrosynthesis of ammonia.

Figure 5.5 shows the operating principle of a PCC cell used for steam electrolysis.

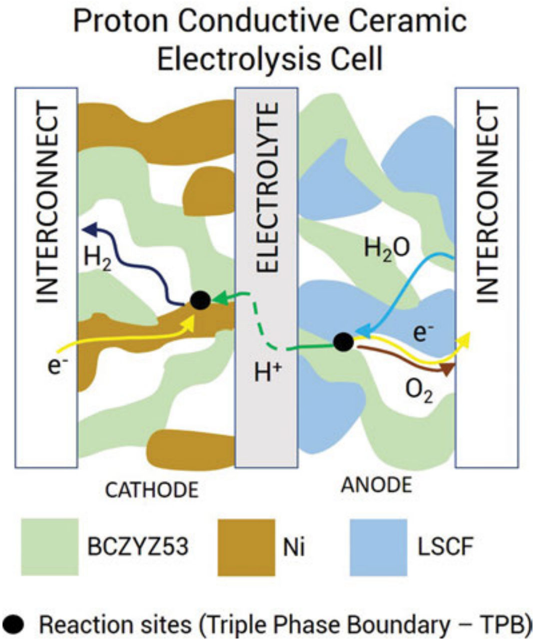

Fig. 5.5: Schematic illustration of a PCC cell for steam electrolysis. The oxygen ion transporting phase is represented in green and, among the several materials under research, can be given by Ni-BaCe$_{0.5}$OZr$_{0.3}$Y$_{0.20}$O$_3$. The electron conducting phases at the cathode and anode side are generally the same used for SOEC: Ni (ochre) and LSCF (light blue), respectively. The pores for the gas transport are represented as transparent. The fluxes of the species involved in the reactions are represented by arrows: light blued for steam, dark blue for hydrogen, red for oxygen, yellow for electrons, and green for hydrogen ions. The reaction sites where the three phases meet each other are indicated by black dots.

PCC electrolyzers generally operate at high temperature. However, as with SOECs, intermediate temperature PCC electrolysis is gaining interest for the various advantages it offers over high-temperature technology. In particular, the reduction of system complexity and cost makes this technology particularly appealing for future use. As already seen, IT-SOEC offers advantages over high-temperature SOEC. However, there are some drawbacks in addition to the ceria reduction already mentioned. For instance, reactions by the frequently used $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) with both Ni on the fuel electrode and MIEC oxide on the air electrode [165]. One of the main advantages of intermediate temperature PCC electrolyzers compared to ceria-based IT-SOEC is the high ion conductivity of the material used in the range of operating temperature. Moreover, let us repeat, one of the main advantages of PCC technology over SOEC is that while the latter requires H_2 to be separated from water after production, pure hydrogen is produced on the fuel electrode side when using PCCs. This fact helps to simplify the system and thus reduce operating costs [275]. At the same time, development of new materials is constantly being investigated. Wu et al. [276] used a novel proton conductor as the electrolyte and a triple-conducting oxide (H^+, O^{2-}, and e^-) as the oxygen electrode. The cell tested by those authors displayed promising performance, reaching a power density of 230 mW/cm^2 at 0.7 V and a current density pf −1.33 A/cm^2 at 1.5 V at 600 °C [276]. The proposed materials yielded higher ionic conductivity [277, 278] and better chemical stability [279, 280] with Ni at intermediate temperatures, and resulted in a cell ASR of 1.37 Ω/cm^2 at 600 °C [276]. The authors [276] operated a cell with a $BaZr_{0.1}Ce_{0.7}Y_{0.2-x}Yb_xO_{3-\delta}$ (BZCYYb) electrolyte, a $BaZr_{0.1}Ce_{0.7}Y_{0.2-x}Yb_xO_{3-\delta}$ (BZCYYb) oxygen electrode, and a Ni-BZCYYb hydrogen electrode below 600 °C achieving 1.33 A/cm^2 at 1.5 V in electrolysis mode.

5.3.3 Application prospects for PCCs

5.3.3.1 Hydrogen separation

Hydrogen can be purified by the process known as hydrogen separation. Usually, proton-conducting membranes with electronic-protonic conductivity are used to separate hydrogen from the components it is alloyed with. Separation can occur only if a chemical potential gradient is established between the two faces of a membrane; the hydrogen flow is driven by this potential gradient that corresponds to the difference in hydrogen partial pressure ($P(H_2)$ on one side of the membrane being lower than $P(H_2)$ on the other side). The pressure gradient is controlled by hydrogen concentration, temperature, and an electric field [281]. Diffusion of protonic defects through the membrane occurs from the region at high $P(H_2)$ to the region at low $P(H_2)$. The overall hydrogen separation process can be summarized as four main steps:

1. The molecules of hydrogen diffuse on the inlet side where they are absorbed by dissociation.
2. Protonic defects diffuse in the ceramic proton-conducting phase of the membrane while electrons diffuse through the electronic phase of the membrane.
3. Protons are reduced on the drain side of the membrane.
4. After re-association and desorption, hydrogen moves away from the surface.

Figure 5.6 illustrates the mechanism of separation from a complex mixture of gas at the anode of the cell to a purified hydrogen at the cathode.

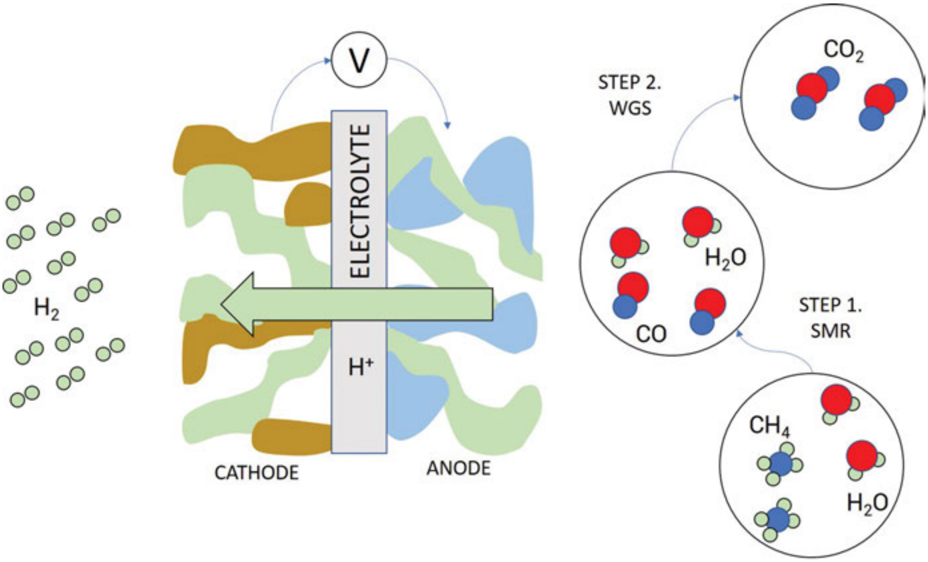

Fig. 5.6: Hydrogen purification: methane is reformed with steam at the anode side (steam methane reforming – SMR) and the hydrogen protons, resulting from the water–gas shift (WGS) reaction, are transported to the cathode side for hydrogen production.

One of the main challenges of proton-conducting membranes for hydrogen separation is ensuring high hydrogen flux. A primary role is here played by the membrane material that heavily affects the rate of hydrogen oxidation and/or electron conductivity and, consequently, the hydrogen permeation rate of the proton-conducting membrane. Adequate hydrogen separation membranes are assumed to have both protonic and electronic conductivity higher than 0.1 S/cm [282]. The most commonly studied proton-conducting materials for hydrogen separation are perovskite-type oxides ($SrCeO_3$, $BaCeO_3$, and $BaZrO_3$) [281]. However, most of the materials being investigated still exhibit low electronic conductivity that prevents high hydrogen flows from being attained. To offset this problem, the development of dual-phase ceramic membranes is gaining interest in this field. Usually, Ni is used in the electron conducting phase thanks to its high conductivity, catalytic activity for hydrogen oxidation, mechanical stability, and low cost of membrane fabrication.

5.3.3.2 Hydrogen compression

The widespread use of hydrogen is conditioned by the storage capacity of this energy vector. Of the various hydrogen storage techniques being studied, compressed hydrogen tends to be the most mature. However, one of the main limitations in terms of cost is the need to add a compressor to the conventional electrolysis technique currently used to reach pressure values suitable for storage purposes. The use of high-temperature PCCs offers the possibility of performing electrochemical hydrogen compression. Proton ceramic electrolyzers can produce hydrogen directly at high pressure [283–285].

Figure 5.7 illustrates the compression mechanism.

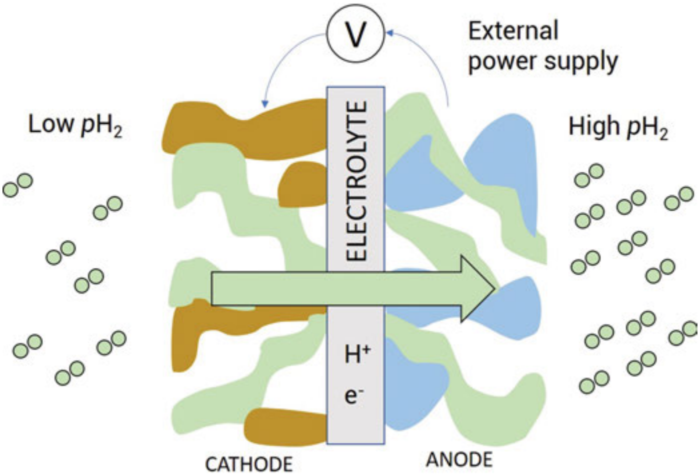

Fig. 5.7: Hydrogen compression: the hydrogen protons pass the membrane from the low-pressure cathode toward the high-pressure anode as a result of the applied voltage.

The first systems utilizing this technology are currently being studied. For instance, a thermodynamic analysis was performed on proton ceramic electrolysis cells used for reforming hydrocarbons or for water electrolysis. The system produces lightly compressed hydrogen, which is then fed into a polymer-based electrochemical membrane compressor to increase the pressure up to 1,000 bar [286]. This approach could be used for hydrogen refueling stations.

5.3.3.3 Hydrogenation and ammonia

Electrochemical hydrogenation/dehydrogenation can be used for different purposes such as synthesizing high-value chemicals (CH_4 from CO_2 and H_2O conversion [287], NH_3 from H_2O and H_2 conversion [288–290]) as well as reforming to higher-value chemicals (C_6H_6 from CH_4 and H_2 conversion [291], conversion of CH_4 to H_2 and CO_2 [283], conversion of C_2H_6 to C_2H_4 and H_2 [292]). Application of PCC cells in this field is acquiring interest for ammonia synthesis. Ammonia is an important chemical frequently used in the fertilizer industry [293]. It is also an important energy carrier thanks to its energy density of 22.5 MJ/kg (HHV), which is approximately half the energy density of a typical hydrocarbon but higher than metal hydrides [294, 295]. Again, ammonia can easily be liquefied and the infrastructure for transportation and storage is already well established [296]. The Haber–Bosh process is currently the most widely used for ammonia production. However, the hydrogen used in this process is produced by external reforming of fossil fuels, usually through steam methane reforming, making the process energy expensive and high polluting [297]. This has encouraged the development of energy-efficient and environment-friendly ammonia synthesis technologies. Both oxygen ion conducting reactors and proton ceramic reactors have been studied and used for ammonia synthesis. The different electrochemical mechanisms occurring in PCC as compared to oxygen ion conducting cells affect reactor architecture. One of the main differences between the two technologies is that water and N_2 are supplied together to the negative electrode in conventional oxygen ion conducting reactors while only N_2 is fed to the negative electrode of PCC-based reactors and thus water is not in contact with a catalytic active interface. In the last decade, PCC cells have been considered as particularly suitable for this purpose for:

1. their ability to synthesize ammonia directly from water and nitrogen without any external reforming process [298];
2. their ability to operate around 400 °C close to the optimal temperature for ammonia synthesis from hydrogen and nitrogen [298];
3. their ability to render the process more efficient by supplying protons directly and by regulating the potential to act on the catalyst activity [298].

The electrochemical synthesis of ammonia was first demonstrated by Marnellos and Stoukides in 1998 when they supplied hydrogen to the anode of a proton-conducting cell that used $SrCe_{0.95}Y_{0.05}O_{3-\delta}$ as its electrolyte [299]. The experimental results spoke of a conversion efficiency (current efficiency or faradaic efficiency) of 78% at 2 mA/cm^2 resulting in an ammonia production rate of approximately 6×10^{-9} mol/cm^2, much lower than commercial requirements. Many studies were performed in the following years without any significant improvement in the ammonia flow rate that remained in the order of 10^{-9} mol/cm^2 when using N_2 and H_2 [300, 301] and in the order of 10^{-10} mol/cm^2 when using N_2 and H_2O [288, 290]. In this regard, the three main challenges to enhancing PCC performance may be summarized as:

1. Thinning the proton-conducting electrolyte to enhance the proton flux. The proton-conducting material for the electrolyte needs to guarantee high proton conductivity with low electronic leakage [298].
2. Materials facilitating the reduction of nitrogen need to be developed for the cathode electrode and/or the cathodic catalyst [298].
3. The cell components’ microstructure needs optimizing so as to maximize the reaction sites and readily exhaust the synthesized ammonia for higher ammonia selectivity.

Once these challenges are overcome, the use of PCC cells for ammonia synthesis could well trigger a transition toward production of renewable ammonia. The use of PCC reactors at intermediate temperatures allows one to operate in a temperature range favorable to the thermodynamic and kinetic conditions of the ammonia synthesis process. Nitrogen hydrogenation is an exothermic reaction facilitated at low temperatures and atmospheric pressure. However, the operating temperature range that gives the maximum ammonia production rate is reported to be around 300–400 °C [302]. It was observed that the Faradaic efficiency of ammonia production decreased with increasing temperature, reaching a value as low as 10^{-5}–10^{-4} in the operating temperature range of 400–600 °C [302] where the balance of kinetics and thermodynamic forces lowers Faradaic efficiency and selectivity for ammonia production. Moreover, the only separation process that will take place is the separation of ammonia from nitrogen and hydrogen fluxes that will then be recycled to the reactor [302]. The ammonia production rate is enhanced at high pressure, so the possibility of producing high-purity and electrochemically compressed hydrogen with PCC technology would prove particularly advantageous for ammonia production, including from an economic point of view. For what concerns ammonia production at ambient pressure, one of the main issues is the lack of ammonia synthesis catalysts compatible with the negative electrode and easily integrated into the cell at such pressure. While operating at high current densities could increase hydrogen concentration at the negative electrode and contribute to ammonia production, high hydrogen concentration can poison the catalyst surface. So active removal of ammonia from the negative electrode may bring about a shift in the reaction equilibrium, improving ammonia selectivity and the production rate [302].

For what concerns the uses of ammonia in the hydrogen sector, one should note that recently Air Products signed a 5 billion $ agreement with ACWA and NEOM for the construction of an ammonia-based facility to produce green hydrogen by renewables (wind and solar) including advanced storage technologies. The project foresees the development of a new model for sustainable living located in the northwest corner of the Kingdom of Saudi Arabia where ammonia will be produced for exportation to global markets. The plant is expected to use electrolysis technology and produce 650 tons of hydrogen per day. The technology developed by Air Products will be used for producing nitrogen. Lastly, Haldor Topsoe technology will be adopted to guarantee the production of 1.2 million tons of green ammonia per year, equal to 0.6% of the annual global production of ammonia. Figure 5.8 illustrates the working principle of a PCC for the three operating modes mentioned: hydrogen purification, hydrogen compression, and ammonia synthesis.

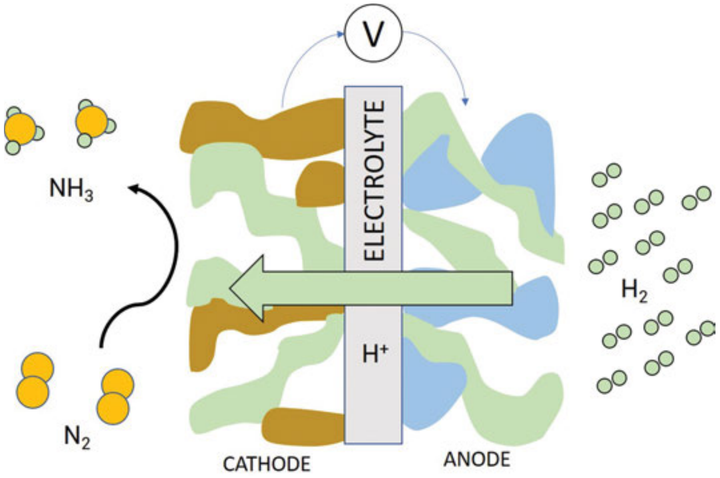

Fig. 5.8: Ammonia synthesis: hydrogen and nitrogen are fed at the anode and cathode side, respectively. The transport of hydrogen protons from the anode to the cathode sides allows the reduction of nitrogen for the synthesis of ammonia at the cathode side.

5.4 Conclusions

The development of highly performing and cost-effective hydrogen production technologies is vital, given the potential of hydrogen in a flexible energy system, with its capacity to attain net zero carbon emissions in sectors hard to decarbonize by other technologies. Electrolysis technology is here rated one of the most promising ways to release green hydrogen for several end-uses in the mobility, industrial, and residential sectors.

Electrolysis is a wide sector embracing many technologies. Among them high-temperature electrolysis holds promise for all end uses, offering a specific set of advantageous characteristics, including flexibility, fuel tolerance, reversible operation, efficiency, and use of waste heat resources.

Two major technologies are likely to meet their targets in terms of performance and cost: the more mature is solid oxide electrolysis, and the more promising, PCC electrolysis.

There is room for improvement with various technologies, from identification of the proper materials and structures for PCCEL, to improvement of performance and reduction of costs with SOEL, including issues with lifespan and degradation. Especially relevant for specific application sectors are fuel tolerance and flexibility, efficiency, and the prospect of power density increasing in future.

These technologies promise some embedded added values such as the use of waste heat to reach net overall conversion efficiencies close to 100%, or the functions of compression, purification, separation, and filtration.

Fuel tolerance may likewise be extended beyond the limits of purity levels, and include the direct use of other carriers, not only methane-rich mixtures, but also ammonia. This option could well pave the way to SOC technology being used in new applications such as transport systems and the maritime sector.

A vigorous research and innovation program in Europe and worldwide is focusing on these technologies that may well evolve to the point of market maturity in the near to mid-future.

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Luca Sementa, Fabio R. Negreiros, Alessandro Fortunelli

6 The use of hydrogen in ammonia synthesis, and in oxygen and carbon dioxide catalytic reduction – the reaction mechanisms

Abstract: We report three paradigmatic examples of atomic-level computational modeling of catalytic processes of hydrogen use in the energy and environmental fields: ammonia synthesis (in particular the Haber–Bosch, HB, process), oxygen reduction reaction (ORR), and the carbon dioxide reduction reaction (CO2RR). Reaction mechanisms for these processes are illustrated first in a general overview and then in the specific cases of: a single-crystal Fe bcc(111) surface for HB, nanostructured systems (nanoporous particles, a small cluster, and nanowire) for ORR, and subnanometer (or ultranano) Ni_3 and Ni_2Cu clusters for CO2RR, respectively. Our goal is to show the potentialities of predictive computational modeling in this field as a basis for progress and possible breakthroughs in the rational design of catalysts satisfying the stringent societal requirements to H_2 utilization for sustainable energy and matter cycles.

Keywords: ammonia synthesis (NRR) - oxygen reduction reaction (ORR) - carbon dioxide reduction reaction (CO2RR) - nanoparticle catalysts - reaction free-energy diagrams - theoretical modeling - rational design - small molecule activation

6.1 Introduction

Catalysis is a crucial enabling technology in view of using H_2 as a sustainable form of chemical energy storage and to support sustainable carbon and nitrogen cycles at the global level. The strength of the H–H bond, and the even greater strength of the C≡O, =C=O, N≡N, and O=O bonds that H_2 is called to reduce, combined with the sheer number of hundreds of million tons of mass to be converted, make the development of appropriate catalysts at the same time mandatory and extremely challenging. Despite the huge efforts spent up to now to solve these challenges, existing catalytic systems do not satisfy the requirements of efficiency, selectivity, sustainability, environmental compatibility, and cost. This suggests that traditional strategies for catalyst design have come to an impasse. To overcome this impasse, alternative routes to discovering new and improved catalytic systems need to be found. Knowledge-based strategies have been proposed to this purpose and appear as the most promising, based on the two pillars of novel in situ characterization techniques and predictive modeling – the latter being the topic of the present contribution.

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In the last decades, continuous advances in hardware, software, and computational methods have widely extended the scope of systems and processes accessible to computational modeling, both in size (length- and timescales) and complexity. We are reaching a stage in which predictive simulations at the force field level can be conducted exceeding the limit: “(number of atoms) X (simulated time) ≈1,” thus allowing: (i) first, an atomic-level understanding of catalytic systems in realistic environments, such as real-size nanoparticles simulated for micro- to milliseconds, and (ii) second, extending the timescale and length scale from microscopic to mesoscale level via accelerated dynamics and multi-scale techniques. With the accuracy of force fields (existing or improved via, e.g., machine-learning algorithms) and of time- and length-rescaling approaches continuously increasing, the feature, unique to modeling, of being able to produce detailed information on energy barriers and transient (short-lived) intermediates that are hard to derive via other means but crucial for singling out and therefore potentially improving the rate-determining steps affecting catalytic efficiency, it is apparent that the long-sought dream of predictive simulations on par with experiment is becoming a reality.

It is equally clear that we are not there yet. Methodological and practical limitations still exist that prevent or delay the full realization of this dream. In the present contribution, we do not have space for discussing these limitations. Rather, we will briefly report the present status of atomic-level theoretical understanding of three of the most important catalytic processes of hydrogen use in the energy and environmental fields: ammonia synthesis (in particular the Haber–Bosch (HB) process), oxygen reduction reaction (ORR), and the carbon dioxide reduction reaction (CO2RR). Our aim is to illustrate the already significant achievements and the great potentialities of predictive computational modeling in this field, so as to provide a basis for future progress and breakthroughs.

Section 6.2 is devoted to preliminary general considerations and a brief discussion of methods. Section 6.3 focuses on non-catalytic steps, that is, mechanistic steps in which the catalyst does not play a direct role in reducing reaction energy barriers, but which are equally important in shaping the overall catalytic landscape. Sections 6.4–6.6 then focus on the HB process, the ORR and the CO2RR, respectively, and discuss our present understanding of these processes, with particular attention on rate-determining mechanistic steps.

6.2 Methods and general considerations

First of all, a brief note on the source of hydrogen. The H_2 molecule is a relatively high-energy intermediate or transient species which do not exist in pure form in sizeable amounts under environmental conditions. Here we adopt the hypothesis that, eventually, the only sustainable source of hydrogen will be via solar-energy-powered water splitting. Alternative sources (presently pervasive) are described elsewhere in this book. Assuming that a sustainable source of hydrogen exists, we will discuss the use of H_2 as a reducing agent in basic catalytic processes, starting from the currently dominant one (ammonia, NH_3, synthesis via the HB process, also called nitrogen reduction reaction (NRR)), to ones which nowadays have a niche diffusion but are expected to play a major role in the future hydrogen energy economy (ORR and CO2RR). The relative simplicity of these small molecules (N_2, O_2, and CO_2) and their activation (reduction) will allow us to illustrate fundamental catalytic concepts and mechanisms of general validity.

Before passing to the main content of this chapter, a few notes on methods. For reasons of space, we will skip here a detailed discussion of technical methodological aspects. Let us simply mention that in the theoretical work reviewed here, a typically atomistic approach is adopted, that is, using an explicit atomistic description of the system, with energy and forces either derived from first-principles or quantum-mechanical (QM) methods (usually at its practical level: density-functional theory (DFT)) or using parametric force fields. Note that we do not discuss and we refer to the original references for a discussion of the choice of the exchange-correlation functional in DFT approaches. Finally, if the catalytic system/event is limited in size, it can be described via finite-size structural models. If, instead, it is extended in size (such as a metal surface), it is best described via periodic models or via embedding within an external reservoir.

At the static level, geometry optimizations (relaxations) are used to single out local minima in the potential energy surface (PES), with such minima interconnected through energy barriers which are typically calculated using the (numerically not so stable) nudged elastic band algorithm [1].

At the dynamic level, molecular dynamics (MD) simulations, either first-principles or ab initio (ab initio molecular dynamics, AIMD) or classical MD using parametric force fields, are a common tool to provide a direct picture of the catalytic event in real time.

For activated processes, however, due to the limited timescale typically accessible to MD (significantly less than 0.1 µs for AIMD and less than 0.1 ms for classical MD), dynamics must be accelerated by various techniques such as raising the temperature artificially or transforming the PES in various ways [2]. In activated processes, it is appropriate to describe the system as basically residing in an ensemble of potential energy basins centered around local energy minima in the PES, interconnected through significant energy barriers. The PES is thus partitioned into a set of regions (energy basins around local minima) and transition energy barriers connecting them. Mathematically, this corresponds to transforming the PES is into a network or “graph.” Once such a network or graph of local minima interconnected via energy barriers is established, individual transition rates among local minima are usually calculated via transition-state theory [3], thus providing the basis for kinetic Monte Carlo (kMC) algorithms [4], that in turn enable predicting the system dynamics over the graph (and thus catalytic rates, etc.). It has been demonstrated that this approach can lead to accurate catalytic reaction (production) rates [5].

Not all the dynamic modes of the system are activated, that is, not all the dynamic modes present energy barriers larger than the thermal energy so that the PES can be described in terms of a network of local minima or graph. In particular, the treatment/description of the solvent in liquid/solid heterogeneous catalysis poses an issue to the strategy just described and to atomistic computational approaches in general. This issue is connected with the diffusive rather than activated energy landscape of the PES when a solvent is present. In other words, the solvent in its dynamics explores a vast number of structural configurations interconnected via very small energy barriers, of the order of thermal energy or less. Such a situation cannot be described as a network of local minima/energy basins, but rather must be dealt with using pure MD approaches.

At the first-principles MD level, in AIMD, a complication arises because of the limited timescale presently accessible to such dynamics (typically 1–2 tens of ps, hundreds of ps only in the most favorable cases). Some solvent dynamical modes that affect the energetics of important electro-catalytic events are of a timescale longer than 1–2 tens of ps, and are therefore hard to describe at the AIMD level. Moreover, solvent dynamical modes exist extending over length scales of several nanometers – tens or even hundreds. These modes are also hard to describe at the AIMD level because practical first-principles simulations are presently typically limited to systems of 1–2 nm in size. In this connection, it can be recalled that boundary conditions in the replicated periodic cells or in the direction perpendicular to the catalyst surface associated with such limited size of the unit cells may also introduce artificial constraints/stresses whose influence on the catalytic energetic is difficult to assess. As a way to overcome these issues, implicit solvent models can be used instead of explicit solvent models. In implicit models, the solvent is replaced with a polarizable continuum medium adding a term to the system Hamiltonian which is then solved self-consistently [6]. An implicit solvent approach entails a much smaller number of atoms than an explicit solvent one; it is, therefore, computationally much less demanding, and all the complicated statistical treatment of the solvent is avoided and buried into effective (semi-empirical) parameters of the polarizable medium.

An alternative solution to the issues presented by explicit solvent description in first-principles AIMD approach is the use of parametric force fields. The accuracy of force fields is much debated, especially for such a complex solvent as water, although recent progresses in force field development promise to enable MD simulations of water as accurate or even more accurate than AIMD [7]. Also, the length scale in MD simulations based on force fields is much larger than that of AIMD and encompasses the majority of solvation phenomena.

Despite all these issues, we should recall the important contribution that AIMD has given and can still give to the simulation of systems containing a solvent such as electro-catalytic systems, in terms of opening new paths, shedding new insight, and at the same time acting as a standard against which to compare alternative approaches. For example, phenomena such as the importance of Grotthuss-like diffusion mechanisms that will be discussed in the next section have been discovered via AIMD [8, 9].

In conclusion, there is no general consensus which is the most accurate and computationally efficient approach to the solvent issue, but it is to be expected that progress in software, hardware, and methods will soon shed further light on this topic.

Before entering into the discussion of specific systems, let us give a brief general overview of the mechanistic steps typically encountered in the following review. In fact, we think that it is useful to keep in mind a general picture of these possible occurrences when dealing with each given reaction and catalyst, not to miss exploring alternative possibilities that could help overcome the present impasse in catalyst design.

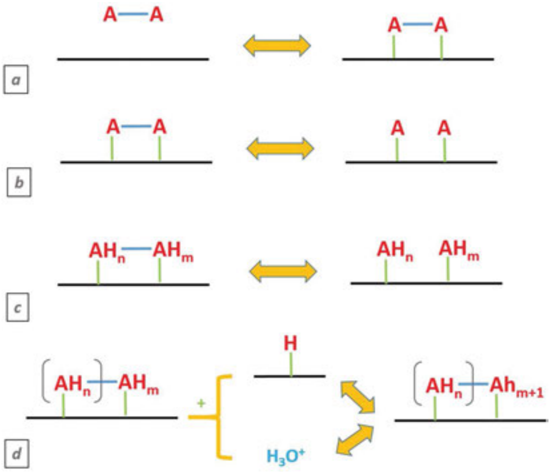

Fig. 6.1: Schematic depiction of the basic mechanistic steps involved in the A_2 reaction reduction (ARR) over a catalyst surface: (a) ad/desorption Eley–Rideal step of A_2; (b, c) dissociation/recombination steps with bond breaking/forming of A_2 (b) or variously hydrogenated A_2 species (c); and (d) hydrogenation step.

Let us focus for simplicity on NRR and ORR, that is, on the reduction of a homonuclear diatomic molecule that we can indicate with A_2 or A–A (representing N_2, O_2, H_2, etc.). The CO2RR case is a variation and a complication of this scheme. Figure 6.1 illustrates schematically the basic mechanistic steps involved in the A_2 reaction reduction over a catalyst surface.

The ad/desorption Eley–Rideal step of A_2 is illustrated in Fig. 6.1(a): A_2 approaches the catalyst surface and adsorbs onto/desorbs from it. A_2 is not the only species that can ad/desorb onto/from the surface: hydronium cations, H_3O^+, and hydroxide anions, OH^-, can also ad/desorbs via Eley–Rideal steps, as illustrated in Fig. 6.2, corresponding to electro-catalytic processes and thus implying an electron coming from/going into the electrode.

Figure 6.1(b, c) then shows dissociation/recombination steps, where, for clarity but at the price of some redundancy, we have distinguished A_2 bond breaking/forming (b) from the process in which the scission/recombination takes place after that A_2 has been variously hydrogenated and is thus transformed into a AH_n–AH_m species (c).

Figure 6.1(d) finally depicts a generic hydrogenation step: a H adatom adsorbed on the surface via a Langmuir–Hinshelwood H-migration mechanism, or a hydronium cation coming from the solution in combination with an electron from the electrode in electro-catalysis via an Eley–Rideal protonation mechanism, transform a AH_m species – or a AH_n–AH_m species – into a AH_{m+1} species – or a AH_n–AH_{m+1} species.

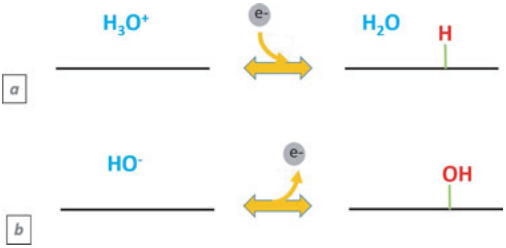

Fig. 6.2: Ad/desorption Eley–Rideal step of hydronium cation, H_3O^+, and hydroxide anions, OH.

Properly speaking, ad/desorption is a non-catalytic step. Dissociation/recombination is a catalytic step which does not involve hydrogen if A_2 is N_2 or O_2. The specific theme of this book is in the catalytic hydrogenation steps of Fig. 6.1(d). As we will see in the following, all these three processes can be rate determining.

The schematics of Fig. 6.1 may hide the chemical aspect of the involved processes. To remind that surface chemistry can be discussed and interpreted in terms of covalence, we have depicted in Fig. 6.3 the AH_m species and detailed them in the case of A = N or O, and added formal chemical bonds between such species and the surface, where a continuous green line represents a covalent single bond and a dotted green line stands for a dative or electrostatic bond. This simple valence bond view of bonding is often rather accurate. For example, when analyzing the spin state of NH_m species bound to the Fe bcc(111) surface, we have shown that there is a good inverse correlation between the spin state of the NH_m species and the number of their formal covalent bonds to the surface, with some provisos due to ligand field splitting (see Tab. 1 in [5]).

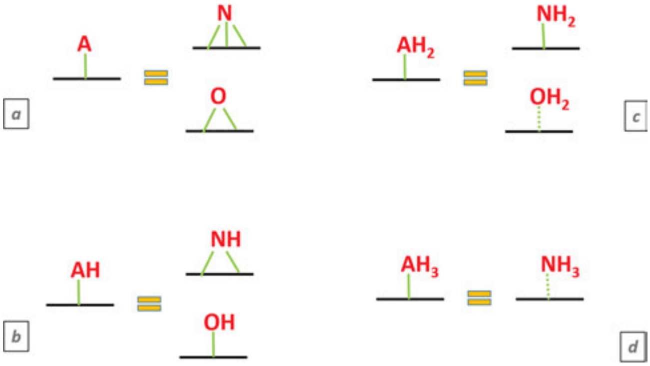

Fig. 6.3: Simple valence bond depiction of bonding of AH_m species (A = N or O) to the catalyst surface. Formal chemical bonds: a continuous green line represents a covalent single bond and a dotted green line stands for a dative or electrostatic bond.

6.3 Non-catalytic steps: diffusion and ad/desorption

As illustrated in Fig. 6.1, (i) diffusion (mass transport) and (ii) ad/desorption onto/from the catalyst surface – Fig. 6.1(a) – represent non-catalytic steps which anyway imply free-energy barriers and can thus contribute to the overall rate-determining effective free-energy barrier of the catalytic process, and thus to the associated catalytic efficiency, as will be discussed herewith.

Mass transport or diffusion (i), although facile in gas/solid heterogeneous catalysis, is anyway a factor to take into account. Indeed, recent simulations tend to include aspects such as explicit reactor modeling to arrive at a complete picture and predictive analysis of the catalytic process [10].

Diffusion may be slower and therefore represent a limiting step in liquid/solid electro-catalysis. In addition, the limited solubility of nonpolar (O_2, N_2) or non-dipolar (CO_2) species in polar solvents such as water may slow down the process and thus decrease reaction rates. Experimentally, the diffusion issue is usually circumvented via the rotating electrode technique. Polar solvents may seem inappropriate to convey nonpolar reactants to the catalysts, but are required to allow fast diffusion of hydronium (H_3O^+) cations or hydroxide (OH^-) anions. H_3O^+ and OH^- species in fact diffuse in water several times faster than most ions. This phenomenon is explained in terms of Grotthuss-like processes in which the diffusive species is not the heavy element (oxygen) but hydrogen (as a proton) jumping from/to the charged species to/from a neighboring water molecule, thus rationalizing the anomalously high proton conductivity of water [11], as illustrated in Fig. 6.4. It can be noted in this connection that collective or better concerted multiproton transfers have also been conceived and proposed to take place in water under standard conditions, a phenomenon corresponding to long jumps in the theory of atomic diffusion over surfaces and that can be in principle dealt with using the same methods [12]. Moreover, such Grotthuss-like (or generalized) diffusion mechanisms have been invoked to rationalize and claimed to play a key role in our current mechanistic understanding of ORR on platinum-based catalysts [8, 9] in other words, proton jumps can be effective in accelerating hydrogen migration processes at the electrochemical double layer (see below).

Fig. 6.4: Schematic depiction of Grotthuss-like processes rationalizing the anomalously high proton conductivity of water – hydrogen (better: proton) jumping from/to the charged species to/from a neighboring water molecule.

Ad/desorption barriers (ii) can also be rate determining.

Especially, in gas/solid heterogeneous activation of small, typically inert, molecules such as N_2, CO, and CO_2, we have recently claimed that adsorption barriers are ubiquitously found. The reason for this claim lies in the following argument. To break a strong bond (N≡N, C≡O, or O=C=O), a significant energy barrier is likely to be encountered, to overcome which high temperatures are needed. At high temperatures, entropic terms stabilize the gas-phase species – for example, for N_2, the entropic term is roughly proportional to the temperature via the formula ≈ 0.5 T/300 (where T is measured in Kelvin and the entropic term in electron Volt). Now, if the adsorption energy term (say – the electronic adsorption energy) is smaller than the gas-phase entropic term (as it is likely, due to the poorly polar character of the small molecules here involved and the fact that the catalyst surface is typically not a bare surface, but a surface at high coverage, that is, close to a saturation coverage of adsorbates), then the free-energy difference associated with the adsorption process (ΔG_{ads}) will be neutral or even positive, and an adsorption barrier ($\Delta G^{\dagger}{}_{\text{ads}}$) will arise. Roughly this adsorption barrier can be estimated via a simple argument as: $\Delta G^{\dagger}{}_{\text{ads}} = \Delta G_{\text{ads}} + |\Delta(\text{ZPE})_{\text{ads}}|$, where $\Delta(\text{ZPE})_{\text{ads}}$ is the zero-point energy contribution to enthalpy, as proposed in [5] for N_2 adsorption onto Fe bcc(111) at the appropriate coverage under reaction conditions. The important point is that, since ΔG_{ads} contains a term proportional to ≈0.5 $T/300$, which scales linearly with T, the beneficial effect of an increase in temperature will be partly cancelled by this increased entropic contribution to the adsorption barrier and thus to the overall effective barrier. This is the reason why experimentally determined apparent Arrhenius barriers and apparent Arrhenius factors are often much smaller than expected. For example, for the HB reaction or NRR over Fe bcc(111) at very low ammonia pressure, experiment finds an apparent Arrhenius barrier of only 0.68 eV [13], whereas the real free-energy barrier is estimated to be 1.62 eV [5], see Section 6.4 for further discussion. To the best of our knowledge, the importance of this phenomenon has been first pointed out for CO adsorption on $Ag_9Pt_{2,3}$ clusters in the catalytic CO oxidation process [14], and in NRR over Fe bcc(111) [5]. Figure 6.5 illustrates this phenomenon for O_2 and CO adsorption on Ag_9Pt_2 clusters functioning as catalysts of CO oxidation to CO_2: given adsorption energies of 0.6–0.77 eV, where these small values are due to the high-coverage status of the cluster catalyst in the real process, and given the relatively high working temperature of these catalysts (up to 300 °C), the adsorption barrier of O_2 onto the Ag_9Pt_2 cluster supported on α-alumina or the adsorption barrier of CO onto the Ag_9Pt_2 free cluster, both necessary steps in the catalytic cycle [14], do give a sizeable contribution to the overall effective free-energy barrier. Indeed, the experimentally measured Arrhenius activation energy for CO oxidation on these cluster catalysts is around 0.6 eV, much smaller than that expected from an estimate based on catalytic rates. From exploratory studies, we believe that this adsorption barrier issue also plays a key role in heterogeneous CO2RR, and is, in general, ubiquitous in small-molecule activation processes.

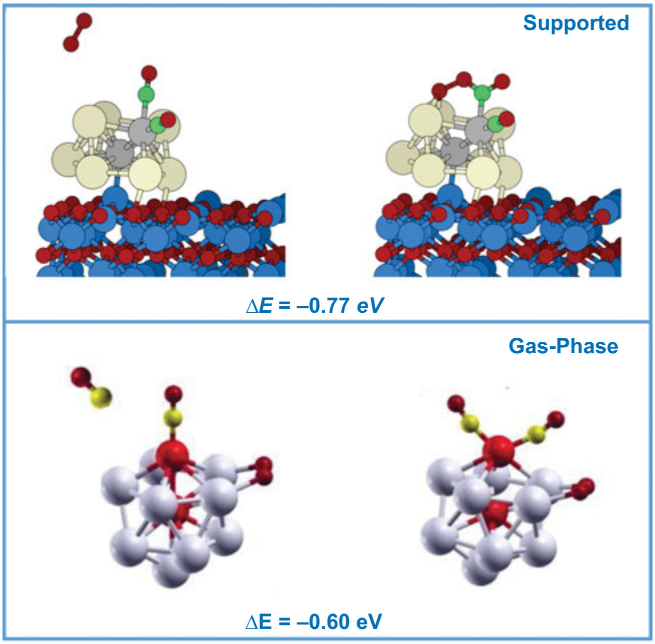

Fig. 6.5: Origin of adsorption barriers for O_2 and CO adsorption on Ag_9Pt_2 clusters as catalysts of CO oxidation to CO_2.

Despite the fast Grotthuss-like diffusion mechanisms discussed earlier and illustrated in Fig. 6.4, adsorption of H_3O^+ and OH^- species to a catalyst surface (see Fig. 6.2) may also suffer from free-energy barriers. We found preliminary indications of the importance of this phenomenon in a study of the hydrogen evolution reaction over a subnanometer $Ag_{12}Au$ catalyst [15]. In this work, AIMD simulations were conducted on a system composed of H_3O^+ (hydronium cation) and $Ag_{12}AuH_{11}^-$ (cluster anion) immersed in surrounding water environment. We found that several picoseconds passed before H_3O^+ migrated to the $Ag_{12}AuH_{11}^-$ cluster surface. Although we were not able to quantify precisely the value of the adsorption barrier, it may be thought of as stemming from the presence of the electrochemical double layer [16] which hinders H_3O^+/OH^- through diffusion. Further studies are needed to prove/disprove these first indications.

6.4 Nitrogen reduction reaction – ammonia synthesis via the Haber–Bosch process

The HB process, or the NRR transforming N_2 into NH_3, currently accounts for the largest use of molecular hydrogen, approximately sharing this record with catalytic hydrocracking of hydrocarbons. About 150 millions of tons of ammonia (NH_3) are produced yearly, most of which are then transformed into nitrates for fertilizers to feed a 7+ billion (and growing) world population. The HB process has enabled the agricultural revolution of the twentieth century, leading to more than doubling the world population. The great stability of the N_2 molecular nitrogen molecule with its strong $N{\equiv}N$ triple bond and the huge mass scale of this conversion necessitate very active, and environmentally friendly, catalysts. The catalysts currently in use in industry are based on iron (undisclosed modifications of the original pure-iron catalyst discovered by Fritz Haber in early twentieth century) and work at extremely high pressures (>200 atm) and high temperatures (>500 °C). Combining these extreme conditions with the huge mass scale of the conversion makes that the HB process is estimated to consume about 2% of the world energy and to produce 450 millions of tons of CO_2 yearly. Considering this enormous energy dissipation, it is clear that improvements of the HB process are strongly needed. Processes and catalysts alternative to traditional HB ones have then been proposed, including more active but environmentally problematic Ru-based catalysts [17] or via alternative paths such as electro-catalytic N_2 reduction or photo-catalytic N_2 reduction which strive to achieve less extreme reaction conditions by providing part of the energy required to split the $N{\equiv}N$ bond from electron or photon sources. Research in this direction is at its beginning, and it is challenging to lower overall free-energy barriers down to – say – 0.6–0.8 eV so as to enable the dream of a room temperature mass production of ammonia. Here, we will focus on recent progress in the understanding of the traditional HB process on Fe-based catalysts, on the issues hereby involved, also mentioning perspectives for improving Fe-based catalyst via, for example, multicomponent doping.

Our strategy, common to all the work expounded in this chapter, is that a sound theoretical mechanistic basis is a unique and potentially crucial tool to enable rapid and breakthrough progress in catalysis. Our hypothesis is that the knowledge of reaction mechanism at the atomistic level as drawn from theory and predictive simulations, starting from first principles and reaching out to the macroscopic level via multi-scale renormalization, can furnish the basis on which to build understanding, first, and then the sought-for rational design, therefore stimulating experiments on synthesis and optimization to arrive at improved catalysts that can work at much lower pressures and temperatures than those presently employed in industry. Irrespective of the fact that this work will pave the way to the preferred solution of the NRR problem or other avenues will be more successful, we trust that our review will illustrate a paradigmatic example of advanced analysis and design of catalysts based on crystalline (possibly multicomponent) surfaces as applied to the field of hydrogen usage.

We took the experimental work conducted on ammonia synthesis over pure iron single-crystal surfaces between the 1980s and the 1990s of the last century by the groups of Gerard Ertl and Gabor Somorjai as a starting point. This work has provided reasonably accurate experimental data to contrast and validate our modeling. In particular, we took the results [13] where HB reaction rates on Fe bcc(111) and bcc(211) surfaces were reported, usually at a total pressure around 20 atm (5 atm of N_2, 15 atm of H_2, and variable but typically low pressures of NH_3) and temperatures in the range 638–773 K, finding, for example at 673 K, ratios in initial reaction rates of 418:25:1 for the surfaces: Fe(111), Fe(100), and Fe(110), respectively. In the work of Somorjai et al., potassium was also added as a promoter, but the resulting systems were much less characterized structurally with respect to those without the promoter, so that we decided not to simulate the promoter data in this preliminary investigation. Another crucial experimental information we used was reported by Kandemir et al. [18] who were able to conduct neutron diffraction characterization measurements on the industrial HB catalyst (so called “ammonia iron” catalyst), and determine that the bulk of the catalyst structure is compatible with bcc α–Fe, showing no indications of bulk nitrides despite these being, in principle, thermodynamically favored under HB reaction conditions. This experimental work provided a sound basis for our modeling: we could restrict and focus our attention on single-crystal Fe bcc surfaces and conduct an extensive QM investigation of these systems in the HB process – to the best of our knowledge, achieving the most extensive theoretical investigation conducted so far in the heterogeneous catalysis arena.

At this point, we had to choose which single-crystal Fe bcc surface to investigate. We selected the bcc(111) and bcc(211) surfaces (for reasons of space, we will here discuss only the bcc(111) case), on the basis of two reasons.

First, experiment shows that bcc(111) and bcc(211) are the two most catalytically active Fe surfaces [13]. This was also confirmed by our preliminary study with a comparison between bcc(100), bcc(110) surfaces on one side and bcc(111) and bcc (211) surfaces on the other side, which suggested that the HB overall free-energy barrier on the former surfaces were higher by ≈0.5 eV than on the latter systems (results not shown).

Second, our choice was supported by a purposely developed “steady-state Wulff construction.” In 1901, Wulff demonstrated that the optimal truncation of a metal particle is obtained when the distance of each facet from the center of the particle is inversely proportional to its surface energy [19]. The Wulff construction provides an easy way to produce optimally shaped particles (i.e., in their energetically most favorable shape) via computation: one simply calculates the surface energy of each facet for a given metal system and then uses the Wulff protocol to build the optimal shape of the particles of that metal – the Wulff construction. The Wulff construction is valid for bare particles. Under reaction conditions, the particle surfaces are invariably covered with various kinds of adsorbates: ligands, reactants, products, and intermediates. This high-coverage state modifies the surface energies, which should then be modified in a “generalized Wulff construction” to predict the optimal shape of the particles under reaction conditions. Moreover, kinetic modeling shows that the specific reaction conditions determine which species are most abundant on the catalyst surface and thus characterize the high-coverage state under steady state. Since our kinetic simulations provide accurate information on the relative time spent by the system in each state/configuration, we proposed a “steady-state Wulff construction” for predicting the shape of catalytic particles under reaction conditions, in which the energies of the various surfaces were calculated on the basis of the adsorbate coverage and populations predicted by the kinetic modeling under the specific reaction conditions.

Next choice was the QM model, for which we selected a bcc(111) (2x2) unit cell. This cell is large enough to describe accurately the energetics of adsorption and HB chemical transformations, and small enough to allow for an extensive QM study. We adopted in fact a methodology based on the accurate QM prediction of surface local minimum configurations and transition rates among them, combined with a full accounting for the detailed kinetic mechanism via kMC modeling. It should be underlined that for each configuration and transition state, we calculated not only the electronic energy, but also the phonon (vibrational) modes and therefore the entropic corrections that enable predicting the free-energy of such states under the given conditions. We were then able to draw a complete free-energy diagram as a function of reaction conditions (temperature and gas pressures of H_2, N_2, and NH_3). The reaction path so determined for bcc(111)-(2 × 2), illustrated in Fig. 6.6 at 673 K, 20 atm of total pressure in stoichiometric ratio of reactants and NH_3 pressure of 1.5 torr, is complex, involving 26 intermediate configurations and 17 transition states connecting them. Such reaction “hyper-graph” was then given as input to the kMC algorithm to determine the steady-state production rate and the population of each given system configuration for each given set of experimental conditions.

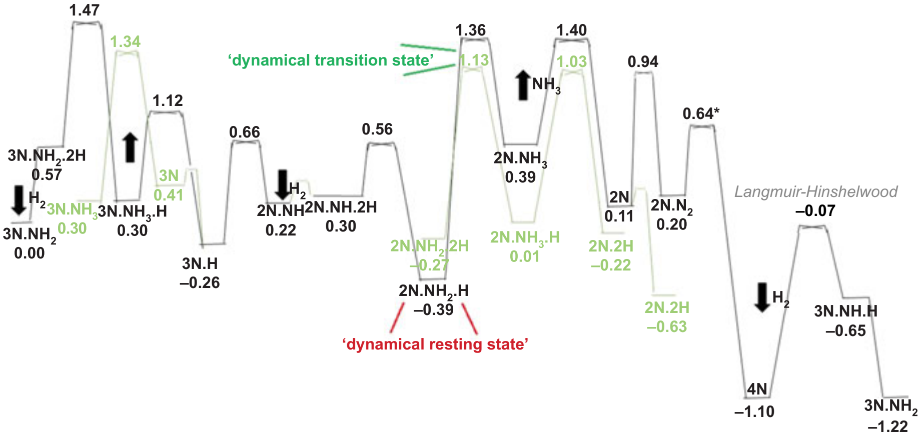

Fig. 6.6: Free-energy diagram for NH_3 synthesis at 673 K, 20 atm of total pressure in stoichiometric ratio of reactants and NH_3 pressure of 1.5 torr (the "3N.NH_2" state is taken as reference, a linear pathway is shown in black while an alternative operative pathway in green) (adapted with permission from [5]. Copyright © by American Chemical Society, 2018).

Let us briefly discuss the results. The predicted "turnover frequency" (TOF) at 673 K and 20 atm of total pressure in stoichiometric ratio of reactants and very low (1.5 torr) pressure of NH_3 is 17.7 NH_3 molecules/s/(2 × 2)-unit-cell (or 5.3×10^{-9} moles NH_3/s/cm^2). This is in excellent agreement with the experimental value of TOF ≈10 NH_3 molecules/s/(2 × 2)-unit-cell (or $\approx 3 \times 10^{-9}$ moles NH_3/sec/cm^2) [13]. Note that there is some uncertainty in the experimental values due to the difficulty of measuring precisely the NH_3 pressure at very low values, but in any case experimentally observed and computationally predicted TOF for HB under these conditions are within a factor of 2, implying an error in the predicted overall energy barrier of the order of 0.04 eV. Such an excellent agreement goes beyond previous qualitative or semiquantitative HB modeling, and validates our approach. This proves that it is possible to use advanced simulations to quantitatively interpret the HB process and therefore quantitatively design improved HB catalysts.

A second outcome of our kMC simulations were the populations of each given configuration or state of the system for each given set of experimental conditions, calculated as the fraction of time spent by the system in that given state. These populations are interesting because they allow, in principle, a more stringent comparison and challenge experiment to develop advanced in situ characterization of the system under steady-state reaction conditions in terms of species adsorbed on the surface. They also provide the weights with which the energy of each configuration must be multiplied to calculate the steady-state surface energies and thus the "steady-state Wulff construction" mentioned previously.

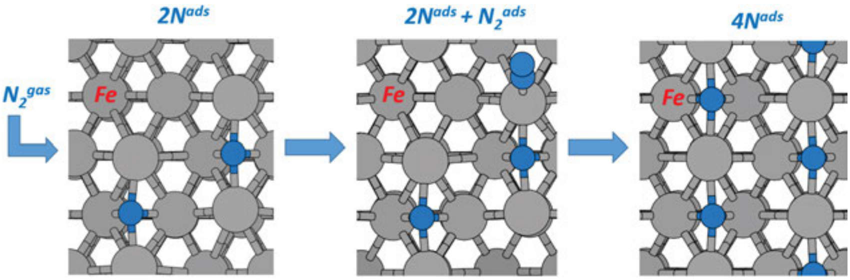

Fig. 6.7: Schematic depiction of "2N" conversion into "2N.N_2" and then "4N" over the Fe bcc(111) catalyst surface.

Let us analyze in more detail the predicted QM free-energy results and diagram. The first state to be singled out is the "resting state" of the catalyst, that is, the state of lowest free-energy under the given conditions without allowing the reaction to take place. Under the set of experimental conditions we explored, this resting state turned out to be either the "3N.NH2" or the "4N" state. Let us focus for simplicity on the "4N" state, illustrated in Fig. 6.7, rightmost side. It is worthwhile underlining that this resting state is a *high-coverage state*, that is, one in which the surface has maximum coverage of N species. This is not surprising, as the strong affinity of iron toward nitrogen that makes Fe potentially a good HB catalyst also entails that this high-coverage state is very stable: in other words, the system is very reactive and indeed it reacts! This however creates the problem that the Fe surface in the "4N" state is completely passivated by N species and unable to catalyze the HB process – in other words, N acts as a *poison*. As shown in previous modeling by Norskov and collaborators [20], two nearest-neighbor N-vacancies or empty sites are needed to adsorb and dissociate an incoming N_2 molecule. This cannot happen on the "4N" state, whose surface is fully covered, so that the system is required to transition at least to a "2N" state to have the two empty neighboring sites necessary to adsorb and dissociate N_2 (illustrated in Fig. 6.7, leftmost side). A basic catalytic cycle is then illustrated in Fig. 6.7: the system starts from the "4N" state, adsorbs and dissociates H_2 (this is possible as H_2 dissociation is an easier process than N_2 dissociation and can occur also on an N-passivated surface), the H adatoms hydrogenate two neighboring N adatoms via Langmuir–Hinshelwood mechanisms transforming them in sequence into NH, NH_2, and NH_3 species which can then desorb from the surface leaving behind two empty sites, as illustrated in Fig. 6.8 for the last steps: "2N.NH_2.H" → "2N.NH_3" → "2N + NH_3(gas)." This picture of a high-coverage catalytic process represents a progress in understanding with respect to previous modeling which was typically limited to the low-coverage régime (providing qualitatively correct but not quantitative indications). Not only this, these findings and methodological approach pave the way to a rational design of improved catalysts.

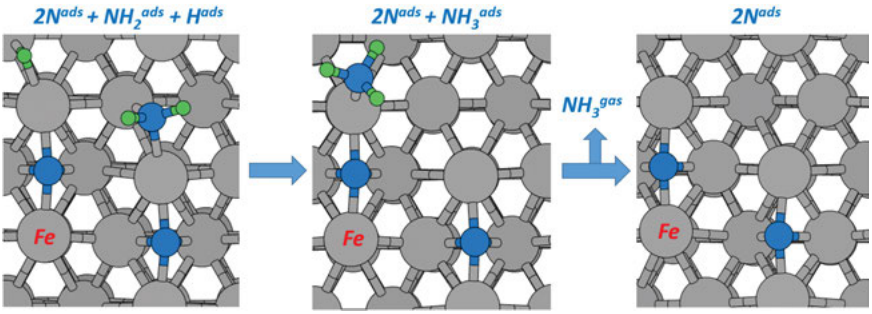

Fig. 6.8: Schematic depiction of “$2N.NH_2.H$” conversion into “$2N.NH_3$” and then “2N” over the Fe bcc(111) catalyst surface.

Looking at the free-energy diagram of the reaction path (Fig. 6.6), in fact, one can single out two most important configurations (highlighted in Fig. 6.6 by red and green colors, respectively): one is the “dynamical resting state” that is the configuration with the lowest free-energy in the diagram, one is the “dynamical transition state” that is the configuration with the highest free-energy in the diagram. In particular, at the beginning of the reaction (very low ammonia pressure, shown in Fig. 6.6), these two configurations correspond to the “$2N.NH_2.H$” local minimum state (the dynamical resting state) and the “$2N.NH_2.2H \rightarrow 2N.NH_3.H$” transition state (the dynamical transition state), respectively, whereas toward the end of the reaction (NH_3 pressure of 1 atm), the dynamical resting state still corresponds to the “$2N.NH_2.H$” local minimum state but the dynamical transition state corresponds to the “$2N+N_2 \rightarrow 2N.N_2$” transition state, respectively. Focusing for simplicity on pressure conditions of 1 atm NH_3, the overall HB reaction rate in a first approximation can then be very roughly described as a single-step reaction with a single barrier connecting “$2N.NH_2.H$” to the products via the “$2N + N_2 \rightarrow 2N.N_2$” saddle point. In this simple approximation, the HB reaction rate can be estimated via transition state theory as $\approx k_B T/h \cdot \exp(-\Delta G^{\dagger})$, where k_B is the Boltzmann constant, h is the Planck constant, T is the temperature, and $\Delta G^{\dagger}$ is the free-energy difference between the “dynamical resting state” (i.e., “$2N.NH_2.H$” under these conditions) and the “dynamical transition state” (i.e., “$2N + N_2 \rightarrow 2N.N_2$” under these conditions). This actually turns out to be a quantitatively good approximation (more refined kinetic analysis will be provided elsewhere).

This result led us to a twofold progress.

First, we were led to the observation that the effective HB reaction barrier under 1 atm NH_3 pressure conditions is composed roughly equally by the free-energy difference between the “2N.NH_2.H” and “2N” configurations, plus the N_2 adsorption barrier onto the “2N” state, that is, the process illustrated in Fig. 6.7, confirming the importance of the adsorption barriers, as anticipated in Section 6.3.

Second, considering that the adsorption barrier is somewhat insensitive to the details of the surface, we are led to the conclusion that – to decrease the overall HB free-energy barrier – we have to decrease the free-energy difference between the “2N.NH_2.H” and “2N” configurations.

Note that these considerations *do change* depending on reaction conditions, such as the pressure of ammonia, that is, they can change during the course of the reaction, from the beginning (low ammonia pressure) to the end (higher ammonia pressure). Hydrogen migration steps (Figs. 6.8 and 6.1(d)) are dominating the rate (i.e., they are rate determining) at low ammonia pressure, whereas N_2 adsorption and breaking – Figs. 6.7 and 6.1(a,b) – are dominating at high ammonia pressure.

We add and strongly underline in this connection that *hydrogen poisoning* is another process that is not rate determining on Fe bcc(111) but can become so for other surfaces/conditions. Let us explain this point in more detail. As we have seen, a good part of the overall HB barrier at high ammonia pressure is due to the free-energy difference between the “2N.NH_2.H” and the “2N” configurations. However, H_2 can competitively absorb and dissociate onto the “2N” configuration and generate a “2N.2H” configuration where the two empty sites of “2N” are filled with H adatoms. At this point, N_2 cannot as easily adsorb and dissociate on the “2N.2H” configuration as on the “2N” state, thus the process of N_2 absorption and bond breaking is slowed down or hindered by H adsorption – that is, hydrogen acts as a *poison*. This becomes particularly relevant if the free energy of the “2N.2H” configuration gets lower than that of the “2N.NH_2.H” configuration, because in such a case “2N.2H” will replace “2N.NH_2.H” as the dynamical resting state, and the overall HB barrier will now be given by the sum of the [“2N.2H” – “2N”] free energy difference plus the N_2 adsorption barrier onto the “2N” state. Note that hydrogen poisoning is also kinetically favored by the typically smaller absorption/dissociation barriers of H_2 with respect to O_2, N_2, CO, CO_2. H_2 adsorption barriers are typically smaller because the entropic translational (volume) term is proportional to the mass of the gas-phase species, which is thus >10 times smaller for H_2 with respect to the other heavier molecules considered here. H_2 dissociation barriers also tend to be smaller because of the higher reactivity of the H_2 bond with respect to the other bonds.

The issue of hydrogen poisoning is haunting all processes that use H_2 as a reducing agent, including, for example, CO2RR via gas/solid heterogeneous catalysis as discussed below. Note that its detrimental effect can be at times reduced by working under non-stoichiometric conditions, that is, by decreasing the H_2 pressure with respect to the stoichiometric ratio with other reactants. A beneficial effect on HB rate when working under non-stoichiometric, lean-H_2 conditions is a feature which had been experimentally observed when investigating alloyed catalysts for the HB process (e.g., for Fe–Ru in the patent [21]) but, to the best of our knowledge, this phenomenon has been rationalized for the first time only [22] by determining that H_2 acts as a poison in the case of a top-layer-Rh-doped Fe bcc(111) catalyst surface.

The picture of the HB process given above is somewhat sketchy. It should nevertheless be possible to understand how, by refining the above considerations, we were able to devise a "hierarchical high-throughput screening" approach and then to suggest optimal surface dopants to improve the HB process [22]. We are now pursuing this strategy further by considering ternary and quaternary doping of the Fe bcc(111) and the bcc(211) catalyst surface.

6.5 Oxygen reduction reaction

The idea of using H_2 as a fuel (energy storage), particularly in the automotive industry, has an old history, starting in the 1930s of twentieth century, but taking its modern form at the beginning of the 1970s, when some pioneers finally realized that, given the exponential increase in world population, an economy (energy production) based on fossil fuels was not sustainable in the long run. Popularizing publications then began to appear [23, 24]. In short, the idea is that H_2 is produced via renewable energy sources (solar, hydroelectric, wind, geothermic, pelagic) and is then burnt with O_2 in H_2 fuel cells (HFCs), for example, for transportation. The catalytic process occurring at the cathode of HFCs is named ORR – the topic of this section. This idea is based on several attractive features of H_2 as a fuel: (i) hydrogen (H) is the tenth most common element on earth by mass, the 4th by molarity (mostly bonded to oxygen in water); (ii) it is already widely used in industry: in 2007, 67 million tons of H_2 have been produced, roughly corresponding to 20% of world consumption of energy; (iii) burning hydrogen with oxygen generates water, with no consequent pollution (no CO_2, no particulates nor fine dusts), not even in case of a large leakage of this fuel; (iv) the energy content per mass of H_2 is high (33.3 kWh/kg); (v) refueling a H_2 car takes only few minutes and ensures an autonomy of hundreds of km; (vi) fuel cells can reach an efficiency of 35–50% versus 20%–30% of internal combustion engines. All this explains the huge investments in research on HFCs by the automotive industry (Toyota, Honda – partnering with GM, Hyundai, Daimler, Volkswagen) of the order of a billion US$ a year. Some issues however hinder the deployment of such an idea: (a) the energy content per volume of H_2 is low: 0.53 kWh/L for H_2 as a gas compressed at 200 atm versus 11.5 kWh/L of petrol; (b) H_2 being a high-energy intermediate, a significant amount of energy is needed to produce H_2; (c) the HFCs most efficient designed so far work in an acid environment, and therefore need proton-exchange membranes that are expensive (Nafion), although there are prototypes of low-cost membranes or membrane-less fuel-cell devices; (d) the only catalysts surviving under the extreme conditions of ORR in acid media are based on platinum, thus presenting issues of cost and sustainability.

Point (d) is the major issue preventing the development of a hydrogen economy, and the problem is basically a catalysis problem. First, a problem of stability: we need catalytic systems in the HFCs that are stable enough to power a H_2 car for 150,000 miles. Second, a problem of efficiency: we need systems that can convert H_2 and O_2 into H_2O fast enough to produce the needed energy with the minimal amount of such a precious element (Pt). With present stability and efficiency, about 80 g of Pt loading (0.25 g of Pt per kW) is needed to power a H -car (although there are prototype converters using only 30 g of Pt). If the 90 million cars yearly produced on the planet use 30 g of Pt each, we would need 2,700 tons/year of Pt, that is, more than 10 times the present yearly production (about 250 tons). Moreover, we would soon exceed the total amount of Pt on earth, estimated around 16/17 thousand tons. It is clear that H_2 cars based on Pt catalysts can become a reality only if each converter contains no more than 1–2 g of Pt at most, meaning that we need to find catalysts that are as stable as the present ones but more active by a factor of 15/30 (we ignore here the alternative option of working in a basic environment, which would enable using Ni-based ORR catalysts). That is, we need to find stable and much more efficient (or containing less precious metals) Pt-based ORR catalysts than the existing ones.

In this context, we will describe hereafter recent and promising results from our lab in understanding and designing Pt-based catalysts for fuel cells [8, 25, 26]. We follow the strategy common to all the work expounded in this chapter of providing a theoretical mechanistic basis as a tool to enable both fundamental and technological progress in catalysis and catalyst design. Irrespective of the fact that this work will pave the way to the preferred solution of the ORR problem or other avenues will be more successful, we trust that our review will illustrate a paradigmatic example of advanced analysis and design of catalysts based on non-crystalline (nanostructured) surfaces as applied in the field of hydrogen usage.

Our research started from previous experimental work in which Pt alloys with various metals such as Ni were tested as an alternative to pure Pt systems in an effort to reduce the amount of Pt in the catalyst. Notably, all these alloy elements were more electropositive than platinum. Oddly enough, experiments found a significant increase in the catalytic activity of alloyed systems, but at the same time discovered that after a few ORR electro-chemical cycles under working conditions most of the alloy element disappeared from the surface layers of the catalysts (we refer to our articles for original references). This represented a puzzle because the surface layers are those believed to be determining the catalytic process and its efficiency, thus the paradox of an alloy element which improved catalytic activity without being directly involved in the catalytic process. More detailed information: the alloy element (say – Ni, for definitiveness), under the harsh conditions of ORR in acid environment at high electro-chemical potential, would leach out of the catalyst and be dissolved as a Ni^{++} cation in solution. Only roughly 15–30% of Ni would remain into the bulk of the catalyst in sites far from the surface and therefore kinetically stabilized against leaching: the first 3/4 surface layers of the catalyst were totally devoid of Ni. The dissolution process would also leave holes in the catalysts particles, thus producing "nanoporous," open structures, a well-known phenomenon since the discovery of Raney nickel via Al dissolution from Ni–Al alloys in the 1920s. To explain the increased ORR activity of these systems, hypotheses on an electronic effect of the residual alloy element buried into the catalyst bulk were advanced, in keeping with previous arguments that a more electro-positive element than Pt would give charge to the surface and therefore reduce the barrier for some catalytic steps, such as O_2 dissociation (bond breaking) on the surface. Other hypotheses were also proposed.

In contrast with this previous modeling, our seminal study [25] adopted an opposite point of view, and the extreme hypothesis that the alloy element would completely leach out of the catalyst. This unexpectedly led us to the prediction that alloy element in fact has a purely sacrificial role, that is, it has no effect on catalysis per se, but acts simply as a tool to produce nanoporous surface arrangements of Pt systems which are more ORR-active than the original catalyst surfaces and indeed are the most ORR-active catalyst. This was impressively confirmed by later experiment, as we will discuss below.

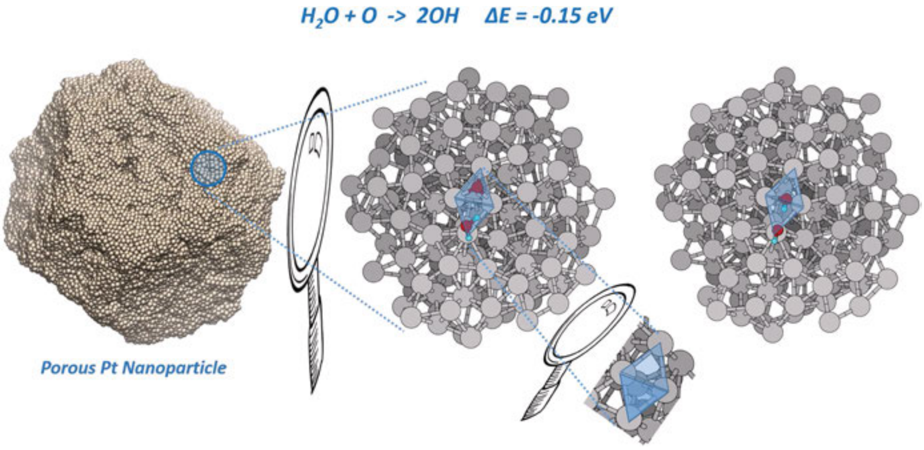

Fig. 6.9: (Left-most side) Atomistic depiction of the structure of a nanoporous particle; (middle) cluster extracted from the same nanoporous particle as in (left-most side) via a local embedded cluster re-optimization (LECR) procedure and adding O, H_2O absorbed on a surface rhombus; (right-most side) same cluster as in (middle) with two OH absorbed on a surface rhombus instead of (O, H_2O). Inset at the bottom four-atom surface rhombus.

We then first used force field modeling to produce structures of nanoporous particles of the same size as those used in experiment (up to 10 nm in diameter) and obtained the corresponding structural models – one of which is shown in Fig. 6.9

(left-most side). Figure 6.10 further illustrates some of our structural models and also shows the nanopores going through the particle. We then analyzed the surface structural motifs, that is, the atomistic arrangements or configurations of these systems, and contrasted them with those of regular pure Pt particles, for which previous research had shown that the most active and abundant surface was the fcc(111) surface. Interestingly, we found that most of the surface of the nanoporous pure Pt particles thus produced was smooth and resembling the fcc(111) surface. In particular, we found that the outermost layer of both fcc(111) and nanoporous particles could be described as tessellated by a typical four-atom motif that we named a "rhombic" motif, see the inset at the bottom of Fig. 6.9. A surface rhombus is an ensemble of four atoms arranged as two equilateral triangles sharing one edge, as shown in the inset of Fig. 6.9.

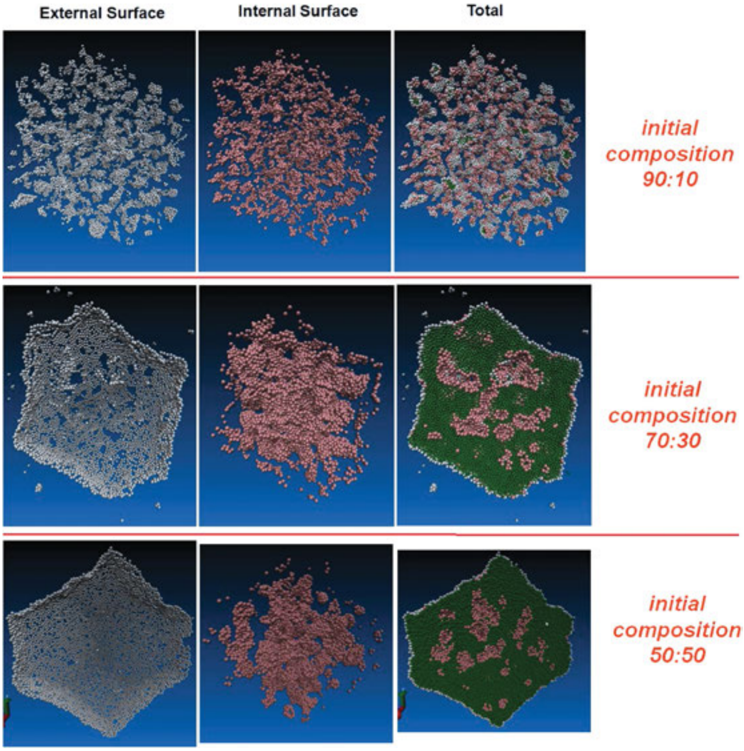

Fig. 6.10: Atomistic depiction of the structures of nanoporous particles generated by ReaxFF dealloying simulations. For each of the three initial compositions (given as Ni:Pt ratio) of the nanoparticles before dealloying as reported on the right-hand-most side, three pictures are reported, showing from left to right: the Pt atoms on the external surfaces in gray, the Pt atoms on the internal surfaces in magenta, and all the Pt atoms with the Pt atoms in the bulk in green.

To achieve a deeper understanding of whether this finding justified a difference in ORR catalytic activity, we resorted to DFT simulations. However, DFT calculations on a particle of 10^5 atoms were out of our (and all present) computational possibilities. To make the problem tractable, we needed to extract smaller pieces of the nanoporous systems and make them amenable to further DFT analysis. We then devised a local embedded cluster re-optimization (LECR) procedure focusing on a given rhombus on the surface of a nanoporous particle, we cut a piece of the particle surrounding the given rhombus and containing around 150–200 atoms (thus a system of a size amenable to DFT calculations). We optimized the so-produced geometry except for freezing the coordinates of the peripheral atoms, that is, of all those atoms which laid at the exterior of the cluster model and were under-coordinated because some of their neighbors had been cut off the model (this procedure is tantamount to imposing some sort of boundary conditions). DFT re-optimization was necessary because the nanoporous particle structures had been derived not via DFT but via force field modeling. At this point, we were able to compare directly ORR catalytic steps on fcc(111) and on rhombi taken from the nanoporous particle.

We were then able, first, to confirm a previous study on fcc(111) that suggested that the rate-determining step assumed so far for ORR did not correspond to O_2 dissociation, as previously assumed, but to later steps in the ORR cycle, such as the "oxygen hydration" step, that is "$O_{ads} + H_2O_{ads} \rightarrow 2OH_{ads}$," which can be described as a hydrogen migration from an adsorbed water molecule to an adsorbed oxygen adatom, as illustrated in Fig. 6.9 (middle and right-most panels) or to a "water formation" step, that is "$OH_{ads} + H_{ads} \rightarrow H_2O_{ads}$," which can be described as a hydrogen migration from the surface (or from the solution as a hydronium cation) to an adsorbed hydroxyl species. Second, we discovered that the overall barrier of the catalytic process was significantly dependent on the structure of the nanoporous particle surfaces. In particular, we found that these surfaces, despite being smooth at their exterior, still differed from the fcc(111) surface in that the surface atoms had a coordination number smaller than 9, around 7–8. Moreover, the overall ORR barrier was strongly affected by the arrangement of the underlying buried layers, and in particular we were able to demonstrate that if the vertex atoms of the rhombus were undercoordinated but had a crystalline-like fcc neighborhood, then the oxygen hydration step was exothermic and thus favored ORR, whereas if they had a fivefold, icosahedral-type coordination environment, then the oxygen hydration step was endothermic and thus disfavored ORR [25]. In other words, we discovered that surface atoms with the same number of neighbors and the same stress tensor but with a different coordination environment had a significantly different ORR catalytic activity, and that only fcc-like coordination environments but in the undercoordinated régime were favorable for ORR. In short, we discovered, within the limits of our exploration, that maximum ORR activity was achieved for undercoordinated but smooth and fcc-like Pt rhombi. This provided a powerful tool to quickly investigating and predicting the ORR activity of any given system via a statistical analysis of the coordination environment of the surface atoms. Indeed, we predicted that the optimum size of the nanoporous particles was around 8 nm in diameter and the optimum initial composition of the Ni–Pt alloy before the ORR-induced de-alloying process was around Ni:Pt = 70:30, in excellent agreement with experimental findings [25].

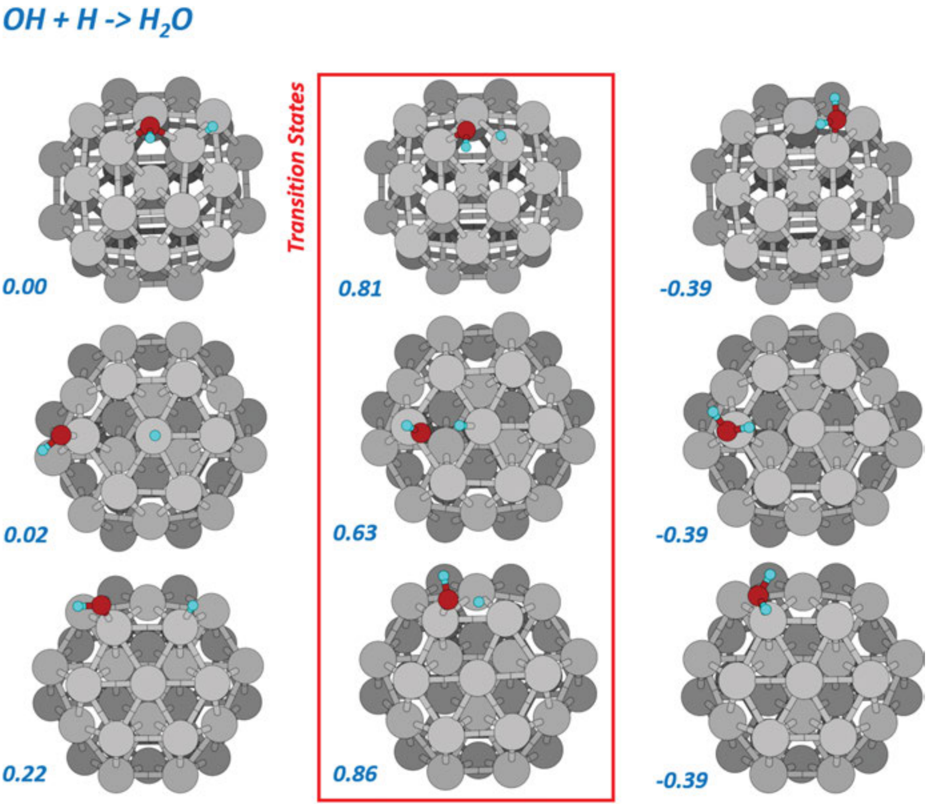

Fig. 6.11: Various H_2O formation steps ($OH + H \rightarrow H_2O$) on the surface of a Pt_{38} truncated octahedral cluster.

A subsequent investigation of ORR over a small cluster, Pt_{38}, in a fcc-like truncated octahedral configuration, confirmed the proposed picture and added further useful details [8]. In particular, we discovered that the reason why small Pt clusters had been found to be less active than larger nanoporous particles was to be sought in the abundant presence of square fcc(100)-like facets on their surfaces with respect to the optimal rhombic motifs. In other words, the nanoporous surfaces exhibited a triangular tessellation similar to that of a fcc(111) surface, which was superior in terms of ORR activity to a square tessellation more likely to be found on small clusters in the same way that the fcc (111) surface is more ORR active than other compact fcc surfaces such as fcc(100). Going into details, the sites at the intersection of (100) and (111) surfaces were sub-optimal in terms of ORR, and the main reason was that the high barrier of the "water formation" step, that is "$OH_{ads} + H_{ads} \rightarrow H_2O_{ads}$," which can be described as a hydrogen migration from the surface (or from the solution as a hydronium cation) to an adsorbed water molecule, due to the high bonding strength of the adsorbed hydroxyl to the stepped site of the surface, as illustrated in Fig. 6.11 for three representative cases.

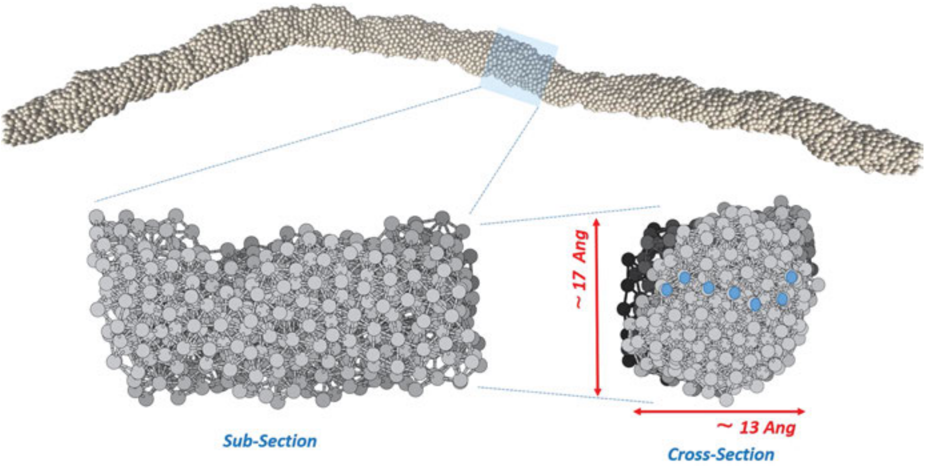

Fig. 6.12: (Top) Atomistic depiction of the structures of nanowires generated by ReaxFF dealloying simulations, starting with an initial composition of Ni:Pt = 70:30. (Bottom-left) Zoom on a piece of the nanowire from (top). (Bottom-right) A cross-section of the nanowire piece from (bottom-left).

The next step was in a way a natural development of this previous modeling. If the function of Ni to enhance ORR catalytic activity of Pt-based nanostructures is simply a sacrificial one, that is, to leach out of the system while leaving behind metastable Pt surface coordination arrangements optimal for ORR, then the best possible system should be obtained by de-alloying a Ni–Pt nanowire in such a way that a pure-Pt nanoporous nanowire would result, roughly 7–8 Pt atom wide in section and no residual Ni in the system. This would simultaneously optimize the surface area of Pt and make it greater than the nanoporous particle case, and confine Pt into the smallest possible nanostructures still however exhibiting either few square arrangements or square arrangements appreciably tilted with respect to triangular neighboring arrangements because of the structural continuity of the nanowires with respect to small clusters. This idea was then actually experimentally realized [26], obtaining pure-Pt nanowires with a cross-section of roughly 7/8 Pt atoms, having a very high surface area of 118 m^2/gPt (whereas the previous highest reported values, obtained for nanoporous particles, were ~70 m^2/gPt), and exhibiting a mass activity of 13.6 A/mgPt (at a bias of

0.9 V vs. RHE), which was ~50 times that of the state-of-the-art commercial Pt/C catalyst (0,26 A/mgrPt), still presently representing the record ORR activity reported so far. Interestingly, it should be noted that the mass activity of such nanowires more than doubled the mass activity value of 5.7 A/mgPt previously reported for Ni–Pt nanoframes of similar cross-section obtained via interior erosion of larger particles, despite the fact that the latter system still contained about 27% residual Ni in their structure, thus definitively disproving the electronic-alloying hypothesis. Schematic picture of nanowires as predicted by our force field simulations are shown in Fig. 6.12, showing the 7/8 Pt atom cross-section. For these systems, we calculated a van der Waals surface area of ~110 m^2/gPt, which agrees well with the experimental value derived from the electrochemically active surface area (118 m^2/gPt). Moreover, according to our statistical analysis these nanowires exhibited an unusually high number of ORR-favorable rhombic structures on the surface: 76% rhombi per surface atom in the nanowire surface with respect to 57% for the nanoporous particles.

Such Pt nanowire systems are reasonably stable and thus could be practically used in HFC devices, in principle requiring ~50 times less Pt than current commercial catalytic systems (therefore only ~1.6 g of Pt would be needed in a H_2-car converter of a standard vehicle). If this laboratory results could be translated into a practical device (even after further improvement, as it is clear that the de-alloying process could be much better controlled, maximizing the abundance of optimal surface configurations) a hydrogen economy could be enabled. The first tests, using competitor Pt nanoframes in HFC devices not optimized for the purpose, achieved an increase in ORR activity only a factor of 2 with respect to the ideal 22 enhancement factor, so it is not clear whether it will be possible to fully achieve the promised enhancement, or whether there are other issues to be solved to enable it, such as O_2 solubility, diffusion or mass transport processes (as recently suggested), etc. Time will say.

6.6 Carbon dioxide reduction reaction

The (photo/electro)-catalytic reduction of carbon dioxide is one of the great challenges that society poses to twenty-first-century chemistry. Major issues to be solved are associated with the complexity of the process, the variety of catalytic paths and the multiplicity of possible reaction products, together with the involved mass scale, and the dispersion of CO_2 in the atmosphere and in the oceans, assuming as our targets not only the achievement of a carbon-neutral energy cycle but also a global reduction of free CO_2 below the present levels. For reasons of space and considering the huge amount of previous literature, we will describe here only a tiny fraction of the many possibilities so far considered or envisioned, limiting to a single example of CO2RR via heterogeneous subnanometer metal cluster catalysts and a few features herein encountered. We hope that our review will be nevertheless illustrative of concepts and issues typical of the field.

Once more, we follow the strategy common to all the work expounded in this chapter of providing a theoretical mechanistic basis as a tool to enable both fundamental and technological progress in catalysis and catalyst design. Irrespective of the fact that this work will lead to the preferred solution of the CO2RR problem or other avenues will be more successful, our aim here is to illustrate a paradigmatic example of advanced analysis and design of catalysts based on multicomponent subnanometer (or ultranano) clusters as applied in the field of hydrogen usage.

We will try to illustrate four main points: (i) the many-body or synergic or coverage dependent energetics on these ultranano systems; (ii) the competition between CO_2 hydrogenation vs. bond breaking into CO + O, and the coverage as its key determining parameter; (iii) the path proceeding via the formation of formate (HCOO) and then formic acid (HCOOH) species, and the related thermodynamic issues; (iv) the formation of high-coverage unreactive complexes or catalyst self-poisoning and how to overcome this issue via alloying. To illustrate these points, we will use results from our study of CO2RR catalyzed by Ni_3 and Ni_2Cu subnanometer (ultranano) clusters deposited on the MgO(100) surface [27–29]. We note in this connection that the MgO(100) surface in this instance is clearly an idealized support, but its simplicity enables a systematic exploration of CO2RR at a level comparable to those of NRR and ORR discussed above, and is therefore appropriate to illustrate a few main concepts and issues typical of the CO2RR field.

(i) The many-body or synergic effects in ligand adsorption, in other words coverage-dependent energetics, play a crucial role in catalysis by ultranano metal clusters. These effects have been first pointed out for gas-phase species in cluster science [30] and first extended and reviewed in the context of heterogeneous catalysis in [28, 31, 32]. An illustrative example in the present context is given in Fig. 6.13, which shows the energetics of the following transformation. The starting state is a $Ni_3(HCOO)H_3$/MgO(100) cluster and the final state is a $Ni_3(HCOO)_2H_4$/MgO(100) cluster, where hydrogen adatoms and formate species are absorbed onto the initial Ni_3/Mg(100) cluster and the transformation consists in adding one CO_2 and one H_2 molecule to the $Ni_3(HCOO)H_3$/MgO(100) cluster – all the configurations are fully relaxed at the DFT level. Now, $Ni_3(HCOO)H_3$/MgO(100) is fully saturated with reducing species (i.e., the hydrogen adatoms, H), so that its transformation into $Ni_3(HCOO)H_5$/MgO(100) increases the system's electronic energy by 0.36 eV. At this point, the cluster is oversaturated with reducing species, and its reaction with the oxidizing species (CO_2) to give a second formate ligand in $Ni_3(HCOO)_2H_4$/MgO(100) is strongly favored energetically by −1.66 eV. Vice versa, if the oxidizing species CO_2 is added to the starting $Ni_3(HCOO)H_3$/MgO(100) cluster that is saturated but not oversaturated with reducing species, a decrease in energy occurs but amounts only to −1.03 eV to give $Ni_3(HCOO)_2H_2$/MgO(100). At this point, the cluster is saturated with oxidizing species and is able to add one more reducing species (H_2) to give $Ni_3(HCOO)_2H_4/MgO(100)$ with a corresponding decrease in energy by −0.25 eV. Given the size of these effects, of the order of several tens of an eV, their importance in determining reaction propensities is apparent.

An important point should be underlined in this connection regarding the source of H species. For these ultrananoclusters, we have considered H_2 adsorption/dissociation as the only source of H species. On an extended surface however H_2 can also dissociate in and diffuse into the considered region of the system from a neighboring region (or unit cell). This means that, ultimately, there is more freedom in stoichiometry and rate to equilibrium is faster. On a substrate different from MgO(100), a source or drain of single H adatoms can be hydrogen spill-over from/to the support to/from the cluster, which needs to be properly be taken into account.

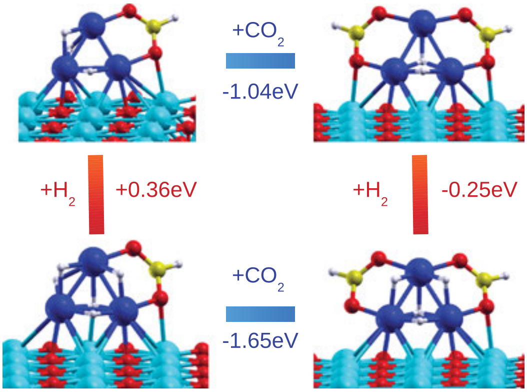

Fig. 6.13: DFT energetics of the transformation from a $Ni_3(HCOO)H_3/MgO(100)$ cluster into a $Ni_3(HCOO)_2H_4/MgO(100)$ cluster via $Ni_3(HCOO)H_5/MgO(100)$ or $Ni_3(HCOO)_2H_4/MgO(100)$ clusters. All the configurations are fully relaxed at the DFT level. Atomic color coding: Mg light blue, O red, C yellow, H white, Ni dark blue.

(ii) One path for CO_2 conversion is via CO_2 bond breaking into CO + O. A C–O bond-breaking step must occur at some point in CO_2 conversion (except when conversion is stopped at the lowest reduction level, that is, formic acid HCOOH). However, if CO_2 splitting into CO + O occurs early in the reaction path, it generates an adsorbed CO molecule, which can then evolve as such into the gas phase, at which point the problem of CO2RR actually turns into that of CORR, the reduction reaction of CO. CORR however presents several issues: CO is a very stable molecule, it can absorb very strongly onto and thus poison several catalysts such as Pt, or it can disaggregate the metal clusters/particles into $M(CO)_n$ carbonyl species [28, 32, 33]. This path is therefore less preferable with respect to a later C–O bond breaking, leading not to CO but to $CO(H)_x$ species. As a practical example, here we use the $Ni_3/MgO(100)$ system to illustrate the competition between CO_2 hydrogenation (preferred) vs. CO_2 bond breaking into CO + O (unwanted). Figure 6.14 exemplifies the main message resulting from our findings.

In particular, we found that coverage is the key parameter determining the propensity toward hydrogenation vs. CO_2 splitting. At low coverage, that is, for Ni_3/MgO(100), the unsaturated valence of the metal atoms in the cluster makes that the barrier to CO_2 breaking into CO + O is very small, of the order of 0.4 eV, and therefore comparable to that for H migration onto CO_2 (see Fig. 6.14). Already at medium coverage, that is, for Ni_3(HCOO)HMgO(100), the smaller interaction between CO_2 and the cluster increases the barrier for the bond-breaking process up to around 1.4 eV, and hydrogen migration is definitively favored.

In passing, we note that the competition here discussed is reminiscent of the competition between ethylene (CH_2=CH_2) adsorption onto a Pt_3 cluster versus oxidative insertion of Pt into a C–H bond of ethylene [34]. We previously found, in fact for this different system, that at high coverage, that is, in the “coordinatively saturated” régime, a π-adsorption mode of CH_2=CH_2 onto Pt_3 is preferred, leading to ethylene saturation on Pt_3, whereas at low coverage, that is, in the “coordinatively unsaturated” régime, a CH_2=CH_2 σ-adsorption mode onto Pt_3 is preferred, opening up reactive channels such as oxidative insertion of Pt into C–H with the corresponding formation of platinum hydride species.

Both these examples (competition between hydrogenation vs. CO_2 bond breaking or between ethylene adsorption vs. oxidative Pt insertion into a C–H bond) lead us to the conclusion that the history of the system, or *catalyst preparation*, is crucial: letting the catalyst interact too strongly with reactants can lead to disruption of potentially useful and effective catalytic species. Note in this connection that high temperatures also favor adsorbate evolution from the cluster into the gas phase, leading to low coverage and opening up undesired reactive channels, so that the temperature profile of the catalytic process is also to be carefully chosen. These considerations may sound simplistic, but they are sometimes disregarded in the literature.

(iii) An alternative path proceeds via the formation of the formate HCOO species. Figure 6.15 illustrates this path on a Ni_3H_4/MgO(100) cluster, that is, Ni_3 with an intermediate coverage of reducing species (hydrogen adatoms). At this coverage of reducing species – see the discussion of point (i) – CO_2 transformation into HCOO is facile. The first step (1)→(2) in Fig. 6.15 is a non-dissociative adsorption of CO_2 onto the cluster. A value of the adsorption energy of ≈–1.4 eV implies that a sizeable adsorption barrier can arise only at high temperatures (over 700 K). The successive Langmuir–Hinshelwood hydrogen migration onto the adsorbed CO_2 to give a formate species, steps (2)→(4) in Fig. 6.15, is also an easy process at this stoichiometry, and is realized via a transition state, depicted in structure (3) of Fig. 6.15, presenting a concerted hydrogen migration and oxygen movement from adsorption onto the support toward adsorption onto an interfacial Ni. It is interesting to speculate in this connection that a different arrangement of the support implying a different arrangement and energetics of oxygen adsorption can facilitate or hinder this concerted movement, marking a difference between this regular MgO(100) surface and amorphous supports

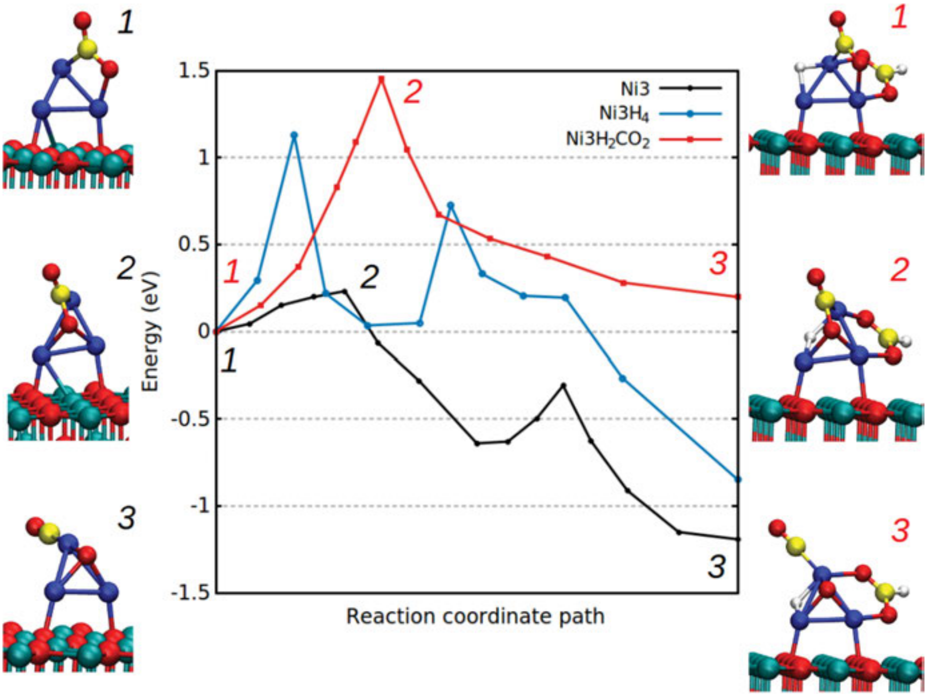

Fig. 6.14: Energy profile and atomistic depictions of the path for dissociating a CO_2 molecule adsorbed on: (left-hand side, black path) a Ni_3/MgO(100) cluster, or (right-hand side, red path) Ni_3(HCOO)HMgO(100) cluster. Atomic color coding as in Figure 6.13.

in which the ligand/cluster/support catalytic complex [28, 32] may create niches with a stronger/weaker interaction among the actors of this step. To progress CO2RR, the so-produced formate HCOO must be hydrogenated via hydrogen migration mechanisms to formic acid HCOOH, and then HCOOH must evolve from the catalyst. HCOOH evolution is often the rate-determining step of the process, due to the weak thermodynamic driving force (small reaction free energy) of the "$CO_2 + H_2 \rightarrow HCOOH$" transformation, as illustrated in Fig. 6.16(b). To avoid self-poisoning, an external thermodynamic driving force must be provided, such as for example formic acid must be taken away from a basic entity (e.g., the oxide support itself) or via HCOOH dimerization with the formation of its strong hydrogen bonds.

(iv) The normal state of a subnanometer catalyst (or, for what matters, of any catalyst) is a high-coverage one, unless the temperature is so high to favor complete ligand evolution into the gas phase, but, under extreme high-temperature conditions, one will encounter the issues of significant adsorption barriers as discussed above. A good catalyst reaches a high-coverage state at the same time avoiding phenomena of self-poisoning. Figure 6.16(a) illustrates the fact that Ni_3/MgO(100) is a moderately

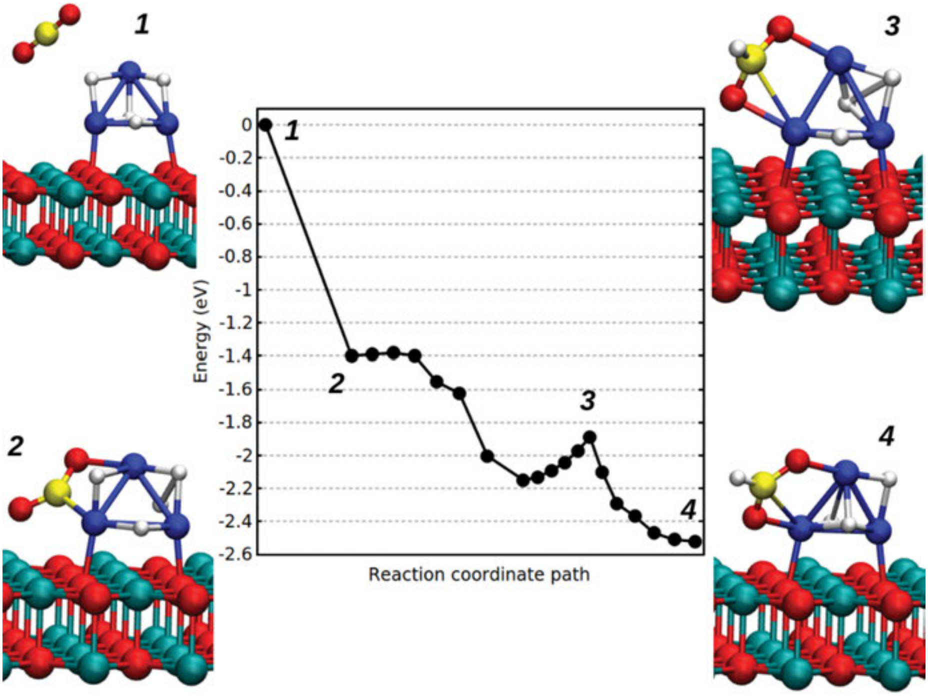

Fig. 6.15: Atomistic depiction of the structures of the local minima and DFT energy profile of the transformation from a Ni_3H_4/MgO(100) cluster into a $Ni_3(HCOO)H_3$/MgO(100) cluster. The configurations (1), (2), and (4) are fully relaxed at the DFT level, whereas (3) is a saddle point. The path (2)→(4) corresponds to a NEB calculation. Atomic color coding as in Figure 6.13.

good catalyst: its resting state is $Ni_3(HCOO)_2H_6$/MgO(100) which cannot process further CO_2 or H_6 molecules and in which the formates are bound a bit too strongly. In concluding this chapter, we briefly mention that, to improve this catalyst, one possibility is to decrease its oxygen affinity and therefore the interaction with HCOO thus making HCOO hydrogenation easier. This can be achieved by alloying with Cu, that is, considering the Ni_2Cu/MgO(100) cluster, as illustrated in Fig. 6.16(b). Indeed, we found that Ni_2Cu/MgO(100) gives rise to a similar $Ni_2Cu(HCOO)_2H_4$/MgO(100) cluster, but in which the reduction of HCOO to HCOOH and HCOOH evolution present a somewhat improved energetics [29]. Figure 6.16(b) illustrates the beneficial effect of Cu doping Ni_3 to Ni_2Cu with respect to reducing the adsorption energy of HCOOH.

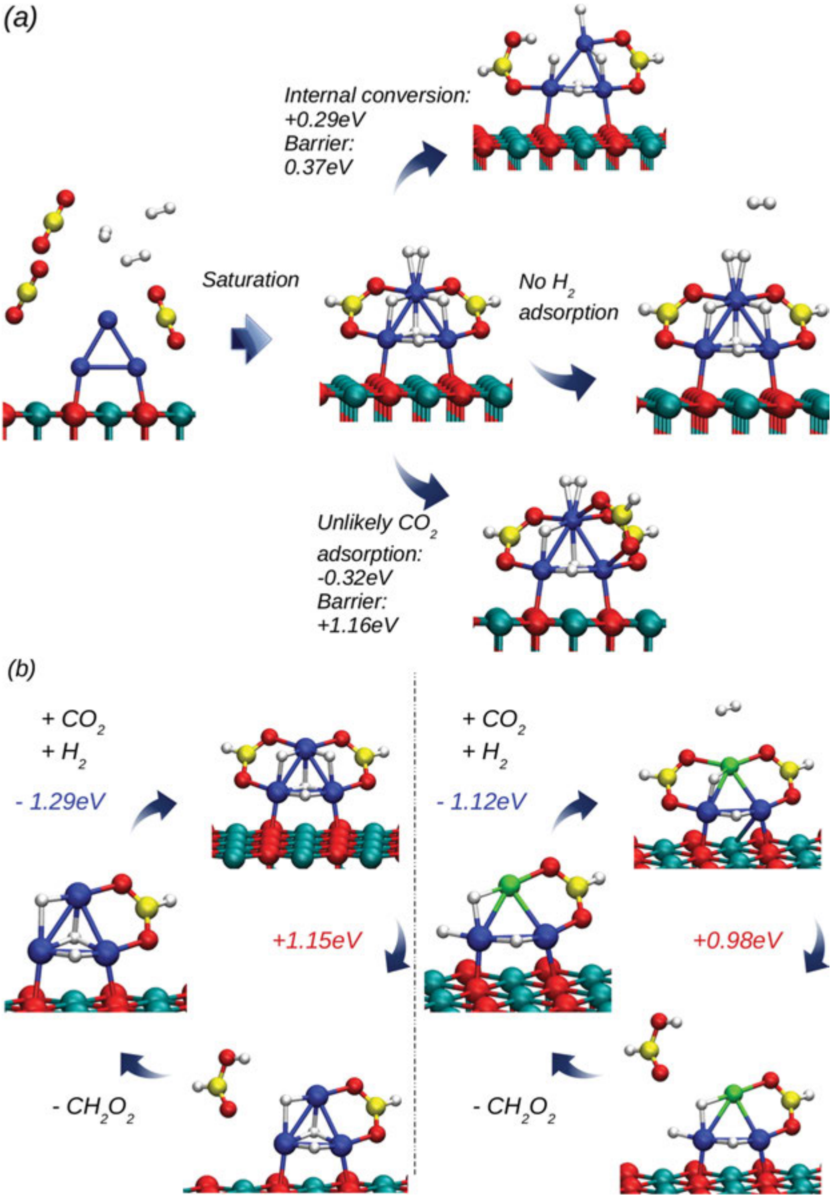

Fig. 6.16: (a) Conversion of Ni_3/MgO(100) + 2 CO_2 + 3 H_2 into a high-coverage $Ni_3(HCOO)_2H_6$/MgO (100) and its possible further transformations. (b) DFT energetics of the transformations from: (Top) $Ni_3(HCOO)_2H_6$/MgO(100) into $Ni_3(HCOO)H_5$/MgO(100) + HCOOH; (Bottom) Ni_2Cu(HCOO)2H_3/MgO (100) + H_2 into $Ni_2Cu(HCOO)H_3$/MgO(100) + HCOOH. All the configurations are fully relaxed at the DFT level. Atomic color coding as in Figure 6.13, plus Cu in green.

6.7 Conclusions and perspectives

Heterogeneous catalysis at gas–solid or liquid–solid interfaces lies at the heart of present energy and environmental challenges, from a sustainable energy cycle to environmental chemistry. Societal needs urgently require finding routes to the catalytic conversion of small molecules: CO, CO_2, H_2, H_2O, O_2, N_2, CH_4, CH_3OH, in mild (close to ambient) conditions and with a high activity and selectivity, this being one of the biggest challenges of twenty-first-century chemistry. In this context, catalysis of hydrogen processes plays a crucial role, hydrogen being a sustainable form of chemical energy storage and able to support sustainable carbon and nitrogen cycles at the global level (so-named hydrogen economy). Presently, an impasse is faced. Traditional catalysts (such as metal or metal oxide particles of several nanometers in size) in all important cases do not satisfy societal specifications, despite having been extensively explored. *New catalysts are urgently needed*.

In this chapter, we reviewed selected paradigmatic examples of a promising and appealing solution to this impasse: a knowledge-based strategy to catalyst rational design. We focused on three of the most important catalytic processes of hydrogen use in the energy and environmental fields: ammonia synthesis (in particular the HB process), ORR, and the CO2RR, and three diverse catalytic systems: large nanocrystallites (8–10 nm Fe bcc particles in ammonia synthesis), exotic nanostructures (metastable nanoporous Pt particles and nanowires for ORR), and small, subnanometer supported aggregates (Ni and NiCu ultrananoclusters for CO2RR). We showed how a predictive modeling approach grounded on first-principles-based stochastic sampling of the PES of the given catalytic systems is able to give reliable, accurate insight into the thermodynamics and the reaction mechanisms of catalyst systems, in situ and under *operando* conditions, thus providing the basis for a thorough understanding of the catalytic phenomenon, in turn paving the way to unprecedented design and control.

We showed how the HB performance of traditional large nanoparticle catalysts [22] (and also for CO2RR of more exotic subnanometer cluster catalysts [29]) can be decisively enhanced by multielemental doping, however not developed empirically over a time period of many decades with major investments in human and infrastructure resources as in the traditional trial-and-error approach, but via a cost-effective and fast high-throughput screening method. We also showed how structurally novel catalytically active sites with precise atomistic configurations can be designed and engineered, exhibiting 1–2 orders of magnitude improved ORR efficiency with respect to commercial Pt catalysts. We finally showed how ultrananoclusters under realistic reaction conditions merge with the support and the adsorbate shell to become one complex entity with a unique and potentially superior CO2RR catalytic chemistry. Engineering the catalytic site via multielemental alloying, novel atomistic configurations, and support effects grounded on predictive modeling based on first-principles-based stochastic sampling of the PES thus appear as effective and practical paths to future rational catalyst design.

In the illustrated examples (and several others not mentioned here for reasons of space), the predictive modeling strategy has achieved significant and potentially breakthrough results. It is therefore natural to propose it as one strongly qualified candidate to overcome the present impasse and find routes for decisive progress in crucial fields such as hydrogen-economy processes and in general the catalytic conversion of small molecules under mild conditions, satisfying all societal requirements of efficiency, selectivity, sustainability, environmental compatibility, and cost.

To fully express these potentialities, further research and resources will be needed. There still exist some methodological and practical limitations that are currently delaying the systematic realization of a complete atomic-level understanding and predictive simulations of catalytic phenomena in realistic environments, in addition to the development of protocols for the synergic coupling of predictive modeling with in situ characterization and precise preparation/synthesis approaches, but the trade-off between such investments and their return in terms of technological breakthroughs is so apparently favorable to expect and hope for their deployment in a next future.

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Michel Noussan

7 The potential of hydrogen passenger cars in supporting the decarbonization of the transport sector

Abstract: Hydrogen may represent an important solution in the necessary shift toward a future low-carbon energy system, especially in sectors that are hard to electrify. While in the transport sector the main potential is represented by long-haul freight transport, some segments of passenger cars may see a penetration of hydrogen solutions in the next years. Still, their success will heavily depend on the effective deployment of a proper hydrogen infrastructure, whose economic and environmental sustainability is related to multiple aspects, mostly focused on hydrogen generation, storage, and transportation. This chapter presents the main challenges and opportunities of hydrogen-based passenger cars, by highlighting the current state of the art and the potential future developments.

7.1 Introduction

Hydrogen is seeing an increasing interest worldwide, as multiple countries are proposing strategies and targets to develop hydrogen technologies to support the decarbonization of their energy systems. The potential of hydrogen is especially valuable in specific sectors that are hard to electrify, such as heavy industry and long-haul transport, in addition to providing a solution for long-term electricity storage.

Still, in the framework of this renewed interest for hydrogen applications, many hurdles remain to reach a sustainable hydrogen economy. In particular, hydrogen production and transport, especially on long distances, remain critical steps in its value and energy chain. When hydrogen is produced from renewables via electrolysis, the low efficiency of the entire pathway remains still low in comparison with alternative solutions, leading to both environmental and economic concerns. Still, given the lower maturity of some technologies, some potential exists to further improve this issue.

Transport represents one of the sectors that are targeted by hydrogen technologies, both in passenger and freight mobility. The sector is currently responsible for roughly one quarter of global carbon emissions, 8.5 Gt in 2018 [1], and a major part is caused by passenger cars. Moreover, the transport sector is one of the most difficult to decarbonize, and it is currently almost totally dependent on oil products, which totaled more than 90% of the transport final energy consumption in 2018 [2]. While other sectors have seen an interesting increase of low-carbon alternatives, mainly through electrification of final uses coupled to electricity generation from

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renewable energy sources, transport applications are still strongly dependent on traditional technologies in most parts of the world. Fossil fuels, and especially oil products, guarantee a very high energy density, and the maturity of internal combustion engine provides a strong reliability and flexibility of operation. In addition, the current oil-based infrastructure is the result of decades of development, and the gradual shift to different solutions requires significant investments.

Hydrogen may become one viable option, as discussed in other chapters of this book. While hydrogen seems most promising for long-haul freight transport, some hydrogen cars have already been deployed and are currently commercially available. Their main advantage is probably the absence of direct emissions of CO_2 and pollutants, just like battery electric cars, but with a refueling speed comparable to the one of internal combustion engines, in addition to a comparable range. However, issues remain on the high investment cost that is required, mostly due to the expensive materials in the fuel cell, and the availability of a proper refueling infrastructure, which is currently lacking in most of the countries, although slightly improving in selected markets.

This chapter discusses the main aspects related to hydrogen applications in the passenger car segment, by presenting the current state of the art and the future potential in the framework of the ongoing decarbonization of the energy systems.

7.2 An historical perspective

The history of hydrogen technologies in the transport sector has a long track record, and different solutions have often been tested successfully, but they ended up being less convenient than other alternative options.

7.2.1 Early history

The use of hydrogen to supply vehicles dates back to 1807, when the Swiss Isaac de Rivaz filed a patent on the first internal combustion engine, which ran on a mixture of hydrogen and oxygen. However, the vehicle he built in 1813, which carried 700 kg of stone and wood for 26 m on a 9% slope, had no success and no practical application. Another hydrogen-fueled internal combustion engine vehicle, the Hippomobile by Étienne Lenoir, was tested in 1862 on an 18-km distance in France, from Paris to Joinville-le-Pont, reaching a speed of 6 km/h. The one-cylinder horizontal engine was powered by hydrogen that was produced by water electrolysis [3]. It is estimated that around 400 units of the engine were produced, both for mobile and stationary applications.

Another application of hydrogen to power vehicles happened out of necessity during the siege of Leningrad in 1941. Due to the scarce supply of gasoline, the military technician Boris Shelishch and his team converted around 200 GAZ-AA trucks to run on hydrogen, and they noted that the trucks burned cleaner and longer than those that had run on gasoline.

However, the use of hydrogen in fuel cell road vehicles was demonstrated only in 1966, when General Motors built the Electrovan, by installing a fuel cell propulsion system connected to cryogenic hydrogen and oxygen tanks in a GM Handivan [4]. The vehicle, whose adaptation required 10 months, was able to reach a top speed of 110 km/h and had a range of around 250 km. The Electrovan was only used on company property, because of safety concerns, and the high costs of the platinum in the fuel cell and the hydrogen and oxygen supply were strong barriers to commercial deployment. Moreover, the fuel cell and the tanks required a lot of space, making the vehicle of impractical use in comparison with other commercial technologies.

In the following decades, after the oil crisis of the 1970s, different hydrogen cars were tested and proposed, mostly by adapting existing cars with internal combustion engines to run on hydrogen, either compressed or liquified. However, they remained at the level of prototypes, and no hydrogen car was in fact commercially available in the twentieth century.

7.2.2 Hydrogen cars in the twenty-first century

Things slowly changed in the following decades. The first 700-bar hydrogen tanks were demonstrated in 2001, expanding the potential range of cars. Some manufacturers (Honda, Ford, Nissan, Mercedes, and Chevrolet) deployed hydrogen cars in selected countries through leasing business models, but most of these models are now out of production.

The models that are currently (as of July 2020) in production, although in selected countries, are produced by Toyota, Hyundai, and Honda. The main performance parameters of the available commercial fuel cell cars are compared in Tab. 7.1 (data from [5, 6]). The maximum range varies from 500 to 600 km, with an average combined consumption of around 100 km/kg of hydrogen. Also, the retail price (which refers to California's market) is very similar, due to the competition of few models in a new and small market, and still higher than other technologies. In addition to the high investment, in California, the most common hydrogen price in refueling stations is currently 13,99 USD/kg (and in the range 12.85–16 USD/kg) [7], which translates to an operating cost of 0.21 USD/mile (0.13 USD/km). However, automakers in California are including three years of hydrogen fuel with their initial sales and lease offerings, to shield early market adopters from this currently high fuel price.

Tab. 7.1: Performance parameters of main commercial models of fuel cell cars [5, 6].

Parameter	Unit	Honda Clarity	Hyundai Nexo	Hyundai Nexo Blue	Toyota Mirai
Vehicle class	–	Midsize car	Small SUV – 2WD	Small SUV – 2WD	Subcompact Car
Curb weight	kg	1,875	1,815	1,875	1,850
Engine power	kW	130	120	120	113
Range	km	580	570	610	500
Consumption (combined)	km/kg$_{H2}$	106	90	97	106
Consumption (city)	km/kg$_{H2}$	108	93	103	105
Consumption (highway)	km/kg$_{H2}$	106	85	90	106
Retail price (California, 2020)	USD	58,490	62,185	58,735	58,550

7.3 Current state of the art and future trends

Notwithstanding the few automakers currently selling hydrogen cars to final customers, the global fuel cell passenger cars stock has continuously increased in the last years, and many countries have already announced challenging targets for the next decade.

7.3.1 Today's hydrogen cars stock

The evolution of hydrogen cars stock in last years is reported in Fig. 7.1. While the growth is noticeable, hydrogen cars are still limited to few countries, where a supply infrastructure is already in place, although limited in comparison with other fuels. The chart highlights the significant contribution of the first four countries for number of passenger cars, which are the United States (mostly California), Japan, South Korea, and Germany.

The tenfold increase of the global hydrogen car fleet from 2015 to 2019, reaching almost 19,000 units, should be put into perspective by considering that the global battery electric car fleet represents almost 5 million units, increased from around 17,000 electric cars on the roads in 2010 [8]. Such a strong growth has been often pushed by generous incentives, which may be limited in the years to come due to the economic crisis caused by the COVID-19 pandemic. Moreover, electric vehicles have suffered less from the lack of refueling infrastructure, since they could have been also charged at home overnight in most cases, though many countries have deployed a large number of public chargers on the roads to provide alternative options to the users. Some experts argue that the competition between hydrogen cars and electric cars could slow down the decarbonization of the sector, due to the additional uncertainty for the users' when buying a new low-emissions car instead of relying on traditional technologies.

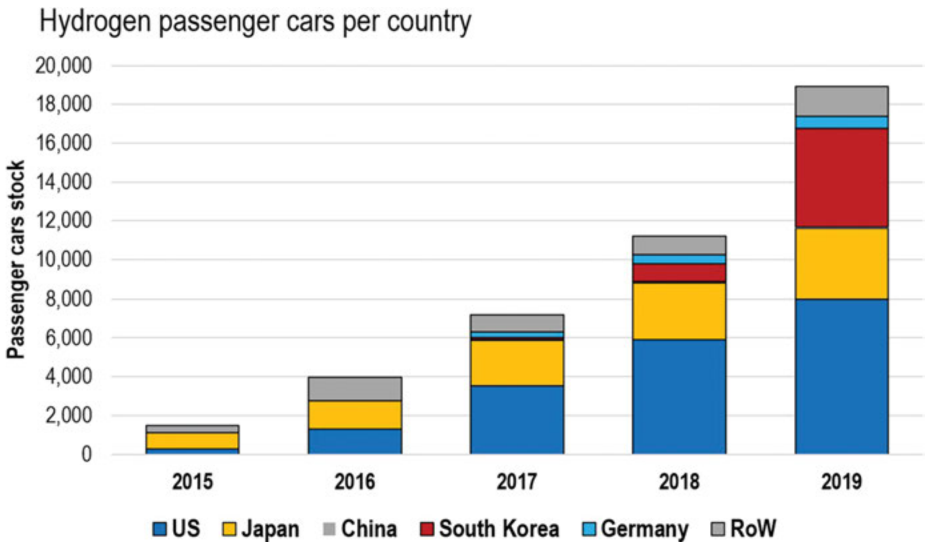

Fig. 7.1: Global hydrogen passenger cars stock per country (see author's elaboration in [8–11]).

Thus, the availability of infrastructure remains a key aspect, and it is often seen as a chicken-and-egg problem: users are reluctant to buy hydrogen cars unless they see a proper refueling network, while companies are waiting to invest in hydrogen stations before they are sure they can count on a reliable and expanding market base. Moreover, refueling stations represent only the final part of a complex supply chain that need to be deployed from scratch. Thus, a quick deployment of a widespread network of hydrogen refueling stations may prove to be more complicated than it is for powering electric vehicles, although potential synergies exist with the supply of hydrogen buses, trains, or trucks, which are expected to play a significant role in the decarbonization of these transport segments. As of the end of 2019, there are 470 hydrogen refueling stations worldwide [12], including private and public ones, and the three countries with the highest number of publicly available stations are Japan (113), Germany (81), and the United States (48).

7.3.2 Specific applications

While a widespread adoption of hydrogen cars is not yet viable, in some cases automakers have put in place pilot projects to demonstrate the reliability of the technology, and to allow potential users to test hydrogen cars. Early adopters, considering the passenger car segment, include taxi fleets and car sharing companies, although the economic profitability needs to be carefully addressed and evaluated.

The longer range and the short refueling times in comparison with battery electric vehicles (BEVs) may prove to be essential features for specific applications, such as taxi drivers. The current largest hydrogen car commercial fleet is operating in Paris since 2015 [13], where 100 hydrogen taxis have accumulated more than 4 million of km, with significant advantages in terms of local pollutants emissions. The company, named Hype, is planning to increase to fleet to 600 cars, thanks to the success of the last years. The high capital cost of the cars has been compensated by the choice of pooling vehicles on several drivers, to increase the utilization times. An additional strategic choice has been to partner with Air Liquide, the French leading company in hydrogen production, which has built four hydrogen-refueling stations in Paris to support the taxis fleet.

A less successful story has been the first hydrogen-powered car sharing, BeeZero, that has been deployed in Munich in 2016 by Linde [14]. The users have driven more than 400,000 km using the available 50 Hyundai ix35 fuel cell cars, before the company stopped their operations after 2 years, due to the lack of economic sustainability of their business model. However, research results [15] highlight that free-floating car sharing could represent an interesting potential to deploy hydrogen cars, although they acknowledge that the current market price in Germany remains challenging.

7.3.3 Future trends

Several countries have announced challenging targets for fuel cell vehicles stocks by 2030 [16], reaching 1 million vehicles in China and the United States, 0.8 million in Japan, and 0.5 million in Korea. Given the limited numbers of cars available today, reaching these targets would require significant investments in the hydrogen supply chain, including the generation, transport, distribution, and also incentives for the users to lower the investment costs of hydrogen cars, which are currently much higher than competing technologies, although they are expected to decrease strongly thanks to mass production.

Still, to put these numbers into perspective it is useful to remember that the global passenger cars production reached 74.2 million units in 2019, down from an historical maximum of 80 million units in 2017 [17]. Even if the COVID-19 crisis has impacted a sector that was already slowing down its historical growth, reaching a noticeable share of the passenger cars vehicles, whose stock is currently estimated around 1 billion, will likely require very significant improvements in the entire value chain.

In fact, the successful deployment of hydrogen cars needs to be part of a broader plan focusing on optimizing the hydrogen supply chain, starting from the final uses where hydrogen is most competitive, such as heavy industry, electricity storage, and freight transport. Many countries are showing interest in developing such a supply chain, by defining specific hydrogen strategies and plans, including Japan, Germany, and the European Union. While Japan is focusing mostly on energy security issues, European countries are seeing hydrogen as a crucial component for the total decarbonization of their energy system by 2050.

In such a perspective, the cost of hydrogen for final customers remains a strong issue, and improvements, both in its generation and transport, are required to improve the energy efficiency of the supply chain, to make hydrogen competitive with alternative technologies.

7.4 Comparison with alternative technologies

As for any technology, the success of hydrogen will be clearly related to its capacity of competing with alternative options. The potential of hydrogen in supporting the decarbonization of the transport system requires that it is produced without emitting greenhouse gases to the atmosphere, either with electrolysis supplied by low-carbon sources (usually referred to as “green hydrogen” when considering renewables and “yellow hydrogen” when coupled to nuclear energy) or with fossil-based solutions coupled to carbon capture, use, and storage (“blue hydrogen”). The most significant comparison should be performed with electric cars, which are being seen by many country as a key pillar of a future decarbonized transport sector.

7.4.1 Features to be compared

While much of the opinions are pushing toward a competition between these two technologies, they may prove to become complementary, provided that hydrogen cars can focus on the right market segment. Although the most promising road transport application for hydrogen is represented by high-duty and long-haul freight, fuel-cell cars can represent a reliable solution for long-distance passenger transport, by exploiting the refueling infrastructure deployed to support the freight transport logistics. Unless major disruptive technologies in electric batteries, their energy density may remain a barrier for an effective and sustainable operation over long distances, allowing hydrogen cars to gain interesting market shares thanks to their higher range.

The other strong advantage of hydrogen over batteries is the faster recharging time, that is, 5 min versus 30 min with fast-charging or hours with traditional charging. This could be compensated by deploying battery-swapping solutions for electric cars, but they would require a strong standardization across different automakers, or either dedicated battery swap stations for each manufacturer or each car model. While in Europe and the United States, this currently appears to be unlikely, in the Chinese market, where the strong state control can easily dictate standards, this option may become a viable solution [18].

An additional aspect in comparing hydrogen supply and battery electric cars recharging is the impact on the power grid, which may become a critical issue in some distribution networks when a large share of fast-charging units are deployed. For this reason, proper smart charging strategies will be required to match the users' demand and the availability of renewable energy generation, either with economic incentives or with different energy storage options to balance the grid.

Hydrogen can be stored easily in comparison to electricity, but the lower efficiency of its supply chain may prove to be a significant hurdle. Figure 7.2 provides a comparison of the overall efficiency of electric cars and hydrogen cars, considering both well-to-tank and tank-to-wheel energy consumption. The figures are based on the average performance of the different components of the supply chain at the current technological level. While these numbers may slightly vary, based on specific assumptions, the difference between the two technologies is clear.

7.4.2 Environmental impact

In addition to the aspects mentioned previously, the main aspect in this competition is probably represented by the environmental impact of each technology, and in particular their carbon emissions. A comprehensive comparison is not easy to perform, as multiple aspects should be taken into account, including the hydrogen and electricity generation mix, the users' behaviors (distance driven, refueling patterns, urban/freeway usage, etc.), and the performance of cars manufacturers.

Still, some reference values for the current performance of passenger cars technologies are reported in Fig. 7.3, considering global average data. The chart presents a comparison of the current lifecycle greenhouse gas (GHG) emissions of fuel cell cars in comparison with the alternative technologies, including electric vehicles and gasoline-powered internal combustion engines.

The values are calculated considering the most recent available data [8], that is, the electricity generation emission factor is set to the current global average (518 g_{CO2eq}/kWh, including transmission and distribution losses), and the hydrogen production is considered from natural gas steam reforming, which is the most used solution worldwide (with an estimated impact of 344 g_{CO2eq}/kWh). Also, the performance of cars is set to representative values of the current models, with 6.8 L of gasoline equivalent per 100 km for internal combustion engine cars, 19 kWh/100 km for BEVs and 34.4 kWh/100 km for hydrogen cars. An additional hypothesis is the specific emission intensity of the production of Li-ion batteries (with

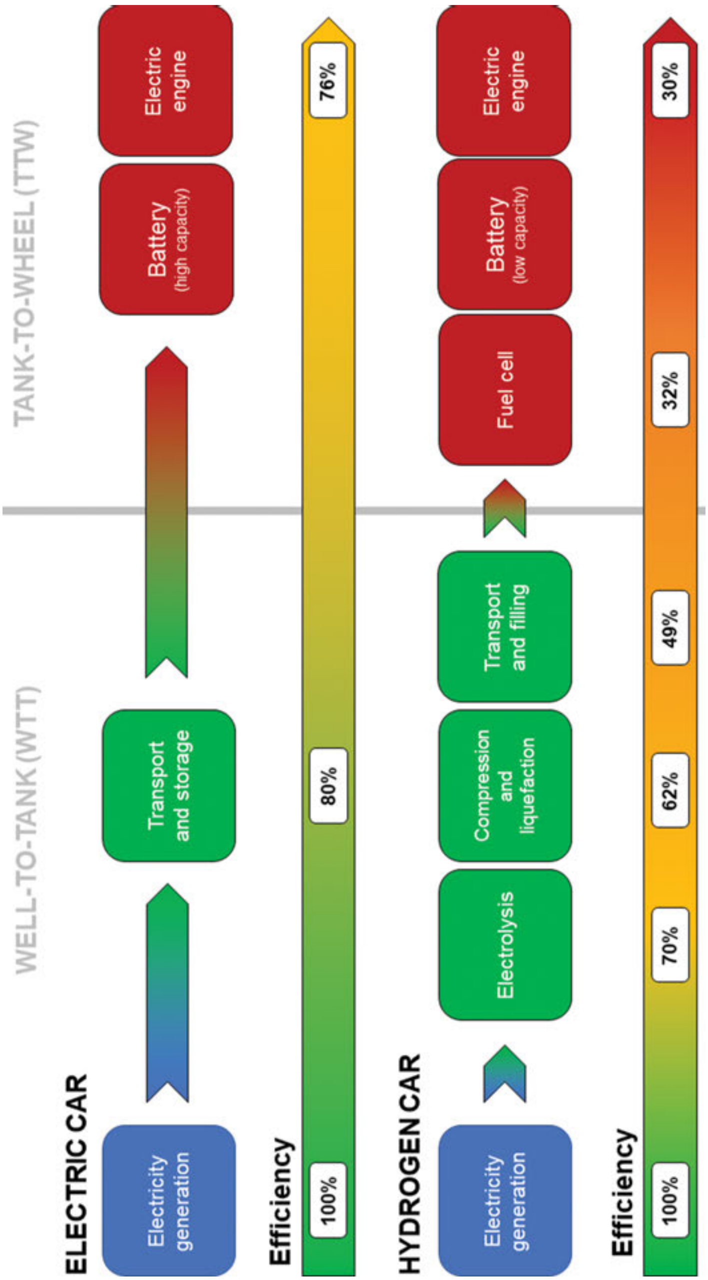

Fig. 7.2: Comparison of overall efficiency of electric cars and hydrogen cars based on current technology. Based on data from Volkswagen, 2019.

NMC 111 chemistry) for BEVs, which is set to two values, 65 and 100 kg/kWh of battery capacity, that are currently representative of the battery production in EU and China, respectively. This aspect has a non-negligible impact on the total BEV emissions, especially for large vehicles.

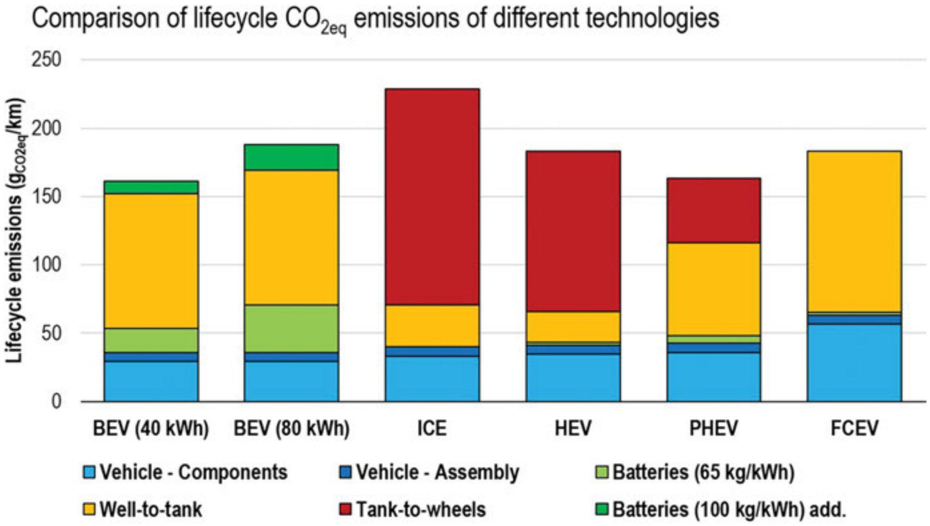

Fig. 7.3: Lifecycle GHG emissions of different passenger cars technologies. BEV, battery electric vehicle; ICE, internal combustion engine; HEV, hybrid electric vehicle; PHEV, plug-in hybrid electric vehicle; and FCEV, fuel cell hydrogen electric vehicle (data source: [8]).

The comparison of the current technologies shows that fuel cell vehicles' emissions level is comparable with large BEVs and hybrid vehicles, and lower than traditional cars, even when the hydrogen is produced from natural gas steam reforming. The potential GHG emissions reductions of future vehicles are strongly related to the electricity and hydrogen supply chains, which represent by far the higher contribution in their lifecycle emissions.

A final aspect to be recalled is that Fig. 7.3 represents average values, while it is important to mention the additional variation related to the vehicle size. In many countries, the continuous increase of the size of new vehicles that are being sold, especially SUVs, is often overcoming the emissions reductions obtained through energy efficiency measures and cleaner vehicles. As an example, the average nominal CO_2 emissions level of new cars sold in the EU has increased in the last three years, after a steady yearly decline from 2010 to 2016 [19], reaching 122.4 g of CO_2 per km in 2019.

While the focus is often limited to new cars, it is important to remember that a number of countries are relying on second-hand cars markets, and often the models that are phased-out for environmental limitations in some countries end up being sold in other world regions. Plus, in addition to the deployment of cleaner technologies in passenger cars, it is important to support the use of adequate vehicles, as well as increasing their average occupancy, which currently remains between one and two passengers per vehicle in most trips in Western countries, with the lower values associated to commuting and other business trips. The technology innovations need to be coupled with alternative measures, with a specific focus on efficiency, to maximize the benefits of switching to low-carbon options.

7.5 Conclusions

Passenger cars are one of the sectors that may benefit from the development of a hydrogen supply chain, although with a minor impact than other transport segments (including freight, railways and maritime transport). While in the short term, the current deployment of electric cars is dominating the market of clean vehicles, in the long term, fuel cell cars may prove to be an interesting solution for long distance car trips, especially if exploiting a refueling infrastructure that is economically justified by the freight transportation.

The performance of fuel cell cars in comparison with electric cars, when considering a lifecycle perspective, is currently strongly affected by the low efficiency of the hydrogen supply chain. Still, other advantages such as the longer range and the quicker refueling times may prove to be crucial aspects for some specific applications, including long trips and high availability uses (e.g., taxis or other commercial fleets).

In any case, the potential development of hydrogen cars seems to be tightly related to the future development of the hydrogen supply chain, whose successful deployment for other sectors may improve the current technological options. Technological advances are required to improve the efficiency in the hydrogen generation from low-carbon sources as well as in the hydrogen storage and transport, especially over long distances. Still, it is important to notice that a strong evolution in the performance of battery electric cars could further affect the potential interest of hydrogen-based solutions.

Given the broad challenges to reach a low-carbon energy system in the next few decades, many different technologies may need to be deployed together, to replace the current solutions based on fossil fuels. While today the focus is strongly put on the competition of battery electric and hydrogen cars, even if the current situation is strongly unbalanced toward the former, in the medium- and long term they may be both play a role in different market segments based on the specific needs of the final users. Technology-neutral policies based on a careful choice of environmental targets will help to support the optimal mix of solutions to shift the current energy systems toward a low-carbon one.

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Massimo Prastaro

8 The hydrogen as a fuel

Eni’s point of view

8.1 Introduction

Hydrogen is an energy carrier with a high potential in numerous applications. In the road transport segment in particular, it could be used to decarbonize the mobility.

The Executive Vice President of the European Green Deal, Mr. Frans Timmermans, recently said that the use and production of clean hydrogen in Europe play very important roles in the energy transition.

Despite its high potential, currently there is no extensive and efficient market for hydrogen: the main obstacles are the still high production costs and the rather low demand.

On the production side, the main problem is the high costs associated with the low levels of efficiency: the energy expenditure that occurs in the conversion process can be adequately compensated only by renewable electricity generation. The reduction in hydrogen production costs is therefore connected to the construction of solar or wind power plants in the hydrogen production sites.

The political and regulatory incentives that the European Commission has recently promoted by presenting the document “A hydrogen strategy for a climate-neutral Europe,” can help to achieve the target.

On the demand side, hydrogen can be used as a substitute for fossil sources for different use cases.

In the domestic heating, there is the possibility to introduce a blending of hydrogen into the methane network and thus reduce the carbon footprint of this sector, as well as the dependence on gas supplying countries.

In the electricity sector, hydrogen has a high potential as long-term storage and backup capacity to the discontinuous production of renewable sources (sector coupling).

In the transport sector, hydrogen can be an alternative fuel. However, its use will require the development of a consolidated production technology and the creation of dedicated logistics and of a refueling infrastructure network.

In the current phase, the manufacturers look into the development of the network before making big investments in new hydrogen vehicles, but the network development depends on the production of vehicle models on a large scale (i.e. the chicken-and-egg dilemma).

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8.2 The market

World production of H_2 is about 70 million tons per year, which is mainly used in refineries (over 50% of the total), for the production of clean fuels. Other 45 million tons a year are used in chemical industries. But the hydrogen production is also a way to store energy, for example, when there is a surplus of renewable energy production.

The current consumption of hydrogen in Italy is very low (about 1% of final energy consumption) and limited to the industrial uses of the refineries and the chemical sector, which mainly use gray hydrogen.

Even in Europe, hydrogen production, which represents less than 1% of energy consumption and concerns a small number of industrial sectors, is mostly of fossil origin; the “green” share only accounts for 4%.

Overall, almost 1,400 hydrogen-powered cars circulate in the EU of which about 200 were registered in 2020. These are distributed in countries with a refueling network (Figs. 8.1 and 8.2).

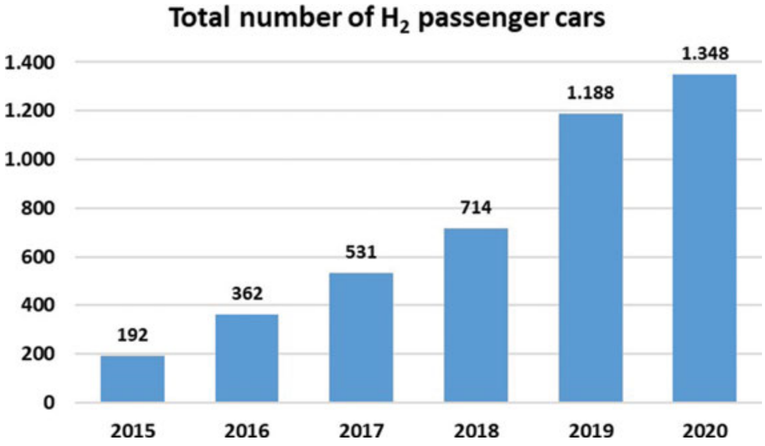

Fig. 8.1: From European Alternative Fuels Observatory.

There are 124 stations in total in Europe, 67% concentrated in Germany, followed by France, Denmark, Austria, and Sweden (Figs. 8.3 and 8.4).

Italy is among the last countries with only one operating station in Bolzano for cars, buses, and trucks, and two distributors not open to the public: one in Milan (that supplies hydrogen to the electric bus line n.84 of the ATM local transport company) and the other one in Capo d’Orlando, Sicily (that refills minibuses).

Lacking both infrastructure and vehicles, a migration to hydrogen is conceivable only in the long run, depending also on the political and economic support to make the necessary investments for the gradual development of the market.

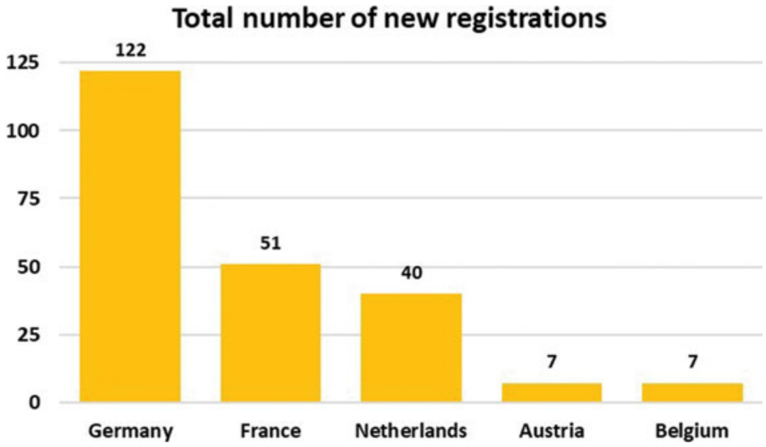

Fig. 8.2: From European Alternative Fuels Observatory.

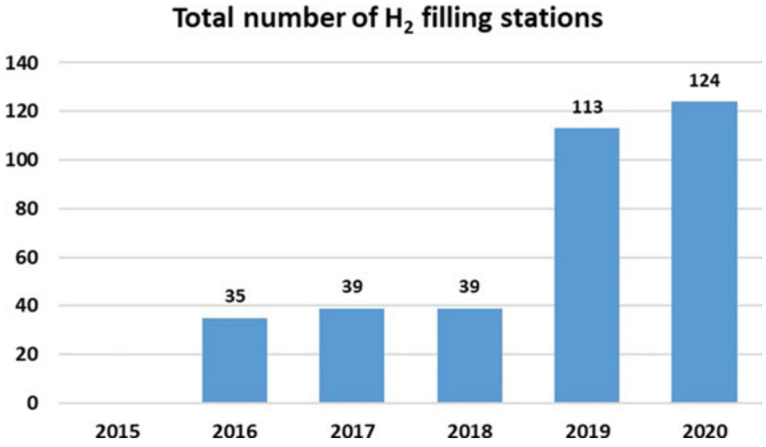

Fig. 8.3: From European Alternative Fuels Observatory.

According to the European Commission's recent strategy, a *three-stage roadmap* would allow the hydrogen economy to reach maturity by 2050.

- 2020–2024: installation of at least 6 GW of renewable electrolyzers for the production of 1 million tons of hydrogen;
- 2025–2030: full-fledged hydrogen in the integrated energy system, with at least 40 GW of electrolyzers for renewable hydrogen and the production of 10 million tons;
- 2030–2050: technologies based on renewable hydrogen should reach maturity and find large-scale application in all sectors which are difficult to decarbonize.

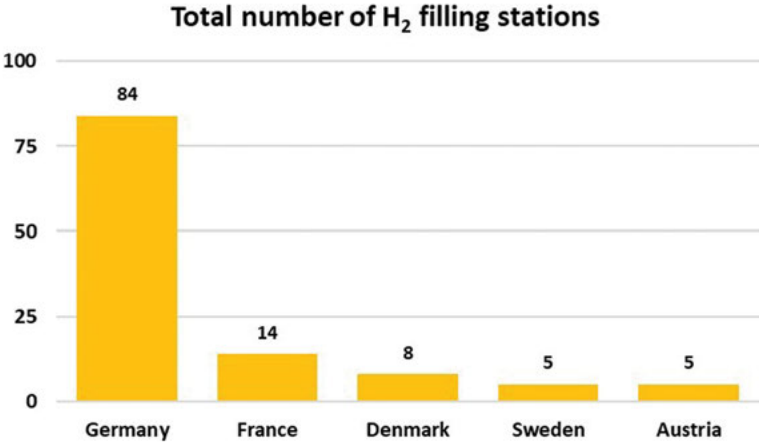

Fig. 8.4: From European Alternative Fuels Observatory.

According to the Italian plan for the future of energy named Piano Nazionale Integrato per l'Energia e il Clima, the contribution of hydrogen to the transport sector in 2030 will account for 1% (of which 0.8% in a mixture with natural gas and 0.2% for direct use in transport).

8.3 The vehicles

Inside the fuel cell electric vehicles, hydrogen is stored in a pressurized tank and reacts with oxygen in a fuel cell for the production of electricity that powers an electric motor (Fig. 8.5). In this technology, the only exhaust is made of water vapor: the hydrogen molecule does not contain carbon atoms and its use does not generate emissions of climate-changing gases, harmful to humans and the environment.

The first fuel cell vehicles were introduced in the last decade mainly in the Japanese and US markets by the pioneers Toyota, Hyundai, and Honda thanks to government incentives for vehicle purchase and the existence of a hydrogen distribution network.

In 2020, there were only two hydrogen car models sold in Europe, the Hyundai Nexo and the Toyota Mirai.

These models are not sold in Italy yet and therefore there is no price list for them, but in Germany, where a hydrogen-refueling network is being developed and the car purchase will not be subsidized, the prices of the Hyundai and Toyota models are between €60,000 and €80,000.

On the other hand, the heavy vehicle market has developed only in the last two years and it is very limited. Today there are only some test projects carried on

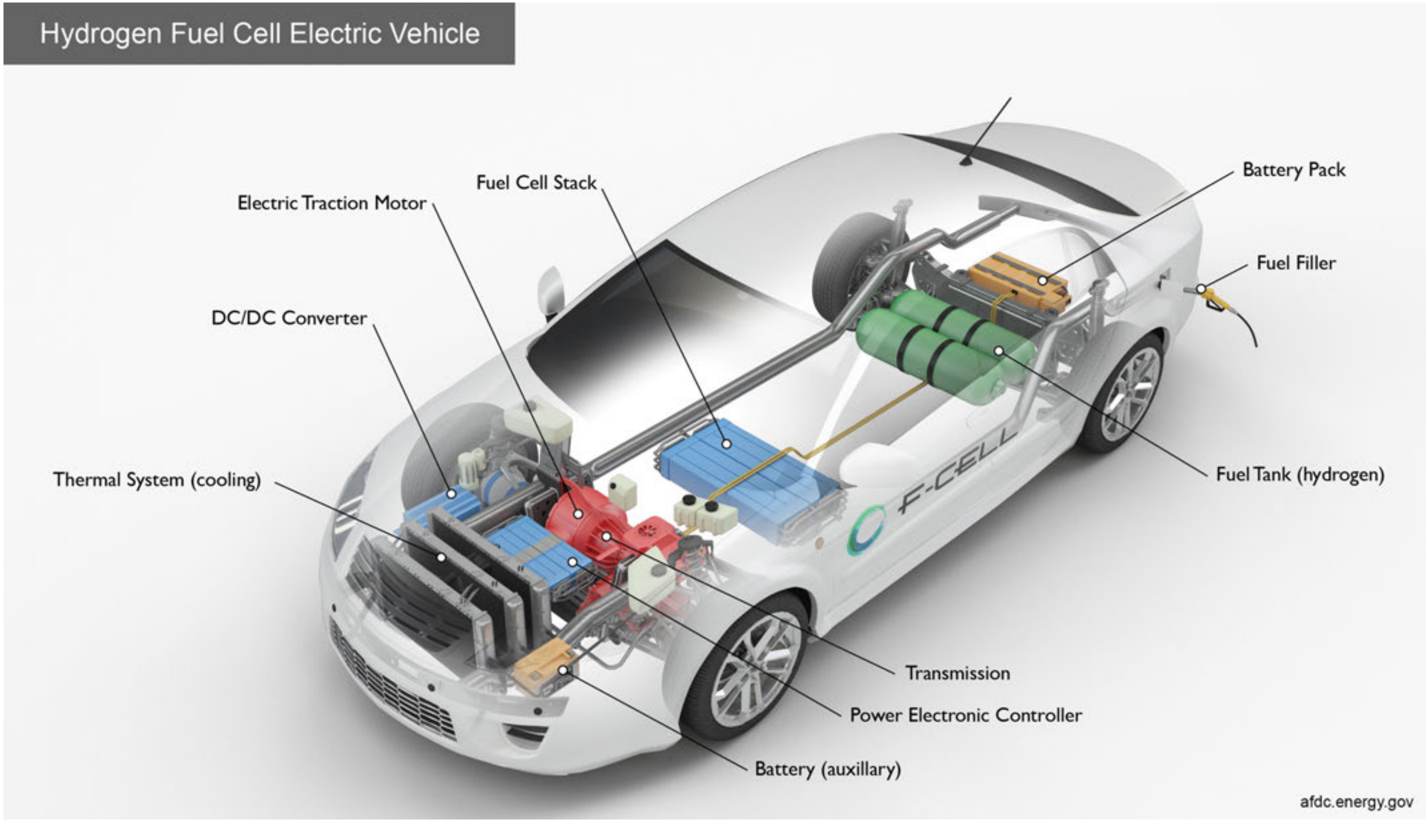

Fig. 8.5: From US Department of Energy website.

in partnership between network developers and manufacturers (including Scania, Kenworth and Nikola). The purchase conditions are not yet defined.

Electric cars with fuel cells overcome some of the limits of pure electricity in relation to refueling times (maximum 5 min) and autonomy of travel (500–600 km), thanks to a 700 bar pressurized tank with a capacity of about 5 kg. The system also includes a small battery used during power peaks to cover delays in the generation of fuel cell current, which recharges by accumulating energy from braking.

For heavy vehicles, the plant would include two 95 kW fuel cell batteries, in addition to seven large hydrogen tanks, for a combined storage capacity of more or less 35 kg at a pressure of 350 bar, which allows a driving distance of 400–500 km. In this case, filling up a tank takes about 10 min on average.

Unlike pure or hybrid plug-in electric vehicles, the load capacity of the heavy fuel cell vehicle is comparable to the equivalent diesel models.

Electric fuel cell vehicles with a hydrogen tank generate no exhaust emissions other than water vapor. However, the possibility that hydrogen is carbon neutral depends, as mentioned, on the percentage of use of renewable sources in the production process. In the recent hydrogen strategy presented by the European Commission, measures are proposed to ensure the “green” origin of hydrogen on the model of “guarantees of origin” already provided in the Renewables Directive.

Finally, the quietness of the electric motor makes the hydrogen vehicle fleets particularly suitable for use in public transport in urban areas.

8.4 The production

Diatomic hydrogen (H_2), simply known as hydrogen, is abundant in nature only in combination with other molecules (such as water or methane), from which it can be produced using primary or secondary sources of energy for the decomposition of the more complex molecules.

Most of the hydrogen is produced from natural gas through the reforming processes whereas only less than 1% of the total hydrogen produced in the world is produced by electrolysis of water using renewable energy such as sun and wind.

The hydrogen can be produced directly at the refueling stations (on-site) but it is usually produced in a large central plant and delivered to the refueling stations.

Five major production pathways can be assessed (Fig. 8.6):

The hydrogen sold at the refueling stations can be “gray,” “blue,” and “green” refer to the different production processes and not to specific varieties of hydrogen.

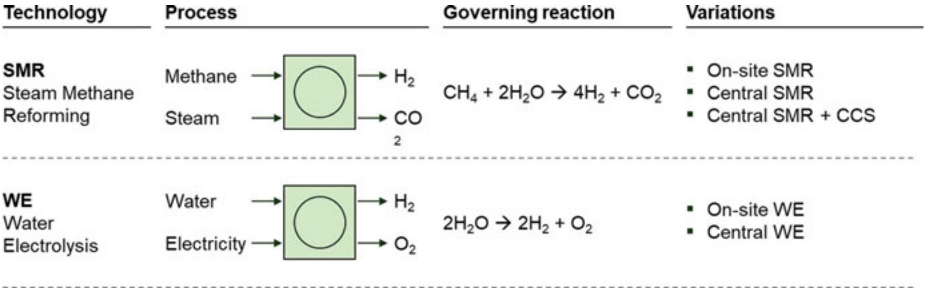

Fig. 8.6: From "A portfolio of power-trains for Europe: a fact-based analysis."

- *Gray hydrogen* is produced through a methane steam reforming process (CH_4) typically inside large chemical and petrochemical plants like refineries where it is used to fulfill internal needs. It therefore has a fossil origin, with a high impact in terms of climate-altering emissions, which will determine its progressive exclusion from usage as part of the decarbonization process of the transport sector.
- *Blue hydrogen* also originates in the methane steam reforming process, but its production is associated with carbon capture and storage processes that reduce the emission of climate-altering agents into the atmosphere. According to the estimates of the International Energy Agency, its carbon footprint would be 10% of that associated with gray hydrogen. The carbon dioxide generated to create blue hydrogen must be stored to prevent its release into the atmosphere. The best way to do this is to use the "spaces" that already exist in nature like those made available by the depleted fields of natural gas or oil. The storage capacity of carbon dioxide in former natural depleted gas fields is not easy to quantify, but it is still important.
- *Green hydrogen* is usually generated through an electrolysis process of water powered by electricity entirely generated from renewable sources, such as wind and solar. But green hydrogen can also be produced from waste. The green hydrogen can certainly make an important contribution to the transport decarbonization and the European Commission will promote its development, but the generation process still has high costs compared to hydrogen originated from methane. Blue hydrogen, although not completely carbon neutral, is a valid "bridge" technology in the energy transition toward a completely decarbonized system, at least in the short to medium term.

Eni strongly believes in the production of blue hydrogen, and is developing a project to submit to the first call of the European Innovation Fund. The project will realize the largest center in the world of carbon dioxide capture and storage in the underground natural gas fields, now empty, off the Ravenna coast. With a storage capacity between 300 and 500 million tons of CO_2, these underground deposits could significantly contribute to the containment of greenhouse gas emissions in Italy. These are natural containers that have already proven their impermeability and resistance for tens of millions of years.

Eni has also ongoing projects to build plants for hydrogen production through valorization of Plasmix (non-recyclable fraction of plastics) and CSS (the non-differentiable solid fraction of waste collection, which today is burned or sent to landfill) as feedstock.

8.5 The transport

In case the hydrogen is not produced on site, there are different methods to transport it from the production site to the refueling stations.

Each method can be more or less convenient depending on the distance and the quantity of hydrogen to be transported.

Four major transport pathways can be assessed:

- *Tube trailers:* transport of hydrogen in the gaseous phase and high pressures (200 bar); the tubes are usually made of steel and have a high net weight. The maximum amount of hydrogen that can be transported by a truck is 500 kg.
- *Container trailers:* transport of hydrogen in the gaseous phase using the new lighter composite storage containers. The hydrogen is pressurized till 500 bar and it's possible to transport about 1,000 kg of hydrogen per truck.
- *Liquid tankers:* transport of hydrogen in liquid phase at low pressures, suitable for long distances.
- *Hydrogen pipelines:* steel pipelines operating at pressures until 70 bar and with a greater thickness than the pipelines for the transport of Natural Gas; this kind of transport is suitable for long distances.

Hydrogen liquefaction and transport by truck are expensive and strongly linked to distance, in fact, it could be convenient for long distances (more than 300 km) and big quantity of hydrogen, while transport via pipeline (P) is convenient for very large quantities and long distances (100 t/day and more than 300 km). Finally, the transport of gaseous hydrogen through gas trucks is convenient for short distances or small quantity of hydrogen and, for this reason, it is the most used in the short period when there are few vehicles on the streets.

8.6 The refueling station

The Italian Legislative Decree of 16th December 2016, n. 257, implementing the European directive on alternative fuels infrastructure (DAFI 2014/94/EU), promotes the development of hydrogen refueling stations.

A hydrogen refueling station is usually integrated into an existing refueling station as an additional fuel offering. The main requirement for this is that there is sufficient space on the existing site for the specific hydrogen facilities according to the fire brigade regulations.

In that respect, in Italy, the firefighters issued on 23 October 2018, the technical fire prevention regulation for the design, construction, and operation of hydrogen distribution systems for vehicles.

For demo purposes or in the future when the market is developed, it will be possible to build a hydrogen refueling station like a greenfield project in a new, standalone facility.

In this case, there will be no need to consider the constraints of existing site infrastructure, but both the investment cost and the operative cost could be higher due to the implementation of typical refueling station services as expected by customers.

In some countries, mobile refueling stations can be used where only relatively small quantities of hydrogen are needed, for example, for a demonstration project. In Italy, mobile stations are not allowed.

8.6.1 Technical components

Hydrogen refueling station has the following technical components: storage tanks, compressor, pre-cooler, and dispenser (Fig. 8.7).

Fig. 8.7: From an Eni's internal study.

8.6.1.1 Low-pressure storage

To store hydrogen, its density must be increased and then operated at high pressures or low temperatures.

There are three storage methods: gaseous storage, liquid storage, and solid storage.

- *Gaseous storage:* Gaseous hydrogen is usually stored in cylinders or tank (200–700 bar) for several days. If the hydrogen is delivered by trailers, the tubes can be used on site as a low-pressure storage tank. The quantities to be stored are calculated on the basis of the number of refueling operations per day. It is possible to plan a modular expansion of the refueling station adding more storage capacity.
- *Liquid storage:* For storing maximum hydrogen in a restricted volume, it is possible to convert hydrogen gas to liquid hydrogen. It requires cryogenic temperatures for the transition from the gaseous to the liquid state (<–253 °C). In order to maintain liquid hydrogen at this temperature, tanks must be perfectly isolated. There are very few hydrogen refueling stations in the word that have liquid tank in the word due to the high cost needed to maintain the cryogenic chain.
- *Solid storage:* hydrogen can also be stored on the surfaces of a material (by adsorption) or within materials (by absorption).

These methods have not yet reached technologically acceptable levels for large-scale use.

8.6.1.2 Compressor

The compressors bring the hydrogen, stored in the tank to the high pressure required for refueling.

A number of different stages can be used to achieve the necessary compression. The most used types of compressors are reciprocating and ionic compressors.

- *Reciprocating compressors* have a motor with a linear drive to move a piston or a diaphragm back and forth. This motion compresses the hydrogen by reducing the volume it occupies. Reciprocating compressors are the most commonly used compressors for applications that require a very high compression ratio.
- *Ionic compressors* are similar to reciprocating compressors but use ionic liquids instead place of the piston. These compressors do not require bearings and seals, two of the common sources of failure in reciprocating compressors. Ionic compressors are available today at the capacities and pressures required at hydrogen fueling stations.

Since the vehicle’s fuel cells need pure hydrogen, it is very important that no contamination with lubricants occurs during compression.

8.6.1.3 Medium- and high-pressure storage tanks

The compressed hydrogen is transferred to the medium and high-pressure storage tank. The pressure in these tanks are 450 bar and 1,000 bar respectively, enough to refuel buses and customer cars.

8.6.1.4 Precooling system

Since hydrogen is compressed during refueling, it heats up. The precooling (normally) is necessary to stay within the temperature limits of the vehicle's fuel storage system.

For 700 bar refueling, hydrogen is generally precooled to −40 °C. Higher precooling temperatures are possible, but can increase the refueling time.

8.6.1.5 Dispenser

The dispenser includes the fueling nozzle, which delivers the compressed hydrogen into the vehicle's pressure tank. The dispensers are designed for the pressure of the hydrogen vehicle's tank, that is, 350 or 700 bar and have various displays to show pressure, quantity, and price to the customers.

The dispenser's fueling process must utilize the SAE (Society of Automotive Engineers) protocols and can support OEM (Original Equipment Manufacturer) specific fill algorithms.

The dispenser is equipped with overfilling protection device that stops filling automatically when it reaches the most suitable filling pressure and an emergency breakaway coupling which prevents gas leakage when vehicles are started by mistake, and it also has a malfunction monitoring system that watches information of various sensors and stops the filling process in case it is abnormal. Nozzles, gas piping, and valves comply with all the safety features required to fuel highly pressurized gas.

8.6.1.6 Electrolyzer (in case of on-site hydrogen production)

The main component of the electrolyzer is the pressurized stack. The stack consists of circular electrolytic cells, each of which contains two electrodes and an inorganic membrane, which can be alkaline, polymeric, or solid oxide.

Hydrogen and oxygen are generated when power is supplied to the stack. The gases produced are then directed to the separator, which consists of a double stainless steel pressure vessel, and then "washed" in the small pressure vessel located above the gas separator.

8.6.2 The scenario

The hydrogen refueling stations are still in a phase of entering the market, with very high development costs (between 1 and 3 million euro) depending on the supply capacity.

Eni estimates that smaller stations will initially be built for captive fleets of cars and heavy vehicles, with deliveries of up to 200 kg/day.

In a subsequent phase, larger stations will be built for larger fleets and for private users.

The final objective would be to build large stations up to 1,000 kg/day, capable of supplying all users and ensuring coverage of the main transport arteries.

Given the significant autonomy of the vehicles (especially compared to the battery electric vehicles), one of the scenarios that Eni see as more likely to happen is the development of a limited number of stations especially in the cities.

This would lead to the creation of an extensive network, in which a centralized production phase in industrial plants is followed by the transport of hydrogen by road (in gaseous form or liquefied) or via pipelines (in gaseous form).

Eni plans to open two hydrogen stations in partnership with Toyota in the next years.

The first one is located in San Donato Milanese (Milan) near the company's headquarter and the second one is located in Mestre along the street that links the airport to the Venice center.

For both stations, Eni presented the executive project and is waiting for the authorizations from the local authorities to start the civil works.

8.6.3 San Donato (Milan) station

The project of the new Eni Station of San Donato was born from a study aimed at the architectural evolution of the service station, which is no longer seen as a traditional refueling station but as a point of sale of diversified products and services, available in a multifunctional innovative structure and perfectly integrated architecturally in the new Eni business center (Fig. 8.8).

The hydrogen distribution plant will be located in the central area between the two existing fuel systems (traditional fuels and natural gas) in an area now partly dedicated to greenery and partly to internal traffic (Fig. 8.9).

8.6.3.1 Principle of operation

Powered by a continuous flow of water <1 L/min, the electrolyzer is capable of producing a hydrogen current of up to 30 Nm^3/h at a maximum pressure of 27 barg (Fig. 8.10).

Fig. 8.8: Enistation San Donato (Milan).

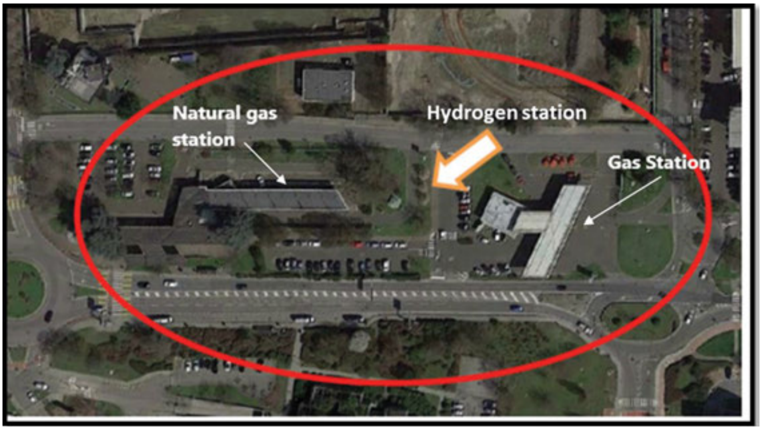

Fig. 8.9: The hydrogen area in the San Donato station.

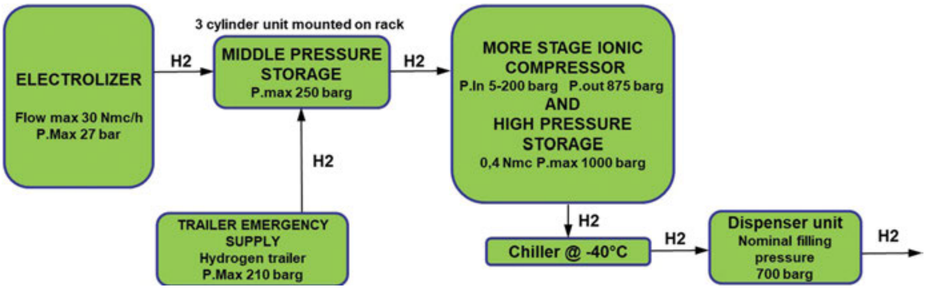

Fig. 8.10: From an internal study.

The hydrogen produced is stored at medium pressure in four suitable containers, each of which can be manually sectioned for future maintenance. The total capacity will be 4 cubic meters.

The gas is brought from 27 to 1,000 bar by means of a unit that uses the proprietary Linde ionic compression technology and is accumulated in the internal storage having a capacity not exceeding 0.4 m^3.

The compressor takes the hydrogen necessary for the filling process directly from the medium pressure storage section and feeds the high-pressure storage.

The compression process is stopped automatically as soon as the gas pressure in high-pressure storage is reached. The station automatically switches to stand-by mode. The compressor is automatically reactivated when the pressure in the high-pressure storage drops below a threshold value. Even during the stand-by mode, the supervision, alarm, and shut-down system is always operational.

A cooling unit always keeps the refrigeration unit within optimum temperature range to allow filling in accordance with SAE TIR J2601 at any time, without waiting times. Several mechanically operated valves are installed in the station to allow the sectioning of the entire station in subsystems in order to carry out checks or maintenance in stand-by phases. During the refueling process, the compressed hydrogen is transferred from the high-pressure storage to the vehicle tank through the refrigeration unit and the dispenser.

During the vehicle refueling process the hydrogen is cooled, through the refrigeration unit, at a temperature of −40 °C according to the SAE TIR J2601 protocol (other temperature conditions can be set according to other Standards or tables optional alternatives).

Thanks to the sophisticated filling control system, vehicles are refueled according to all the parameters and requirements of the SAE TIR J2601 filling protocol.

In addition, the station control system has an infrared interface for communication between dispenser and vehicles in accordance with the SAE TIR J2601 specifications.

8.6.3.2 Main characteristics

- H_2 production: Minimum 40 kg/24 h in standard operating conditions
- H_2 Compression: Minimum 26 kg/h at 20 °C for compression from 3 to 75 MPa
- Number of vehicles to be refueled in 24 h (4 kg tank): Minimum 10 cars
- Maximum refueling time (with empty tank, 4 kg of H_2 refueling, 20 °C): 360 s
- Maximum electricity consumption for H_2 production: 65 kWh/kg
- Total connection power: 380 kW
- System noise level: 70 dB (A) at 10 m

8.6.4 Venice station

Metropolitan City of Venice, Eni and Toyota signed on 5th September 2019 an agreement for the development of the hydrogen mobility.

As part of the agreement, Eni will build a hydrogen refueling station.

This site was chosen taking into account the following characteristics:

- location along the route from Venice to the “Marco Polo” airport and therefore a site with high visibility;
- proximity to the depot of the ACTV., the municipal public transport company operating in Venice that is supposed to buy up three hydrogen buses according to the signed agreement (Fig. 8.11).

Fig. 8.11: Enistation Venice.

The Mestre hydrogen plant, unlike the one in San Donato, will not include the production of hydrogen on site but the supply by means of a tube trailer (Fig. 8.12).

Fig. 8.12: Rendering of the Eni hydrogen station in Venice.

8.6.4.1 Principle of operation

The main elements belonging to the technological system are (Fig. 8.13):

1. Two covered bays for the supply of hydrogen from a cylinder car;
2. H_2 medium-pressure storage consisting of four cylinders for a total of 650ltx4 at a pressure of 500 bar located on the side of the cylinder car, separated by a concrete septum with a height of 3.5 m.
3. Compressor 700–40 kg/day – absorption 11 kW with H_2 storage at 93 MPa (930 bar) (0.4 mc) integrated in the compressor container;
4. Compressor 200–100 kg/day – absorption 22 kW with H_2 storage at 50 MPa (500 bar) (0.4 mc) integrated in the compressor container;
5. One nozzle dispenser for refueling "light" H_2 vehicles at 700 bar;
6. One nozzle dispenser for refueling H_2 heavy vehicles at 350 bar;
7. Chiller (external and underground under the dispenser).

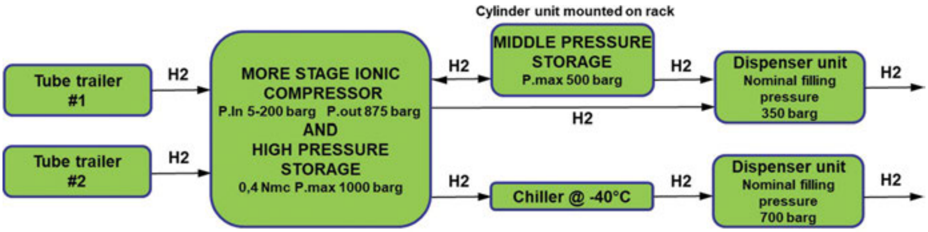

Fig. 8.13: From an Eni's internal study.

1. Two covered bays for the supply of hydrogen fromtube trailers.
2. 5 stages Compressor pressure: 5–200 barg in – 875 barg out.
3. H_2 high-pressure storage (0.4 Nmc) max pressure 1.000 barg integrated in the compressor container.
4. H_2 medium-pressure storage consisting of four cylinders mounted on rack each of 650lt at a pressure of 500 bar located on the side of the tube trailer bays separated by a concrete wall with a height of 3.5m.
5. Chiller under the 700 barg dispenser.
6. One nozzle dispenser for refueling H_2 vehicles at 700 barg;
7. One nozzle dispenser for refueling H_2 buses at 350 barg;

The areas of the hazardous elements will be fenced and screened with protection walls with a minimum height of 3.5 m and a thickness of 30 cm.

In order to mitigate the visual and environmental impact, Eni will use a special paint in various shades of green, based on Titanium Dioxide that, as a reaction to the exposure of ultraviolet rays, it activates its photocatalytic characteristics, reducing the main pollutants (organic and inorganic) present in the environment. The ability of this type of finish is to decompose in 1 h 90% of pollutants present in the surrounding 80 cubic meters.

8.6.4.2 The main characteristics

- Refueling time: approx. 5 min/vehicle (5 kg) and approx. 20 min/bus (30–37 kg)
- Refueling up to 10 cars and 2/3 buses/day
- The plant will allow for the delivery of a maximum of 150 kg/day of hydrogen.

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Urs Cabalzar, Christian Bach, Stefan Hiltbrand,
Patrick Stadelmann

9 Hydrogen refueling of cars and light-duty vehicles

9.1 Design of hydrogen refueling stations

Generally, a hydrogen refueling station (HRS) consists of a compression unit, end storage cylinders, a cooling system, and a dispenser (Fig. 9.1). Depending on the type of supply, the station additionally incorporates a storage upstream of the compression unit. In existing stations, the hydrogen is either supplied by trailers in gaseous or liquid state or produced on-site. Very few stations are fed via pipelines which only become economically viable for very high hydrogen turnover and long transport distances. Currently, for the majority of HRS worldwide hydrogen supply and dispensing takes place in gaseous state [1] which is why this chapter focuses on this type of station and Fig. 9.1 shows the components of a respective setup.

Strictly speaking, hydrogen is in a supercritical state as the prevailing temperature and pressure at such stations lie beyond the critical point of hydrogen. However, the physical state is commonly specified as gaseous in literature and also in this chapter.

In gaseous state, hydrogen is refueled up to a nominal working pressure of 35 and 70 MPa which is standard for utility vehicles and passenger cars, respectively. These pressure values represent the target values at a uniform gas temperature of 15 °C. To ensure an equal filling amount independent of ambient conditions (e.g., winter/summer), the refueling target pressure is decreased for lower and increased for higher ambient temperature. Furthermore, compression heat release within the vehicle tank during refueling causes a significant temperature increase. This requires the station to cool the dispensed hydrogen and to refuel to a higher pressure in order to reach the desired target pressure in the vehicle tank once the hydrogen cools down to ambient temperature again. Both the outlined temperature dependence and the pressure drop in the piping between storage cylinders and vehicle tank make it necessary to maintain hydrogen in the storage cylinders at a pressure around 20–30% above the standard pressure values as shown in Fig. 9.1.

Higher pressure in storage cylinders is also needed as pressure decreases during refueling. By dividing the storage cylinders into sections, part of the stored hydrogen can be kept at higher pressure. With this so-called cascade refueling concept, the vehicle is sequentially filled by commonly three sections called low, middle, and high bank. Thereby, most of the dispensed hydrogen is provided by the low bank. This leaves the high bank, which is only used at the end of the refueling, at

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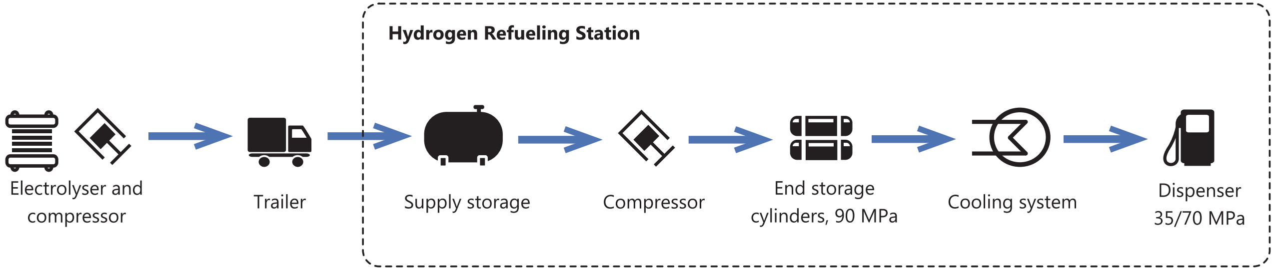


Fig. 9.1: Main components of a typical hydrogen refueling station.

higher pressure compared to undivided storage cylinders with the same volume. Cascade refueling increases the number of vehicles which can be refueled consecutively. Smaller HRS often only allow for one to three of such back-to-back refills. However, there are no limitations in this respect, if storage capacity, compressor, and cooling system are designed sufficiently large.

9.2 Hydrogen compression

In conventional gasoline and diesel refueling stations, the liquid fuel is pumped directly from a large supply storage into the vehicle. Gaseous fuel, in contrast, is compressed and stored in end storage cylinders and dispensed into the vehicle using the pressure difference between end storage cylinders and vehicle tank. There are station concepts without end storage tanks or with fuel stored at medium pressure levels (e.g., 50 MPa) where the compressor directly fuels the vehicle. Generally, this causes a significant increase in refueling time so that such concepts are not state of the art.

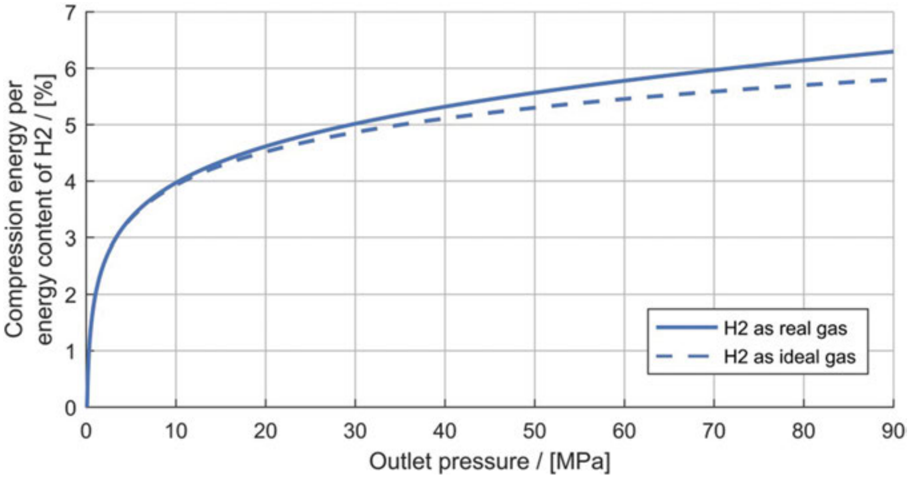


Fig. 9.2: Energy needed to isothermally compress hydrogen normalized by the energy content (HHV) of the hydrogen delivered (inlet pressure: 0.1 MPa, temperature 15 °C).

The specific electrical energy needed to compress hydrogen normalized by the energy content (HHV) of the delivered amount is shown in Fig. 9.2. The curve is calculated based on the simplification of isothermal compression:

$$w_{\mathrm{T=const.}} = RT \int_{p_{\mathrm{inlet}}}^{p_{\mathrm{outlet}}} \frac{Z(p,T)}{p} dp \tag{9.1}$$

Due to an increase in gas temperature and further losses, the actual energy consumption of compressors is higher if waste heat is not recovered. Nevertheless, the logarithmic tendency observable in Fig. 9.2 remains. Note that, for instance, a pressure elevation of 10 MPa is considerably more energy intensive at lower than at higher pressure.

In existing HRS, different types of compressors are employed, such as piston, membrane, and ionic compressors. Commonly, compressors of all types consist of several stages with intercooling in order to get closer to the thermodynamically favorable isothermal compression. In reality, the compression from 0.5 to 90 MPa requires 7–13% of the delivered hydrogen (HHV) in electrical energy if waste heat is not recovered [2]. Existing compressors that recover waste heat can reduce energy consumption below this range.

9.3 The process of refueling hydrogen in gaseous state

9.3.1 Basics of the overall process

For station users, refueling of gaseous hydrogen is very straightforward and similar to refueling conventional fuels. After activating, the dispenser at the payment terminal the refueling nozzle needs to be connected to the vehicle's receptacle and the filling can be started by pressing a button. From an engineering point of view, however, the refueling process is more challenging compared to liquid fuels. Rather than just filling the tank to top level, the stop criterion for gaseous fuels is set by a predefined target pressure. As stated above, the target pressure depends on ambient conditions, thermodynamic effects in piping and tanks as well as unknown vehicle parameters. To improve process control, an infrared communication system was introduced which allows transmitting data from the vehicle to the dispenser (Fig. 9.3). This data includes, inter alia, information on volumes and number of vehicle tanks, as well as in-tank temperature and pressure. If the communication system fails, refueling is still possible, however, the degree of filling is slightly reduced. Note that communication system, nozzle, receptacle and refueling process are standardized worldwide (see, e.g., SAE J2799, SAE J2601).

According to the standardized refueling process, the pressure increase within the car tank is dictated by a so-called pressure ramp controller which is a pressure regulator governing the pressure elevation over time. Depending on refueling conditions, the ramp rate is set to a value as high as 28 MPa/min. Figure 9.4 shows measurement results for pressure, temperature, and mass flow of a typical hydrogen refueling. The pressure in the refueling station immediately downstream of the ramp regulator and within the vehicle tank during an exemplary refueling are displayed in orange.

Fig. 9.3: Hydrogen dispenser, nozzle with infrared receiver and vehicle receptacle with infrared transmitter (from left to right).

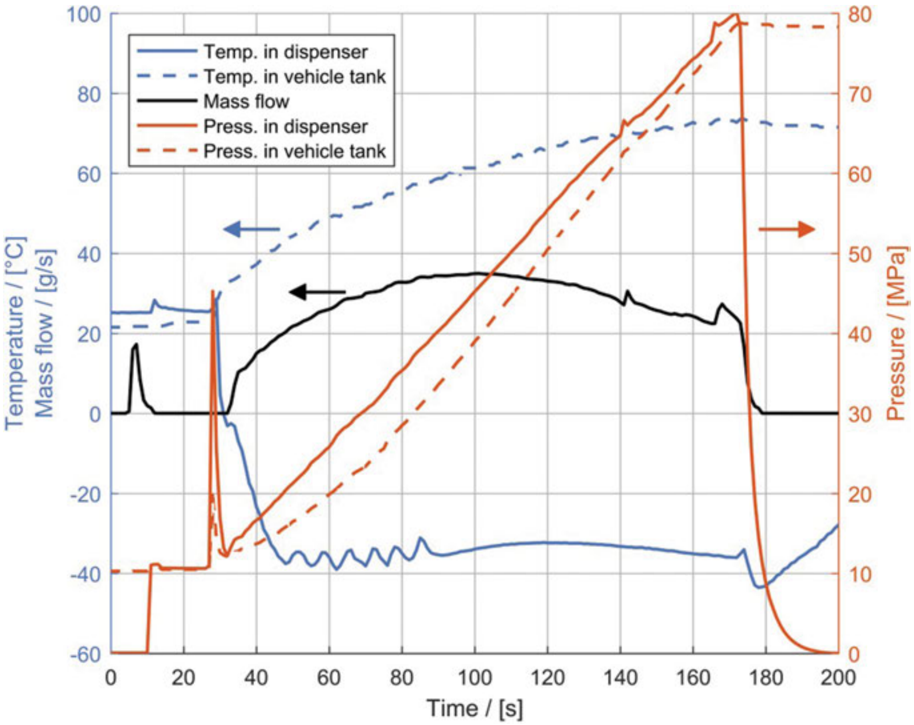


Fig. 9.4: Temperature and pressure profile in dispenser and vehicle tank as well as mass flow during a typical hydrogen refueling process.

Before the main refueling starts at $t = 27$ s, the pressure in the dispenser is increased at $t = 10$ s to reach vehicle tank pressure level. This allows the dispenser control to determine initial vehicle tank pressure which is then compared to the value communicated via infrared or replaces the latter if communication fails. The pressure is then maintained at this level for around 17 s to check for possible leaks in the joints and fueling lines to the vehicle tank. As pressure builds up upstream of the refueling valve during this leak check, a sharp spike is apparent when main refueling starts. Subsequently, the pressure in the dispenser rises linearly. Due to pressure drop within the fueling lines, the vehicle pressure curve shows a small bulge downwards, however. At the end of refueling at $t = 173$ s, the remaining hydrogen in the refueling hose connecting HRS and vehicle is vented to the atmosphere as can be seen by the dispenser pressure curve falling to zero. The complete refueling process takes approximately 2 to 3 min.

As stated above, hydrogen is cooled during refueling which can be observed in Fig. 9.4 as a decrease of gas temperature within the dispenser. After the start of the main refueling, the temperature falls and is kept within the range of −33 to −40 °C. This range is predefined in the category “T40” of the standard SAE J2601 and has to be reached within 30 s after start of the main refueling. Other categories such as “T30” or “T20” allow higher dispenser temperatures but will lead to certain restrictions and or increased refueling times. Figure 9.4 shows that by delivering low-temperature hydrogen at the dispenser nozzle, the temperature within the vehicle tank still rises significantly above ambient level but stays below the standardized limit of 85 °C.

9.3.2 Thermodynamics in pathway from storage to vehicle

To get an idea of the dominant thermodynamic effects, the process of hydrogen refueling can be strongly simplified to the setup shown in Fig. 9.5. Omitting piping and valves as well as reducing the number of reservoirs the refueling process is described by one storage cylinder of larger volume and a vehicle tank of smaller volume which are connected by an orifice. This setup allows for a straightforward thermodynamic analysis which, despite its simplicity, yields tendencies that also hold for the actual process.

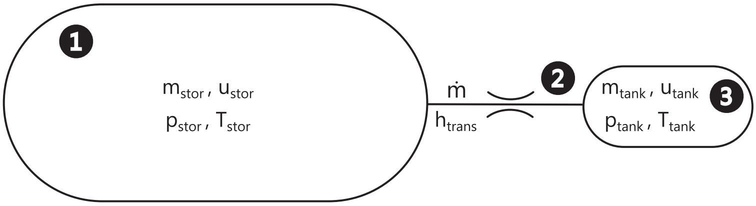


Fig. 9.5: Strongly simplified schematic of the hydrogen refueling pathway to show the dominant thermodynamic effects of the refueling process.

The relation describing this setup is derived from the energy conservation equation according to the first law of thermodynamics. Considering all components adiabatic and neglecting kinetic as well as gravitational potential energy, the following relation is valid for each of the reservoir:

$$mu(p,T) - m_i u(p_i, T_i) = \int_{t_i} \dot{m} h_{\text{trans}}(t) dt \tag{9.2}$$

whereby

$$m = \int_{t_i} \dot{m} dt + m_i \tag{9.3}$$

where m and u are the mass and the specific internal energy of either the storage cylinder or the vehicle tank. The subscript i denotes variables at initial conditions and h_{trans} the enthalpy transferred with the gas from the storage cylinder to the vehicle tank.

As hydrogen flows out of the storage cylinder, the remaining gas undergoes an isentropic expansion and cools down. Similarly, the hydrogen flowing into the vehicle tank compresses the gas already present in the vehicle tank. However, since the temperature of the inflowing gas is not equal to the temperature within the vehicle tank, the change of state in the vehicle tank is not isentropic. Nevertheless, the compression leads to an increase in temperature. A third change of state occurs within the orifice where the pressure drops from storage cylinder level to vehicle tank level. This expansion can be described as isenthalpic and in case of an ideal gas also as isothermal. Whereas intermolecular forces are negligible and hydrogen acts as an ideal gas at atmospheric pressure and 15 °C, the prevailing temperature and pressure range during hydrogen refueling does not allow a respective simplification. Therefore, hydrogen needs to be considered as real gas and the isenthalpic expansion leads to a change in temperature. This change can be described by the Joule–Thomson coefficient

$$\mu_{JT}(p,T) = \left.\frac{\partial T}{\partial p}\right|_{h=\text{const.}} \tag{9.4}$$

where μ_{JT} is specific to an individual gas and depends on pressure and temperature. At the conditions present during refueling in gaseous state, the coefficient is negative for hydrogen. This means that a drop in pressure leads to an increase in temperature.

Figure 9.6 shows the temperature at the positions indicated in Fig. 9.5 for hydrogen during a simplified refueling process assuming real gas behavior. On the x-axis, the current transferred mass is plotted normalized by the total transferred mass from storage cylinder to vehicle tank.

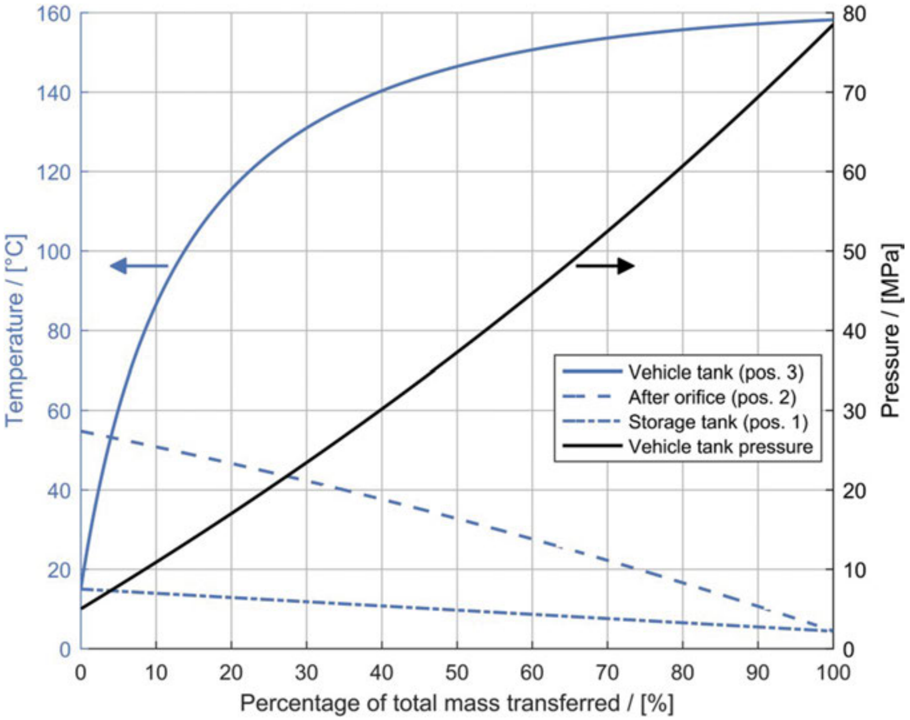


Fig. 9.6: Temperature profile at positions 1, 2, and 3 as indicated in Fig. 9.5 as well as pressure profile at position 3 for a calculated adiabatic hydrogen refueling process.

The cooling effect in the storage cylinder is rather low since its volume is selected to be 10 times larger than the volume of the vehicle tank and hence pressure change is much lower. Furthermore, in reality, the surroundings are not adiabatic and the thermal capacity of the cylinder wall and the fueling lines will reheat the hydrogen towards ambient temperature as it flows to the vehicle. The temperature increase over the orifice caused by isenthalpic expansion amounts to several tens of degrees in the beginning of refueling when the pressure difference between the storage cylinder and vehicle tank is high (Fig. 9.6). As refueling continues, the temperature increase regresses. Here again, in reality, the expansion within the fueling lines is not isenthalpic and the heat transfer to the piping material will cool down the hydrogen towards ambient temperature. However, depending on the length of the fueling lines, the temperature of the hydrogen entering the vehicle tank could still be elevated significantly.

By far, the highest contribution to the temperature increase within the vehicle tank has the compression of hydrogen within the tank itself as can be seen in Fig. 9.6. Note that the temperature increase per unit of mass transferred is considerably higher in the beginning of refueling when pressure of the vehicle tank is lower. Figure 9.6 shows that starting from 15 °C the end temperature within the vehicle tank rises up to almost 160 °C. Of course, in reality heat will be transferred to the vehicle tank wall and eventually to the ambient leading to a lower end temperature. Despite this, end temperature remains high also in reality and will considerably exceed the abovementioned limit of 85 °C depending on the prevailing conditions of refueling (e.g., for low initial vehicle tank pressure). The compliance with the temperature limit for all expected ambient conditions can only be ensured when hydrogen is cooled prior to entering the vehicle. Please refer to Fig. 9.4 to get an idea of the order of magnitude for the end temperature of an actual refueling with cooled hydrogen.

Note that the temperature stability of the used materials and therefore the compliance with the limit of 85 °C is not the only reason to aim for low-end temperature in the vehicle tank. A high-end temperature also implies a high refueling target pressure considering that the final mass within the vehicle tank is to remain equal for all ambient conditions and is targeted to correspond to the mass present at 70 MPa at 15 °C. This means that refueling to an end temperature significantly above 85 °C would also require an increase regarding the pressure level of the storage cylinders and the preceding compressor.

9.3.3 Thermodynamics within the vehicle tank

In the preceding chapter, the refueling process is described by a zero- or one-dimensional approach which inherently considers one average value for the gas temperature within the storage cylinder or the vehicle tank. Particularly in the vehicle tank, however, local temperature may significantly deviate from the average value. Measurements and simulations conducted at Empa show that under certain refueling conditions the temperature distribution is rather heterogeneous [3]. Conditions favoring the inhomogeneity for instance are low gas velocities and reduced gas circulation within the tank. To generate turbulence, a tank injection nozzle with small diameter is favorable. Also, the geometry of the tank affects temperature distribution.

Figure 9.7 shows simulation results for the temperature distribution within a vehicle tank in the vertical cross-section toward the end of a hydrogen refueling process. Note that the velocity of the gas entering the tank will decrease throughout refueling. This holds even if mass flow would be kept constant since density increases steadily. With decreasing inlet velocity, gravitational effects become more dominant and the cooled entering gas is deflected downward.

For the shown simulation results, the inner diameter of the injection nozzle was set to 6 mm and the diameter and length of the vehicle tank amounted to 260 and 700 mm, respectively. Such a setup leads to strong vertical temperature stratification toward the end of the refueling. Measurements confirmed that even for nonadiabatic conditions, the temperature difference between top and bottom areas may exceed 20 °C [3]. Depending on the dimensions of the vehicle tank, also a horizontal stratification can emerge as shown by Devilliers et al [4]. Particularly, for tanks with

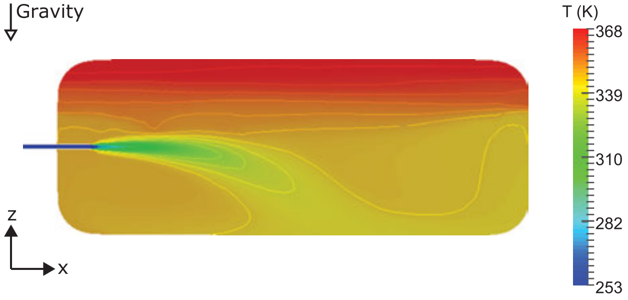


Fig. 9.7: Simulation results for the temperature distribution within a vehicle tank toward the end of a refueling process under adiabatic conditions.

high length to diameter ratios as installed in buses or trucks are prone to an uneven temperature distribution along the horizontal axes.

Note that if stratification occurs local temperatures may exceed 85 °C even if the average temperature lies below this limit. Therefore, it is essential to take into account the influence on the refueling process when designing a vehicle tank and its injection nozzle.

9.4 Remaining challenges for rollout of hydrogen stations

The maturity of the components of HRSs has reached a high level so that not technological but economical aspects pose the main challenge in the process of mass-market development of hydrogen mobility. Besides the issue of economic viability, uncertainties still exist regarding the regulatory framework as well as the verification of the hydrogen purity and the amount dispensed to the vehicle.

Note that all statements presented in this section correspond to the status as of 2019.

The regulatory framework governing the permission to construct a HRS is mainly determined on a national level and in many cases based on outdated or unadapted standards and guidelines. Particularly the dimensioning of hazardous areas (ex zones) as well as the applicable fire protection measures are unclear to station builders and authorities. The lack of explicit guidelines regarding this matter leads to time delays and an increase in expenses for the permission process. In many countries, the prevailing regulatory framework even differs between subnational entities which prevents for a completed permission process in one entity to be used as example case in another. Currently efforts are underway to address this issue on a European level and thus to reach intracontinental harmonization for the majority of the regulations for HRSs.

Due to the particular characteristics of hydrogen in comparison with other gaseous fuels as well as the prevailing temperature and pressure conditions in a hydrogen dispensing system, the mass flow measurement during refueling is challenging. Moreover, currently worldwide no standardized methods exist to calibrate the flow meters of HRSs, thus traceability is not established and the legal metrological control in accordance with the standard for refueling compressed gases OIML R 139-1 is not executable. This means that the validity of the amount of hydrogen, for which the customer is charged, cannot be legally verified yet. Two ongoing projects address this issue on a European level. Alongside a metering study funded by Fuel Cell Hydrogen Joint Undertaking FCH JU (FCH/OP/Contract 196), the project *MetroHyVe* [5] pursues the introduction of a hydrogen field test standard which will allow the verification of the hydrogen mass dispensed. Figure 9.8 shows the standard in operation at the refueling station of Empa in Switzerland in 2018.

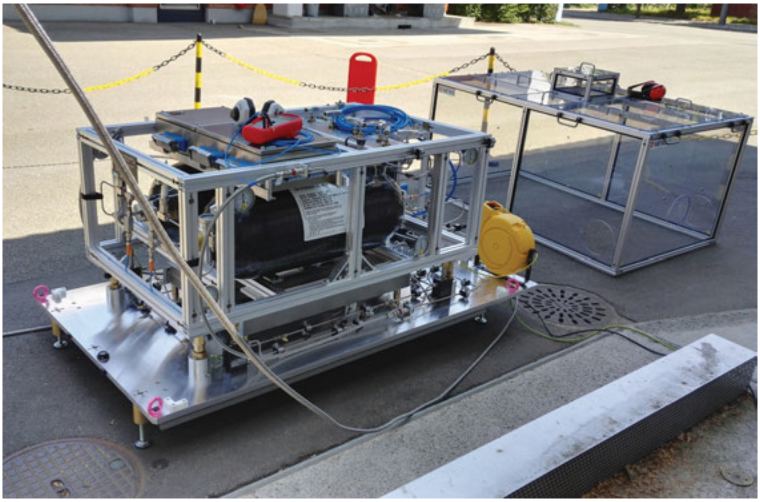
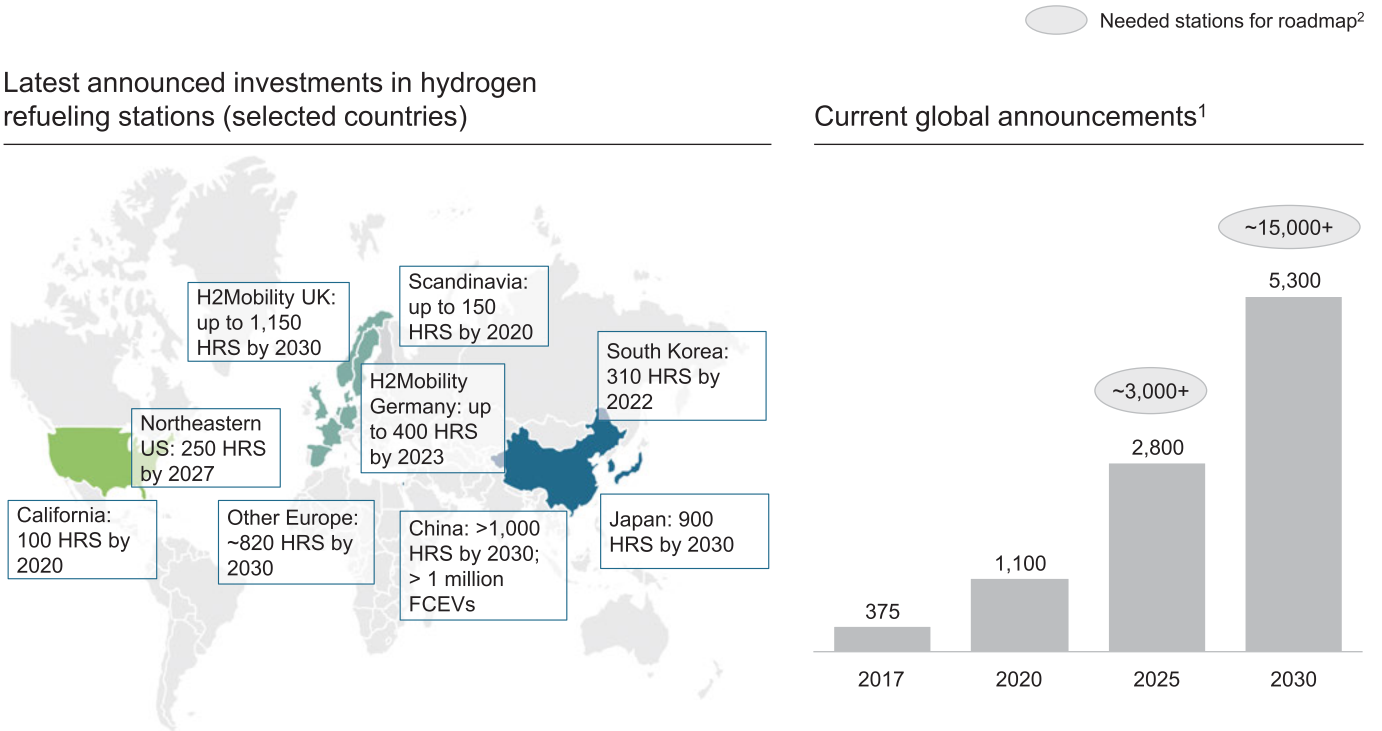


Fig. 9.8: Hydrogen field test standard of the Swiss Metrology institute METAS in operation at the HRS of Empa in Duebendorf.

In simple terms, the standard consists of two storage tanks which can be lowered to a high-precision scale. By weighing the tanks before and after refueling, the increase of mass is determined. This mass has to correspond to the mass displayed on the dispenser with a certain accuracy. Since the mass of refueled hydrogen is comparably small and remains in the order of a few kilograms, various uncertainties have to be taken into account. For instance, the cooled hydrogen coming from the dispenser leads to ice formation on the piping which results in an increase in weight. Also the volume expansion of the storage tanks when pressurized as well as wind and weather conditions will affect the reading on the scale. Furthermore, an improper design of



1 Announcements for shaded countries/regions: California, Northeastern US, Germany, Denmark, France, Netherlands, Norway, Spain, Sweden, UK; Dubai; China, Japan, South Korea

2 Equivalent number of large stations (1,000 kg daily capacity)

SOURCE: Air Liquide; Honda; Hydrogen Mobility Europe; H2Mobility; E4tech; NREL; web search

Fig. 9.9: Status and announcements regarding the rollout of hydrogen refueling stations worldwide [6].

the refueling station may present a major source of uncertainty. Long pipes between flow meter and vehicle particularly promote measurement deviations since pressure in these pipes may be different before and after refueling. An increase in pipe pressure, for example, implies that a certain amount of hydrogen passed the flow meter but did not enter the vehicle. Solutions to cope with such source of errors and uncertainties are currently developed.

Another issue presently addressed internationally is the lack of standardized methods to assure the quality of the dispensed hydrogen. Fuel cell systems are very sensitive to impurities and may suffer reduced lifetime if fuel quality is not appropriate. The standards ISO 14687 and SAE 2719 stipulate the limits for specific impurities. Currently, methods are developed for both online measurements and inspection by periodical sampling [5]. In hydrogen mobility, standardization is generally well advanced and applied on an international level. For instance, the deployed refueling nozzle and vehicle receptacle as well as the entire refueling process are equal across all countries. This is of great importance as a high level of international standardization will strongly support the rollout of hydrogen mobility. In the area of rail and maritime applications, globally valid standards still need to be developed, however.

So far, a few hundred HRSs have been installed worldwide. These stations are mainly located in North America (US west coast), Europe, and the major economic countries of Asia. Currently, a wide variety of roadmaps and initiatives from governments and the private sector intend to significantly increase the number of refueling stations and develop a basic infrastructure for hydrogen mobility in the upcoming years [6]. Recent announcements were gathered by the Hydrogen Council and are depicted in Fig. 9.9.

Symbols

h	J/kg	Specific enthalpy
m	kg	Mass
p	Pa	Pressure
R	J/kg/K	Specific gas constant
T	K	Temperature
t	s	Time
u	J/kg	Specific internal energy
w	J/kg	Specific compression energy
Z	–	Compressibility factor

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Thomas Von Unwerth

10 Fuel cells for mobile applications

Abstract: The increasing ecological awareness nowadays leads to a high demand for environmentally friendly energy conversion, especially in mobile applications. Therefore, hydrogen is seen to be one of the most purposive options, ideally utilized in fuel cells. Those, almost known for two centuries, have been already tried and tested in many prototypes and demonstrators. From different types of fuel cells, the proton exchange membrane fuel cell turned out as the most suitable, consisting of several components with very specific requirements. Its working principle uses hydrogen and air to form no harmful emissions, just water vapor. Assembled with a hydrogen, air, and cooling module and equipped with a control unit the fuel cell forms a system delivering electric power, with addition of an electric powertrain and an adequate hybridization then suitable for propulsion.

Since fuel cells headed to overcome more and more their challenges, an increasing number of mobile applications in different fields occurred. But for a widespread market entry still some research and development tasks have to be performed, aiming, among others, at high reliability and low costs, comparable to conventional powertrains.

Keywords: hydrogen, hybridization, mobile applications, propulsion, proton exchange membrane

10.1 Brief history of fuel cells in mobile applications

Since the birth of the fuel cell (FC) with its invention in 1839 by Richard Friedrich Schönbein and Robert Grove [1] it lasted more than a century until first mobile applications occurred. With experiences from space, for example, in Gemini missions, first serious vehicle usages are known from the early 1960s. A first tractor with an FC was demonstrated by Allis Chalmers, Milwaukee, United States, propelled by a 5 kW alkaline FC consisting of 1,003 cells [2], demonstrating the suitability for traction use cases (Fig. 10.1).

Later prototypes occurred also from car manufacturers, for example, a van from General Motors, but most of the trunk compartments are filled with FC and hydrogen reactor equipment (Fig. 10.2). Also the self-modified car of one of the pioneers of FC technology, Karl Kordesch, still had to deal with package problems due to size and weight of those days' FC technology, leading to a concept with hydrogen vessels on the roof, like shown in Fig. 10.3.

But from those days on, now knowing that FCs were generally suitable for mobile applications, an increasing number of car manufacturers started into dedicated development programs. Starting with first prototypes and feasibility studies soon some cars

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Fig. 10.1: One of the first mobile applications with a fuel cell in the 1960s [3].

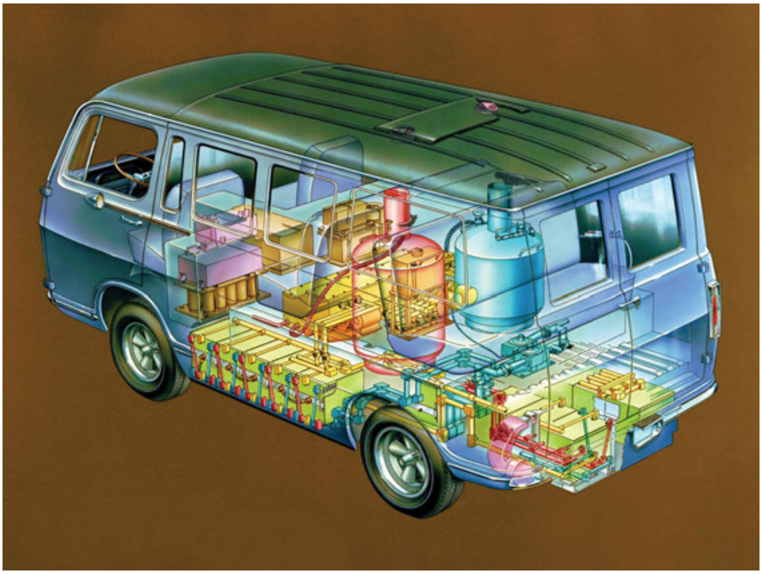

Fig. 10.2: First van with a fuel cell from General Motors 1967 [4].

showed up, most of them based on vehicle bodies from series types due to the huge investment load no one wanted to carry for the overall development of a completely new car platform just for FCs. Under those constraints some compromises had to be taken in terms of packaging a FC system and a storage system not specifically designed for vehicles into compartments that were usually laid out for holding an internal combustion engine and a simple gasoline or diesel tank.

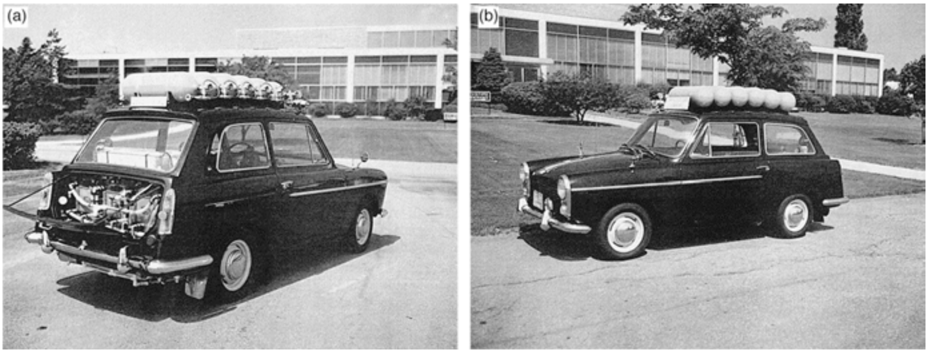

Fig. 10.3: Modified Austin with a fuel cell by Karl Kordesch 1970 [5].

Only later some first approaches towards an own FC car concept arose from companies who very early saw the market entry of FC cars in their country like Honda or Toyota. Nowadays following the market introduction of battery electric vehicles with their own platforms, it's to foresee that also the FC versions will have an own design for their different specifications concerning package space.

In other mobile applications FCs also started their entrance already in the last century. First buses were equipped with FC powertrains mainly in Europe and North America as well as heavy-duty trucks occurred with first FCs as APUs (auxiliary power units for onboard electric energy supply) and later also as main propulsion system. Trains and airplanes equipped with FCs as well. A widely noticed project was the Cryoplane from an EU consortium, showing that even for aviation systems FCs can be principally suitable. But the high needed energy and power densities for flying a big airplane would lead to tremendous loss of passenger space for storing the respective amount of hydrogen. Therefore, FCs are projected to enter this sector in a later stage of decarbonization of traffic.

Other interesting developments went on in the maritime field of applications. Submarines were tested with FCs already at the end of the last century and a number of ships with FCs were built over the latest 20 years, most of them as prototypes and took out of service later, because there was no real business case. Nowadays even the big shipping companies are rethinking emission-free navigation especially for the big ocean ships, carrying more and more ecologic aware tourists into nature-sensitive regions around the world. FCs can power ships or at least their onboard power supply while berthing or docking at a harbor.

10.2 Fuel cell types in mobile applications

There are some main types of FCs consisting of different components, more or less suitable for mobile applications (Tab. 10.1).

Tab. 10.1: Types of fuel cells and their characteristics for use in mobile applications (green: favorable, red: less suitable).

Fuel cell	Electrolyte	Temp	Fuel/oxidant	Characteristics
Alkaline (AFC)	KOH	~90 °C	H_2/O_2	🟥 Liquid electrolyte, pure O_2
PEM (PEMFC)	Polymer membrane	~80 °C	H_2/O_2, air	🟩 Suitable temperature, robust, rel. cheap
Direct methanol (DMFC)	Polymer membrane	~130 °C	CH_3OH/O_2, air	🟥 CO_2 as by-product, low efficiency
Phosphoric acid (PAFC)	Phosphoric acid	160–220 °C	Natural gas, H_2/O_2, air	🟥 Elution of acid, high temperature
Molten carbonate (MCFC)	Molten carbonate	620–660 °C	Natural gas, biogas, coal gas, H_2/O_2, air	🟥 Liquid electrolyte, high temperature, complex process technology
Solid oxide (SOFC)	Yttrium-stabilized zirconia	800–1,000 °C	Natural gas, biogas, coal gas, H_2/O_2, air	🟥 Very high temperature, long starting time, expensive materials

For early prototypes mostly the alkaline fuel cell (AFC) has been used, since this was the most proven and those days easiest to handle assembly due to its quite moderate operating temperature, well-known components and fluids, and the broad experiences from usage in space missions. But knowing that the AFC strictly needs a supply of pure hydrogen and oxygen because of the intolerance against contaminations – especially carbon dioxide, leading to carbonate formation solidifying the liquid potassium electrolyte – the search towards other possibilities increased. FCs with acids as electrolytes like the phosphoric acid fuel cell (PAFC) can often be found in stationary applications like power plants, where in closed cycles liquid acids can be handled and recirculated. On the other hand for the transport sector those are more critical and less suitable, in addition the necessary higher operating temperatures and the resulting need for specific high-temperature, acid-proof materials the PAFC is not the preferred solution. Also the other high-temperature FCs, molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC) are inferior choices. Both run only on temperatures above 600 °C and 800 °C, respectively, and require expensive materials. Moreover, the MCFC uses a molten carbonate as electrolyte, which has to be costly circulated, cleaned, and held in its molten liquid state. Because of the ceramic solid electrolyte, only conductive above ca. 800 °C, the SOFC suffers the same challenges and additionally has a ceramic core and usually glass sealings that tend to fracture under harsh vibration and shock conditions in a mobile application.

At last the proton exchange membrane fuel cell (PEMFC) started its triumphal procession with the development of a polymer material named Nafion by Walter Grot in 1960 [6]. As a derivative from well-known Teflon, the new plastic was capable of conducting protons, the core blocks of hydrogen, when simply swelled by water. Coated with catalyst layers as electrodes, assembled with carbon paper as gas diffusion layers and outer bipolar plates with channels for hydrogen and air supply, therefrom a robust and reliable FC could be derived. The operating characteristics at relative low temperatures with high efficiencies and the simple design made it very promising for use in mobile applications. Today after further intensive development and a lot of intensive testing in different kinds of vehicles and fleets, the PEMFC is the chosen state of the art, converting hydrogen and oxygen from air into pure water vapor, heat, and electric energy.

Another FC type, based on the PEMFC, was on and off seen as another possibility for mobile use, the direct methanol fuel cell (DMFC). Owing to the advantage of being fed by methanol as a liquid energy carrier with high energy density in a very common fuel tank, it uses similar components and is therefore also robust and simple. But the more complex conversion of methanol and oxygen in a DMFC leads to lower efficiencies than the PEM and the non-avoidable emissions of carbon dioxide, thus it being not really superior to a combustion engine.

With further research and development, a derivative of a PEM FC towards a PAFC might become suitable for mobile applications, the so-called high-temperature PEM (HT-PEM). With use of a phosphoric acid–doped membrane as electrolyte the operating temperature can be increased to a level comparable to a common internal combustion engine. This offers the advantage of more efficient cooling, leading to higher installable FC power and by avoiding the otherwise necessary humidification it also leads to significant simplifications of the FC system. But up to now, there’s no solution for running this FC type with acceptable power densities at lower temperatures or even starting the FC from subzero.

10.3 The PEM fuel cell components and working principle

A single PEM FC (Fig. 10.4) typically consists of different single components. The heart of a PEM is the polymer membrane, mostly a web of polytetrafluorethylene as backbone filled with Nafion, a brand name for sulfonated tetrafluoroethylene–based fluoropolymer-copolymer [6]. This specific ionomer in combination with water in its pores is capable of conducting positive charged ions, for example, the atomic cores of hydrogen, H^+ ions.

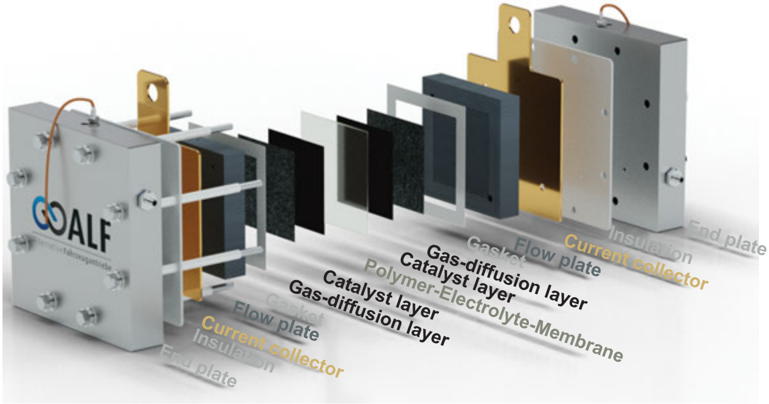

Fig. 10.4: Main components of a single PEM fuel cell. (Graphic by J. Hrdlicka, Chemnitz University of Technology).

Such a membrane commercially available as a foil is then coated with paste or ink for the electrodes. This paste is mainly made from carbon black powder with a specific content of precious metal as a catalyst, for example, platinum. The catalyst particles in the electrodes are responsible for dividing the hydrogen on the so-called anode side into its core parts, protons and electrons, and on the cathode side for the oxygen reduction reaction (ORR) as a pre-step for the recombination to water from protons, oxygen and the electrons conducted through the outer electric circle from the anode to the cathode side. The so built membrane with its electrodes is widely named as membrane electrode assembly (MEA) or catalyst coated membrane (CCM).

Directly connected to the electrodes on each side a gas diffusion layer (GDL) follows. The GDL can be made from carbon fibers, forming a kind of mesh capable of leading hydrogen and air to the reaction zone in the catalyst layer and conveying produced water from the reaction zone outward. Additionally, it conducts the electrons from and to the electrodes and supports and stabilizes the very thin and limp membrane. An assembly of CCM and GDLs often is named 5-layer-MEA.

For a reliable sealing of anode against cathode and the outer side as well as to keep the MEA stretched, the membrane is framed by a sub gasket (e.g., made from polyimide), applied on each side then forming a so-called 7-layer-MEA.

To complete a single PEM cell, two plates finally hold such an MEA in between. Next to mechanically stabilizing the cell, these bipolar plates own various other important functions and therefore have to meet specific requirements, both stated in Tab. 10.2.

Tab. 10.2: Functions and requirements for bipolar plates.

Function	Influencing parameters
Conduct current	Electric conductivity through plane, thickness
Conduct heat	Heat transfer to a cooling fluid
Seal one cell from another	Tightness, diffusivity
Transport gases	Flow field, pressure drop, equal hydrogen, and air distribution
Transport water	Flow channels with prevention of droplet blocking and flooding
Structural integrity	Stiffness, thickness

Moreover, in a tradeoff between lifetime, installation space, fabrication, costs, and sustainability they also should be

- lightweight,
- corrosion resistant/durable,
- capable of retaining ions or radicals otherwise affecting the membrane,
- thin, flexible, and stiff,
- efficiently mass fabricable at low emissions,
- cheap, and
- recyclable.

Due to these numerous restrictions, two main development lines are currently taken. One, the more classical variant, is the graphitic bipolar plate. Derived from the early stages of FC development, when pure graphite had been used, nowadays plates are made from graphite-polymer-compounds with the main advantage of being very durable but in contrast with a minimum thickness for being gastight and stable. Furthermore, those are not that well suited for mass fabrication considering the cycle times of the production process. The other is the metal bipolar plate. Taking into account that metal sheet forming is a well-known and mature mass-manufacturing technology, especially for mobile applications the property of reaching a thickness below 0.1 mm is a main benefit. Against that, a lot of effort is currently spent to find basic materials together with coatings that meet the requirement for high lifetimes. Meanwhile the needed durability of 5,000 h for passenger car applications is reached [7], but higher lifetimes for use in light-/heavy-duty vehicles or buses for the time being are more suitable on a graphite basis.

For cooling purposes, a bipolar plate often consists of two half-plates, both welded or glued together, forming a cooling flow field in between, designed to be passed by a cooling fluid. For lower power ranges of the cell air can be a reasonable solution, but due to its relatively low heat capacity and heat transfer coefficient for mobile applications with higher power outputs, that means also higher thermal losses, a liquid becomes inevitable.

To keep the overall cell tight between anode and cathode as well as to the ambient, sealings need to be placed appropriately. Those can be similar to O-rings or flat gaskets, optionally embedded into the bipolar plate, with a geometry adapted to cell in- and outlets, typically made from silicon-based materials. Among various other options one mentionable can be found in dispensing the seal onto the bipolar plate or the MEA with the aim to have higher durable tightness, but accepting longer fabrication times and hard disassembly for later repair and recycling.

Finally, since the electric current output of a cell is defined and though limited by the cell's area, for an appreciable power output more cells have to be put together in a row, followed by an addition of voltage, and held by a clamping system. The latter can consist of two current collector plates with connectors for electric cables, each placed at the end sides of the so gained FC stack, two stable endplates with insulations to the connector plates to apply the necessary clamping force, induced by simple threaded rods with torque controlled mounted nuts. Next to systems like metal tie straps, rudimentary taken from packing industry, many other developments with bolts and springs can be found to secure the durable stack compression.

The endplates additionally hold the fittings for mounting of tubes and hoses that deliver the media – hydrogen, air, and cooling fluid. More newer versions of endplates are more integrated and compact, even hold some process components inside like valves or ejectors and are made from plastics instead of full metal material. This makes them more lightweight, cheaper, and more eligible for series (Fig. 10.5).

Often for diagnostic purposes a connector is placed at each cell of the stack, where a cell voltage monitoring system can be installed. Herewith problems during operation can be detected; at least if a voltage drop in one or more cells occurs, actions can be initiated to countervail.

Fig. 10.5: Modern automotive fuel cell stack [8].

10.4 The fuel cell system for mobile applications

For the operation of a PEM FC some components are essential, forming together a FC system. Those can be clustered in four main modules: the air management module, the hydrogen management module, the cooling module, and the control module, as shown in Fig. 10.6.

10.4.1 Air management module

The air management module at the intake side sucks air from the ambient through a filter. In contrast to internal combustion engines the filter is more than a paper for filtering particles. It also has to hold back aerosols and gases that harm the FC stack, for example, CO and sulfur compounds. Some suppliers already are in the market with specific series solutions for FC air filtering.

A compressor then increases pressure to a level needed at least to compensate pressure losses through the subsequent flow path according to the needed sufficient mass flow to operate the stack at a wide range of operating points with different power loads.

From the variety of air compressors available, only a few meet the requirements for charging a FC. The delivery of absolute oil-free air definitely is the most important but also hardest achievable condition, because for many concepts oil for lubrication is vital. Secondly, the pressure ratio for a wide range of mass flow has to fit to the operating points for different power loads.

So summarized, all the main requirements for FC air charging are:

- delivery of absolute oil and contaminant free air,
- even (constant) maximal pressure ratio over a wide range of mass flow,
- mass flow with minimal pulsations,
- electrically driven (no crankshaft in FC system),
- high efficiency,
- speed controllable with high operating dynamics,
- low noise level,
- small and lightweight,
- low costs, and
- efficiently mass fabricable.

Under these restrictions many compressor types are less suitable. For example, common reciprocating piston machines at least deliver air with high pulsations and have to be oil lubricated; most blowers only achieve low pressure ratios and quite low efficiencies. However, only two variants made their way into FC systems: screw compressors and centrifugal turbo-compressors. Former came up with early mobile FC systems because of their capability of running oil free and a

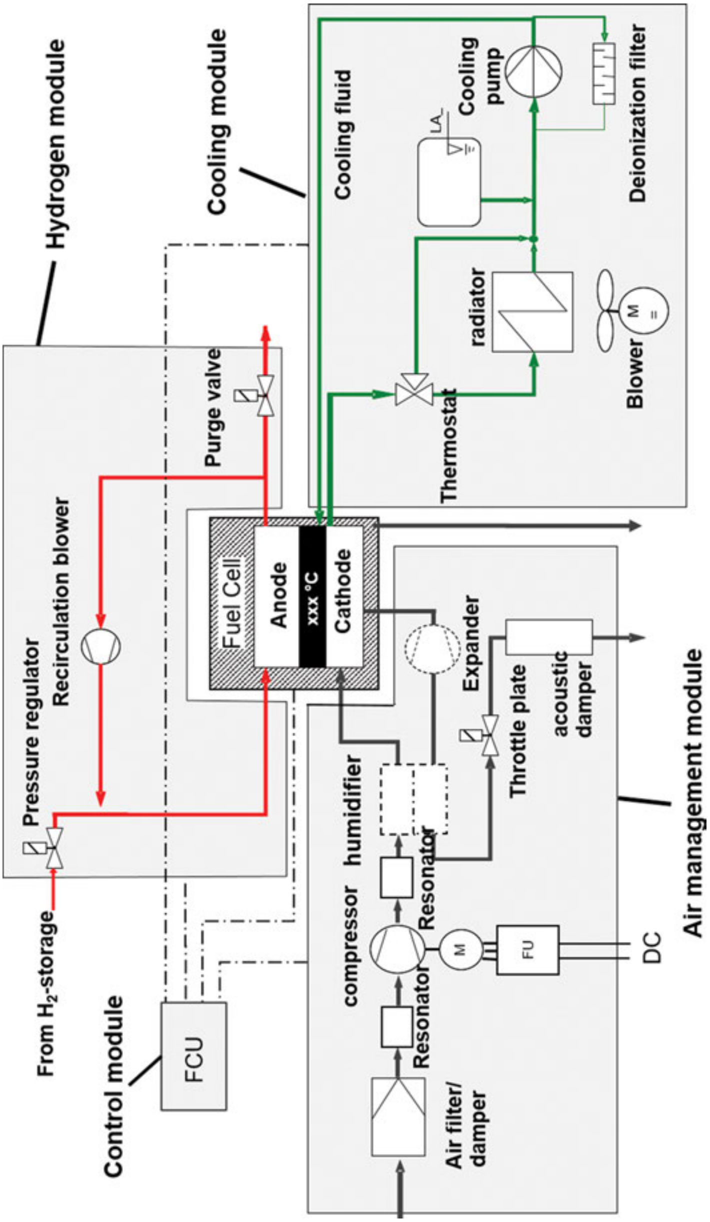

Fig. 10.6: Main modules with key components of an automotive PEM fuel cell system.

characteristic map, properly matching the needed flexibility in pressure and mass flow. But still combined with relatively heavy weight, bad acoustics, and high costs it soon became obvious that a potential better solution could be simple turbochargers, well known from internal combustion engines. Meeting most of the above other targets, yet equipped with a narrow operating map, since then a lot of effort was spent to get them oil free with different approaches for air lubricated or magnetic bearings. Additional measures, for example, flow bypasses, to expand their map to the operating conditions of a FC, are today used in a wide field of applications.

Before entering the FC, downstream the air management module the compressed air flows through a humidifier. This can be a kind of water injection device, or a membrane device, transporting water through a membrane from a fluid or from the water saturated FC outlet gas to the dry air induced by the compressor. Due to the limited humidifier inlet temperature, the compressor outlet air has to be cooled down, otherwise harming the membrane material, especially at high pressure ratios of the compressor, the compressor outlet air has to be cooled down, otherwise that explains the sometimes-seen installation of an air intercooler.

Even newer developed FCs with MEAs working with low pre-humidified gases, thus with no need for an external humidification, anyway need a lowered temperature at the air inlet, not damaging the stack materials.

Streaming through the FC the oxygen partly reacts with hydrogen to water and so at the outlet the exhaust gas has decreased oxygen and increased or even saturated water content. For this reason, the gas flows back through the humidifier, transferring the high water content to the fresh gas. A backpressure valve then is put in place to control the pressure of the overall cathode side and the air is released to the ambient. Finally, a few dampers or resonators in the cathode stream can take care of a smooth acoustics.

10.4.2 Hydrogen management module

On the anode side the FC is fed with hydrogen from a storage compartment, usually in mobile applications implemented as gas vessels, holding hydrogen at 35 or 70 MPa, depending on needed energy content and live storage space for each specific use case. Liquid, cryo-compressed, or metal hydride storages have also been proven many times, but weighing up different factors, stated in Tab. 10.3, led to the wide consent of gaseous compressed hydrogen. The nowadays mostly used so-called Type IV vessels contain polymer inliners as a permeation barrier and are wrapped with carbon fibers to carry the stresses induced by the inside high pressure.

Tab. 10.3: Advantages and disadvantages of different hydrogen storage options in mobile applications.

	Pressurized gaseous	**Liquid**	**Metal hydride**
Specs [9]	– (35) 70 MPa – −40–85 °C – (1.6) 1.8 kWh/kg[a] – (0.5) 0.9 kWh/L[a]	– < −253 °C, – 0.1–0.5 MPa – 2 kWh/kg[a] – 1.2 kWh/L[a]	– 0–150 °C – 0.1–10 MPa (eligible) – 0.4 kWh/kg[a] – 0.8 kWh/L[a]
Advantages	– Proven technology – Long time gastight – High filling and defilling dynamics – Fast emergency blow off – No auxiliary power	– Higher energy density – Variable tank geometry – Fast filling	– Intrinsic safety – Durable storage – Free tank geometry
Disadvantages	– Lower energy density than liquid – Geometric constraints (cylinder, sphere)	– Need for permanent cooling (aux power) – Extensive insulation – Hydrogen loss due to deflation – Cryogenic handling	– Slow dynamics – Complex thermal management – High amount of inert storage material – High filling/defilling time
Favored applications	– Passenger cars – Light- and heavy-duty vehicles – Buses – Trains	– Heavy-duty vehicles – Ships – Airplanes	Stationary autonomous intralogistics vehicles

[a] Including storage housing and system.

After leaving the storage vessel, the hydrogen pressure is decreased by a first pressure reducer inside the tank valve, latter a specially designed component that also holds, for example, a pressure and temperature sensor, a temperature pressure relief device, and a manual shut off. Afterward the hydrogen flow from eventually more vessels is combined in a high-pressure tubing interconnection; a second external pressure reducer sets the pressure to a level of ca. 1–2 MPa to only handle a quite low pressure in the following hydrogen lines down to the FC system. A system isolation valve is built in to cut off the hydrogen flow for shut off and a pressure control valve then sets the corresponding pressure for each operating point on the anode side.

For operating the PEM FCs' anode principally three basic schemes are suitable. One is a dead-end flow, just blocking the outlet port and using all inlet hydrogen for the reaction. Sometimes used for smaller FC systems, disadvantage for this option is the highly uneven hydrogen concentration downstream the flow channels, followed by an also unbalanced power and temperature density with bias to harmful defects of the MEA.

To elude this so caused hydrogen starving, the second possibility is to open the anode outlet to the ambient and vent the gas well regulated to the ambient. Current and temperature inhomogeneity this way can be eliminated, but losing hydrogen results in a vast loss of energy and a possible safety issue. So, most systems use a third option, recirculating the outlet flow back to the inlet. That can be done by using a passive ejector pump and an electrically propelled active recirculation blower. An ejector makes use of the inlet pressure to increase the flow velocity through its specific geometry and transfers the momentum from the fresh hydrogen to the recirculated mass flow. That is why the ejector only works as long as a minimum of fresh mass flow passes through. Thus, for part-load operating points with only low need for hydrogen, the recirculation needs an active pump or blower. Although such blower can substitute the ejector for the overall range, in the majority of cases it is placed conjoined in a row. At lower power outputs, the active blower keeps the recirculation alive, whereas the ejector takes over whenever possible, with aim of increasing system efficiency by saving electric power by switching off the blower.

Nevertheless, the recirculation contains a purge valve, necessary to vent the loop in certain time intervals, depending on the contamination content on the anode side, in particular nitrogen that diffuses mainly from the nitrogen carrying cathode air through the membrane.

10.4.3 Cooling module

Cooling circuits for a PEM FC generally look very similar and can be adapted from internal combustion engines. There’s of course need for a radiator and a fan to transfer heat from a cooling fluid to the ambient as well as for a temperature regulation valve and a controllable pump. The differences are two main issues, making the cooling of a FC more challenging. First, the coolant must not be electrically conductive. Due to the parallel fluid flow through all the single cells, otherwise it would short-circuit the stack. Therefore, deionized water charged with frost protection is a preferred fluid. But because of the inevitable elution of ions over time from all the surrounding tubes, hoses, and components, an additional deionization filter filled with an ion-scavenger resin has to be installed in-line. Second, the amount of heat to be cooled is higher. At first sight, it seems weird having a better efficiency than an adequate combustion engine and at once transporting more heat to the coolant. A closer look at the energy flows for both then reveals the reason. The heat conveyed by the exhaust gas from the FC at a much lower temperature level leads to higher amounts of heat to the coolant, also running on a low temperature level, and so at least to bigger radiators. The latter can become a hard engineering issue, especially in mobile applications with narrow package space.

10.4.4 Control module

FC systems for mobile applications, put together from the former three modules, are interspersed with many sensors and actors to get operating data and to react on different load conditions by controlling specific parameters. Important control loops cover the regulation of mass flow, temperature, pressure, and humidity for the FC media – coolant, hydrogen, and air. Also measures, important when a voltage drop of the stack or a single FC occurs, are initiated by the FC control unit (FCU). The FCU can be a derivative from a common vehicle control unit and carries software that's mostly based on a lot of long-time expert experience in operating FCs and can represent a future key intellectual property. Especially diagnostic algorithms for FC health and lifetime prediction and self-adapting control strategies with artificial intelligence are the aim of current research and development. Finally, as in automotive industry many onboard networks are CAN-bus handled, the FCU and all the sensors and actors should own CAN-bus interfaces.

10.5 Fuel cell powertrain and hybridization

To complete an overall mobile FC powertrain some supplementary components are needed; see Fig. 10.7.

The electric power from the FC system is distributed by a power distribution unit (PDU). The PDU is a connector in the intermediate current link between the system, the main electric drive, and the battery branch. While a powertrain in principle can be powered stand-alone by a FC system, at least a common lead acid battery is needed for starting purposes, and powering the usual board net. With a voltage converter between system and 12 V battery level also the battery can be recharged. An additional high-voltage hybrid battery supports the acceleration dynamics and allows the recuperation of otherwise dissipated braking energy.

A high-power voltage converter, placed near the hybrid battery or the FC system, defines the intermediate voltage. Even two or three of these can be integrated, each near a power sink or source, aiming to gain high efficiencies by running at highest possible, most constant voltage levels. But in terms of package, costs, and extra switching losses, often only one is favored.

The electric drive, for numerous applications a permanent magnet synchronous machine, needs an inverter to alternating current from direct current fed by the FC and the battery into the intermediate circuit. To the latter also the main auxiliary

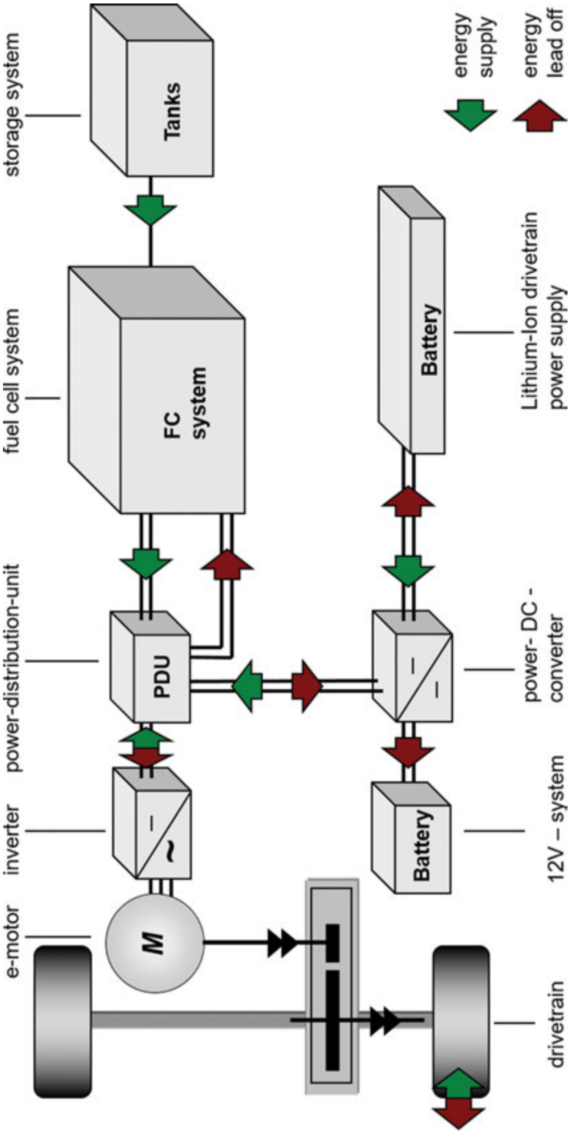

Fig. 10.7: Sample fuel cell powertrain layout in mobile applications.

components can be connected via the PDU, for example, the FC compressor, the recirculation blower, and various pumps responsible for vehicle safety and comfort issues.

The hybridization concept is mainly defined by the size of the battery and the FC. A big FC with a small battery as booster is suitable for longer driving ranges and leverages the high energy densities of hydrogen and the short refueling durations. Reversely, a smaller FC combined with a big battery works more as a range extender, beneficial when starting from a pure battery vehicle basis and trying to increase range. But taking into account that volume, mass, and costs do not linearly fall with FC power output, mobile applications head more toward the former stated option.

10.6 Challenges for FC in mobile applications (energy, power, safety, lifespan, costs, life cycle assessment)

In mobile applications energy storage and conversion plays a key role. Therefore, the engineer's area of conflict for FCs is mainly framed by a pentagram of system requirements as shown in Fig. 10.8.

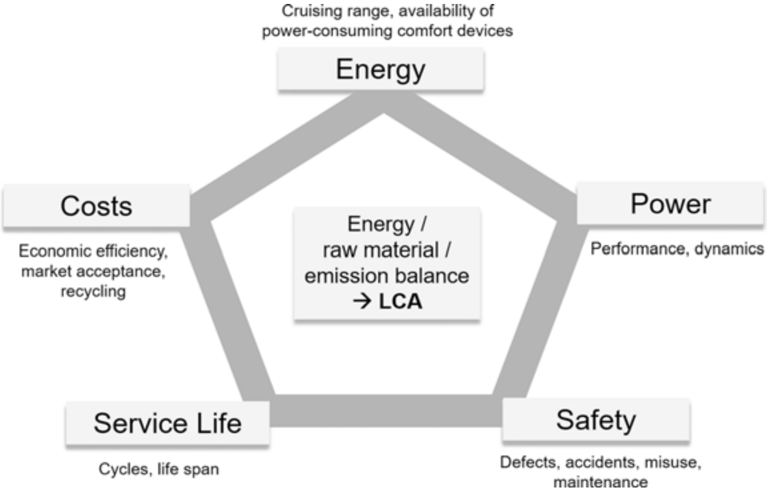

Fig. 10.8: Pentagram of requirements for fuel cells in mobile applications.

Concerning energy and power an ongoing challenge is the further increase of energy densities in hydrogen storage and a power density growth of the FC to gain smaller systems or higher power outputs from a given package space. The aims here are long ranges without waiving of convenience issues combined with adequate driving performance known from conventional powertrains. Next, safety is an indispensable system characteristic and has to be taken into account for each development step toward higher energy and power densities. That has to cover issues of system failure, emergency, misuse, as well as maintenance aspects. Furthermore, lifetime has to meet the minimum application requirements, for example, for passenger vehicles more than 5,000 h, with at once reaching a defined number of operation cycles without significant aging. At last, costs have to be cut down to a minimum for economic viability and market acceptance.

Additionally, since ecology plays a major role nowadays, a look at the overall value chain becomes more important. So, at last a life cycle assessment for each part of the mobile FC system including the used hydrogen as a fuel has to be performed [10]. Starting with a look at the exploitation of used raw materials, each step of the production phase has to be analyzed in consideration of energy demand and emissions, through the operating phase of the application to the point of recycling, remanufacturing, or disposal.

10.7 Mobile applications for fuel cells

Since FCs are principally suitable for wherever energy conversion from hydrogen to electric energy is needed, FCs so far found their way into a variety of mobile applications. Nowadays highest interest seems to be in the heavy-duty sector. Wherever high mobile power outputs over a long time are needed, FCs are seen as a very applicable solution. That means e.g. trucks, buses, construction machines, boats, ships, ferries, trains etc. For all those, the advantages of no emissions with long range and fast refueling times predominate in contrast to pure battery solutions, package space is not that small, and cost targets are not that hard to achieve.

On the way towards systems mainly designed for pure propulsion purposes, another idea is at least to power the auxiliaries of a vehicle by a FC, a so-called APU. By using electric power from hydrogen during, for example, idle times, energy consuming times of only the board net and warm-up or even keep-warm phases for a large main powertrain system, emissions can be reduced severely, additionally still independent from a stationary clean power source connected by a cable.

The next consequent step then might be a spread of the series-produced FC systems to first light-duty vehicles, large passenger vehicles like vans and SUVs, and later also to smaller cars, with good cause for now configured as pure battery vehicles. There’s no reason, once FCs are mass manufactured and therefore cheap and meeting all other development targets, why they should not be used also there.

In the logistics sector currently FCs are already widely economically established [11]. The main driver here has been the big advantage of needing only one fast refillable vehicle for each shift instead of more running on batteries while at least one of them is out of operation to be recharged at a power plug.

Perhaps the latest use of FCs for main propulsion may occur in commercial aviation. There is the need for very high energy and power densities, while in parallel maximum space is wanted for passengers and goods. A part-solution also here is the emission-free APU, coming with extra advantages, the use of nitrogen from the FC exhaust gas as fire-extinguishing measure and the use of product water from the FC for hygiene and onboard food and beverage issues. But mid- to long-term also FCs as main drive for planes might be used, several demonstrations with drones or sport aircrafts already proved feasibility.

Of course, mobile applications for FCs own one common demand, the need for a comprehensive hydrogen infrastructure. But, in contrast to a battery recharging infrastructure, this can be achieved with a finite number of refilling stations. Those can be placed as supplement to existing gasoline stations, utilizing the present facilities with all the comfort issues known and valued by customers. And the filling stations can be supplied by hydrogen from decentral on-site or centralized large-scale production. Hydrogen can be delivered in gaseous or liquid state by trailers or pipelines, just as needed for different specific use cases.

In many countries around the world the build-up of hydrogen stations already has begun and the formerly known chicken-egg dilemma between mobile applications and infrastructure is going to be resolved soon.

10.8 Outlook to further research and development

Nowadays, no real technological job killers for FCs exist anymore; the principal feasibility is proven for almost all mobile applications. But, of course a number of topics still remain to be researched and further developed. Even more, the still steep development gradient for FCs is promising a vast increase in optimized technologies due to further intensive research.

On the agenda are, for example, new materials for membranes, bipolar plates, and their coatings with the aims to be more durable, higher conductive, and cheaper. Lightweight issues for the FC stack as well as for each component up to now have rarely found their way into the design process.

Cost reductions can still be found with a variety of approaches; the decrease in use of precious metals especially for the platinum catalyst is a major topic. Although platinum content has been lowered the latest years to a level almost comparable to a catalyst for diesel exhaust gas after treatment, there’s still potential for further reductions. Therefore, new membrane coating technologies, contra-aging operating strategies and entirely other catalyst materials with optional, nanostructured particles are noteworthy efforts.

The extensive use of components known from other series manufactured applications should as well lead to decreased costs as a reduced system complexity by potentially leaving out nonessential components, even with accepting a slightly lower overall efficiency.

Finally, the manufacturing processes for each of the components have to be developed towards low or even zero emissions, low energy consumption, and reproducible quality for mass production. Additionally, with the approach for an overall circular economy the lowest possible environmental impact.

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Jens Mitzel, K. Andreas Friedrich

11 Hydrogen fuel cell applications

11.1 Utilization of hydrogen in fuel cells

The utilization of hydrogen as energy carrier and its highly efficient conversion to electrical energy is one of the most promising technologies to address the challenges of air pollution (NO_x, CO, particulates) and global warming (mainly CO_2, CH_4) caused by anthropogenic emissions. Conventional energy converters transform the chemical energy of a fuel in several steps. For example, a coal power plant converts the chemical energy of the coal via thermal energy and kinetic energy to electrical energy using water steam and turbines. Due to energy dissipation in each step the efficiency of such a power plant is about 30–50% [1]. In contrast, fuel cells can convert this chemical energy directly to electrical energy (Fig. 11.1) using electro-catalytic reactions and direct charge transfer. Depending on the used fuel cell technology system efficiencies of 50% (low-temperature fuel cells) to 60% (high-temperature fuel cells) can be achieved [2]. Most important, hydrogen-fed fuel cells do not use carbon-based fuels and consequently do not emit CO_2 and particulate matter. Due to the direct catalytic conversion and lower temperatures (<1,200 °C) also the emission of NO_x is avoided.

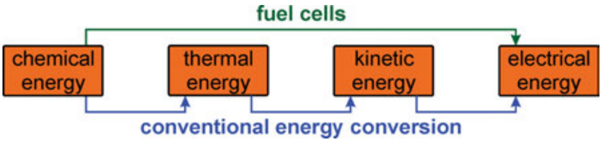

Fig. 11.1: Energy conversion in fuel cells and in conventional energy converters.

The high potential of hydrogen as energy carrier for emission-free energy supply was published in 2017 by the Hydrogen Council in their study “Hydrogen scaling up – A sustainable pathway for the global energy transition” [3]. The Hydrogen Council is a global, industrial initiative founded in 2017 to promote market initiation of hydrogen and fuel cell technologies. This includes the commitment of the council members (Air Liquide, Alstom, Anglo American, BMW, Daimler, Engie, Honda, Hyundai, Kawasaki, Shell, Linde, Total, and Toyota) to invest annually 1.9 billion euros within the next 5 years for this purpose. This study represents the perception of the council how to establish a hydrogen-based energy market up to 2050. According to this vision, up to 20% of the intended reduction of CO_2 emissions can be achieved in the transport sector by establishing more than 400 million passenger cars, 15 million heavy-duty trucks, and 5 million buses powered by fuel cells, a market share of about 25%. By fulfilling the targets of this study 18% of global energy demand can be covert by hydrogen technologies and 10 million barrel of crude oil

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can be saved every day. This would result in a reduction of 6 GT of annual CO_2 emissions worldwide. The CO_2 avoidance potentials for 2050 for the different sectors and more detailed for the transport sector are summarized in Fig. 11.2. This chapter provides an overview of the current status regarding market implementation and of new developments in fuel cell technologies.

11.2 Working principle

The simplest chemical reaction in a fuel cell is the reaction of hydrogen and oxygen from air. The basic principle is explained with regard to the proton exchange membrane fuel cell that uses hydrogen ions as charge carriers in the electrolyte. The fuel cell is driven by the supply of air flow and hydrogen flow into the cathode and the anode, respectively. Hydrogen is used as fuel, and oxidized at the anodic catalyst allowing the hydrogen ions, basically protons, to migrate through the membrane. On the other hand, the electrons travel through an external electric circuit to the cathodic catalyst. Oxygen from the air flow is reduced with the electrons at the cathodic catalyst combining with protons to form water molecules completing the redox reaction. The overall redox reaction is given as follows:

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O \tag{11.1}$$

As the general redox reaction is an exothermic reaction, heat is released beside the usable external electric power. The general redox reaction comprises of several intermediate chemical reactions taking place at anode and cathode. At the anodic catalyst hydrogen is first dismantled to hydrogen atoms at the Pt catalytic sites and oxidized. As a result, two protons are produced and two electrons are released per disintegrated hydrogen molecule. The reactions at the anode are indicated by

$$H_2 \rightarrow 2H^+ + 2e^- \tag{11.2}$$

The released electrons move to the cathode side over an external circuit. Most of hydrogen ions are bonded to liquid water in the membrane, so hydrogen ions with solvation shell are created, which are often denoted as H_3O^+- ions.

At the cathode the reduction reaction of oxygen takes place after each oxygen molecule is decomposed into two oxygen atoms. The reduction is provided by the released electrons moving from anode to cathode outside the cell. The reactions at the cathode taking place at catalytic sites (e.g., of a platinum catalyst) are indicated by

$$\frac{1}{2} O_2 + 2e^- + 2H^+ \rightarrow H_2O \tag{11.3}$$

As a result, water molecules, which are the products of the general redox reaction, are formed.

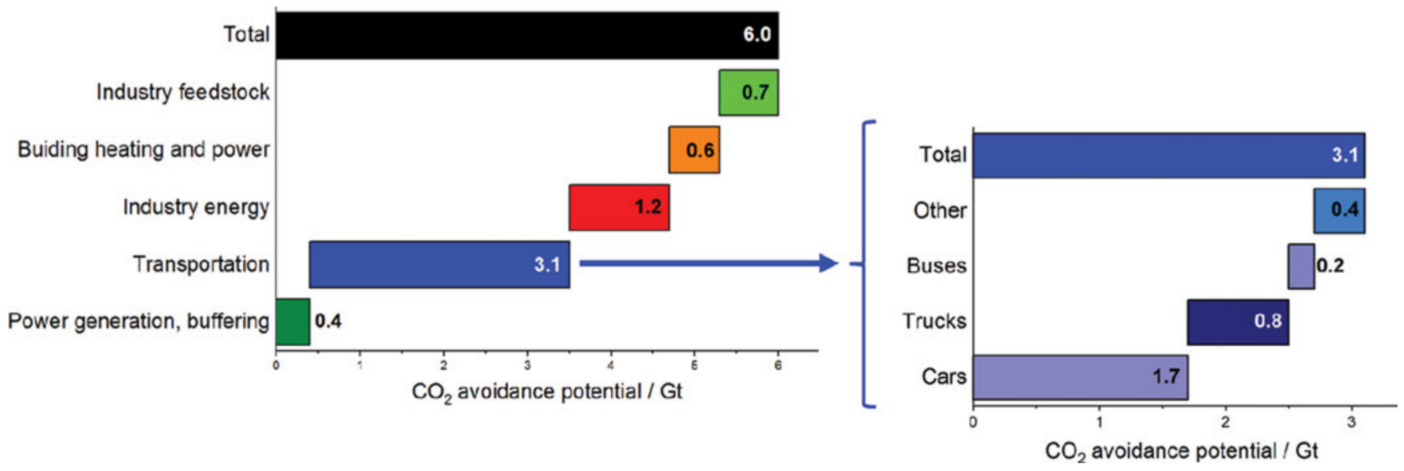

Fig. 11.2: CO_2 avoidance potential until 2050 according to the Hydrogen Council [3].

Figure 11.3 illustrates schematically the functional principle of fuel cells with either hydrogen ion or oxygen ions as charge carriers.

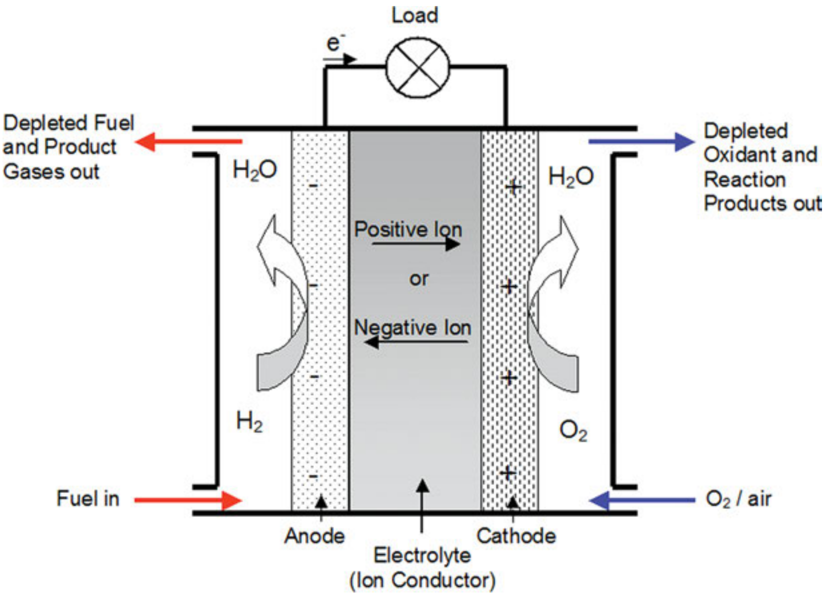

Fig. 11.3: Principle of fuel cell operation.

Due to a focus in this chapter on the applications we will not elaborate further on materials, components, and cells for different types of fuel cells with large variance of operation temperatures. The interested reader is referred to reviews on fuel cell technology [4–6].

11.3 Passenger transport applications

The frequently exceeded air purity limits in cities have shown in recent years that a reduction in pollutant emissions from vehicles is urgently needed in order to achieve existing environmental protection goals and to ensure the quality of life. These goals can be achieved through the use of electric vehicles. The marked introduction of battery power electric vehicles is still challenging due to current high prices, short ranges, and long recharging. By using fuel cell electric vehicles (FCEVs), it is possible to address these challenges of electrically powered vehicles. Due to the high storage density of compressed hydrogen, higher ranges can be achieved and refueling takes about 3 min, no longer than conventional refueling of a car with gasoline.

For automotive fuel cell applications, the last 5 years were dominated by the launch of FCEVs, which are manufactured in small series. These are hybrid vehicles based on the use of polymer electrolyte membrane fuel cells (PEMFC) and lithium-ion batteries. Thus, the transfer of the prototypes, which dominated the fuel cell activity for many years, into a close-to-mass-production manufacturing was successful, and Asian automakers have taken a leading role. An automotive fuel cell system is shown in a simplified block diagram in Fig. 11.4.

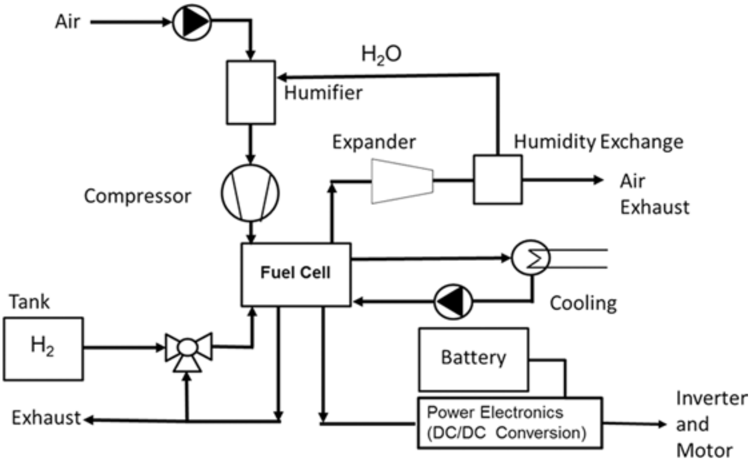

Fig. 11.4: Scheme of a fuel cell automotive system.

An automotive fuel cell system is normally hybridized with a battery that can exhibit quite different capacities depending on the vehicle design (e.g., the GLC from Daimler with a plug-in battery reaches 50 km battery range). The fuel cell system consists of 4 subsystems: (1) the hydrogen supply system, (2) the air supply system, (3) the cooling system, and (4) the electronics/power management system. From a high-pressure tank (700 bar) hydrogen is released at lower pressures to the fuel cell and recirculated to achieve high fuel utilization and to avoid fuel depletion in the fuel cell. A main feature of the air supply system is the humidification of the input air by water exchange from the exhaust air. Cooling systems for fuel cells are similar to internal combustion engine (ICE) radiators but larger cooling areas of the radiators are needed due to the low temperature of polymer membrane fuel cell and the difficult rejection of heat to the environment. The power management needs to be quite sophisticated to account for high currents, voltage conversion, and optimized hybrid operation between fuel cell and battery. Due to the high power of the battery, dynamic operation of the fuel cell can be limited improving the durability of the cells significantly. Also the battery enables regenerative breaking increasing the efficiency of the overall system. With a plug-in battery efficiencies can be further increased reaching similar values as a battery drive but with higher driving range. The main requirements for automotive fuel cell systems are high maximum power output, high power density, and reliability under real world driving conditions including freezing conditions and repetitive system shut-down and restart.

11.3.1 Close-to-mass-production manufactured FCEVs

The world's first FCEV of this kind was established 2013, the Hyundai ix35 Fuel Cell (134 hp and 594 km range). It was manufactured in a small series of 1,000 SUVs. About 100 vehicles have been deployed in the United States, focused on California because of the existing incentives and hydrogen infrastructure. In February 2016, this US fleet reached a total of 1 million miles. Another 250 vehicles had been delivered to 13 European countries. The remaining vehicles of the small series were distributed in the Japanese and South Korean market. In 2018, the newest Hyundai FCEV has been introduced: the Hyundai Nexo. The data of both FCEVs are summarized in Tab. 11.1 [7].

The Nexo, a 5-seater SUV, is a dedicated fuel cell car development and no longer an adaption of an existing vehicle as the ix35. It can be clearly seen that the Nexo has significantly improved acceleration values and driving range. With 754 km it demonstrates the largest range of all FCEVs on the market so far. This range is achieved through three hydrogen tanks with 52.2 L hydrogen each. Unlike most other FCEVs, all three tanks have the same dimensions, significantly reducing manufacturing and supply costs. The entire fuel cell stack is now 10% more efficient and 20% lighter than the model in the ix35 Fuel Cell, which has increased energy density by 30% [8]. The world premiere of the new NEXO was at the Consumer Electronics Show in Las Vegas on 9 January 2018. The launch for Korea was July 2018 and for Germany August 2018. First, 3,600 Nexo are to be manufactured in a factory in Chungju, South Korea. The Nexo is available in Europe for a price of 54,000 euros. Due to national subsidies this purchase price is reduced in South Korea significantly to just about € 29,000 [9].

On 15 January 2015, the first Toyota Mirai (154 hp and 500 km range) was delivered to Japanese Prime Minister Shinzo Abe. After the first FCEVs were sold on the Japanese market for the equivalent of about 48,000 €, the sale in the United States began in California in October 2015 at a price of about 52,000 €. The other US states followed in mid-2016. In Europe, sales started in September 2015, initially in Germany, the United Kingdom, and Denmark due to the existing hydrogen infrastructure. Sales in other European countries followed in 2017. On the German market, the Mirai costs about 78,500 € including taxes [10]. Just a month after launching the Mirai, Toyota had 1,500 orders, which significantly exceeded its production capacity for 2015 and resulted in lead times of more than 2 years, depending on the country. In 2015, a total of 700 vehicles were manufactured, of which 400 were intended for the Japanese market. For the coming years, Toyota expanded the production capacity, but with quantities of 2,000 for 2016 and 3,000 for 2017, the Mirai is still not a fully mass-produced vehicle [11].

Tab. 11.1: Comparison of performance data from Hyundai's Nexo and ix35 fuel cell.

		Nexo	**i×35 fuel cell**
Hybrid system	Total power	135 kW	124 kW
Fuel cell	Stack	440 cells	250–450 V
	Stack voltage	255–450 V	100 kW
	Stack power	95 kW	100 kW
Electric engine	Power	120 kW	100 kW
	Torque	395 Nm	300 Nm
Battery	Power	40 kW	24 kW
	Voltage	240 V	180 V
	Capacity	1.56 kWh	0.95 kWh
Tank	Capacity	6.33 kg 156.6 L	5.64 kg 144.0 L
Velocity	Max.	170 km/h	160 km/h
Acceleration	0–100 km/h	9.7 s	12.5 s
Driving range	NEDC	754 km	594 km

Following the presentation of the Clarity Fuel Cell (Fig. 11.5) at the Tokyo Motor Show in October 2015 and at the Geneva Motor Show in March 2016, the first new-generation FCEV by Honda was handed over to the Japanese Ministry of Economy, Trade and Industry (METI). In mid-March 2016 the sale of Clarity Fuel Cell started in Japan [12] and the first vehicles in Europe were delivered as part of the HyFIVE project in London and in Copenhagen [13]. Since December 2016, the car is also available as a leasing vehicle in California. The Clarity Fuel Cell is a four-door sedan with a 130 hp electric motor and a range of 589 km with a hydrogen storage capacity of 5 kg. The compact 103 kW fuel cell system is located completely in the engine compartment, allowing space for five passengers in the interior. In 2016, initially 200 vehicles were manufactured predominantly for the Japanese market [14].

In Europe, the first close-to-production manufactured FCEV was launched by the Daimler AG. The GLC F-cell is an SUV available since December 2018 [16]. In order to meet the gradual build-up of the hydrogen refueling infrastructure, it is the first fuel cell plug-in hydride vehicle on the market. In addition to the fuel cell, the GLC has significantly larger lithium-ion batteries compared to other FCEVs. About

Fig. 11.5: Honda Clarity Fuel Cell [15].

9 kWh assures up to 50 km range based purely on battery electric power. The 4.4 kg of hydrogen from the 700 bar pressure tanks increases the range to about 500 km [17]. The PEMFC system used is about 30% more compact than previous systems [18], which (as with the Honda Clarity Fuel Cell) allows the complete integration of the system in the classic engine compartment, an important prerequisite for the progressive mass production of FCEVs. The entire fuel cell system of the GLC uses only 20 g of the most expensive raw material of fuel cell production, the noble metal catalyst platinum. The associated cost reduction is another important criterion for the competitiveness of the vehicles and the price of the GLC F-Cell should be around 60,000 € [19].

In recent years, the objectives for the commercial introduction of PEMFCs to passenger transport applications have already been achieved in terms of efficiency, power density, and cold start capability as shown for the mentioned FCEVs [20]. However, the costs of the systems and their lifetimes must be further improved. To achieve cost targets the noble metal content in a FCEV has to be decreased to numbers that are used in the exhaust system of ICEs, namely about 3 g in gasoline engines and 6–8 g in diesel engines. The amounts of catalyst in the electrodes should therefore be reduced below 0.1 mg/cm^2. Because of the slower kinetics of oxygen reduction, especially the reduction of the loading of the oxygen electrode is the most challenging target for fuel cells. As published by General Motors in March 2016 [21], low cathode loading results in strong power losses at high current densities while the power requirements at low current densities can be achieved. This problem is due to the occurrence of additional mass transfer resistance near the catalyst. As the platinum loading decreases, the available catalyst surface area decreases and the oxygen transport rate increases. As a result, the local transport resistance close to the catalyst surface increases disproportionately due to oxygen diffusion through the ionomer film in the electrode. To counteract the problem, stable catalysts with large surfaces as well as special ionomers with high oxygen permeability in the catalyst layer have to be developed. As shown in General Motors' publication, stacking costs could be reduced by up to

25% by implementing electrode structures with low local oxygen transport resistances and thus commercialization cost targets could be achieved.

11.3.2 Alternative mobility concepts

In general, it has been observed in recent years that both the entry into electro mobility and the entry into hydrogen mobility are less implemented by private users, but rather by vehicle fleet operators. This is noticeable through the establishment of alternative mobility concepts. The higher range and fast refueling of FCEVs compared to other electrically powered vehicles are promising for applications such as car sharing or taxi operation. This allows increasing the number of FCEVs on the road, improving the utilization of hydrogen refueling stations, and increasing the public awareness of FCEVs. The anticipated high utilization of these vehicles also enables faster conclusions about the behavior of the FCEVs over the entire service life.

In Munich, Germany, the gas suppling company Linde has founded a subsidiary called Linde Hydrogen Concepts to establish the car sharing system BeeZero using FCEVs. For this purpose, 50 Hyundai ix35 fuel cells were purchased, which could be rented since August 2016 and which are operated exclusively with green hydrogen produced from renewable energy sources. In contrast to already established car sharing formats with battery electric vehicles BeeZero did not aim for short, spontaneous city trips, but provided emission-free vehicles for weekend trips or longer commute journeys. Unfortunately, this concept was only planned for demonstration of the technology and BeeZero ceased operations at the end of June 2018 due to economic reasons [22]. During the 2 years of operation the FCEVs were used for 850,000 h and 400,000 km.

Other car sharing fleets are still in operation in Germany. The BMW leasing subsidiary Alphabet Germany, specialized on mobility solutions for companies, has been expanding its vehicle offering by FCEVs since December 2017 [23]. About 30 Toyota Mirai will be added to the fleet within 3 years. The vehicles are used by major alphabetical customers, especially as service and pool vehicles. Also in Frankfurt, FCEVs can be used since September 2017 via car sharing [24]. Here, the company book-and-drive has taken a Toyota Mirai into operation, in order to demonstrate its suitability for everyday use and to dismantle initial fears of contact with the new technology. The booking of this Mirai costs 4 euros per hour, not more than conventional vehicles.

Additionally, the taxi concept using FCEVs seems to be a success story. For this application, the long recharging times of batteries are particularly negative. In December 2015, the start-up STEP (Société du Taxi Electrique Parisien) began testing FCEVs for taxi rides in Paris, France. A small taxi fleet of five Hyundai ix35 fuel cells under the name HYPE (Hydrogen Powered Electric) were taken into operation [25]. During the last 3 years, this fleet was expanded by another 60 vehicles of the same type [26] and 25 Toyota Mirai [27]. This makes HYPE the world’s largest fuel cell–powered taxi fleet using 100 FCEVs. Within the next 5 years, it is aimed to expand the fleet to several hundred vehicles, gradually replacing older taxis with ICEs, and launching equivalent services in Brussels and London [26].

The start-up company CleverShuttle from Berlin, Germany, uses hydrogen-powered taxis based on the ride sharing principle [28]. Here, a taxi ride is booked via a smartphone app and is possibly combined with trips of other customers, so that several passengers can be transported together. CleverShuttle promises fares that are 40% cheaper than comparable trips with conventional taxis, regardless of whether other passengers board or not. About 20 Toyota Mirai are used in Hamburg since 15 September 2017 in Munich since October 2017 [29] and additional 10 in Stuttgart since May 2018 [30].

11.3.3 Fuel cell–powered buses

In addition to the previously introduced FCEVs, hydrogen buses have enormous potential to reduce global CO_2 emissions. The study “Hydrogen scaling up” assumes that even a single city bus in 16-h operation annually emits 50 tons of CO_2, as much as 15 mid-range cars [3]. The hydrogen roadmap proposed in the study sets the target of converting up to 30% of all buses to hydrogen by 2050, which would require selling about 20,000 buses a year globally. Looking at the very ambitious plans for the new acquisition of fuel cell buses, this seems quite realistic, with the main driver for commercialization being in Asia. For example, South Korea plans to convert 26,000 natural gas (NG) buses into hydrogen technology by 2030, and Shanghai alone plans to use 3,000 fuel cell buses by 2020 [3].

Different projects have been initiated promoting the fleet construction of fuel cell buses in the coming years. In February 2018, it was announced that China, like Japan at the 2020 Summer Olympics in Tokyo, is planning to put more emphasis on hydrogen technologies, in particular on fuel cell buses, at the 2022 Winter Olympic Games in Beijing. For this purpose, an agreement has now been signed for the purchase of 74 fuel cell buses for the city of Zhangjiakou, in which the ski competitions are taking place [31]. This world’s largest fuel cell bus fleet consists of 49 Foton AUV buses from Beiqi Foton Motor Co. and 25 buses from Zhengzhou Yutong Group Co.

In Europe, fleet building is currently driven mainly by the JIVE project, which started in January 2017 [32]. Within 6 years, a total of 139 fuel cell buses will be installed in European public transport, 56 in the United Kingdom, 51 in Germany, 12 in Italy, 10 in Denmark, and 10 in Latvia. As it became known, this project was extended to include a second batch of buses in JIVE 2, which began in January 2018 [33]. In this extension, the segmentation of the buses is no longer based on countries, but on clusters. Thus, there will be 50 buses in the Benelux, 15 buses in the France, 37 buses in Germany/Italy, 32 buses in the United Kingdom, and 18 buses in the North/Eastern Europe cluster. In the next 6 years, 291 fuel cell buses will be put into operation on

Europe's roads, 139 in JIVE, and another 152 in JIVE 2. In addition, these projects are pursuing other goals, such as the construction of a reliable and fleet-capable refueling infrastructure within the accompanying MEHRLIN project and the reduction of the acquisition costs for a fuel cell bus to 625,000 euros [34].

Additionally, many busses are on the road or planned to operate in different countries. In the final report of the European CHIC project, an overview of the worldwide progress of hydrogen-powered bus fleets was published in December 2016 [35]. A total of 109 buses were in operation at the end of 2016 and the commissioning of more than 700 additional buses was planned for the coming years, the above-mentioned recent projects not included. The distribution of the fuel cell–operated bus fleets across the different countries is summarized in Fig. 11.6, whereby it can be seen that especially in Europe, China, Japan, and South Korea a strong increase is expected in the coming years.

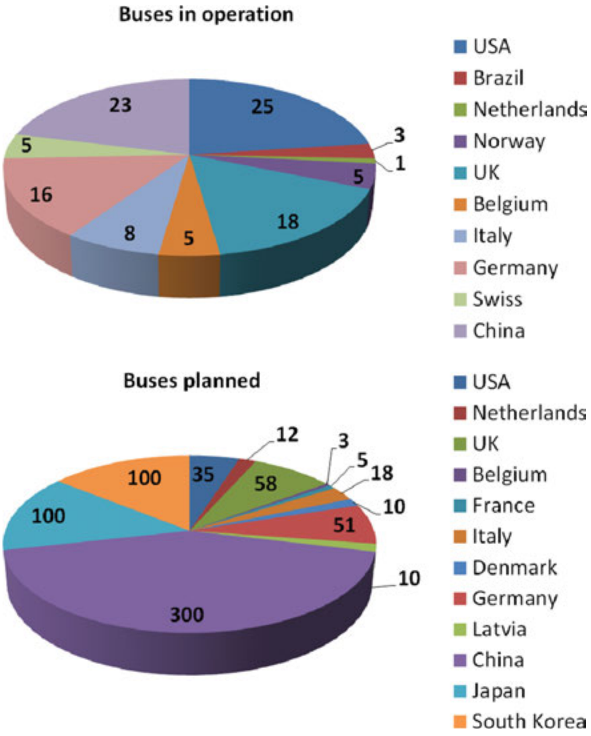

Fig. 11.6: Fuel cell buses in operation (left) and planned (right) at the end of 2016.

11.3.4 Fuel cell–powered trains

Fuel cell–powered rail electromobility represents an emission-free alternative to diesel-powered trains on non-electrified lines, which accounts for about 50% of regional and freight transport in industrial countries and even more in emerging and developing countries. Thereby, the fuel cell is an alternative not only in terms of environmental protection, but also in economic terms as shown, for example, in Austria. The plans for the electrification of a 32-km-long, previously non-electrified line between Jenbach and Mayrhofen in the Zillertal were reevaluated [36]. The first planning in 2015 envisaged electrifying the line conventionally via overhead wires, for which a total of 156 million euros should be invested. In February 2018, these plans were changed and the new plan relies on the conversion to hydrogen operation. In addition to the landscape aspect by the avoidance of overhead wires the main driver for this decision was the required investment. The hydrogen solution H2Zillertal (Fig. 11.7) is estimated to cost just about half of the original solution at around 80 million Euros and will be implemented until 2022. This includes the hydrogen train based on the 4090 EMU of the Austrian Federal Railways (ÖBB), a facility for hydrogen refueling as well as hydrogen production, which will take place via electricity from a nearby hydroelectric power station.

Fig. 11.7: H2Zillertal fuel cell train [45].

In cooperation with Hydrogenics, Xperion, and Akasol, Alstom Transport Deutschland GmbH developed a traction vehicle concept for rail in Germany, which uses fuel cells. In September 2016, Alstom introduced the Coradia iLint at the InnoTrans railway exhibition in Berlin [37]. This emission-free commuter train for 300 passengers reaches speeds of 140 km/h. The hybridization of the 200 kW PEMFC systems with high-performance lithium-ion batteries and the energy recovery during braking of the train can cover a distance of 600–800 km and guarantee the entire onboard supply of electricity. In addition to the train, Alstom and its partners provide operators with the maintenance and construction of the required hydrogen infrastructure [38]. So far two prototypes are available, which are tested and approved by the Federal Railway Authority (EBA). The Coradia iLint was the first hydrogen-powered low-floor train on the European public railway network during this intensive test program between September and October 2017 [39]. Since 17 September 2018, the two prototypes are used for public transport on the route between Buxtehude and Cuxhaven in Lower Saxony. Additional 14 vehicles are planned to run regularly on the rails of Lower Saxony [40]. Furthermore, the federal states of Baden-Württemberg, Brandenburg, Hessen, and North Rhine-Westphalia signed declarations of intent to install a total of 60 trains in the 5 federal states by 2021 [41].

Another fuel cell integration project was announced by Ballard Power Systems in November 2017 [42]. The Canadian fuel cell supplier has signed a contract with Siemens to integrate a fuel cell drive into the Mireo. This is a new, electric railcar for passenger transport from Siemens with a maximum speed of 160 km/h. For this purpose, Ballard is developing a 200 kW PEMFC system and the first deliveries of the train are planned until 2021. This development contract is part of a German-funded project of Siemens, Ballard, and RWTH Aachen with the aim of developing a modular and scalable fuel cell–based hybrid concept.

In China, the world’s largest rail vehicle manufacturer CRRC Corporation Limited also announced two such train projects. In March 2017, it was published that a contract was signed for the construction of eight hydrogen-powered trams for the Chinese city of Foshan [43]. These trains are designed for 285 passengers and a top speed of 70 km/h. Their use is planned on the 17.4-km-long Gaoming line, which has a total of 20 stops. Furthermore, it was announced in October 2017 that FCveloCity is developing a prototype low-floor train [44]. The 336-passenger train consists of 3 wagons and reaches a top speed of 70 km/h, which is achieved through the installation of PEMFC systems from Ballard Power Systems, a powerful battery and capacitors. The 15-min refueling with 12 kg of hydrogen takes place at one of the two terminal stations of the new 14-km-long public transport line in Tangshan. Due to the short distance, the relatively small amount of hydrogen and the short range of up to 40 km are enough to enable designated services.

11.3.5 Fuel cells in aircraft

For aviation, the use of hydrogen as an energy source appears difficult at first because of the very high energy demand in commercial aircraft. But nevertheless there are attractive applications for fuel cells. In 2016, easyJet has announced an environmental-friendly fuel cell–based concept for shunting their aircraft on the ground, which could save about 4% of their fleet’s total kerosene consumption [46]. The aircrafts will be equipped with electric motors in the nose wheel, a concept that has already been tested together with Airbus and Lufthansa Technik by the German Aerospace Center (DLR) in tests using the DLR research Airbus A320 ATRA [47].

Further kerosene savings are possible by replacing the auxiliary turbines in the rear of the aircraft, which take over the power supply for air conditioning and onboard electronics on the ground. DLR and its partners have demonstrated that the use of a multifunctional fuel cell system cannot only carry out these tasks, but can also enable the onboard water and heat supply as well as provide oxygen-depleted air to the kerosene tanks for fire protection [48].

Even if challenging, the fuel cell can also be used as an aircraft engine. So far, this is limited to small lightweight construction aircraft. As early as 2009, Gérard Thevenot crossed the English Channel on a fuel-powered trike, and in 2014, the motor glider Antares, developed by DLR together with Lange Research Aircraft GmbH, flew from the ILA Berlin Air Show to its home airport of Oberpfaffenhofen in a total of three 200-kilometer-long stages [49]. Both aircraft were designed for a single pilot, but DLR also equipped the world's first four-seater aircraft powered solely by a fuel cell hybrid system. The HY4 (Fig. 11.8) was developed by the Institute of Engineering Thermodynamics of the DLR together with Hydrogenics, Pipistrel, H2FLY, the University of Ulm, and with support from the Stuttgart Airport. The first flight took place on 29 September 2016, at the Stuttgart Airport [50]. The integrated system includes four 45 kW PEMFC systems and 45 kW lithium-ion batteries with a capacity of 21 kWh. This hybrid system drives the 80 kW electric motor of the 1,500 kg HY4, which achieves a top speed of 200 km/h. Due to the entrained 9 kg of hydrogen in two tanks in the fuselage, ranges of 750–1,500 km can be achieved depending on speed, altitude, and payload. For the DLR and its partners, the HY4 represents an important development platform for fuel cell–operated aircraft to enable the further development of regional aircraft for up to 19 passengers.

Fig. 11.8: HY4 powered by a fuel cell hybrid system [51].

11.4 Cargo transport applications

Vehicles for the transport of goods require both a high performance and a long range. In order to electrify these vehicles and thus avoid pollutant emissions, these boundary conditions must be taken into account. Long battery charging periods are neither time- nor cost-efficient. Especially for these requirements, the use of fuel cells with rapid hydrogen refueling seems to be the best solution. Therefore, various concepts have been demonstrated in the recent years that can facilitate the decarbonization of cargo transport.

11.4.1 Heavy-duty trucks

As shown by the Hydrogen Scaling-up Study mentioned earlier [3], heavy-duty trucks are responsible for around a quarter of CO_2 emissions in the transport sector worldwide, expected to increase to 35–40% by 2050. Therefore, the electrification of trucks with fuel cells has a high potential for the significant reduction of CO_2 emissions. Even the conversion of 350,000 trucks, as assumed by the study, would have the same saving potential as the introduction of 2.5 million FCEVs. Several prototypes were already developed that could pave the way to realize this potential in cargo transport.

In Switzerland, the installation of the first hydrogen-powered fleet of trucks is ongoing. For this purpose, the Swiss development company ESORO AG has covered several thousand test kilometers with a first prototype and obtained road approval in June 2017 [52]. The developed refrigerated truck (Fig. 11.9), whose drive and cooling unit are powered by a fuel cell hybrid system, will be operated by the COOP logistic retail group to supply goods using the roads of Zurich. It is based on a MAN

Fig. 11.9: Fuel cell truck by ESORO AG [55].

truck equipped with two 60 kWh CALB lithium-ion batteries and a 100 kW PowerCell S3 stack based on PEMFC technology. The system was integrated by Swiss Hydrogen and by Esoro. The hydrogen is stored in 7 tanks at 350 bars directly behind the driver's cab. Up to 35 kg of hydrogen can be refilled in just 9 min resulting in a range of about 400 km. The truck is approved for up to 19 tons and can be operated with an additional trailer for up to 16 tons. Thus, this vehicle represents the first approved, hydrogen-powered truck in the 35-ton category. The truck covered 20,000 km test operation in real-world delivery use at COOP up to now. Thereby, the longest run was 375 km in one day covering three tours in the region of Basel and Zürich with truck and trailer and including two mountain passes (Staffelegg and Albispass).

Toyota is also working on a solution for this weight class. In April 2017, the company launched the Project Portal for demonstration in the United States by equipping a track for 36 tons with a fuel cell system. The truck will be operated at the harbor of Los Angeles [53]. Two PEMFC stacks as used in the Toyota Mirai and a lithium-ion battery with a capacity of 12 kWh are used. This should result in a total output of 670 hp and a torque of 1,800 Nm. The hydrogen storage takes place in tanks of the Norwegian company Hexagon, whereby a range of about 320 km is targeted.

In December 2016, the US company Nikola Motor Company (NMC) also presented a futuristic concept study of an electric truck in Salt Lake City [54]. The Nikola One is equipped with both a large lithium-ion battery and a fuel cell system, the latter based on PEMFC technology and provided by PowerCell. Thus, a total power of 735 kW and a torque of 2,700 Nm should be achieved. The battery is designed for a capacity of 320 kWh and the fuel cell system for a power of 300 kW. The refueling of this Nikola One is announced to only 15 min and the production should begin 2020. The truck will be powered by six electric motors, one per drive wheel, which are co-developed by Bosch. The range target is 1,600 km and a speed of 100 km/h should be reached after 30 sec. Energy recuperation is planned to enable this enormous range and reduce the braking distance. The purchase price is announced to 375,000 US dollars. The hydrogen for 1.6 million km will be provided for free to the first 5,000 buyers. The delivery of these first 5,000 units is scheduled for 2021.

11.4.2 Maritime applications using fuel cells

Emissions of nitrogen oxides, sulfur oxides, and fine particulate matter are particularly high in the maritime sector due to the heavy fuel oil and marine diesel fuel used. The development of low-emission propulsion systems for ships is driven by increasingly stringent regulations and the fact that 90% of all goods are transported by ship. In January 2017, the "Study on the Use of Fuel Cells in Shipping" by the European Maritime Safety Agency (EMSA) summarized the results of a total of 23 maritime fuel cell projects and concluded that fuel cell technology can be considered as an alternative ship propulsion systems and that the technology used is mainly based on the size of the systems [56]. In systems for onboard energy supply and for driving smaller passenger boats the use of low-temperature fuel cells up to 100 kW is advantageous. For energy supply of large container ships high-temperature fuel cells up to 650 kW can be used. Some selected projects will be presented in this chapter.

In September 2016, the preliminary results of the project e4ships and thus the related fuel cell activities in Germany were presented at the international trade fair for the shipping industry (SMM) [57]. This included a methanol-operated 90 kW system installed on the Scandinavia ferry MS Mariella in the Pa-X-ell sub-project managed by the Meyer shipyard. The system consists of three standardized racks from Fischer eco solutions and SerEnergy. Each rack uses six air-cooled high-temperature PEMFC modules (160–200 °C) of 5 kW electrical power with an internal methanol reformer. The sub-project Schibz, which is managed by Thyssenkrupp Marine Systems, develops diesel-powered solid oxide fuel cells (SOFC) systems with scalable outputs of between 100 and 500 kW for main energy supply of deep-sea vessels. In the first project phase, a 50 kW demonstrator was installed for real-life testing on the MS Forester. The long-term testing and further development of the demonstrators will continue until 2022.

Since August 2017, the MS innogy (Fig. 11.10 top left) is operating on the Baldeneysee in Essen, Germany, as an excursion and conference ship [58]. The integrated fuel cell propulsion is based on seven H3 5000 systems by Serenergy of 5 kW maximum electrical output power each. These systems are supplied with “green” methanol and they use methanol reformers and high-temperature PEMFC stacks to provide up to 28 kW rated power during operation [59]. Together with two 50 kWh batteries, the propeller is powered by an 80 kW electric motor. The included methanol tanks have a capacity of 330 L and assure the operation for 14 h before the methanol has to be refilled. The adaption and fuel cell integration was carried out as part of “greenfuel” pilot project. To cover the total methanol demand of the MS innogy, “green” methanol from Iceland is provided by Helm AG. The entire operation of the ship is thus CO_2 neutral.

Furthermore, the Jules Verne 2 (Fig. 11.10 right) started operations on the Erdre in Nantes, France [60]. After a 5-year construction and test phase in the French NavHybus project, the 10-m-long and 3.80-m-wide river boat was launched in June 2017 for ferry services. The two redundant PEMFC systems are provided by the company SYMBIO. These are integrated into the roof of the small ferry and provide not only the required power for propulsion but also the heat for the passenger compartment. This allows up to 25 passengers and 10 bicycles to be comfortably transported [61].

And even a hydrogen-powered world tour on the water is ongoing. However, the Energy Observer (Fig. 11.10 bottom left) does not rely exclusively on hydrogen, but is a solar-wind-hydrogen catamaran [62]. It is 30.5 m long, 12.8 m wide, and weighs 30 tons. The Energy Observer is powered by two electric motors with 41 kW each, which are supplied by various technologies. The catamaran is equipped with 130 m^2 of solar cells providing up to 21 kW and with two wind turbines, each with 1 kW output power. To save energy for the night and unfavorable weather

Fig. 11.10: MS innogy (top left) [64], Jules Verne 2 (right) [65] and Energy Observer (bottom left) [66].

conditions, the Energy Observer also has an electrolyzer and a hydrogen tank on board. By using desalinated water via reverse osmosis up to 4 Nm^3 of hydrogen can be produced per hour. The reconversion takes place in an integrated fuel cell system. The launch of the catamaran was on 4 July 2017, in Paris. Its world tour will take a total of 6 years and will cover more than 100 stops in 50 countries in order to promote hydrogen as an energy carrier. The entire journey can be followed via online tracking [63]. After almost 2 years' sailing, the catamaran is currently under construction to modify the boat. The surface area of the solar panels is increased to 168 m^2 for up to 28 kW and a breakthrough technology in wind propulsion is installed. Two rotating, self-supporting, fully automatic "Oceanwings" will enable both an increase in the vessel's speed and the production of hydrogen by electrolysis of sea water.

11.4.3 Material handling powered by fuel cells

Forklifts in department stores and distribution centers are largely equipped with electric drives to prevent accumulation of pollutants in warehouses. These are usually equipped with batteries, which, however, can limit the operating time. To ensure the required operating times even in multi-shift operation, empty batteries of the truck are replaced with charged ones. This is a time-consuming and costly process because replacement batteries must be kept on stock and loaded. On the other hand, the refueling of a fuel cell system can be realized in a few minutes. In addition, a fuel cell provides a constant rated voltage and the truck thus has a constant power during operation, while this decreases using batteries with increasing discharge. Summarized, the total cost of ownership analysis of hydrogen propulsion is much better than that of battery propulsion for the forklift application.

Because of these advantages, sales numbers of PEMFC-based solutions are increasing significantly in the last years, mainly in the United States. While about

7,700 units were operated in October 2015 [67], this number increased to more than 20,000 in November 2018 [68]. Main suppliers are Plug Power and Nuvera Fuel Cells, which distribute fuel cell systems as well as refueling infrastructure.

In Europe, the technology is still in the demonstration phase. For example, a total of 200 fuel cell forklifts and aircraft tugs and 10–20 hydrogen refueling stations will be installed as part of the HyLIFT demonstration project [69]. To facilitate the market initialization in Europe, a new intralogistics network was initiated in Germany. The CIN (Clean Intralogistics Net) is an association of 11 companies with the aim of promoting less polluting and less expensive infrastructure using hydrogen as an energy carrier [70]. The CIP includes Air Liquide, BMW, Bosch Engineering, Daimler, ElringKlinger, Fronius Germany, Heraeus Fuel Cells, Jungheinrich, Linde Material Handling, Linde Gases Division, and STILL. The first General Assembly was held on 30 May 2017 in Berlin.

11.4.4 Last mile delivery

In addition to the already mentioned heavy-duty trucks, a change in the transport of goods to the end customer is also needed. New so-called last mile delivery concepts with electric drives are emerging and finding their way into the market. This is urgently needed since parcel deliveries have increased significantly as a result of e-commerce [71]. Thereby, problems in cities due to increased emissions of exhaust fumes and increased traffic are rising [72]. For this application, fuel cells are used to increase the range of battery electric vehicles in the so-called range extender systems.

For small vans, systems with an electric power in the order of 5 kW are used, which charge the batteries of a commercially established electric vehicle during delivery operation and thus more than double their range. An example of such a vehicle is the Kangoo ZE-H2 (Fig. 11.11 left) from the French company SYMBIO. A Renault Kangoo ZE with a battery capacity of 22 kWh is being extended by the 5 kW PEMFC range extender ALP5. Thereby, the range of this electrically powered delivery vehicle was increased from 100 km to over 300 km. Depending on the hydrogen storage used, the Kangoo will have an additional 26 kWh of 1.78 kg of hydrogen (350 bar tank) or 30 kWh of 2.03 kg of hydrogen (700 bar tank) per refill [73]. This can increase the range even up to 400 km. In September 2016, this vehicle achieved a new range world record for light electric utility vehicles in real city traffic, covering a delivery distance of 367 km in about 10 h [74].

Founded in 2010, StreetScooter GmbH has been a subsidiary of Deutsche Post AG since 2014 and manufactures the electrically powered StreetScooter, which is well known in German cities for the delivery of parcels. However, the range of the van is limited. During delivery operation, this small van with a payload of up to one ton and a loading volume of 8 m^3 provides a range of only about 80 km covered by the installed 30 kWh lithium-ion battery. As a consequence, StreetScooter announced in October 2017 to test fuel cells to increase this range to up to 500 km [75]. The development of this new model based on the StreetScooter WORK L is being carried out in cooperation with the RWTH Aachen and will initially involve 500 vehicles that will prove their suitability for everyday use.

An alternative for parcel delivery in cities is the use of cargo bikes, which are also becoming increasingly common in cities. As early as 2014, the study “Cyclelogistics – Moving Europe forward” concluded that electrically powered cargo bicycles, known as e-pedelecs, could be used for up to 51% of all urban cargo transport [76]. However, these e-pedelecs do not yet meet the requirements of the logistics industry in terms of range and service life. This problem significantly increases under freezing winter conditions. The study “Investigation of the use of bicycles in commercial traffic,” published in 2016 by the DLR, identified the batteries as the bottleneck [77]. Consequently, the DLR started to develop a fuel cell system specially designed for this application [78]. The so-called fuel cell range extender (FCREX, Fig. 11.11 right) is designed for a rated output of 300–500 W and is able to ensure a long range of heavy e-pedelecs in all climatic conditions. Various system components, including the PEMFC stack and hydride-based thermostats, have been developed for this project. After the completion of a first prototype, the FCREX module will be validated within the 3 years project “FCCP – Fuel Cell Cargo Pedelecs” until 2021.

11.5 Stationary applications

In the stationary use of fuel cells, the market entry has already been successful, mainly in Asia. There are currently three main applications: the decentralized supply of residential buildings with electrical and thermal energy through small combined heat and power plants (µCHP), the energy provision for industrial use, and the protection of critical loads in case of disturbances in the power grid using a fuel cell system for uninterruptible power supply (UPS). Most stationary applications use NG as fuel,

Fig. 11.11: SYMBIO Kangoo ZE-H2 (left) [65] and FCREX for e-pedelecs (right).

since NG distribution systems are well established in industrialized countries. We will discuss these systems here as an indirect hydrogen application as NG is first reformed to a hydrogen-rich gas which is provided to the fuel cell. Therefore, mainly hydrogen is converted at the anode. In future, hydrogen can be used as fuel in these applications when hydrogen is generated completely by renewables and its price is competitive. A typical system layout for a µCHP system is shown in Fig. 11.12.

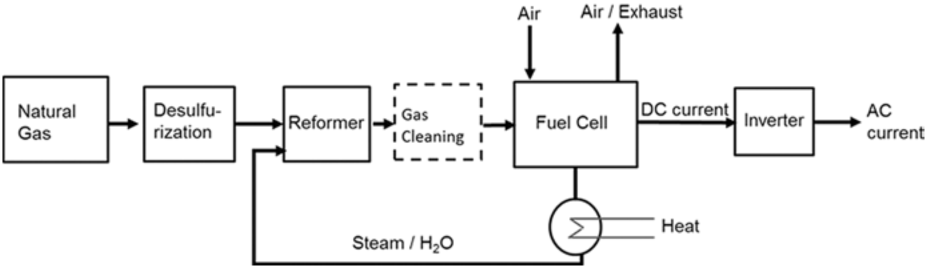

Fig. 11.12: Block diagram for a µCHP system. Often an additional parallel boiler is used for higher heat and warm water requirements.

In high-temperature fuel cells NG can be converted directly by so-called internal reforming to hydrogen-rich gas at the electrodes of the cell thereby also cooling efficiently the fuel cell. This effect leads to higher hydrogen utilization and superior efficiencies. However, a pre-reformer for higher hydrocarbons is normally required. For low-temperature fuel cells a reformer and an additional gas cleaning reactor is needed to provide hydrogen-rich gas with high purity to the fuel cell. Low-temperature fuel cells can tolerate just a few ppm of contaminants like carbon monoxide. All fuel cells require a desulfurization unit since sulfured components (e.g., odorants) in NG block catalyst sites of reformer and fuel cells. In high-temperature fuel cell the exhaust gases are often burned to provide heat for pre-heating air and fuels. Different reforming technologies are applied with steam reforming leading to higher efficiencies compared to autothermal reforming and partial oxidation reactors. Heat of the fuel cell is commonly used leading to overall efficiencies in the range of 80–95%. The main requirement for stationary fuel cell systems is long lifetime of several 10,000 h. For more detail we refer the interested reader to reviews on stationary fuel cells [79, 80].

11.5.1 µCHP for residential houses

The µCHPs are usually designed for the supply of residential houses for one or two families. In contrast to the conventional boilers, they cannot only provide heat but also electricity. Thereby, they reduce the energy consumption of the houses significantly and temporarily cover the entire energy demand. Depending on the device, the electrical power output varies between 0.3 and 1.5 kW. Meanwhile, these systems are offered by a variety of manufacturers and are based on three different fuel cell types: low-temperature PEMFCs, high-temperature PEMFCs, and SOFCs. These µCHPs are connected to the NG grid and convert the chemical energy from the NG to heat and electricity. This process can be realized directly using an SOFC or after reformation to hydrogen using the PEMFC technologies.

In Japan, µCHPs have already overcome the hurdle of market introduction and several tens of thousands of such plants are newly installed every year due to the Ene-Farm program (Fig. 11.13). Beginning in 2009, a total of more than 260,000 µCHP units using fuel cells are deployed until September 2018 and supply Japanese households with electricity and heat. The increased volumes led to a major reduction of installation costs. In 2009, the cost per unit was around 24,000 Euro (3.03 million yen), while in 2017 it had decreased to about 9,000 euro (1.14 million yen) [81]. The aim of the Japanese government is to equip 10% of all households (5.3 million) with this innovative technology until 2030.

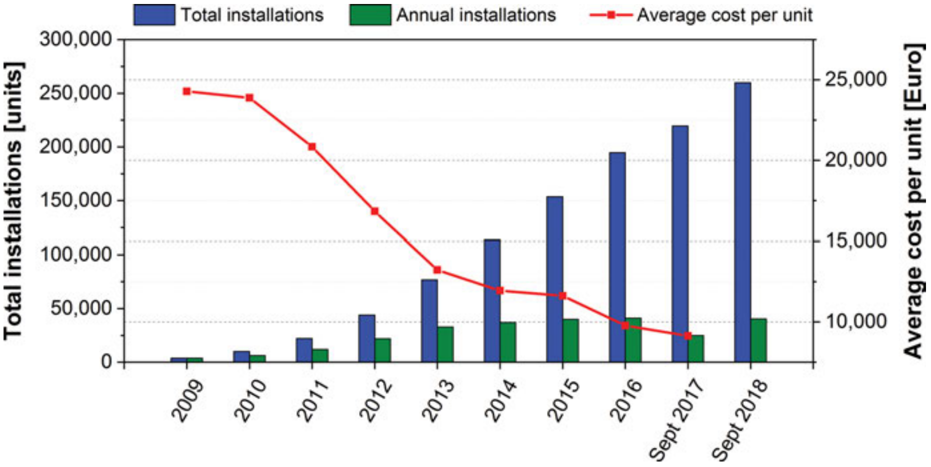

Fig. 11.13: Annual and total installations as well as costs per unit for µCHPs in Japan.

By contrast, the introduction of such systems in Europe was limited to European and national demonstration projects with a few hundred devices for the last decade. For example, the market launch was supported by the ene.field projects at European and Callux at German level. In ene.field up to 1,000 µCHPs were installed in 11 countries between 2011 and 2017. Due to installation in different climatic zones, the monitoring of the unit's operation was used to analyze and further improve their suitability for everyday use [82]. In Germany, the practicability of this technology was demonstrated in the Callux project between 2008 and 2016 and a total of 1,000 µCHPs were installed [83]. The cost of such devices in Europe has been significantly reduced in recent years also driven by these projects. For example, Viessmann currently offers the Vitovalor 300-P (0.75 kW_{el} and 1 kW_{therm}) for 19,500 € and Hexis the module Galileo 1,000 N (1 kW_{el} and 1.8 kW_{therm}) for 19,000 €.

To further promote the deployment, the larger-scale PACE project (Pathway to a Competitive European Fuel Cell micro-CHP Market) aims to install a total of 2,650 new units until 2021 [84]. The objective is to reduce costs by a further 30%, increase the service life to more than 10 years and expand annual production capacity to 1,000 units per year.

In order to support the next step into the commercial market, Germany initiated the technology introduction program for stationary fuel cells for domestic energy supply (TEP). Launched in December 2016, the TEP supports the installation of up to 75,000 systems until 2023 and create additional incentives to buy initially for private users. But due to modification in July 2017, also small- and medium-sized enterprises, service providers, and local authorities can apply for non-residential buildings [85]. The subsidy is granted for the purchase of a new fuel cell µCHP in the power range between 250 W and 5 kW and up to 40% of the costs will be subsidized [86]. In addition to this purchase funding, operators will receive a surcharge in Germany, which is based on the amount of electricity generated. This is four cents per kilowatt-hour for self-consumption and eight cents for supply to the power grid [87]. Taking this into account, the ASUE ("Arbeitsgemeinschaft für sparsamen und umweltfreundlichen Energieverbrauch e.V.") has calculated and compared the consumption and operating costs of various heating systems using the example of a 150 m^2 house (Fig. 11.14) [88]. It was shown that annual costs are lowest when using fuel cell systems. Consequently, fuel cell–based µCHPs have become a very attractive alternative for supplying customers with electricity and heat. Due to the TEP, new residential districts in

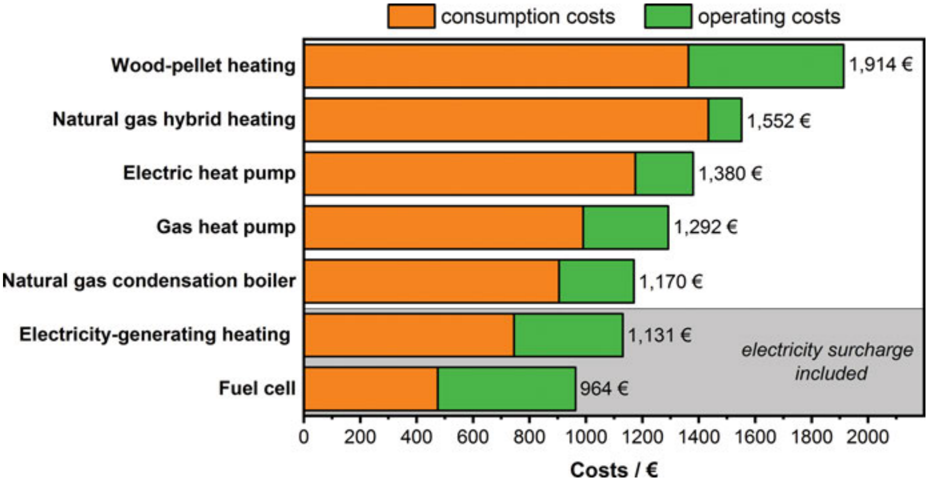

Fig. 11.14: Annual costs for energy supply of a residential house of 150 m^2 in Germany.

Langweid am Lech and in Mering, both near Augsburg in Bavaria, can be completely equipped with fuel cell–powered µCHPs [89]. In these areas, a total of 105 units of the Vitovalor 300-P from Viessmann will be installed using the PEMFC technology.

11.5.2 Energy provision for industrial use

For industrial use, steady generation of electricity and heat from NG and biogas in larger power plants in the MW range is required. High-temperature fuel cells are usually used because high dynamics are not needed but the highest possible efficiency and longevity as well as low investment costs are key requirements. Although the technology is not emission-free, it can significantly reduce CO_2 emissions due to an electrical efficiency of up to 47%, which is significantly higher than that of conventional power plants at around 27%. In the United States alone, the rated power of fuel cell–based power plants increased to over 235 MW by November 2016 [90].

The largest connected fuel cell power plant with an output power of 59 MW is the Gyeonggi Green Energy Fuel Cell Park in South Korea. Installed in 2014, it consists of 21 DFC3000 plants of the US company FuelCell Energy, each with a electrical output power of 2.8 MW and equipped with molten carbonate fuel cell (MCFC) [91]. In the United States, FuelCell Energy is constructing a 63 MW power plant park in Connecticut using the same modules. Based on the smaller DFC1500 module, the first megawatt-class industrial fuel cell power plant in Europe is operating since 2016. The 1.4 MW power plant is built by E.ON Connecting Energies at the facilities of Friatec AG, a material manufacturer in Mannheim, Germany [92]. In October 2016, it was also revealed that FuelCell Energy is investigating an interesting possibility of this technology for CO_2 capture and storage (CCS) in underground deposits with a 2.3 MW MCFC pilot plant in Alabama, USA [93]. The plant is directly connected to a conventional ExxonMobil power plant and aims to reduce the CO_2 emissions of this power plant by concentrating parts of the exhaust CO_2 through the MCFC and making them accessible for storage. In contrast to other CCS techniques, no energy is needed to separate the CO_2, but rather the MCFC is generating energy and thus it significantly improves the energy balance of the process.

Based on the SOFC technology, BloomEnergy installs small power plants in the United States using 160 to 250 kW modules to assure the energy supply of companies such as Walmart, Coca-Cola, Apple, IKEA, and many more in order to reduce the CO_2 emissions of factories and shopping centers [94]. Coupled with the biogas network, a low-carbon energy supply for many companies in California is thereby established. In order to further increase the fuel efficiency of SOFC power plants, hybrid power plants have been developed, in which SOFCs are coupled with gas turbines. The over 850 degrees hot exhaust gases of the SOFC are fed to the gas turbine, which can convert the residual fuel highly efficient. This hybrid power plant can significantly increase the efficiency, since the SOFC can operate at higher pressure and thereby achieves higher efficiencies and better performance. In Germany, with the support of EnBW, DLR is developing the fundamentals of this concept. It is aimed to build up a 30 kW prototype with electrical efficiencies of around 60% [95]. Another demonstrator for this technology is installed at Kyushu University, Japan. The 250 kW prototype Model 15 with a total efficiency of 55% by Mitsubishi Hitachi Power Systems is in operation since March 2015 [96]. After this test phase, the prototype was further developed into a market-ready product. The new unit was installed in the Senju Techno Station of Tokyo Gas Co. and commenced operation in September 2016 [97]. Three more test rigs will be installed at Toyota Motor Corporation, NGK Spark Plug Co., and Taisei Corporation to improve efficiency, operability, operating cost, and longevity in industrial environments before the commercial launch.

11.5.3 Backup power for critical loads

Assuring UPS is an important issue in the reliability of various installations and is used, for example, in the telecommunication and in the transport sector. Fuel cell–based solutions are offered by various suppliers such as Ballard, Intelligent Energy, Proton Motor, Heliocentris, and Zebotec. The corresponding systems use PEMFC systems to react quickly to a power supply issue. These systems represent an environmentally friendly alternative to the frequently used diesel generators and have the advantage compared to battery systems that the power can be reliably supplied over a longer period of time by suitably designing the hydrogen tanks. The Indian market in particular is highly interesting for this application. In a market study published in 2015, Intelligent Energy has shown that there are more than 400,000 cell towers in this world's second largest telecommunications market, of which 70% need to be powered by diesel generators for at least 8 h per day [98]. From financial as well as environmental point of view, this represents a great potential for the use of fuel cell systems. In October 2015, Intelligent Energy announced that they had signed a £ 1.2 billion contract to convert the power supply of a total of 27,400 cell towers from diesel to hydrogen over the next 10 years [99].

In Germany, a cooperation of Proton Motor and Deutsche Bahn (the German railroad company) was announced in 2015 [100]. It is planned to evaluate the replacement of diesel-based UPS units by fuel cell systems within the next few years. For this application, Proton Motor developed an UPS container solution in the power range between 6 and 250 kW. Additionally, fuel cell–based UPS systems are used in Germany for the digital radio for authorities and organizations with security tasks (BOS). Since the end of May 2016, 44 BOS stations in Bavaria have been protected by PEMFC systems in the power range between 4 and 8 kW, which can ensure radio operation during power outages for at least 72 h [101]. The units are installed at locations with difficult accessibility and climatic conditions in pre-alpine and alpine regions, thereby they are aimed to demonstrate the technical readiness of fuel cell technology under these conditions. Overall, about 220 BOS stations throughout Germany are equipped with emergency power units based on fuel cells.

11.6 Summary and outlook

Hydrogen and fuel cell technologies have shown that they can play an important role in the transition of energy supply from fossil fuels to renewable energy sources. In addition to electricity generation from wind, water, and solar energy, other challenges such as the distribution of energy among the different industrial sectors and the interim storage of energy have to be considered. Fuel cells using hydrogen as an environmentally friendly source of energy can be a key technology and the market maturity is progressing steadily.

For special applications and in individual markets, the market launch has already been successful. The sales figures of fuel cell–powered μCHP units for domestic energy supply are rising rapidly, especially in Japan and Germany. The use of fuel cells in material handling with forklifts and in powering factories and shopping malls is becoming increasingly prevalent in the United States, especially in California. By contrast, the use of fuel cells in the transport sector is just initiated. But due to the small series production of FCEVs and the increased refueling infrastructure, the elements for further deployment are available now. It is notable that the introduction of this hydrogen mobility is less a matter of private users, but rather of vehicle fleet operators. In addition to cars and buses, it is becoming increasingly clear that heavy-duty applications are of great interest. Trains, ships, and trucks using fuel cells have been evaluated in real operation. It was shown that new transport applications for fuel cells are currently focusing on areas with high energy demand and with high range requirements. Although first vehicles are commercially available throughout the transport sector, the maturity of this technology needs to be further increased. The implementation of mass production for compact, robust, durable, and cost- and application-oriented systems is the main task of the coming years. It can already be observed that the production of fuel cell systems is becoming closer to production and a rapid cost decrease due to economies of scale is expected.

As the US central government is currently promoting fossil fuels, Asia has become the strongest center of hydrogen technology. In addition to Japan and South Korea, China is massively increasing its efforts to be a major player in the electromobility and hydrogen technologies sectors. In Europe, significant efforts continue to develop fuel cell technology toward market maturity. In some applications, such as the μCHPs, the implementation in the market seems to be achievable in a timely manner.

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Christophe Coutanceau, Marian Chatenet, Deborah Jones, Gael Maranzana

12 Materials for proton-exchange fuel cell for mobility and stationary applications

12.1 Introduction

In future, hydrogen will be represented as a key energy vector to compete with fossil fuels, which will be produced from renewable energy sources (wind, solar, tidal, etc.) [1], for instance, when coupled with water electrolysis. This will become an important compound to help rapid development of low-carbon energy economy and will gain a central role in the energy transition and in the integration of renewable energies in the energy mix [2].

One of the main targeted uses of clean hydrogen is the production of electricity through feeding of fuel cells, and particularly proton-exchange membrane fuel cells (PEMFCs). Indeed, hydrogen possesses a very high energetic density (32.9 kWh/kg) [3] and PEMFC systems are versatile enough to open a wide range of applications from nomad/portable devices, to electric vehicles and stationary cogeneration of heat and power (CHP systems) [4]. However, in an industrial point of view, the most important applications of PEMFCs are electric transportation (cars, trucks, buses, trains, etc.) and CHP for buildings, industries, isolated remote locations [5]. Therefore, more and more countries worldwide are developing roadmaps for intensive development of hydrogen production, storage, distribution, and uses. In Europe, for instance, the Clean Hydrogen Alliance has been announced by the European Commission to accelerate the decarbonization of industry and maintain industrial leadership, with the objective of a float of ca. 5 million fuel cell vehicles in 2030. The United States, China, Korea, and Japan have developed very ambitious implementation programs around hydrogen and fuel cell technologies [6], as well as Germany (H_2 Mobility Germany) and France (Plan National Hydrogène) but the spreading of PEMFC technology must lean on a strong research and development (R&D) activity from their conception to their validation and their use in real conditions in order to allow transferring innovations to industry. Among the main issues, durability is a strong limitation to commercialization. The targets are very ambitious, being in accordance with the Department of Energy (DOE) 8,000 h in automotive drive cycle and 60,000 h for CHP application [7].

Fuel cell stacks are composed of several unit cells connected in parallel or in series depending on the targeted stack outputs (voltage and current). Similarly for

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all electrochemical generators (alkaline cells, batteries, redox flow cells, etc.), these unit cells contain two electrodes, where electrochemical reactions occur (here the hydrogen oxidation reaction (HOR) at the anode and the oxygen reduction reaction (ORR) at the cathode), an electrolyte allowing the migration of ions (here a proton conductive solid polymer) and two current collectors (here bipolar plates), as shown in Fig. 12.1. But, conversely to alkaline cells and batteries, the electrodes in PEMFC are not consumed to provide electric energy, and the electrochemical reactions (HOR and ORR) at the electrodes must be activated by a catalytic material. All these components constitute the core and the heart of the fuel cell: the efficiency, feasibility, cost-effectiveness, and durability of PEMFCs will greatly depend on the characteristics of the materials used for their manufactures. The R&D effort on materials for PEMFCs has two main objectives: in short term to improve the performances (mainly efficiency and durability) of existing materials by proposing mitigation methods and in mid and long terms to develop the next generation of materials and components for more durable and less costly systems, based on less strategic metals and more environmentally friendly compounds and processes to meet the requirements necessary to this technology to be really part of the sustainable development.

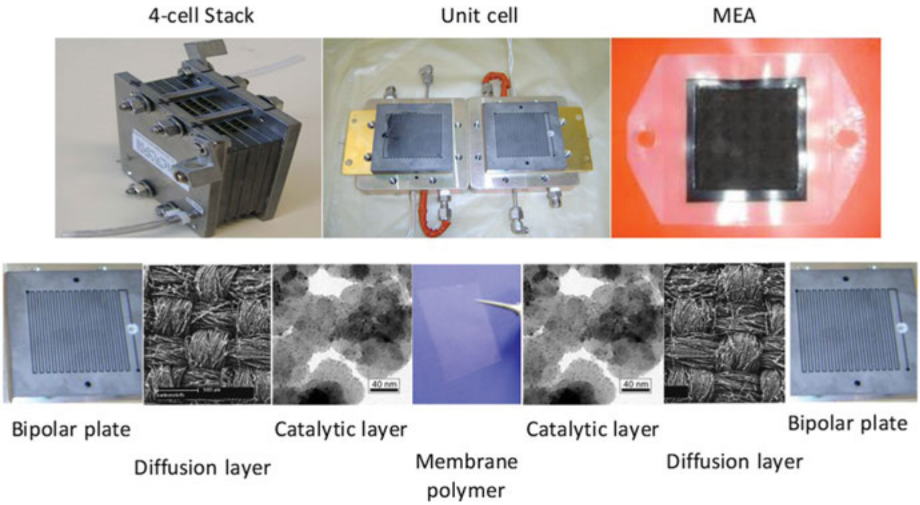

Fig. 12.1: Top: photographs of a small PEMFC stack, a unit cell, and a membrane electrode assembly (MEA). Bottom: photographs of components of MEA and of typical bipolar plates.

In this chapter, we present the working principle of a PEMFC (Section 12.2) in order to point out the different phenomena and constraints that could alter the materials constituting the different components of the fuel cell core, and further the performance of the fuel cell in terms of efficiency and durability. Then the state-of-the-art materials are presented, as well as the main directions for the development of future materials for the next generation of PEMFCs: catalysts and supports in Section 12.3, proton-conductive polymers as solid electrolyte membranes between both electrodes and as ionomer impregnating the electrodes in Section 12.4, and materials for the gas diffusion layers (GDLs) and the bipolar plates in Section 12.5.

12.2 Working principle of PEMFC

A PEMFC converts hydrogen and oxygen into water, heat, and electricity according to the following electrochemical equations:

$$\text{At the anode:} \quad H_2 = 2H^+ + 2e^- \tag{12.1}$$

$$\text{At the cathode:} \quad \tfrac{1}{2}O_2 + 2H^+ + 2e^- = H_2O \tag{12.2}$$

$$\text{Overall reaction:} \quad H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \tag{12.3}$$

Hydrogen is oxidized at the anode of the cell into protons (H^+) releasing also electrons. Protons cross the electrolyte and electrons circulate in the external circuit, both toward the cathode of the cell, providing electric energy. At the cathode of the cell, oxygen is reduced into water in the presence of protons and electrons (Fig. 12.2).

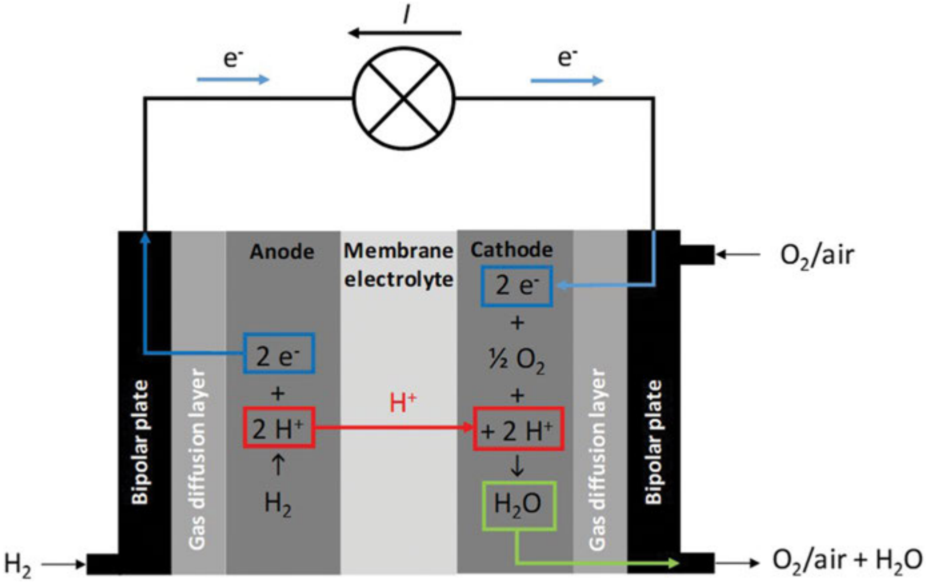

Fig. 12.2: Schema of the working principle of a PEMFC.

The reversible voltage ($U_{\text{rev}}(T)$) of a PEMFC is defined according to the following equation [8]:

$$U_{\text{rev}}(T) = -\frac{\Delta G_{\text{rev}}(T)}{2\text{F}} + \frac{\text{R}T}{2\text{F}} \ln\left(\frac{P_{\text{H}_2} \times (P_{\text{O}_2})^{1/2}}{P_{\text{H}_2\text{O}}} \times \frac{1}{(P^0)^{1/2}}\right) \tag{12.4}$$

where $\Delta G_{\text{rev}}(T)$ is the free Gibbs energy; R the perfect gas constant ($R = 8.41433$ J/K mol); T the cell temperature; F the Faraday constant ($F = 96{,}485$ C/mol); P_{H2}, P_{O2}, and P_{H2O} are the partial pressures of hydrogen, oxygen, and water, respectively; and P^0 is the reference pressure ($P^0 = 1.013 \times 10^5$ Pa).

But the voltage deviates from the reversible one as soon as the cell provides electric current to an external load, owing to different limitations: rate of reactions and decrease of reactant concentrations in the electrode, resistance to proton migration and electron circulation, and so on. These limitations translate into activation and concentration overpotentials at the anode and cathode, and into ohmic resistance in the system. The cell voltage at a current density j (current per unit geometric surface area), $U_{\text{cell}}(T, j)$, can be expressed as follows:

$$U_{\text{cell}}(T, j) = U_{\text{rev}}(T) - \left(\left|\eta_{\text{a}}^{\text{act}}\right| + \left|\eta_{\text{a}}^{\text{conc}}\right| + \left|\eta_{\text{c}}^{\text{act}}\right| + \left|\eta_{\text{c}}^{\text{conc}}\right|\right) - Rj \tag{12.5}$$

where $\eta_{\text{a}}^{\text{act}}$ and $\eta_{\text{c}}^{\text{act}}$ are the activation overpotentials for the HOR at the anode and ORR at the cathode, respectively; $\eta_{\text{a}}^{\text{conc}}$ and $\eta_{\text{c}}^{\text{conc}}$ are the concentration overpotentials at the anode and cathode, respectively; and R is the ohmic resistance (sum of the proton resistances of the membrane and electrodes and the electronic resistances of materials and interfaces).

The concentration overpotentials can be determined in a first approximation by combining the Nernst equation (eq. (12.6)) and the expression of the current derived from the first Fick's law (eqs. (12.7) and (12.8)):

$$\left|\eta_i^{\text{conc}}\right| = \left|\frac{RT}{n_i F} \ln \frac{C_i}{C_{i,0}}\right| \tag{12.6}$$

$$j_i = \frac{n_i F D_i}{\delta_i} \times (C_{i,0} - C_i) \tag{12.7}$$

$$j_i^l = \frac{n_i F D_i}{\delta_i} \times C_{i,0} \tag{12.8}$$

where η_i^{conc} correspond to the concentration overpotentials at the anode and cathode and n_i to the number of faradays exchanged per mole of hydrogen oxidized ($n = 2$) or oxygen reduced ($n = 4$); C_i represent the concentrations of hydrogen or oxygen at the electrode surface and $C_{i,0}$ the concentrations of hydrogen and oxygen in the feeding gas; D_i is the diffusion coefficient of hydrogen or oxygen in the experimental medium; F is the Faraday constant; δ_i is the thickness of the diffusion layer for hydrogen and oxygen; and j_i and j_i^l are the current and limiting diffusion current densities for hydrogen oxidation and oxygen reduction, respectively.

Combining these equations leads to the following expression for the global concentration overvoltage:

$$\left|\eta^\mathrm{conc}\right| = \left|\frac{RT}{2\mathrm{F}}\ln\left(1-\frac{j}{\left|j_{\mathrm{O}_2}^\mathrm{l}\right|}\right)^{\frac{1}{2}}\left(1-\frac{j}{j_{\mathrm{H}_2}^\mathrm{l}}\right)\right| \tag{12.9}$$

The activation overpotential can be determined in a first approximation from the anodic and cathodic branch of the Butler–Volmer expression of the current densities for the HOR and for the ORR, respectively:

$$j = j_{\circ,\mathrm{H}_2}\exp\left(\frac{\alpha_\mathrm{a} n_\mathrm{a} F\eta_{\mathrm{H}_2}^\mathrm{act}}{RT}\right) \tag{12.10}$$

$$\left|\eta_{\mathrm{H}_2}^\mathrm{act}\right| = \frac{RT}{\alpha_\mathrm{a} n_\mathrm{a} F}\ln\frac{j}{j_{\circ,\mathrm{a}}} \tag{12.11}$$

$$j = \left|j_{\circ,\mathrm{O}_2}\right|\exp\left(-\frac{\alpha_\mathrm{c} n_\mathrm{c} F\eta_{\mathrm{O}_2}^\mathrm{act}}{RT}\right) \tag{12.12}$$

$$\left|\eta_{\mathrm{O}_2}^\mathrm{act}\right| = \frac{RT}{\alpha_\mathrm{c} n_\mathrm{c} F}\ln\frac{j}{\mathrm{I}j_{\circ,\mathrm{c}}\mathrm{I}} \tag{12.13}$$

where j is the current density, $j_{\circ,\mathrm{H}_2}$ (or $j_{\circ,\mathrm{a}}$) and $j_{\circ,\mathrm{O}_2}$ (or $j_{\circ,\mathrm{c}}$) are the exchange current densities for the hydrogen and oxygen reactions, respectively, n_a and n_c are the number of moles of faradays exchanged per mole of oxidized hydrogen and reduced oxygen, respectively, and $\eta_{\mathrm{H}_2}^\mathrm{act}$ and $\eta_{\mathrm{O}_2}^\mathrm{act}$ are the activation overpotentials for the HOR and ORR, respectively. Note that the exchange current density for the electrochemical reaction $A + ne^- = B$ is expressed as follows (eq. (12.14)), which also depends on the concentration of reacting species:

$$j_\circ = \frac{nF}{S}k_S^\circ\left(C_A^\circ\right)^\alpha\left(C_B^\circ\right)^{(1-\alpha)} \tag{12.14}$$

where C_A° and C_B° are the concentrations of A and B species in the solution, α is the transfer coefficient ($0 < a < 1$), k_S° is the reaction rate constant, and S is the electrode surface.

Assuming $\alpha_\mathrm{a} = \alpha_\mathrm{c} = 0.5$, the total activation overvoltage can be expressed as follows:

$$\left|\eta^{\mathrm{act}}\right| = \frac{RT}{2F}\ln\left(\frac{j}{\mathrm{I}j_{0,\mathrm{c}}\mathrm{I}} \times \left(\frac{j}{j_{0,\mathrm{a}}}\right)^{1/2}\right) \tag{12.15}$$

The cell voltage can then be expressed as follows:

$$U_{\mathrm{cell}}(T,j) = U_{\mathrm{rev}}(T) - \frac{RT}{2F}\ln\left(\frac{j}{\mathrm{I}j_{0,\mathrm{c}}\mathrm{I}} \times \left(\frac{j}{j_{0,\mathrm{a}}}\right)^{1/2}\right) + \frac{RT}{2F}\ln\left(\left(1 - \frac{j}{\left|j^{\mathrm{l}}_{\mathrm{O}_2}\right|}\right)^{\frac{1}{2}}\left(1 - \frac{j}{j^{\mathrm{l}}_{\mathrm{H}_2}}\right)\right) - Rj \tag{12.16}$$

This simplified equation displays four terms on which it could be possible to play to increase the efficiency of the cell, that is, to reach high cell voltage at high current densities. The first term, $U_{\mathrm{rev}}(T)$, is fixed by thermodynamics, and few actions are possible, except by varying the working temperature and pressures of reactants (which are generally fixed by the manufacturer or end-user). The second one indicates that increasing the exchange current densities, $j_{\circ,\mathrm{H}_2}$ and $j_{\circ,\mathrm{O}_2}$, would decrease the activation overpotential. However, those exchange current densities are directly related to the intrinsic activity of the electrocatalytic materials. The third one indicates that increasing the limiting diffusion current densities, $|j^{\mathrm{l}}_{\mathrm{O}_2}|$ and $j^{\mathrm{l}}_{\mathrm{H}_2}$, will lead to decrease in the concentration overvoltage. However, the limiting diffusion current densities are directly related to the nature and structure of the electrodes, GDLs, and geometry of the bipolar plates. The last term, Rj, indicates that the decrease in the resistance of the system will also help increase its efficiency. However, this resistance is related to the proton migration through the electrodes/electrolyte interfaces and across the polymer electrolyte, and of electrons from the catalytic sites toward the external circuit through the electrode, GDL, and bipolar plates.

The simple and approximated method presented here to explain the working principle of a PEMFC has the advantage to comprehensively point out the importance of materials and of their characteristics, for the improvement of the electrical performance of such system. The following sections then focus on the state of the art and future developments of the different components and materials for the core of PEMFCs and will complete their roles.

12.3 Catalysts and supports

PEMFCs started to emerge upon the development of sufficiently stable membranes (perfluorosulfonated polymers) [9], researchers and engineers having demonstrated unique creativity to optimize the catalysts and their use in active layers and electrodes [10]. Formerly, platinum was used at the two electrodes in the form of unsupported Pt-black, but the scientific community soon realized that this strategy could not be successful at the large scale, owing to its inefficacy to properly valorize scare and expensive Pt. So, several *quantum jumps* were successfully adopted and enabled the transition from thick and inefficient ionomer-free Pt-black electrodes (1960s) to thin carbon-supported Pt nanoparticle (NP)-based active layers; these embed the "proper amount" of ionomer and present "adequate porosity" for efficient mass transfer to achieve performance that is compatible with industrial deployment (2000s) [10]. In this strategy, while Pt-based catalysts are still the norm, they are shaped into NPs supported on electron-conductive nanostructured carbon materials, conferring porosity to the active layer, for both reactant/product mass transfer and ionomer incorporation, a mandatory composite structure for high-performance PEMFC electrodes [11].

12.3.1 Classical materials

12.3.1.1 Pt-based catalysts

Platinum has been and remains the most widely used catalyst for the ORR and HOR, the reactions proceeding at the cathode and anode of a PEMFC, respectively. Pt indeed exhibits a good compromise between (rather) fast reaction kinetics and significant stability against corrosion in the physicochemical and electrochemical environment of a PEMFC membrane-electrode assembly (MEA). However, its availability and price are not necessarily compatible with a wide deployment of Pt-based systems [12], or at least require that the PEMFC performance to Pt-content ratio is maximized. This strategy has precisely been at the origin of four decades of intense scientific and technological improvements, which led to the present standard: the active layers are now composed of high-surface-area carbon-supported Pt-based NPs of 3–4 nm in diameter and contain "appropriate amounts" of proton-conducting ionomer [9, 10]. It is mostly the ORR cathode that has been under intense target [13] and not the HOR anode, as it has been soon discovered and later rationalized that minimal amounts of Pt were sufficient to promote nonlimiting HOR in a PEMFC [14]. Hence, the following paragraphs will mostly address ORR catalysis.

The first breakthrough in ORR catalysis optimization was to decrease the size of the Pt structures (hence, NPs), in order to reach large Pt dispersion (ratio of surface Pt atoms to total Pt atoms) and high surface area. However, simply increasing the dispersion (decreasing the NPs size) is not practical, since it leads to activity and durability issues. The seminal works of Stonehart and coworkers [15] and Kinoshita [16] (related to phosphoric acid fuel cells, PAFC) were soon confirmed by that of Takasu et al. [17] and Durand and coworkers [18] for PEMFC environments, indeed clearly demonstrated that smaller NP size leads to less active Pt: the specific activity of ORR (activity expressed per Pt electrochemical surface area, ECSA) monotonously decreases from bulk Pt structures to atomically disperse Pt; hence, increasing the Pt dispersion is only beneficial (in terms of mass activity, the activity expressed per gram Pt, i.e., the activity-to-cost ratio) until ca. 3–4 nm [13]. Most catalyst development efforts until the 2000s focused on producing highly dispersed carbon-supported (Pt/C) catalysts, composed of isolated and “round-shaped” Pt NPs. There are many commercial providers for such structures, which can be varied in terms of weight percentage of Pt (ca. 5–70 wt%), NP size (ca. 2–7 nm), and nature of the carbon support (Vulcan XC72, Ketjen Black 600, graphitized carbon black, etc.; more details on the support materials are provided in Sections 12.3.1.2 and 12.3.2.3).

While initial activity is important, it is not sufficient: the performance must be maintained for the operating life of the device (8,000 h for automotive operation and above 60,000 h in stationary applications) [7]. Unfortunately, despite being a noble metal, Pt does corrode in oxidizing conditions [19]: the small NP size needed for high platinum dispersion is not compatible with long-term stability [20]. Ferreira et al. [20] note that coarsening of Pt/C NPs occurs via two parallel processes in PEMFC environments: “(i) Ostwald ripening on carbon at the nanometer scale, which is responsible for platinum particle coarsening from similar to 3 to similar to 6 nm on carbon, and (ii) migration of soluble platinum species in the ionomer phase at the micrometer scale, chemical reduction of these species by crossover H_2 molecules, and precipitation of platinum particles in the cathode ionomer phase, which reduces the weight of platinum on carbon.” The fundamentals of such processes were not discovery at the time, since it had been fully documented decades earlier in the field of heterogeneous catalysis [21]. These theoretical predictions rationalize the spontaneous dissolution of smaller (instable) NPs and the concomitant growth of larger (stable) ones, to minimize surface energy; therefore, the active area (ECSA) decreases, leading to reduced PEMFC performances. Theory has been fully confirmed by numerous practical observations, originating from accelerated stress tests in model environment/conditions [22] or small unit PEMFCs [23], or from on-the-field long-term stack test-rounds [24, 25]. One could argue that the loss of active surface area can, to some extent, be counter-balanced by a growth of the average NPs size (larger particles being more active than smaller ones), but this only minors the losses of performances and never leads to improved apparent activity for aged Pt/C [22, 25]. Of course, the intrinsic stability of the Pt NPs is not the only source of degradation, as these may migrate on the carbon support, agglomerate, and coalesce (if the conditions are sufficiently reducing [26]), all these processes leading to ECSA losses and decrease of apparent performances [27]. These processes, associated with the carbon support stability, will be detailed in Section 12.3.1.2.

A second strategy employed to minimize the content of Pt-group metals (PGM) in PEMFC catalysts, also derived from PAFC catalysis [28], is to consider alloys or composites. The literature on these aspects is extraordinary rich (see, e.g., [13, 29, 30]) and the main outcomes of this strategy will be briefly listed hereafter. Besides “diluting” platinum, hence minimizing its proportion in the final catalyst (which is interesting in terms of cost of the MEA), combining Pt with another metal (usually a 3d metal), enables to modulate the electronic structure of the alloy/composite and can lead to enhanced activity and stability for the ORR. This electronic effect, rationalized by the group of Norskov [31], enables to tune (shift) the metal NP d-band center position versus Fermi level, so that it corresponds to the optimized position in terms of bound strength of the desired reaction intermediate. One can therefore explore Volcano plots of activity to reach optimum activity [32]. This was latter experimentally verified by many groups around the world (see, e.g., [13, 33]). The rationale for the improved activity/durability is multifold. Firstly, in alloys, the 3d element (e.g., Ni or Co) usually exhibits smaller lattice parameter than Pt, hence induces lattice strain and advantageously modifies the adsorption strength of ORR intermediates, thereby accelerating the ORR. A similar effect can be provided by using composites (e.g., core–shell particles), in which the inner material (core) exerts a mechanical strain on the outer one (shell); this is the ligand effect. Of course, in practice, it is hard to separate the ligand from the strain effects, as the less-noble 3d element is usually leached in the acidic electrolyte, leaving a superficial skeleton of Pt atoms (which can be modified into a smooth skin upon proper annealing or long-term operation) [34, 35]. The catalysts and MEA providers now perfectly play with these effects, and Pt alloys are now commonly encountered in industrial/commercial PEMFC, the most popular being Pt–Co-alloyed NPs, used in the Toyota Mirai PEMFC cathode [36, 37], or in Axane-Air Liquide's stationary PEMFCs [33, 38]. In parallel to these industrial developments, the research community has been particularly active in preparing multielement (alloyed) Pt–M catalysts with many different co-metals (Co, Ni, Fe, Cu, Pd, Au, rare earth elements, etc.) [39–45]. All these strategies enable to non-negligibly enhance the intrinsic activity of the PtM/C catalyst over the Pt/C benchmark. However, the activity enhancement is not sufficient to meet the activity targets set by most organizations [37], and their durability in operation is open to question; it is linked to the inherent poorer stability of the non-noble component of the alloy and leads to non-negligible loss of performance in operation [13, 33, 38]. These losses are associated with the loss of intrinsic activity (due to the leaching of the co-metal) [33, 38] but also to the possible poisoning of the ionomer by the co-metal cations [46].

All these effects called for the development of more advanced catalysts that exhibit larger intrinsic activity and durability, which is presented in Section 12.3.2. Another manner to improve the practical performances of the catalyst is to support them onto proper supports and include them in proper electrode structures, which is discussed in Section 12.3.1.2.

12.3.1.2 Carbon supports

As stated in Section 12.3.1.1, the catalyst NPs are usually immobilized on high surface area carbon supports, which enable high dispersion but also electronic conductivity and provide the required porous texture to the electrode for ionomer insertion and mass transfer [9–11, 47]. The most widely (and commercially) used carbon supports are carbon blacks, owing to their extremely low cost and high availability in multiple textures/sizes. It is thanks to the dispersion of the Pt-based NPs on these carbon supports that initial performance of PEMFC became compatible with practical operation, and these materials are nowadays encountered in all the commercial/industrial PEMFCs at both electrodes [9, 11]. The most widely encountered carbon blacks in PEMFC electrodes are Vulcan XC72 (which presents a turbostratic structure with 1–2 nm wide organized domains of graphitic carbon separated by amorphous (likely oxygenated) domains (BET (Brunauer, Emmett and Teller) area ≈ 240 m^2/g_{carbon})), Ketjen Black 600 (a very high surface area carbon, ca. 800 m^2/g_{carbon}), essentially amorphous, and graphitized carbon black (which is more organized than the two others but presents lower BET area, ca. 120 m^2/g_{carbon}). Evidently, better dispersion of the catalyst NPs is achieved with larger BET areas, but more graphitized carbons (of lower BET area) exhibit larger corrosion resistance in PEMFC environments (see below). In addition, the porous structure generated by the pilling of carbon grains is of utmost importance for ionomer insertion in the active layer and mass transfer of the reactant/products in the electrode; it strongly depends on the geometry of the carbon grains (size and shape). The properties of carbon support in electrocatalysis are thoroughly described in [48].

Carbon nanotubes and in particular aligned structures of carbon are also popular, owing to the emphasized mass transfer in their very well-defined porous geometry, high BET area, and inherent robustness against corrosion (these materials are highly graphitized) [49, 50]. Unfortunately, it is still complex to prepare such structures at sufficiently low cost and large dimension to enable practical implementation. They, however, remain a structure of choice for modeling and understanding purposes [50, 51]. Carbons presenting tailored porous structures have also been proposed as a manner to enhance the rate of mass transfer and optimize the ionomer distribution in PEMFC electrodes, like carbon aerogels [52–56] and xerogels [57–59], but these supports are still not employed in commercial systems, essentially owing to poorer resistance to corrosion in operation.

Indeed, carbon is not a stable element in the environment of the PEMFC, being stable as CO_2 above ca. 0.2 V versus RHE (Reversible Hydrogen Electrode) [19]. The degradation of the carbon support is highly correlated to the structure of the carbon, graphitic (organized) carbon being more robust than amorphous (disorganized) ones [30, 60–62]. This explains why aerogel and xerogel structures failed (until now) to be commercially deployed in PEMFCs. Because of this, graphitized carbons start to be fundamentally studied [63–65] and employed in PEMFC systems [33].

Of course, the corrosion of carbon also depends on the operating conditions [66]: (i) higher potential values and presence of oxygen (a strong oxidant) led to more intense intrinsic corrosion of the carbon support, for example, at open-circuit voltage [67]; (ii) dynamic conditions (e.g., potential sweeping) are always detrimental to the stability of the carbon support [61], hence, intermediate characterizations are detrimental to the materials stability [62]; this is particularly documented for start/stop conditions [68, 69] and for fuel-starvation events [70], which are severely harmful to the carbon support and should be avoided or at least controlled if long-term operation is desired; and (iii) the presence of the Pt-based catalyst NPs may severely assist the corrosion of the carbon support, and hence accelerate the agglomeration/loss of Pt NPs [25, 71–73].

12.3.2 Future materials

12.3.2.1 Pt-based catalysts

Advanced Pt-based catalysts are explored since ca. 20 years but still need optimization to meet practical expectations. Monolayer catalysts put forth by Adzic and coworkers [74] indeed enable reaching high activity with respect to the Pt mass [75] but remain awkward to upscale and do not maintain their promises upon long-term operation. Shaped NPs (e.g., PtNi octahedra), derived from seminal works on single crystals [76], also present extremely interesting initial ORR activity [77]. Unfortunately, they suffer the same drawbacks as monolayer-based catalysts, in terms of upscaling ability and durability in operation [78, 79]. More work is ongoing in these areas.

One major breakthrough was brought by dealloyed catalysts, and the group of Strasser has been highly active in the field [80]. In this strategy, the natural acid-leaching/dealloying of a PtM alloy initially rich in M (e.g., $M = Cu$) forms a platinum-rich shell that exhibits compressive strain, thereby shifting the electronic band structure of platinum and weakening chemisorption of oxygenated species, hence enhancing the ORR kinetics [81]. He massively employed this strategy, as well as others, to tune highly active ORR catalysts. It is worth noting that initially alloyed catalysts, like the commercially employed Pt_3Co/C, lead to similar leaching upon long-term PEMFC operation, ending into more intrinsically active catalysts [82]. In that case, the leaching of Co can, in certain conditions (fast leaching in highly oxidizing conditions), promote inclusion of vacancies in the NP structure, which are very active for ORR, the so-called hollow Pt NPs [33]. This strategy was also used with success to prepare PtNi nanoframes that combine dealloyed structures and preferential orientations, therefore leading to extraordinary ORR-specific activity [83], or PtNi aerogels [84]. In such structures, the spectacular gain in ORR activity is, to some extent, linked to the presence of defects in the crystalline structure, the so-called surface distortion [85]. Unfortunately, to date, the promises of extraordinary activity derived from model experiments at the lab scale have still not been validated in practice for large surface PEMFC stacks in real operation.

12.3.2.2 Non-PGM catalysts

Another major breakthrough in PEMFC ORR catalysis resulted from the development of non-PGM containing ORR catalysts that exhibit sufficient performances to be tested in PEMFCs [86]. Since this discovery, there is an extraordinary worldwide effort to understand the operation of these materials [87–90] and improve their catalytic activity [91, 92]. These materials are now benchmarked in the United States and European Union and tested on the industrial scale. Their Achilles' heel is however their durability, both after ink formulation [93] and in operation [94–96]. This seriously threats the future of these materials in commercial/industrial systems; hence, the research community is inventive to find mitigation strategies [97], which yet must be validated in on-the-field applications.

12.3.2.3 Alternative supports

While carbon is still the norm in terms of catalyst support in PEMFC electrodes, its intrinsic instability in PEMFC conditions forced the PEMFC community to look for more robust supports. Strategy to functionalize the carbon surface for protection is not rare [64, 98] but none of these really led to the required enhancement of durability. In an effort to suppress corrosion, 3M explored nonconductive supports, the so-called nanostructured thin film [99] but these suffered their loss of electron conductivity and poor capabilities to manage water and are still not employed in practical PEMFCs. Based on this, conductive metal oxides have been widely explored as support for Pt-based NPs [100]. There is a wide variety of possible metal oxides [101]. Among these, TiO_2 and SnO_2, usually doped to enhance their electron conductivity, are the most popular. However, these materials usually exhibit low surface area that are incompatible with proper dispersion of the catalyst NPs and organization into efficient active layers in PEMFC. A solution to these issues was recently brought by Jones, Maillard, and Beauger, in which nanostructured doped metal oxides were optimized to heighten their BET area and enable good Pt NPs dispersion and also to present proper porous texture for their integration in PEMFC active layers. These structures were in the form of aerogel [102, 103] or nanotubes [104], and successfully tested in PEMFC. Unfortunately, their durability in operation still remains insufficient, as a result of leaching of the doping element (which can adsorb/poison the Pt-based NPs) and loss of the oxygen vacancies, which both led to depreciated electron conductivity in the vicinity of the catalyst particles, hence, deactivation of the catalyst [103, 105].

12.4 Ionomers and membranes

The proton-exchange membrane is at the heart of PEMFC, where it ensures conduction of protons from anode to cathode, separation of reactant gases, and electrical insulation of the electrodes. The requirements for proton-exchange membranes in fuel cells have long been known and the target of much research. These requirements have triggered the development of many types of fuel cell electrolytes, for example, of sulfonated polyaromatics and polyheterocyclic polymers, and acid-doped basic polymers [106–109]. Notable advances through strides in new material developments and in understanding of the mechanisms leading to degradation [110] under operando conditions of a fuel cell have led to membranes combining high proton conductivity (low electrical resistance) and chemical and mechanical durability. These endeavors have also notably advanced perfluorosulfonic acid (PFSA) polymer technologies [111, 112] that have thence produced new generations of state-of-the-art fuel cell membranes. Indeed, apart from the use of phosphoric acid-doped polybenzimidazole (PBI) in high-temperature PEMFC applications, PFSA polymers represent the state of the art and are the ionomer and membrane materials used in commercial fuel cells.

12.4.1 Current materials and structures

PFSA polymers are characterized by a poly(tetrafluoroethylene) (PTFE) backbone with pendant side chains terminated by sulfonic acid groups, and the length of which has given rise to the current terminology for PFSA ionomers of (i) long side chain (LSC) for the Nafion® (as well as Fumion®, Flemion®, and Aciplex®) type and (ii) short side chain (SSC) for the Aquivion® type, as well as the 3M™ ionomer that both lack the perfluoroether group typical of the LSC ionomer [113]. The compositional and structural differences between LSC and SSC ionomers impart specific properties: SSC ionomers are more crystalline and a given polymer equivalent weight (EW) SSC ionomer has higher glass transition temperature (T_g Nafion® ca. 100 °C, 3M™, ca. 125 °C, Aquivion®, ca. 140 °C) than that of the LSC congener. These properties of SSC ionomers are of prime importance, since they extend the usable range of operating temperature to higher values [114, 115].

Acid-functionalized ionomer membranes have a distinct morphology that arises from self-organization of the ionomer chains, similar to that shown by amphiphilic systems, into hydrophobic and hydrophilic regions that, respectively, provide the proton conduction properties and membrane mechanical integrity. In this phase-separated microstructure, the anisotropy of individual ionic clusters is superimposed on heterogeneity in the overall spatial organization, and hydrophobic and hydrophilic regions are separated by transitional interphases [116]. Water is an extended phase in sufficiently hydrated samples. PFSAs form dispersions and not solutions in low boiling alcohols and water, and the morphology and properties of dispersion-cast membranes differ from those of the more crystalline material produced by extrusion of sulfonyl fluoride from polymers. Small-angle scattering profiles of solution-cast membranes show that without heat treatment the structure retains an essential amorphous colloidal morphology with little or no entanglement between polymer aggregates. High-temperature processing is required for the polymer chains to reorganize and entangle, and ultimately to give a sufficiently robust and highly conducting membrane [117].

The PFSA membrane developed by DuPont as Nafion® in the late 1960s, and commercialized by Chemours since 2015, has been the object of several thousands of investigations for use in PEMFC. Its original development was as a permselective separator in chlor-alkali electrolyzers (sodium (Na) fast ion exchanger). Nafion® is produced by free radical-initiated copolymerization of a perfluorinated vinyl ether sulfonyl fluoride comonomer with tetrafluoroethylene (TFE), while the monomer used by 3M in copolymerization with TFE is prepared by electrochemical fluorination of a hydrocarbon starting material. Reactive oxygen species can be generated directly in a fuel cell via chemical or electrochemical reaction of crossover gases over the electrocatalyst surface, or through homolysis of hydrogen peroxide, giving $OH^\bullet$ radicals that can react further with hydrogen peroxide to give hydroperoxyl radicals $OOH^\bullet$. Post-polymerization fluorination is designed to remove the chain-end carboxylic acid groups, recognized as being the starting point for chain “unzipping” through free-radical attack [118]. Nevertheless, the chain ends are not the only point of origin for chemical attack on the ionomer structure, and other mitigation strategies have been implemented that are effective against attack on the side chain, thus preventing the ensuing unraveling of the structure.

Conventional approaches to increase the performance of the membrane include reducing membrane thickness to reduce the membrane resistance and facilitate back-diffusion of water from the cathode to the anode during fuel cell operation and using lower EW ionomers. Both routes potentially compromise membrane durability. For the same ionomer type, gas crossover through thin membranes is higher than through a thicker membrane, constituting reduced fuel efficiency and enhancing the likelihood of degradation processes. Furthermore, thin membranes are prone to earlier failure since there is less bulk material to erode prior to events such as cracks, pinholes, and shorting. The effectiveness of low EW ionomers stems from the increased density of sulfonic acid groups, and hence, the affinity of the resulting membrane for water. Correspondingly, membranes made with these materials typically undergo high swelling, increased plasticity, and softening in wet conditions, while they shrink under dry conditions. Repeated swelling and contraction as occur on fuel cell operation leads to mechanical strain that compromises lifetime. Various chemical and physical routes have been employed to increase membrane mechanical resistance, including thermal annealing and chemical cross-linking and development of composite membranes [119, 120] incorporating polymer reinforcements, electrospun nanofibers, carbon nanotubes, inorganic particles, and clays. Of these approaches, the embedding of ionomer into expanded PTFE (ePTFE) [121] as developed by W. L. Gore [122] was a critical step forward. Although the proton conductivity of such membranes is lower due to the presence of the non-conducting PTFE component, the membrane electrical resistance is reduced significantly simply by the use of the thin membranes that the approach authorizes. As such, current start-of-the-art PEMFC membranes are 15–20 µm composites of ePTFE and PFSA ionomers of ~800 EW, where the ionomers have undergone chemical modification to improve their inherent chemical stability, which comprise other stabilization components for radical scavenging and gas recombination.

Inorganic radical scavengers and hydrogen peroxide decomposition catalysts are routinely implemented in current membrane materials. The role of the latter is to lower the H_2O_2 concentration and indirectly decrease the formation of free radicals, whereas introduction of a regenerative radical scavenger into the membrane (or electrodes) lowers the concentration of oxidative species already formed through parasitic reactions. Examples of hydrogen peroxide decomposition catalysts and radical scavengers applied for mitigation of membrane degradation include metal oxides such as CeO_2, MnO_2, SnO_2, TiO_2, MnO_2, ZrO_2, heteropoly acids, tungsten oxide, and Ce^{3+} and Mn^{2+} ions [123, 124]. The antioxidant properties of organic radical inhibitors [125–127] such as sterically hindered phenols (e.g., terephthalic acid, α-tocopherol, and catechin) or amines, and non-hindered aromatic amines and heterocycles can be used to stabilize PFSA membranes against free radical attack, due to their proton-donating character resulting in a resonance-stabilized radical.

12.4.2 Alternatives and future developments

The technology pull toward simplification of fuel cell systems for automotive applications has driven the need for a high-performance membrane that operates under conditions of low relative humidity and temperatures exceeding the boiling point of water. The higher temperature of operation facilitates the elimination of waste heat from the fuel cell stack, while exclusion of a pressurized system ensures full membrane humidification throughout the temperature range of operation that increases the overall system efficiency. These conditions put a severe constraint on the amount of water that can be maintained in the fuel cell MEA, and limit the proton conductivity in conventional membrane materials, among other effects. Formulating new concepts leading to novel proton-conducting membrane systems that have high proton conductivity at high temperature through the full range of relative humidity remains the most difficult challenge now. Polymer materials comprising protogenic functions other than sulfonic acid, typically phosphonic and heterocycle functionalized materials, have been investigated for higher temperature PEMFC application [128]. Most successful to date has been the approach of acid "doping" PBI for PEM fuel cells operating at 140–200 °C, well above the temperature at which PFSA membranes can be used. Operating features such as no humidification, high CO tolerance, better heat utilization, and possible integration with fuel processing units are among the benefits conferred with the use of high-temperature acid-doped PBI-type membranes [129]. Other basic polymers also have the property of complexing phosphoric acid, most notably pyridine-based aromatic polyethers having pyridine in the main and/or side chains [130].

Many routes have been developed to non-fluorinated, polyaromatic sulfonated polymers over the past two decades, with significant focus on polyarylenesulfones, polyarylene ether ketones, polyaryleneethers, polyphenylenes, polyimides, and polybenzimidazoles [131]. Initially considered as offering the possibility to extend the operation temperature, their advantages are now considered to lie in their low gas crossover and their composition free from fluorochemicals and the associated recyclability. Preparation routes to sulfonated polyaromatic polymers include direct sulfonation of a polymer backbone, grafting of a sulfonated functional group onto a polymer main chain, graft polymerization followed by sulfonation of the graft component, and copolymerization of functionalized monomers to random, alternating, or block copolymers. Of all of these, direct sulfonation has been most frequently used, since it has the advantage of simplicity. However, development of a polymer with a defined sulfonation pattern is generally not possible by direct sulfonation, and the ionomers prepared generally show random substitution along the polymer chain, and a more amorphous structure than the PFSA archetype. Well-defined ion-conducting channels in a phase-separated arrangement are required for efficient proton transfer, and such control is only possible through better tailoring than can be attained by simple polymer modification. Control of the position, number, and distribution of protogenic functions along the polymer backbone is of great consequence to the ultimate membrane properties, and the use of presulfonated monomers allows the synthesis of sulfonated polymers having a tuned polymer micro- and nanostructure. Recent examples of sulfonated polyaromatics showing stability to oxidative degradation and high proton conductivity include development of sulfonated polyphenylenes [132] and phenylated polyphenylenes [133]. It is of interest to note that recent work converges on polymer families related to some of the original Ballard Advanced Materials' membranes [134], although free from the ether linkages that are susceptible to oxidative degradation and elegantly designed from bottom-up. The block copolymer approach is also being used for the synthesis of polymers comprising sulfonated and non-sulfonated (poly)aromatic, and perfluoroalkyl segments [135], or multiblock polyaromatic hydrocarbon and fluorocarbon segments bearing PFSA side chains [136], with the expected attendant benefits associated with the more hydrophobic character and enhanced phase separation.

Inorganic radical scavengers and hydrogen peroxide decomposition catalysts, although routinely implemented in current membrane materials, are not however optimally located or immobilized, such that their efficacy is lost with time in operation. Means are required to encapsulate [137], tether, or anchor these components to avoid their migration to the fuel cell electrodes or their leaching in the fuel cell exhaust. Furthermore, phenol-type antioxidants are depleted over time and must be stabilized by grafting on inorganic or organic supports and, unlike the Ce^{3+}-based radical scavengers, they are not regenerated but are consumed and themselves undergo oxidative aging.

Most advanced membranes in commercial MEAs are reinforced by ePTFE film. This development of some 30 years ago radically increased the membrane mechanical strength and thereby the MEA lifetime, and yet ePTFE has several shortcomings, which must be overcome through alternative compositions and designs in order to achieve the very high operation hours required of heavy-duty transport applications in particular. The tensile properties of ePTFE decrease strongly with temperature (even between 40 and 80 °C), and their efficacy as mechanical reinforcement of ionomer membranes is severely affected [138]. Furthermore, conventional ePTFE reinforcements have highly anisotropic tensile properties in two dimensions parallel to the surface of the film. When impregnated with ionomer to form a reinforced membrane, this anisotropy in the mechanical strength of ePTFE is conserved in the reinforced membrane, which shows significant differences on swelling in water in the directions parallel to the membrane surface. Within a complete MEA, such anisotropic swelling introduces stresses at the membrane/catalyst-layer interface. Moreover, perfluorinated polymers are good solvents for oxygen, and an ePTFE reinforcement does not provide additional oxygen barrier properties [139]. Finally, because of the chemical composition of ePTFE, only hydrophobic–hydrophobic interactions can develop with a sulfonated ionomer, which can be insufficient to avoid delamination under certain operation conditions. Most of these shortcomings are essentially inherent to ePTFE as a material and little can be done to overcome its limitations. New approaches to membrane reinforcement include the use of electrospun polymer webs of basic (heterocyclic) thermostable polymers having high fiber tensile strength at high temperature, and essentially identical mechanical properties in the machine and transverse directions [140]. On impregnation, the non-welded electrospun polymer web absorbs ionomer and relaxes outward to develop a novel architecture where the ionomer membrane is reinforced across its whole thickness. In addition, such reinforcements are functional, since they are basic in character and interact with PFSA through ionic cross-linking or hydrogen bonding. Delamination between reinforcement and ionomer is no longer an issue in this membrane construction, which has a modified interface between the reinforcement and PFSA. Such reinforcements in association with new-generation high-molecular-weight ionomers hold great promise for future MEAs with exceptional stability and durability.

12.5 Gas diffusion layers and bipolar plates

The technical solution chosen so far for distributing the reagents from the cylinders or ambient air to the catalytic sites consists of two components: a feed plate in which a network of millimeter-sized channels is formed and a GDL with micrometer pore size. The reactive gases are transported in the channels between the inlet and outlet of the feed plate by means of the pressure gradient (inlet/outlet pressure drop) and diffuse through the GDL to the electrode. A plate, called bipolar plate, within the stack will feed a hydrogen anode on one side and an air cathode on the other side. This is not the case for the two end plates of the stack, which are monopolar. The functions of these two components are not limited to the transport of gases. They must allow the evacuation of reactants (vapor and liquid water), the transport of electrons from the plate to the catalytic sites (and vice versa), and the evacuation of heat produced essentially at the cathode electrode and in the membrane. They also have a structural role in ensuring the mechanical stability and tightness of the stack. Depending on performance, cost, and durability constraints, different solutions have been developed by the scientific community and industrials. Given the recent progress made on membranes and electrodes, current solutions can be limiting; hence, alternatives will be considered.

12.5.1 Classical materials and structures

12.5.1.1 Bipolar plates

The qualities of a bipolar plate are derived from the material used and the way it is shaped [141]. It must allow (i) good electrical conductivity in its bulk and (ii) at the interface with the GDL, (iii) be light and (iv) small in volume, (v) hydrogen tight, (vi) corrosion resistant, (vii) mechanically strong, (viii) chemically compatible with the MEA, (ix) inexpensive (materials and manufacture), (x) allow good thermal control of the MEA, and (xi) maximize oxygen and hydrogen transport to the catalytic sites without creating too much pressure drop. In practice, a bipolar plate consists in the assembly of two plates, themselves bipolar, allowing the distribution of a gas on one side and the flow of the cooling fluid on the other.

12.5.1.1.1 Materials

The materials used to make bipolar plates depend essentially on the intended application and its intrinsic constraints. For stationary or heavy transport applications, carbon-based materials are preferred because they guarantee better durability, at the expense of cost and compactness. For automotive applications, cost constraints are such that most manufacturers have turned to stamped metal sheets.

Carbon-based materials [142, 143] can be pure graphite (isostatic) impregnated with a polymer such as PTFE to ensure hydrogen tightness. The plates are sliced from the impregnated graphite blocks and then machined. This solution is less and less used because of the cost of machining and the brittleness of the obtained plates. Nevertheless, it has the advantage of leading to a very good thermal (150 W/m K) and electrical (1,000 S/cm) bulk conductivities. The thermal and electrical contact resistances between the plate and the GDL, itself made of graphite fibers, are also minimal. The production of a polymer filled with graphite particles, fibers, or carbon black represents a cheaper and more robust solution. This material can be machined, molded, or even injected. Mass production should take advantage of molding techniques although in practice it is very difficult to avoid re-machining to finalize the plates. The graphite particle (~ 30–60 µm) loading must be enough (77–87 wt%) to obtain percolation, which leads to very viscous pastes that are not easily injectable. This generally results in materials that are mechanically stronger than pure graphite but have lower thermal and electrical conductivities, in the order of 10–20 W/m K and 100–300 S/cm, respectively.

The advantage of using these carbonaceous materials compared to metals is that good corrosion resistance is achieved. Even if the carbon is oxidized, it is evacuated as CO_2 and therefore does not form a semiconductor layer on the surface of the plate. No metal ions that could pollute the ionomer are produced and the contact resistance with the GDL remains very low. However, the resulting plates are larger, heavier, more fragile, and more expensive than stamped metal plates.

Different metals have been tested to produce bipolar plates [144, 145]: stainless steel, titanium [146], aluminum [147], nickel [148], copper [149], and even carbon steel [150]. However, 316L stainless steel alloy is the most used because it is a good compromise between ease of stamping and corrosion resistance. The main constraint associated with the use of metals is the existence of a high electrical contact resistance between the bipolar plate and the carbon GDL. Due in particular to the semiconducting oxide layer that develops on the metal, the coating is mandatory to meet the DOE objective of a contact resistance lower than 10 mΩ cm^2. This coating must be thick and tight for non-stable metals (Al, Cu, etc.) but can be quite thin on stainless steels or titanium. PVD (Physical Vapor Deposition) coatings of gold, platinum, or zirconium can be used. A thickness of 10 nm of gold is a minimum on a stainless steel sheet to sufficiently improve the contact. However, its cost is of the same order of magnitude as that of stainless steel, that is, around 3 $/kW for mass production, that is, a total cost of more than 6 $/kW for the bipolar plate, which is double of the target cost set by the DOE. Alternative coatings based on non-precious materials have therefore been developed. These include graphite CVD coatings, graphite-filled composite sprays [151] that have the advantage of not using vacuum installations. Coatings of nitrides (TiN and CrN) or carbides (TiC and CrC) of a few micrometers or even less have also proven to be effective but do not reduce the contact resistance to the same level as for a gold-passivated stainless steel or carbon-based plates. The durability of the coatings is also a very important issue. To minimize the contact resistance, it is tempting to increase the clamping stress between the GDL and the plate. However, this method can result in damages to the GDL and the passivation layer, where the mechanical stresses are concentrated. Decreasing the contact resistance can also be achieved by surface treatments. For example, thermal carburizing or nitriding has been used with good results. It is possible to produce a surface roughness of the order of 10 µm, that is, the characteristic size of the GDL carbon fibers to increase the number of contact points.

To summarize, the choice of the material constituting the bipolar plate has a direct influence on the performance of the fuel cell due to the variability of the electrical contact resistance with the GDL. It also conditions the compactness of the stack and its durability. In addition, the choice of material leads to certain shaping constraints. For instance, it can be difficult to obtain very thin channels by stamping. However, as it will be explained in the following paragraph, the performance of a fuel cell in terms of efficiency and durability is very sensitive to the design of flow fields.

12.5.1.1.2 Flow fields design

A convenient flow field geometry should lead to (i) uniform gas distribution, (ii) maximum gas concentrations at the electrodes, (iii) optimal humidification of the ionomer and membrane, and (iv) good electrical conduction, at the expense of (v) minimum inlet/outlet pressure drop.

There is an optimal pressure drop (inlet/outlet pressure gradient), below which liquid water will be difficult to drain off, and saturation in the channels (defined as the ratio of liquid water volume to total volume) and in GDLs will be high and will prevent good gas transport. A low pressure drop can lead to a poor distribution of the gas flow between the different cells of a stack and between the different channels of a cell. If the hydrogen flow rate is locally too low, the phenomenon of fuel starvation appears, which causes the irreversible degradation of the cathode by carbon oxidation [152]. A good supply of gas, especially hydrogen, is therefore essential to guarantee the durability of the system. To do so, channels are usually designed for leading to a rather important pressure drop. But, on the other hand, a too high pressure drop will increase the electrical consumption of the auxiliaries (air compressor/hydrogen recirculator) and penalize the energy efficiency of the system. The difficulty lies in the management of partial load operation, when the current density is low, and the gas flow rates are reduced to prevent drying out. The pressure drop is therefore low and flow distribution problems may occur.

A large number of channel geometries have been proposed [153–155] to facilitate the flow of liquid water (in the channels and in GDLs) and to promote oxygen transport through the GDLs, the three main types of geometry are presented in Fig. 12.3. In the case of parallel straight channels, the pressure difference between two adjacent channels is quite small. Oxygen transport from the channel to the catalytic site thus takes place mainly by diffusion. This is not the case for the serpentine channels. A pressure gradient exists under the rib between two adjacent channels. This gradient causes a flow in the GDL that improves oxygen transport and facilitates the evacuation of liquid water appearing under the rib. It has been shown experimentally [156] and through modeling studies [157] that liquid water appears under the rib, which is a preferred cold point of condensation. In the case of interdigitated channels, the entire flow of reactive gas, vapor, and liquid water passes through the GDL under the rib. This geometry allows the transport limit to be pushed back at the cost of pressure losses that are too great for a commercial application. In addition, these interdigitated channels and to a lesser extent serpentine channels are not suitable for dry gas operation because they reduce the diffusion barrier for water vapor allowing the membrane to remain wet.

Currently, manufacturers are trying to reduce the width of the channels and rib to improve the electrical conductivity in the GDL, decrease the operating heterogeneity between the electrode located under the rib and under the channel [158], and improve oxygen transport. However, channels with smaller hydraulic diameter must be shorter to avoid creating too much pressure drop. Thus, more and more geometries of the "straight parallel channels" type are considered. Sometimes the channels can be corrugated: this is a compromise between straight and serpentine flow fields. Another advantage of parallel straight/corrugated channels is the absence of angles that can trap water drops. Finally, they generally led to a more homogeneous coolant flow on the reverse side of the stamped sheet. This results in a more homogeneous cooling and a longer service life.

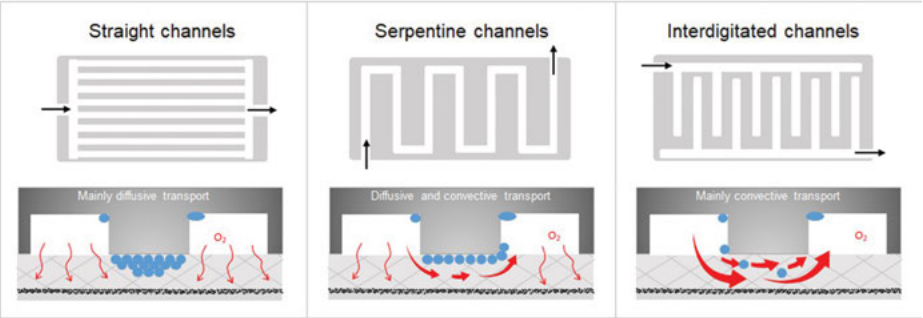

Fig. 12.3: Main geometries of channels and the associated modes of transport.

12.5.1.2 Gas diffusion layer

GDLs bridge the gap between millimeter-sized channels and micrometer-sized electrodes. They allow gases to diffuse under the rib of the channels. They consist of two different layers of carbonaceous materials [159]. The thicker layer in contact with the bipolar plate is made of carbon fibers with a diameter of about 10 µm impregnated with PTFE to give them a hydrophobic character without which they would fill with liquid water. There are carbon felts, papers, and even cloth with a thickness of between 100 and 400 µm. The most commonly used are SGL®, Freudenberg®, Toray®, or Avcarb®

papers. The thinnest layer in contact with the electrode is called microporous layer (MPL). It consists in a layer of carbon black impregnated with PTFE (20%) whose pore size is approximately the same as in the electrode. Its hydrophobic character is therefore more pronounced than that of the fibrous part. The role of MPL is to improve the electrical contact with the electrode and to prevent the return of liquid water from the GDL to the electrode which would result in flooding of the catalytic sites and also to constitute a thermal barrier necessary for the evacuation of the water produced in vapor phase. The main mechanism for transporting water from the electrode to the channels is the heat pipe effect [160] (evapo-condensation). The temperature of the electrodes being higher than the temperature of the channels, the saturating vapor pressure is therefore higher in electrodes than in channels. This concentration gradient is at the origin of the phenomenon of diffusion of water vapor from the electrodes to the channels. The MPL acts as a thermal resistance in which water cannot condense because it is very hydrophobic. It thus makes it possible to maintain the temperature difference [161] necessary for the transport of the water produced in vapor phase. The GDL must also have a low bulk electrical resistance and a low electrical contact resistance with the bipolar plate. The mechanical rigidity of the GDL is a decisive factor because the greater it is, the greater the clamping force that can be applied and the lower the electrical contact resistance. Unfortunately, these fibrous carbon materials remain fairly soft and degrade when over-tightened [162]. Mechanical degradation of the GDL but also chemical degradation with a loss of hydrophobicity can be responsible for significant performance losses and acceleration of the degradation of electrodes [163].

The GDL must be chosen according to the operating conditions of the stack. For example, for operation with dry gases, a GDL with a relatively small opening or a thick GDL is preferred, which will limit the diffusion of water vapor at the expense of a limited diffusion of oxygen. There is an interest in reducing the thickness of the GDL to improve compactness while reducing electrical resistance and cost. To do this, the size of the channels must be reduced at the same time; otherwise, diffusion under the rib is compromised.

12.5.2 Alternatives and future developments

Short-term research is oriented toward optimizing the current architecture to reduce its cost. A recent technoeconomic study seems to demonstrate that flexible graphite-based bipolar plates can be competitive for automotive applications [164]. Their cost would be 3 $/kW, that is, that of the DOE’s target. Progress is expected to be made on passivating coating on stamped metallic bipolar plates. For example, it is possible to make the coating before stamping [165], which represents a gain in the manufacturing process. Dotted metal plate technologies have been shown to be as efficient as continuous plating [166], which reduces the amount of precious metal deposited. Other doped titanium oxide-based deposits show great promises in terms of electrical conduction, durability, and cost [166]. The mastery of stamping techniques and the selection of stainless steels should make it possible to use thinner, cheaper stainless steel sheets and at the same time to form channels with smaller hydraulic diameters. It will then be possible to reduce the thickness of GDLs and their cost, while increasing the power density of the stacks. The optimization of transfers requires a judicious choice of GDLs. It is possible to choose two different GDLs for the anode and cathode. From a system point of view, to limit fuel starvation, one idea is to use a more closed GDL (with a lower effective diffusion coefficient) on the anode side to limit the water flow evacuated at the anode [167]. It is also possible to favor the evacuation of water at the cathode by creating a temperature gradient between anode and cathode with a cold cathode [168].

In the longer term, the current density objectives above 3 A/cm of the automotive industry will be difficult to achieve without technological breakthroughs because of the electrical resistance of GDL and of the electrical contacts between GDL and bipolar plate. One can imagine replacing the bipolar plate and GDL with a metallic porous medium with higher electrical conductivity [169]. Channels could be formed in this diffusion layer. A more rigid porous medium than GDL will have to be chosen in order to increase the clamping force and reduce the contact resistances. The solution developed by Toyota for the Miraï is very original and innovative even if it is already on the market. The bipolar plates are made from a 3D structure of expanded titanium, a bit like in some electrolyzers. GDLs are very thin and thanks to a very powerful hydrogen recirculation, among other things, the air humidifier has been removed.

Another idea to simplify the system would be to implement phase change cooling [170]. By means of a specific treatment of the GDL, liquid water could be injected into the anode compartment to both humidify and cool the cell. This would eliminate the flow of cooling fluid, thus dividing the cost of the bipolar plates by a factor of 2, increasing compactness, and eliminating the need for a humidifier.

12.6 Conclusion

All examples described in this chapter shed light on the very active domain of PEMFC materials for catalysts, supports, ionomers, diffusion layers, and bipolar plates, both for automotive and stationary applications, and show that despite dramatic improvements that led to the present commercial systems, more work is still needed to witness their wide deployment.

Indeed, if exceptional progresses in PEMFC materials have been achieved over the last decades, there is still room for improvement. In a short term, performances (mainly efficiency and durability) of existing materials have to be improved by proposing mitigation methods in order to ensure industrial deployment of the technology; in mid and long terms, the next generations of materials and components have to be developed to proposing more durable and less costly systems, based on less strategic metals and more environmentally friendly compounds and processes to meet the requirements necessary to this technology to be really part of the sustainable development. These will likely originate from disrupting strategies, among which a few were listed in this chapter.

Therefore, wealth of works in terms of catalysts, ink formulation, active-layer preparation (composition and structuration), combination with proper components (GDLs, membrane, and bipolar plates) for membrane–electrode assemblies, cell assembling, and operating conditions are still needed, which means that material scientists and electrochemical/mechanical engineers should work hand in hand if one wants to successfully include these advanced materials in real PEMFC systems. Of course, many labs and industrial companies are on the start line.

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Ciro Caliendo, Paola Russo, Paolo Ciambelli

13 Hydrogen safety, state of the art, perspectives, risk assessment, and engineering solutions

Abstract: The final goal of realizing the hydrogen economy requires also the solution of safety issues related to the properties of hydrogen and to the technologies for storage, transport, and utilization. The hydrogen transport has been treated with an engineering approach. Hydrogen transportation via pipelines or by road and tunnel is analyzed and the respective risk evaluated. Risk acceptability criteria for transportation in tunnel adopted in some countries are compared. Transport scenarios strictly related to hydrogen release from liquid hydrogen were analyzed and their characteristics were computed by implemented DG-QRAM method.

Finally, the main safety strategies to mitigate the effects of hydrogen release and the minimum safety requirements to be taken into account are suggested. Safety engineering issues such as alignment and the length of road section or tunnel, expected traffic volume, and the relevant percentage of dangerous goods vehicles should be taken into account in order to mitigate the effects of hydrogen transport.

Keywords: GH2, LH2, Transport of hydrogen, perspectives, risk assessment, safety strategies, pipeline, road tunnel

13.1 Introduction

The hydrogen safety science and engineering has made tremendous progress in the last years. Today it is also driven by the current concrete interest to the realization of a hydrogen economy in the next 30 years, as recently planned by the European Commission. Hydrogen as zero-carbon fuel means water as emission in mobility, but also carbon-free production when water is the source of hydrogen from electrolysis and renewable energies; hydrogen can decarbonize big industrial productions such as steel and cement. Really, the so-called green hydrogen will be the final destination of a journey starting from the current fossil-based grey hydrogen production and passing through the intermediate stage of blue hydrogen (CO_2 capture and storage). Really, the final goal requires also the solution of critical safety issues related either to the intrinsic properties of hydrogen or to the various technologies involved after the production step for storage, transport, and utilization. Due to the huge amount of aspects to be treated, this chapter mostly focuses on hydrogen transport with an engineering approach. The connections inside an integrated hydrogen safety engineering system are very clearly represented by rows and columns of a matrix developed by

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the HySafe consortium and reported by Molkov [1]. Rows contain activities relevant to basic phenomena, such as releases and dispersion, ignition and thermal effects from fires, pressure effects from deflagrations and detonations, mitigation technologies and safety devices, hazards, and risks; columns refer to safety of applications and infrastructure, such as hydrogen production and distribution, transportation, storage, micropower applications, refueling stations, garages, and tunnels. Moreover, the unavoidable necessity of establishing regulations, codes, and standardization for a safe hydrogen is a strict consequence of advanced knowledge of phenomena and realization of engineering solutions [1].

13.1.1 Transport of hydrogen

13.1.1.1 Background

The transportation of hazardous materials (hazmat) attracts a great amount of attention for the growing concern of safety and environmental damage. Due to its dangerous nature, the transportation of hazmat requires to be dealt in greater depth when compared to the issues of other goods transported.

Hazardous materials are generally classified into nine classes and several subclasses [2] on the basis of their physical and chemical characteristics that may cause a specific risk.

Among the hazardous materials, hydrogen (which belongs to class 2 ADR) is now generating a great interest because its growth prospects are highly attractive.

However, it will inevitably be necessary to allow a wider distribution of this resource from production sites to consumers. Hydrogen might be transported via road, rail, water, pipeline, and air. The intermodal transport, in which multiple modes are considered simultaneously, may also be an appropriate approach. However, the main issue is that hydrogen is the lightest element on earth so that in order to be transported it must be pressurized and delivered in the form of compressed or liquefied gas.

13.1.1.2 Transportation by pipelines

In the long run, the best and safest way might be transportation by pipelines, which has already been performed in some European countries. Large quantities of hydrogen from production area to utilization area are already transported via dedicated pipelines. All over the world H_2 pipelines reach a total length of 4,542 km, most of which (2,608 km) are located in the United States and some more (1,598 km) in Europe, and only a small part (337 km) in the rest of the world (data updated to 2016) as reported in Fig. 13.1 [3].

As the establishment of a global European network is not feasible in the short-term perspective, the intermediate step will be the transport of H_2/CH_4 mixtures in

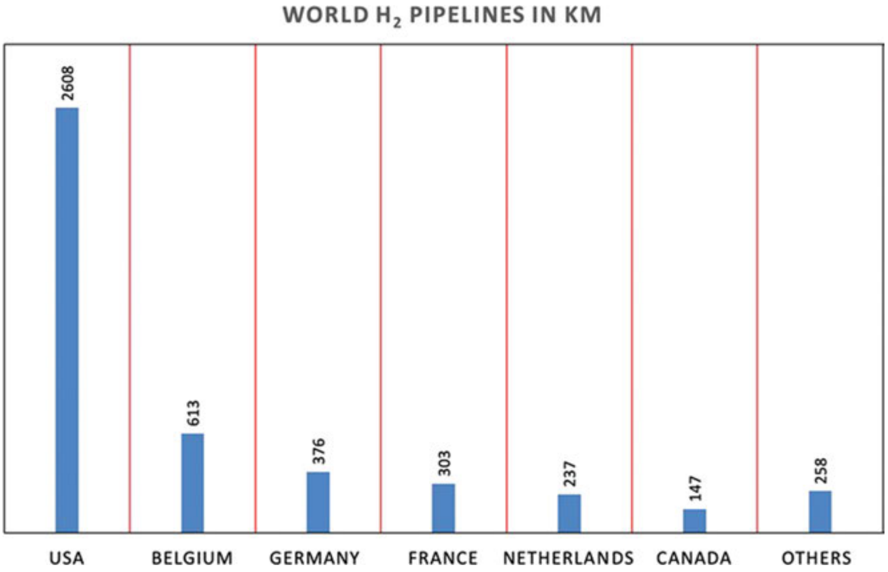

Fig. 13.1: H_2 pipelines km in the world (adapted from [3]).

gaseous form through pipelines, exploiting the existing natural gas transportation network as alternative to the expensive construction of a dedicated infrastructure. Current European plans call for the capability to add up to 20% hydrogen to the natural gas.

It is worth remembering that at the beginning of nineteenth-century street lamps and households were fed by a piped gas mixture (town gas) containing up to 50% hydrogen, produced by coal or petroleum products, and only at the middle of twentieth-century natural gas completely eliminated this production. First application of the concept of blending natural gas and hydrogen dates back to 50 years ago, but now, pushed by wind power installations and diffusion of fuel cell fed automotive electric vehicles, it is strongly supported by many stakeholders.

A review of key issues of blending hydrogen into natural gas pipelines was reported by NRL [4]. Hydrogen content is a critical issue with respect to safety, as the risks are increased by adding hydrogen to natural gas. It was found that the probability of ignition and the severity of explosion of pipeline systems are only slightly increased for hydrogen addition up to 20% [4]. Assuming that the three main risks relate to (i) gas buildup, (ii) explosions in enclosures, (iii) transmission pipelines [5], the assessment analysis showed that gas buildup behavior of blends was similar to that of pure natural gas. A more significant increase in overpressure, and therefore risk or damage, was observed for blends with more than 50% hydrogen. Moreover, the risks in distribution mains and service lines are different, depending on the hydrogen concentration in the system. At less than 20% hydrogen the overall risk is not significant, but the service lines are more involved than mains, because of the most confined spaces. Over 50% hydrogen, the overall risk in service lines significantly increase and the potential hazards severity can become very high.

Attention must be especially paid to gas loss from service lines, as leaking in a confined space may increase hydrogen concentrations, resulting in a threat from the safety point of view. Moreover, plastic seals can have high permeability for hydrogen and confined spaces with high number of sealed joints may represent very unsafe situations, due to leaked gas accumulation.

In 2019, Snam became the first company in Europe to launch a 1-month experiment of introducing natural gas blended with 5% hydrogen into the Italian gas distribution network at Contursi Terme (Italy). The experiment was replicated in December 2019: they successfully tested the transport of 10% H_2 in methane to two industries, doubling previous tested concentration [6].

13.1.1.3 Transportation by road

Gaseous hydrogen can be transported in small to medium quantities in compressed gas containers (up to 3,000 L at 200–250 bar) inside tube trailers. For transport in larger scale pressure of up to 500–600 bars or even higher may be employed. The low density of hydrogen has also an impact on its transportation: in standard conditions (about 1 bar and 0 °C), hydrogen has a density of 0.09 kg/m^3. When hydrogen is compressed to 200 bar, the density increases to 15.6 kg/m^3, and at 500 bar pressure it reaches 33 kg/m^3. For this reason, single tube trailers can carry approximately 500 kg of hydrogen, depending on the pressure and container material. An advantage of the tube trailers is the lower loss of hydrogen during transportation with respect to liquid hydrogen (LH_2).

In comparison with the tube trailers, a greater quantity of hydrogen can be transported by a LH_2 tanker, since the density of LH_2 is much higher than that of the gaseous phase. In this respect, hydrogen is generally cooled to its atmospheric boiling point of 20 K (−253 °C) and loaded into 45 m^3 tanker at around 4 bar pressure. Since the density of LH_2 is about 70.9 kg/m^3, considering a degree of filling equal to 80%, a tanker can contain up to 2.5 tonnes of hydrogen. Moreover, studies on low-temperature phenomena [7], and advances in designing and building of large-scale prototype tanks [8] have strongly contributed to open new horizons in the field of hydrogen storage [9]. Therefore, different industrial sectors can profit from this advances, from high purity hydrogen requiring electronic industries [10] to transportation utilizing high density fuels [11].

Finally, hydrogen may be transported by other chemical carriers such as ammonia. Liquid organic hydrogen carriers (e.g., toluene) are considered more emerging technologies. Other means are metal and liquid (complex) hydrides and adsorption bed on various materials, such as nanocarbons, zeolites, and metal-organic framework compounds. Although material carriers have a higher hydrogen density, all retain an additional energy penalty and cost associated with the recovery of hydrogen from the carrier molecule. They might be safer methods to applicate, presently. However, storage pressure is not the only safety risk factor. For instance, metal hydrides are more sensitive to heat or impact than hydrogen gas.

Since the greater part of hazmat is transported by trucks, it is also logical to assume that nowadays the most effective option for the transportation of hydrogen is by road.

13.1.1.4 Risk of hydrogen transportation by road

The risk of road accidents involving vehicles carrying hydrogen might increase in importance with a higher number of these vehicles being employed. The presence of tankers carrying hydrogen is certainly an additional risk for road transport, given the hazardous nature of this substance (e.g., its wide flammability range, low ignition energy, and high heat of combustion). Therefore, the transportation of hydrogen on public roads poses a direct threat to users, residents, and environment. Moreover, its transportation through tunnels may cause major negative consequences due to confined space compared to open roads. In this respect, a distinction between gaseous and liquefied hydrogen has also to be made. In the light of the above considerations, the transport of LH_2 by road seems to be the most effective short-term option, but at the same time it entails different risks from those associated with compressed gaseous hydrogen.

Hydrogen has a high buoyancy due to its extremely low density. This makes hydrogen a less dangerous substance than other flammable goods in unconfined spaces because the high buoyancy causes the hydrogen to disperse rapidly. But in confined spaces (such as tunnels) hydrogen can accumulate and increase the risk of explosions significantly. Moreover, hydrogen evaporates very quickly in case of leakage and tends to form a flammable mixture with air more easily. In contrast, for example, gasoline evaporates slowly, resulting in a widespread distribution with a minor probability of fire and/or explosion; propane gas is denser than air so that it accumulates in the lowest spots and disperses slowly; methane gas, instead, is lighter than air but not as light as hydrogen, so it disperses rapidly, but less rapidly than hydrogen. The energy released by hydrogen in the event of an explosion might be about 2.5 times greater than that of the other fuels mentioned above; and since it has a lower minimum ignition energy, even tiny sparks (caused, for example, by the agitation of hydrogen itself) might generate an explosion.

13.1.2 Quantitative risk assessment (QRA)

The hazardous substances generally considered by the most common risk assessments that are available in the literature are those traditionally transported on road (gasoline, propane, methane, toxic materials, etc.). For hydrogen transport, instead, there is not a specific risk assessment methodology. This is mainly due to a limited knowledge of the consequences of accidents involving hydrogen in confined spaces and/or on open roads, as well as to the characteristics of associated scenarios, and time response of users in the event of an accident.

Due to the lack of a specific quantitative risk assessment (QRA) methodology for the transportation of hydrogen, the consequences of accidents involving this hazmat are prevalently investigated using different analysis tools: fluid dynamic simulations, reduced-scale experiments, and/or full-scale experiments. We report selected useful references below.

The effects of deflagration and detonation of hydrogen in a reduced-scale tunnel were investigated in [12], while experimental data of hydrogen-air mixture explosions in a tunnel are reported in [13], and the effects due to the release of hydrogen from storage systems are evaluated in [14]. The consequences for both instantaneous and continuous LH_2 releases are studied in [15]; the risk presented by road transportation and storage at a re-fueling station of LH_2 is assessed in [16]. By carrying out some experiments, the danger associated with the transport of hydrogen is discussed in [17]. The highest-risk scenarios for a hydrogen plant in an oil refinery are identified in [18], as well as specifying that the intolerable regions of social risk of the plant should be based on the “As Low As Reasonably Practicable” principle. By carrying out experimental tests, the risk of explosion in gaseous hydrogen-mixtures was characterized in [19]. In [20], by means of experimental tests, it is shown that the flame length increases with the release of hydrogen. In [21] it is proved that the increase in fire resistance of the hydrogen storage tank might reduce the magnitude of risk to acceptable levels. The state-of-the art on the hydrogen hazards with associated risks in tunnels, and similar confined spaces, are recently described in [22]. The mentioned report also discusses the tools available for assessing the consequences of different accident scenarios involving hydrogen.

The lack of a specific method for a quantitative risk analysis of transporting hydrogen by road poses also a relevant issue of research. With reference to transportation on open roads and/or through tunnels it is to be mentioned that different QRA methods are available in the literature, for example, the Austrian TuRisMo, the Italian IRAM, the Dutch TUNPRIM, the QRAFT model from Singapore, and the DG-QRAM developed jointly by PIARC [23] and Organization for Economic Co-operation and Development. It is to be stressed that none of them is aimed at a quantitative analysis of the risk of transporting hydrogen, but some methods, such as the DG-QRAM, which is considered in Europe as one of the most appropriate for dealing with dangerous goods, might be helpful, at a preliminary analysis step, for providing an approximate evaluation of the risk level due to transported hydrogen.

13.1.2.1 Description of the risk assessment process

The general process of risk assessment applied to roads may be divided more especially into five main steps:

- selection of a target outcome,
- identification of system,
- definition of hazards,
- determination of the probability (or frequency) of occurrence of events,
- evaluation of the consequences.

The definition of the hazard (i.e., accident scenario), as well as the determination of its probability (or frequency) of occurrence, comes from the event tree. It is a graphical representation used in risk analysis to draw different chronological series of subsequent events (or scenarios) starting from an initial event. In the event tree the probability of occurrence of each event is also defined once the probability of the initial event has been identified. The probability of occurrence of the final scenario is given by the product of all the conditional probabilities corresponding of each bifurcation. This will depend on the properties and conditions of the hazmat, the presence of safety measures, and specific circumstances.

With reference to LH_2 release, a typical event tree is presented in Fig. 13.2. Starting from the initial event, the LH_2 release is assumed to be followed by three types of release: instantaneous, continuous, and continuous from small-sized hole. The continuous release of liquefied hydrogen from a small-sized hole is assumed to cause no significant effect. The instantaneous or continuous release can be with or without ignition. The ignition can also be direct or delayed, depending on the time of ignition. The direct ignition of instantaneous release may lead to the final fireball scenario; whereas the delayed ignition may lead to the flash fire scenario or VCE (vapor cloud explosion). Furthermore, the immediate ignition of continuous release is connected to the Jet fire scenario, whereas the delayed ignition may lead to the flash fire or VCE scenario.

It is worth remembering that when LH_2 is used, further hazards and related scenarios should be considered. And some of these have not been fully understood or forecasted yet. As an example, boiling liquid expanding vapor explosion (BLEVE) and rapid phase transition (RPT) are two physical explosions as a consequence of a loss of containment and they are two atypical accidental scenarios [24].

Among the various projects on hydrogen safety, the FCH JU project IDEALHY has been focused on the LH_2 risk assessment, considering BLEVE among the potential consequences [25]. Moreover, the Norwegian project SH2IFT [26], in which the

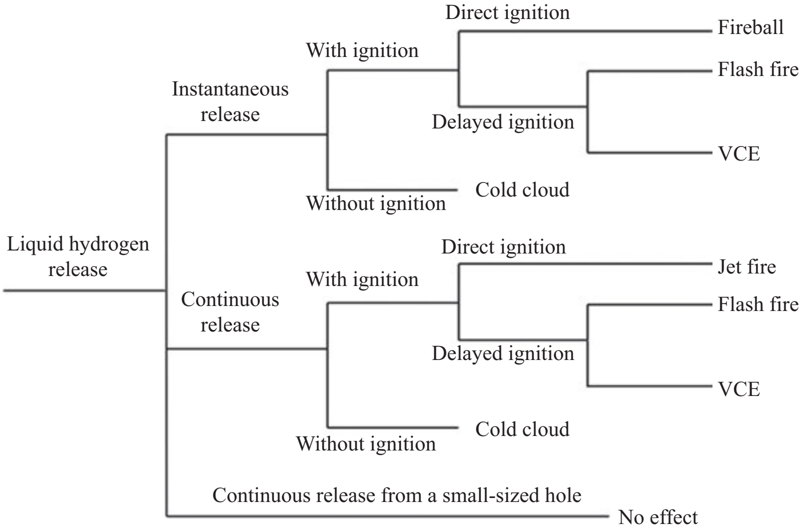

Fig. 13.2: A typical event tree of liquid hydrogen release [15].

safety aspects of both liquid and gaseous hydrogen are carefully investigated, will analyze BLEVE and RPT in the case of the LH_2, carrying out experimental tests and developing numerical models both to assess the formation and to estimate the related consequences. Moreover, LH_2 RPT has been theoretically predicted in a few studies such as in [27]. On the other hand, RPT has never happened for LH_2, while three past LH_2 BLEVE accidents have been identified [28].

The results of a risk analysis are generally expressed in terms of the societal risk, which represents the resulting risk to a group of people, due to all hazards starting from a specific event. The level and nature of consequences are measured in terms of fatalities. The representation of societal risk is commonly the F/N curve and expected value (EV). The F/N curve is graphically reported in a bi-logarithmic chart in which N represents the number of fatalities and F the cumulative frequency that the number of fatalities is $\geq N$. The EV of risk is, instead, defined as the integral between 1 and the maximum number of fatalities N. The results of a risk analysis then need to be compared to predefined acceptability criteria.

13.1.2.2 Consequence analysis

Consequence analysis is carried out for evaluating the extent of the possible consequences associated with a top event and it is usually an integral part of QRA.

13.1.2.2.1 Consequence analysis for gaseous hydrogen

In the case of gaseous hydrogen, the fundamental science for non-premixed flames is very good. The hazards from these flames are also well characterized. Reduced order models used to establish thermal radiation hazard and safety distances from hydrogen jet fires are often based on simplified, empirical models previously developed for hydrocarbon jet fires [29, 30]. The capability of these models of predicting the thermal radiation of hydrogen jet fires has often been validated against small-scale or medium-scale jet flame experiments [31–33]. They work reasonably well to predict thermal load consequences and are being used in integrated platforms (e.g., HyRAM) [34]. Large-scale hydrogen jet fire experiments have shown that thermal radiation levels can be significantly higher than one might expect from extrapolation of model results based on smaller hydrogen flames [35, 36]. Moreover, real jet fires are often significantly affected by various geometries, ventilation, and atmospheric conditions, while reduced models are normally developed for unobstructed, idealized free jet flames and will typically not be able to account properly for effects of more complex conditions involved in realistic scenarios. Predictive tools based on computational fluid dynamics (CFD) may be very useful for quantitative consequence analyses of fire hazards in realistic environments [37].

On the contrary, premixed combustion requires further investigation. The phenomena are well understood from a fundamental perspective but modeling for large-scale applications with obstacles needs further work – particularly the understanding and modeling of deflagration detonation transition.

13.1.2.2.2 Consequence analysis for liquefied hydrogen

In the case of liquefied hydrogen, despite a well-known advantage in volumetric capacity, there is not yet a full understanding of the hazards from cryogenic releases of hydrogen, and validated predictive tools to be used in hydrogen safety engineering are currently missing. From a hazard's management point of view, the complexities and extreme conditions implied with LH_2 handling put different demands on safety assessments and the modelling of accidental release, mixing, and combustion. The quality and level of detail of experimental data available in literature are insufficient to allow complete and accurate validation of CFD. Unfortunately, criteria for model performance in another field (e.g., LNG) cannot be easily adapted. They need to be revised for LH_2 because of the significant differences in its physical properties.

Recently, some significant knowledge advances in understanding the hazard behavior of LH_2 and cryo-hydrogen have been done. As an example, Cirrone et al. [38] demonstrated that the similarity law for concentration decay in momentum-dominated jets and the dimensionless flame length correlation can be used as engineering tools for calculation of hazard distances for hydrogen releases at different temperatures, including cryogenic. To this aim the correlations were applied to tests conducted at Sandia National Laboratories (United States) on cryogenic unignited and ignited jets. While there has been some progress in this area a number of knowledge gaps still exist in all of the areas including dispersion, jet and pool fires, general ignition, and BLEVE/fire resistance.

With regard to modeling tools available in the literature to evaluate the consequences of various scenarios related to hydrogen jets release, they can be classified in engineering tools (e.g., HyRAM consequence models [34], H2FC Cyberlab SAGE Network [39], and NET-Tools [40]) and CFD tools (e.g., FireFOAM [41], FLACS [42]).

In particular, for engineering tools the priorities indicated in [43] are: the development of suitable models for accounting for the effects of different mitigation measures appropriately, and the development of a realistic model for high-pressure hydrogen releases inside ventilated enclosures.

13.1.2.3 Risk of hydrogen transportation by pipeline

Nowadays, H_2 pipelines are mainly adjoined to industrial areas, so their breakage may cause significant risk to the surrounding environment and the people likely getting in touch with them. Therefore, the risks associated with a possible breakage of a pipeline carrying gaseous hydrogen must be taken into careful consideration. Dry hydrogen often ignites when it is discharged to air in normal weather. Apparently, the electric field developed by ejection of this charged gas can develop enough of a potential gradient to cause ignition by corona discharge; it has to be noted that the minimum ignition energy of hydrogen is only about 0.02 mJ. Consequences of gaseous hydrogen pipelines accidents can cause rather serious damage to people and buildings located in proximity of the pipeline involved in the hazard.

Following an accidental release of gas, a flammable cloud of gas is formed that mixes it with air and can be immediately ignited giving a jet or trench fire, or later generating either a flash fire or an explosion. For a fire the worst hazard for people and buildings is the direct contact with flames and thermal radiation, while in the case of an explosion it is the impact of the blast wave. From the analysis of preexisting literature, it results that, as consequence of a pipeline failure, the event with a higher frequency of occurrence is represented by a fire while that with worst consequences by an explosion [44].

In a previous work carried out by one of the co-authors [45] of the present chapter, a procedure has been proposed to assess the potential direct damage to building structures caused by a gas explosion as consequence of release by a high-pressure pipeline. This procedure has been applied to both natural gas [46] and hydrogen pipelines [45]. The probability of occurrence of an explosion event as a result of a pipeline breakage has been estimated, and the consequences of the explosion (overpressure and impulse) have been evaluated. To simulate the hydrogen release, a one-dimensional integral model, SLAB model [47], has been used, while results of the explosion in terms of overpressure and impulse are calculated by means of the multi-energy method developed by TNO [48]. Explosion damage to building structures has been assessed using pressure-impulse diagrams that describe the ability of structural components to withstand various types of explosion loads defined as blast capacity.

More recently [49], the same procedure is applied to estimate harm to people as well as the direct structural damage associated with high-pressure hydrogen pipeline explosions (Fig. 13.3).

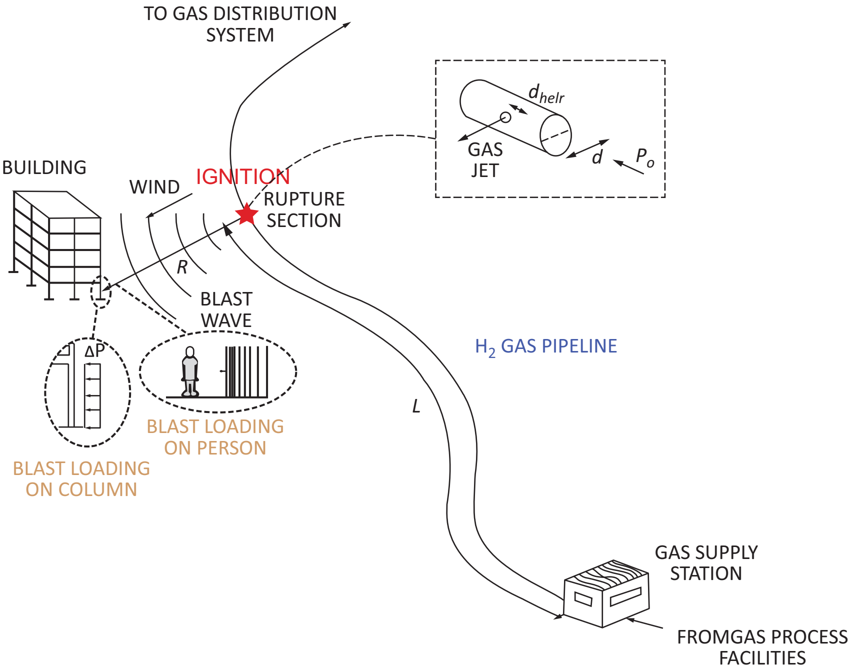

Fig. 13.3: Damage associated with high-pressure hydrogen pipeline explosions (adapted from [49]).

Specifically, the analysis refers to transmission and gathering pipelines located in industrial and rural areas. For people both direct and indirect effects of blasts are considered in order to evaluate the annual probability of damage. As a main direct effect, the damage to pressure-sensitive organs, such as lungs and ears, due to the sudden increase in pressure, is considered. Among indirect effects both the impact of the head and the whole-body due to whole-body displacement are observed. During the whole-body displacement, in fact, the overpressure and impulse of the explosion interact with the body in such a way as to be essentially picked up and translated. On the contrary, the damage due to flying fragments hitting someone's body, and owing to the impact caused by a collapsed structure to people inside buildings, is not evaluated. With regard to building structures, direct damage from an explosion can be of various kinds, such as deflection of structural steel frames, collapses of roofs, leveling of walls, shattering of panels, and broken windows. Specifically, direct damage to both reinforced concrete columns and walls of load-bearing masonry buildings are examined. What is finally evaluated is a minimum safety distance between hydrogen pipelines and people (Fig. 13.4). The presented procedure can be applied for the design and risk assessment of new pipeline networks in industrial or rural areas and for existing building assets.

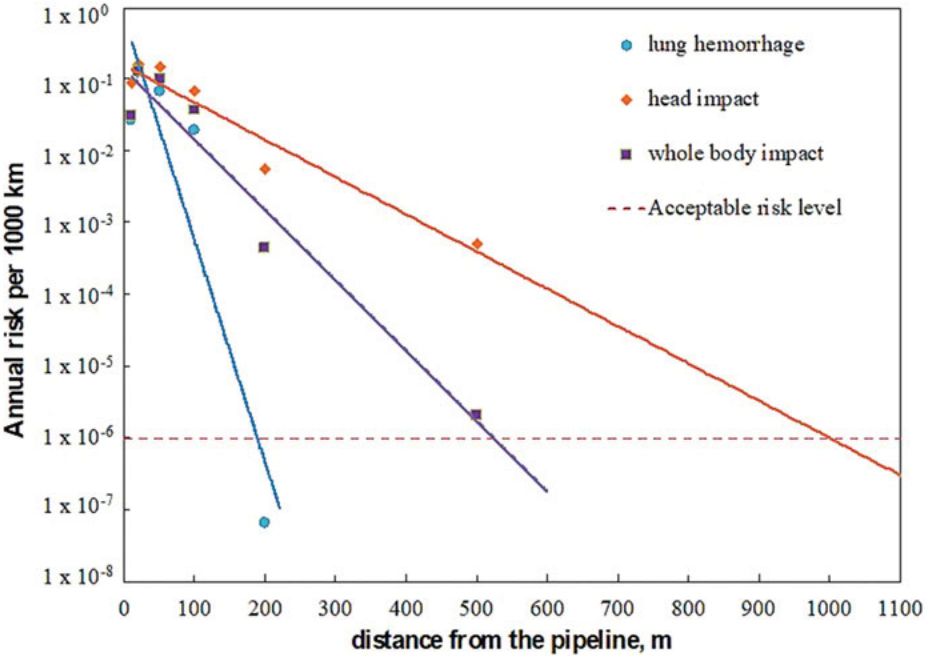

Fig. 13.4: Damage associated with high-pressure hydrogen pipeline explosions (adapted from [49]).

13.1.2.4 Risk acceptability criteria

The definition of an acceptability criterion is affected by many factors involving more especially legal, social, and cultural aspects. Although there is not a risk-acceptability criterion universally recognized, several criteria in use in some countries exist for specific applications. Moreover, some criteria are appropriate for the risk of overall traffic, while other criteria are valid only for the transportation of dangerous goods and may also be more restrictive. With reference to transportation through tunnels, which may be extended also to open roads that include tunnels, a short summary of acceptability criteria is presented in this paragraph from [50]. In Italy, for example, the risk is evaluated as not being acceptable if the F/N curve lies above the upper limit, which is defined by the following function: $F = 10^{-1} \cdot N^{-1}$ for $N \geq 1$ fatality. Note that the reference criterion mentioned is for overall traffic, recommended per year, and is based on a legal requirement. However, certain applications regarding dangerous goods vehicles (DGVs) can also be found in [51]. In the Czech Republic, the acceptability criterion is referred to a 1-km-long road tunnel (per year), and for the overall traffic: the upper limit is $F = 10^{-2} \cdot N^{-1}$ for $1 \leq N \leq 1{,}000$ fatality. In Switzerland, the acceptability criterion is referred to a 100-m-long road tunnel (per year) and the transport of dangerous goods on transit roads including tunnels: the upper limit is $F = 10^{-3} \cdot N^{-2}$ for $N \geq 10$ fatality. In Germany, it is referred to 1-km-long road tunnel (per year) and the transport of dangerous goods through road tunnels: the upper limit is $F = 10^{-2} \cdot N^{-2}$ for $N \geq 10$ fatality. In Austria, the acceptability criterion refers to the transport of dangerous goods through tunnels (per year), and the upper limit is: $F = 10^{-1} \cdot N^{-2}$ for $N \geq 10$ fatality; however, for tunnels longer than 1 km the upper limit is: $F = 10^{-1} \cdot N^{-2} \cdot L^{0.5}$ for $N \geq 10$ fatality. In the Netherlands, the acceptability criterion for road tunnels indicates that the risk is evaluated as being not acceptable if the F/N curve lies above the upper limit defined by the following function: $F = 10^{-1} \cdot N^{-2}$ for $N \geq 10$ fatality. In the United Kingdom, the upper limit is $F = 10^{-1} \cdot N^{-1}$ for $N \geq 1$ fatality [52]. Finally, both France and Greece have set an EV threshold value in road tunnels for DGVs equal to 10^{-3} fatalities/year [53].

When the F/N curves lie above the upper limit, additional safety measures and/or appropriate traffic control strategies should be implemented for reducing the risk level.

13.1.2.5 Case study

Although there is not a specific risk assessment method for the transportation of hydrogen on open roads and/or through tunnels, it appears useful to summarize here the results of a study [54], carried out by one of the authors of the present chapter. The work is based on an extension of the aforementioned DG-QRAM to potential accident scenarios involving vehicles transporting liquefied hydrogen. Since the DG-QRAM considers only 13 standard accident scenarios, which do not include the transport of hydrogen, certain modifications are necessary in terms both of the event tree and additional scenarios for taking into account the liquefied hydrogen transported. For this purpose, the event tree of the release of LH_2 from a tanker was built according to the framework of the aforementioned Fig. 13.2, and the probabilities of occurrence of each event – such as are reported in the literature – were used. Three additional scenarios were implemented, which are strictly related to the transport of LH_2 (i.e., fireball, VCE, and flash fire). The main characteristics of the accident scenarios related to the hydrogen release, expressed in terms of the amount of substance contained in the tanker, the size of breach, and the mass flow rate from the breach, which are explicitly required by the DG-QRAM method, were computed and implemented. Once the conditional probabilities had been defined, the maximum emitted radiation intensity was evaluated in order to estimate the physical consequences of fireball and flash fire. The implementation of the aforementioned three additional accident scenarios related to the transport of hydrogen allowed us to evaluate the increase in the societal risk, both in terms of F/N curves and EV of risk. In particular, the entity of the increase in risk level due to LH_2TVs (liquid hydrogen transport vehicles) in road tunnel as a function of the fluctuation of geometric and of traffic characteristics was quantified. It was found how the risk level increases with the tunnel length (L), the average annual daily traffic (AADT), and the percentage both of heavy goods vehicles (HGVs) and DGVs. It was also found that for certain combinations of the geometric characteristics and traffic conditions, some accident scenarios with LH_2TVs presented F/N curves that lay beyond the upper limit, while the same did not happen without LH_2TVs. This means that engineering interventions should be implemented for reducing the risk level. Alternatively, the road management agencies (RMAs) might temporarily forbid or limit the circulation of DGVs, including more especially those carrying hydrogen.

However, it is to be stressed that the DG-QRAM cannot predict exactly the real risk due to hydrogen, as a result a certain degree of uncertainty is expected. Therefore, the results obtained should be considered only to a certain order of magnitude and should be supported by additional studies based on fluid dynamic simulations or reduced-scale experiments and/or full-scale experiments.

13.1.3 Hydrogen safety engineering

The main safety strategies to deal with the hydrogen release in order to mitigate its effects might be:

- minimizing its mass flow rate;
- isolating hydrogen from other hazardous materials;
- separating and protecting people from the potential negative effects due to hydrogen;
- preventing hydrogen from accumulating in confined spaces (such as tunnels), reducing the risk of explosions (e.g., by means of appropriate characteristics of ventilation systems or hydrogen traps on ceiling);
- permitting the drainage of liquefied hydrogen by means of slot gutters;
- providing alternative itineraries on open roads for the circulation of vehicles carrying hydrogen;
- considering operating measures to reduce the risk such as, for example, of escorting the vehicles carrying hydrogen and/or permitting their circulation through tunnels by night;
- placing road signs at the portals of tunnels on which are reported speed limits, prohibition of overtaking, safety distance between vehicles;
- providing tunnels with water supply systems, as well as monitoring systems;

- providing tunnels with systems to allow communications between RMAs and emergency services such as the police, fire brigades, and rescue teams;
- using alarm systems and warning devices;
- wearing personal protective equipment;
- training of the emergency services;
- observing safe operational requirements.

In the light of the above considerations, a variety of mitigation techniques appear available to limit the negative consequences of the transport of hydrogen on open roads and/or through tunnels. For a balanced approach due to the costs of the engineering measures, RMAs should ensure minimum safety requirements taking into account: both the horizontal-vertical alignment and the length of road section or tunnel; the expected traffic volume expressed in terms of the AADT per lane; the percentage of both HGVs and DGVs, considering particularly those transporting hydrogen.

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Giuseppe Ricci, Laura Prosperi, Maurizio Dessi, Marco Tripodi

14 Hydrogen applications in ENI: from Industrial applications to power generation

14.1 Foreword

Eni is an energy company employing over 30,000 people in nearly 67 countries around the world. Eni is working to build a future where everyone can access energy resources efficiently and sustainably. Eni's work is based on passion and innovation, on unique strengths and skills, on the quality of the people, and by recognizing that diversity across all aspects of operations and organization is something to be cherished. Eni believes in the value of long-term partnerships with countries and communities where it operates.

Eni's commitment is to respond with concrete, rapid, and economically sustainable solutions to the challenge of improving access to reliable and clean energy and fighting climate change. Eni recognizes the Intergovernmental Panel on Climate Change's scientific evidence on climate change and was among the signatories of the Paris Pledge for Action, supporting the objectives of the Paris Agreement to limit temperature increases to well below 2 °C.

Eni's strategy combines the objectives of continuous development in a rapidly evolving energy market with a significant reduction in the group's carbon footprint coupled with ambitious net lifecycle emission (scope 1, 2, and 3) reduction targets: −30% by 2035 and −80% by 2050.

Eni believes that hydrogen will have importance in the European economy and has defined a strategy that comprises all clean hydrogen production pathways, including natural gas reforming with carbon capture and storage, circular economy technologies for production of low carbon hydrogen from plastic waste, and from renewable electricity.

Currently, hydrogen is mainly used in refinery applications, while uses in other applications are still at an early stage. Some long-term opportunities could come from blending hydrogen into the existing natural gas network for heating purposes and power generation, or in transport application with fuel cell vehicles.

In fact, Eni currently uses hydrogen in many of its downstream plants and is probably the company with the highest hydrogen consumption in Italy. It is mainly used in refineries and biorefineries for HVO (Hydrotreated Vegetable Oil) biofuel production.

In Eni, there are also some ongoing activities in the Enipower Company, an Eni subsidiary and the largest Italian operator of cogeneration heating power plants (CHP) and the second national grid service provider. The last paragraph will describe the expertise of Enipower, both in hydrogen power generation and in new research, to leverage the opportunity of converting overgeneration of renewables

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into hydrogen through water electrolysis during the less remunerative hours of the day in the power market in order to offer a flexible service to the power market.

14.2 Hydrogen use in petroleum refineries and biorefineries

Laura Prosperi

14.2.1 Introduction

In the refining industry, hydrogen is used mainly for the following purposes:
1. Reduction of pollutants from fuels combustion
2. Pre-treatment of upstream feedstock in some specific production units
3. Conversion of heavy crude oil cuts into lighter and more profitable products

1. Environmental regulations impose limits on the content of contaminants in fuels, in particular, on sulfur content in gasoline and gasoil, in order to reduce the emissions of pollutants from motor vehicles. The refining process that allows this is a catalytic hydrogenation where hydrogen is used to mainly remove sulfur from petroleum products to meet market specifications. This process is usually referred to as hydrodesulfurization (HDS).
2. In some refining units, the contaminants in feedstocks are poisons that can reduce or even compromise the performance of the unit itself. In these cases, hydrogen is used to reduce the content of contaminants such as sulfur, nitrogen, oxygen, and metals. This process is generally referred to as hydrotreating (HDT).
3. Environmental regulations also call for reducing the use of heavy fuel oils because of their high sulfur content. Therefore, it becomes necessary to reduce the production of heavy fuel oil by converting them into lighter and more profitable products (naphtha, kerosene, and gasoil). In this case, hydrogen is used to convert the heavy petroleum cuts into products with higher added value via hydrocracking (HDC).

14.2.2 Petroleum refineries

14.2.2.1 Hydrotreating and hydrodesulfurization

HDT is a process in which hydrogen is necessarily used to remove undesired species from feeds to other process or from fuels for the market. In the latter case, the HDT process is called HDS because the main function is to reduce the sulfur content in fuels to comply with legislations.

The general scheme of a HDT/HDS unit is as follows (Fig. 14.1):

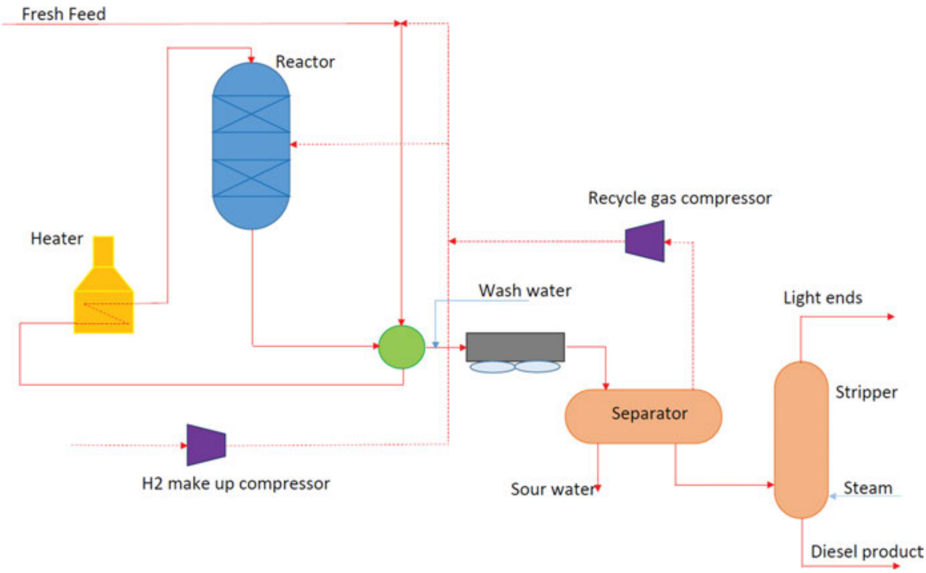

Fig. 14.1: General scheme of a hydrotreating/hydrodesulfurization unit.

The feed to be treated is mixed with hydrogen (make up + recycle) and heated to the reaction temperature before entering the reactor (one or more, depending on the unit configuration) where the reactions occur in the presence of a catalyst. The effluent from the reactor is cooled down and then in one or more separators, the liquid product is separated from the gas phase that is rich in H_2. The gas is sent back to the reactor while the liquid product goes to storage if it is a final product or is fed to another process. The makeup hydrogen is the reagent consumed in the reactions, while the recycled hydrogen is necessary to stabilize the catalytic activity and reduce the coke formation that decreases the lifetime of the catalyst.

In the reactor, different reactions take place in the presence of the catalyst. Hydrocarbon molecules lose the undesired atoms (S, N, O, etc.) and in some cases, their structure is modified as follows:

$$R - CH = CH_2 + H_2 - > R - CH_2 - CH_3 \ \text{(saturation of olefins)}$$

$$R - SH + H_2 - > RH + H_2S \ \text{(desulfurization)}$$

$$R - SH + H_2 - > RH + H_2S \ \text{(desulfurization)}$$

$$R - NH2 + H_2 - > RH + NH_3 \ \text{(denitrification)}$$

$$R - OH + H_2 - > RH + H_2O \ \text{(deoxygenation)}$$

where R indicates the hydrocarbon portion of the molecules.

The reactions take place differently, depending on the complexity of the hydrocarbon portion “R –,” which depends on the boiling point of the petroleum cut. In particular, the higher is the boiling point of the petroleum cut, the more difficult the HDT reactions become and the higher is the hydrogen consumption.

Indeed, the concentration of undesired atoms (S, N, metals, etc.) varies among the different petroleum cuts as per the following figure (Fig. 14.2):

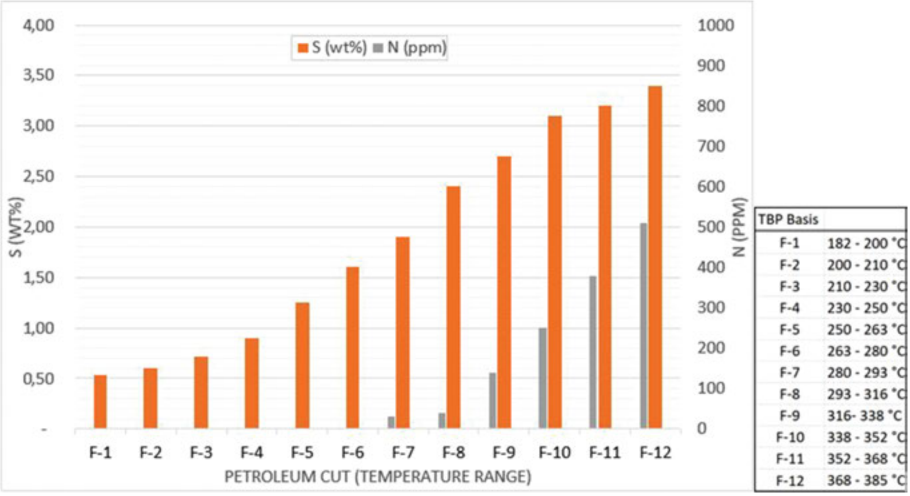

Fig. 14.2: Concentration of undesired atoms (sulfur and nitrogen) according to different petroleum cuts.

So, the higher the boiling point range of the petroleum cuts, the higher is the concentration of contaminants. Moreover, in heavier cuts, the contaminants are bonded to more complex hydrocarbon molecules, which makes their removal difficult.

In Tab. 14.1, the relative reactivity of different hydrocarbon molecules and their boiling points are reported:

Tab. 14.1: Relative reactivity and boiling point of different hydrocarbon molecules.

Compound	Boiling point (°C)	Rel. rate
Diethylsulfide	92	600
Thiophene	84	30
Benzothiophene	221	10
Dibenzothiophene	333	1
4,6-Dimethildibenzothiophene	360	<0.1

When the molecules also contain aromatics rings, saturation of the aromatics can take place depending on the operating conditions (temperature and pressure). Note that aromatic saturation requires H_2 as well.

In brief, the heavier is the hydrocarbon cut to be treated, the higher is the hydrogen consumption.

The HDT scheme is almost the same for all the processes operating in the hydrogen cycle. Reactor configuration, catalyst, and operating conditions vary depending on the different feedstocks and the target product quality.

A generic scheme of a complex refinery is shown in the following picture (Fig 14.3). Within the refinery, there are several HDT units treating different feedstocks for obtaining different products.

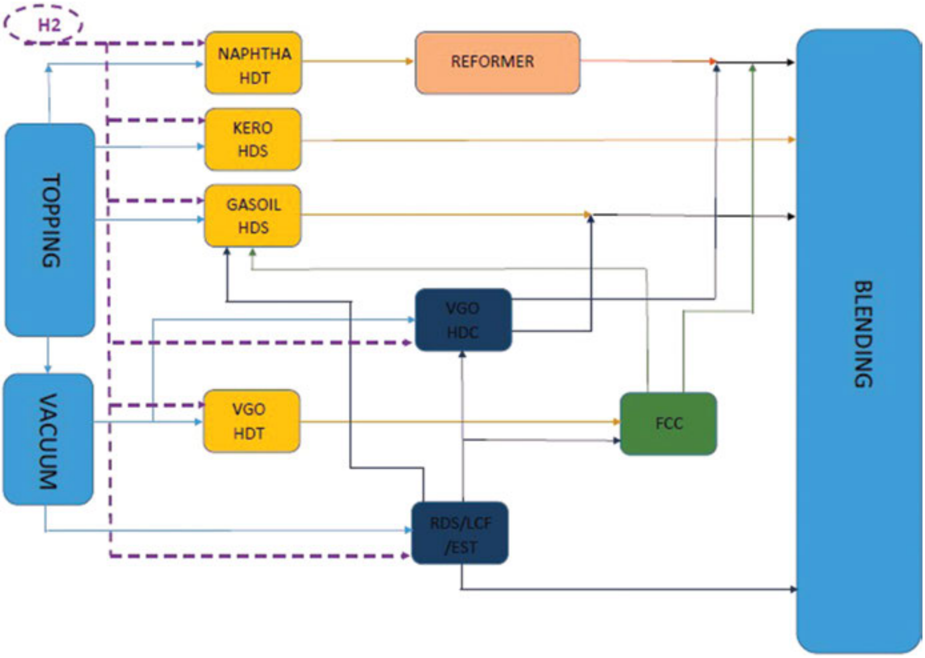

Fig. 14.3: Typical scheme of a complex refinery.

14.2.2.1.1 HDT for naphtha feed

The naphtha HDT prepares the feed (boiling range = 40–200 °C) for the subsequent naphtha treatment (catalytic reformer), reducing the sulfur and nitrogen content that are poisons for the reformer catalyst.

The specifications of the naphtha feeding the reformer are:

- $S \leq 0.5$ ppm
- $N \leq 0.5$ ppm

The naphtha HDT scheme is relatively simple because the naphtha feed is easy to be treated compared to the heavier cuts of crude, but the operating conditions can vary depending on where the stream comes from.

The main HDT feed is the straight naphtha from topping unit and the typical characteristics are:

- S ~ 500 ppm
- N ≤ 15 ppm

Naphtha may also come from other refinery processes which involve cracking reactions, such as visbreaking, thermal cracking, coking, and delayed coking.

In this case, it is usually known as "cracked naphtha."

In Tab. 14.2, typical characteristics of the cracked naphtha are reported.

Tab. 14.2: Main characteristics of naphtha.

	VB naphtha	Coker naphtha
Sulfur (ppm)	8,000	6,000
Nitrogen (ppm)	350	800
Br n°	25	80

where the bromine number (Br n°) indicates the concentration of olefins created during the process of thermal cracking.

Typical operating conditions of a naphtha hydrotreater are as follows:

- Reaction temperature: 250–350 °C
- Pressure: 20–40 bar
- H_2 consumption: 2.5–20 Nm^3/m^3 of feed

The lifetime of the catalyst is typically between 2 and 4 years.

14.2.2.1.2 HDT for kerosene feed

HDT of kerosene (boiling range = 180–260 °C) is used to produce jet fuel as the final product.

The process is similar to the naphtha HDT and Jet Fuel product specifications are generally achievable at low to moderate processing severity. The typical sulfur content in kerosene is between 0.1 and 0.4 wt% and the specification of sulfur concentration in the jet fuel is ≤3,000 ppm. Typical operating conditions of a kerosene HDT are the following:

- Reaction temperature: 250–300 °C
- Pressure: 20–60 bar
- H_2 consumption: 25–40 Nm^3/m^3 of feed

The catalyst can have a lifetime of 5 years.

14.2.2.1.3 Gasoil HDS

As previously mentioned, the main purpose of a gasoil HDS unit is to obtain a gasoil that meets diesel specifications for the fuels market. In particular, the required sulfur content is less than 10 ppm wt.

The scheme of a gasoil HDS (Fig. 14.4) is similar to what has been described above, but due to the higher amount of sulfur, high H_2S is produced. Hence, the recycle gas back to the reactor has to be washed by an amine absorber column before it enters the reactor. Desulfurization reactions are inhibited by the presence of H_2S – the higher the concentration of H_2S, the higher is the impact on the catalyst performance. Another difference when compared with the previous processes is that a gasoil HDS often has more than one reactor.

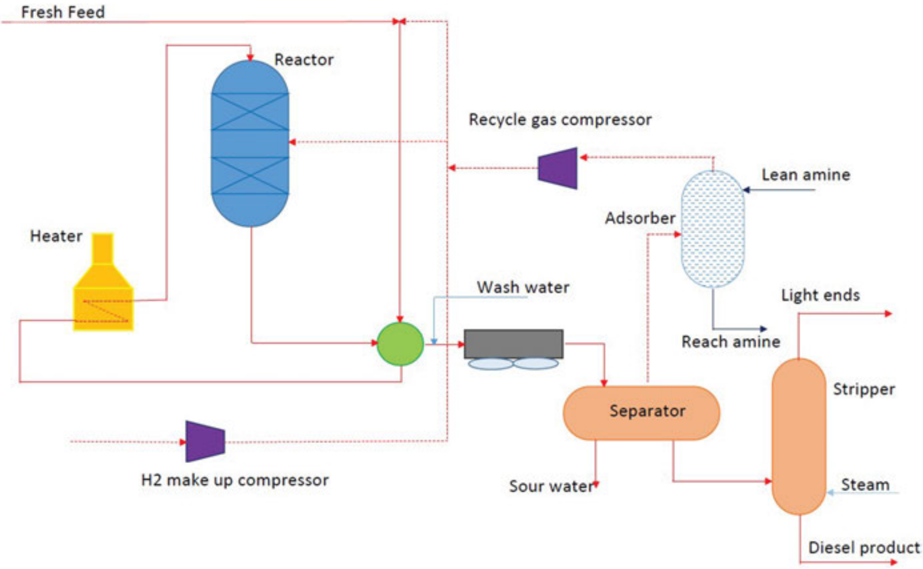

Fig. 14.4: Scheme of a typical desulfurization plant.

The feed to a HDS for diesel production has a boiling point range of 250–370 °C and the level of its contaminants depends on the crude oil source, which depends on the process from which the gasoil comes. Table 14.3 shows how the characteristics of different gasoils vary depending of the process that generates them.

Tab. 14.3: Characteristics of different types of gasoil according to the different production processes.

	SRGO	FCC LCO	VB AGO	RDS AGO	GO EST
Density (kg/L)	0.87	0.97	0.85	0.87	0.85
Sulfur (wt%)	0.8	1	2.3	0.12	0.37
Nitrogen (ppm)	350	870	1,000	230	2,870
Br n°	2	3	20	1	1
Aromatics (vol%)	35	85	40	30	34

Gasoils coming from a cracking process (LCO, VB GO) contain more aromatics and more nitrogen. For these streams, more severe operating conditions (higher reaction temperature or higher pressure) are required to remove nitrogen and more hydrogen is consumed for aromatic saturation (Table 14.4).

Tab. 14.4: Hydrogen consumption range in Nm^3/m^3 of inlet stream in different refinery processes.

	SRGO	FCC LCO	VB AGO	RDS AGO	GO EST
Nm^3/m^3	30–80	200–300	100–150	60–70	80–100

The typical operating conditions for a gasoil HDS are the following:
- Reaction temperature: 350–380 °C
- Pressure: 50–80 bar
- H_2 consumption: 60–200 Nm^3/m^3 of feed

The lifetime of the catalyst can be 1–2 years.

14.2.2.1.4 Vacuum gasoil HDT

There are two main processes related to the vacuum gasoil (VGO; boiling range = 370–520 °C) hydroprocessing:
- FCC feed pretreatment
- HDC pretreatment

The typical properties of VGO are the following:
- Sulfur = 1.0–2.5 wt%
- Nitrogen = 500–2,000 ppm
- Aromatics = 35–50% vol.

The operating conditions of a FCC pretreaters are less severe than those of hydrocracker pretreaters.

The main objective of a FCC pretreater is to reduce the metal content, the sulfur content (2,000 ppm), and the nitrogen content (500–1,000 ppm) in order to optimize the FCC performance.

The main target of the hydrocracker pre-treater is to remove nitrogen down to 50 ppm or less: Higher values have an impact on the activity and performance of the cracking catalyst.

The main operating conditions for the VGO pretreaters are as follows:

- Reaction temperature: 330–370 °C (FCC)/360–400 (HDC)
- Pressure: 40–100 bar (FCC)/90–150 bar (HDC)
- H_2 consumption: 85–170 Nm^3/m^3 of feed

14.2.2.1.5 Resid hydrodesulfurization (RDS)

Typically, a resid hydrodesulfurization (RDS) is a complex unit in which more than two reactors are needed for the residue to be desulfurized and obtain a product that meets the fuel oil market specifications (Table 14.5). Due to required high reaction temperature (380–400 °C) cracking reactions also take place.

High hydrogen consumption, 135–200 Nm^3/m^3, is due to the extremely high content of sulfur, nitrogen, and metals of the resid:

Tab. 14.5: Typical resid properties before and after RDS unit.

	FEED	**PROD**
Density (kg/L)	0.9986	0.9801
Sulfur (wt%)	4.1	1
Nitrogen (wt%)	0.315	0.258
Metals (ppm)	108	14.6

14.2.2.2 Hydrocracking of VGO and hydroconversion of resid

HDC and hydroconversion are processes that allow the conversion of heavy petroleum fractions into lighter fractions in the presence of hydrogen.

The reactions occur at a high pressure (100–190 barg) and the hydrogen consumption is in the range 250–550 Nm^3/m^3.

The severity of VGO HDC operation depends on the type of VGO feed quality (VGO straight run or VGO from a cracking process).

There are two types of reactions that occur in HDC: HDT reactions in order to eliminate the impurities from the feed (S, N, metals, and aromatics) and HDC reactions in order to crack C–C bond with hydrogen addition.

The flow scheme of a HDC/hydroconversion unit (Fig. 14.5) can be divided into four sections:

- High-pressure reaction section
- Gas-liquid separation section
- Hydrogen recycle section
- Fractionation section

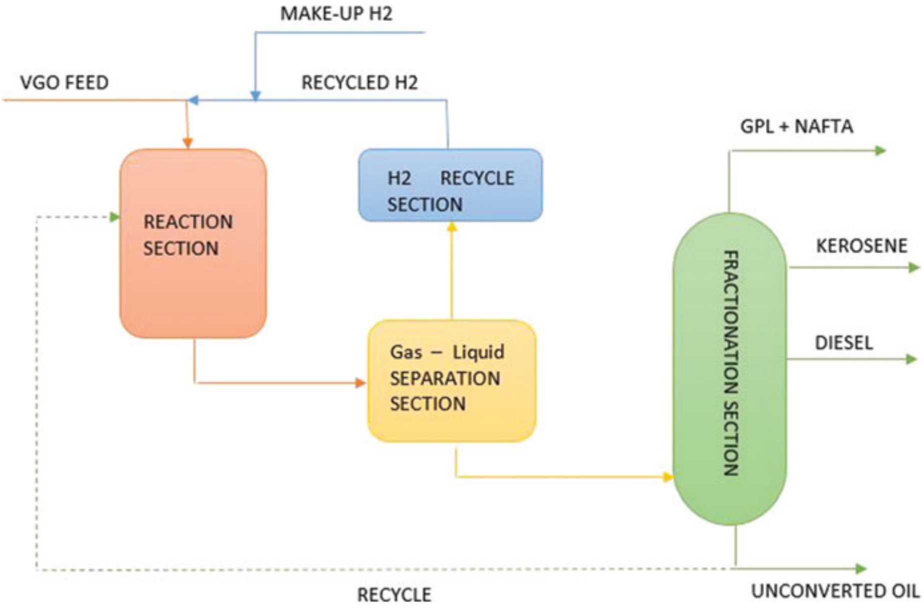

Fig. 14.5: Scheme of a hydrocracking/hydroconversion unit.

For a VGO HDC, the reaction section is typically based on two reactors:

- Hydrotreater or hydrotreater/HDC reactor
- HDC reactor

and depending on the process, the unconverted oil can be recycled to the reaction section in order to increase the conversion of the unit.

The typical conversions are:

- 75 wt% for a VGO hydrocracker without recycle (one through configuration)
- 95–98 wt% for a VGO hydrocracker with recycle
- 65 wt% for the LC-Finer resid hydroconversion
- 95 wt% for the EST (Eni slurry technology resid hydroconversion)

The scheme of resid hydroconversion units is different from that of VGO Hydroconversion units because the high viscosity and high concentration of the undesired elements in the feed require a different type of catalyst.

In particular, residue hydroconversion units do not employ fixed bed reactors:

- For the LC finer, the catalyst is suspended by the circulation of the feed and hydrogen from the bottom to the top of a reactor that is the called "ebullated bed."
- For the EST, the catalyst is dispersed into the feed and the hydrogen, circulating from the bottom to the top of a particular type of reactor named "slurry bubble column," where the mixture of feed, hydrogen, and catalyst is optimized in order to maximize conversion. The EST technology uses molybdenum disulfide as catalyst that is formed in the dispersed phase by a reaction between molybdenum and sulfur contained in the feed. After the fractionation section, the bottom – composed of "nonconverted material" plus catalyst – is recycled back to the reactor to increase the overall conversion and to recover the catalyst.

14.2.2.3 Lube cycle

- In the lube cycle, hydrogen is used to improve the final product quality. In this case, the units are usually called "hydrofinishing" and their scheme is similar to that of the HDT units previously described.
- Hydrofinishing is the final treatment for improving the quality of the base oil and/or waxes by bringing in contact such feedstocks with hydrogen in the presence of a catalyst, under predetermined processing conditions.

14.2.3 Biorefineries

In Eni's biorefineries, biofeedstock is transformed in HVO through two main reaction steps: hydrodeoxygenation followed by hydroisomerization through Ecofining^{TM} process technology (Fig. 14.6).

The high content of oxygen and olefins inside bio-feedstocks requires significant amounts of hydrogen. The feedstock can be vegetable oils, used cooking oil, animal fats, greases, or tallow oil.

These feeds mainly consist of triglycerides typically with 1–2% free fatty acid content and roughly 11% oxygen, and they have a high degree of unsaturation.

The first stage involves oxygen removal from the molecules by hydrodeoxygenation while also saturating the olefins present in the vegetable oil and grease. Since all olefinic bonds are saturated, the product consists of only paraffins that are downstream to the first stage.

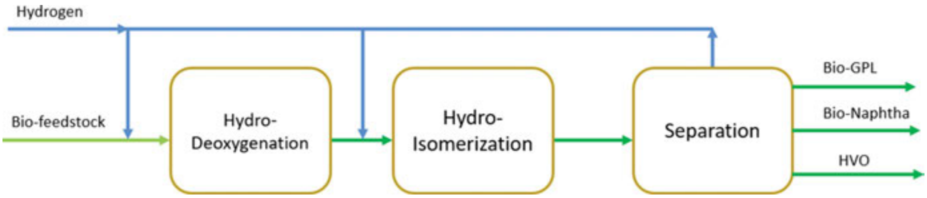

Fig. 14.6: Simplified scheme of a biorefinery with deoxygenation and isomerization reactors.

In the second stage, hydroisomerization is done to isomerize the *n*-paraffins, produced in the first stage, into iso-paraffins. Since n-paraffins have extremely poor cloud point properties, this step is important to improving the cold flow properties and making the product compatible with the fuel specification.

The reactions occurring in the deoxygenation section (Fig. 14.7), in the presence of a catalyst, are the following:

In the isomerization section (Fig. 14.8), in the presence of a specific hydroisomerization catalyst, n-paraffins are converted into iso-paraffins with a better cloud point.

The properties of renewable fuels are similar or even better that the properties of traditional diesel product. In the following table are shown the main typical properties of mineral diesel, compared to typical average properties of a generic HVO (Table 14.6).

14.3 Hydrogen in power generation

Maurizio Dessì, Marco Tripodi

As far as power generation is concerned, since early 90s, gas turbine manufacturers have developed gas turbine machineries in order to elaborate pure hydrogen as well as mixtures of natural gas and hydrogen.

The technological challenge is to elaborate a gas that requires specific technical and safety solutions with respect to safety, explosiveness, and flammability. After the first design of the hydrogen-based power plants, the lack of large volumes of hydrogen hindered the development of these technologies. Currently, blue hydrogen and the emerging hydrogen economy are stimulating new manufacturing interest in hydrogen gas turbines.

Today, hydrogen plays a marginal role in power generation, representing less than 0.2% of the global electricity production [1].

Currently, manufacturers have, in their catalogue, gas turbines that capable of covering the entire range of hydrogen-natural gas mixtures (0–100%), allowing a very flexible operation in terms of fuel flexibility. The gas turbines fueled by hydrogen have no carbon emissions and they provide cleaner reliable energy, which can significantly help in complying to the national energy grids regulations.

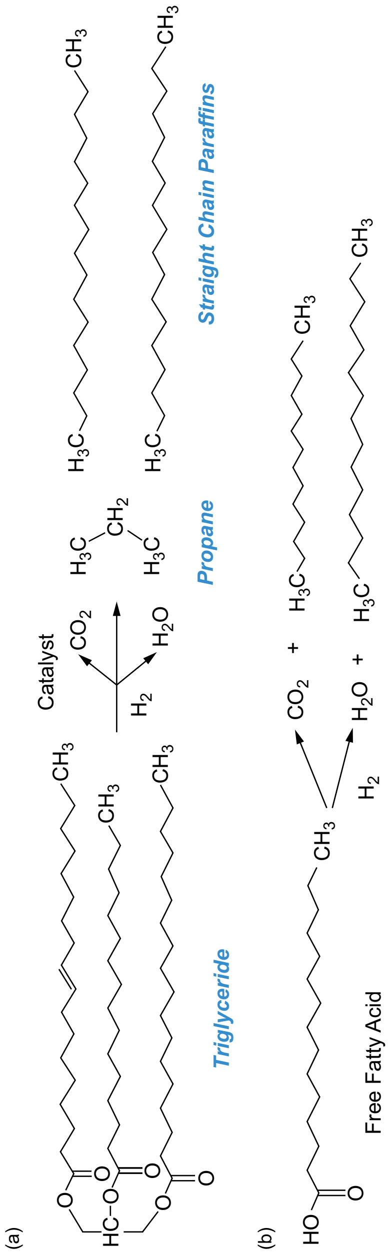

Fig. 14.7: Reactions occurring into deoxygenation reactor.

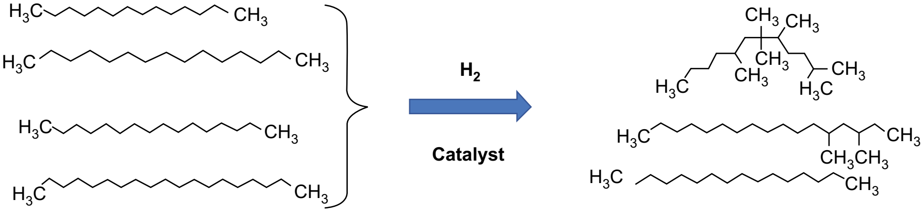

Fig. 14.8: Reactions occurring into isomerization reactor.

Tab. 14.6: Properties of HVO compared to ULSD (ultra low sulfur diesel).

	Mineral ULSD	**Renewable Diesel**
% O	0	0
Specific gravity	0.84	0.78
Sulfur content, ppm	<10	<1
Heating value MJ/kg	43	44
Cloud point C	−5	−10 to +20
Distillation	200–350	265–320
Cetane	40	70–90
Stability	Good	Good

Actually, the combustion of pure hydrogen is possible only through combustion systems based on diffusion flames. These burners require NO_x control with steam or nitrogen injection in the combustion chamber to contain the flame temperatures, but they entail an efficiency reduction in natural gas-based turbines.

The major gas turbine providers have declared that in 10 years' time, a new generation of hydrogen dry-low NO_x burners will be available enabling a new clean, reliable, and highly efficient full-hydrogen power generation. Nevertheless, a wider hydrogen deployment will be possible only if several hydrogen producers are in the market offering a competitive hydrogen price and also if production, transport, and storage of hydrogen become economically viable.

Hydrogen gas turbines could provide highly flexible thermal power generation, giving the regulatory services that are needed by both the electrical and the gas grids. Hydrogen production will allow a deeper market coupling between gas and electricity.

Eni, through its Enipower company, the largest Italian operator of cogeneration CHP and the second national grid service provider, has developed a significant expertise in the combustion of hydrogen-natural gas mixtures in existing gas turbines. Indeed, one gas turbine model, Ansaldo Energia AE94.K, has been operating with a mixture of syngas and natural gas (up to 23 vol% hydrogen) since 2004.

In addition, the two gas turbines model, Ansaldo Energia AE94.3A, has been equipped with a special dry-low NO_x burner since 2007 and is able to process a blend of hydrogen and natural gas (up to 15 vol% hydrogen). The aim is to operate the dry-low NO_x burners with hydrogen content up to 30% in volume by 2022.

Summarizing, Enipower's experience reports that after more than 15 years, the combustion of hydrogen mixtures has shown no significant issues on the overall operating efficiency, giving confidence to the future development of hydrogen power generation.

Furthermore, Eni has been working on the opportunity of converting overgeneration of renewables into hydrogen through water electrolysis during the less remunerative hours of the day in the power market. In this way, Eni could provide a new regulation service valuable to the power grid. All in all, the electrolyzer itself can provide additional balancing services to the power grid, properly modulating its power consumption.

Produced green hydrogen can be:

a) directly used in the existing gas turbines, displacing natural gas in the industrial must-run power generation processes;
b) injected into the gas grid, enabling the energy transition toward a low carbon economy.

According to the above, Eni has been studying the opportunity to install new fully hydrogen-powered gas turbines, already commercially mature, that could handle larger volumes of hydrogen. They can produce electrical energy without carbon dioxide emissions and also granting the ancillary services needed by the energy networks. This can contribute toward new balancing services that could become the key to the growth of renewable power generation.

Reference

[1] IEA, The Future of Hydrogen, IEA, 2019, Paris. https://www.iea.org/reports/the-futureofhydrogen

Marco Chiesa, Alessio Zolla

15 Hydrogen for mobility

15.1 Hydrogen production

Hydrogen is the most abundant element on our planet, but it is hard to find it in its pure form. It is for this reason that, in order to produce it, it must be taken out from other chemical composites. To do so, energy is required as a necessary input to the process and this energy can be of different nature, fossil or renewable. Therefore, hydrogen could be produced from fossil fuels such as natural gas and coal, nuclear, and biomass and from renewable energy sources such as solar, wind, and hydroelectric in order to obtain the hydrogen from the water molecule [1].

15.1.1 Reforming

Nowadays, most of the hydrogen produced in the world is of a fossil nature (96%), since it is produced through the reforming of methane in the steam methane reforming (SMR) process or in the autothermal reforming (ATR) which results in the high emission of CO_2 (9–10 kg CO_2/kg H_2) [2]. These processes account for almost 50% of the total hydrogen production today (which was 70 MT in 2019) [3].

15.1.1.1 SMR

In this process, high-temperature steam between 700 and 1,000 °C reacts with methane under 3–25 bar and in the presence of a catalyst produces hydrogen, carbon monoxide, and carbon dioxide. The process is endothermic since heat needs to be provided to the system for the reaction to happen. Subsequently, in the “water–gas shift reaction,” carbon monoxide and steam react in the presence of a catalyst to produce carbon dioxide and more hydrogen. As part of the final process called “pressure-swing adsorption,” carbon dioxide and other impure substances are removed from the gas stream, and hydrogen is the sole substance that is finally obtained [2].

Steam-methane reforming reaction:

$$CH_4 + H_2O\,(+\,\text{heat}) \rightarrow CO + 3\,H_2$$

Water–gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2\ \ (+\,\text{small amount of heat})$$

https://doi.org/10.1515/9783110596274-023

15.1.1.2 ATR

In the ATR process, oxygen and carbon dioxide or steam are used in a reaction with methane. The reaction takes place in a single chamber where the methane is partially oxidized. Unlike the SMR, the reaction is exothermic due to oxidation.

The reactions can be described in the following equations, using CO_2:

$$2CH_4 + O_2 + CO_2 \rightarrow 3H_2 + 3CO + H_2O$$

And using steam:

$$4CH_4 + O_2 + 2H_2O \rightarrow 10H_2 + 4CO$$

The outlet temperature of the syngas is between 950 and 1,100 °C and the outlet pressure can be up to 80 bar.

The main difference between the SMR and the ATR is that SMR uses air for only combustion as a heat source, while ATR uses purified oxygen. The advantage of ATR is that the ratio between H_2 and CO can be varied according to the process input H_2:CO, and this can be useful to produce other specialty processes [4].

15.1.1.3 Partial oxidation

In this process, methane and some other hydrocarbons present in natural gas react with a limited quantity of oxygen that is not enough to oxidize the hydrocarbons completely to carbon dioxide and water. In this way, the reaction products contain mainly hydrogen and carbon monoxide, apart from a small amount of carbon dioxide and some other compounds. The second part of the process, the water–gas shift reaction, is substantially the same as that occurs in the SMR process. Unlike the SMR process, partial oxidation is an exothermic process, since heat is an output [1, 4].

Partial oxidation of methane reaction:

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2\,H_2\ (+\,\text{heat})$$

Water–gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2\ \ (+\,\text{small amount of heat})$$

15.1.2 Electrolysis

Electrolysis is the most important process for producing the so-called green hydrogen. In this case, the electrolyzer receives water as input, which is then split into hydrogen and oxygen using electricity. Green hydrogen is the output of this process only if 100% of the energy used for the electrolysis process is of renewable nature (e.g., wind, solar, or hydropower) and when there is no emission of CO_2 in this process. The electrolysis process takes place in an electrochemical cell. Each cell is structured as a layered combination of two electrodes (cathode, at the hydrogen production side, and anode, at the oxygen evolution side), an electrolyte (liquid or solid, depending on the technology) that allows ion exchange, and in some cases, like in alkaline cells, a diaphragm or separation element that avoids product mixing. Individual cells are assembled in stacks by joining them in series with intermediate separation plates between the adjacent positive and negative electrodes, which separate the hydrogen and oxygen evolution channels. Starting from the stack, which is the "building block" of a larger plant, the resulting system is modular with the possibility of sharing balance-of-plant components by different groups of stacks. A DC current is applied to the electrodes flow across the electrolyte, causing hydrogen gas to evolve at the cathode and oxygen gas at the anode [4].

The **overall electrochemical reaction** is

$$H_2O \rightarrow H_2 + {}^1\!/_2O_2$$

Different *electrolysis cell technologies* have been developed that operate either at *low temperature* (lower than 100 °C), using liquid water and with predominant electrical demand, or at *high temperature* (600–800 °C), using water steam and with increased heat demand but at higher electrical efficiency. Electrolysis technologies are, therefore, classified commonly into two groups:

- low-temperature electrolysis (below 100 °C), including alkaline electrolyte cells, polymeric electrolyte membrane cells (PEMEC), and anion exchange membrane electrolyte cells;
- High-temperature electrolysis (600–900 °C), including solid oxide electrolyte cells and proton conducting ceramic cells.

Today, only two technologies are in commercial use: "alkaline" electrolyzers and "proton exchange membrane" electrolyzers (PEMEL). Solid oxide electrolyzers are in the pre-commercial phase, while anion exchange membrane electrolyzers are just emerging, with currently few suppliers for small scale solutions [1].

15.1.2.1 Alkaline electrolyzers

Hydrogen can be produced at significant rates by means of *alkaline electrolyte cell* units, which represent the most developed technology for stationary hydrogen generation. The liquid electrolyte, usually a caustic aqueous solution of KOH or NaOH, is circulated between metallic (Ni-based) electrodes carrying OH- ions. A diaphragm, permeable to the electrolyte, avoids the internal mixing of hydrogen and oxygen. The outlet streams, oxygen and electrolyte from the anode and hydrogen and electrolyte from the cathode, are fed to gas-liquid separators, which act as storage drums and pressure equalizers and from which the residual electrolyte is recirculated to the cell after cooling. This technology is mostly suited for large-scale production of hydrogen and performs at its best when the source of energy is continuous and not intermittent.

15.1.2.2 PEM electrolyzers

PEM electrolyzers (PEMEC) are also commercially available, although they at an early industrialization stage. They use pure water as an electrolyte. A non-caustic solid electrolyte consisting of a polymeric membrane (usually Nafion®) separates the electrodes and allows only proton (H +) transfer, offering an almost nil presence of oxygen impurities in the outlet hydrogen flow. Water is supplied at the anode and is transported partly to the cathode by diffusion and by *electro-osmotic drag*, which is sustained by the transport of protons. The main drawback of this technology is the need for precious metals as catalysts (e.g. Platinum and Iridium). There is ongoing research to reduce their amounts. PEMEL are able to produce highly compressed hydrogen for decentralized production and storage at refueling stations (30–60 bar compared to 1–30 bar for alkaline electrolyzers) and offer a flexible operation, such as the capability to provide frequency reserve and other grid services.

Electrolyzers can feed hydrogen-refueling stations for fuel cell vehicles, buses, or trucks as well as for hydrogen trains and ships. The typical range of system sizes goes from a production of 50–100 kg_{H2}/day up to 500–2,000 kg_{H2}/day for larger stations. On-site electrolysis may have advantages with respect to delivery from larger centralized electrolyzers or other hydrogen production plants, incurring distribution costs [3].

15.2 Hydrogen refilling station configuration

15.2.1 HRS location

There is no clear guidebook for how to roll out alternative fuels into a dominant incumbent market where gasoline and diesel availability is widespread, with tens of thousands of fueling stations. A conceptual approach has been proposed for infrastructure planning that could be applied to all early hydrogen fueling networks. The first component of this concept is clustering. Here, stations are clustered together within a limited geographic area, predicted to include potential early adopters. In this way, the early market benefits from reliable and convenient access to stations, which ideally supports a majority of trips. This serves early adopters and is a cost-efficient way of using limited funding for hydrogen infrastructure where it is most likely to be of higher use. Of course, driving outside the cluster is hindered by lack of access to fuel. Hence, the second key component is to connect the clusters by placing stations strategically to create a corridor system or a “hydrogen highway” through which fuel cell vehicle drivers can travel more widely than the initial cluster. The benefit of this design is a broad coverage and access to many more locations, enabling drivers to move about freely in the network. Even though lower daily usage is likely, such corridor stations are widely viewed as a prerequisite for most prospective owners, even for the relatively infrequent trips that drivers take outside their home area.

Both basic tactics have complementary benefits and are thus being widely developed in combination. The early market cluster is typically located in a city or community with a high percentage of potential early technology adopters. Such areas typically have been identified by consortia of automakers and public-private partnerships that find common cause to share resources, as in the case of optimally placing publicly funded hydrogen stations.

Corridors help to extend the effective fuel cell vehicle driving range beyond areas served by the early clusters. Intercity stations are generally placed at connector communities. These stations link nearby clusters and help to plant seeds for new clusters. Destination stations offer a third important aspect in the design and development of a fueling network. These stations are located at popular sites, for example longer distance weekend destinations that may not be considered lighthouse communities in their own right. As with connector stations, destination stations may eventually seed new markets, as nearby residents can purchase and fuel a fuel cell vehicle.

Choosing the specific location of stations within clusters and on connecting roadways offers its own challenges. One method is to locate cluster stations nearer to the homes or workplaces of the anticipated early adopters. Another theory recommends locating these stations along commonly travelled routes or commutes of early adopters. This latter option could potentially lead to stations that are outside the cluster itself and is more dependent upon accurate daily traffic data. Providing enough infrastructure near homes is an ideal solution, but may only serve a small group initially, whereas locating stations along commuter routes is an important complementary solution for a large group of potential customers. In this way, both strategies can coexist and be part of a phased plan to convince the greatest number of people to purchase fuel cell vehicles with the least number of stations. Early stations can be selected for both their proximity to customer homes and proximity to a commuter route. An important attribute in early station placement is coverage which is generally determined by convenience or proximity to a station and network reliability (e.g., maintaining fuel availability if one station is out of service). Research indicates that current fossil fuel station networks are overbuilt in terms of convenience and reliability and that hydrogen networks can achieve comparable coverage with only 10%–30% of as many locations as existing gasoline stations. Population density, region size, and existing fossil fuel infrastructure all affect the minimum level of hydrogen infrastructure required.

The remaining questions of standardization are related to creating a consistent and user-friendly customer experience, such as the ability to accept universal payment. Such standards can encourage faster fuel cell vehicle adoption by minimizing changes to consumer behavior, reduce costs using uniform testing, design, and approval procedures. For context, a counterexample of note is the frustration that many electric vehicle users experience when charge types and payment methods restrict the use of some infrastructure to specific customers.

15.2.2 HRS configuration

15.2.2.1 HRS – CGH2 (compressed gaseous hydrogen) station

Figure 15.1 illustrates the possible configurations of a gaseous hydrogen refueling station. Tube trailers or an on-site production units typically supply fuel stations today, but future stations may also be supplied by pipelines. On-site production units, which may include an SMR or an electrolyzer, typically supply hydrogen at a pressure of 20 bar, although some electrolyzers are capable of higher-pressure production (30 bar). The tube trailer, with a capacity ranging from 250 to 1,000 kg, supplies hydrogen to the station at pressures ranging from 200 to 500 bar, which are drawn down to 20–50 bar before replacing it. Low pressure hydrogen is stored in bottles (“cylinder racks”), tanks, or tube trailers. The gaseous refueling stations include a high-pressure compressor, which draws hydrogen from the supply source and compresses it before storing in a high-pressure buffer storage system. The hydrogen from the high-pressure system is later directed by a dispenser into the vehicle’s onboard tank via a refrigeration unit, which pre-cools the hydrogen to about −40 °C to allow fast fueling without overheating the vehicle’s tank (based on SAE J2601).

15.2.2.2 HRS – LH_2 (liquid hydrogen) station

Figure 15.2 shows possible configurations of a liquid hydrogen (LH_2) station with an onsite cryogenic tank, which is replenished through LH_2 delivery by cryogenic tankers with about 4 metric tons of payload. In one possible station configuration, cold gaseous hydrogen that has vaporized (due to ambient heat) and accumulated in the head space of the cryogenic tank (i.e., “boil off”) and supplemented by liquid is conditioned in a heat exchanger before it is supplied to a compressor, which compresses it into a high-pressure buffer storage system. A dispenser then directs hydrogen into the vehicle’s onboard tank via a chiller, which pre-cools the hydrogen to −40 °C. Alternatively, the LH_2 from the cryogenic storage tank is pressurized by a cryogenic pump and then gasified via an evaporator. The high-pressure gaseous hydrogen from the evaporator is stored in the high-pressure buffer storage system, which is later precooled to −40 °C by the

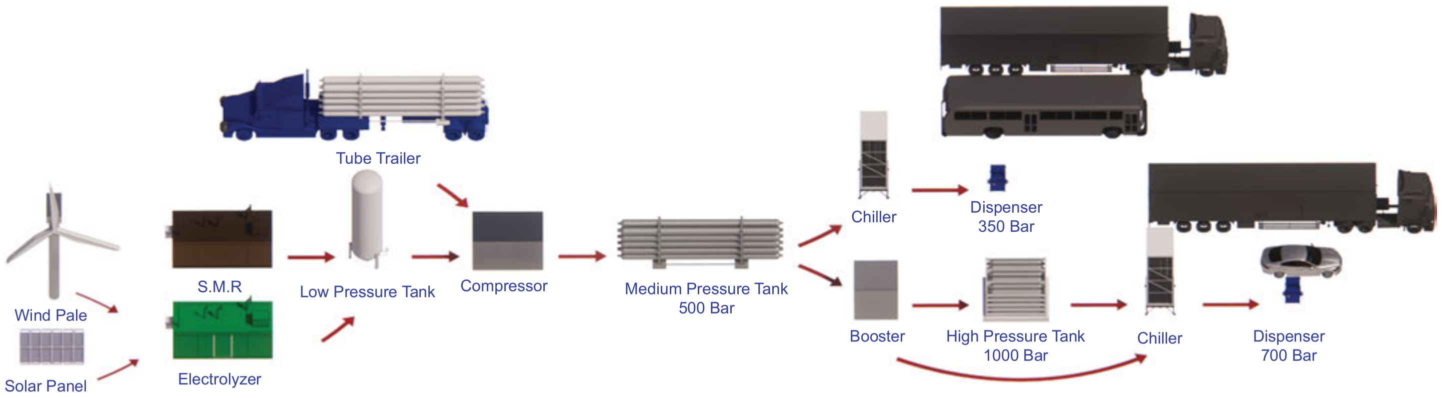

Fig. 15.1: Compressed gaseous hydrogen station overall components.

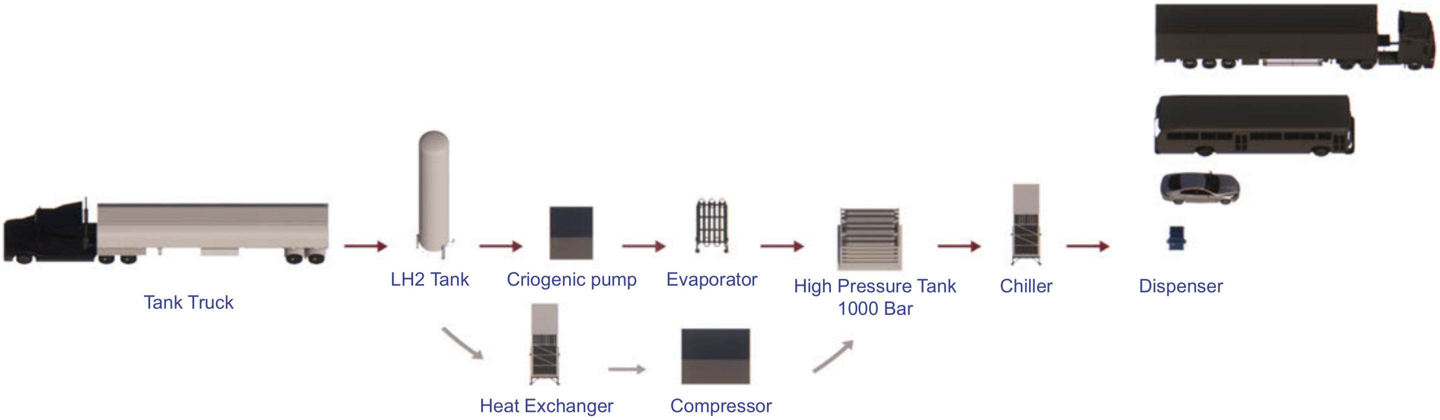

Fig. 15.2: Liquid hydrogen station overall components.

cooling unit before being dispensed into the vehicle tanks. The pre-cooling unit in this configuration utilizes the cryogenic hydrogen to cool the hydrogen.

15.2.3 HRS components

15.2.3.1 Compression

The compressor unit is the key component of a hydrogen fueling station because the fueling is carried out using compressed gaseous H_2 at pressures from 35 to 70 MPa. Apart from the initial state – gaseous or liquid – the technology used for fueling also depends on a range of other factors, as for example, the throughput and the type of vehicle to be fueled. A number of different compressors can be used to achieve the necessary compression. Customary types are piston, compressed air, diaphragm, or ionic compressors, which are selected according to the design of the refueling station (capacity utilization, energy consumption, cost-effectiveness, etc.). Hydrogen compression is a way of overcoming the pressure difference between storage (from 10 to 200 bar) and refueling (up to 1,000 bar). The refueling process should not exceed the target time of three to five minutes for light-duty vehicles (passenger cars). The gaseous refueling stations include a high-pressure compressor, which draws hydrogen from the supply source and compresses it to about 1,000 bar before storing in a high-pressure buffer storage system. The hydrogen from the high-pressure system is later directed by a dispenser into the vehicle's onboard tank via a refrigeration unit, which precools the hydrogen to about −40 °C (based on SAE J2601 H70-T40 protocol) to allow fast fueling without overheating the vehicle's tank. Two compressors usually cover the pressure gap between delivery/production and dispensing needs (350 and 700 bar): A main compressor that increases the pressure from a feeding stock that can be between 10 and 200 bar to a medium pressure that is usually set between 350 and 500 bar. Fuel cells are very sensitive to contamination of the hydrogen supplied. Impurities may result in an irreversible damage to the membrane and the fuel cell as a whole. This is the reason that the SAE J2601 standard sets a purity level for hydrogen of up to 99.99%. The compression system plays a large role in this regard, as it can be the primary on site source of hydrogen's contamination if an improper technical solution is chosen.

15.2.3.2 Storage

A major advantage of hydrogen is that, unlike electricity, it can be stored in large amounts for extended periods of time. The storage tanks must hold enough hydrogen to meet customer demand. When there is hydrogen production on site, a low-pressure storage system is usually required to avoid the continuous functioning of the compressor. Low-pressure tanks are those that contain hydrogen between 20 and 200 bar. If the hydrogen is delivered by compressed hydrogen gas trailer(s), the trailer(s) itself can be considered and used as a temporary on-site low-pressure storage tank(s). The quantities to be stored are calculated based on the number of anticipated refueling operations per day and can be adapted with a modular expansion of the refueling station. The hydrogen from the low-pressure storage tank is transferred via a high-pressure compressor to the medium- or high-pressure storage tank. Medium- and high-pressure storage tanks, with pressure stages of 200 to 500 bar (medium) and 800 to 1,000 bar (high), respectively are used to refuel the customer's vehicle. The first range is suitable for buses and trucks with a 350 bar onboard tank; the second range is suitable for passengers' cars and other vehicles with an onboard tank designed to be refilled up to 700 bar. The two storage systems can also be cascaded in order to provide their contribution in different stages of the refilling process (medium-pressure storage for the startup and high-pressure storage to complete the process). There is also the option of using only a medium-pressure storage tank to refill the customer's vehicle tank until the pressure balance is reached. To fill up the tank completely, the hydrogen can be compressed from the medium pressure storage tank up to the necessary pressure, by a booster compressor.

In the real hydrogen refueling stations setup, the different configurations described above are not free-standing but connected, in order to create the best response to the station's needs in terms of sales expectations and modularity for future developments. Particular attention should be paid to the design, installation, operation, and maintenance of hydrogen handling equipment in order to reduce the likelihood and size of any leak.

When high-pressure storage is used, it should be designed and built to an appropriate design code or standard and located in a secure open-air compound. Measures appropriate to the location should be taken to prevent unauthorized access, vandalism, and impact from vehicles. Storage equipment costs depend on many different equipment characteristics (material, pressure, quantity, dimensions, etc.) and market readiness.

15.2.3.3 Cooling and refueling

To provide a customer experience similar to that of gasoline ICEVs, SAE J2601 was developed to enable stations to fill hydrogen fuel cell electric vehicles (HFCEVs) with 5–7 kg of hydrogen within 3–5 min. Fast refueling of hydrogen is constrained by the thermodynamic properties of hydrogen under compression and the material properties of the type IV (all composite) tanks used to store hydrogen onboard HFCEVs. The operating temperature of type IV storage tanks must stay between −40 and 85 °C to prevent degradation of the tank liner. At a fueling station, hydrogen in bulk storage is approximately at ambient temperature. However, fast dispensing increases the temperature of both the hydrogen and the tank liner, such that the hydrogen must be cooled to −40 °C before it is dispensed to keep the FCEV (fuel cell electric vehicle) tank from exceeding its operating temperature. In order to ensure hydrogen fueling safety, the SAE fuel cell standards committee interface working group has worked with experts from gas companies, fuel suppliers, and the automotive industry to develop the SAE J2601 standard, which includes two fueling protocols for light-duty FCEVs:

- lookup table method
- MC formula method

Hydrogen fueling protocols have been developed based on computational modeling and experimental data. Fueling protocols are implemented at stations to keep the fueling process within specific temperatures and pressures to ensure that vehicles can be safely filled within a given time frame.

The SAE J2601 protocol defines specific assumptions of fueling conditions that must be met for the protocol to be used. The HFCEV's storage capacity should be between 2 and 10 kg if its NWP (Nominal Working Pressure) is 70 MPa. The ambient temperature must be between −40 and 50 °C. The hydrogen fuel delivery temperature cannot be less than −40 °C or greater than −17.5 °C at any time during the fueling process. The vehicle pressure at the beginning of a fill must be between 0.5 MPa and the nominal working pressure of the vehicle (usually 70 MPa). Finally, the hydrogen flow rate cannot be allowed to exceed 60 g/s at any time during the fueling process.

Irrespective of the type of fueling, communication or non-communication, the station monitors the communications interface with the vehicle. For communication fueling, the vehicle temperature and pressure are monitored throughout the fueling to control the fueling process such that the vehicle tank does not exceed preset upper limits. If the temperature of the tank reaches the maximum compressed hydrogen storage system (CHSS) operating temperature or if the pressure exceeds 1.25 times the tank's nominal working pressure, fueling is aborted.

The temperature of the hydrogen being dispensed is an important parameter to ensure safety of the fueling process; so it is monitored throughout the fill. The rolling average and total mass average fuel delivery temperature is calculated and used to terminate the fueling, to prevent vehicle tank over-heating in the event of equipment failure. The station should achieve the pre-cooling temperature, consistent with the station type, within the first 30 s of fueling. For example, for a T40 station with an H70 hose, if the pre-cooling temperature falls within the expected range (window) at the end of 30 s, the fueling continues as expected, by maintaining the calculated APRR (average pressure ramp rate) at the dispenser.

SAE J2799 standardizes unidirectional wireless communications between the FCEV and the hydrogen station. Communication signals such as temperature, pressure, CHSS volume, start of fueling, abort, and pressure rating are specified. The advantage of using this optional communications standard, when coupled with J2601 fueling, is that the state of charge can be further improved to 95–100%, allowing for more driving range than without communications. The SAE J2799 IrDa transmitter is located on the receptacle of the fuel cell vehicle and the receiver is located on the hydrogen station dispenser nozzle.

A hydrogen dispenser needs to control the fueling process so that limits are not exceeded and performance targets for fill time and density are achieved over a wide variety of ambient and vehicle conditions.

15.2.4 Case study

The current hydrogen vehicle deployment and the number of HRS in operations do not yet provide a valuable amount of data appropriate for taking clear strategic decisions. Nevertheless, waiting for suitable data entails not to act as a leader in this new challenging market. Therefore, any decision should take into account the huge dynamism inherent to the HRS market at this stage: The right approach would then be the modularity/scalability of the station. This is connected to the dimension of the greenfield (the bigger, the better) and a predictive design development that takes into account, since the beginning, the next steps, by a meticulous allotment of technical areas (e.g., H_2 production, storage area, type and positioning of compressor(s), delivery area, dispensers location, and traffic flow).

First decision to take is about liquid or compressed hydrogen. Nowadays, LH_2 is interesting in terms of H_2 amount that can be transported and stored. The downside is the liquefaction process that requires huge amount of energy and the low efficiency of the actual process that requires to refill onboard tanks with compressed H_2; the higher cost of technology and the cost of energy required for the liquefaction process and transportation is paid back only in the case of high sales volumes. When FCEV is widely available and/or the onboard tanks technology allows the use of LH_2, then LH_2 will be a valuable option. The present status of FCEV deployment and the cost of technology make the CGH2 (compressed gaseous hydrogen) option preferable.

Nowadays, the H_2 on-site production is an option that can be considered (suitable only for CGH2), but it introduces further variables to the system.

Electrolyzers, specifically the PEM ones, have the great advantage of a short start-and-stop dynamics with ramp-up and ramp-down time in seconds. This is not the case with SMRs, which have the advantage of a higher efficiency once they attain operating speed. Electrolyzers are less noisy than SMRs and with no CO_2 production, they are more suitable to be located in urban context, while lower electrical power consumption makes SMRs preferable where the energy costs are a huge constraint. H_2 outcome pressure is higher with electrolyzers (usually 20–30 bar compared to less than 10 bar for SMR) and this is an advantage while calculating the low-pressure storage needs. To avoid the compressor running at all times, a low-pressure storage must be dimensioned to store the H_2 produced during the compressor downtime; considering the very low hydrogen density at ambient temperature, this will have an impact in terms of tanks costs and landscape (number of vertical tanks on site). These very-low-pressure tanks may also be used to partially store the hydrogen delivered by lorry, but this is usually not a recommended choice since it is a "downgrading" in terms of pressure for the delivered hydrogen. Further energy must be spent to raise up the pressure again to complete the process flow. This is an impacting energy consuming option.

Compressor is a critical equipment in the HRS process in terms of cost per unit, H_2 quality (e.g., hydrogen purity) and business continuity (risk of embrittlement, downtimes, faults, maintenance needs, etc.).

The challenge for designers is to find the right balance between many factors: pressure leap, CGH2 storage steps and quantities, type of H_2 supply (trailers, pipeline, on-side production or a mix of them), business continuity plan (e.g., predictive maintenance, backup equipment, operations algorithm), and costs control.

Moreover, the booster compressor is part of the compression stage and it covers the pressure gap between medium and high pressure. It also contributes to close the refilling process when the flow from the storage system is not sufficient. With respect to an awareness of the criticality of this equipment in terms of decisions to take in the design phase, there is no further general guidance to provide about compressors.

The storage system is the element with higher flexibility and modularity in the whole process. The storage requirements for low, medium, and high pressures will depend on the compressor's characteristics and target refueling rate. Low-pressure tanks will be very impacting in terms of dimensions. Daily deliveries by CGH2 lorries must be considered as further low-pressure storage tanks; there are refueling stations designed considering a number of lorries always on site providing a flexible feeding stock without the need for further low-pressure fixed tanks. The correct dimensioning of medium-pressure tanks is critical because it will provide the first step of the refueling process to any vehicle connected to the dispensers' hoses. It then prevents a huge contribution from the booster. High-pressure storage is a valuable option when light vehicles with on-board tanks at 700 bar are expected, for the same reason earlier mentioned for medium-pressure tanks. Medium- and high-pressure storage tanks should be considered as a unique system when the storage dimension is to be balanced: the recommended layout requires a cascading connection between the different pressure tanks to facilitate pressure-steps refueling process and relieving the booster compressor duty (and compensating the booster pressure ramp-up when it is triggered).

Dispensers are the most technologically advanced equipment because, as discussed in the relevant section in this document, they have to control and manage any single step of the refueling procedure in order to grant a safe refueling time comparable to the one required on conventional fuel stations. Considering the present trucks per day rate for this case study (40) and the average on-board tank content at 350 bar – no more than 40 kgH_2 – we have to target 1,600 kgH_2/day.

15.2.4.1 Scenario 1 – Fig. 15.3

- 500,000 kgH_2 per year
- Trucks with onboard tank suitable only for 350 bar filling pressure
- One dispenser dedicated to light-duty vehicles (@700 bar)
- Hydrogen delivered only by tube trailer at 200 bar
- Peak flow set at 8% of total flow

Minimum equipment requirements for Scenario 1 – Unit Qty.
- Dispensers single nozzle @700 bar – n. 1
- Dispensers single nozzle @350 bar – n. 2
- Tube trailers per day @200 bar – n. 5
- Heat exchanger – n. 1
- Booster – n. 1
- Compressors 150 kgH_2/h – n. 1
- Mid-pressure (500 bar) storage kgH_2 – 138
- High pressure (1,000 bar) storage kgH_2 – 138

15.2.4.2 Scenario 2 – Fig. 15.4

- 1,000,000 kgH_2 per year
- Trucks with onboard tank suitable for 700 bar filling pressure (no 350 bar dispensing)
- Hydrogen delivered only by tube trailer at 500 bar
- Peak flow set at 8% of total flow

Minimum equipment requirements for Scenario 2 – Unit Qty.
- Dispensers single nozzle @700 bar – n. 2
- Tube trailers per day @500 bar – n. 5
- Compressors 150 kgH_2/h – n. 2
- High pressure (1,000 bar) storage kgH_2 – 46

15.2.4.3 Scenario 3 – Fig 15.5

- 2,000,000 kgH_2 per year
- Trucks with onboard tank suitable for 700 bar filling pressure (no 350 bar dispensing)
- Hydrogen delivered at 70% by tube trailer at 500 bar
- Remaining 30% produced on site by Steam Methane Reforming
- Peak flow set at 8% of total flow

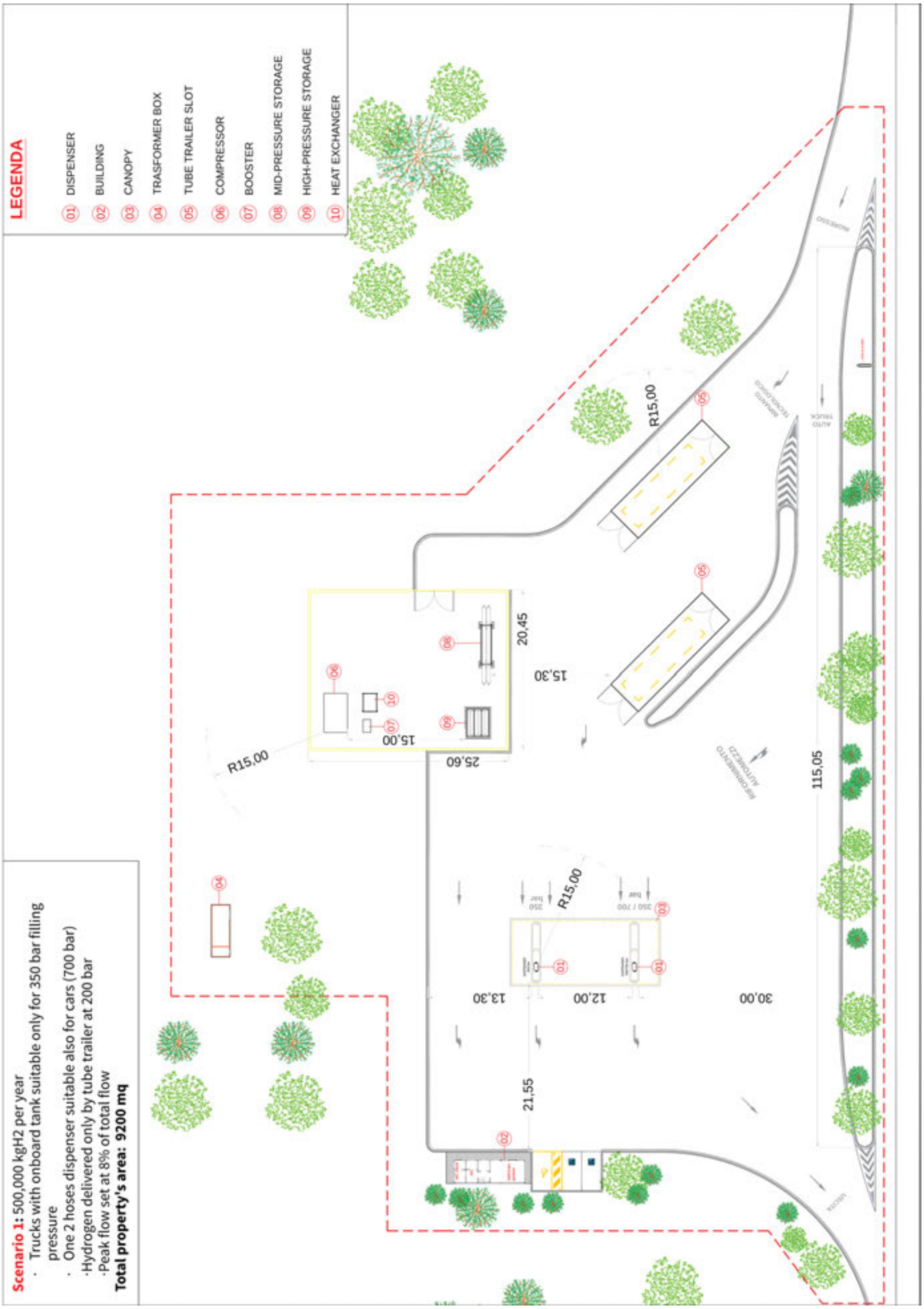

Fig. 15.3: Scenario 1–500.000 kgH$_2$ per year.

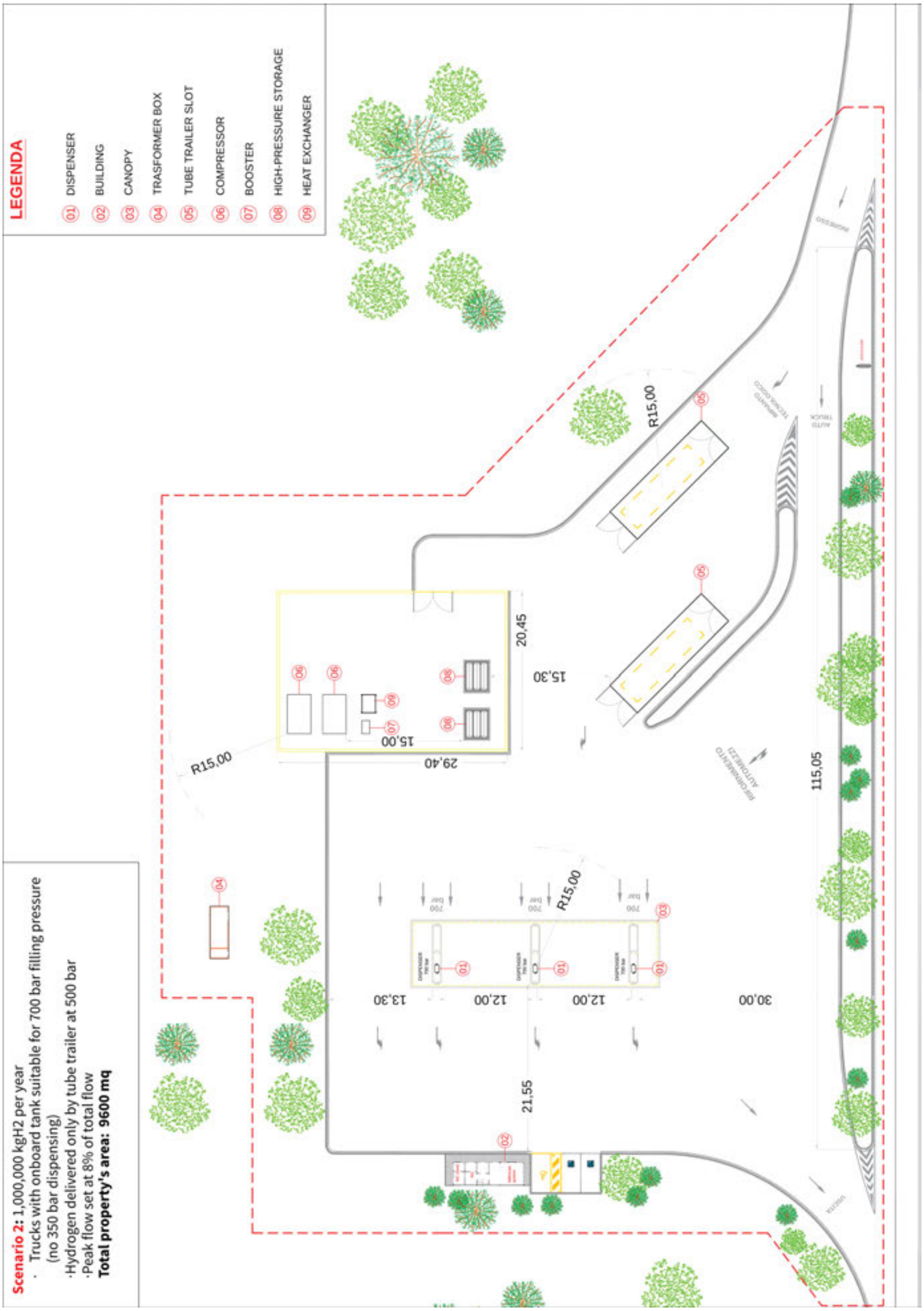

Fig. 15.4: Scenario 2 – 1,000,000 kgH_2 per year.

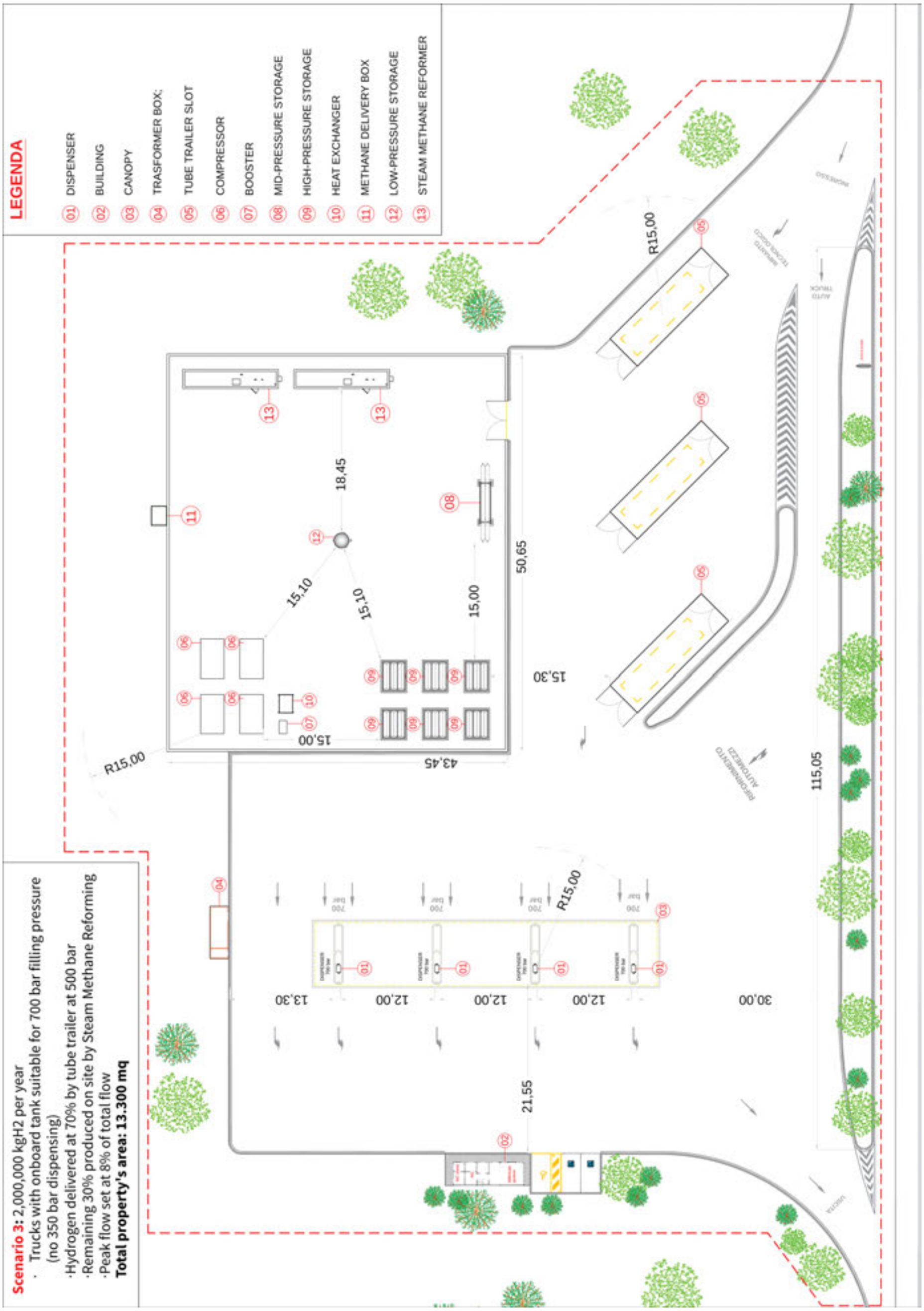

Fig. 15.5: Scenario 3 – 2,000,000 kgH$_2$ per year.

Minimum equipment requirements for scenario 3 – Unit Qty.

- Dispensers single nozzle @700 bar – n. 4
- Tube trailers per day @500 bar – n. 6
- Compressors 150 kgH_2/h n. – 4
- Mid-pressure (500 bar) storage kgH_2 – 635
- High pressure (1,000 bar) storage kgH_2 – 142
- SMeR – 1,000 kgH_2/day – n. 2
- Low-pressure (30 bar) storage kgH_2 – 835
- SMR output compressor n. 1

15.3 Hydrogen application as a fuel

15.3.1 Passenger cars – Tab. 15.1

Along with battery electric vehicles, hydrogen-powered fuel cell passenger cars are the only zero-emission alternative drive option for motorized private transport. The first fuel cell passenger cars were tested back in the 1960s as demonstration projects. In most cases, the fuel cell test vehicles were converted cars that had originally been fitted with an internal combustion engine. At the time, however, the early test models were still not competitive, either technically or economically.

Up until about 10 years ago, petrol engine prototypes were still being tested with hydrogen as an alternative energy and low-emission fuel. These were vehicles with modified bivalent engines, which could run on both petrol and hydrogen. Owing to the fuel, hydrogen-powered internal combustion engines not only achieved somewhat higher efficiencies than in petrol operation, they also emitted much lower levels of pollutants. Although hydrogen is a clean fuel with excellent physicochemical properties, it has been unable to gain acceptance as a fuel for motorized road transport. For passenger cars, the focus is now almost entirely on hydrogen-powered fuel cells as a source of drive energy, using the new 700 bar standard.

15.3.2 Rail/hydrail (hydrogen trains) – Tab. 15.2

Rail transport is one of the most energy-efficient means of mechanical land transport. It generally needs less energy than traditional ways of transport via road and it pollutes even less CO_2 when (clean) electricity is used to power them.

Today, there are still many non-electrified routes operated by diesel trains that cannot be electrified via overhead since it is very expensive or that do not allow it due to technical reasons. In UE, 46% of railway lines in use are not electrified. To decarbonize these routes, the main alternatives are battery-powered trains and FCEVs.

Tab. 15.1: Passenger cars' key points.

	Passenger cars at a glance
Market maturity	Technology proven worldwide (Europe, North America, Asia) throughprototypes/ small fleets, first production vehicles in moderate numbers. Incentive schemes for passengers car purchase still necessary
Requirements	Comparable to internal combustion engine vehicles in terms of equipment, performance, range; sufficiently dense hydrogen refueling infrastructure
Advantages	Pollutant-free driving; range and performance close to petrol cars.
Disadvantages	Still much more expensive than internal combustion engine cars; poorrefueling station infrastructure.
Alternatives	Internal combustion engine cars; battery electric cars.

Battery-powered trains are a feasible solution for railway lines whose length is limited but they also pose a constraint in terms of weight and autonomy due to physical limits of existing batteries. On the contrary, FCEV-powered trains represent the best solution for the decarbonization of diesel routes from different point of views: They do not need massive infrastructure investments such as overhead application. They also guarantee comparable autonomy than diesel convoys and the capability to go over steep slopes. More in detail, FCEV trains are the best alternative to diesel on non-electrified routes when the length of the line is above 80–100 km or where steep slopes (>20‰) are present along the route. FCEV-powered trains have since been tested globally and so they have already moved beyond the proof-of-concept phase. The most advanced segment is the regional passenger train but the technology is also suitable for shunts and mainline locomotive applications.

Tab. 15.2: Rail/hydrail key points.

	Rail/hydrail at a glance
Market maturity	To date, demonstration projects for light rail vehicles (based on bus technology). Various shunting locomotives as pilot projects/one-off vehicles.
Requirements	Sufficient and reliable hydrogen supply.
Advantages	Lower infrastructure costs (no overhead lines/conductor rails); (locally) emission-free operation, dependent on hydrogen production.
Disadvantages	Expensive drive system; additional tank space.
Alternatives	Diesel (-electric/-hydraulic) with diesel or PtX fuels; electric traction; battery-powered trains

15.3.3 Industrial trucks (forklifts/tow trucks) – Tab. 15.3

Industrial trucks are another area of use for fuel cell technology. The most common types are forklifts and tow trucks, which are used in intralogistics. Worldwide, more than 10 million industrial trucks are used every day and the fleet is growing. Fuel-cell industrial trucks are especially suitable for indoor operation because they produce no local pollutant emissions and only low noise emissions. Fuel cell vehicles have advantages over battery-operated industrial trucks in terms of refueling. Instead of having to replace the battery, the trucks can be refueled within two to three minutes.

They take up less space and are cheaper to maintain and repair. Fuel-cell industrial trucks allow for uninterrupted use and are, therefore, particularly suitable for multi-shift fleet operation in material handling. In the case of larger industrial truck fleets in multi-shift operation, (moderate) cost reductions can be achieved in comparison to battery technology and productivity in material handling can also be increased.

The United States has the largest hydrogen-powered industrial truck fleet at present. In Europe, there are around 140 fuel cell industrial trucks in operation at present. In order to drive commercialization forward, a further 200 fuel-cell-operated material handling vehicles are set to be brought into circulation in small fleets at 10 to 20 selected locations as part of the HyLIFT Europe project (2016).

Tab. 15.3: Industrial trucks' key points.

	Industrial trucks at a glance
Market maturity	Over 11,000 fuel cell material handling vehicles in North America; demonstration fleets in Europe; prototypes in Japan.
Requirements	Sufficient and reliable hydrogen supply.
Advantages	Lower infrastructure costs (no overhead lines/conductor rails); (locally) emission-free operation, dependent on hydrogen production.
Disadvantages	Expensive drive system; additional tank space.
Alternatives	Diesel (-electric/-hydraulic) with diesel or PtX fuels; electric traction.

15.3.4 Buses – Tab. 15.4

In terms of road transport, buses in the public transport network are the most thoroughly tested area of application for hydrogen and fuel cells. Since the early 1990s, several hundred buses have been and are being operated with hydrogen worldwide – predominantly in North America, Europe, and also increasingly in Asia. Although hydrogen was initially used in buses with internal combustion engines, bus developers are now concentrating almost entirely on fuel cell electric buses (FCEB).

The use of small FCEB fleets is being promoted in urban areas as a way of contributing to technological development and to the clean air policy.

Fuel-cell buses have now reached a high level of technical maturity, although they are not yet in series production. Owing to the small numbers, until now they have been expensive, at around 1 million EUR, than standard diesel buses, which cost in the region of 250,000 EUR (2017). The maintenance costs have also significantly reduced and the reliable operating times increased. Depending on the annual production numbers, production costs for FCEBs should continue to fall, however, in future projects.

Modern fuel cell buses draw their energy from two fuel cell stacks, each with an output of approx. 100 kW. They also have a relatively small traction battery and are able to recover brake energy. In addition, they carry approximately 30–50 kg of compressed hydrogen on board, stored in pressure tanks at 350 bar. On the other hand, some battery electric bus models have large traction batteries and only small fuel cell stacks, which are used as range extenders.

Fuel-cell buses now have a range of 300–450 km and so offer almost the same flexibility as diesel buses in day-to-day operation. While some older municipal buses still consume well over 20 kg of hydrogen (rather than 40 L of diesel) per 100 km, newer fuel cell buses now use only 8–9 kg per 100 km, giving FCEBs an energy efficiency advantage of around 40% as compared to diesel buses.

In order to develop the market, demonstration projects with large fleets for long-term use are planned. The FCEB fleet in Europe is expected to expand to between 300 and 400 vehicles by the end of 2021.

The use of fuel cell technology and hydrogen in buses is also regarded as a model that can be transferred to other commercial vehicles.

Tab. 15.4: Buses key points.

	Buses at a glance
Market maturity	Technology tried and tested in numerous small fleets worldwide (Europe, North America, Asia), larger projects with several hundred buses at the planning stage; currently only in publicly funded transport projects, studies on commercial use
Requirements	Flexible, reliable use in scheduled services with short downtimes (for refueling/charging); ideally no space and restrictions for passenger transport
Advantages	Higher efficiency, lower emissions
Disadvantages	Range 300–450 km, no public infrastructure needed for municipal buses, range still too shot for coaches; no air pollutants, low noise emissions, little additional weight from hydrogen tanks
Alternatives	Gas buses, diesel hybrid buses, electric buses

15.3.5 Lorries and light commercial vehicles – Tab 15.5

Almost all lorries are fitted with diesel engines; this is especially true of heavy goods vehicles used for long-distance road haulage. Alternative drives and fuels – mostly gas vehicles (CNG (compressed natural gas) and liquid petroleum gas) – are mainly used for light commercial vehicles. Electric drives have so far been unable to achieve significant numbers in lorries because of the weight and volume of the batteries that are needed to provide the necessary range reduce the payload to an unacceptable level.

However, a gradual increase in hybridization/electrification is anticipated in the future for light commercial vehicles and small lorries. In terms of lorries, in California and Germany, there are as yet just a few vehicles that draw their drive energy from hydrogen-powered fuel cells. The prototypes are mostly light to medium lorries, which, because of their low noise emissions and absence of pollutants, are intended for use in urban delivery services. They are generally battery electric vehicles, which have been fitted with a fuel cell as a range extender. The use of fuel cells in long distance road haulage lags further behind. Meanwhile, concepts or prototypes for heavier lorries and trucks are available, with autonomy comparable to the equivalent of diesel-powered ones (about 1,200 km with 80 kg@700 bar H_2).

Prerequisites for use in long-distance road haulage are considered to be minimizing losses in payload (and volume), competitive fuel prices, the maximum possible range, and an adequate refueling station infrastructure.

Finally, the use of fuel cells to supply auxiliary equipment with electricity is also discussed. Here, reformers convert diesel fuel into hydrogen, which is used efficiently and with few or no air pollutants, by appropriately dimensioned fuel cells to operate refrigeration systems and the like.

Tab. 15.5: Lorries and Light Commercial vehicles key points.

	Lorries and Light Commercial Vehicles at a Glance
Market maturity	Vehicles (around 50), mostly in the United States, with individual examples inGermany/EU. Concepts and prototypes primarily for smaller lorries in urban areas with air quality issues, but also first concepts/prototypes for heavy goods vehicles.
Requirements	Space-saving hydrogen storage; reliable supply; reduction in total cost ofownership.
Advantages	Higher efficiency, no air pollutants, low noise emissions.
Disadvantages	Expensive drive technology/fuel; still shorter range than diesel; low density of refueling stations.
Alternatives	Diesel vehicles; LNG/CNG and battery-electric commercial vehicles (BEVs).

15.3.6 Motorcycles – Tab 15.6

Light motorcycles were an early commercial application of fuel cell technology in motorized private transport. In emerging and developing economies, motor scooters and small motorcycles are an indicator of an increase in motorization. However, two-stroke or four-stroke motorcycle engines running on fossil fuels lead to increased air pollutant and noise emissions in conurbations. Electric scooters and motorcycles, in contrast, offer the advantage of zero-pollutant and low noise emission travel. In the past, however, they suffered from low storage density and, hence, range of batteries. Due to technical advances in battery technology, however, the typical daily distances travelled in cities can now often be covered. The last two decades saw a succession of two-wheel prototypes equipped with a variety of fuel cell types and storage systems. The commercial implementation of fuel cell motorcycles foundered, however, partly because of the higher purchase/running costs for the fuel cell technology and the inadequate hydrogen supply infrastructure. In addition, battery technology can cover the moderate performance requirements for electric motorcycles in urban commuter traffic.

Tab. 15.6: Motorcycles key points.

	Motorcycles at a glance
Market maturity	Only prototypes so far; were regarded as an early commercial application, but e-bikes advanced faster. Hydrogen to extend the range of heavy motorcycles in future
Requirements	Low purchase/running costs; adequate range; simple storage
Advantages	Fuel cell motorcycles are zero pollutant and low noise. Longer range in comparison to all electric motorcycles
Disadvantages	Expensive especially in comparison to cheap internal combustion engines; inadequate hydrogen supply infrastructure
Alternatives	Motorcycles with internal combustion engine; e-bikes and e-scooter

15.3.7 Nautical applications – Tab 15.7

In the shipping industry, diesel engines are used almost exclusively today. To date, the only relevant alternative drive option is the use of LNG or CNG to fuel ships. Fuel-cell modules have been tested successfully in maritime conditions. Fuel cells work more efficiently than comparable diesel-generator sets in the partial load range and through the possibility of combined heat and power generation. In many cases, fuel cells are operated not with hydrogen but with other fuels, including methanol, natural gas, or diesel fuel. These offer the advantages of greater availability, lower price, and easier storage. They are converted into hydrogen with the aid of internal or external reformers. The use of hydrogen-powered fuel cells for ship propulsion, by contrast, is still at an early design or trial phase.

Moreover, in comparison to the efficient slow-running diesel engine, which runs on heavy fuel oil, the power train and fuel are still far too expensive.

Submarines are a niche application of fuel cells. For instance, electrolyzers have been used in submarines for some time now to produce oxygen for breathing air. Submarines operated with fuel cells have been developed in the United States and Germany. The submarines developed in Germany use PEM fuel cells and metal hydride hydrogen stores. In terms of submarine applications, fuel cells are characterized by low noise emissions, low operating temperatures, and air-independent operation.

Tab. 15.7: Nautical applications key points.

	Nautical applications at a glance
Market maturity	Use of fuel cells for on-board power generation being trialed. Concepts for small ship/boat propulsion system; propulsion system for commercial maritime shipping unlikely.
Requirements	Low emissions combined with low prices for drive-trains and fuels.
Advantages	Higher efficiency, lower emissions.
Disadvantages	Expensive drive system; additional tank space.
Alternatives	Diesel engine with heavy fuel oil, marine diesel, (commercial) diesel fuel; gas turbine with LNG/CNG.

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Paul E. Dodds, Daniel Scamman, Paul Ekins

16 Hydrogen distribution infrastructure

Abstract: Hydrogen has to be supplied to end-users using safe, reliable, and cost-effective distribution infrastructure. The choice of distribution infrastructure should take into account the varying pressure and purity requirements of end-users and the hydrogen production methods being used. Hydrogen can be transported as a gas through pipelines, or compressed and transported in tube trailers, or liquefied and transported in road tankers, or produced at refueling stations or industrial sites. All of these technologies are in use in different parts of the world.

It is difficult to justify investment in expensive distribution infrastructure such as a pipeline network for a very small initial market that might not grow in the future. Onsite electrolysis or tube trailers are likely to be most cost-effective for refueling stations, in the short term. Pipelines could be introduced sooner, if an industrial cluster or a gas distribution network were converted to use hydrogen, as a substantial demand would be created that would enable economies of scale in hydrogen production and distribution.

Hydrogen purity and pressure requirements are often overlooked but require significant energy inputs. Compressor technologies for refueling stations are currently expensive or unreliable, and alternatives are in early stages of development. Purification costs can be minimized through careful system design.

Keywords: hydrogen distribution, hydrogen trade, liquefaction, hydrogen tankers, hydrogen pipelines, hydrogen storage, hydrogen pressure, hydrogen purity, hydrogen infrastructure

16.1 Introduction

If hydrogen is to have a substantial role in a future low-carbon economy, it must be supplied to end-users using safe, reliable, and cost-effective distribution infrastructure. The choice of distribution infrastructure will depend on end-use requirements and on how the hydrogen is produced, among other factors.

Hydrogen could potentially contribute to every sector of the energy system, but requirements differ between sectors. Fuel cell vehicles require high-purity hydrogen that is compressed to 700 bar, and hydrogen demand for refueling is likely to be very low in the early years, when only a few fuel cell vehicles are in use [1]. Industrial and

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domestic boilers, on the other hand, can cope with substantial levels of impurities and do not require compressed hydrogen, and a substantial demand for hydrogen would develop immediately if an industrial cluster were converted to use hydrogen.

Hydrogen can be produced from a range of feedstocks. The principal technologies to produce low-carbon hydrogen in the future are most likely to be steam methane reforming (SMR) with carbon capture and storage (CCS), electrolysis [2]. Biomass gasification with CCS may also have a role. Electrolysis could be large scale (i.e., centralized, with the hydrogen delivered to the end-user) or small scale (i.e., decentralized, for example through onsite production at refueling stations) [3]. Economies of scale and the need for CO_2 capture and transport infrastructure mean that natural gas and biomass are only likely to be used in large-scale plants.

16.1.1 Challenges for hydrogen distribution infrastructure

The chemical properties of hydrogen pose a challenge for distribution infrastructure. Hydrogen is a gas at standard temperature and pressure. As a very small and highly buoyant molecule, it escapes easily from defective infrastructure. Hydrogen has a very broad flammability range, from 4% to 74% concentration in air [4], which poses safety challenges for unplanned releases. Although it has a very high specific energy (142 MJ/kg), its energy density is around a third of natural gas under the same conditions, which makes it more difficult to transport in bulk than, for example, liquid fuels. While natural gas can be cooled to liquid natural gas (LNG) at −160 °C, the condensation point of hydrogen is much lower at −259 °C, and the energy density of liquid hydrogen is only a quarter of the energy density of gasoline.

Despite these challenges, a range of infrastructural options exist to deliver centralized hydrogen to end users. These are summarized in Fig. 16.1. Hydrogen can be transported as a gas through pipelines or can be compressed and transported in tube trailers. Another option is to liquefy and transport the hydrogen in road tankers. All of these options are currently used in different parts of the world.

16.1.2 Hydrogen trade

Many hydrogen studies in the past have made an implicit assumption that countries would be self-sufficient and hydrogen would not be traded internationally, even when modelling the global energy system [6]. Yet there is increasing international interest in the development of a global hydrogen market, particularly from countries such as Australia [7] and Chile [8], which have ample solar and wind resources to produce cheaper renewable electricity than elsewhere.

For countries with land borders, hydrogen is most likely to be traded as a gas via large transit pipelines. For example, a plan to create a dedicated hydrogen pipeline

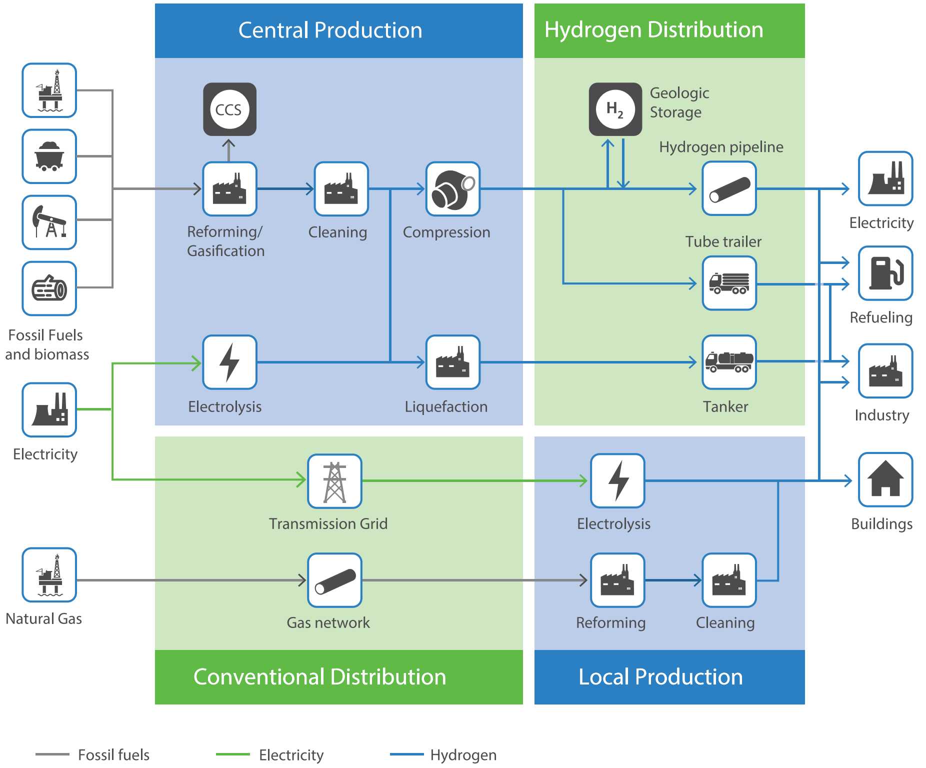

Fig. 16.1: Overview of hydrogen distribution pathways. The diagram is simplified and aims to highlight the diversity of options. Source [5].

network across Europe of almost 23,000 km by 2040 has been proposed by a group of eleven European gas infrastructure companies [9]. For other countries, the low energy density means that hydrogen is unlikely to be traded as a gas by sea. It could be shipped as liquid hydrogen, but this would require liquefaction and active cooling. Another option would be to produce and transport hydrogen in the form of ammonia, which is easier to handle [8]. Ammonia would be particularly valuable if there were ammonia end-uses, as it would avoid energy losses resulting from the need to convert it back to hydrogen. Liquid-organic hydrogen compounds and liquefied synthetic methane would be alternative carbon-based possibilities, if a CO_2 sources that could not otherwise be abated were available.

When designing hydrogen distribution infrastructure, it would therefore be prudent to consider potential imports of gaseous hydrogen by pipeline, and liquid hydrogen or ammonia at seaports.

16.1.3 Structure of this chapter

This chapter examines hydrogen distribution infrastructure options in detail. Section 16.2 reviews the various hydrogen distribution options. Energy storage is an important part of all systems, so Section 16.3 has an overview of hydrogen storage options. Section 16.4 examines pressure and purity requirements in more detail. Finally, Section 16.5 considers strategies to cost-effectively develop hydrogen infrastructure over time to meet growing demands, and Section 16.6 draws a few conclusions.

16.2 Hydrogen distribution technologies

The four broad routes to deliver hydrogen to end users in a country are illustrated in Fig. 16.1. One option is to produce hydrogen onsite and to deliver the feedstock (e.g., electricity) to the site. The other options are tube trailer, road tanker, and pipeline transport from a centralized production or import site. Moreover, an international hydrogen market might emerge in which hydrogen and/or ammonia was traded by ship to major ports and perhaps industrial clusters.

16.2.1 Onsite production

Onsite hydrogen production at refueling stations, using electrolyzers, offers the advantages of producing high-purity hydrogen [10] and not requiring expensive hydrogen distribution infrastructure at the start of a transition, when total consumption is very low. Disadvantages are the need for a high-voltage electricity supply, no opportunity to benefit from any economies of scale, a likely need for additional onsite hydrogen storage, and the loss of the space that is taken by the electrolyzer.

16.2.2 Tube trailers

Tube trailers are constructed of a number of compressed hydrogen cylinders mounted on a trailer. The cylinders are filled at a hydrogen plant, and the trailer is then towed to the point of use. Tube trailers are well established for low-purity industrial uses, with 200 bar transport pressures and 300 kg capacity, but new trailers are being developed specifically for fuel cell vehicle refueling with 1,000 kg capacity at 500 bar, for economies of scale [10]. The trailer can be parked at a refueling station to refuel vehicles directly, reducing onsite storage and compression requirements, as compression begins from a much higher starting pressure [11].

Tube trailers have two principal disadvantages compared to other distribution technologies. First, since many cylinders are only partly filled for much of the time, they have high capital costs. Second, the quantity of hydrogen that can be transported in a tube trailer is relatively small compared to the weight of the cylinders, so the fuel required to transport the cylinders from the production plant to the end-use site and back could even exceed the amount of delivered fuel if the distance is too far (i.e., the energy return on energy invested is negative) [12]. This means that tube trailers are only really appropriate for transport applications where hydrogen demand is low and the trailer is being transported over a short distance. They might also be justified as provision for an emergency hydrogen supply in remote regions or as specialist hydrogen supply for industry.

16.2.3 Liquefaction and road tankers

In contrast to tube trailers and pipelines, road tankers transport hydrogen as a liquid rather than a gas. Liquefaction greatly increases the energy density and enables smaller amounts of hydrogen to be transported over long distances, for which pipelines would not be economical [12]. For 200-km round-trips, the energy efficiency is virtually 100% (no losses). For 1,600-km round-trips, the efficiency drops to around 90% due to the higher fuel consumption. Over 90% of merchant hydrogen is currently transported in liquid form in the United States, indicating an advanced state of technological maturity [13]. The first step is to clean and liquefy the hydrogen. It is then transported to the point of use, where it is either supplied as a liquid or more commonly regasified.

Theoretically, only about 1.1 kWh/kg must be removed to liquefy hydrogen gas, but the cooling process has a very low Carnot cycle efficiency [14], so the energy input is considerably higher, in practice. The US 2020 target for the energy consumption of large-scale liquefaction is 11 kWh/kg (i.e., 28% of the energy content of the fuel vs HHV), with the potential to reduce to 6 kWh/kg in the long-term [13]. This means that liquefaction consumes considerably more energy than hydrogen compression. Moreover, liquefiers use electricity, which is more expensive than hydrogen, as a fuel. Cost estimates for liquefaction plants range from 220–1,200 €/kW [15], with the higher values for existing plants and the lower values for larger plants that would benefit from economies of scale [16].

Liquid hydrogen tanker capacities are typically 2,000–7,500 kg, depending on the jurisdiction. Countries with tighter controls on vehicle sizes, for example in Europe, are likely to have smaller payloads. Given the substantial energy content of a liquid hydrogen tanker, refueling stations handling liquid hydrogen might be subject to strict industrial safety regulations in some countries that could make them unviable; for example, in the UK, the threshold for compliance with Control of Major Accident Hazards regulations is 5,000 kg of onsite hydrogen. Moreover, although liquid hydrogen is substantially denser than compressed hydrogen; it still has only a quarter of the energy density of petrol, so larger tanks would be required to store and supply the same quantity of energy.

16.2.4 Ships

It is unlikely that ships would transport gaseous hydrogen over long distances due to the low energy density. It would be economically viable to transport liquid hydrogen, and the first liquid hydrogen carrier is due to commence shipments between Australia and Japan in 2021 [17].

Another option would be to transport ammonia internationally. Ammonia is easier to handle and has a higher energy density than liquid hydrogen. Transporting ammonia by ship is relatively straightforward. Moreover, ammonia could be a zero-carbon fuel for ships in the future.

16.2.5 Pipelines

Pipelines are the lowest-cost method of transporting large quantities of hydrogen [12]. Almost 3,000 km of hydrogen pipelines have been constructed since 1938 in Europe and North America [18]. The majority of these are high-pressure pipelines connecting industrial sites.

Pipeline investment costs can be split into four main categories: materials, labor, right-of-way fees, and miscellaneous [18]. Only the material costs are likely to differ from pipelines used for natural gas. Cost estimates per km vary widely due to differing topography, land use and labor costs, and the lengths of pipelines vary widely between regions. Using information from [18], the cost can be estimated as the equivalent methane pipeline cost plus 20%.

16.2.5.1 High-pressure pipelines

It is likely that hydrogen would be transported over long distances and delivered to refueling stations and major industrial sites using high-pressure pipelines (20–90 bar). Transporting hydrogen through high-pressure steel pipelines is more difficult than transporting methane because of hydrogen embrittlement, which makes hard steel pipes vulnerable to cracking, and because of hydrogen attack, in which reactions with the steel carbon atoms under certain operating conditions again lead to cracks. This means that it is unlikely that existing natural gas pipelines, which use hard steels, could be repurposed to use hydrogen, so a new national hydrogen pipeline network would have to be constructed, if required.

Pipeline energy losses are lower than for tube trailers and road tankers. The amount of energy required for transporting hydrogen over a distance of 1,000 km across Europe is comparable to around 2% of the energy content of the transported hydrogen, with the levelized cost estimated between 0.09 and 0.17 €/kg [9].

Hydrogen has a lower energy density by volume than methane but a faster flow rate; this means that the total pipe capacity is around 20% lower for hydrogen than methane, but the total hydrogen stored within the pipe is only a quarter of the total methane at the same pressure in energy terms (hence the loss of linepack described in Section 16.3) [19]. This means that hydrogen pipeline flows and pressures would have larger fluctuations with demand changes than for natural gas, and so would need to be more carefully monitored.

16.2.5.2 Low-pressure pipes

Low-pressure hydrogen pipelines are not generally used for hydrogen except in a few niche areas, such as hospitals, but town gas, a mixture of hydrogen and carbon monoxide, was delivered at low pressure to buildings in many countries for many years prior to the adoption of natural gas [20]. A low-pressure distribution network would be required if hydrogen were adopted for residential and commercial heating.

There is much interest in the UK in converting the existing low-pressure gas distribution networks to deliver hydrogen [21, 22], and this could be an option in other countries such as the Netherlands, Denmark, and Germany. Embrittlement is a pressure-driven process and is less of a concern at lower pressures. However, many older pipes were constructed of iron and can have high leakage rates. Since the 1970s, polyethylene pipes have been used instead of iron pipes, and these are thought suitable for delivering hydrogen [21]. In the UK, the Iron Mains Replacement Program is replacing all iron pipes near buildings with polyethylene pipes for safety reasons, so the gas networks are gradually becoming “hydrogen-ready.” Other countries that continue to have networks with substantial numbers of iron pipes would have greater conversion costs that would make hydrogen a more expensive option.

16.3 Hydrogen storage

Hydrogen is much cheaper to store for long periods than electricity. The most basic type of hydrogen storage is an above-ground metal cylinder, as for other gases, but carbon fiber tanks have been developed for high-pressure storage in vehicles and large quantities of hydrogen can also be economically stored underground.

A hydrogen economy would require hydrogen storage at a range of scales. Refueling stations would require buffer storage, and perhaps additional storage if hydrogen were being produced onsite. If hydrogen were used in building heat, then there could be large changes in both intraday and interseasonal demands. Intraday demand variations are at least partially met in natural gas systems though “linepack,” which is effectively storage resulting from large quantities of natural gas being in transmission pipelines at each moment. However, hydrogen would have much lower linepack at the same pressures than natural gas because of its lower energy density. This means that large-scale storage would probably be required, which would most likely be in underground caverns.

16.3.1 Geological storage

Interseasonal storage of natural gas is already used in some countries, and could be an important part of a low-carbon system to meet winter heating demand. Hydrogen stored in salt caverns or depleted gas fields could have a similar role in a low-carbon future. Underground hydrogen storage can achieve energy densities of 280 kWh/m^3, which is about one hundred times the energy density of compressed air storage [12]. Comparatively low construction costs make salt cavern storage much cheaper than surface storage in cylinders.

Underground storage is limited to areas with suitable geology [23]. Hydrogen salt cavern stores have been used in several countries. Some salt deposits are deeper and costlier to excavate and operate, but are capable of storing more hydrogen at higher pressures of up to around 200 bar. Salt caverns are the cleanest form of geologic storage but some post-storage cleaning would probably be required, particularly for hydrogen used by fuel cells.

Aquifers and depleted gas fields are alternative geologic stores for regions without appropriate salt deposits, but the hydrogen recovered may need additional cleaning, and these options have undergone little testing to date.

16.3.2 Hydrogen storage in the transport sector

The low energy density of hydrogen has led to a need for high-pressure storage, particularly at refueling stations and in vehicles. Higher pressures require more stringent tank material and compressor specifications, greater compression work requirements, and additional safety measures such as minimum separation distances and safety barriers between storage and people using the refueling station [24]. Low (~45 bar) and medium (200–500 bar) pressure vessels are common in industry, but high pressure tubes and tanks (700–1,000 bar) are rarely used outside the refueling sector and are currently produced in low quantities [12]. Hydrogen tanks at refueling stations must have higher pressures than vehicles (e.g., 925 vs 700 bar) to allow rapid refueling without requiring a slow compressor to fill vehicle tanks.

Underground storage is commonly used at petrol refueling stations to reduce surface land usage. Since compressed hydrogen gas has only 15% the energy density of petrol, space for storage is a key consideration for hydrogen refueling stations. Fuel cell vehicles are more efficient than existing petrol vehicles, and a refueling station could receive a continuous supply of hydrogen by pipeline rather than receiving a fuel delivery every few days, so the space requirement for storage might not be dissimilar to what it is today. There would likely be trade-offs between storage and compression costs; for example, a larger hydrogen tank would allow for a smaller (and cheaper) on-site compressor that would trickle-feed the storage through the night.

Hydrogen could also be stored at refueling stations in liquid form, in large, well-insulated tanks with active cooling, and then be dispensed as a liquid or a gas.

16.4 Pressure and purity

The pressure and purity at which hydrogen is produced and at which it is needed have important implications for hydrogen infrastructure design and have often been overlooked. Production routes that appear cheaper than others may become more expensive if extensive compression and purification are required. Likewise, it may be unnecessarily costly to generate high-purity hydrogen if high purity is not required. One approach for infrastructure might be to match low-purity demands for hydrogen with low-purity sources, and to match high-purity demands for hydrogen with high-purity sources. Table 16.1 summarizes purity and pressure requirements for a range of hydrogen applications.

Tab. 16.1: Purity and pressure requirements for a range of hydrogen end-uses. Purity requirements are from [25]. Pressure requirements are typical ranges, where 0.075–7 bar signifies a distribution network supply, 7–90 bar a distribution or transmission network supply, and 950 bar a hydrogen refueling station. All pressures are gauge pressures (i.e., above atmospheric pressure).

Application	Purity	Pressure
Combustion (internal combustion engines)	98%	950 bar
Combustion (residential/commercial combustion in boilers, cookers, etc.)	98%	0.075–7 bar
Industrial fuel for power generation and heat, excluding fuel cell applications	99.9%	7–90 bar
PEM fuel cells for road vehicles	99.97%	950 bar
PEM fuel cells for stationary applications	99.9%	0.075–7 bar

16.4.1 Compression technologies and costs

Highly compressed gas is currently the preferred option for on-board storage of hydrogen in most transport applications, as this avoids the expense and boil-off losses of liquefaction, the conversion losses of synthetic fuels such as ethanol, and the technological immaturity and weight of metal hydride storage.

Hydrogen is normally produced at low pressures, but can be generated at up to 15–80 bar to reduce subsequent compression requirements. Hydrogen transmission pipelines typically operate in this pressure range, and centrifugal compressors achieve higher pressures if necessary. Pressure falls as gas travels through a transmission network, so regularly-spaced pipeline compressors are sometimes used to repressurize the gas.

16.4.1.1 Compression needs for the transport sector

Hydrogen must be compressed to very high pressures in vehicle tanks to enable fuel cell vehicles to achieve similar driving ranges as those of existing petroleum-powered vehicles. Buses tend to use 350-bar hydrogen storage as they have more on-board storage space, while most passenger cars use 700-bar storage. Refueling stations store hydrogen in a series of cascade tanks at pressures up to 825–950 bar (typically 900 bar), due to the significant pressure drop across the dispenser control system [26]. Although this increases tank capital costs and compression work, it allows faster refueling and the use of smaller compressors to replenish storage tanks overnight.

The energy penalty for compressing hydrogen to 900 bar can be substantial, as can be seen in Fig. 16.2 for different inlet pressures. Isothermal compression represents the theoretical minimum compression work requirement, where compression heat is continuously removed during the compression process. Real-world compressors typically do not remove much compression heat during compression, leading to a less-efficient adiabatic process. Other losses (e.g., friction) reduce efficiency further, with 70% being a typical efficiency versus the adiabatic value for mechanical compressors. Compression up to 900 bar requires a number of stages, as the pressure ratio per stage of a reciprocating compressor is typically limited to 3–10. Interstage cooling is normally used to remove compression heat to prevent overheating and to improve efficiency towards isothermal values. Using more stages increases efficiency and lifetime but also increases complexity and capital costs. Figure 16.2 shows that a compressor with a 70% efficiency but no interstage cooling requires about 9% of the hydrogen's energy content for compression from a 20 bar pipeline to 900 bar, but that interstage cooling with a pressure ratio per stage of 4 reduces this to 6.5%, which is closer to the isothermal value of around 3.5%. For buses, compression from 20 to 450 bar (suitable for 350-bar refueling) requires 5% compression work at 70% efficiency. While these compression work values are notably less than required for liquefaction (see Section 16.2.3), they are still substantial energy penalties.

If hydrogen were only used for vehicles, then it is unlikely that the refueling station supply pressure would be lower than around 20 bar. However, if existing gas networks were converted to supply hydrogen to buildings, then there would be an option to connect refueling stations to lower-pressure parts of distribution networks. The low pressure network operates at pressures of 0.075 to 2 bar, which

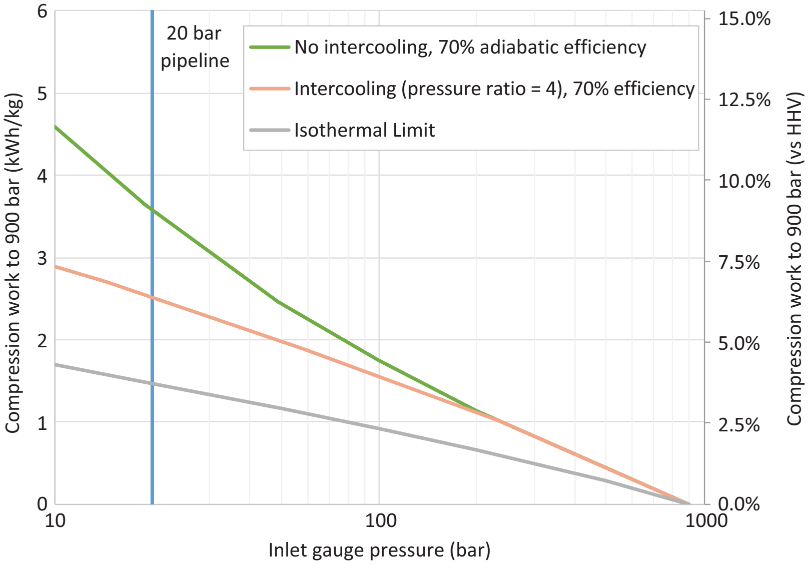

Fig. 16.2: Hydrogen compression work requirements to 900 bar. Efficiency is reported relative to the adiabatic input required (where compression heat is not removed during compression) and assumes ideal gas behavior.

would require substantially larger compression work to reach 700 bar for FCEV refueling than from 20 bar, and might not be able to deliver the volumes of hydrogen required. Intermediate pressure (2–7 bar) would require more reasonable compression work (7%–8%), but forms only a small part of the distribution networks.

16.4.1.2 Compressor technologies

Mechanical compressors are the incumbent and mature technology for hydrogen and are similar to those used for natural gas. Centrifugal compressors tend to be used for large flowrates and low pressure ratios, in centralized production facilities and in pipelines [27], while piston compressors are used to achieve high pressures at refueling stations. Interstage cooling is normally used to lift efficiency towards the isothermal limit (Fig. 16.2), though real-world efficiencies are still well below adiabatic values. The US Department of Energy has targeted 80% compressor efficiency by 2020, compared to adiabatic compression [26]. Mechanical compressors suffer poor reliability and are a leading cause of refueling station unavailability [28]. This is exacerbated by a large number of moving parts and frequent start-ups; compressor rings currently need replacement every 1,000 hours [26], leading many operators to pay for a spare compressor onsite or for fast-responding service engineers. Lubricants can contaminate the hydrogen, necessitating post-compression cleaning;

this can be addressed with lubricant-free compressors, but these can suffer from rapid wear. In some cases, particularly for hydrogen from tube trailers with lower pressure ratios required for onsite compression, diaphragm compressors are preferred due to their greater efficiency and reliability.

The advantages and disadvantages of the principal compressor technologies are listed in Tab. 16.2. Electrolysis can generate hydrogen at pressures up to 200 bar; additional stack voltage is needed, but at power inputs nearer isothermal than adiabatic efficiency levels. High-temperature electrolysis further increases efficiency due to improved reaction kinetics. However, higher differential pressures lead to increased crossover (where too much hydrogen can cross the membrane electrolyte), stronger material specifications, and a need for more steady-state operation with fewer startups. Electrochemical compression has been demonstrated at up to 1,000 bar, and offers high efficiency, high reliability, no contamination, and reduced cooling requirements [29]. In fact, electrochemical compression has been suggested as a means for purifying as well as compressing hydrogen [10], although impurities at the inlet may compromise compressor lifetime. High-strength membranes and materials would also be needed to withstand extreme differential pressures. Ionic compressors are based on mechanical piston compression but with an ionic liquid layer to prevent lubricant contamination. However they are currently expensive and may have to limit throughput to prevent foaming [30]. Hydride compressors that adsorb hydrogen at low pressure and release it at high pressure are compact and reliable, but are currently expensive and heavy. Mechanical compressors remain the incumbent technology for refueling stations, but ionic compressors are increasingly being adopted. Compressors remain a priority development technology for the hydrogen transport sector.

Compression costs can be significant. A US study estimated current HRS (hydrogen refuelling station) costs of €1.70/kg[1] for compression from both 20-bar pipelines and onsite production to 875 bar, and €0.46/kg for compression from tube trailers to the same pressure [26]. With compression a key technology for hydrogen storage, and scarce information on very high pressures due to the small production numbers currently involved, further work is needed in this area to ascertain compression cost forecasts [33].

16.4.2 Hydrogen purity for fuel cell applications

The current ISO 14687-2 standard for PEM fuel cells in transport applications requires highly pure hydrogen in excess of 99.97%. The technologies required to achieve this purity are discussed below. In addition to the costs of purification itself, technologies for compositional measurement and verification are also required to avoid invalidating warranties [10]. This is a particular challenge, given the large number of

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[1] USD in 2007 have been converted to EUR in 2019 in this paragraph.

Tab. 16.2: Advantages and disadvantages of compression technologies [31, 32].

Technology	Advantages	Disadvantages
Mechanical	+ Commercially available + Wide operating range	– Low efficiency (~70%) and expensive – Poor reliability due to many moving parts – Regular maintenance needed due to start-ups – Purification required due to oil contamination
High-pressure electrolysis	+ High efficiency + Production at 50–200 bar + High temperature further reduces energy use	– Strong materials needed (increasing cost) – Increased crossover and back-diffusion losses (where water flows from cathode to anode) – Long start-up times requires stable supply
Electrochemical	+ High efficiency + 1,000 bar demonstrated + High reliability (no moving parts) + Pure output (no oil contamination)	– Strong materials needed (increasing cost) – Back-diffusion and resistive losses – Low throughput needed to increase efficiency – Pure inlet required and needs drying
Ionic	+ Low contamination + High efficiency + Reliable (few moving parts)	– Expensive and unproven – Limited throughput to avoid foaming
Hydride	+ Compact, reversible + Reliable (few moving parts)	– Expensive and unproven – Heavy

impurities with different limits, the purity required, and the measurement frequency particularly during start-up or operation in extreme temperatures.

Purity requirements for stationary applications tend to be lower, as summarized in Tab. 16.1. Most existing stationary fuel cells are supplied with natural gas rather than hydrogen, so purification equipment is incorporated within the fuel cells systems themselves.

16.4.2.1 Hydrogen from electrolysis

Hydrogen produced from water electrolysis is typically pure enough for FCEV applications. Recombination catalysts are used to remove oxygen that crosses the membrane. The main contaminant is normally water vapor. Water vapor is not a problem for fuel cells; indeed, dry hydrogen normally has to be humidified to provide efficient proton transport. However, water vapor is a problem when compressing, storing and transporting hydrogen; water vapor condenses on compression, which can cause rust, corrosion, or increased wear in moving parts as it washes away lubrication. It can also freeze in cold temperatures, damaging pipework and valves. This applies to decentralized hydrogen generated onsite as well as hydrogen transported from centralized facilities. Hence electrolyzers normally include dryers, typically regenerative desiccant towers, which are low-cost with low power consumption. Regeneration either involves electrical heating or sending some dry gas back through the wet tower to pick up the accumulated moisture, and it typically reduces yield by around 10%, though there is scope for reducing losses [34].

16.4.2.2 Hydrogen from steam methane reforming (SMR)

Hydrogen generated from SMR needs significantly more cleaning than hydrogen from electrolysis if used in a fuel cell. Pressure-swing adsorption (PSA) is the incumbent technology for purifying hydrogen and is typically incorporated into the SMR process. It is capable of achieving hydrogen purities of >99.9%, but higher purity is achieved only through a greatly increasing loss of yield [21]. For example, PSA can generate hydrogen with a purity exceeding 99.999%, but the net recovery reduces to 84% [35]. Hydrogen purification costs from SMR have been estimated as €0.70/kg in 2015 and €0.36/kg in 2025, with the claim that well-designed SMR and PSA systems are already capable of achieving the required purity levels, and that, once quality assurance technologies are developed, the high-purity SAE J2719 standard should not add to the cost of hydrogen production [10].

An alternative to PSA is pressure-driven diffusion membranes, which are typically palladium-based. Palladium filters achieve exceptionally high purity but are expensive, require a 400 °C operating temperature and a pressure differential of 10–15 bar [36], reduce yield by 3–5%, and can suffer short lifetimes. One study found a palladium-based separation system that is potentially cheaper than PSA [36], and diffusion membranes have been recommended for further research [10].

16.4.2.3 Hydrogen from pipelines/salt cavern storage

Hydrogen extracted from pipelines and/or salt-cavern storage would need additional onsite cleaning prior to use in PEM fuel cells to remove lubricants, odorants, colorants, and any debris or dust that has been acquired. An odorant would probably be needed to warn against leaks; cyclohexene has been found to be compatible with fuel cell technology in Japan, but is described as having too pleasant a smell and lacking the stench of mercaptan-based odorants used in Europe [37, 38]. A colorant may also be required to warn users of the location of flames as hydrogen burns with a colorless flame; an extremely dilute strontium solution is being considered [37]. PSA or activated carbon filters may be appropriate for onsite purification. The cost of cleaning hydrogen from pipelines is not well understood [10].

16.5 Developing hydrogen infrastructure to meet a growing demand

Three principal distribution options are compared in Tab. 16.3. The most appropriate infrastructure distribution option depends on a number of factors:

- The end-use pressure and purity requirements, and to a lesser extent, whether impurities might enter the hydrogen during distribution, for example from dirty pipelines.
- Whether production is centralized or decentralized at the point of use.
- The scale and geography of demand. Pipelines are primarily suited to large demands, whether over small or large distances [39]. Road tankers are suitable for small and medium demands over long distances. Tube trailers are only cost-effective for very small demands over short distances.
- Whether any existing infrastructure can be converted to use hydrogen, for example, by repurposing existing polyethylene distribution pipe systems or underground salt caverns to use hydrogen, instead of natural gas [19].

Tab. 16.3: Qualitative overview of technologies for hydrogen distribution [33].

Distribution route	Capacity	Transport distance	Energy loss	Fixed costs	Variable costs	Deployment phase
Gaseous tube trailers	Low	Low	Low	Low	High	Near term
Liquefied road tankers	Medium	High	High	Medium	Medium	Near to long term
Hydrogen pipelines	High	High	Low	High	Low	Longer term

16.5.1 Developing hydrogen infrastructure in the early stages of a transition

Pipelines are the lowest cost method of distributing large quantities of hydrogen. However, they have high initial infrastructure costs, and low demand for hydrogen at the start of a transition would result in their having a low capacity factor. This would mean the return on the investment would be very low at first, and investors would also have to consider the risk premium of the expected increase of hydrogen demand in the future not materializing. Moreover, it might even not be possible to operate a pipeline, if demand were substantially lower than the capacity, due to the risk of pipeline collapse. Hence if demand grows slowly, the choice of distribution infrastructure is likely to change over time.

16.5.1.1 Transport-led transition to hydrogen

Fuel cell cars have been viewed as the primary market for hydrogen in the past. Vehicles would have a very small demand at the outset of a transition [40]. It would be geographically disparate, as vehicles need to refuel across a country. It is most likely that onsite refueling would be primarily used at first [41], perhaps supported by gaseous tube trailers in areas of high or very low population densities, and liquid road tankers in other areas or where liquid hydrogen imports are available.

The lack of an existing network of hydrogen refueling stations is often cited as creating a “chicken-and-egg” barrier to the adoption of fuel cell cars. One approach for hydrogen transport might be a number of public-private stakeholder initiatives to fund the early rollout of hydrogen vehicles and infrastructure, until the industry becomes self-sustaining. The various European H2Mobility programs have suggested a rollout of refueling stations at critical locations. For the UK, a network of 65 refueling stations by 2020 was suggested to provide a basic coverage of high-population areas, with this growing to 1,150 stations by 2030, to cover the whole population [41], but this ambition has not materialized to date. Another study suggested a global target of more than 3,000 refueling stations by 2025, which would be sufficient to provide hydrogen for about 2 million fuel cell cars and would enable the development of refueling infrastructure to become economically self-sustaining [42].

Heavy duty vehicles (e.g., buses, refuse trucks, taxis, and trains) might be more prosperous markets for fuel cells vehicles than cars, in the near team [43]. Many such vehicles use centralized refueling depots, which avoid the low capacity factor issue and encourage economies of scale, and could reduce distribution costs more rapidly than would be possible for the private car sector.

16.5.1.2 Industry- or heat-led transition to hydrogen

Hydrogen is increasingly seen as a means of decarbonizing heavy industry [44] and also providing low-carbon heating in some countries [19]. If an industrial cluster or gas distribution network were converted to use hydrogen, then a large demand would emerge that would enable economies of scale in hydrogen production and distribution infrastructure [45]. A pipeline network might be justified that would also enable lower-cost hydrogen to be supplied to the transport sector.

16.5.2 A mature hydrogen infrastructure

In the longer term, a mature distribution system is likely to develop. In many countries, a transmission pipeline network will be constructed, and this might be linked to networks in other countries to create supranational networks such as the envisaged

European Hydrogen Backbone [9]. Hydrogen for the transport sector would likely be supplied from centralized sources to take advantage of economies of scale. A global hydrogen market would likely develop, which could lead to liquid hydrogen and/or ammonia displacing gaseous hydrogen in some markets.

One new market that might emerge could be peak electricity generation using hydrogen turbines. This would require large hydrogen inflows for short periods. While gas turbines have historically been supplied by gas transmission or high-pressure distribution networks, this might be more difficult for hydrogen due to the lower linepack discussed in Section 16.3. An alternate option might be to build a large hydrogen turbine on top of a hydrogen salt cavern store [23].

16.6 Conclusions

Hydrogen infrastructure must be safe, reliable, and cost-effective. However, hydrogen is relatively difficult to handle compared to many fuels, as it highly buoyant, escapes through very small holes, has a broad flammability range, and has a very low energy density. Yet, it has been used by industry for decades, and there are several mature approaches to delivering hydrogen to end users. It can be transported as a gas through pipelines, compressed and transported in tube trailers, liquefied and transported in road tankers, or produced at refueling stations or industrial sites.

The introduction of fuel cell vehicles in many countries has been impeded by a lack of refueling infrastructure. It is difficult to justify investment in expensive distribution infrastructure for a very small initial market that might not grow in the future. Onsite electrolysis or tube trailers are therefore likely to be the most cost-effective methods of supplying hydrogen at refueling stations in the short term. An alternate approach would be to focus on heavy duty vehicles that operate from depots, which could have a higher capacity factor. While these have higher costs per kg of delivered hydrogen than using pipelines, the lower initial investment is easier to justify until demand is established.

Pipelines become increasingly cost-effective as hydrogen demand increases. Pipelines have lower costs per kg of delivered hydrogen than other methods and are likely to be safer as the hydrogen is not being transported on roads. It is likely that pipelines would have an increasingly important role in a transition to hydrogen. This role could be accelerated if an industrial cluster or a gas distribution network were converted to use hydrogen, as substantial demand would be created that would enable economies of scale in hydrogen production and distribution. While existing transmission pipelines are unlikely to be suitable for distributing hydrogen due to embrittlement, there is evidence that some gas distribution networks could be converted. It is possible that international hydrogen pipeline networks could also be created to enable hydrogen trading.

Liquid hydrogen could have a role throughout a transition to a hydrogen economy. In the short term, liquid road tankers could supply refueling stations at long distances from a central production hub. In the longer term, even if a hydrogen pipeline network were constructed there might be liquid hydrogen imports by ship that could be transported to refueling stations that are not connected to a network. There is a need to reduce liquefaction capital costs and improve its energy efficiency.

Hydrogen purity and pressure requirements of different end uses are often overlooked. For example, PEM fuel cells require very pure hydrogen at very high pressure, while combustion applications such as boilers can use 98% pure hydrogen at low pressure. Compressor technologies are currently expensive and unreliable; alternative technologies have been proposed but are at early stages of development. Both purification and compression require significant energy input and there is a need to consider these when designing a hydrogen distribution system to minimize these losses.

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Henning Zoz, Tejas Bopardikar

17 Power to gas to fuel – P2G2F®

Abstract: In this world, where resources are naturally limited while the world's population is steadily growing, the availability of affordable energy is essential. This refers not only to the question of energy generation but also to its storage and utilization. The following chapters introduce energy generation and storage systems, particularly in regard to future-oriented solutions. The key summary names present and future components as "power to gas to fuel – P2G2F®."

17.1 Introduction

Governments have recently declared CO_2 as the climate-relevant gas responsible for the expected global warming and have declared war on it. It should be noted that about 4% of the CO_2 gas is globally emitted by humans, of which, it is believed, that saving half, that is, saving 2% could be possible. For this reason, the agenda is for a significant reduction in CO_2 emissions that has been defined the socio-political goal of the energy transition [1]. Here, it is envisaged that, by 2035, about 55–60%, and by 2050, even 80% of the electricity produced in Germany must be generated from renewable energy sources, primarily wind energy and photovoltaic (PV) energy. In 2017, greenhouse gas emissions could be lowered by 177 million tons, of which around 135 million tons were CO_2 equivalents from electricity generation [2].

The need to achieve the targets set by the German Renewable Energy Sources Act (EEG) was intensified by the accident at the nuclear power plant at Fukushima in 2011, along with and caused by the flood disaster, after a seaquake. As a result, all nuclear reactors in Germany shall be shut down by 2022 [1]. The insofar challenge is that no nationwide energy supply could be guaranteed by renewable energies, among other things, due to the constant change of solar and wind conditions and the associated lack of continuity. For a base-load energy supply of the country, therefore, the electricity from renewable energy sources must be permanently stored, so that, for example, in times of overproduction with favorable wind and sun conditions, energy can be retained in case of energy shortages. A worldwide energy transition would require a global storage capacity of more than 15,000 TWh in 2050 [3].

Unfortunately, there is no existing method to store these large amounts of energy currently, so the so-called energy transition in Germany can only work in a way that allows independence from fossil fuels; for example, all water pump storages in Germany together can only store so much energy to power the country for 30 min, given that all other supply systems shut down, and unfortunately, the given geological formations do not allow any significant increase. Therefore, one of the

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most important challenges in the future will be to find alternate, feasible, and economical storage solutions.

Although there is no large market, at the moment, r for electrolyzers that convert water into hydrogen and oxygen using only electricity, or for big enough hydrogen storage tanks, or even the appropriate methods for the reconversion of hydrogen into electricity, for example, large fuel cells or H_2 turbines. Even today, it would be at least possible to build a demonstrator that combines all of the above mentioned technologies, giving an example for the possible decentralized clean energy of the future.

Hydrogen storage and hydrogen mobility have become two of the key issues during this period, not least because of the 2050 Climate Action Plan, which defined the CO_2 reduction targets for different sectors [4]. The targets are based on the “Impulspapier Strom 2030” [5] and the report on the Green Paper on Energy Efficiency [6].

Based on all these assumptions, the power to gas to fuel (P2G2F®) concept has been developed, the subsections of which are described and summarized below.

17.2 Part 1: Power – renewable energies

Renewable energies represent the focus of the concept of the energy transition and also the “source” of the concept P2G2F®. Here, electricity is generated from sustainable resources, such as geothermal energy, sunlight, wind or hydropower, or gas combustion from biomass (Fig. 17.1).

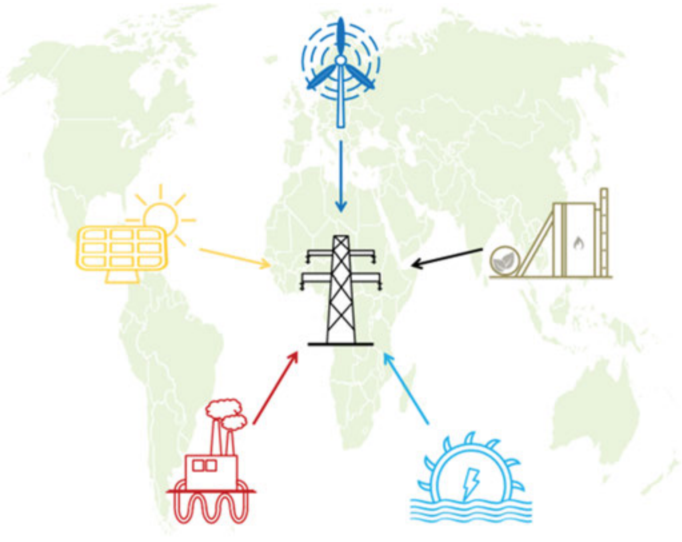


Fig. 17.1: Renewable energies are applied globally.

In 2018, 648.9 billion kWh (648.9 TWh) of energy were generated in Germany [7]. More than one third of these have been derived from renewable sources (Fig. 17.2) [7].

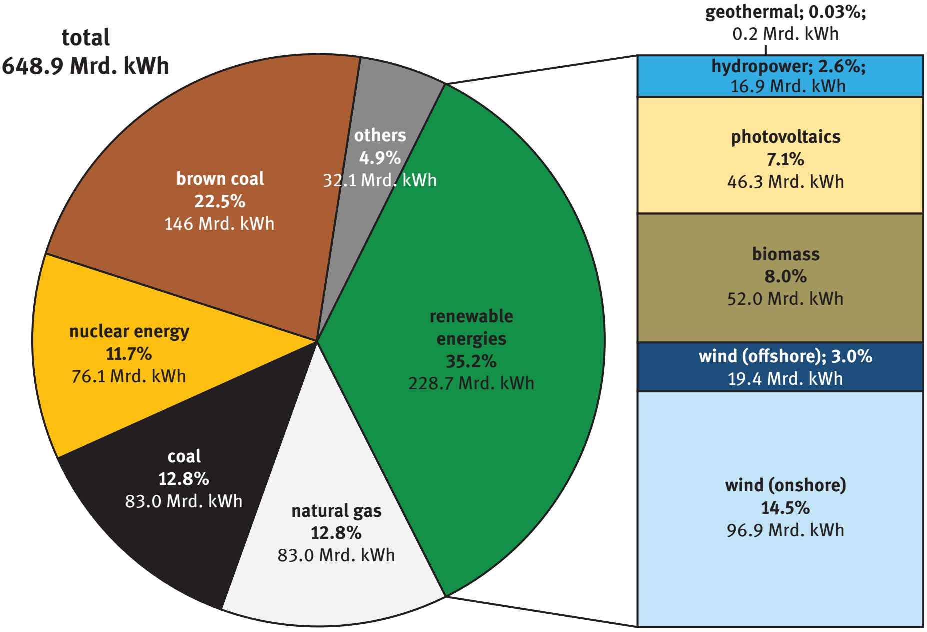


Fig. 17.2: Share of respective energy generation systems in total electricity production in Germany in 2018 [7].

Energy production from non-fossil resources is preferable due to general sustainability. A few facts about the most important sources of alternate energy production, wind and PV energy, are given below:

Wind energy is generated by wind turbines. These can be located on land (onshore) as well as on the sea (offshore). Wind energy is the main electricity supplier of renewable energies in 2018, as it already accounts for 17.5% of the total electricity volume in Germany. At the end of 2017 alone, 5,407 MW of wind power was achieved at sea [8]. According to the plans of the Federal Government, 15,000 MW have to be generated by wind energy, by 2030 [2].

In PV energy, electricity is generated directly from sunlight, using solar cells. More than 1.6 million PV systems in Germany provided approx. 43 GW of power in 2017. This makes PV the second largest electricity producer in the field of renewable energies [2].

17.3 Part 2: gas–water electrolysis and energy storage

Global efforts were taken in order to reduce greenhouse gases significantly through the expansion of renewable energies, with the aim of staying below the global warming threshold of 2 °C. On that score, the importance of hydrogen as a chemical energy source is dramatically increasing [4].

“GAS” is the second of three parts of the P2G2F® concept and already known in the power-to-gas (P2G) concept, which refers to a chemical process in which hydrogen is produced from water by electrolysis and then used for a later combustion or reconversion. For this process, preferably excess energy through the production of renewable energy is used. Since hydrogen can be stored in various different ways, this indirectly becomes a form of energy storage. There is also the possibility of converting hydrogen by subsequent methanation into a fuel gas. This can, for instance, be used as fuel for ships, aircraft, or vehicles. This transformation is also known as “power-to-fuel.” The conversion of wind or solar power into hydrogen (via electrolysis) with time-shifted back conversion into electricity, however, is, from an energetic point of view, too intricate and will only establish itself economically if, for instance, natural gas and/or other fossil fuels become too expensive.

Conversion to fuel however would again be more economical, since fuel is considerably more expensive than stationary energy per unit of energy. The use of fuel contributes so much to the economy that the stationary power back-up (P2G) could be co-financed with it. In summary, P2G2F® is linking the aforementioned energy storage systems, but is not economical, presently. However, P2G2F® will be the first of all strategies to potentially become an economical alternative to current energy storage systems in the future.

17.3.1 Water electrolysis

Electrolysis, particularly water electrolysis, is an important step in the field of sustainable energy storage and electromobility. Here, the energy is transformed in an electrochemical process where applied voltage causes an electron deficiency at the cathode and an electron excess at the anode. The water, then, is oxidized to oxygen at the anode, and protons are released. These diffuse through the so-called *proton exchange membrane* (PEM) into the cathode space, where they are reduced to hydrogen at the cathode (Fig. 17.3).

Electrolyzers that use this principle are commercially available [9]. In Germany, a significant expansion of installed capacity in the double-digit gigawatt range is expected by 2050 (Fig. 17.4) [4]. However, today’s systems are usually produced under manufactory conditions in small batches. Alkaline electrolysis and, to a large extent,

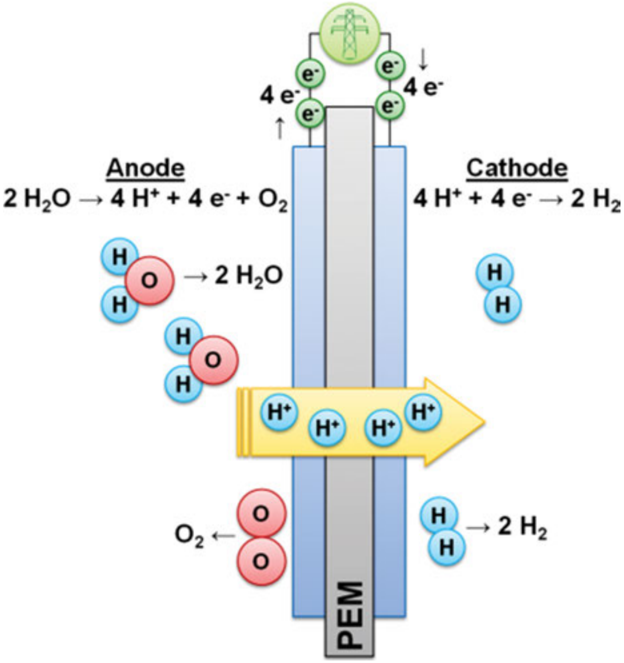


Fig. 17.3: Scheme of the water electrolysis.

PEM electrolysis [4] are technically mature. The development of novel electrolyzers with certain components is still going on, particularly in the field of new membranes. Here, the capability can potentially be enlarged.

17.3.2 Energy storage systems

Over the past decades, various types of energy storage systems have been developed. In general, these can be divided into short-term and long-term storage units.

Short-term storage systems can be charged and discharged in the range of seconds to minutes with a high ratio of power to storage capacity, and refer to the so-called power storage systems. They may be used several times a day and are mainly utilized for network services, as they are suitable for short-term energy fluctuations. These include batteries, capacitors, and, for example, flywheel energy storage [10].

Other short-term storage systems are the so-called shift storages, which can be charged and discharged in the range of minutes to hours. They can be charged and discharged once or twice a day offering energy stability within one day. These not only include batteries, but also compressed air storage systems and pumped storage power plants [10].

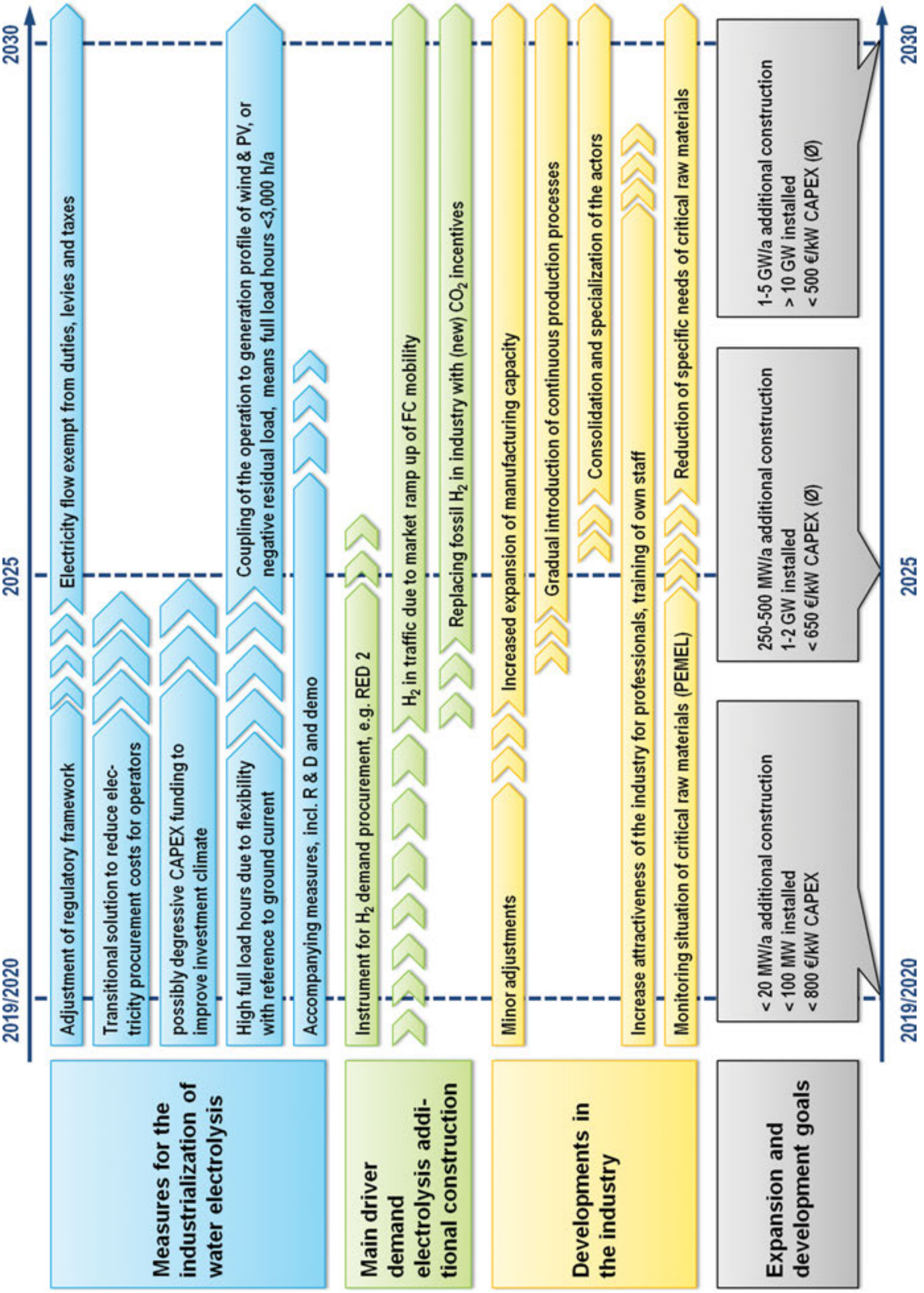
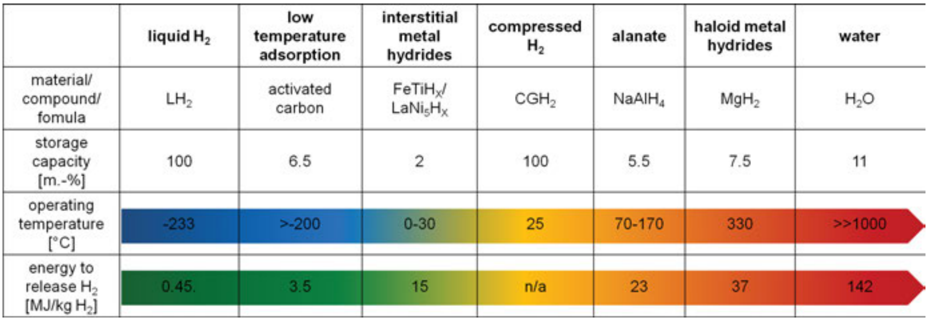


Fig. 17.4: Roadmap for the industrialization of water electrolysis, adapted from [4].

The long-term storage systems, designed to last for days to weeks, may serve as a potential source of energy in times of energy shortfall, or for long-term weather doldrums, when energy production from renewable energy sources is insufficient. These types of storage pass only a few cycles per year and are based on chemical P2G storage, such as hydrogen or methane or even on hydroelectric power plants [10].

17.3.3 Hydrogen storage

The core of the P2G2F® concept revolves around hydrogen storage systems for mobile applications. Many methods of storing hydrogen at various capacities and different operating/conversion temperatures are available (Fig. 17.5).



	liquid H_2	low temperature adsorption	interstitial metal hydrides	compressed H_2	alanate	haloid metal hydrides	water
material/ compound/ fomula	LH_2	activated carbon	$FeTiH_x$/ $LaNi_5H_x$	CGH_2	$NaAlH_4$	MgH_2	H_2O
storage capacity [m.-%]	100	6.5	2	100	5.5	7.5	11
operating temperature [°C]	-233	>-200	0-30	25	70-170	330	>>1000
energy to release H_2 [MJ/kg H_2]	0.45.	3.5	15	n/a	23	37	142

Fig. 17.5: Different types of hydrogen storage, adapted from [11–15].

In general, four different types of hydrogen storage systems are discussed in the framework of road mobility: the CGH_2 variant with compressed hydrogen at 35–80 MPa and at room temperature, the liquid gas variant LH_2, in which hydrogen is present at temperatures between 20 and 30 K and pressures of 0.5–1 MPa, solid-state storage, such as hydrides and other materials with a high specific surface area, and hybrid solutions using at least two of the above variants. The LPG and compression gas variants have been used by the automotive industry so far [11–15].

In the transportation sector, fuel storage tanks have been used in fuel cell-powered cars to date, with a pressure of 700 bar. This comes with some degree of uncertainty for users and for road traffic, or for mobility in general. The preferred variant with a promising future outlook is therefore solid-state storage. This is because the hydrogen can be stored practically pressure free, making this technique very attractive for mobile purposes. Solid-state storage examples include Hydrolium® and reactive hydride composites (RHC).

17.3.3.1 Hydrolium® and reactive hydride composites (RHC)

Hydrogen storage by means of solid-state storage is based on a simple principle. Certain metals and metal compounds absorb hydrogen like a sponge. Hydrogen is atomized here as on a metal catalyst on the surface of the storage material and not in molecular form, as is the case with high-pressure tanks (Fig. 17.6).

Hydrolium® is a metal alloy solid-state storage material. It is capable of storing 50–100 g of hydrogen per 1 L tank-volume, equivalent to ~556-1.112 standard liters or 1.64/3.28 kWh of chemical energy. It is loaded into the H2Tank2Go® cartridges as a loose powder. Hydrolium® has the same advantages as other solid-state storage materials and also shares quite long hydrogen charging times (it can take an hour to fully charge H2Tank2Go® at about 1 L volume). This, in terms of economic profitability, requires an efficient tank system, since any on-board refueling would be too slow and costly. The solution is given in Section 4.1.

Also, the development of hydrogen solid-state storage materials has progressed. One of the next-generation materials insofar developed is metal hydride-based storage materials, particularly by RHC. The so-called complex metal hydrides [16–18] could predictably represent a class of the best hydrogen energy storage in the future. The largest known storage capacity in this case has lithium borohydride ($LiBH_4$) with a theoretical H_2 capacity of 18.3 wt% and is therefore with 2–4 wt%, about 6 times higher than the hydrides known today at room temperature [19, 20]. However, substantial research effort is needed to make it commercially available.

Research has been performed in this field within the framework of two EU projects. The successful “BOR4STORE” project (GA 303428)[1] under the Seventh Research Framework Program, in collaboration with partners from all across Europe, investigated a cost-effective method for producing boron-based storage materials that can store more than 8% hydrogen by mass. It also considered low raw material, disposal, and material costs on an industrial scale. The project also identified the most promising candidates for boron-based storage materials, structural, dynamic, thermodynamic, and kinetic modelling, as well as various thermal management simulations, and a cost analysis for wet-chemical and mechanochemical production. The project ended with the conception of a complete hydrogen tank system, the Zoz-B4S-SM/MM. Right after the project, one tank (Zoz-B4S-SM) was manufactured and certified (Fig. 17.7). As a result, this worldwide innovation is commercially available but still far away from economics [21–23].

It can work with an solid oxide fuel cell and is fully functional at a loading pressure of 50–60 bar and an operating temperature of max. 650 °C. The B4S-SM is based on Li-RHC ($2\ LiH + MgB_2 + 2H_2 \leftrightarrow 2\ LiBH_4 + MgH_2$) with a theoretical storage capacity of ~10 wt%, which corresponds to about 60–100 kg H_2/m^3.

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[1] https://www.hzg.de/science/eu_projects/fp7/key/047584/index.php.en

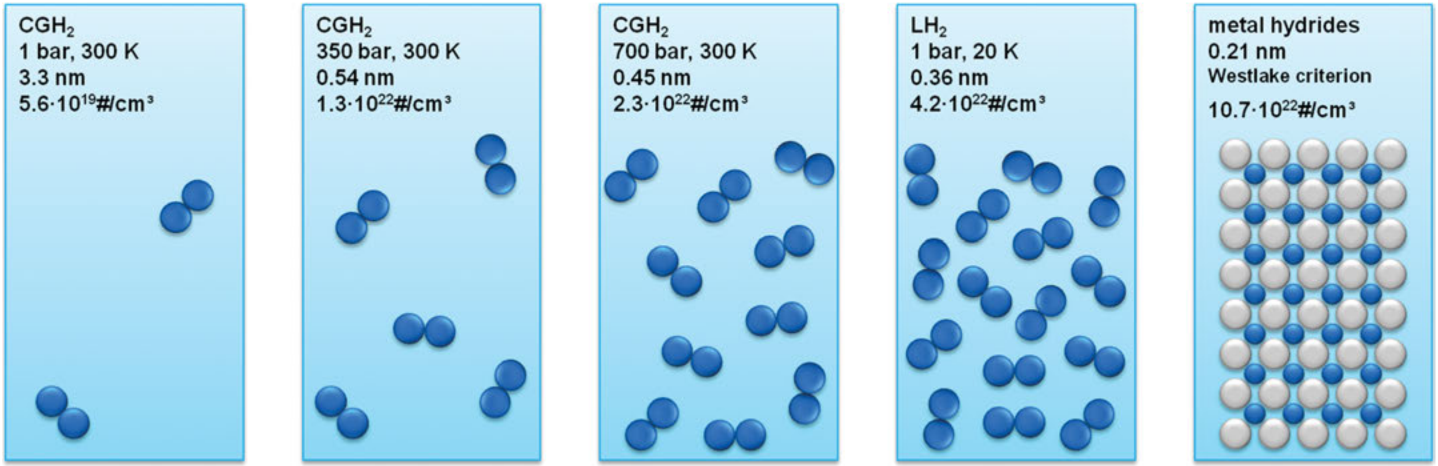

Fig. 17.6: Volumetric hydrogen densities on materials basis, adapted from [11, 15].

Fig. 17.7: H_2 tank system B4S-SM in the Helmholtz HZG – Hydrogen Technology Center in front of the Zoz-Simoloyer® CM100-s2, a process plant for the production of complex metal hydrides.

The also-successful "ECOSTORE" project (GA 607040),[2] as part of the Marie Curie Initial Training Network program, has also established a network with partners from all across Europe and associate partners from Japan, focusing on the topic of novel complex metal hydrides for efficient and compact storage of renewable energy such as hydrogen and electrochemistry. Here, joint research has been promoted and new professionals trained in this field. In the end, a complete hydrogen tank system was built, too (see chapter *"Room temperature hydrides of the AB-type: activation via ball milling," Bellosta von Colbe et al.*).

17.4 Part 3: fuel – electromobility

Energetically, mobility based on regenerative hydrogen is inefficient. The poor energy efficiency of <40%, in fact, does not play any role, as long as the technology can become economical. Insofar, this often used knock-out criterion for H_2 as a potential fuel is not relevant. The same non-relevance brings millions of combustion engine vehicles on the road that do not provide a much higher energetic efficiency.

The difference in the scenario is that energy efficiency with respect to hydrogen, overall does not need to be taken into account, if it is "renewable." Only then, we can afford to consider economic efficiency. Ultimately, hydrogen as fuel cannot be

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[2] https://www.hzg.de/science/eu_projects/fp7/key/047589/index.php.en

more expensive than gasoline and ultimately, hydrogen transportation can only become economical, if gasoline becomes too expensive. This explains why fossil fuels could not successfully be used to generate the desired hydrogen with no resources consumed and no pollutants emitted.

From the early days, the electric motor has been technologically preferable compared to the heat engine driving technology. The electric motor immediately delivers 100% torque, contains hardly any mechanics, has comparatively no wearing parts, and needs no lubricants. In a battery car, the same electric motor converts electrical energy into kinetic energy, as in a hydrogen-powered car. There is no standard solution. Short distances can be served with battery and medium to long distance with hydrogen propulsion.

At present, the overall balance of an electric car, whether battery or hydrogen-powered, is worse than that of a conventional car with an internal combustion engine. But this is also justified, among other things, in the mass production of vehicles. The electric engine is the future. A mass production would be desirable here, but has failed so far, due to the high cost of the fuel cell.

From the corresponding author's view, it is quite clear, that for the next 30 years, it will be the modern diesel-engine that will provide the most economical and ecological passenger driving solution. However, this shall not at all stop us from working for the future!

One present critical fact to be pointed out here is the mass of battery-driven cars, for example, the new E-SUV from Mercedes Benz at a weight of 2.5 t is 650 kg heavier than the corresponding gasoline-driven model [24].

17.4.1 H2Tank2Go® – tanks with solid-state storage material for hydrogen

Any technology comes with associated risk and danger. Over the years, we get used to our environment which explains, why, for example, compared to gasoline, people are afraid of hydrogen, when even with a realistic view, hydrogen represents the far better option. Hydrogen is clean, non-toxic, and inexpensive and can be obtained from water at a large scale everywhere in this world (at sufficient energy supply). Using solid-state storage material, it is possible to transport huge loads of hydrogen practically pressure free in a container. Due to the technically parameters, hydrogen has a higher potential for mid-long distance transportation, compared to battery.

In recent years, Zoz GmbH in Germany has been working on the development and manufacturing of small hydrogen storage 0.95 L tanks namely H2Tank2Go® that are based on a solid-state storage material, at present nanostructured Hydrolium® (cf. Section 3.3.1 and Fig. 17.8). To prevent Hydrolium®-powder from leaking out of the cartridge, special filters have been developed.

Fig. 17.8: H2Tank2Go® cartridges.

Due to the large internal surface of the metallic alloy, large quantities of otherwise gaseous hydrogen can be stored in a relatively small volume. At room temperature, therefore, the pressure in the tank is about 5 bar, and the amount of hydrogen stored therein would easily exceed 700–1,000 bar. In terms of volumetric storage density, H2Tank2Go® even surpasses cryogenic tanks that store hydrogen at extremely low temperatures (−253 °C) in liquid form (Fig. 17.9).

The pressure inside the tank depends on the temperature. Thus, due to the released hydrogen, the pressure increases as the temperature increases. However, at standard operating conditions, the pressure never exceeds 10 bar, which corresponds to the pressure in a standard water pipe. As a result, H2Tank2Go® is a relatively safe storage method for large volumes of H_2. With fuel cells, the hydrogen is converted into water for energy generation with an efficiency factor of about 60%.

The stored content of the H2Tank2Go® cartridge again corresponds to approximately 1 kWh of electrical energy, depending on the efficiency of the fuel cell. A Li-ion battery, today, stores about 250 Wh/L, or 150 Wh/kg energy. The filled H2tank2Go® tank weighs just over 4 kg and offers about twice the gravimetric, or four times the volumetric energy storage capacity when compared to the Li-ion batteries.

The above advantages support the application of H2Tank2Go® technology in electromobility. This was shown by a demonstration: a formerly battery-operated electric kickboard isigo®1.0 was reconstructed and presented to the public at the Hannover Fair 2010 as a H_2-powered isigo®H2.0 prototype. The isigo®H2.0 could reach a range of up to 60 km with one H2Tank2Go® cartridge, while the battery-powered isigo®1.0

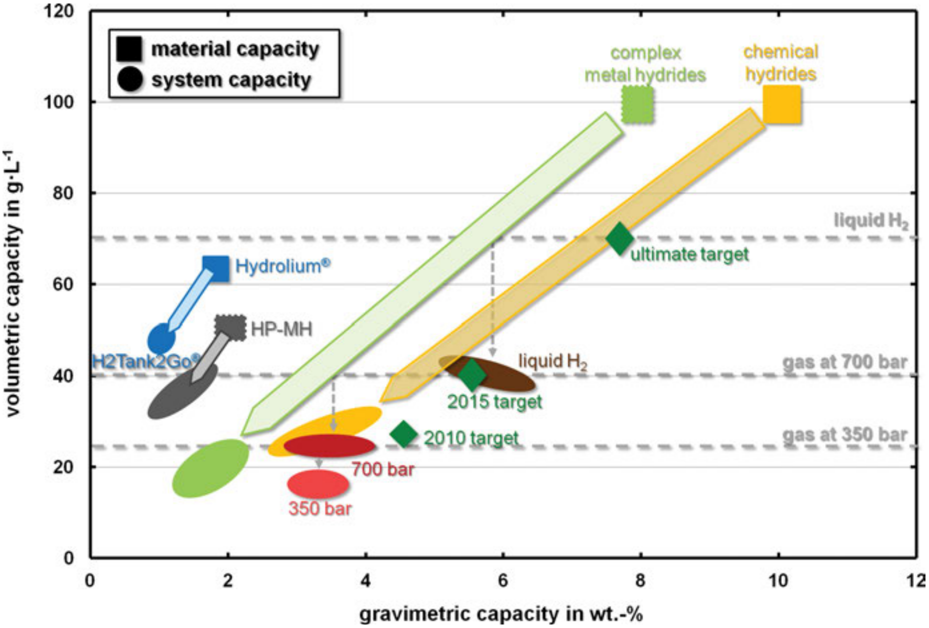

Fig. 17.9: Hydrogen storage systems – gravimetric and volumetric capacities [1].

only has a range of about 20–25 km. In 2012, at the next Hannover Fair, the advanced semi-serial version of the isigo®H2.0 with two H2Tank2Go® tanks, which now has a range of 120 km was presented (Fig. 17.10). Use of cryogenic or high-pressure tanks is not even conceivable for this type of mobility for safety reasons and due to the design.

A very high volumetric storage density and relatively high safety of the H2Tank2Go® cartridges are not the only advantages of this product. Another advantage is the very simple, and therefore, fast way to exchange the empty cartridges with full ones applying a click'n-go system. The actual loading of Hydrolium® powder with gaseous H_2 usually takes about 1 h (cf. Section 3.3.1). For this reason, although the metal hydride technology is superior to that of Li-ion batteries due to its storage density, the automotive industry generally has no particular interest in the metal hydride technologies. Here, a refueling on site would take too long and for the system itself, special cooling would be necessary, which would make the tank unnecessarily heavier and more expensive. The time to "refuel" the vehicle with the H2Tank2Go® using the click'n-go system takes just a few seconds, saving valuable time at the gas station. The H2Tank2Go® tanks can be purchased not only from gas stations, but also from mail-order companies or from a home depot. Another possibility would be the installation of vending machines at each gas station, where empty cartridges can be exchanged with filled ones mainly contributing to the very low hydrogen costs from the tank filling (Fig. 17.11).

This type of loading station could circumvent the problem of developing an H_2-infrastructure based on LH_2, which represents a major obstacle to the breakthrough of

Fig. 17.10: Isigo®H2.0 prototype with two H2Tank2Go® cartridges.

Fig. 17.11: Example for a vending machine for the exchange of H2Tank2Go® cartridges.

hydrogen-powered mobility. The vending machines can be placed anywhere more easily than the corresponding high-pressure hydrogen refueling systems, and would also be necessary for high-pressure gas storage tanks. This would allow the H2Tank2Go® and associated infrastructure to completely revolutionize the field of H_2 mobility.

17.4.2 Iron bird – modular system for mobile energy generation

Since Zoz GmbH is a relatively small company with limited resources, the step to finally turn this type of H_2 infrastructure revolution into reality is not possible without financial and technical assistance. That is how the H2-OnAir + project, a European cooperation project of the EUROGIA + initiative, a program aimed at all areas of the energy industry, from renewable energies to efficiency and the reduction of CO_2 emissions from fossil fuels, was born.

The main objective of the H2-OnAir + project is to equip a solar- and battery-driven aircraft with an additional fuel cell range extender to increase the range to at least three times the current value (in periods of no sunshine from 33 to >100 km). This is to prove that H_2 is a serious candidate for the primary power supply of clean aviation. If the project is successful, the next step is its application to the electric car mobility and finally to all personal transportation systems.

The hydrogen-powered fuel cell range extender functions as an onboard charging station for the existing Li-ion battery and, for cost, performance and weight reasons, is made up of several H2Tank2Go® hydrogen tanks that produce power in conjunction with PEM fuel cells (PEM-FCs). A dual system of 2 kW fuel cell stacks is used to ensure a rated power of 4 kW. The total weight of the range extender should not exceed 50 kg. All H2Tank2Go® tanks have the same quick release system.

This project is based on the aircraft platform Icaré 2 (Fig. 17.12) of the University of Stuttgart, which is operated today in cooperation with SEIKO [25]. Icaré 2 was built for solar flight, which is why it was designed for extremely low power consumption under all flight conditions.

The typical energy requirement for a long-term flight is less than 2 kW electrical power. For the start, the electric motor needs up to 14 kW, which is provided by a rechargeable battery system. Icaré 2 is, due to its low power consumption, especially at cruising altitude, an ideal test platform for new energy systems. In addition, Icaré 2 includes all features such as low energy consumption, solar generator and battery system for future flight platforms, and other transport platforms.

Currently, batteries have a recharge time. To this end, Zoz GmbH developed the *Iron Bird* as a mobile range extender (Fig. 17.13). Here, six H2Tank2Go® are used as energy storage in a manageable small energy pack, and these can be exchanged empty for full, within seconds, if necessary, as described in Section 4.1.

Fig. 17.12: Icaré 2 – record aircraft powered by solar power [25].

Fig. 17.13: Iron Bird, range extender for electromobility [26].

The Iron Bird can be carried in almost any trunk of a battery car, and the battery can be recharged by hydrogen generated electricity constantly (Fig 17.14). The Iron Bird, today, would be more like a reserve canister than a power plant [26].

Fig. 17.14: Modular system of the iron bird containing H2Tank2Go®.

17.4.3 Fuel cells

Fuel cells are the centerpiece of electromobility and work exactly the other way around as the electrolytic cell.

As of today, only cost-effective fuel cells for economic efficiency are missing, which are to be developed with several partners from industry and academia in the LOCOPEM joint project [27–29]. The iron bird does not represent the future, but a bridge to the future, in order to overcome short distances without significant loading times.

Project "LOCOPEM" (low-cost gas diffusion electrodes for PEM fuel cells), funded by the state government of North Rhine Westphalia, aims at significant cost reduction in PEM fuel cell production. A technology that contributes to the reduction of catalyst material inside the MEAs (membrane electrode assembly) should be developed. With PEM fuel cells, currently, platinum (nano)particles supported by graphite are used most to catalyze the reactions on both electrodes. The critical reaction takes place where the gas-flow of H_2 (anode) and O_2 (cathode) meets the catalyst layer, which is electrically connected to the gas-diffusion layer (GDL), the bipolar plates, and the proton conducting membrane. This leads to an increase of costs of the whole PEM-FC as the fraction of active catalyst-particles is very limited, and a lot of platinum is "wasted" as inactive catalyst-material. LOCOPEM directly addresses this problem by development of a new technology to significantly reduce the amount of inactive Pt particles retaining (and even increasing) the fraction of active catalyst material [30].

Therefore, the GDL, and not the membrane, is coated with the catalyst by means of carbon nanotubes and carbon nanofibers, which are deposited onto the GDL via high-velocity oxygen fuel spraying. Afterward, platinum (or other substitutes) are brought onto the carbon nanotubes/carbon nanofibers by pulsed electroplating before the newly formed gas diffusion electrodes are hot-pressed together with the membrane to build up MEAs. As this procedure will be developed with the aim of an easy up-scale to industrial production, LOCOPEM targets to significantly reduce the costs of fuel cell production, thus contributing to the hydrogen economy as a whole [30].

All these attempts should lead to an efficient use of hydrogen as fuel for cost-efficient, ecological, and economical electromobility.

17.5 Power to gas to fuel® – sustainability in hydrogen form

The Zoz GmbH has proposed a kind of demonstration power plant, which includes as an alternative, and as part of the P2G concept also, the possible methanation of hydrogen with CO_2 gas (Figs. 17.15, 17.16, 17.17) [1]. The methane gas produced in this way could be stored in the existing natural gas grid.

Although all the components of the proposed concept already exist, its technical realization is economically inefficient, as it cannot compete with the established technology based on fossil fuels in terms of household power supply. In the near future, this scenario can only be economical if gasoline is replaced by hydrogen technology for mobility.

In order to avoid the complex and expensive construction of a high-pressure H_2 infrastructure in this context, the P2G2F® approach with H2Tank2Go® or the use of solid H_2-storage systems could make a major contribution to the energy transition.

The concept of P2G2F®, thus, goes through several phases in the field of energy generation, energy storage, and energy consumption, in the context of electric mobility. All aspects along a value chain are considered here. It is essential for the entire concept and its sustainability that the entire processes run absolutely without the use of fossil fuels.

The company Zoz GmbH was nominated for the concept P2G2F® 2013 for the annually awarded "German Environmental Award" of the German Federal Environmental Foundation (DBU) by "Die Familienunternehmer," (Fig. 17.18) an association that represents the economic interests of 180,000 family entrepreneurs – ASU e. V. in Germany, which employs a total of about eight million employees subject to social security [https://www.familienunternehmer.eu/].

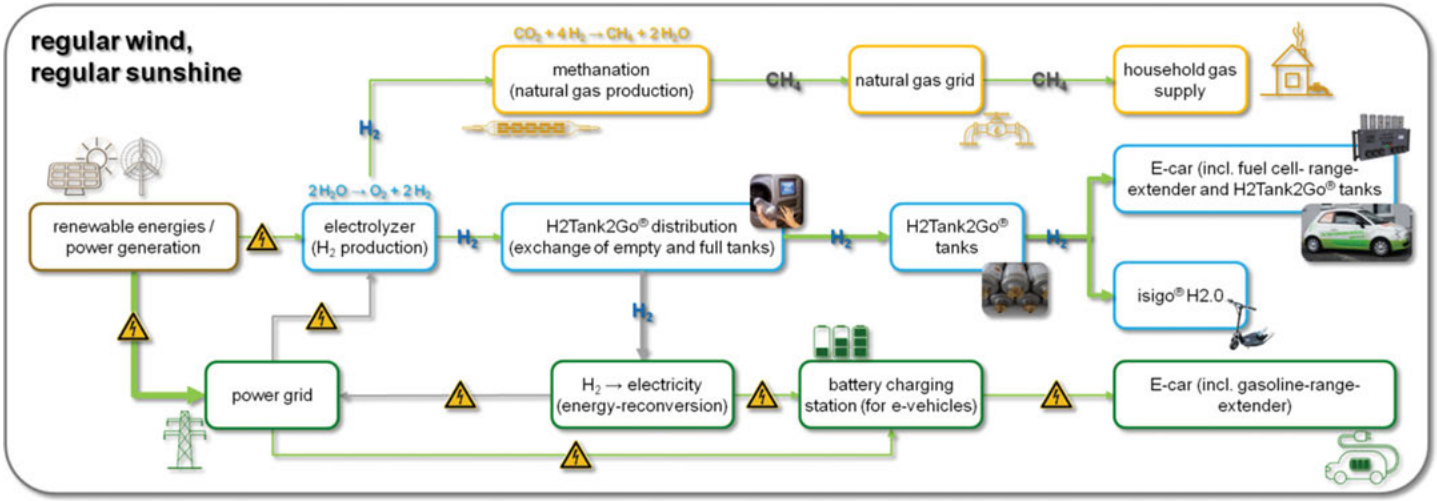

Fig. 17.15: P2G2F® power plant scheme, normal conditions, adapted from [1].

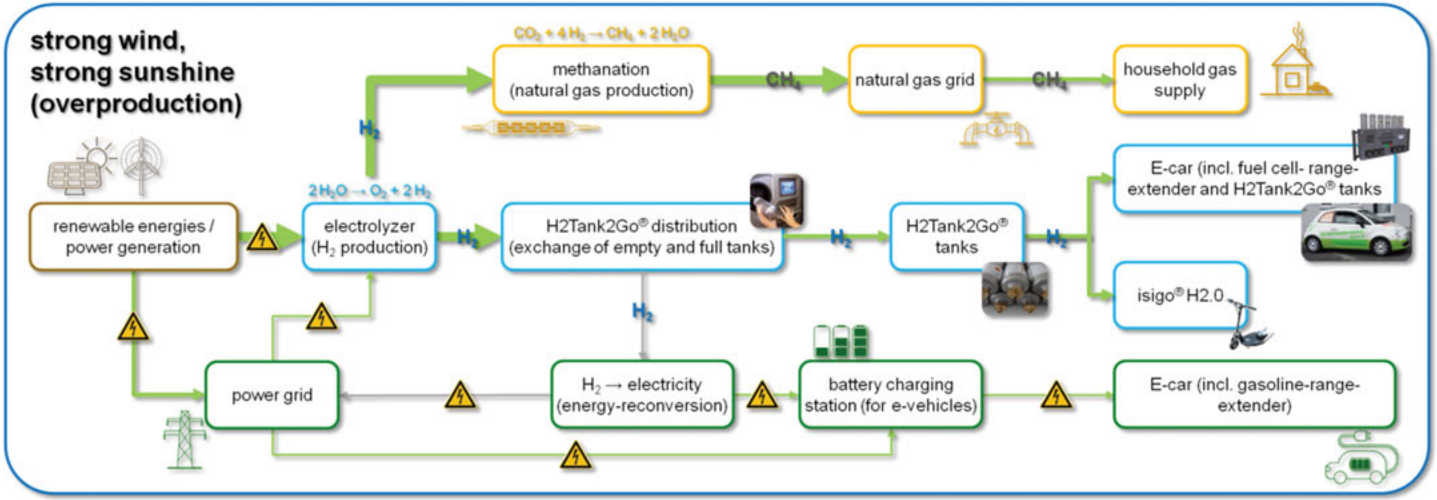

Fig. 17.16: P2G2F® power plant scheme, overproduction, adapted from [1].

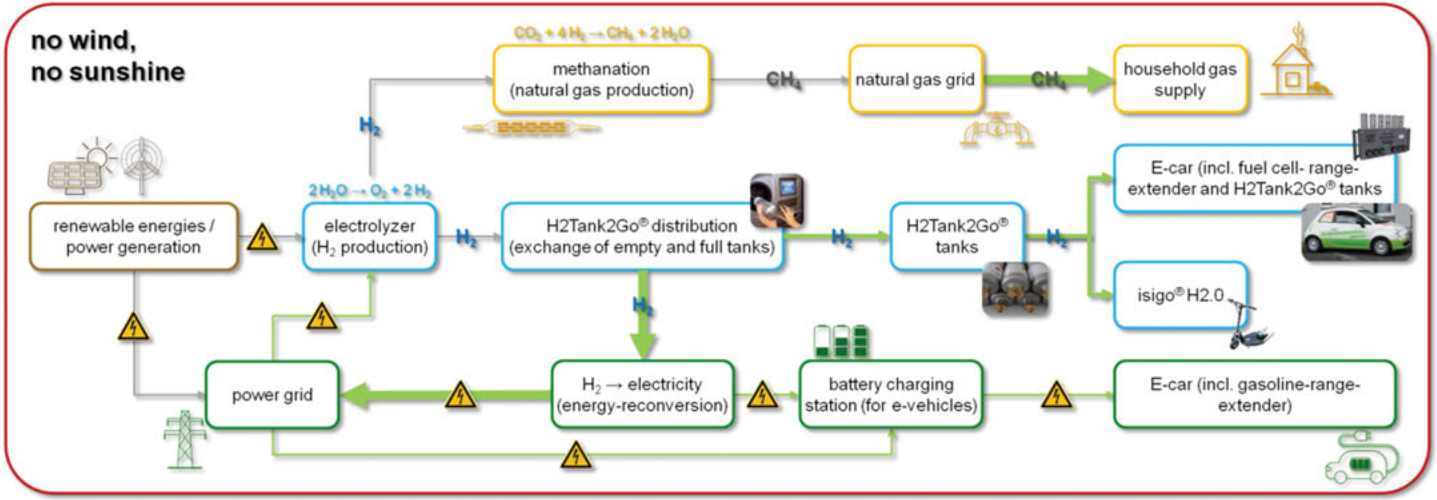

Fig. 17.17: P2G2F® power plant scheme, undersupply from renewable energies, adapted from [1].

Fig. 17.18: Nomination for the “Deutscher Umweltpreis” from the “Deutsche Bundesstiftung Umwelt” in 2013, nominated by Die Familienunternehmer – ASU e.V.

17.6 Summary

“P2G2F®” is an all-embracing concept for using renewable energy for electromobility, with hydrogen as fuel. This is shown by the fact that research in all sub-areas of the concept still continues, and there is also further high research potential. In addition to efficient systems for generating renewable energy, efficient systems for industrial hydrogen production must be developed. The existing hydrogen storage technology has come farther than a few years ago, but once again, the potential has not yet been fully exploited and higher capacity storage materials could be developed. These can then be used by both mobile and stationary users. At the end of the chain is the implementation of hydrogen in mobile systems. The development of high performance and, above all, affordable fuel cells is essential here, to enable the economic use of hydrogen as fuel. Nevertheless, it remains undisputed that hydrogen is the energy storage and sustainable fuel of the future.

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Marcel Van de Voorde, Paolo Ciambelli

Conclusions and Recommendations: “The Future of Hydrogen”

The book series at hand analyzes the current state of affairs for hydrogen and offers guidance on its future development.

Hydrogen is currently enjoying unprecedented momentum, with the number of policies and projects around the world expanding rapidly. Together with renewable electricity, hydrogen constitutes the major energy vector substituting the use of fossil fuels, and its large-scale introduction could be the point of no-return in transformation to a sustainable and climate change responsible for society and economy. The combination of serious concerns about our changing climate, which are aggravating every month, and the economic emergency triggered by the pandemic provide the hydrogen industry with a unique opportunity to participate fully in the ongoing energy transition.

Japan and South Korea were forerunners in designing development plans based on hydrogen, but in the latest months Europe has clearly implemented a strategy to be at the forefront in the world for the energy transition, assigning to hydrogen a fundamental role in the race to reach a climate-neutral and zero-pollution economy in 2050. Several European countries have now initiated strategies aiming at promoting their competitive advantage (wind energy in Northern Europe, photovoltaics (PV) in Southern Europe; usage and deployment in industry and transportation in Northern and Central Europe; diverse methods of decarbonization in the Netherlands and Scandinavia). China’s President Xi Jinping announced last September the objective of a pledge to achieve carbon neutrality before 2060, and it remains to be seen whether China will really intend to overcome its persistent hesitation (as presently the largest carbon emitter), for a policy addressed to decarbonize their coal-based hydrogen production. On the other hand, China currently gives Asia a head start in the upcoming electrical mobility market based on batteries or hydrogen.

Moreover, the major energy players in the Middle East are now looking very seriously at hydrogen as a potential carrier of fossil fuels decarbonization, subject to development of carbon sinks, whether through capture and sequestration (carbon capture and storage) or through storage and reuse (carbon capture and utilization, CCU). Australia has the same approach, and projects are already well underway with its main Asian energy partners.

Finally, the United States is currently a home to the world’s largest pool of fuel cell electric vehicles and forklift trucks (more than 30,000 already operational), with a lead from the US pioneering state, California. But political differences stand in the way of a nationwide scale-up. Yet, the biggest companies active in relevant technologies, and some of the most advanced and valuable start-ups, are developing on the American

https://doi.org/10.1515/9783110596274-026

soil. All that is missing for the rest of the industrial world to embark is, finally, in a unified and proactive policy on hydrogen's silent and virtuous revolution that is presently emanating from the United States.

The book series provides an extensive and independent survey of hydrogen that lays out where things stand now; the ways in which hydrogen can help to achieve a clean, secure, and affordable energy future; and how we can proceed to harvest its full potential. As the ultimate goal is the realization of a revised, much more comprehensive concept of the "hydrogen economy", the overview is not only limited to technical aspects, to allow scientists, company managers, policy makers, and society as well to better understand this fast-moving area in terms of technologies but also of possibilities, thereby offering a privileged glimpse into the future.

The world should not miss this unique chance to make hydrogen an important part of our clean and secure energy future.

Where is today's starting point to achieve cost reduction, hydrogen usage adoption in new sectors, such as transport, buildings, and power generation, and shifting to clean, hydrogen-based industrial processes? Clearly, these three aspects are strictly related. Supplying hydrogen to industrial users is now a major business around the world, and the demand for hydrogen has grown more than threefold since 1975 and continues to rise (about 70 million tons in 2019). Hydrogen use today is dominated by industry, namely, oil refining, ammonia production, methanol production, and steel production. However, it is almost entirely supplied from fossil fuels: about 6% of global natural gas use being currently the primary source of hydrogen production, accounting for around three quarters of the annual global dedicated hydrogen production, and about 2% of global coal go to hydrogen production. As a consequence, this production of hydrogen (termed *grey* H_2) is responsible for CO_2 emissions of around 830 million ton/year, equivalent to CO_2 emissions of a country such as Germany.

A range of technical and economic factors influences the production cost of hydrogen from natural gas, with gas prices and capital expenditures being the two most important ones. Fuel costs are the largest cost component, accounting for between 45% and 75% of production costs. Low gas prices in the Middle East, Russia, and more recently North America (shale gas) give rise to some of the lowest hydrogen production costs. Gas importers like Europe, Japan, Korea, China, and India have to contend with higher gas import prices, resulting in higher hydrogen production costs.

In contrast to the hydrogen production from fossil fuels, today less than 0.1% of global dedicated hydrogen production comes from water electrolysis, since producing hydrogen from low-carbon energy is costly at the moment. With declining costs for renewable electricity, in particular from solar PV and wind, interest is growing in electrolytic hydrogen, and there have been several demonstration projects in recent years. In particular, building electrolyzers at locations with excellent renewable resource conditions could become a low-cost supply option for hydrogen, even after taking into account the transmission and distribution costs of transporting hydrogen from (often remote) renewable locations to the end-users.

The cost of producing hydrogen from renewable electricity could fall 30% by 2030 as a result of declining costs of renewables and the scaling up of hydrogen production. This forecast supports the position that the energy transition should be strongly accelerated toward the production of "clean" (*green*) hydrogen from water as hydrogen source (water splitting process), and solar PV and wind as renewable energy drivers. Even more ambitious and integral is the view that the acceleration should be directed right away to the production of the *green* hydrogen by "artificial photosynthesis," that is, directly from solar energy without the intermediate production of renewable electricity.

The last mentioned option of direct hydrogen production is pursued in research laboratories around the world at a much lower technological readiness level; similarly, the ramping up of renewable electricity production will still require time. Consequently, it appears mandatory to invest today in producing so-called *blue* H_2. One pathway for the latter is driving electrolyzers for water splitting with a CO_2-free electricity mix that may include nuclear energy. A dedicated *local* electricity generation from renewables or nuclear power offers an alternative to the use of *grid* electricity for this production route of hydrogen. The second approach to produce *blue* hydrogen starts from fossil fuels, coupled to carbon sequestration. This strategy opens up a way to enable still the use of fossil fuels and constitutes an effective and presently available positive step paving the way for the transition to a "hydrogen economy." The associated momentum appears to outweigh concerns that the latter approach would result in a delay of implementing *green* hydrogen.

A parallel discussion deals with storage/transportation of H_2 (pressurized, liquefied, or mixed with natural gas via gas pipelines). Indeed, the distribution as a mixture with methane, with the highest potential in multifamily and commercial buildings, particularly in dense cities, can be seen as an effective solution or a way to promote the co-use of hydrogen and natural gas, while longer term prospects could include the direct use of hydrogen in hydrogen boilers or fuel cells. It is worth remembering that an alternative solution, strongly sustained in Japan, is the use of H_2 carriers (ammonia or liquid organic hydrogen carriers, for example), which could really enable a world-scale "hydrogen economy" available to all countries.

What is missing is a real debate about pros and cons, sustained by independent studies. These should address in detail the costs, especially providing predictions of their future changes, discuss technology barriers, and assess how fast they could be overcome.

With reference to transport, the competitiveness of hydrogen fuel cell cars depends on fuel cell costs and the accessibility of refueling stations, while for trucks the priority is to reduce the delivered price of hydrogen. Shipping and aviation have limited low-carbon fuel options available and represent an opportunity for hydrogen-based fuels.

In power generation, hydrogen is one of the leading options for medium- and long-term storage of renewable energy, and hydrogen and ammonia can be used in gas turbines to increase power system flexibility. Co-firing of ammonia in coal-fueled power plants could also help reduce CO_2 and pollutant emissions.

Referring to the future of hydrogen a great focus on safety issues is necessary, not only about the actual safety level of systems but also about its perception in the public eyes, mostly relying on training, education, and public awareness. The risks related to hydrogen do not change in nature with its wider distribution but the rapidly widening reach will generate significant demand for skills, projects, and players who will need to acquire know-how rapidly, which certainly requires more specific "hydrogen energy" training courses at universities and technical colleges. It is critical to set and harmonize rules and norms to ensure that equipment needed to roll out hydrogen technology is operated to the strictest safety standards.

This book series did not aim at giving definite answer to the various questions mentioned. Rather, it presents the state of the art, accounts for advanced research, outlines development perspectives, and proposes road maps toward the "hydrogen economy." It provides clues to analyze all aspects dealing with the future of hydrogen and should thereby support decision makers in their quest which scientific and technological aspects should be investigated, which opportunities exist for companies, or which political strategies should be chosen.

Practical opportunities at near term can be summarized as follows:

1. **The time is right to tap into hydrogen's potential to play a key role in a clean, secure, and affordable energy future.**
   Scale up technologies and bring down costs to allow hydrogen to become widely used. Pragmatic and actionable recommendations provided to governments and industry will make it possible to take full advantage of this increasing momentum.
2. **Hydrogen can help tackle various critical energy challenges.**
   Decarbonize a range of sectors, including long-haul transport, chemicals, and iron and steel industry, where it is proving difficult to achieve substantial emission reductions.

   This achievement can also help improve air quality and strengthen energy security.
3. **Hydrogen is versatile.**
   Wide variety of pathways and fuels being available to produce hydrogen, including renewables, nuclear, natural gas, coal, and oil.

   Hydrogen can be transported as gas by pipelines or in liquid form by ships, much like liquefied natural gas. It can be transformed into electricity and methane to power homes and feed industry, as well as into fuels for cars, trucks, ships, and planes.
4. **Hydrogen can enable renewables to provide an even greater contribution.**
   H_2 as the leading option for storing energy from renewables.

   Hydrogen appears to be promising to become the lowest cost option for storing electricity over days, weeks, or even months. Hydrogen and hydrogen-based fuels can transport energy from renewables over long distances – from regions with abundant solar and wind resources to energy-hungry cities thousands of kilometers away.

5. **New technologies are becoming available.**
   Impressive advances of solar PV, wind, batteries, and electric vehicles.

   These successes have shown that policy and technology innovation has the power to build global clean-energy industries. The versatility of hydrogen is attracting stronger interest from a diverse group of governments and companies. Support is coming from governments that both import and export energy, from cities, as well as renewable electricity suppliers, industrial gas producers, electricity and gas utilities, automakers, oil and gas companies, and major engineering firms. Investments in hydrogen can help foster new technological and industrial development in economies around the world, creating skilled jobs.
6. **Hydrogen can be used much more widely.**
   Hydrogen penetrating into all sectors of the economy, enabling their coupling. Today, hydrogen is used mostly in oil refining and for the production of fertilizers. For it to make a significant contribution to clean energy transitions, it also needs to be adopted in sectors where it is almost completely absent at the moment, such as transport, buildings, and power generation.
7. **International cooperation is vital to accelerate the growth of versatile, clean hydrogen around the world.**
   Governments working together to scale up hydrogen in a coordinated way.

   This would help to spur investments in factories and infrastructure that will bring down costs and enable the sharing of knowledge and best practices. Trade in hydrogen will benefit from common international standards. As the global energy organization that covers all fuels and all technologies, the International Energy Agency(IEA) will continue to provide rigorous analysis and policy advice to support international cooperation and to conduct effective tracking of progress in the years ahead.

Clean, widespread use of hydrogen in global energy transitions faces several challenges:

- **Hydrogen is almost entirely supplied from natural gas and coal today.**
  Hydrogen is already in use at large industrial scale all around the world but its production is responsible for substantial CO_2 emissions.
- **Producing hydrogen from low-carbon energy is costly at the moment.**
  The cost of producing hydrogen from renewable electricity could fall 30% by 2030, as a result of declining costs of renewables and the scaling up of hydrogen production.
- **The development of a hydrogen infrastructure is slow and holding back widespread adoption.**
  Hydrogen prices for consumers are highly dependent on how many refueling stations are available, how often they are used, and how much hydrogen is delivered per day. Tackling this issue is likely to require planning and coordination that brings together national and local governments, industry, and investors.

- **Regulations currently limit the development of a clean hydrogen industry.** Government and industry must work together to ensure that existing regulations are not unnecessary barriers to investment. Trade will benefit from common international standards for the safety of transporting and storing large volumes of hydrogen, and for tracing the environmental impacts of different hydrogen supplies.

Key recommendations to help governments, companies, and others to seize this chance to enable clean hydrogen to fulfill its long-term potential:

1. **Establish a role for hydrogen in long-term energy strategies.** European national and regional governments can guide future expectations. Companies should also have clear long-term goals. Key sectors include refining, chemicals, iron and steel, freight and long-distance transport, buildings, power generation, and energy storage.
2. **Stimulate commercial demand for clean hydrogen.** Clean hydrogen technologies are available but costs remain challenging. Policies that create sustainable markets for clean hydrogen, especially to reduce emissions from fossil fuel-based hydrogen, are needed to underpin investments by suppliers, distributors, and users. By scaling up supply chains, these investments can drive cost reductions, whether from low-carbon electricity or fossil fuels with CCU (carbon capture and utilization).
3. **Address investment risks of first-movers.** New applications for hydrogen, as well as clean hydrogen supply and infrastructure projects, stand at the riskiest point of the deployment curve. Targeted and time-limited loans, guarantees, and other tools can help the private sector to invest, learn, and share risks and rewards.
4. **Support R&D to bring down costs.** Alongside cost reductions from economies of scale, R&D is crucial to lower costs and improve performance, including investigations of fuel cells, hydrogen-based fuels, and electrolyzers (the technology that produces hydrogen from water). Government actions, including use of public funds, are critical in setting the research agenda, sharing risks, and attracting private capital for innovation.
5. **Eliminate unnecessary regulatory barriers and harmonize standards.** Project developers face hurdles where regulations and permit requirements are unclear, unfit for new purposes, or inconsistent across sectors and countries. Sharing knowledge and harmonizing standards are key, including norms for equipment, safety rules, and certification of emissions from different sources. Hydrogen's complex supply chains imply that governments, companies, communities, and the civil society need to consult regularly.
6. **Engage internationally and track progress.** Enhanced international cooperation is needed across the board but especially on standards, sharing of good practices, and cross-border infrastructure. Hydrogen

production and use need to be monitored and reported on a regular basis to keep track of progress toward long-term goals.

It is clear that the hydrogen technology will reach great challenges in future with focus on:
i) promotion of research, development, and new technologies;
ii) support of governments with respect to infrastructure, regulations, and uprising new companies;
iii) impact and encouragement of the society to accommodate the emerging renewable energy world.

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