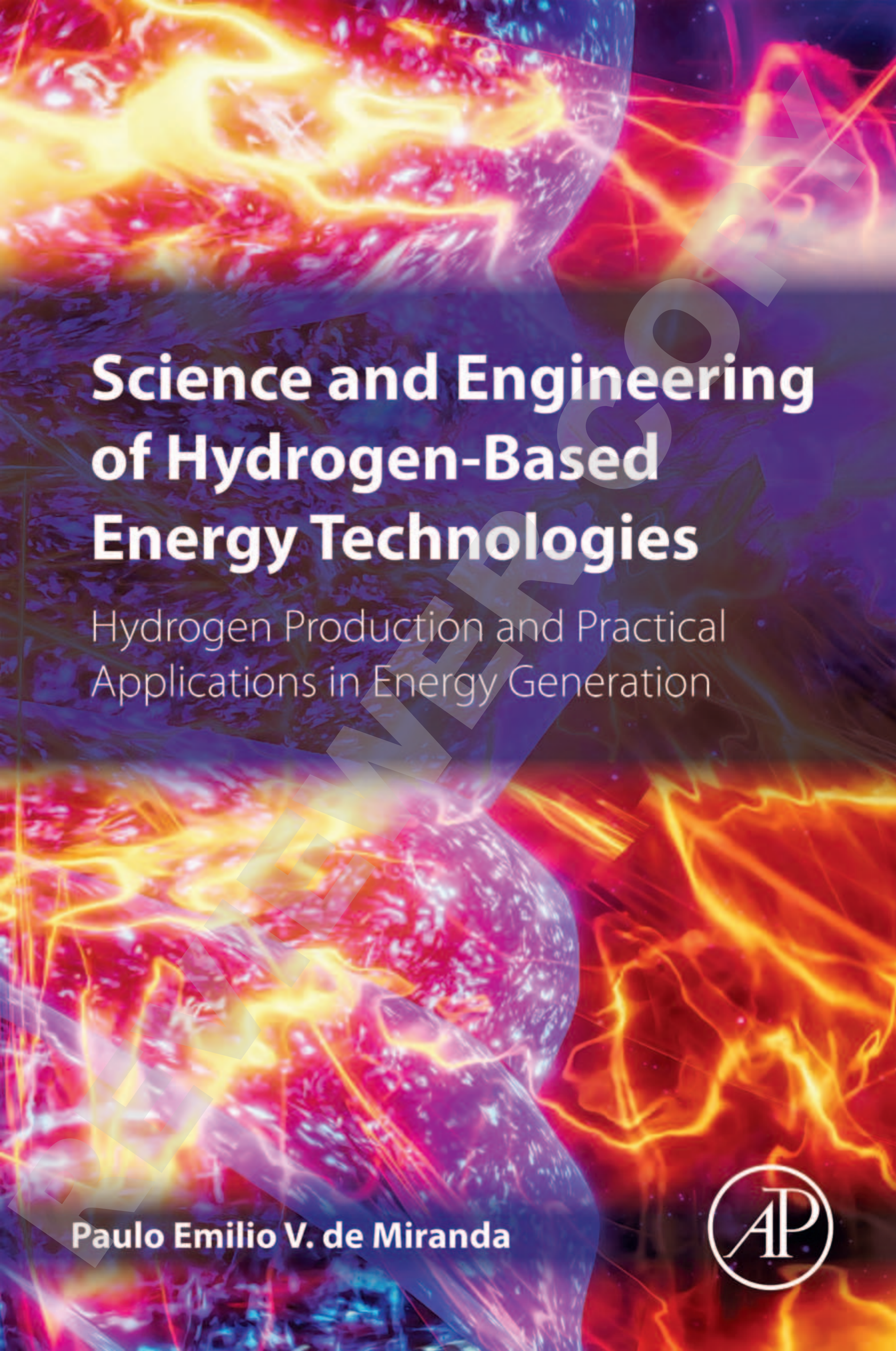

Science and Engineering of Hydrogen-Based Energy Technologies

Hydrogen Production and Practical Applications in Energy Generation

Paulo Emilio V. de Miranda

Science and Engineering of Hydrogen-Based Energy Technologies

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Hydrogen Production and Practical Applications in Energy Generation

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Foreword

I am delighted to write this foreword, not only because Paulo Emílio V. de Miranda has been a friend and colleague for the past several years, but also because I strongly believe in the way he has been serving in the areas of science and engineering of hydrogen-based energy technologies. Interestingly, the title of this edited book has become the same. Paulo has tried his best to bring the key people on board to contribute to this edited book with their distinct chapters, covering basic aspects of hydrogen and hydrogen energy, fuel cells, hydrogen production methods, energy storage via hydrogen storage, hydrogen transportation, hydrogen stations, hydrogen deployment, hydrogen energy engineering practices and demonstrations, hydrogen energy policies, hydrogen energy roadmaps, hydrogen safety, hydrogen marketing, etc.

This book has educative and training values of interpretive discussions in many subjects for all readers, including students, engineers, practitioners, researchers, scientists, etc. I am sure this book will inspire many young and senior people to advocate about hydrogen energy for sustainable economies. The specific details and discussions on every specific topic make this particular book even more appealing to all readers in every age group. In addition, there is a remarkable set of science-related material in every hydrogen-related subject to emphasize the importance of the applied nature of science. Furthermore, there is huge engineering-related material from A to Z type covering entire spectrum of hydrogen energy from the production to the deployment in various sectors, ranging from residential to industrial and from industrial to utility sectors.

In closing, I am quite satisfied with the authorship of each specific subject and the material presented as well as the science- and engineering-related examples and case studies tailored for the readers, and I am sure that this will be an excellent asset to the hydrogen energy literature.

Last, but not least I warmly congratulate Paulo and his contributors who have brought this unique edited book to fruition.

Prof. Dr. Ibrahim Dincer
Vice President for Strategy
International Association for Hydrogen Energy
Vice President, World Society of Sustainable Energy Technologies

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Preface

The world is experiencing its steepest ever-observed growth of energy consumption and population. These two factors coupled with progressively growing urbanization rates at very high levels have threatened the planet and life on it. This has motivated the vision of a sustainable society capable of implementing the creative and innovative concept of a circular restorative economy. Such a vision can be implemented only by transitioning to a new energy era in which hydrogen and renewable energies play a main role. Hydrogen energy is about utilizing hydrogen and hydrogen-containing compounds to generate and supply energy for all practical uses with high-energy efficiency, overwhelming environmental and social benefits, and economic competitiveness. The implementation of hydrogen energy for widespread utilization requires the use of currently available technologies that resulted from intense long-lasting scientific developments involving fuel cells, hydrogen production methods, selection of specific application options, safety and regulations, policies and planning for early adoption, as well as market introduction.

The dawn of hydrogen energy, which brought the practical deployment of sustainable devices and mobility, called for the present text on science and engineering of hydrogen-based energy technologies. Its content was structured in such a way that both knowledgeable professionals in the area, as well as newcomers possessing a strong basis on engineering, energy, or sustainability, will be attracted and interested.

The general approach to hydrogen energy establishes a broad vision of technological possibilities and future prospects. It explores emerging technologies to show that additional efficiency gains and environmental benefits will be progressively achievable as conventional technologies are surpassed. Upon unveiling the occurrence of natural hydrogen on earth, once believed nonexistent, hydrogen energy was presented as sustainable and perennial.

Fuel cells are deeply discussed, with an emphasis on polymeric membrane electrolyte fuel cells and on solid oxide fuel cells and their technological variants, either to generate electrical energy or to consume it for hydrogen production, independently or reversibly.

Biomass is one of the major renewable sources for energy generation and acts as a natural medium for sunlight energy storage. Its enormous availability as residues and wastes (agricultural, industrial, domestic household, municipal) makes its energetic use very beneficial to society. Focus on the production of hydrogen from biomass through biological routes using fermentation processes, in special dark fermentation, is provided.

The progressive increase in the use of renewable energies, which represents the main future prospects of countries and regions for environmental and energy-security reasons, motivates and facilitates the large-scale production of green hydrogen by water electrolysis. Electrolyzer technologies and hydrogen storage methods are thoroughly analyzed and discussed.

Hydrogen utilization applications from the dawning of the hydrogen energy era to the present include transitional technologies, such as the use of hydrogen as fuel in turbines and internal combustion engines. However, the use of hydrogen to feed fuel cells will ubiquitously dominate engineering, mobile, and stationary applications. These options are explored and exemplified with emphasis on technological and engineering procedures.

New regulations, codes, and standards (RC&S) and the adaptation of existing codes are necessary to introduce such technologies into use by the society. This also requires thoroughly understanding and systematizing the roles of the different active regulating institutions as well as establishing and guaranteeing safety protocols. RC&S, metrology, and safety are defined and understood within the ample variety of official world and regional active actors.

Hydrogen may be made available in different world regions depending on local specificities. Also, early deployment of hydrogen energy technologies may be based on niche applications for a specific society. It results that identifying suitable sectors, actions, timing and actors is mandatory for planning and to create adequate policies. Roadmapping techniques were defined, exemplified and discussed as an important tool to make the necessary transition to the hydrogen energy era.

Most of hydrogen, effectively produced in large scale, has a captive use as a chemical product. To be traded as a world energy commodity and also in order to guarantee the market entrance of hydrogen-based technologies, alternative approaches to determining total cost of ownership must be adopted. This approach is explored by taking into consideration externalities associated with the use of conventional technologies that include hidden costs of environmental and societal damage.

I apologize for not being able to include so many other topics of interest, and I hope the selected content will fill the gap of scientific and technological information to understand and foster engineering applications of hydrogen-based energy technologies.

Rio de Janeiro
Brazil, June 2018
Paulo Emílio V. de Miranda

Chapter 1

Hydrogen Energy: Sustainable and Perennial

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OVERVIEW

Hydrogen energy unveils perennial and sustainable energy production and utilization methods to fulfill all needs required by the human society. It represents an opportunity to utilize a great possible variety of raw materials and an energy source, such as electricity, heat, or mechanical work, to obtain fuel to be used in energy-efficient devices and therefrom to generate the same energy elements, such as electricity, heat, or mechanical work, with very limited noise and no aggressive wastes. This circular path concerning energy production and use had not been achieved and made possible for large-scale utilization until the advent of hydrogen energy became a reality.

The adoption and implementation of hydrogen energy makes more clean and sustainable energy available and introduces the creative and innovative concept of a circular economy, restorative by nature. This requires the use of intermittent renewable energy and the adequate control of seasonal energy storage. It also calls for a transition from the present fossil fuel—based energy system that is hitherto characterized for being structured in such a way that it possesses fuel ownership spotted in selective geographical locations, that it presents growing consumption of known reserves to depletion, that its exploitation devastates the environment, and that its utilization is made using energy-inefficient and pollutant engineering procedures and technologies. Such transition is able to create a system that is based on renewable energies, such as hydroelectric, solar, wind, geothermal, and oceanic energies, and is also based on a host of raw materials as source of the energy carrier that includes water and virtually any type of biomass. It makes the selection of primary energy and raw material to be adopted under judicious local possibilities and the possession of fuel to be widely distributed throughout the world, potentially decreasing concentrated ownership for market control. It also introduces the utilization of the most efficient energy converter known,

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the fuel cell. It abandons the sequential and inefficient conversion of energy forms used by heat engines, turbines, and motors, to make the direct, unique, and highly efficient electrochemical energy conversion of the chemical energy contained in the fuel into electric energy and heat, thereby producing water.

Other energy transitions have been experienced before. Since several thousand centuries ago, biomass, mainly wood, has been used as a source of energy, and watermills and windmills were known since several thousand years ago. Renewable energies and fuels dominated the scene for the period the human kind continuously developed to enter modern times. A transition to the fossil fuel era was made with the use of coal and the steam engine and characterized the Industrial Revolution from the 18th century. The peak supply of world energy with wood occurred around 1850 and that of coal to transition to petroleum happened by 1930. The internal combustion engine was the invention that accelerated the use of oil derivatives and the supply of world energy with oil peaked in 2000. Curiously, the world's first automobile powered with an internal combustion engine used hydrogen as fuel, which was designed and demonstrated by François Isaac de Rivaz in 1806. Due to political and economic crises related to the commercialization of oil, since the years 1970 the consumption of natural gas increased steadily and is expected to peak by 2050, when the hydrogen economy will be installed and will have paved the way to take the world lead for energy supply. The transition from one fuel to another has not eliminated the use of previous ones. Instead, their utilization has been superimposed with progressive higher amounts. Wood, coal, oil, and natural gas are all simultaneously supplied, as well as the electricity from hydropower, nuclear, thermal, and geothermal plants. In complement to that, much electricity is also generated using modern windmills and photovoltaic solar cells.

It is remarkable to observe what the fuel transitions are able to tell. Wood is chemically more complex and has smaller specific energy (20.6 MJ/kg) than coal (23.9 MJ/kg). Conversely, coal is also chemically more complex and has smaller specific energy than oil (45.5 MJ/kg), which, in turn, repeats this trend with natural gas (52.2 MJ/kg). In addition to that, one may observe that there is an ongoing progressive decarbonization of fuels. The carbon content decreases from wood, to coal, to oil, to natural gas. It is also amazing to realize that the content of hydrogen increases continuously from wood, to coal, to oil, to natural gas, to reach the ultimate, perennial, and carbon-free fuel, hydrogen, for which specific energy equals 142.2 MJ/kg for its high heating value. Fig. 1.1 shows the carbon to hydrogen ratio for selected fuels that demonstrates the spontaneous decarbonization that is taking place, as our society aggregates new fuels to massive utilization [1]. Wood, not shown in Figure 1, has an average carbon to hydrogen ratio of 0.68. Among these, ethanol is usually obtained as a biofuel, made in large scale from sugarcane in Brazil and from corn in the United States. In this case, the photosynthesis process that consumes CO_2 from the environment during crop growth compensates the

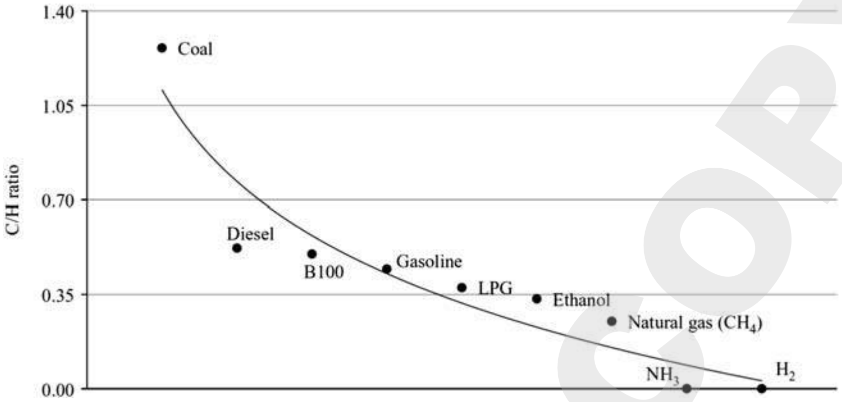

FIGURE 1.1 Carbon to hydrogen ratio in selected fuels. Reproduced from [1].

waste carbon resultant from its utilization for energy production. It is noticeable that the use of clean hydrogen and, eventually, ammonia does not involve carbon emission.

The ability to harvest fuels of all types and the talented development of ingenious forms for utilizing them have resulted in very steep, ever-growing, world fuel consumption since the Industrial Revolution. This is depicted in Fig. 1.2 and shows that while the world needed an annual energy delivery of 43.5 EJ for all needs in the year 1900, about 575 EJ was required for the year

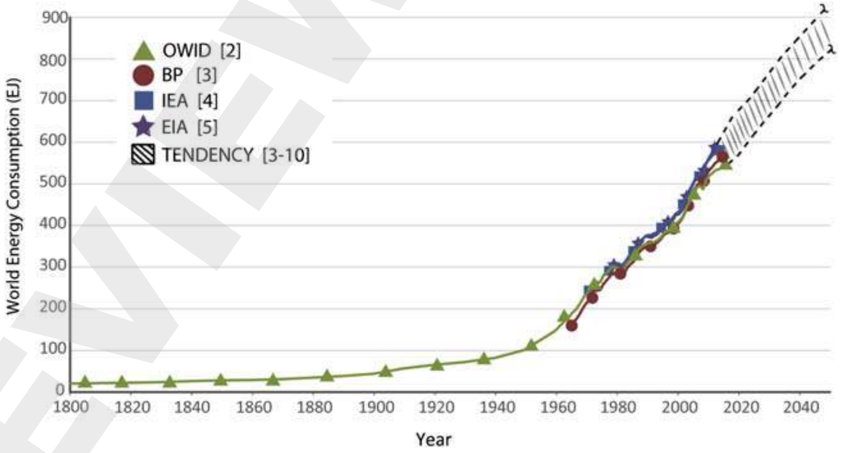

FIGURE 1.2 World energy consumption. 1 EJ is equal to 10^{18} J. It is approximately the energy contained in 7 million tons of gaseous hydrogen or in 170 million barrels of oil. The historical data to the present was gathered from [2–5], including data started in 1800 [2] and the curves showed closed together depicting values for the second half of the twentieth century to the present [3-5]. The shaded area presents extrapolations gathered from [3–10].

2016 and the amazing amount of 760 EJ is expected to be necessary for the year 2040. The later result is deduced using data from several different origins, which were extrapolated based on their historical series of actual measurements.

This is pushed by a five- to sixfold increase in world population in the total period mentioned, but also because of the widespread use of energy for food production, storage, and distribution, for all sorts of vehicles, appliances, and devices, as well as for closed ambient heating or cooling, which has raised the level of practical, comfortable, and healthy living. However, life on the planet and the planet itself were threatened by such a huge kinetics of liberation to the environment of the carbon contained in fossil fuels, producing greenhouse effect gases and other contaminants.

The world has collectively awakened to worries regarding the environment during the United Nations' 1992 Conference on Environment and Development (Rio-92). An analysis made of the world environmental situation before that moment and from it onto the present shows alarming results, as depicted in Fig. 1.3 [11]. Although the use of products that are sources of allogeneic stratospheric gases under ultraviolet solar radiation, which destroy the ozone layer, has decreased 68%, allowing forecasting that a significant recovery of the ozone layer will occur by 2050, other results have markedly worsened. Per capita freshwater availability decreased 26% in the period especially because of the population increase of 35.5%. In addition, coastal dead zones that are mainly caused by fertilizer runoff and fossil fuel use increased 75.3%, killing large swaths of marine life. The latter, coupled with an annual increase in CO_2 emissions of 62.1% and a reduction of 2.8% in total area of forests, has markedly affected the biodiversity with a decrease of 28.9% on vertebrate species abundance. Moreover, the 10 warmest years from a 136-year record have occurred since 1998, and the most recent year of the data treated, 2016, ranks as the warmest on record. The ample recognition of these effects increased the relative importance of environment mitigation actions for controlling climate changes and preserving life in comparison with previous worries about fossil fuels shortage.

In fact, in addition to the pollutants already mentioned, the indiscriminate use of fossil fuels also produces small particulate material with size of up to 2.5 μm, PM2.5, which are especially present in large world metropolitan areas, affecting local population. Dispersed in the air, they are easily inhaled, going through the whole respiratory system until the alveolus, being mainly responsible for the occurrence of respiratory and cardiac illnesses and eventually contributing to injure human life. Made of micrometric solid carbon particles with condensed hydrocarbons on their surfaces, they still bear adhered particles of liquid hydrocarbons that are soluble in organic media, hydrated sulfates, and eventually, small particles of toxic heavy metals. In addition to that, they play the role of bacteria, viruses, and toxic chemical product carriers and pollute the water, soil, plants, food, and also the air. The

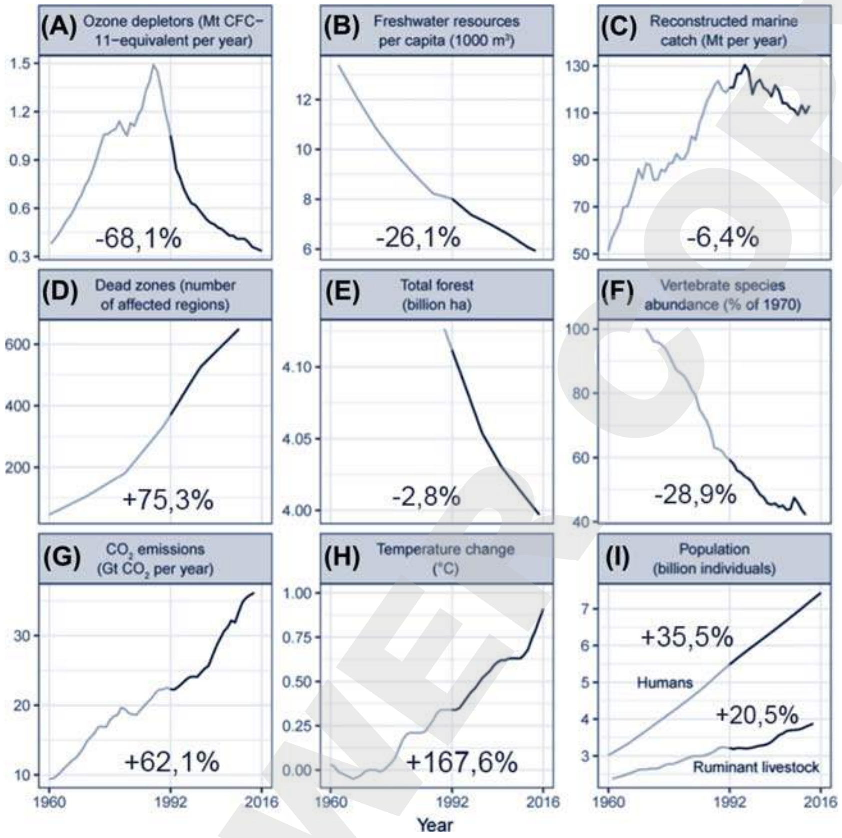

FIGURE 1.3 Variation on the planet's environmental variables before (*faded line*) and after (*black line*) the United Nations' 1992 Conference on Environment and Development Convention, named Rio-92, which was held in Brazil. *Reproduced from [11].*

World Health Organization, WHO, establishes that a safe level of PM2.5 contamination in urban centers is below 10 μg/cm^3. Fig. 1.4 presents data gathered in previous publications [12,13] built with data taken from Pascal et al. [14]. It unveils a correlation between mortality peaks and greater levels of air pollution with particulate materials with sizes up to 2.5 μm.

The inexorable transition to the hydrogen energy era is taking place with a marked participation of renewable energies. Their inherent intermittent output is well complemented with the production and storage of hydrogen, projecting a perennial renewable circular sustainable cycle. Hydrogen, as an energy carrier, is versatile, clean, and safe. It can be used to generate electricity, heat, and power and still finds many applications as a raw material for the industry. It can be stored and transported with high energy density in the liquid or gaseous states and may be produced from raw materials where it is contained

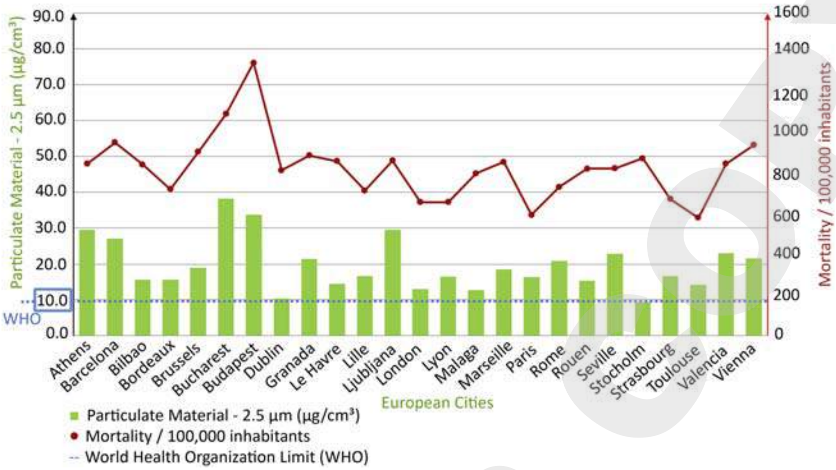

FIGURE 1.4 Average level of environmental contamination with particulate material in air suspension with sizes up to 2.5 µm (*green bars* [light gray in print version]) and mortality per 100,000 inhabitants owing to respiratory and cardiac problems (*red curve* [dark gray in print version]) in the European cities indicated. *[12], using information from [13] and data from [14].*

and an energy source. Hydrogen is mostly produced from natural gas, by the steam reforming of methane, which constitutes its cheaper fabrication procedure. Direct consequences of that are the possibilities to include carbon capture, storage, and utilization technologies during the energy transition and/or the use of biomethane to mitigate carbon emissions when producing hydrogen. This can also be achieved by water electrolysis technologies to produce hydrogen, using renewable energies, or yet by gasification of biomasses that opens an enormous opportunity for different regions in the world with their own local specificities in terms of raw materials and energy sources. Natural sources of hydrogen, once thought nonexistent, have been proved in several geographical spots with huge amounts, some with high purity and others combined with methane, nitrogen, helium, and other gases.

Fuel cells that use hydrogen as fuel and oxygen from the air as oxidant constitute the most energy-efficient devices known to date to generate electricity. Their market entry represents an era in the 21st century in which their utilization assumes importance comparable with the one the computers had for the 20th century. They are being applied in all sorts of electric energy—powered applications, with emphasis on the distributed stationary generation of electricity, heavy-duty vehicles, and automobiles. The descriptions about hydrogen energy that follow will inevitably involve the use of fuel cells.

This chapter will describe what hydrogen energy is about, what it is needed to implement its use, the types of applications possible, the challenges faced, and the benefits gained by using it. New possibilities for harvesting hydrogen for perennial energetic use will also be unveiled.

WHAT HYDROGEN ENERGY IS ABOUT

The annihilation of matter by its collision with antimatter is the most energetic per unit mass energy conversion envisioned, though out of our reach. Interstellar stars, such as our sun, make incredibly effective energetic use of hydrogen; the fusion of four atoms of such light element to produce helium liberates an enormous amount of energy. A small fraction of the hydrogen atoms mass is not converted into mass of the helium atom, and it is enough to generate much energy following the well-known Einsteinian equation. Although nuclear fusion has been developed and experimented for long, it is not practical, economical, or easily feasible to date as an energy generation procedure for large-scale utilization by mankind. Although the energy produced in a fusion reaction is measured in millions of electron volts, the ionization energy to displace an electron from a hydrogen atom in a typical chemical reaction is only 13.6 eV. Even though nuclear fusion might eventually become viable, it is not expected to happen soon. Chemical and electrochemical reactions are, however, accessible as feasible procedures to generate energy. And that is not bad. In fact, it is very good compared with the inefficient 20th century's thermal machines that burned fossil fuels to generate energy using successive conversion steps. The energy-efficient direct, one-step, conversion of the chemical energy contained in the fuel into electric and heat energies using fuel cells is well established to dominate the energy scenario in this century.

Hydrogen energy is about utilizing hydrogen and hydrogen-containing compounds to generate energy to be supplied to all practical uses needed with high energy efficiency, overwhelming environmental and social benefits, as well as economic competitiveness.

The dawning of the hydrogen energy era revolutionizes several aspects of civilized life to allow a circular path concerning energy production and use, giving convenient and beneficial utilization to the huge amount of wastes resultant from developed life style, decarbonizing different sectors of intense energy consumption, making viable to implement large-scale production of renewable energy, better homogenizing the distribution of energy throughout different regions of the world, and facilitating the access to it. To transition from the fossil fuel—based economy to the hydrogen energy economy, provided that technology is available, new approaches have to be put in place, as depicted in Fig. 1.5. These include

1. circular, clean, and beneficial path for energy production and use;
2. widespread use of renewable energies, including
    - **2.1** production and storage of hydrogen to stabilize the delivery of electric energy, regulating the inherent intermittence associated with renewable energies;

FIGURE 1.5 The various characteristics and possibilities related to hydrogen energy technology application.

  2.2 production and storage of hydrogen to act as a buffer to increase resilience of a country or region energy system;

3. use of sewage and of urban and rural organic wastes to produce hydrogen and hydrogen-rich gases and compounds;
4. use of hydrogen to decarbonize activities in sectors such as
   4.1 the industry
      4.1.1 supplying electrical and thermal energies;
      4.1.2 supplying renewable feedstock produced by conveniently reacting hydrogen with biomasses;

  - **4.2** energy supply, as combined heat/cooling and power, to buildings and households, thereby introducing the distributed generation of electrical and thermal powers;
  - **4.3** transportation, including light-duty and heavy-duty vehicles and automobiles for terrestrial, nautical, and aeronautical applications;

5. energy distribution across sectors, countries, and regions using hydrogen and hydrogen-rich gases and compounds as carriers and also hydrogen trading as an energy commodity;

6. facilitating the access to energy in different countries or regions because of local specific options of primary energy source and raw materials to produce hydrogen and also local production of natural hydrogen.

When hydrogen is produced from water electrolysis and used in fuel cells, water appears once again, as a by-product, closing an advantageous circular cycle. Such hydrogen production is considered environmentally friendly when renewable energies are used as the source of energy. This is facilitated in countries such as China, Brazil, Canada, the United States, and others, where much electrical energy is generated by hydroelectric power plants, in which in some periods of the year there is a surplus of turbinable water creating availability of turbinable discharge energy, because of difficulties associated with storing electrical energy once produced. That is, when demand to dispatch electricity decreases, either water is accumulated in a dam, which cannot be done with run-of-river hydroelectric plants, or water is spilled aside, not going through the turbines. Conversely, electricity generated may be used for hydrogen production as a way to store energy. Hydrogen then produced may be used for the various energetic or conventional chemical applications it finds. Similarly, hydrogen production from water electrolysis may also be done using electrical energy originated from other renewable energies, such as wind energy, solar energy, or ocean energy. In such cases, there are two additional benefits concerning the production of hydrogen by water electrolysis using renewable energies. The first one is that hydrogen may be used to complement and adjust electrical energy—delivering issues related to the inherent intermittence of renewable electric energy production. When there is shortage of water, wind, sun or ocean activity but the demand for electricity consumption exists, the hydrogen already produced and stored is available to generate electricity using fuel cells and/or turbines. The second benefit of storing hydrogen is that it can act as a buffer to increase resilience of the whole energy system of a country or region, considering all procedures used to generate electricity, either renewable or not, thereby stabilizing a regional electric energy distribution network.

The world population, once dispersed in rural areas, has modernly been concentrated in large, intensively built and structured environment and densely populated areas, where the exceeding production of wastes challenges the quality of life, threatens the health of living beings, and harms the local ecosystem. Table 1.1 presents data on measured and simulated population and urbanization rate in selected parts of the world. Although there is an ongoing tendency of decreasing the world population average annual growth rate, the world will have more than 9 billion inhabitants in 2040 with a very high rate of urbanization. It is remarkable that a very young society, such as the Brazilian one, is expected to reach 90% of urbanization rate in 2040. It is also important to observe that highly populated countries, such as India and China, will possibly move to urban centers until 2040 about 300 million or 230 million people, respectively, which is a significant increase of urban population, amounting more than the whole population of other countries.

All these urban concentrations generate a host of waste, and an important fraction of the waste collected is organic. In addition to this, there is also an important production of sewage, which in many places is largely untreated, or only primarily treated, before being discarded to the environment. Sewage usually contains and is a carrier of bacteria, viruses, protozoa, and parasites. All urban organic wastes and wastewater (sewage) may be treated to produce hydrogen or hydrogen-rich gases, giving a useful destination to a huge urban problem. Similarly, rural and agribusiness wastes may also potentially be used for the production of hydrogen, hydrogen-rich gases, and solid fertilizers.

A fundamental advantage of the widespread use of hydrogen energy is the possibility to help to decarbonize different sectors of activity, with inherent social and environmental benefits. Such decarbonization affects industry in two different aspects. One is related to the supply of clean electricity and high-grade thermal energy. Powering of all sorts of equipment and systems may be made using fuel cells, and the supply of low-grade and high-grade heat may be achieved, feeding hydrogen to burners and heat exchangers. The other concerns the supply of feedstock, mainly for chemical industries, once produced using fossil fuels and consisting of a host of hydrocarbons, which can be alternatively made out of hydrogen and biomasses, thus becoming of renewable origin, while allowing the use of the same industrial methodologies already in place to fabricate the end products.

Two additional sectors of activities are likely to be decarbonized by the use of hydrogen energy and gain very much importance for being, not only, but also located in urban environment, where there is dense concentration of human lives. Their decarbonization causes therefore direct and strong social benefit. One of them is the supply of combined heat/cooling and power to all sorts of residential, business, and public buildings using fuel cells. It presents the additional advantage of shifting from centralized production of electricity

TABLE 1.1 World Population and Urbanization Rate [10]

	Compound Average Annual Growth Rate (%)			Population (million)		Urbanization Rate (%)	
	2000–16	**2016–25**	**2016–40**	**2016**	**2040**	**2016**	**2040**
North America	1.0	0.8	0.7	487	570	81	86
United States	0.8	0.7	0.6	328	378	82	86
Central and South America	1.2	0.9	0.7	509	599	80	85
Brazil	1.1	0.7	0.5	210	236	86	90
Europe	0.3	0.1	0.1	687	697	74	80
European Union	0.3	0.1	0.0	510	511	75	81
Africa	2.6	2.4	2.2	1216	2063	41	51
South Africa	1.5	0.7	0.6	55	64	65	75
Middle East	2.3	1.7	1.4	231	321	69	76
Eurasia	0.4	0.3	0.1	230	236	63	67
Russia	−0.1	−0.2	−0.3	144	133	74	79
Asia Pacific	1.1	0.8	0.6	4060	4658	47	59
China	0.5	0.3	0.0	1385	1398	57	73
India	1.5	1.1	0.9	1327	1634	33	45
Japan	0.0	−0.3	−0.4	127	114	94	97
Southeast Asia	1.2	1.0	0.7	368	763	48	60
World	1.2	1.0	0.9	7421	9144	54	63

UN Population Division databases; IEA databases and analysis.

and distribution across long distances, which involves energy losses causing high overall inefficiency, to the distributed generation of combined heat/cooling and power. This procedure benefits from the legal framework already put in place for using the well-established distributed generation of electricity with wind and solar energy systems and also the technological adaptation already made to avoid and control the dispersion of harmonics into the grid. Harmonics are unwanted voltage and/or current frequencies eventually generated in distributed energy devices that overload wiring and transformers, heating them up and possibly even causing fires in extreme cases. Such voltage and/or currents are harmful to equipment, decreasing usage reliability and life expectancy. The other sector mentioned for which decarbonization bears magnificent importance for postmodern society is transportation. The ever-growing number of automobiles in the cities and heavy-duty vehicles covering high distances introduces a heavy environmental and social hurdle to human kind, as depicted in Fig. 1.4. Although automobiles call so much attention because of the personal use made with them and the mobility freedom they represent, light-duty vehicles, such as forklift, and heavy-duty vehicles, such as buses, have gained market rapidly powered by hydrogen with fuel cells.

The hydrogen energy era brings an innovation with respect to fuel availability that was not imaginable during the fossil fuel era. The latter has clearly established a strong ownership relation between fuel, countries, and regions. Regional or world political and market-based power has been directly correlated to be proprietary of petroleum, natural gas, and once important coal reserves. Particular land and marine extensions possessing the privilege of such resources have been the motivation for harsh disputes and military actions all throughout the 20th century. In certain cases, politically unstable or unprepared civil organizations in specific countries have easily enriched and threatened other countries with their petro power, contributing to world instability. Conversely, powerful countries have found momentary excuses to occupy and explore certain such regions, once again creating world political instabilities. The hydrogen energy economy changes completely this situation because any country or any world region is able to find its own particular options to combine primary energy source, preferably renewable, and raw material for local hydrogen production to satisfy its own needs while harvesting natural hydrogen has not yet become a reality. Water electrolysis with renewable energy varieties represents an option that gains economic viability with the increase of the magnitude of the particular undertaking in terms of installed power. The enormous experience already accumulated on reforming natural gas to produce hydrogen may also be used with biogases. The immense availability of biomasses in several world regions facilitates to implement gasification or biodigestion processes for hydrogen production. The extra need of hydrogen fuel in a country or region has easy solution by transnational distribution and trading across the world of hydrogen, hydrogen-rich gases, or hydrogen-rich compounds, as new energy carriers, reestablishing a specific world fuel market. The existence of such energy commodity that could eventually recreate the previous unbalanced fuel proprietary condition of the fossil fuel era is, nevertheless, alleviated by local possibilities of hydrogen production for partial supply of the total amount needed. And, in addition to all that, amazingly, natural hydrogen wells begin to have their existence proved in specific world regions.

FULL IMPLEMENTATION OF HYDROGEN ENERGY TECHNOLOGIES

Green Hydrogen Production

An important aspect concerning the utilization of hydrogen energy technologies is that its main fuel, hydrogen, has been produced and used in very large scale by different industrial sectors for many years. Although hydrogen has been used as a chemical product and not as a fuel for energy production, the main methodologies for hydrogen production, storage, and transportation are well dominated. Fig. 1.6 presents prospects for hydrogen utilization until 2050, when hydrogen energy technologies will be well established. It shows energy values expressed in EJ (10^{18} J) calculated from the energy contained in the amount of hydrogen that is expected to be necessary, using the higher heating value of hydrogen, equal to 142.18 MJ/kg [15]. All energy sectors are expected to increase the amount of hydrogen used, especially transportation, industry, and feedstock production.

The increase in the amount of hydrogen required in the next decades is so significant that a variety of technological options, raw materials, and energy sources for hydrogen production must be made viable, taking into

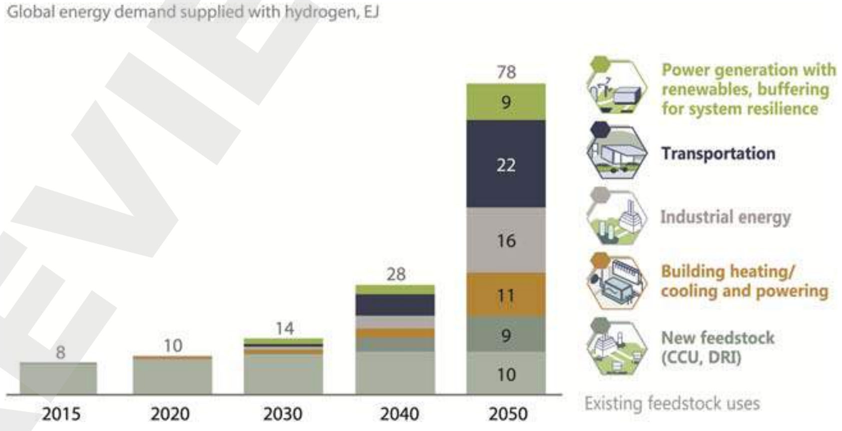

FIGURE 1.6 Global energy demand supplied with hydrogen. Energy quantities are shown in EJ. 1 EJ = 10^{18} J. *CCU*, carbon captured and utilized; *DRI*, direct reduced iron. *Reproduced from [15].*

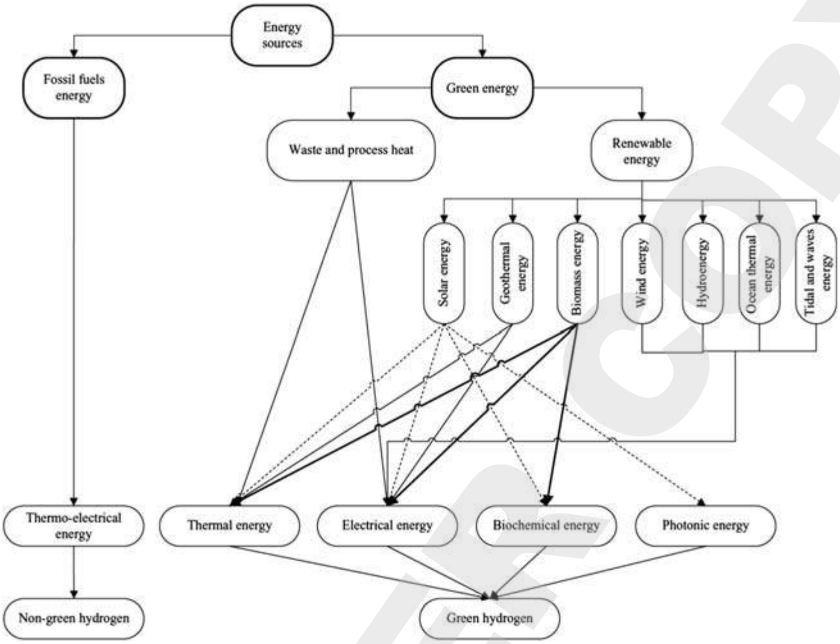

FIGURE 1.7 Energy conversion paths for hydrogen production. *Reproduced from [1].*

consideration that low environmental impact technologies will be preferred. A great variety of energy conversions will be possible, as depicted in Fig. 1.7 [1]. The chemical energy contained in fossil fuels that undergo thermoelectrical energy conversions will follow on playing an important role, however, resulting in hydrogen that is not considered green because of the deleterious emissions associated with such technologies. These represent, however, well-established mass production approaches that are cheaper than others because of mass production and also for not taking into account externalities associated with their processing and use, such as those discussed in Fig. 1.3.

There is a host of green energy possibilities for hydrogen production, associated with wastes from several origins and process heat, as well as with renewable energies, all of them used to harvest four forms of energy that are thermal, electrical, biochemical, and photonic. Wastes and process heat may be used for thermal energy and electrical energy generation, which are then utilized for green hydrogen production. The renewable energies such as solar energy, geothermal energy, biomass energy, wind energy, hydroenergy, and ocean thermal, tidal, and wave energies, give origin to all four forms of energies aforementioned for green hydrogen production. Solar energy, of course, is dominant with the generation of all four forms of energy mentioned for green hydrogen production and is expected to undergo large-scale utilization throughout the world. This is foreseen by the data presented in Fig. 1.8. Fig. 1.8A shows how the global average levelized[1] cost of electricity from utility-scale solar photovoltaic (PV) has been decreasing and is expected to vary until 2040. It declined 70% from 2010 to 2016 and is projected to decline an additional 60% to 2040, period in which the solar PV electricity costs will become competitive to those of other fuels described in Fig. 1.8B, thereby progressively facilitating its adoption by consumers. According to Fig. 1.7, biomass energy also presents versatility for generation of thermal, electrical, and biochemical energies for green hydrogen production, gaining special importance because of its great availability all throughout the planet. The ensemble of renewable energies and the energy contained in wastes and process heat may all generate electrical energy that is required for electrolytic, electrochemical, electrophotochemical, and electrothermochemical processes, which, in addition to photobiochemical methods, give origin to an ample variety of technologies for green hydrogen production.

The total Gibbs free energy necessary to break the water molecule for hydrogen production by water electrolysis is composed by a smaller portion of electricity that is converted to work if there is heat energy concomitantly available to complement the work to be done. At temperatures above steam formation, the increase in heat energy offered to the system decreases progressively the requirement of work to be done by the electric current. That is the reason why high-temperature electrolysis is more advantageous. Fig. 1.9 [16] represents the basic thermodynamic variables associated with this process, showing that it is energetically more beneficial to process steam than liquid water. In addition to that, the higher the temperature, the smaller the amount of electric energy needed, ΔG (the molar Gibbs energy of the reaction), to convert directly steam into hydrogen and oxygen. This happens because the total energy needed, ΔH (the molar enthalpy of the reaction), remains approximately constant while the heat, $T\Delta S$ (absolute temperature multiplied by the variation in entropy), is progressively augmented. Consequently, Fig. 1.9 shows that less electricity is required for the electrolysis of steam per cubic meter of hydrogen produced compared with the electrolysis of liquid water. However, heat must be provided and it is costly to be produced. If electricity from renewable source is available, the solid oxide electrolysis cell

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[1] The levelized cost of an energy carrier, either electricity or hydrogen, is calculated in a consistent way that takes into account the initial capital, discount rates and costs of operation, feedstock, and maintenance. It represents an economic assessment of the average total cost to build and operate the power generation or hydrogen production infrastructure over its entire lifetime divided by the total electrical energy or hydrogen output using such asset over its lifetime.

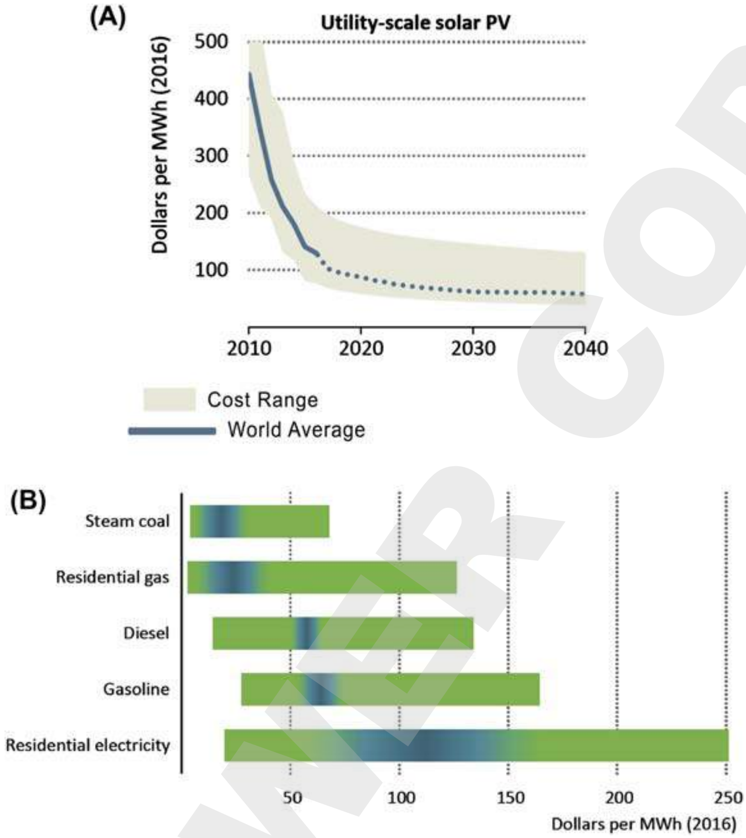


FIGURE 1.8 (A) Global average levelized cost of electricity from utility-scale solar photovoltaic (PV), *blue solid line* (dark gray in print version), world costs range, shaded, and cost projections to 2040, *dotted line*; (B) Fossil fuels and residential electricity range of world average prices paid by consumers, 2015. *Notes: MWh*, megawatt-hour. A utility-scale solar facility is one which generates solar power and feeds it into the grid, supplying a utility with energy. The areas shaded in blue (dark gray in print version) represent the range of reference prices used for the purposes of calculating energy consumption subsidies. Variations in quality may explain a part of the variations in price, especially for electricity where differences in reliability of services mean that it is not a homogenous product across countries. *Reproduced from [10].*

(SOEC) is a more energy-efficient technology for green hydrogen production. It is a high-temperature electrochemical device, which when coupled with an electrical energy source promotes the reduction of a gaseous reactant to generate products such as hydrogen and oxygen [17–22].

The SOEC operating at high temperatures, 700–900°C, has the advantage that the unavoidable Joule heat inherent to its operation is used in the

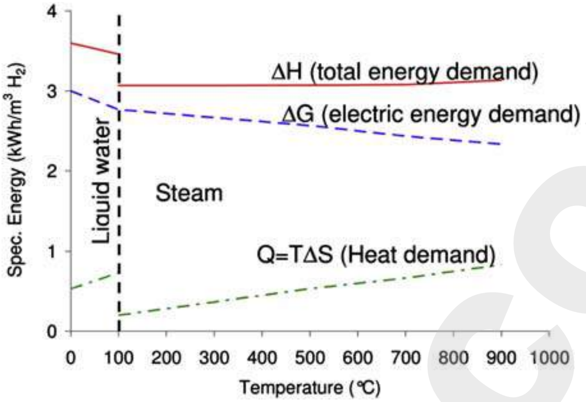


FIGURE 1.9 Thermodynamic approach of the high-temperature water/steam electrolysis process. *Reproduced from [16].*

electrolysis process. It consists of an apparatus similar to a solid oxide fuel cell (SOFC), in which the oxygen ion–conducting electrolyte may be made of yttria-stabilized zirconia (YSZ); the air electrode, the anode, may be composed of perovskites such as lanthanum strontium manganese oxide (LSM), lanthanum strontium cobalt iron oxide (LSCF), and nickel-YSZ cermet for the hydrogen electrode, the cathode. The electrochemical reactions involved are as follows:

$$\text{SOEC fuel electrode, cathode: } H_2O + 2e^- \rightarrow H_2 + O^{2-} \quad (1.1)$$

$$\text{SOEC air electrode, anode: } O^{2-} \rightarrow \tfrac{1}{2}\, O_2 + 2e^- \quad (1.2)$$

The SOEC benefits from the intense development being made for SOFCs because it basically utilizes similar materials and systems. The special advantage is that SOECs and SOFCs may be used reversibly, for the production of hydrogen or the generation of electricity, respectively, in the same device, alternating the role of anode and cathode, the fuel utilized, as well as either the input or the output of electricity as it is used to produce hydrogen or to generate electricity.

Other technologies of water electrolysis are presently very well developed and have successfully reached market application [23]. Like fuel cells, they are subdivided according to the type of electrolyte used. In an alkaline electrolysis cell (AEC), the electrolyte is made of liquid solutions of NaOH or KOH, thereby possessing OH^- as charge ion conductor; it uses carbon and transition or noble metals as catalysts, electrodes, and interconnectors and is operated at low temperatures, 40–90°C. A polymeric electrolyte membrane electrolysis cell (PEMEC) has electrolyte composed of a hydrated polymeric membrane that possesses H^+ as charge ion conductor, moving through the membrane by the aid of another charge ion conductor that is H_3O^+, using carbon and platinum as electrode and catalyst, carbon–metal as interconnector with an operation temperature ranging between 20 and 150°C. The main intrinsic and operational features for the AEC, PEMEC, and SOEC are summarized in Table 1.2 that also simulates a specific comparison between these devices, in which the AEC and PEMEC are set to be operated at 80°C and the SOEC at

TABLE 1.2 Summary of Different Electrolyzer Types, Their Particular Features, and a Specific Comparison Among Them

Electrolyzers	**AEC**	**PEMEC**	**SOEC**
Electrolyte	Solution of NaOH or KOH	Hydrated polymeric membranes	Ceramic
Charge ion conductor	OH^-	H^+, H_3O^+	O^{2-}
Cathode reaction	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$2H^+ + 2e^- \rightarrow H_2$	$H_2O + 2e^- \rightarrow H_2 + O^{2-}$
Anode reaction	$2OH^- \rightarrow H_2O + \frac{1}{2} O_2 + 2e^-$	$H_2O \rightarrow \frac{1}{2} O_2 + 2H^+ + 2e^-$	$O^{2-} \rightarrow \frac{1}{2} O_2 + 2e^-$
Electrodes	Ni, C	C	Ceramic/cermet
Catalyst	Ni, Fe, Pt	Pt	Ni, perovskites (LSM, LSCF)
Interconnector	Metal	Carbon–metal	Stainless steel, ceramic
Operating temperatures (°C)	40–90	20–150	700–900
Specific Comparison			
Operating temperature (°C)	80	80	800
Operating potential (V)	1.9	1.7	1.15
Internal resistance (Ω cm^2)	2.5	0.5	0.15
Hydrogen production rate (mol H_2/m^2h)	50	175	211
Hydrogen production per energy consumed (mol H_2/kWh)	27	40	110

AEC, alkaline electrolysis cell; *PEMFC,* polymeric electrolyte membrane electrolysis cell; *SOEC,* solid oxide electrolysis cell.
Adapted from [24].

800°C [24]. It is remarkable that the SOEC presents outstanding results, including smaller operating potential and internal resistance, as well as higher hydrogen production rate and hydrogen production per energy consumed. In a situation in which the electrical energy needed to produce hydrogen using the AEC or PEMEC varies from about 1 to 2 kWh/Nm^3H_2, the SOEC may require less than 0.5 kWh/Nm^3H_2. This exemplifies the advantageous energy efficiency characteristics of the SOEC compared with the present conventional technologies for hydrogen production by electrolysis. In addition to that, the SOEC has also prospects to become a cheaper technology than the present conventional ones [25]. Fig. 1.10 presents levelized cost of hydrogen production using SOEC current and future advanced technologies in comparison with the use of the AEC and PEMEC as a function of the electricity cost. It shows that within all ranges of electricity costs the SOEC presents better future prospects to produce cheaper hydrogen.

There are novel, yet to become commercial, electrolysis methods for hydrogen production. Among them, the microbial electrolysis cell (MEC) utilizes, just like the AEC, the PEMEC, and the SOEC, similar fixture as the microbial fuel cell (MFC) does [26]. The MEC makes use of exoelectrogen bacteria that are microorganisms with ability to transfer electrons extracellularly. In an MEC, they generate electric current in a suitable medium where an extra external power is also supplied and combined to reduce protons, thereby producing hydrogen. Fig. 1.11 [27] depicts schematically the MEC setup and functioning as a two-chamber reactor. Electrochemically active bacteria (EAB) colonize in the MEC's anode, consume an energy source and a substrate, such as organic waste materials, and produce protons that diffuse through the electrolyte solution, trespassing the separator membrane toward the MEC's cathode. They also generate electrons that are driven to an external circuit and CO_2 as reaction waste that is discarded. At the MEC's cathode,

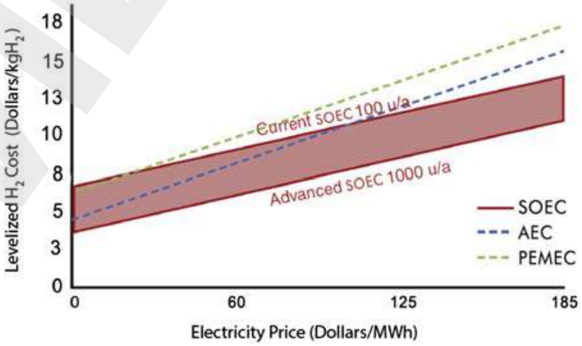


FIGURE 1.10 Levelized cost of hydrogen production as a function of electricity cost using an alkaline electrolysis cell (AEC), a polymeric electrolyte membrane electrolysis cell (PEMEC), or a solid oxide electrolysis cell (SOEC). *Adapted from [25].*

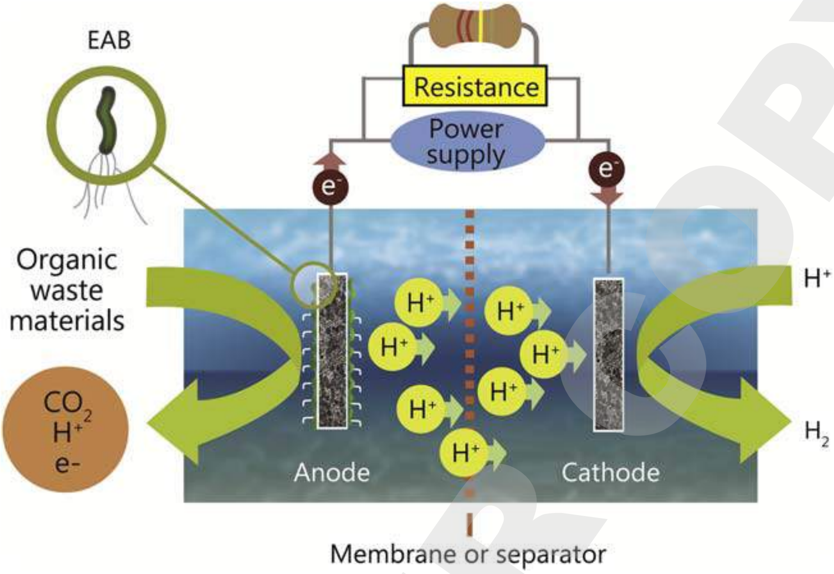


FIGURE 1.11 Schematic representation of a microbial electrolysis cell as a two-chamber reactor, showing the role of electrochemically active bacteria (EAB) in the anode chamber on waste material substrate to produce protons that diffuse through the separator membrane and reach the cathode where combination with electrons promotes hydrogen production. *Reproduced from [27].*

protons are reduced to produce gaseous hydrogen, what is achieved by superimposing an external electrical potential to the system. In the SOEC case, heat was supplied by the cell's electrochemical exothermic reactions to vaporize water and to decrease the work to be done by the electric current imposed to the system, thereby allowing electrolysis to be performed with a much smaller external power than that of conventional water electrolysis. In the MEC case, the external power needed for electrolysis is even smaller. The electrochemical potential needed for hydrogen production by electrolysis using the different technologies previously discussed are 1.9 V for the AEC, 1.7 V for the PEMEC, and 1.15 V for the SOEC for the specific comparison example presented in Table 1.2. Conversely, the electrical power needed for hydrogen production in an MEC can be as small as 0.25 V [26] and may result in energy consumption as low as that of the SOEC, of the order of 0.6 kWh/$Nm^3 H_2$ [28]. Virtually, any biodegradable organic electron donor may be used as a substrate in MECs, which include domestic wastewater, ocean and marine sediments, anaerobic sewage sludge, acetate, butyrate, glucose, ethanol, polymeric materials such as cellulose and proteins, complex mixtures such as dairy manure, swine wastewater, brewery wastewater, and a host of industrial and agribusiness wastes. Table 1.3 presents a list of possible EAB and their substrates used in MECs. MECs use microbes as biocatalysts to produce hydrogen with purity level that does not require expensive hydrogen purification

TABLE 1.3 Electrochemically Active Bacteria and Substrates Used in MECs [27]

Electrogenic Microorganisms	Substrates	References
Rhodopseudomonas palustris DX-1	Volatile acids, yeast extract thiosulfate	[29]
Ochrobactrum anthropi YZ-1	Acetate, lactate, propionate, butyrate, glucose, sucrose, cellobiose, glycerol, ethanol	[30]
Acidiphilium sp. strain 3.2 Sup 5	Ferric iron, Ferrous iron	[31]
Rhodoferax ferrireducens, *Citrobacter* sp. SX-1	Glucose, citrate, lactose, sucrose, acetate, glycerol	[32,33]
Shewanella putrefaciens MR-1, IR-1, SR-21	Lactate, pyruvate, acetate, glucose	[34]
Shewanella oneidensis MR-1	Lactate	[35]
Klebsiella pneumoniae strain L17, *Enterobacter cloacae*	Glucose, starch, cellulose	[36,37]
Aeromonas hydrophila KCTC 2358	Acetate	[38]
Aeromonas sp. strain ISO2-3, *Geobacteraceae*	Glucose, acetate	[39,40]
Geobacter metallireducens, *Geobacter sulfurreducens*	Acetate	[41–44]
Desulfobulbus propionicus	Pyruvate, acetate	[45]
Propionibacterium freudenreichii ET-3	Acetate, lactate	[46]
Arcobacter butzleri strain ED-1	Sodium acetate	[47]
Clostridium beijerinckii, *Clostridium butyricum* EG3	Starch, glucose, lactate, molasses	[48,49]
Firmicutes Thermincola sp. strain JR	Acetate	[50]
Geothrix fermentans, *Gluconobacter oxydans*	Acetate; glucose	[51,52]

MEC, microbial electrolysis cell.

procedures, and specially, they integrate pollution treatment and hydrogen production with the advantages of cleanness, energy saving, and waste utilization [27]. Future development of MECs is very much dependent on the development prospects of MFCs, presenting the benefit of a wide variety of different applications that MFC-based technologies may reach. In addition to electricity generation and remote power supply, these include alternative technologies such as carbon capture, desalination, resource recovery, wastewater treatment, bioremediation that is a process used to treat contaminated media, electrochemical biosensors, medical diagnostics tool, and on-chip power sources and ecobots, that is, ecological robots that present a self-sustaining operation using, for example, waste as raw material for energy production [53].

Natural Hydrogen

In spite of all the well-known or the new and sophisticated technologies for hydrogen production and the belief kept for so long that these are the possible ways to make hydrogen fuel viable for use on earth, exploration of natural hydrogen, not once considered possible, is beginning to become reality. There is no doubt that hydrogen is the most abundant element in the Universe. On earth it was thought to exist only bound to compounds, into any hydrocarbons and water, being one of the constituents of all flora and fauna. The gas hydrogen was not considered to be available on earth, either mixed with other gases or in high proportion, almost pure, because it is composed of such a reactive chemical element. However, recent evidence proves the contrary. Fig. 1.12 shows a circular geological structure on the earth's surface in Brazil where measurements are made to detect continuous outgassing of natural hydrogen [54]. These circular, sometimes elliptical, structures that may possess a few meters or kilometers of diameter are zones of deformation of the soil, resulting from basement faults, bounded by rounded depressions of a few meters, presenting inside a flat bottom.

They have also been found elsewhere, such as in North America, the Sultanate of Oman, Philippines, Mali, Turkey, New Caledonia, and Russia [54–56]. The following are considered as characteristics and mechanisms related to natural hydrogen existence on earth [55]:

FIGURE 1.12 Geological structure composed of a circular depression on a craton zone formation in Brazil where hydrogen gas is detected flowing out. *Reproduced from [54].*

1. Natural hydrogen outgassing is now understood to appear in craton formation regions that are rock formations on the earth's continental crust that have remained stable for a period of time as extended as 500 million years.
2. Hydrogen is found at the earth's free surface and in fairly shallow depths of up to about 500 m [56].
3. Natural molecular hydrogen also occurs in ophiolitic[2] formations, eventually associated with nitrogen and abiotic methane, whose generation is not linked with organic matter thermal cracking but by reduction of any source of carbon. That is, there is no organic matter accumulation associated with the sites of occurrence, situation in which hydrocarbons would rather be produced.
4. The effect of serpentinization[3] in peridotite, a very dense, coarse-grained, olivine-rich [$(Mg^{2+}, Fe^{2+})_2SiO_4$] ultramafic rock, which is a silicate mineral rich in magnesium (forsterite end-member[4]) and iron (fayalite end-member), is twofold [55]:
   - **a.** The hydration of the forsterite end-member of olivine (Mg_2SiO_4) produces much hydroxide ion, such as in Eq. (1.3), to make it an ultrabasic rock:

$$2Mg_2SiO_4 + 3H_2O \rightarrow Mg_3Si_2O_5(OH)_4 + Mg^{2+} + 2OH^- \tag{1.3}$$

Fosterite + water → serpentine + magnesium + hydroxide ion

   - **b.** Since Fe^{2+} is by far the most important electron donor in ultrabasic rocks, hydration of the iron end-member (fayalite) of olivine minerals induces the formation of Fe^{3+} minerals such as magnetite, leading to the formation of hydrogen as depicted in Eq. (1.4):

$$3Fe_2SiO_4 + 2H_2O \rightarrow 2Fe_3O_4 + 3SiO_2 + 2H_2 \tag{1.4}$$

Fayalite + water → magnetite + silica + hydrogen

The existence of aquifers under the earth's surface in geologically stable craton formation regions may represent a mechanism of continuously promoting the formation of natural hydrogen, as far as ferrous iron is present in their surrounding (as olivine, or as any other mineral containing ferrous iron being able to decompose and liberate soluble Fe^{2+} in water). This may eventually be consistent with the amazing possibility of replenishing natural hydrogen wells with new-formed gas.

---

[2] Ophiolite is a stratified igneous rock complex in the earth's oceanic crust and the underlying upper mantle that has been uplifted and exposed above the sea level, emplaced onto continental crustal rocks. Meaning snake rock, from Greek, it contains *serpentinized* rocks that present a scaly, greenish brown—patterned surface resembling snakeskin.

[3] Serpentine rocks are formed as a result of hydration processes, such as serpentinization, when the spreading tectonic plates in the earth's crust lift them up from the ocean and they are chemically altered by water or, alternatively, when a similar process is induced by the presence of the underlying aquifers that promote water movement.

[4] *End-member* is a mineral that is at the extreme end of a mineral series in terms of purity. Fayalite Fe_2SiO_4 and forsterite Mg_2SiO_4 are *end-members* of the olivine series $(Mg,Fe)_2SiO_4$.

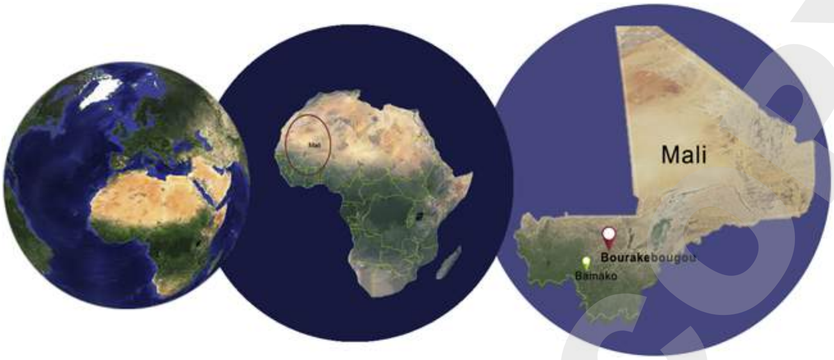


FIGURE 1.13 Localization of Bourakebougou, in Mali, Africa, where the first world hydrogen wells have been producing natural hydrogen, used locally for electricity generation.

The first hydrogen wells actually producing natural hydrogen in the world are being explored in Bourakebougou, in Mali, Africa, in the region depicted in Fig. 1.13, by the company Petroma Inc. It was the search for water in that region that unveiled the presence of gaseous occurrence composed of 98% of pure natural hydrogen 1% of nitrogen and 1% of methane that is explored and used locally for electricity generation [54]. The natural hydrogen wells are a little over 100 meters below the earth's surface in that region, confirming that this energy resource may be available in shallow wells for which the technological setup for exploration becomes simpler and cheaper. This may result on the extraordinary possibility of harvesting natural hydrogen at a cost smaller than that of hydrogen produced by any of the methods known to date, from the conventional natural gas steam reforming and the well-developed water electrolysis to the innovative technologies hitherto discussed.

Because it has been herein showed that the first world's natural hydrogen wells are under production in Mali, on the northeast of Africa (Fig. 1.13) and because natural hydrogen occurrence has also been proved to exist in the northeast of South America, in Brazil (Fig. 1.12), considering that it is known that the South American and African continents once joined together, in old geological era, forming the Pangea supercontinent as depicted in Fig. 1.14, and that they may share similar geological structures, an analysis was made of the potentiality of discovering simultaneous occurrence of craton formation regions on the top of the underlying aquifers in these continents, which would bring the possibility to identify other possible regions where natural hydrogen wells would likely be found. The resulting analysis is shown in Fig. 1.14. It is absolutely amazing to verify that there are several coincident occurrences of craton rock formations onto the underlying aquifers both in South America and in Africa, Fig. 1.14. The formation verified in the Amazon region calls attention for its enormous extension.

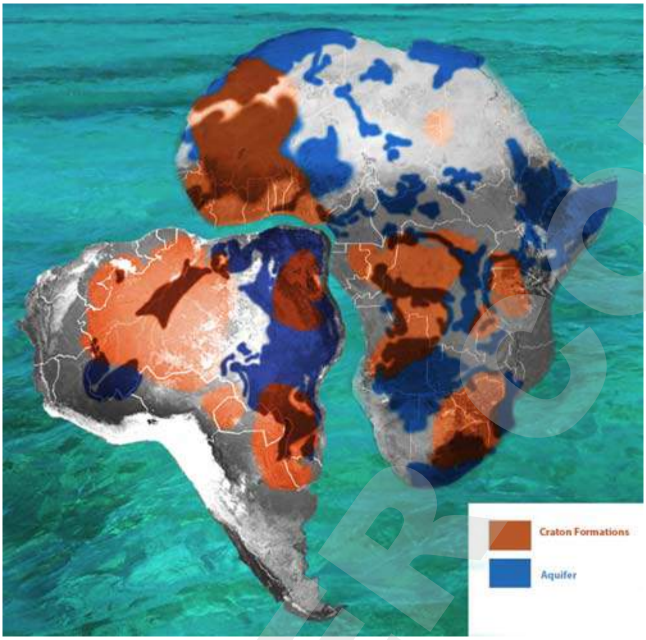


FIGURE 1.14 South American and African continents joining together in old geological era that once formed the Pangea supercontinent. Regions where craton rock formations are found on the top of the underlying aquifers in South America and Africa are indicated with different color contrasts.

In addition, taking into account that natural hydrogen-rich gaseous formations were found on the paleo ocean floor in New Caledonia (ophiolite) such as depicted in Fig. 1.15 [55], it is conceivable to admit that in the vast intercontinental oceanic extensions, there might exist several sites where natural hydrogen is likely to be found and explored, the feasibility of which will be very much dependent on the depth and local conditions but will benefit from the experience already accumulated with the exploration of hydrocarbons in the ocean. It is also important to remark that an eventual future exploration of subsea natural hydrogen will never submit such sites to the danger of extraordinary environmental disasters such as the ones already occurred with the exploration of hydrocarbons, oil and natural gas, simply because hydrogen would be partially absorbed by water and partially vented to be consumed in open air, thereby producing water.

HYDROGEN ENERGY APPLICATION

Once hydrogen is available, either industrially produced or naturally harvested, it becomes the 21st-century ultimate fuel commodity for clean,

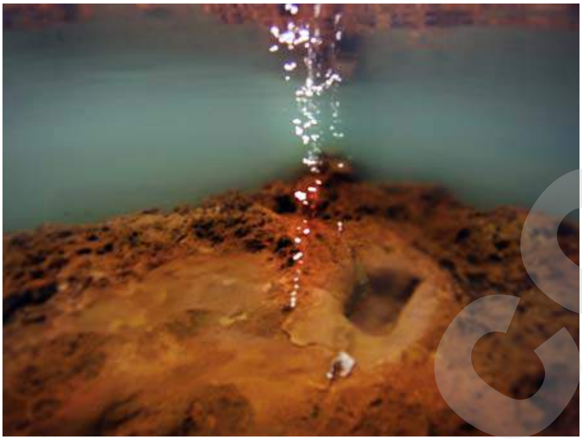
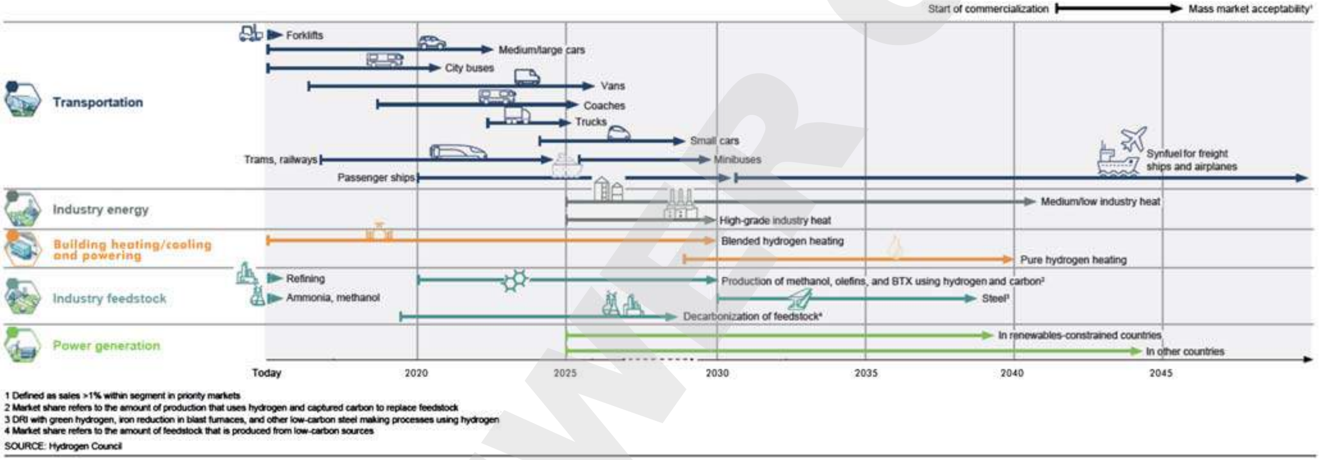


FIGURE 1.15 Natural bubbling of a gaseous mixture of nitrogen, hydrogen, and methane on the ocean floor in the bay of Carénage, New Caledonia. *Reproduced from [55].*

environmentally friendly, energy commercial application. Fig. 1.16 presents future prospects for hydrogen energy technologies start of commercialization to mass market acceptability in the sectors of transportation, industry energy, building heating/cooling and power, industry feedstock, and power generation.

Transportation is the sector that calls so much attention because it includes automobiles, the 20th century's star of the vehicles because of the freedom associated with personal mobility. However, dense-populated urban regions and their inhabitants suffer the effects of deleterious externalities never taken into account when new technologies for mobility are considered more expensive than the conventional ones. In the transition period to a new and cleaner energy era, different options are considered in parallel to the introduction of the ultimate solution represented by fuel cell automobiles. In particular, both battery and fuel cell vehicles possess electric drivetrains, presenting the advantage of coupling well with growing renewable energy sources utilization and sharing the burden of striving for a new refueling infrastructure to be installed, requiring heavy investments [57]. Intermediate transitional efforts also include a variety of hybrid vehicles and the use of renewable fuels such as ethanol [58] in conventional internal combustion engines. The advancement concerned with the direct utilization of methane or ethanol in fuel cells without previous reforming [59] may open new strategies for clean vehicles with an electric power train.

It is interesting to see that fuel cell—powered forklifts that are used in confined ambient of companies have already reached plenty application and represent brand new hydrogen energy technology that needs no subsidies for acceptation. Moreover, fuel cell hydrogen buses are a class of vehicles comprising a niche market for reasons such as:



1 Defined as sales >1% within segment in priority markets
2 Market share refers to the amount of production that uses hydrogen and captured carbon to replace feedstock
3 DRI with green hydrogen, iron reduction in blast furnaces, and other low-carbon steel making processes using hydrogen
4 Market share refers to the amount of feedstock that is produced from low-carbon sources
SOURCE: Hydrogen Council

FIGURE 1.16 Future prospects for hydrogen energy technologies start of commercialization to mass market acceptability in the sectors of transportation, industry energy, building heating/cooling and power, industry feedstock, and power generation. *From [15].*

1. they are very much used in huge urban areas throughout the world, where local pollutant emissions represent a problem requiring urgent solution;
2. they represent mass transportation mode and their use contributes to decrease the need for automobile utilization;
3. they are much more silent than conventional buses, making their use to decrease local noise pollution;
4. they are refueled in their central garage, which simplifies and makes infrastructure needs much cheaper than for automobiles, dispersedly used.

Fig. 1.17 presents a version of a series hybrid battery-dominant electric hydrogen fuel cell plug-in city bus for which the power train and the auxiliary system were developed and demonstrated [12]. In this case, emphasis has been given to the design of the hybridization energy engineering with predominance of power in batteries and predominance of energy with hydrogen. It succeeded to take 46.6% of the total energy embarked to effective motion at the vehicle axle, resulting in a fuel economy of 6.7 kg H_2/100 km and on the achievement of working ranges normally above 300 km.

Hydrogen energy is ready to positively and directly influence the industrial sector in a number of ways. In addition to the supply of electric energy, it opens the possibility to offer high-grade heat for a host of industrial processes. However, a certain time span will be necessary to modify industrial infrastructure, which means that several years will be required for such a transformation. Creative adaptations are being designed such as the case of the chemical industry that has industrial procedures established for the use of a variety of hydrocarbons normally derived from fossil fuels, oil, and natural gas. A huge facility is designed to be created for hydrogen production from water electrolysis using renewable wind energy, including massive amounts of

FIGURE 1.17 Example of a series hybrid battery-dominant electric hydrogen fuel cell plug-in city bus.

hydrogen storage in underground wells and transportation to an industrial site, where an infrastructure is being built to produce the same feedstock hydrocarbons presently obtained from fossil fuels by locally reacting hydrogen with selected biomasses as sources of carbon [60]. The advantage of such an endeavor is to transform the chemical industry into renewable, while keeping in use the same present industrial methodologies because the same hydrocarbon feedstock will continue to be used.

With respect to the steel industry, there is also an extraordinary transformation in course. In this case, renewable energy is also the energy source chosen to produce hydrogen by water electrolysis to displace the use of an ancient industrial apparatus that is the blast furnace for metallic iron production from iron ore. Fig. 1.18 compares the procedures presently used for

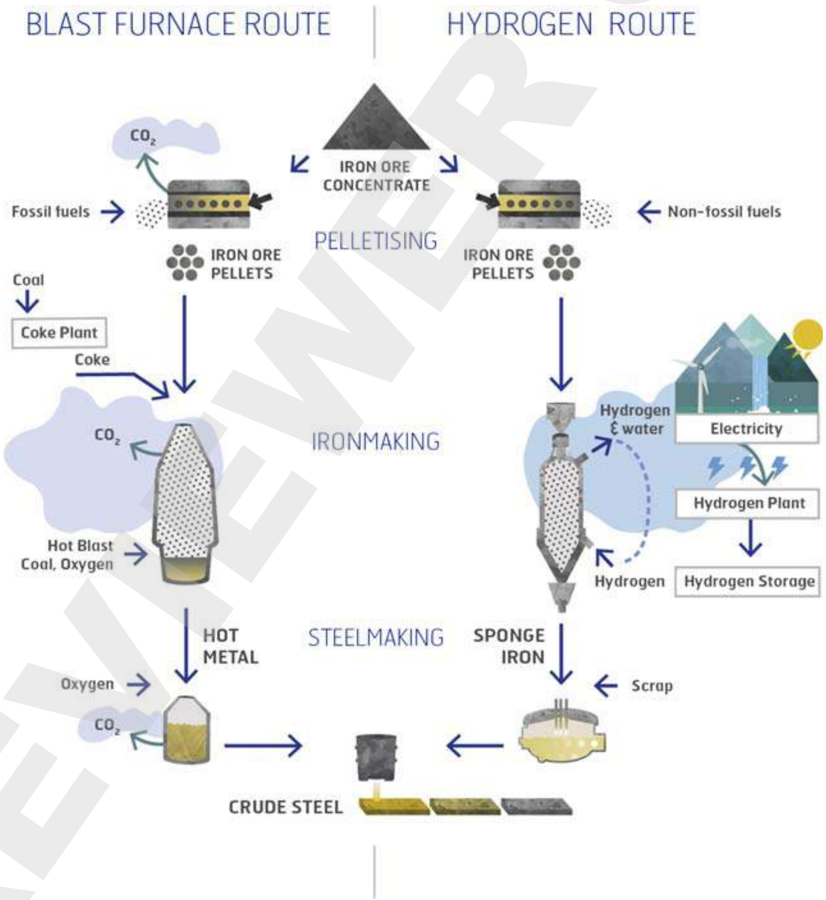


FIGURE 1.18 Conventional environmentally unfriendly, on the left-hand side, and hydrogen-based clean, on the right-hand side, procedures to fabricate metallic iron from iron ore. *From [61].*

metallic iron production with the new hydrogen-based procedure under development by a particular industry [61], which is concomitantly under development with similar engineering approaches by other companies in a few different European and Asian sites. The left-hand side of Fig. 1.18 shows that iron ore concentrate is pelletized using fossil fuels, so that the mineral pellets and coke are fed into a blast furnace, which produces hot metal that is, subsequently, used to be transformed into crude steel. Coke and fossil fuels are used, and greenhouse effect gases and much particulates and ashes are emitted with this conventional procedure. Alternatively, the right-hand side of Fig. 1.18 presents a "hydrogen route" in which iron ore concentrate is also used to produce pellets, but no fossil fuel is used for that. Hydrogen is produced from water electrolysis on site or nearby using renewable electricity and is stored in large amounts to be used for two purposes: one is for the production of high-grade industrial heat and the other one is for the procedure of direct reduction of iron ore into metallic iron, which gives origin to sponge iron without using coke as a reducing agent, without using fossil fuels for heating, without deleterious environmental emissions, and also without having to convert the iron ore, the raw material, into liquid form as it has to be done in the blast furnace. The sponge iron is then used for crude steel production. Such a hydrogen route for the production of direct reduced iron from pelletized iron ore is very innovative and encompasses a future vision of using hydrogen energy to clean the ancient and pollutant steel industry into an environmentally friendly one.

Among the different possibilities available to speed up the commercialization of hydrogen energy technologies, the small-power distributed generation of electricity and heating/cooling devices are effectively ready for use. Although this has called the attention of and has motivated organizations throughout the world, it was in Japan that it succeeded to reach impressive numbers, as a result of an enduring public—private partnership, with the introduction and programmed withdrawn of subsidies. It gave a solid demonstration of how a well-programmed and well-implemented long-term road mapping for the introduction of a new and disruptive technology may be accomplished. Two types of fuel cells were chosen for utilization in urban homes connected to the city gas distribution system, the polymeric electrolyte membrane fuel cell, PEMFC, and the solid oxide fuel cell, SOFC. Fig. 1.19 presents the steep increase of the number of systems installed throughout the years to reach more than 220,000 in 2017. However, this will remain small compared with the prospects of installing 1.4 million units by 2020 and 5.3 million units up to 2030 [62].

The increase on the number of units to be installed in the near future will certainly contribute to force down the decreasing trend already observed for the devices' retail prices. Although the distributed generation of electricity is a known tendency for the near future and hydrogen energy technologies may effectively contribute to it, the centralized generation of electricity and its distribution to consuming centers coupled with hydrogen energy technologies

FIGURE 1.19 Evolution as a function of the years of the number of low-power fuel cell–based devices effectively installed for distributed generation of electricity and heat, as well as their selling prices. *Modified from [62]. Currency was converted from Yens to Dollars.*

is likely to be developed in conjunction to power generation with renewable energies. This will benefit from the significant capacity presented by hydrogen for long-term carbon-free seasonal energy storage [15] and the importance energy storage gains when much renewable energy is produced.

CONCLUDING REMARKS

The world has gone through a few energy transitions and presently experiments the dawning of a new one with much better prospects concerning the energy availability, energy efficiency, and environmental impact on the planet resulting from intensive use. With a smaller population and fewer methods to make use of energy, the total amount of energy used in the world during the 19th century was equal to 22 EJ. However, the Industrial Revolution was so intense that the two first decades of the 20th century were enough to use the same amount of energy consumed during the whole 19th century. From thereon, with a steady and important increase in human and ruminant livestock population, the century of marked evolution in the fields of science and technological innovation has eagerly demanded more and more energy, however, using it inefficiently, with regrettable losses, unequally shared by the enormous variety of the world's ethnicity, and causing an environmental disaster on the planet.

In the 21st century a harsher trend of energy requirement and use is imposed. Once again, a little over three decades will have used energy in an amount equivalent to the whole previous century. By 2050 the world might need 900 EJ of energy supply. This calls for more than a simple energy transition to make more energy available. Instead, a perennial, renewable, environmentally friendly, and prone to be extensively shared form of energy enters the scene all throughout the world. In addition to that, it has been conceived for use with very efficient energy conversion devices, the fuel cells. Hydrogen energy is the solution for the huge present and future energy requirements. It consists of utilizing hydrogen and hydrogen-containing compounds to generate energy to be supplied to all practical uses needed with high energy efficiency, overwhelming environmental and social benefits, as well as economic competitiveness.

In spite of the inventiveness that has given origin to a host of procedures for hydrogen production from water, biomasses, and hydrocarbons, making use of well-known as well as of innovative technologies with the necessary action of primary energy forms, it is herein unveiled that hydrogen is recognized to be no longer only an important energy carrier, such as electricity. It is also a primary fuel. It is available on earth to be harvested and used. It may be found with very high purity or mixed to other gases. It evolves from the earth's surface on several, probably all, continents from fairly shallow reservoirs, and it also degases in varied locations yet to be explored of the huge oceans' bottom extensions. It contains no carbon. It is not the result of biomass transformation, having rather an inorganic origin. It does not harm the planet. It may be renewable and perennial, through the permanent serpentinization, hydration, of ophiolitic rocks, existent all through the Planet, by water from aquifers that are replenished by rainwater percolation. The first hydrogen wells are already being explored. Others will also be as the 21st century goes by.

The hydrogen energy era is born.

The consumption of natural hydrogen by human beings and its transformation into water somehow mimics nature's superficial biological activity and atmospheric oxidation on Earth in terms of circular water cycles. While the use of natural hydrogen by humans is a modern subject of the present times, natural hydrogen was a precursor of life on Earth, before the apparition of chlorophyll and photosynthesis, through a succession of conditions during which the Earth's atmosphere changed from a generally reducing to a strongly oxidizing one. An era is being inaugurated in which, just like the fossil fuels coal, oil, and natural gas, hydrogen is a primary fuel and, just like electricity, it is also an energy carrier. Hydrogen carries with it only energy, not the environmentally harmful carbon. Moreover, in terms of energy it is the fuel that carries the largest specific density among all others.

Because of the facts of being able to be produced by a host of different raw materials and renewable energy sources, projecting its availability to become ubiquitous in the world; of being able to be harvested in natural form on earth without the requirement of any further treatments or conversions to other compounds for practical use; of, eventually, being perennial, being continuously processed in the earth guts; of possessing the highest energy density among all known fuels; of being chemically the simpler fuel among all others; of being environmentally friendly and not possessing carbon; of acting as a buffer for short- or long-term energy storage in conjunction with and solving issues associated with the intermittent renewable energies; of, if naturally or if artificially produced from water, thus being originated by reactions occurring with water and, whenever used, either conventionally burned or efficiently converted into electricity and heat by feeding a fuel cell, giving origin once again to water, hydrogen is the suitable fuel for a circular economy, that is, a perennial renewable circular sustainable fuel utilization cycle that will characterize the highly efficient engineering and the energy technological choices of the 21st century.

The interaction of humanity with natural existent hydrogen is not new, but it was not known to be natural hydrogen.

To understand it, it is first important to recall that only in the 20th century it was accepted that the movement of tectonic plaques made the earth's oceanic crust and the underlying upper mantle to be uplifted and exposed above sea level, emplaced onto continental crustal rocks, giving rise to many present mountains. That is the reason why ophiolite is frequently found on top of mountains, sometimes associated with limestone rocks. Subsequently, it is needed to consider that the natural formation of hydrocarbons such as methane, ethane, ethylene, and propane may occur without participation of biomasses, with inorganic origin, by reaction of hydrogen with CO_2 or bicarbonate ions dissolved in water. Methane formation follows the well-known Sabatier equation:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{1.5}$$

It could even be possible that this would be the source of hydrocarbon compounds giving inorganic origin to natural shale gas formations without the intervention of biomass. It could also be possible to develop new hydrogen and hydrocarbons production methods and CO_2 sequestration procedures by mimicry of the natural processes.

Once this explanation is taken into consideration, one can refer to Yanartaş, flaming rock in Turkish. It is situated close to Olympos, in Lycia, in the province of Antalya, Turkey, where the Chimaera Mountain presents ever-lasting flames, known for more than 2500 years. Fig. 1.20 presents the site localization and a photograph of the flames. The composition of the gas that gives origin to these flames was found to be 12% of hydrogen, mainly methane, and traces of nitrogen and helium [63].

However, there is an alternative explanation for the ever-lasting flames of Yanartaş on the Chimaera Mountain that was given by Homer, in the Iliad, as follows:

> *Chimaera, daughter of Echidna, breathed raging fire, a creature fearful, great, swift-footed and strong, who had three heads, one of a grim-eyed lion; in her hinderpart, a dragon; and in her middle, a goat, breathing forth a fearful blast of blazing fire. Her did Pegasus and noble Bellerophon slay.*

FIGURE 1.20 Map of Turkey with indication of the localization of the Chimaera Mountain on the Southeast and Yanartaş, ever-lasting flames from sustainable perennial natural gases.

Defeated by Pegasus and Bellerophon, Chimaera (Fig. 1.21) was sent to the guts of the earth, from where she breathes fire through the rocks for ever…

FIGURE 1.21 Bellerophon fighting the Chimaera. Side A of an attic black-figured "overlap" Siana cup, ca. 575–550 BC. Found in Camiros (Rhodes). Courtesy Louvre Museum.

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Science and Engineering of Hydrogen-Based Energy Technologies

Hydrogen Production and Practical Applications in Energy Generation

Edited by Paulo Emílio V. de Miranda

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The Editor

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