Hydrogen-Based Energy Systems

Subjects: Energy & Fuels

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The current state of hydrogen as an energy vector is marked by its growing importance and recognition worldwide. Despite its still formidable challenges, once it achieves some maturity, it might be seen as a promising solution to address climate change, reduce emissions, and facilitate the transition towards a sustainable energy future. Collaborative international efforts highlight its significance. While challenges exist and these should not be underestimated, the momentum behind hydrogen suggests that policymakers all around the world see a promising future in the global energy transition towards a cleaner future for both developed and developing countries, and thus for the world.

hydrogen hydrogen energy systems electrolysis transportation storage fuel cell

1. Hydrogen

Hydrogen is the most abundant element in the Universe, and it is primarily found on Earth in molecules such as water and organic compounds [1]. It is the first and simplest element in the periodic table, having the smallest atomic mass of 1.008 g/mol and being composed of only one proton and one electron [2][3]. Atomic hydrogen does not exist under normal conditions [3]. In turn, hydrogen is found as a two-atom combination, forming the hydrogen molecule (H_2).

Under normal conditions, hydrogen is a colourless and tasteless combustible gas [4]. Because it is renewable, non-toxic, and carbon-free, it is expected to significantly improve air quality [5]. In the remainder of the article, the term “hydrogen” will mainly be used as a synonym for the H_2 molecule.

Physical and chemical properties both have an impact on how a substance is used and handled. This is especially true when it comes to the safe handling and storage of energy carriers such as hydrogen.

Under normal conditions, hydrogen exists as a gas. In fact, its normal boiling point at normal pressure (1.013 bar) is very close to absolute zero, at −252.8 °C (20.4 K) [1]. Of course, temperature and pressure influence the hydrogen aggregation state. By increasing the pressure, gases can be liquefied. Regardless of the pressure, there is a critical temperature above which they can no longer be liquefied. The critical temperature for hydrogen is −240 °C (33.2 K) [6]. As a result, in order to liquefy hydrogen, its temperature must be lower than this point. The pressure known as hydrogen’s critical pressure is 13 bar [6]. Thus, the critical temperature and pressure of a substance, which in the case of hydrogen are −240 °C and 13 bar, define its critical point. At this point, the hydrogen density is 31 g/L [6].

At normal pressure, the melting point of H_2 (the temperature at which it changes from solid to liquid) is −259.2 °C (13.9 K), which is slightly lower than the boiling point [1]. A substance’s triple point is the point on the phase diagram at which all three aggregation states are in thermodynamic equilibrium. This point for hydrogen is −259.3 °C and 0.07 bar [1]. The triple point is also the vapour–pressure curve’s minimum point. The pressure–temperature combination at which the gaseous and liquid states are in equilibrium is indicated by this curve (purple). Hydrogen is a liquid to the left of that curve and a gas to the right of that curve. Above and to the right of the critical point, hydrogen transforms into a supercritical fluid, which is neither gaseous nor liquid. In comparison to other substances, hydrogen's vapour–pressure curve is rather steep and short [3]. As a result, hydrogen liquefaction occurs primarily through cooling and less through compression.

Figure 1 represents the hydrogen phase diagram, which shows the critical point (green), triple point (orange), melting curve (pink), vapour–pressure curve (purple), and solid, liquid, and gaseous states of aggregation.

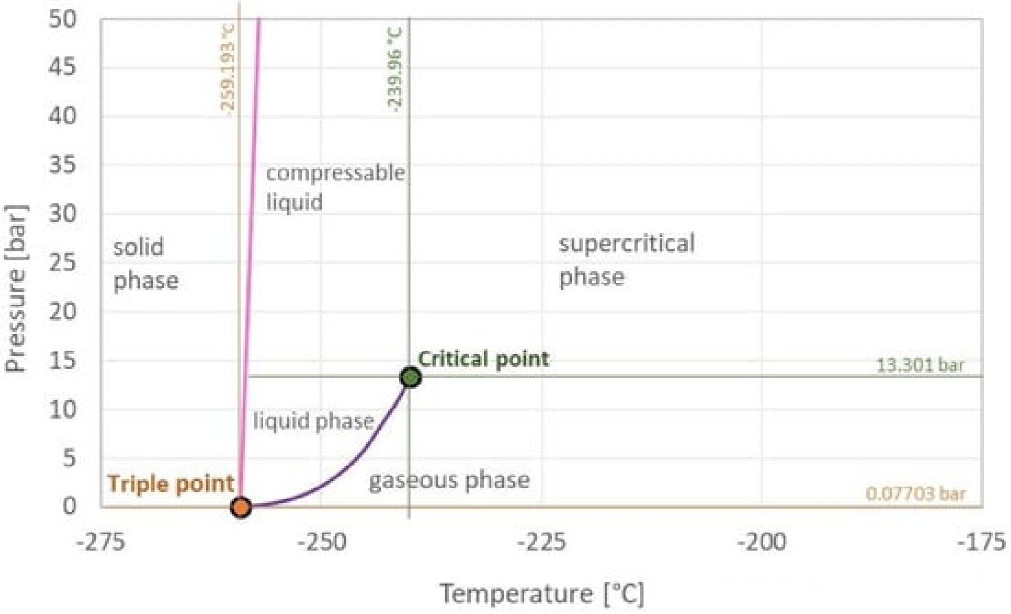

Figure 1. Hydrogen phase diagram [7].

The negative Joule–Thomson coefficient of hydrogen is a unique property [6]. Under normal conditions, when air adiabatically expands, it cools down, which is used in gas liquefaction. However, hydrogen behaves differently; when it is adiabatically expanded, it heats up. Hydrogen exhibits "normal" Joule–Thomson effect behaviour only below its inversion temperature of −73 °C (200 K) [6].

Density is defined as the mass-to-volume ratio. At 0 °C, the density of hydrogen in its gaseous state is 0.089 g/L [8]. With a density of 1.29 g/L, air is approximately 14 times heavier than hydrogen gas, giving hydrogen high buoyancy in the atmosphere and making it highly volatile in open air [6]. Hydrogen has a density of 70.8 g/L in liquid form at the boiling point [9]. It has a density of 76.3 g/L at the melting point of −259.2 °C and 1.013 bar [3]. Thus, liquefaction increases the density of hydrogen by a factor of 800 (0.089 g/L to 70.8 g/L) while considerably decreasing its storage volume [3]. To compare, the corresponding factors for liquefied petroleum gas (LPG) and liquefied natural gas (LNG) are approximately 250 and 600, respectively [3].

The energy content of an energy carrier greatly influences how it is stored. The calorific value of an energy source, or more accurately, its lower and higher heating values, determines its energy content. The amount of net heat released in a (theoretically) complete combustion is defined as the lower heating value (LHV). The higher heating value (HHV) additionally considers the energy released during the condensation of the water vapour produced during combustion [3]. The calorific value usually has a mass basis, expressed in MJ/kg. It is also possible to describe it on a volume basis, MJ/L, using density (kg/L). The gravimetric and volumetric energy densities of hydrogen in various states of aggregation, as well as those of other common fuels, are depicted in **Figure 2** [10]. As can be seen, in terms of gravimetric energy density, hydrogen has by far the highest LHV of 120.1 MJ/kg [11]. The HHV (not shown in the figure) can be as high as 141.8 MJ/kg [1]. As a result, the LHV is nearly three times greater than that of liquid hydrocarbons. The volumetric energy density of hydrogen, on the other hand, is relatively low. Its value is only of 0.01 MJ/L under normal conditions [3]. As a result, in order for hydrogen to be used in practice, its density must be strongly increased so that it can be stored in a reasonably small volume.

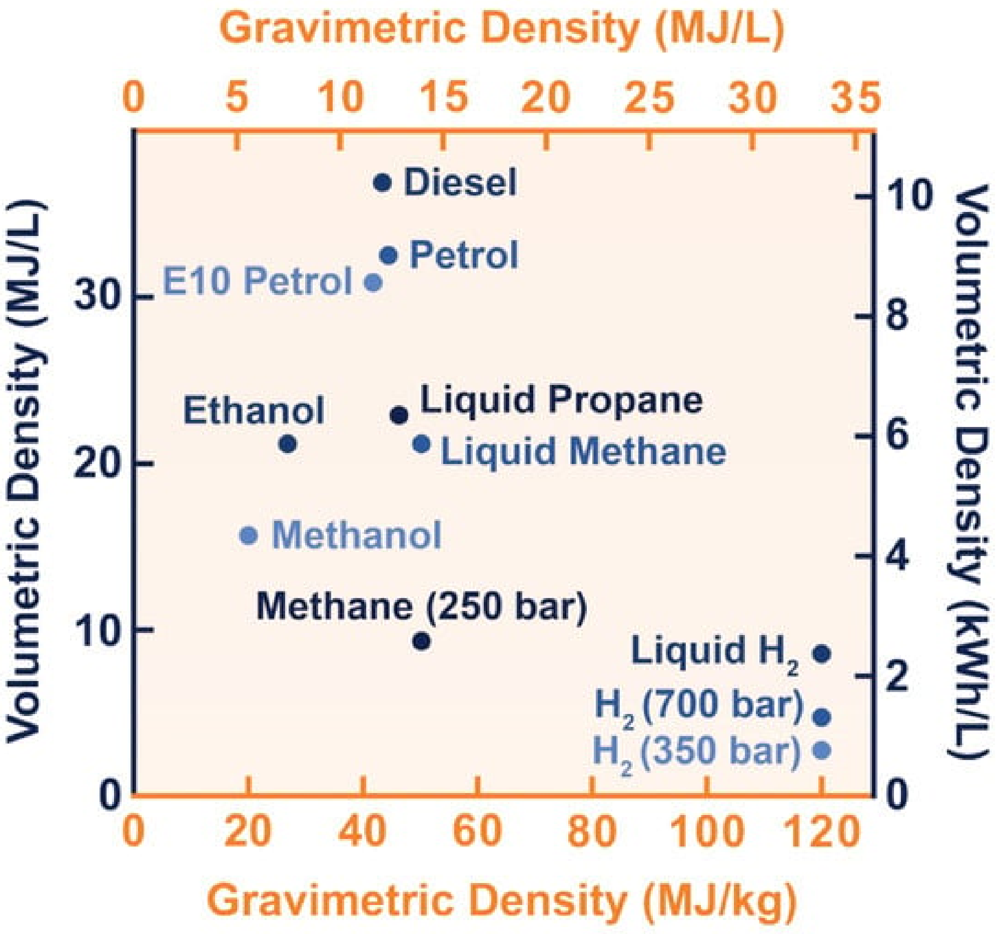

Figure 2. Volumetric and gravimetric energy density of hydrogen in various states of aggregation, as well as of other common fuels [12].

Another important property of hydrogen is its extreme diffusivity. Because hydrogen is the lightest of gases, it can diffuse into other media at a rate of 0.61 cm2/s, causing embrittlement in porous materials and even in metals [11].

The flammability of hydrogen is an important chemical property. When hydrogen is burned in the open air, the flame is barely visible in daylight, as it has low heat radiation and a high ultraviolet radiation component [3]. Hydrogen has a broad ignition spectrum when compared to other fuels. This range is constrained by the lower and upper flammability limits, which for H_2 are 4% and 76% concentrations in air, respectively [8]. Only methane has an upper limit close to 15%, which still falls short of that of hydrogen as shown in **Figure 3**.

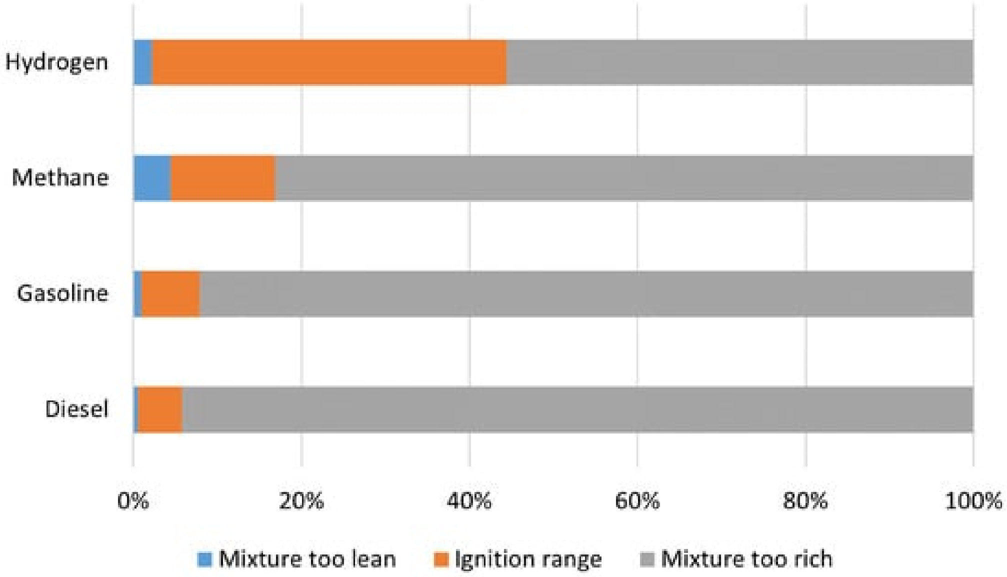

Figure 3. Ignition range of hydrogen and of other common fuels, adapted from [8].

Hydrogen is an interesting fuel due to its combustion properties and absence of carbon in its composition. Its wide ignition range would allow for fairly lean air/hydrogen mixtures in internal combustion engines. While gasoline engines use a stoichiometric combustion air ratio $\lambda=1$

and diesel engines use $\lambda=2$, hydrogen combustion engines could use λ values as high as 10 [3][8]. Because lean combustions are more efficient, they use less fuel for the same amount of energy used.

Pure hydrogen has a higher self-ignition temperature than conventional fuels, at 585 °C [11]. The minimum energy required for hydrogen ignition, on the other hand, is of only 0.02 mJ, which is lower than for other common fuels [8]. As a result, hydrogen is classified as a highly flammable gas. A single electrostatic discharge of around 10 mJ, on the other hand, is sufficient to ignite other fuels [3]. Hydrogen has a maximum flame speed of 346 cm/s, considerably higher than those of other common fuels [3].

The hydrogen molecule is a relatively inert substance. However, by heating a 2:1 hydrogen/oxygen mixture to 600 °C, a chain reaction can begin, resulting in a spread of temperature rise throughout the mixture [3]. The water vapour produced by the reaction's heat expands to a greater volume than the original mixture. The rapid spread of water vapour causes an oxyhydrogen reaction, also known as the Knallgas reaction [3].

Hydrogen possesses various physical and chemical properties that render it an intriguing fuel option. However, it requires careful handling and adherence to safety regulations, as not all of its properties are equally favourable.

2. Green Hydrogen Production Processes

2.1. Introduction

Hydrogen can be generated using a wide range of energy sources and technologies. It is thus an energy vector because it is a substance that stores energy as a result of the transformation of primary energy. Fossil fuel sources dominate its current production [13]. As seen in **Figure 4**, by the end of 2021, natural gas (69.5%), coal (29.5%), and oil (0.79%) accounted for more than 99% of global hydrogen production. Only 0.14% is generated by electricity, with the remainder (0.04%) being generated by biomass. As a result, hydrogen can be extracted not only from fossil fuels but also from biomass and even water [14].

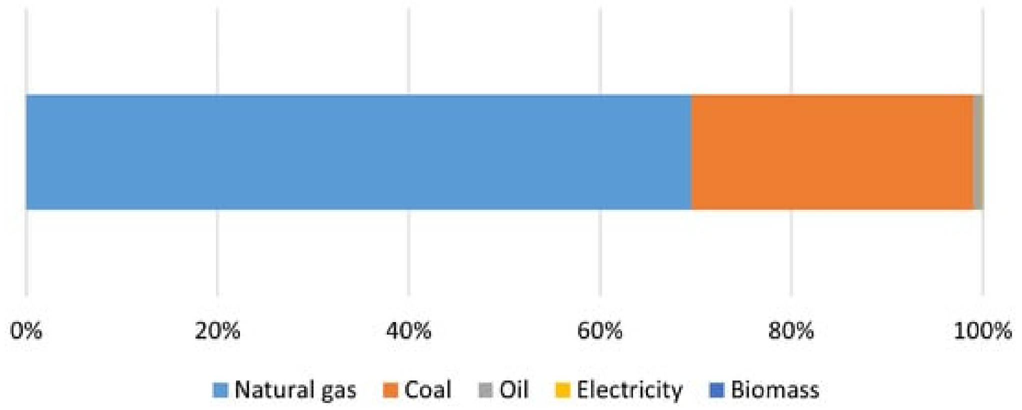

Figure 4. Energy demand for hydrogen production by fuel in 2021, adapted from [13].

2.2. Hydrogen Production Processes

Because of their low production costs, fossil fuels continue to dominate hydrogen production. There are currently several mature technologies for producing H_2 from fossil fuels, the most common of which being hydrocarbon reforming and pyrolysis. In **Figure 5**, one can understand the different processes for the production of hydrogen from fossil fuels and from renewable energy sources.

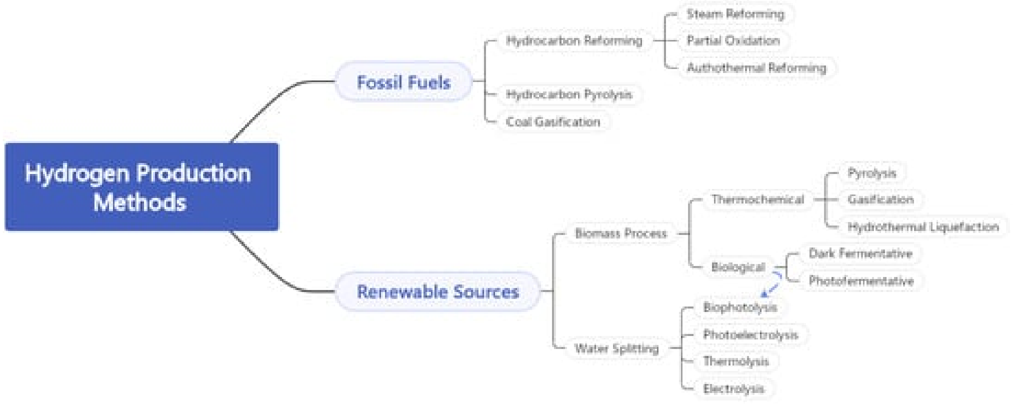

Figure 5. Hydrogen production processes from fossil fuels and from renewable energy sources.

2.2.1. Hydrogen Production from Fossil Fuels

Hydrocarbon reforming is the most advanced technique for producing H_2. Other reactants, such as water vapour or oxygen, are required for the process in addition to hydrocarbons. However, carbon monoxide (CO) is also produced in addition to hydrogen. Steam methane reforming (SMR) is the reaction of steam with hydrocarbons, usually natural gas (methane), at high temperatures (800–1000 °C) [15]. Because this is a highly endothermal reaction, a significant amount of heat is required for it to take place. An alternative to steam reforming is partial oxidation (POX). It is a process that uses high temperatures to convert heavy fuel oil or coal into a mixture of H_2 and CO. One advantage of this process is that it is exothermal, which means that no external heat sources are required [16]. When the two preceding processes, SMR and POX, are combined, the result is known as autothermal reforming (ATR). In this way, POX, in conjunction with O_2, provides the energy required for SMR, thereby rendering the process thermally neutral [17]. It requires less energy than other processes due to its high thermal efficiency. The Global Warming Potential (GWP) of SMR and ATR is fairly high, rated at 11–13 and 13.3 kg CO_2eq/kg H_2. But it could drop to values as low as 1.14 and 0.64 kg CO_2eq/kg H_2 if carbon capture and storage are implemented [18].

Pyrolysis is a thermal decomposition process that converts various light liquid hydrocarbons into elemental carbon (C) and hydrogen in the absence of oxygen [19]. It is typically processed in two stages: hydrogasification and methane cracking. Because the recovered carbon is in the solid state, the pyrolysis of methane (CH_4) does not produce carbon dioxide (CO_2). Coal gasification is a thermochemical process that converts coal into synthesis gas, which is a mixture of H_2 and CO. At high temperatures and pressures, coal is converted into syngas using steam and oxygen (or air) [20]. The main issue with this hydrogen production method is the high CO_2 emissions, at around 16 kg CO_2eq/kg H_2 [21].

2.2.2. Hydrogen Production from Biomass

The amount of hydrogen obtained through biological processes has increased in recent years as a result of increased attention to sustainable development and waste minimisation. Dark fermentative H_2 production and photo-fermentative processes are the primary processes. Anaerobic bacteria are used in dark fermentative processes to produce H_2, organic acids, and CO_2 on carbohydrate-rich substrates in the absence of light and under low-oxygen conditions [22]. H_2 can be produced at any time because no light is required. In photofermentation, on the other hand, photosynthetic bacteria use sunlight as an energy source and assimilate small organic molecules present in the biomass to produce H_2 and CO_2 [23].

Some of the most efficient methods for producing H_2-rich gases from biomass are thermochemical processes. Pyrolysis, gasification, and hydrothermal liquefaction are the most common ones. When gasification and pyrolysis are used, the thermochemical conversion of dry biomass is similar to that of fossil fuels. Both the aforementioned technologies generate CO and CH_4, which can be used to increase H_2 production via steam reforming and water–gas shift reactions. Biogas reforming has an average GWP of 3.61 kg CO_2eq/kg H_2, but depending on the circumstances, it could be negative or exceed 8 kg CO_2eq/kg H_2 [21]. Hydrogen could be obtained from humic biomass through a combination of hydrothermal liquefaction and steam reforming [14].

2.2.3. Hydrogen Production from Water

Water is a plentiful resource for hydrogen production, and it can be split into hydrogen and oxygen with enough energy while emitting no harmful emissions. In its most basic form, water splitting uses an electric current (electrolysis) passing through two electrodes to split the water into H_2 and O_2. However, other energy sources, such as thermal energy (thermolysis), photonic energy (photo-electrolysis), and biophotolysis using microorganisms, can also be used to split it.

One of the most basic methods for producing hydrogen from water is electrolysis. It is the conversion of electrical energy into chemical energy in the form of hydrogen and oxygen as a by-product (this process is further detailed in the following section) [24]. It is regarded as a promising technology, but its production costs are high. Thermolysis is a thermochemical water-splitting process that uses high temperatures to decompose water into H_2 and O_2 [25]. Although it is a simple process, water decomposition requires temperatures above 2500 °C. Because this is a reversible process, one of the primary challenges in its application is the separation of the produced H_2 and O_2, as recombination of these gaseous products can result in an explosive mixture.

Photoelectrolysis is similar to electrolysis, but it includes the absorption of solar energy from a photoelectric cell. This is a process that requires both solar and electrical energy and converts it into chemical energy as H_2 [26]. Biophotolysis is a photonic biochemical process that produces H_2 from water. Under anaerobic conditions, microorganisms such as green microalgae or cyanobacteria use photosynthesis to split the water molecule into H_2 and O_2 [27]. Under these conditions, hydrogen can be produced in an aqueous environment.

2.3. Hydrogen Colour Code

The climate benefit of hydrogen is dependent on how it is produced. As illustrated in **Figure 6**, hydrogen can be distinguished by colour grading based on its production method and carbon footprint.

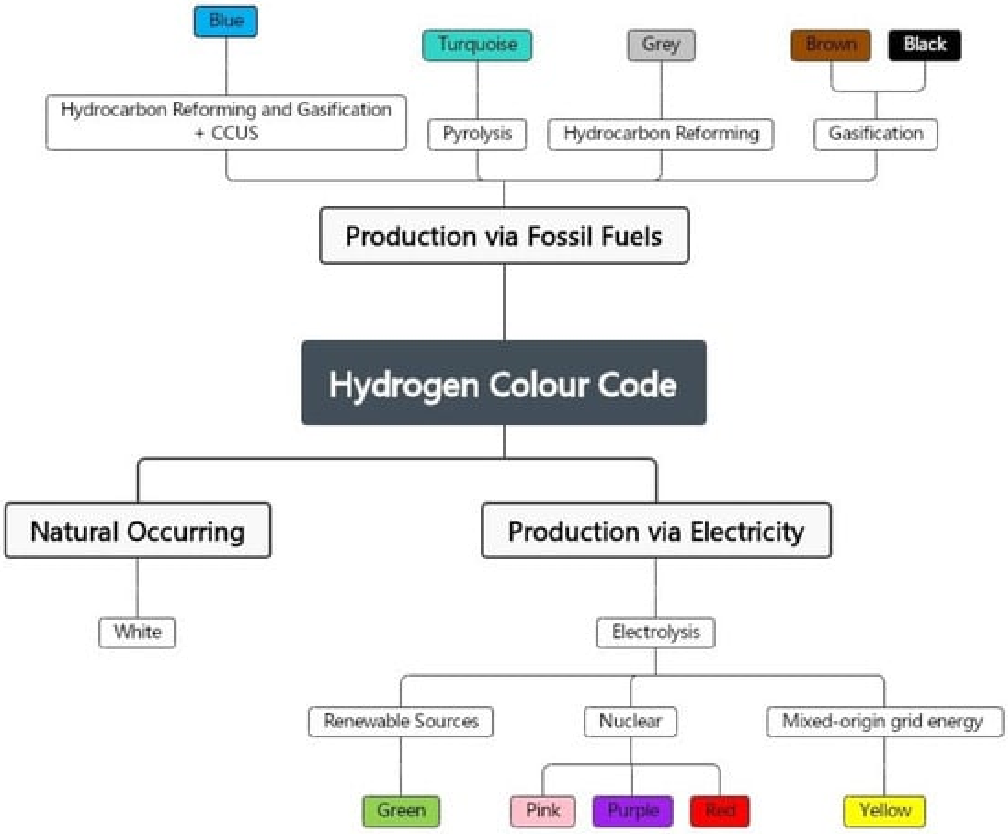

Figure 6. The hydrogen colour spectrum.

2.3.1. Black and Brown Hydrogen

Coal is used to produce black and brown hydrogen, the colours referring to the types of coal used in the process: bituminous (black) and lignite (brown) [28]. H_2 is produced in a process by gasifying coal, where high quantities of GHGs such as CO_2 and CO are produced [29].

2.3.2. Grey Hydrogen

Grey hydrogen is the most common method of production right now [30]. Hydrogen is produced using fossil fuels, and while it is not as harmful to the environment as black or brown hydrogen, the CO_2 produced is still quite significant in terms of its GWP because it is released into the atmosphere [31][32].

2.3.3. Turquoise Hydrogen

Turquoise hydrogen is extracted by the pyrolysis of methane [33]. This is a relatively new process that removes solid carbon rather than emitting CO_2 [34]. Solid carbon is an essential raw material that can be used to make tyres, plastics, batteries, etc. The process uses natural gas as a feedstock, and if the energy used is renewable, the carbon footprint will be close to zero [35][36].

2.3.4. Blue Hydrogen

Blue hydrogen is derived from fossil fuels, just like grey hydrogen [37]. To reduce its emissions, however, much of the CO_2 emitted during the process is captured and stored underground or extracted as a solid and thus used [38]. This is referred to as carbon capture, utilisation, and storage (CCUS) [5].

2.3.5. Yellow Hydrogen

Some authors also consider yellow hydrogen, in which water electrolysis is powered by grid electricity, so its carbon footprint is dependent on how the electricity used is produced [39].

2.3.6. Pink, Red, and Purple Hydrogen

Pink, red, and purple refer to hydrogen produced by splitting water using nuclear power plant electricity. Pink hydrogen is produced by the electrolysis of water [40]. Red hydrogen can also be produced through thermolysis, with the chemicals used in the process being reused in a closed loop [35]. Finally, purple hydrogen is obtained by combining nuclear energy and heat with chemo-thermal electrolysis for water splitting [41].

2.3.7. White Hydrogen

White denotes naturally occurring hydrogen produced by a natural process within the Earth’s crust [35]. There are projects underway to extract it, which is similar to natural gas extraction in that it requires drilling deep underground to access natural H_2 wells. It is regarded by some as the least expensive alternative to green H_2.

2.3.8. Green Hydrogen

Hydrogen that conforms with specific sustainability criteria is called green hydrogen (GH_2). However, there is no universally accepted definition, as there is no international standard for green hydrogen. Several sources refer to GH_2 as being produced through electricity generated from renewable energy sources with minimal CO_2 emission [35][42][43][44].

2.4. Water Electrolysis

Water electrolysis is an electrochemical technique for separating water to produce hydrogen and oxygen using electricity [42]. Based on IRENA—International Renewable Energy Agency (Abu Dhabi, United Arab Emirates)—the electrolyser is composed of three stages (**Figure 7** [45]):

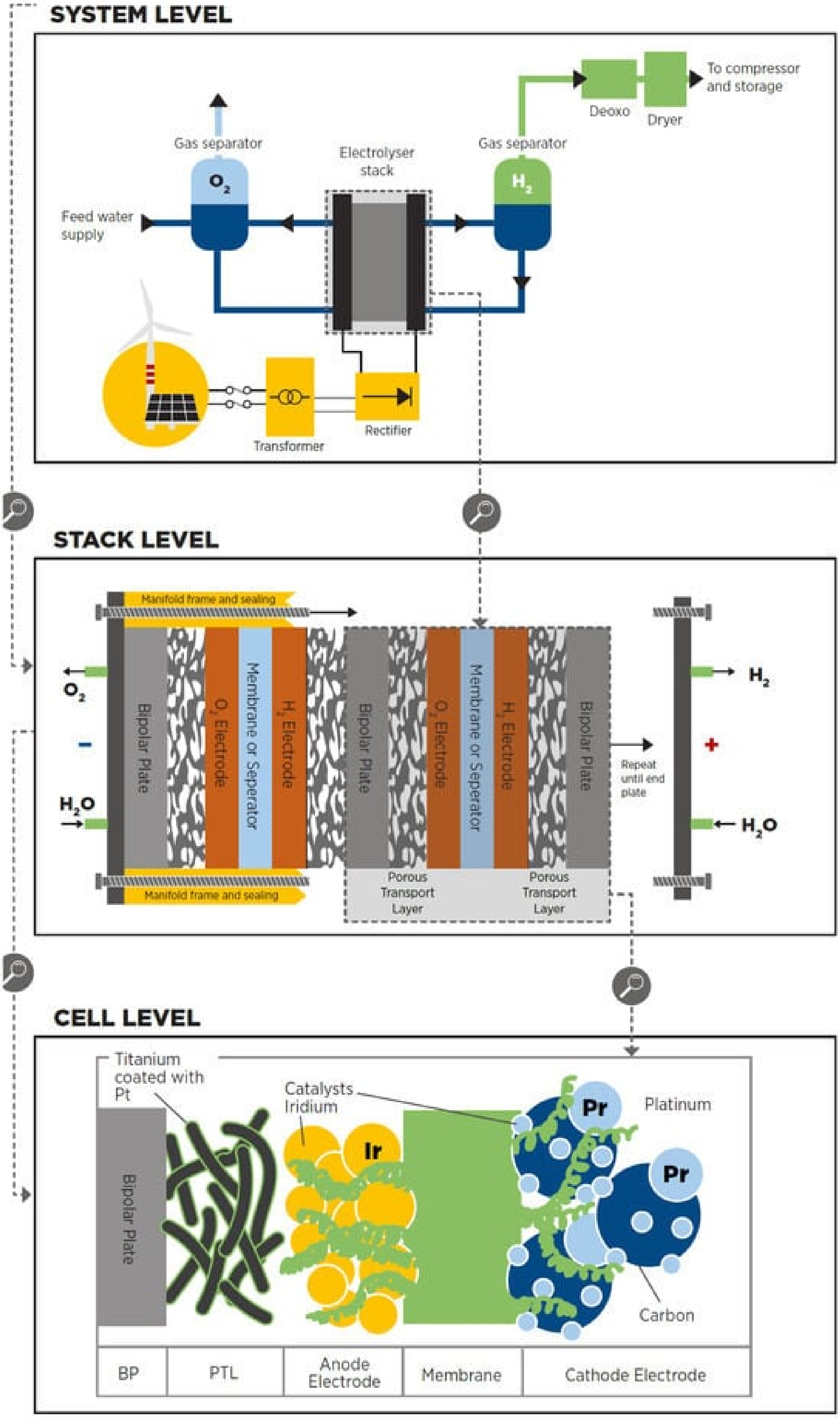

Figure 7. Examples of the components found on water electrolysers in their three levels: system, stack and cell [45].

- The cell is the electrolyser's heart and the site of the electrochemical process. Common cells consist of two electrodes—anode and cathode—immersed in a liquid electrolyte or adjacent to a solid electrolyte membrane, two porous transport layers (PTLs) that facilitate reactant transport and product removal, and bipolar plates (BPs) that provide mechanical support and flow distribution.

- The stack generally serves a broader purpose by incorporating multiple cells connected in series, insulating material spacers between opposing electrodes, seals, frames for mechanical support, and end plates to prevent leakage and collect fluids.

- The system level usually includes cooling equipment, hydrogen processing (e.g., for purity and compression), electricity input conversion (e.g., transformer and rectifier), water supply treatment (e.g., deionisation), and gas output (e.g., from oxygen output).

Using circulation pumps or gravity, purified water (or an aqueous solution containing elements to improve the ionic exchange) is introduced into the system. The electrolyte then flows through the BPs and PTLs to reach the electrodes.

$$\mathrm{H_2O} + \mathrm{Electricity}\left(237.2\ \mathrm{kJmol^{-1}}\right) + \mathrm{Heat}\left(48.6\ \mathrm{kJmol^{-1}}\right) \rightarrow \mathrm{H_2} + \frac{1}{2}\mathrm{O_2} \quad (1)$$

At room temperature, the previous reaction requires a theoretical thermodynamic cell voltage of 1.23 V to split water into hydrogen and oxygen [42]. However, the cell voltage required for efficient water splitting was experimentally determined to be 1.48 V [42]. The additional voltage is the voltage required to overcome the kinetic and ohmic resistances of the electrolyte and the electrolyser's cellular components [42]. This is a well-known technology for producing green hydrogen two centuries after the first water electrolysis was performed. However, it is still a technology that is not cost effective for producing large volumes of hydrogen. Water electrolysis technologies have been developed and used in industrial applications since the 18th century. Different trends influenced its development during this evolution, so it can be divided into five generations. According to IRENA—International Renewable Energy Agency—each generation of water electrolysis brings its own set of challenges, breakthroughs, and significance (**Figure 8** [45]).

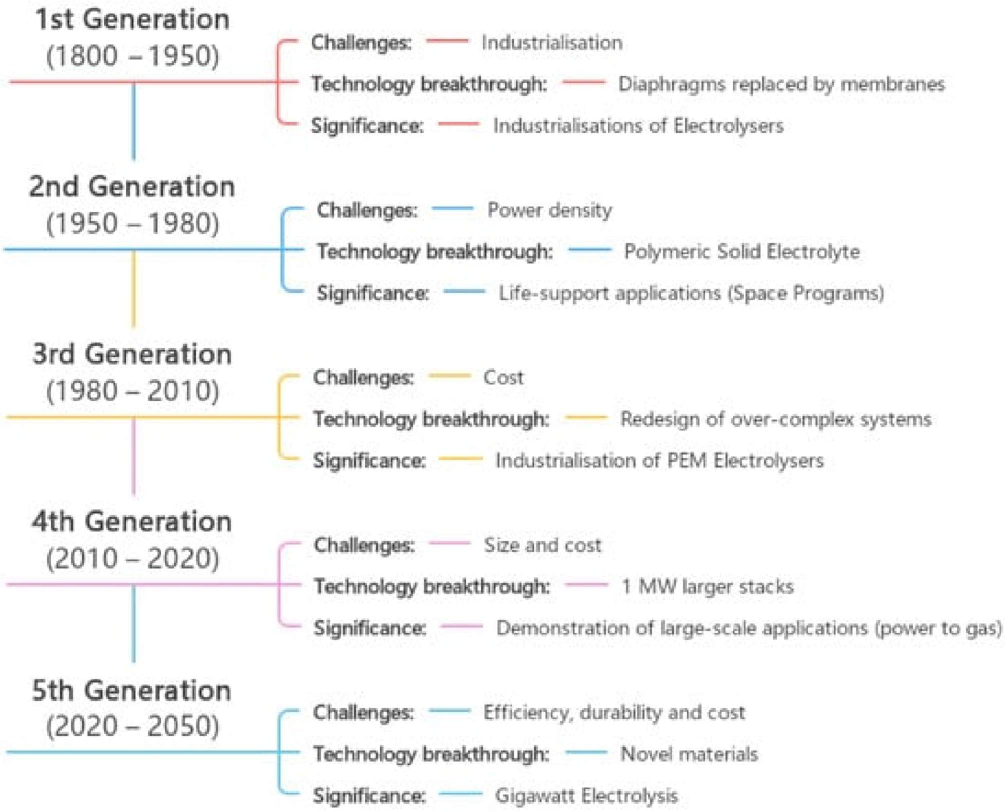

Figure 8. The five generations of water electrolysis development, adapted from [45].

2.4.1. Alkaline Electrolysis

Alkaline water electrolysis is a well-established and mature technology for producing MW-scale industrial hydrogen in industrial applications [42]. There have been several developments from the first introduction of water electrolysis until the operation of the first alkaline water electrolysis plant.

One technique for electrochemically splitting water in the presence of electricity is alkaline water electrolysis. As shown in Equations (2) and (3), this splitting consists of two individual reactions in each half of the cell, the hydrogen evolution reaction (HER) at the cathode, and the oxygen evolution reaction (OER) at the anode:

Cathode reaction (HER):

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (2)$$

Anode reaction (OER):

$$2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^- \quad (3)$$

During this electrolysis process, two moles of alkaline solution are reduced to produce one mole of hydrogen and two moles of hydroxide ions (OH^-) [42]. The H_2 produced can be removed from the cathode surface, and the remaining hydroxide ions are transferred to the anode side via the porous separator under the influence of the electric circuit between the anode and cathode [42]. Already at the anode, the OH^- ions are discharged to produce half a mole of oxygen and one mole of water as shown in **Figure 9** [42].

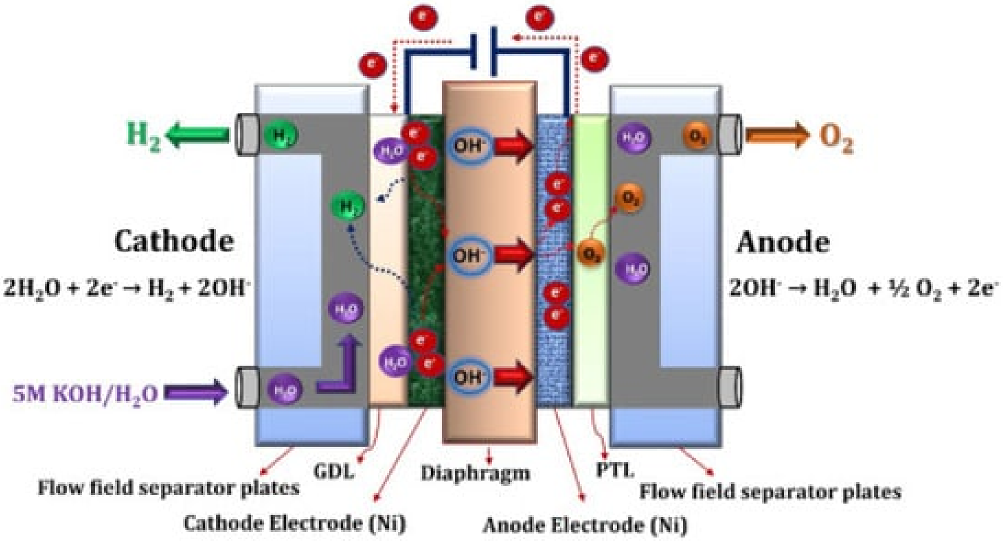

Figure 9. Schematic representation of the alkaline water electrolysis operating principle [42].

2.4.2. Anion Exchange Membrane Electrolysis

Anion exchange membrane (AEM) water electrolysis is a new green hydrogen production technology [42]. Wu and Scott published the first paper on alkaline exchange membrane water electrolysers in 2011 [46]. The first implementation of this system took place in 2012 [47]. The process of AEM water electrolysis is similar to that of alkaline water electrolysis [42]. The main difference is that the diaphragms have been replaced with an anion exchange membrane. This type of water electrolysis has several advantages, including the use of less expensive transition metal catalysts rather than noble metal catalysts, and the ability to use a low-concentration alkaline solution (1 M KOH) as an electrolyte rather than a high-concentration one (5 M KOH). Despite its benefits, this technology requires additional research and development to achieve the assembly stability and cell efficiency required for commercial and/or large-scale applications. Enapter (Crespina Lorenzana, PI, Italy), the leading manufacturer of AEM electrolysers, currently reports a lifetime of 35,000 h [48].

AEM water electrolysis is one method of electrochemically splitting water using an anion exchange membrane and electricity. The electrochemical reaction is made up of two half-cell reactions, HER and OER, which are already shown in Equations (2) and (3) [42].

The water molecule is initially reduced on the cathode side by the addition of two electrons to produce H_2 and OH^- ions. Hydrogen is released from the cathode surface, and hydroxide ions are diffused across the anion exchange membrane to the anode side by the anode's positive attraction, while electrons are transported through the external circuit [42]. The hydroxide ions recombine as water and oxygen molecules on the anode, losing electrons in the process. The anode releases the oxygen produced. **Figure 10** illustrates the fundamental principles of AEM water electrolysis.

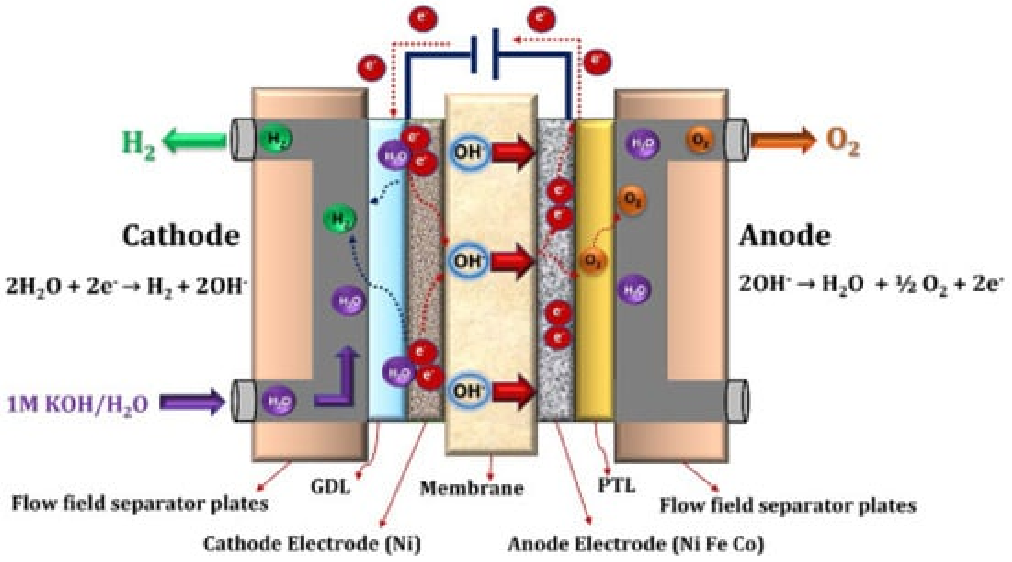

Figure 10. Schematic representation of the AEM water electrolysis operating principle [42].

2.4.3. Proton Exchange Membrane Electrolysis

In 1966, General Electric Co. (Boston, MA, USA) developed the first water electrolysis device based on a proton exchange membrane (PEM) to overcome the drawbacks of alkaline water electrolysis [49]. As an electrolyte, a sulfonated polymeric membrane is used in this technology. The ionic charge carrier is H^+, and deionized water permeates the proton conductive membrane, allowing the electrochemical reaction to function [42]. Because of the kinetics of the hydrogen evolution reaction in PEM water electrolysis, which is faster than alkaline water electrolysis due to the highly active metal surface area of the Pt electrodes and the lower pH of the electrolyte, it typically operates at lower temperatures (30–80 °C) with higher current densities (1–2 A/cm^2) and produces high-purity (99.999%) gaseous (H_2 and O_2) [42].

Like other water electrolysis technologies, PEM technology electrochemically splits water into hydrogen and oxygen. The water molecule is first broken down on the anode side to produce O_2, H^+ protons, and electrons as shown in Equation (5). The produced oxygen is then expelled through the anode's surface. The remaining protons travel to the cathode via the proton exchange membrane, while the electrons travel to the cathode via the external circuit. As shown in Equation (4), protons and electrons recombine at the cathode to produce gaseous H_2.

2.4.4. Solid Oxide Electrolysis

A solid oxide electrolysis cell (SOEC) converts electrical energy into chemical energy. General Electric and Brookhaven National Laboratory (Upton, Suffolk County, New York, USA) pioneered the development of solid oxide water electrolysis in the USA in 1970 [42]. This electrolyser operates at high temperatures (500–850 °C) with water in the form of steam, reducing the energy required to split the water and thus increasing energy efficiency [3]. This increase in energy efficiency is expected to lower the cost of produced hydrogen, energy consumption accounting for the majority of the cost of H_2 production in electrolysis.

Compared to other electrolysis technologies, solid oxide water electrolysis has several advantages. Because of the high operating temperatures, the process has beneficial thermodynamics and kinetics, allowing for an increase in conversion efficiency. It is also a technology that can be easily thermally integrated with downstream chemical synthesis, such as methanol and ammonia production. It also does not require the use of noble metal electrolysers. Despite its advantages, its commercialisation has been challenged by the absence of long-term stability.

2.5. Analysis of Green Hydrogen Production Processes

Green hydrogen production (from renewable energy sources such as solar and wind) using water electrolysis technologies is expected to be a defining moment in the energy transition to meet the proposed zero-emission challenges. Water electrolysis is a well-known electrochemical process for producing green H_2 that requires widespread adoption in order to reduce production costs while maintaining high energy efficiency [42]. As a result, advancements and innovations in current technology are required. In this context, the various technologies presented above each have unique challenges and potential solutions in terms of cost reduction and commercialisation.

Different cost-cutting strategies can be implemented at the cell level. Examples include changing the cell's composition to use less critical materials and changing the stack design to improve the energy efficiency, durability, and current density. Another option is to increase the module's size. This strategy should take into account the trade-off between a small module size that allows for mass manufacturing, standardisation, and replication and a large module size that can achieve cost reduction as a function of the plant size at the expense of fewer units deployed and thus less learning per deployment [45].

Table 1 outlines the general technical characteristics of each water electrolysis technology, as well as the various materials and elements for each electrolyser component. The values associated with the operationalisation of the electrolyser systems and their estimated production cost based on plant size are then stated. Finally, each process is evaluated in terms of its TRL based on all of the values presented in the table.

Table 1. Technical characteristics of typical water electrolysis technologies: alkaline, proton exchange membrane, anion exchange membrane and solid oxide water electrolysis [42][45].

	Alkaline	AEM	PEM	Solid Oxide
Electrolyte	KOH/NaOH (5–7 mol/L)	DVB polymer support with KOH/NaOH (1 mol/L)	PFSA membrane	YSZ
Separator	Asbestos, Zirfon, Ni	Fumatech	Nafion®	Solid electrolyte YSZ
Electrode/catalyst (oxygen side)	Nickel-coated perforated stainless steel	Nickel or NiFeCo alloys	Iridium oxide	Perovskites-type (LSCF, LSM)
Electrode/catalyst (hydrogen side)	Nickel-coated perforated stainless steel	Nickel	Platinum nanoparticles on carbon black	Ni-YSZ
PTL anode	Nickel mesh (not always present)	Nickel foam	Platinum-coated sintered porous titanium	Nickel mesh or foam
PTL cathode	Nickel mesh	Nickel foam or carbon cloth	Sintered porous titanium or carbon cloth	None

	Alkaline	AEM	PEM	Solid Oxide
BP anode	Nickel-coated stainless steel	Nickel-coated stainless steel	Platinum-coated titanium	None
BP cathode	Nickel-coated stainless steel	Nickel-coated stainless steel	Gold-coated titanium	Cobalt-coated stainless steel
Operating temperature	70–90 °C	40–60 °C	50–80 °C	700–850 °C
Operating pressure	<30 bar	<35 bar	<30 bar	1 bar
Nominal current density	0.2–0.8 A/cm^2	0.2–2 A/cm^2	1–2 A/cm^2	0.3–1 A/cm^2
Voltage range (limits)	1.4–3.0 V	1.4–2.0 V	1.4–2.5 V	1.0–1.5 V
Electrode area	10,000–30,000 cm^2	<300 cm^2	1500 cm^2	200 cm^2
Efficiency	50–68%	52–67%	50–68%	75–85%
H_2 purity	99.9–99.9998%	99.9–99.999%	99.9–99.9999%	99.9%
Lifetime (stack)	60,000 h	>5000 h	50,000–80,000 h	20,000 h
Cold start	<50 min	<20 min	<20 min	>600 min
Stack unit size	1 MW	2.5 kW	1 MW	5 kW
Capital costs (stack) minimum 1 MW	270 USD/kW	n.d.	400 USD/kW	>2000 USD/kW
Capital costs (stack) minimum 10 MW	500–1000 USD/kW	n.d.	700–1400 USD/kW	n.d.
Development status	Early Adoption	Large Prototype	Early Adoption	Demonstration
TRL Scale	TRL 9	TRL 6	TRL 9	TRL 7

n.d.—no data.

3. Hydrogen Storage Processes

3.1. Introduction

It has long been acknowledged that the future of energy production aims at the independence on the fossil fuels currently in use, so a long-term solution to this problem must be found. However, production is only one aspect of the problem, several questions must be addressed. Specifically, how does one meet energy demand when production is lower than demand, and how does one do so in a safe and efficient manner [50]. With the increased use of unpredictable and intermittent renewable energy sources such as wind and solar, it is critical to store excess energy for use in periods of deficit.

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Only through efficient energy storage will renewable energy exploitation reach a critical point. Renewable energies are, indubitably, highly regarded for energy production, for both direct and indirect use. Their unpredictability and fluctuations in time and geography, on the other hand, require energy storage systems that can store energy when and where available and provide it when and where needed. The development of good, clean, and efficient energy storage materials is an impediment to using only renewable energy instead of depending heavily on fossil fuels.

Energy storage systems (ESSs) help to increase the reliability and sustainability of renewable energy resources by overcoming unpredictability and fluctuations. ESSs are proposed to store excess energy generated to be reused during peak demand periods to address time mismatches between energy production and consumption [51]. Furthermore, when it comes to electricity storage, the current methods are limited in terms of capacity as well as charge and discharge times [52]. Large-scale energy storage can help to balance fluctuations in energy use and production.

Hydrogen is one of the most viable long-term storage options for renewable energy [53]. The basic idea is that excess solar and/or wind energy is used to produce electric energy, immediately used to produce hydrogen through water electrolysis during periods when renewable energy production exceeds energy consumption. The hydrogen thus produced is then stored as a compressed gas, or as a liquid. When the electricity generated by wind and/or solar is less than what is consumed, the stored hydrogen can be used to generate electricity, for example, in fuel cells.

Energy storage requirements vary depending on the end-user application in terms of capacity, energy density, storage time, discharge time, operating conditions, and overall storage economics [54]. In a developed hydrogen economy, hydrogen is expected to be used for both stationary and onboard applications. The storage of hydrogen in stationary applications is far less difficult than in onboard application. The weight of the ESS is less important in stationary applications than its volume, which is related to the volumetric density of hydrogen. On-board applications, on the other hand, require both high gravimetric and volumetric energy densities, though volumetric energy density is less important for large vehicles, trains or ships.

3.2. Underground Hydrogen Storage

Power-to-gas technology has given rise to a demand for underground hydrogen storage (UHS) sites around the world due to its ability to maximise the use of renewable energy sources and minimise pollutant and GHG emissions. Large-scale energy storage is required to compensate for the unpredictable and intermittent nature of renewable energy sources, like wind and sun; hence, large-scale hydrogen storage devices are critical. UHS allows for the long-term storage of huge amounts of hydrogen gas.

UHS is generally preferred over surface storage options because it allows for high storage pressures, high safety standards, and security against external influences due to their deep underground locations, reduced investment and storage costs, and a high storage capacity to meet supply needs during energy shortages. This type of hydrogen storage, however, is not without its own issues. The chemical reactivity of H_2 with metal hydrides, dissolved solutes, and microbial metabolisms is well expected, as is the strong propensity for hydrogen leakage due to low viscosity and high reactivity with steel components. The coupled system of excess renewable energy generation and hydrogen production varies with RES availability, causing pressure oscillations in the compressors and hosting rocks. Seismic or volcanic activities can cause H_2 leaks, which escape to the atmosphere via fault zones or abandoned wells. The low molecular weight of H_2 allows it to quickly diffuse through any (even very narrow) existing routes.

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Underground hydrogen storage facilities, **Figure 11**, are classified into two main categories. These are naturally-occurring porous structures such as depleted oil and gas fields and water aquifers, as well as man-made structures that include salt caverns, rock caverns, or abandoned mines. Cushion gas is required in all of these hydrogen storage systems to ensure that the stored gas is delivered at pressures that do not require considerable re-compression prior to processing and transport. The usefulness of the various energy storage structures is mainly reliant on the energy storage availability and end-use requirement in terms of energy storage times.

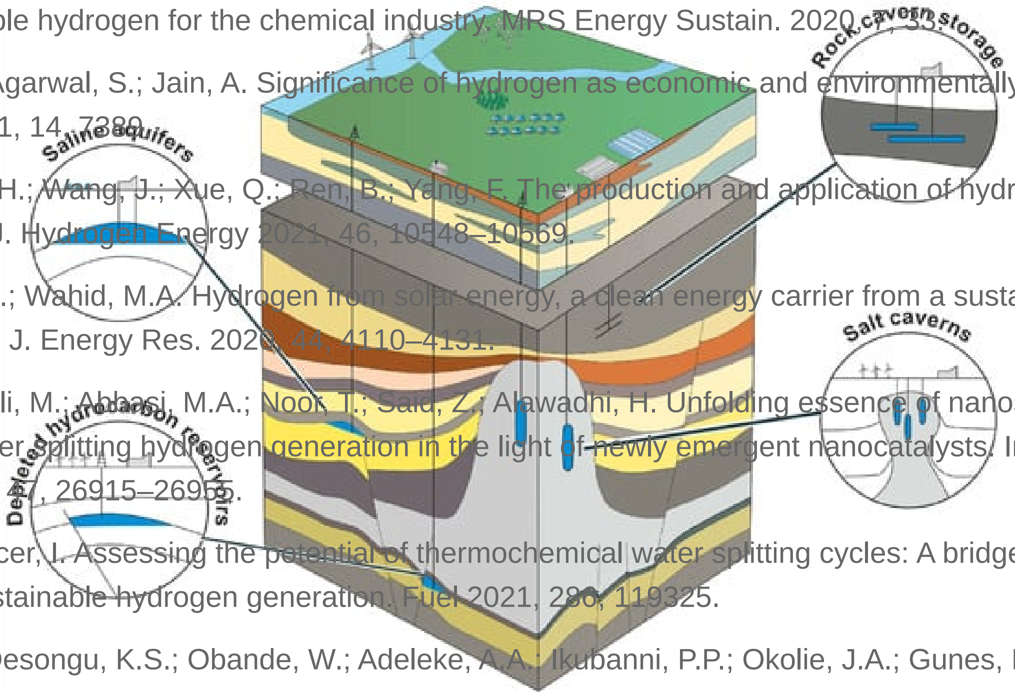

Figure 11. Underground hydrogen storage [55].

3.3. Physical Storage

Physical storage methods, including compressed gas storage, cryogenic (liquid) storage, and cryocompressed storage, are considered the most mature and frequently used technologies for hydrogen storage. These methods are distinguished by high-pressure or refrigerated storage, and in the case of hydrogen, cryogenic storage is required due to its low boiling point. Hybrid storage, which combines both compression and cooling methods, is also an option. However, since hydrogen has a lower volumetric energy density, one of the following conditions must be maintained to make storage reasonable: high pressure, low temperature, or materials with a higher affinity to hydrogen molecules.

3.4. Material-Based Hydrogen Storage

Material-based hydrogen storage refers to the processes of storing hydrogen gas in solid materials. Based on the storing technique, material-based hydrogen storage could depend on the material adsorption or absorption of hydrogen molecules.

Adsorption and absorption are two different methods for storing hydrogen gas. Adsorption involves the adhesion of hydrogen molecules to the surface of solid material, such as activated carbon, metal–organic frameworks, or zeolites. This method relies on the ability of the adsorbent material to form weak bonds with hydrogen molecules, which are attracted to the surface due to the material's high surface area and porous structure. Adsorption has the potential to store hydrogen at high densities

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while avoiding some of the safety concerns associated with high-pressure hydrogen storage. However, it also has limitations in terms of the amount of hydrogen that can be stored and the energy efficiency of the hydrogen storage process.

In contrast, absorption involves the uptake of hydrogen gas into a liquid or solid material. One common example is the use of metal hydrides, which can absorb large amounts of hydrogen through a chemical reaction that forms a metal–hydrogen compound. Absorption has the advantage of allowing for the high-density storage of hydrogen, some metal hydrides being able to store up to 5 wt% hydrogen. However, absorption also has drawbacks, including the need for high temperatures and pressures to release the stored hydrogen and the potential for degradation (ageing) of the absorption material over time. As such, both adsorption and absorption offer potential solutions for hydrogen storage but also face challenges that must be addressed for widespread adoption.

Material-based hydrogen storage is considered to be a viable long-term solution due to its potential to provide higher storage capacities and be perceived as safer option compared to physical hydrogen storage methods. Moreover, material-based hydrogen storage methods are viewed as a favourable alternative to lithium-ion batteries due to their lighter weight. These materials have the potential for higher storage capacities and can operate under moderate temperature and pressure conditions. Various characteristics are required for materials capable of reversibly storing hydrogen. These characteristics include good reversibility, fast kinetics, operating conditions near ambient temperature and pressure, high gravimetric and volumetric energy densities, and acceptable economics [54].

4. Hydrogen Transportation Processes

Trucks

Depending on the required quantity, gaseous hydrogen can be transported in medium amounts as compressed gas in containers. This can be done by using trucks with gas cylinders or tubes, as shown in **Figure 12**, under pressures ranging from 200 to 500 bar [3].

Figure 12. Tube trailers for pressurised hydrogen gas transportation [56].

Ship

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To transport hydrogen by ship, it is necessary to convert it into a form with higher energy density and then convert it back upon arrival at the importing terminal [57]. Compression is the most energy-efficient method for this process. Although compressed hydrogen gas ships can achieve shipping distances of up to 2600 km when compressed to 275 bar, this falls short of typical long-distance routes exceeding 5000 km [57]. Therefore, due to the substantial increase in cost per unit of hydrogen delivered and the limited quantity of hydrogen that can be transported, compressed hydrogen gas ships are not considered a viable option for hydrogen transportation.

Three options remain for shipping hydrogen: ammonia, LOHC, and liquid hydrogen. Each of these options involves a three-step process: transforming gaseous hydrogen into a suitable form for transport, the hydrogen transportation itself, and reconverting the carrier back to gaseous hydrogen at the destination [57]. However, further R&D is required for each carrier to reach full commercial scalability, as there are still aspects of the value chain that need improvement and refinement.

Pipelines

Globally, there is an extensive network of natural gas transmission pipelines spanning approximately 1.4 million km, according to the available data [57]. In contrast, pure hydrogen pipelines cover only about 4600 km, mainly located in the United States and Northwest Europe [58][59]. The United States has the largest natural gas pipeline network, accounting for nearly one third of the total global length, followed by Russia as shown in **Figure 13**. The existing natural gas pipelines offer a potential opportunity for repurposing them to transport hydrogen, which could result in reduced transportation costs.

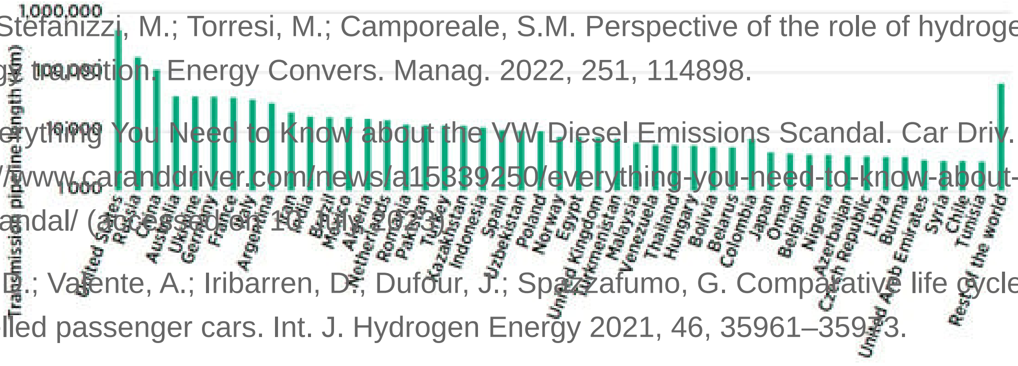

Figure 13. Total natural gas transmission network length by country [57].

The main cost elements associated with hydrogen pipelines consist of the pipeline structure, compressors, the energy required for compression, and the expenses involved in replacing components such as seals and meters [57]. The investment required for a new pipeline depends on its diameter and operating pressure. Increasing the diameter results in a non-linear increase in steel usage (the main cost factor) and capacity [57]. Therefore, it is generally more cost-effective to build a larger pipeline designed to accommodate future capacity needs rather than multiple smaller pipelines. However, a new hydrogen pipeline can be 10–50% more expensive than a new natural gas pipeline [57].

5. Use of Hydrogen in Energy Conversion Processes

Hydrogen Internal Combustion Engines

The automotive industry has experienced a significant transformation in the past decade towards sustainable propulsion technologies. This transformation was likely triggered by events such as the Dieselgate emissions scandal [60] and also the

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boost in electrical propulsion technologies made by advances in electrical energy storage and industry disruptors such as Tesla Inc. (Austin, TX, USA) This made electric vehicles a viable and attractive option for many consumers. However, the increasing use of plug-in hybrid and fully electric vehicles has raised concerns about the actual life cycle footprint of EVs, namely, the sustainability of battery manufacturing and end-of-life, as well as the indirect emissions associated with the production of the electric energy needed to propel the vehicle. This is because the production of electric energy and its associated emissions of CO_2 and NOx are often concentrated in conventional power plants, which are fuelled by fossil fuels such as coal, typically the worse fossil source in terms of specific GHG emissions, or natural gas, and by renewable energy sources only to a limited extent. Given this scenario, green hydrogen is seen by many policy makers as playing a crucial role in the future of clean mobility.

To begin with, hydrogen has the potential to be used directly as a fuel in internal combustion engines (ICE) in place of conventional fossil fuels [10][61]. Over the past few decades, various research groups have studied the combustion of hydrogen using either port-fuel injection (PFI) or direct injection (DI) in the combustion chamber [8][11]. Due to its unique chemical and physical properties, such as its low density, high diffusivity, and temperature inversion during rapid expansion, direct hydrogen injection has emerged as the most promising solution. This is because hydrogen's minimum auto-ignition energy at stoichiometry is about ten times lower than standard hydrocarbons, and its flame speed in air is faster than standard hydrocarbons. Consequently, PFI is susceptible to pre-ignition, knock, and backfire in the intake manifold. In contrast, hydrogen's wide flammability range and high molecular diffusion make it easier to achieve efficient combustion inside ICE, especially with DI. However, the location and timing of the injector cap are critical parameters that require further investigation. Additionally, the control of NOx emissions, wall heat losses, fresh mixture formation, and stratification within the cylinder are issues that require further studies [59]. Naturally, one of the main obstacles for the use of hydrogen in ICE-based vehicles is the low density of hydrogen, which requires hydrogen to be compressed and stored in high-pressure vessels, with all the hurdles that were already mentioned in the present study regarding this issue.

Hydrogen Gas Turbines

In January 2019, the gas turbine industry made a resolute pledge to advance the development of gas turbines capable of running on 100% hydrogen by 2030 [62]. This commitment demonstrates a strong endorsement of the European gas grid's transition into a renewable-based energy system. The industry aims to tackle technical hurdles and ensure a rapid and seamless transformation towards this goal.

Gas turbines play a crucial role in balancing the electric energy system, and by expanding their fuel capabilities to include hydrogen, they can have a prominent role in both transitional and long-term energy strategies. In their current combined cycle configuration (in which a vapour turbine is added to extract energy from the exhaust gases of the gas turbine), these systems already represent the cleanest form of electricity generation from fossil sources. Compared to coal-fired power plants, gas turbines running on natural gas emit roughly half of the CO_2 for the same electricity output [62].

According to the European Turbine Network (ETN Global) report on hydrogen gas turbines, these turbines have several advantages [62]. First, they can enable deep emissions reduction while integrating more renewables in the power sector through the use of hydrogen produced by them. Second, gas turbines can burn 100% hydrogen fuel and can be retrofitted to existing natural gas infrastructure allowing for scalability, from small decentralised units to large-scale systems. Third, the shift from coal-fired to gas-fired power generation could play a crucial part in decarbonising the sector during the next ten years with relatively limited efforts and investments and with the small update of already proven technology and the existing manufacturing infrastructure.

Although gas turbine manufacturers have made significant efforts to determine the tolerance of existing gas turbine systems to operate with hydrogen and understand the potential negative effects (such as increased NOx emissions and reduced lifespan of hot gas path components), there is still much work to be done to certify existing gas turbine technology for high hydrogen content gaseous fuels, particularly when hydrogen is mixed with natural gas.

Fuel Cells

Fuel cells are becoming more popular as environmentally friendly sources of electric energy. They are electrochemical devices rather than thermal engines. They have no moving parts and convert hydrogen or hydrogen-rich fuels and oxygen into electricity and heat, with only water as the emission by-product. This process directly converts the chemical energy of a fuel into electrical energy without the need for intermediate aerial combustion and conversion to thermal energy, thus avoiding the thermodynamic limitations of thermal engines, which have an efficiency limited by the theoretical Carnot efficiency. The concept of a fuel cell dates back to William R. Grove's invention of two platinum electrodes in an electrolyte, where hydrogen underwent a catalytic reaction at one electrode and oxygen at the other. Electrolysis breaks down water into its constituents, oxygen and hydrogen, using a direct current [3]. The process occurring in a fuel cell is basically the reverse of the electrolysis process, that is, the recombination of O_2 and H_2 to form H_2O with the production of a direct electric current. The basic structure and operation of a fuel cell is illustrated in **Figure 14**. Grove referred to his invention as a "gas cell" and described it as a "curious voltaic pile" in a letter to Michael Faraday in 1842 [63].

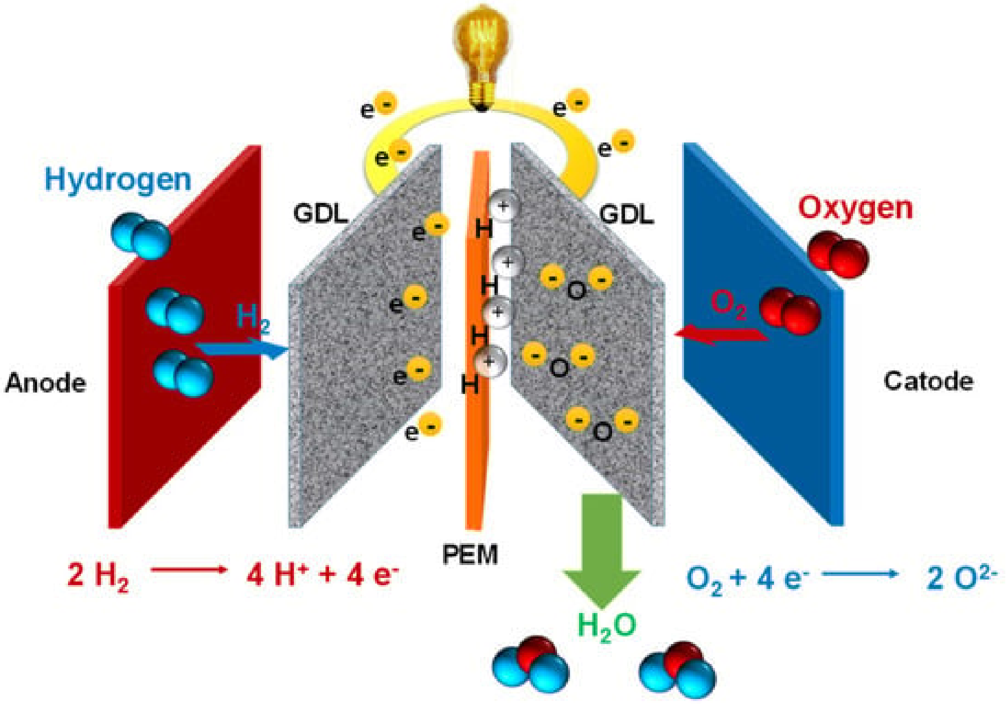

Figure 14. The basic structure and operation of a fuel cell [64].

Ludwig Mond, an industrialist in 1889, is credited with coining the term "fuel cell" after realising that the electrochemical oxidation of hydrogen is a more efficient process for releasing energy compared to its oxidation in an aerial combustion process. He recognised that since hydrogen can be continuously supplied to the cell, it can be considered a "fuel", leading to Grove's electrochemical cell being referred to as a "fuel cell" instead of a battery [63].

There are various types of fuel cells, but they all share a fundamental design. Each unit comprises a series-connected stack of multiple individual cells. At the core of this design is the membrane electrode assembly (MEA), which determines the fuel cell’s performance. The MEA consists of two porous electrodes, namely the negative electrode (anode) and positive electrode (cathode), both equipped with catalysts to speed up the reactions. It also includes an electrolyser and gas diffusion layers. The electrolyte plays a crucial role by allowing only specific ions to pass between the electrodes. If any other substances flow through the electrolyte, they disrupt the chemical reaction and thereby reduce the efficiency of the cell.