

The Survey of Key Technologies in Hydrogen Energy Storage

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Abstract

Hydrogen is believed to be an important energy storage vector to fully exploit the benefit of renewable and sustainable energy. There was a rapid development of hydrogen related technologies in the past decades. This paper provides an overall survey of the key technologies in hydrogen energy storage system, ranging from hydrogen production using both fossil fuels, biomass as well as electricity generated from renewable power sources, to hydrogen storage in both pressurised gas, liquefied and material-based methods, as well as associated electricity generation technologies using hydrogen. The state-of-the-art and the future development of individual technology is also discussed.

Keywords: Hydrogen energy storage system, Hydrogen production, Hydrogen storage, power generation

1. Introduction

Energy is a topical subject in our daily life. The rapid growth of population and increase of personal income are the key drivers behind growing energy demand. It is projected that by 2035, an additional 1.6 billion people will demand energy when the global population reaches 8.7 billion [1]. The major problem faced is the conflict between increasing energy demand and the scarceness of existing fossil fuel supply, together with concerns associated with the utilisation of conventional fossil fuels, such as greenhouse gas emissions leading to climate change, as well as the negative impact on human health from other associated pollutants.

There is an urgent need to source clean alternative and sustainable fuel to replace existing non-renewable fossil fuels. The world has seen a rapid growth in the development of renewable power generation. According to [2], the renewable power capacity installed globally reached 1560 GW at the end of year 2013, almost double the figure of 895 GW at the start of year 2004. However, there are numerous disadvantages inherent in renewable power plants. Typically, renewable power plants are far away from the demand site, as a result, the transport of renewable energy presents a difficulty. The inherent intermittent nature and fluctuation of renewable power sources indicate that the power generation is unpredictable and there is an inevitable mismatch between the renewable power generation and the load demand. Hence, with existing centralised power generation and distribution networks, increasing decentralised renewable power plants, like PV arrays and wind farms, will have significant impact on the stability of the grid. As a result, curtailment is a mechanism currently used to solve those problems which is expensive and prevents the further penetration of renewable power. Energy storage is a solution to address the aforementioned problems.

Among various energy storage mechanisms, such as pumped hydro, battery, compressed air, flywheels, capacitor, and others, hydrogen is a promising candidate to help construct our future energy system. Currently, as an important industrial material, hydrogen is widely used in food industry, petroleum refining, ammonia production, as well as metal refining. However, hydrogen also has great potential to provide energy to all sectors of the economy, including transportation, buildings and industry and can further lead to a low carbon energy system sometimes called the Hydrogen Economy.

The Hydrogen Economy is an attractive concept. It was published in 1972 [3] and was further developed along with the progress of the environmental, political and economic development as well as the advancement of the technologies [4, 5]. The fundamental philosophy of this concept is a new system that utilises hydrogen for energy delivery.

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Such system includes the integration of hydrogen production, storage, transportation, distribution and applications, as well as other aspects such as education, safety, codes, standards and regulations. Nowadays, there are a lot of research activities in analysing and investigating the necessity, impact, opportunities and challenges of transition and implementation of hydrogen economy, either nationally, e.g. in Australia [5, 6], Brazil [7], Canada [8, 9], China [10–12], Ecuador [13], Germany [14], Japan [15], Korea [16–18], Lithuania [19], Mexico [20], New Zealand [21], Nigeria [22], Pakistan [23], Poland [24, 25], Portugal [26], Romania [27], Slovenia [28], Spain [29, 30], Taiwan [31, 32], United Kingdom [33, 34], United States [35], or regionally, e.g. in Asia [36], Southwest Europe [37], EU [38], even the whole world [39, 40].

In this report, a thorough survey of the key technologies in hydrogen energy storage is carried out. It provides an overview of hydrogen technology from production to storage and utilisation, ranging from hydrogen production from fossil fuels, biomass, as well as from renewable power sources, to hydrogen storage as compressed gas, cryogenic liquid and in chemical compounds. Finally, it reviews the application of hydrogen technology not only in fuel cell systems, but also in the latest power-to-gas technology. This report also surveys the current development and state-of-the-art of those technologies.

2. Technologies in Hydrogen Production

Hydrogen can be produced from a large number of different feedstocks such as water, coal, natural gas, biomass, hydrogen sulfide, boron hydrides, and others, through thermal, electrolytic or photolytic processes. A brief summary of the methods, along with their concise descriptions, materials and required energy supply is provided in Table 1. The production of hydrogen can be catalogued as four main routes; renewable, non-renewable and nuclear, biomass as demonstrated in Fig. 1.

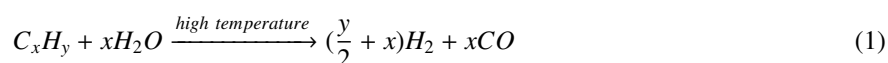
Currently, over 50 million tons of hydrogen is produced worldwide annually. However, an estimated 95% or more is from fossil fuels [41]. Meanwhile, a large amount of the hydrogen produced is used for industrial applications, such as metal refining, chemical production as well as fats and oil production.

2.1. Reforming, gasification & partial oxidation

Reforming, gasification and partial oxidation (POx) are the three common methods in industry to produce hydrogen from fossil fuels using thermal energy with reforming being the dominant process route. These methods can also be used to process renewable biomass for hydrogen production, which will be discussed later in Section 2.4. Hydrogen is produced from the reaction of hydrocarbons with water (e.g. steam-reforming and steam-gasification), oxygen (e.g. POx, gasification), and oxygen/water sequence (e.g. autothermal reforming).

Steam methane reforming

The difference between reforming and gasification in terminology is the nature of the incoming fuel [42]. Gasification defines the use of solid fuel, such as coal, biomass or solid waste to produce hydrogen gas or synthesis gas (hydrogen and monoxide mixture), while reforming addresses the utilisation of a fluid fuel, either in gaseous or liquid form, for synthesis gas production. The steam-reforming and steam-gasification process can be expressed by the following simplified net reaction:



The carbon monoxide produced from this reaction can be shifted to H_2 via the catalytic water-gas shift reaction at a lower temperature as shown in equation (2). The carbon dioxide can be separated and removed from the final H_2 product, together with any other remaining impurities e.g. nitrogen, methane, carbon monoxide.



Steam methane reforming (SMR) is the most well-known and commercially available technology for bulk hydrogen production. It is a catalytic conversion of light hydrocarbons such as natural gas, propane, butane, naphtha, biogas, or landfill gas, using steam. Approximately half of the global supply of hydrogen is provided by reforming of natural gas [43]. Due to the use of a catalyst, the natural gas is first desulphurised to remove sulphur which is the

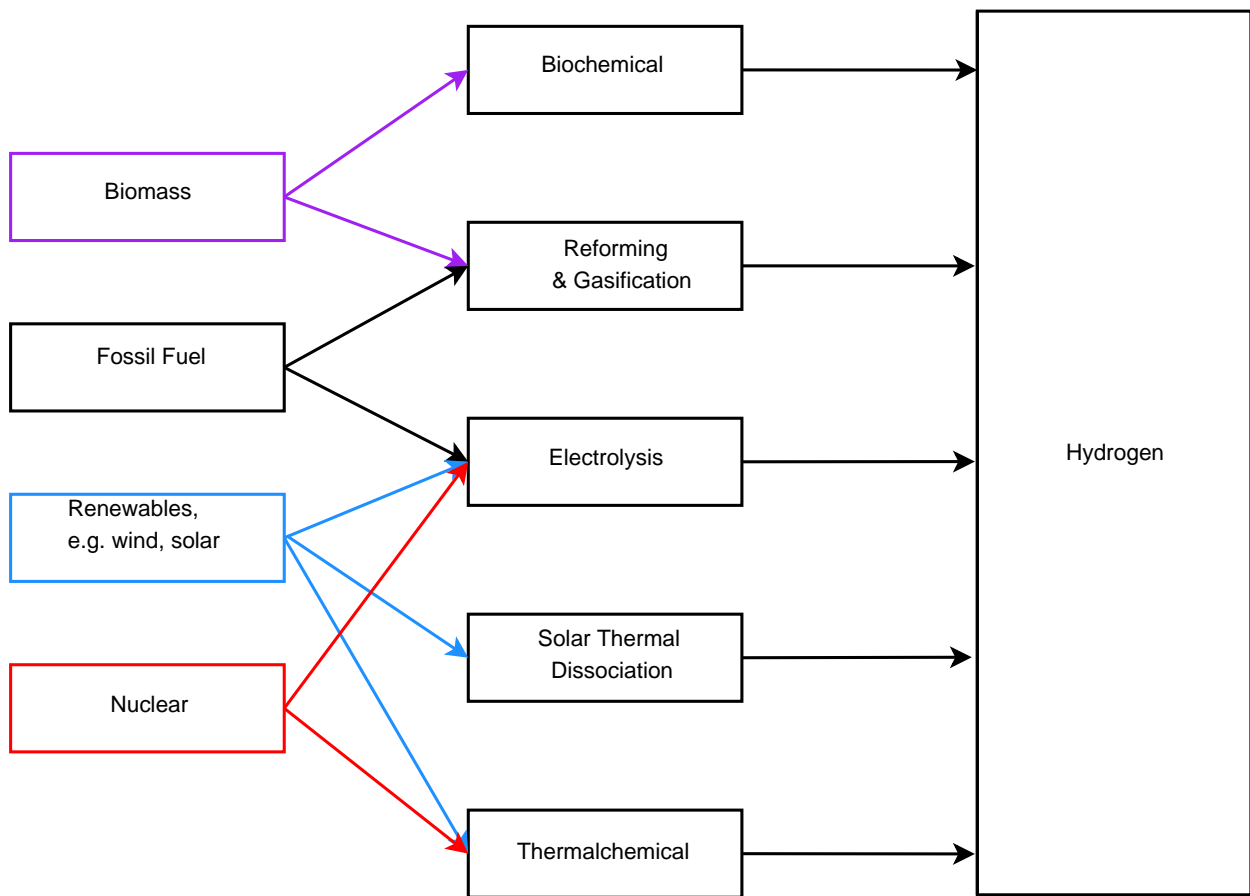


Figure 1: The route of hydrogen production

Table 1: General hydrogen production methods [42] p524

Method	Description	Material	Energy
Water electrolysis	Water decomposition into oxygen and hydrogen by passing a direct current that drives electrochemical reactions	Water	Electrical
High-temperature steam electrolysis	Steam decomposition by using direct current assisted by thermal energy to drive electrochemical reactions to split water molecule	Steam	Electrical, Thermal
Photoelectrochemical water splitting	Uses electric and photonic energy to electrolyse water and generate H_2 and O_2	Water	Photonic, Electric
Photocatalysis	Uses photonic energy and catalysts to decompose water molecule	Water	Photonic
Biophotolysis	Uses a reversible reducible cofactor and photometabolically active microbes to generate hydrogen from water	Water	Photonic, Biochemical
Anaerobic digestion	Uses biological energy manipulated by microbes to extract hydrogen from biodegradable materials in the absence of oxygen	Biomass	Biochemical
Thermolysis	Uses thermal energy to decompose water molecule at very high temperature ($2500^\circ C$)	Water	Thermal
Thermochemical water splitting	Thermally driven chemical reactions performed in a loop with the overall result of water splitting	Water	Thermal
Thermocatalytic cracking	Uses thermal energy to break the carbon-hydrogen bonds of hydrocarbons and eventually generate hydrogen	Fossil fuels	Thermal
Gasification	Converts solid carbonaceous materials into carbon monoxide and hydrogen by reacting them with O_2 and/or steam	Water, fossil fuels, biomass	Thermal
Reforming	Reacts carbon-based liquid or gaseous fuels with steam at high temperature to produce carbon dioxide and hydrogen	Water, fossil fuel or biofuels	Thermal

main catalyst poison. Then, at temperature of $700 - 1100^{\circ}\text{C}$ and typical pressure of $3 - 25\text{atm}$, steam is reacted with methane to generate carbon monoxide and H_2 . The reaction is expressed in equation (3).



Generally, in order to increase the efficiency of the process, the carbon monoxide goes through the water-gas shift reaction, as expressed in equation (2), to increase the hydrogen yield. The generated hydrogen is purified commonly using pressure swing adsorption (PSA) process to remove the carbon dioxide and other residues, such as carbon monoxide. The heat required for reforming is usually provided by combustion of a portion of the incoming hydrocarbon feed and by burning waste gases which contain H_2 and CO [44]. The major disadvantages are the large size and high cost of plant materials due to the requirement of the pressure and temperature of the process [45, 46]. The environmental impact of SMR as this process is accompanied by large quantities of CO_2 emission [47].

SMR is a fully developed process and there is limited space for significant technological breakthrough or cost reductions in the main process. However, there are still research efforts in catalyst selection, materials for reformer tubes, control of carbon emission, and development to improve the cost efficiency of the process [46]. There is also major interest in the development of compact reformers that operate at lower pressures and temperatures. Interest in performance of catalysts is a popular subject in the literature, attracting great research interest in both high temperature [48–51] and low temperature operation [46].

Partial oxidation

Partial oxidation (POx) is another commercially available method for hydrogen production from hydrocarbons. This process is used in oil industry to process heavy hydrocarbons, like heavy oil or sulphurous organic residues. In this process, under high temperature, methane is reacted with oxygen gas (partially oxidised or combusting) to produce carbon monoxide and hydrogen according to (4).



POx is exothermic which means no external heat source is required, as the heat is provided by the controlled combustion. Similar to the steam methane reforming process, the produced hydrogen is passed through a water-gas shift reactor and then purified by a suitable method e.g. PSA. The major disadvantage of POx is the lower efficiency when compared with the SMR process and higher operating costs as the process demands large quantities of pure oxygen [46].

Gasification & auto-thermal reforming

Gasification is an established process to produce syngas from solid fuels from which pure hydrogen can be extracted. Gasification and partial oxidation are closely related. In gasification of solid fuel such as coal, a wide temperature range is used between 300 to 2000°C , the fuel is reacted with a gasification agent, for instance air, oxygen, steam or their mixture to produce synthesis gas. The synthesis gas includes hydrogen which can be separated as we as CO which can be converted to CO_2 via water gas shift, liberating more hydrogen [45].

Depending on how heat is provided for the gasification process, it can be catalogued as auto-thermal or all-thermal process [42]. Auto-thermal reforming/gasification combines the POx and steam reforming process. It uses the POx to provide the heat and steam reforming to increase the hydrogen yield which resulting in a thermally neutral process [52]. The reaction can be expressed as



2.2. Thermocatalytic cracking

Another way to produce hydrogen from hydrocarbons using thermal energy is the thermocatalytic cracking process which is a process of decomposition.

With catalysts, thermal cracking process can be conducted as an oxidative or nonoxidative process. The simplified reaction of nonoxidative process can be illustrated as



where $C(s)$ represents carbon that is precipitated as a powder or granulate matter [42].

This process is also known as pyrolysis where the hydrocarbon is decomposed into hydrogen and carbon with no carbon oxides generation due to the absence of water or oxygen in the reactor [52]. This approach eliminates the requirement for water-gas shift and CO_2 removal as required in SMR and POx processes besides produces valuable clean carbon as a byproduct which can be used by industry for carbon fibres and nano-material production [42, 53]. Due to its single step and environmentally favourable nature, the thermocatalytic decomposition of methane has attracted great research attention, especially in the catalyst development [54–56].

The oxidative thermal cracking can be implemented as cyclic redox reactions on metals. Consisting of two steps, the endothermic reduction step and the exothermic oxidation, as expressed in



where M denotes a metal and M_xO_y is the corresponding metal oxide. This process eliminates the requirement of high-temperature H_2 and O_2 separation as they are produced in different reactors [42].

Steam-iron process is a well known example of redox process for hydrogen production. At temperature around $1000^\circ C$, following reactions take place



The carbon monoxide consumed in this process can be found in metal processing plants [42].

2.3. Thermolysis & thermochemical water splitting

Thermolysis

Thermolysis is a single-step direct thermal splitting of water process, the reaction is given as



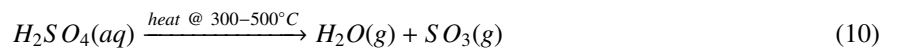
For a reasonable degree of dissociation, the process requires a high level of temperature, generally above $2500K$ [42]. The selection of materials to cope with such high temperature, reduce the heat lost due to re-radiation from the reactor, along with the development of effective technique to separate H_2 and O_2 are the major challenges for this method [42, 45].

Thermochemical water splitting

Thermochemical water splitting method is a modification of the water thermolysis process by combining chemical reactions without the presents of catalyst which significantly reduces the temperature requirement down to $900^\circ C$ [45]. This approach involves a series of chemical reactions cycles in which all chemicals, except water, involved in the process are recycled. In this process, the hydrogen and oxygen are produced separately. Hence, this method tackles the problems caused by high temperature and gas separation in water thermolysis process.

Among different thermochemical cycles, such as zinc-zinc oxide, nickel-manganese ferrite [57], copper-chlorine [58], the sulphur-iodine process (S-I cycle) has the highest system efficiency. Although still in demonstration stage, it has some potential for further improvements and commercialisation. The process complexity is the major disadvantage of the sulphur-iodine process.

Firstly, at $300^\circ C$ to $500^\circ C$, the sulfuric acid is decomposed to release water without the presents of catalyst,



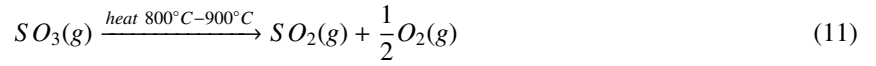
Then, SO_3 is separated for the steam and decomposed at temperature between $800^\circ C$ to $900^\circ C$ to release oxygen:

Table 2: Advantages and disadvantages of hydrogen production from biomass [61]

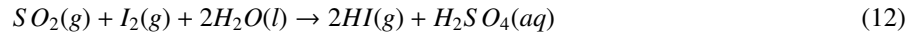
Advantages	Disadvantages
Mitigating CO_2 emissions	Seasonal availability and high handling costs
Crop residues conversion increases the value of agricultural output	Non-total solid conversion (char formation) and tars production
Replacing fossil fuels with sustainable biomass	Fuel process limitations: corrosion, pressure resistance and hydrogen aging
Costs of getting rid of municipal solid wastes	

Table 3: Basic reactions biomass gasification processes [59]

Reaction mode	Reaction Equation
Pyrolysis	$C_xH_yO_z \rightarrow (1-x)CO + \frac{y}{2}H_2 + C$
	$C_xH_yO_z \rightarrow (1-x)CO + (y-4)H_2 + CH_4$
Partial oxidation	$C_xH_yO_z + \frac{1}{2}O_2 \rightarrow xCO + \frac{y}{2}H_2$
	$C_xH_yO_z + O_2 \rightarrow (1-x)CO + \frac{y}{2}H_2 + CO_2$
	$C_xH_yO_z + 2O_2 \rightarrow \frac{x}{2}CO + \frac{x}{2}CO_2 + \frac{y}{2}H_2$
Steam reforming	$C_xH_yO_z + H_2O \rightarrow xCO + yH_2$
	$C_xH_yO_z + nH_2O \rightarrow aCO + (x-a)CO_2 + yH_2$
	$C_xH_yO_z + (2x-z)H_2O \rightarrow xCO_2 + (2n + \frac{y}{2} - z)H_2$



The following Bunsen reaction combines the separated sulfur dioxide with iodine and water to produce sulfuric acid at low temperature



Finally, the hydrogen iodine is further decomposed at temperature $425^\circ C$ to $450^\circ C$ to generate hydrogen



During this process, the chemical (H_2SO_4 in this case) is recycled, and water is the only material used for hydrogen production [42].

2.4. Biological

Generating hydrogen from renewable biomass has a number of advantages and disadvantages compared with fossil fuels, as listed in Table 2. By means of the thermochemical approaches mentioned above, for example, gasification, reforming and partial oxidation, hydrogen can be produced from a range of biomass. The basic reactions are listed in Table 3. A number of process variables will have influence on hydrogen yield such as characteristics and compositions of the biomass, moisture content, particle size, heating rate, temperature, reactor system, carrier gas and catalysts, as reviewed in [59, 60].

Another way to produce hydrogen from biomass utilises biological technologies such as anaerobic digestion process which grows bacteria fermentatively in the dark in bioreactors, or a photofermentative process which utilises algae and bacteria in photobioreactors in the light [62]. The biological methods are considered to be promising ways to produce hydrogen with low pollution and high efficiency [63].

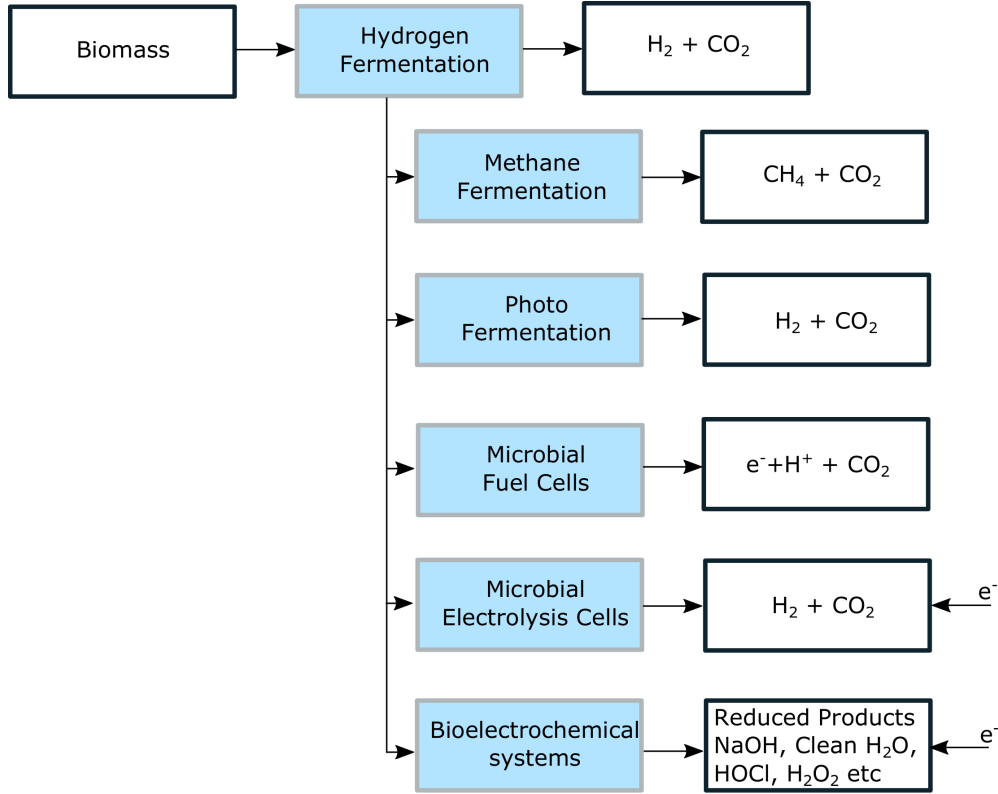
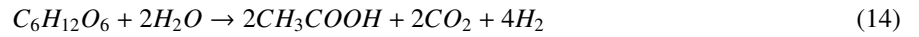


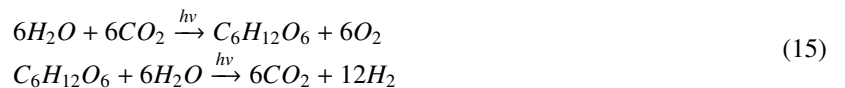
Figure 2: Overview of the two stage biohydrogen production process [66]

The dark fermentation reaction is carried out by anaerobic microorganisms that convert carbohydrate rich matter into hydrogen, CO_2 and other acid end products [57, 64], the reaction can be expressed as



Such fermentation has several advantages including simple reactor design and operation, the fermentative microbes are readily available, diverse waste materials can be used, and high rates of hydrogen production can be achieved compared with other biological processes. One of the major challenges of dark fermentation is the relatively low production capacity per unit of capital investment [65]. To tackle this, there are extensive research efforts in developing two stage systems to extract additional energy, as those volatile fatty acids can be used to produce methane easily using well-established anaerobic digestion technology [66]. The schematic of the overall process of two stage process is demonstrated in Fig. 2. Another advantage for this two stage integration is that each phase of the process can be optimised separately which makes the fermentation more efficient.

The well known photosynthesis process is used by green plants to convert solar radiation into biochemical energy. This process can be adapted to certain extent for hydrogen production and forms the base of biophotolysis [42]. Photofermentative process, involves water splitting to produce hydrogen and oxygen using green and blue-green algae as well as bacteria. With the help of photo-activated enzymes, hydrogen can be produced from water in an aqueous environment at standard temperature and pressure, the reactions are [65]:



where $h\nu$ represents the photonic energy required for this process.

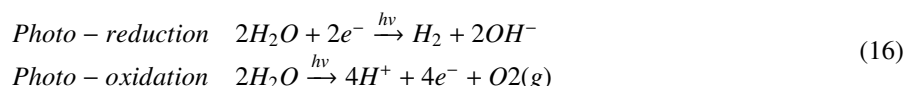
However, photosynthesis is still in research stage and not yet commercially available.

2.5. Photonic

Both methods discussed here, photocatalytic water splitting and photoelectrochemical water splitting, together with biophotolysis mentioned in the previous section, use the photon energy to produce hydrogen.

Photocatalytic water splitting

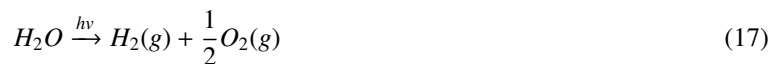
In principle, hydrogen can be released from water when water molecules absorb energy at a rate of 285.57kJ/mole from ultraviolet radiation [47]. Various supramolecular complexes can be used to convert energy from photon to liberate the constituted gases from water. Two actions, photo-reduction and photo-oxidation occurs during this process [42]:



Photocatalytic water splitting is a direct method of hydrogen production from water using ordinary light, however, this method suffers low production efficiency [47]. Semiconducting oxides such as titanium oxide (TiO_2) are commonly used in this photolysis reaction. There is a lot of research interest, especially in photocatalyst development [67–71].

Photoelectrochemical water splitting

Photoelectrochemical water splitting, also called photoelectrolysis, utilises the solar irradiation to generate electric current which drives the water electrolysis process. The so-called photoelectrochemical (PEC) cell which consists of photosensitive semiconductors immersed in an aqueous electrolyte, and counter electrodes are used for this process [42]. The reaction at the PEC cell is illustrated as



One of the remarkable features of PEC cell is that this device is effectively a compact integration of solar electric energy generation (PV) and water electrolysis (electrolyser). Although this technology is still under development, it is reported that 18.3% efficiency can be achieved for a single bandgap system in the laboratory, while over 30% conversion efficiency can be achieved for dual bandgap systems [72].

2.6. Water electrolysis

Water can be decomposed using direct electric current, hydrogen and oxygen will be produced from water through redox reactions. The overall reaction is $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$. An electrolyser is the device that combines the oxidation and reduction reactions to produce hydrogen and oxygen gas. In principle, any electric power generation source, e.g. PV, wind and other renewable energy sources, nuclear, even fossil fuel or biomass electric power plant, can be connected to an electrolyser to produce hydrogen and oxygen.

Three different types of electrolyte can be used in a typical electrolysis process, i.e., a liquid electrolyte, a solid polymer electrolyte in the form of proton conducting membrane, and oxygen ion conduction membranes [42]. Therefore, according to the adopted electrolyte types, there are three types of electrolysers, named alkaline, proton exchange membrane or polymer electrolyte membrane (PEM) and solid oxide electrolysers (SOE). Typical specifications of these three water electrolysis technologies are listed in Table 4.

Physically an electrolyser stack consists of several cells linked in series. Two distinct cell designs exist: *monopolar* and *bipolar*. In the monopolar design the electrodes are either negative or positive with parallel electrical connection of the individual cells, while in the bipolar design the individual cells are linked in series electrically and geometrically. One advantage of the bipolar electrolyser stacks is that they are more compact than monopolar systems. Another advantage of the compactness of the bipolar cell design is that it gives shorter current paths in the electrical wires and electrodes. This reduces the losses due to internal ohmic resistance of the electrolyte, and therefore increases the electrolyser efficiency. However, there are also some disadvantages with bipolar cells. One example is the parasitic currents that can cause corrosion problems. Furthermore, the compactness and high pressure of the bipolar electrolysers require relatively sophisticated and complex system design, and consequently increases the manufacturing

Table 4: Typical specifications of alkaline, PEM and SOE [73]

Specification	Alkaline	PEM	SOE
Technology maturity	State of the art	Demonstration	R&D
Cell temperature, °C	60-80	50-80	900-1000
Cell pressure, bar	< 30	< 30	< 30
Current density, A/cm^2	0.2-0.4	0.6-2.0	0.3-1.0
Cell voltage, V	1.8-2.4	1.8-2.2	0.95-1.3
Power density, W/cm^2	Up to 1.0	Up to 4.4	-
Voltage efficiency, %	62-82	67-82	81-86
Specific system energy consumption, kWh/Nm^3	4.5-7.0	4.5-7.5	2.5-3.5
Partial load range, %	20-40	0-10	-
Cell area, m^2	< 4	< 300	-
Hydrogen production, Nm^3/hr	< 760	< 30	-
Stack lifetime, hr	< 90000	< 20000	< 40000
System lifetime, yr	20-30	10-20	-
Hydrogen purity, %	> 99.8	99.999	-
Cold start up time, min	15	< 15	> 60

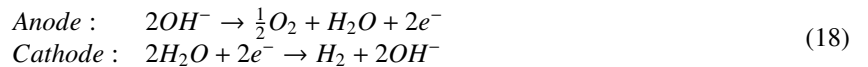
costs. The relatively simple and sturdy monopolar electrolyser systems are in comparison less costly to manufacture. Nevertheless, most commercial alkaline electrolysers manufactured today are bipolar [74].

Depending on the requirement of temperature, there are three possibilities to conduct the electrolysis for splitting H_2O molecule [42]:

- Cold electrolysis of liquid water at or close to the ambient temperature. Alkaline and PEM electrolyser cells can be used.
- High-pressure electrolysis. The high-pressure electrolysis is attractive because it facilitates hydrogen and oxygen compression and storage. In order to increase the efficiency of the process, both temperature and pressure must be increased; moreover, the water is given in pressurised liquid form. It is thermodynamically efficient to pressurize water rather than to compress hydrogen and oxygen products. However, there is a design trade-off in the sense that too high an operating pressure leads to reduced efficiency and higher cost.
- High-temperature steam electrolysis in solid oxide electrolysis cells. In this case, water is converted to steam with the expense of thermal energy. Moreover, the electrochemical bath is heated, directly (through steam) or indirectly (through heat transfer).

Alkaline electrolysers

The alkaline electrolyser is the most mature and commonly used electrolyser technology, especially at large scale. An alkali solution which normally is 20 – 40% potassium hydroxide (KOH), is used as electrolyte to raise the ionic conductivity in the cell stack [45]. Other electrolytes like sodium hydroxide (NaOH), sodium chloride (NaCl) have also been used [57]. The use of liquid and corrosive alkali solution is one of the major drawbacks of alkaline electrolyser. In alkaline electrolysers, a diaphragm separates the two electrodes. Previously, asbestos was used as diaphragm with a thickness in the range of 3mm [73]. The operation temperature of the electrolyser is hence limited to 80°C due to the use the asbestos. The water is reduced at cathode to generate hydrogen and hydroxide. The hydroxide will be circulated through the diaphragm to the anode and recombined to generate oxygen. The reaction is expressed in equation (18)

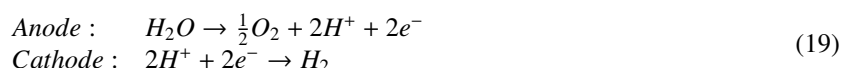


In the past years, research had been focused on reducing the operating costs associated to the consumption of electricity hence improving the efficiency, meanwhile, the operating current densities have been increased in order

to reduce the investment costs [73, 75]. New advanced materials are also being developed to be used as diaphragms to replace the conventional used asbestos. Those include membranes based on antimony polyacid impregnated with polymers, porous composite composed of a polysulfone matrix and Zirfon, and separators based on polyphenyl sulfide.

PEM electrolyser

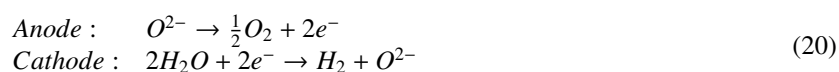
The major difference between alkaline electrolysers and PEM electrolysers is the use of electrolyte. PEM electrolysers employ a solid polymer membrane electrolyte instead of the corrosive liquid electrolyte used in alkaline electrolysers. However, high purity deionized (DI) water is required for the electrolysis process [57]. At the anode, water is oxidized to produce oxygen, electrons and protons. The protons will travel across the proton exchange membrane to the cathode side while the electrons will reach the cathode side via an external circuit. At the cathode, protons will be reduced to generate hydrogen. The following reactions take place in a PEM electrolyser:



The PEM electrolyser is more suitable to work under fluctuating power supply. This is due to the fact that the transportation of protons across the membrane responds quickly to fluctuating power supplies [73]. Currently, the major drawback of PEM electrolysers is the high manufacturing cost.

Solid oxide electrolyser

The above two electrolyser technologies are all operated under low temperature (less than $100^\circ C$), whereas SOE operates at high temperature (up to $1000^\circ C$). This results in high efficiency compared with alkaline and PEM technology. At the cathode side, water, or rather steam is reduced to produce hydrogen. The generated oxide anions will pass through the solid electrolyte to the anode where they form oxygen [75]. The following reactions take place in a SOE:



SOE is not suitable for fluctuated power input, such as power generated by renewable energy sources. This is mainly due to the reason that the change of load will cause heat losses as well as changes in cell temperature. Such changes will result in micro cracks in the membrane, and as a result, significantly reduce the lifespan of the electrolyser [73].

3. Technologies in Hydrogen Storage

Hydrogen storage is an important component in hydrogen economy, and one of the most urgent and challenging applications is to develop safe, reliable, efficient and effective storage mechanisms. In its natural form, hydrogen has a high gravimetric energy density while the volumetric energy density is low. It is known that under ambient temperature and pressure, $5kg$ of H_2 would fill a ball of $5m$ in diameter which is similar to an inflated hot-air balloon in volume [45]. As a result, dependent on the application, the emphasis of hydrogen storage is different. For example, for automobile applications, the gravimetric density is the most important factor as the hydrogen storage system must suit the size of the vehicle without adding too much weight while providing reasonable driving range. In other words, in transportation sector, it is preferable to store H_2 in a lightweight and safe container with high density. On the other hand, in stationary applications, high volumetric density is more preferable, as the weight is not the dominant factor that will affect the efficiency of the system.

There are three typical approaches to store hydrogen:

- Physical storage as compressed gas
- Physical storage as cryogenic liquid hydrogen
- Materials-based storage or solid state storage

Table 5: Target and Current Status of H₂ Storage Technologies [76]

Storage Targets	Gravimetric <i>kWh/kg</i> (<i>kgH₂/kg system</i>)	Volumetric <i>kWh/L</i> (<i>kgH₂/L system</i>)	Costs \$/ <i>kWh</i> (\$/ <i>kgH₂</i>)
2017	1.8 (0.055)	1.3 (0.040)	\$12 (\$400)
Ultimate	205 (0.075)	2.3 (0.070)	\$8 (\$266)
Projected H ₂ Storage System Performance	Gravimetric (<i>kWh/kg</i>)	Volumetric (<i>kWh/L</i>)	Costs (\$/ <i>kWh</i>)
700 bar compressed (Type IV)	1.5	0.8	17
350 bar compressed (Type IV)	1.8	0.6	13
Metal Hydride (NaAlH ₄)	0.4	0.4	TBD
Sorbent (MOF-5, 100 bar)	1.1	0.7	16
Chemical Hydrogen Storage (AB-50 wt. %)	1.7	1.3	16

Among them, the first two methods, i.e. store hydrogen as compressed gas and in its liquid form, are the most mature and widely used methods. The last method (or range of methods) is still largely under research and development, and it is highly dependent on the development of advanced materials.

The technical and economical targets for hydrogen storage were set and revised by U.S. Department of Energy (US DoE). The latest 2017 targets along with current status are listed in Table 5. The ultimate target for hydrogen storage system is to achieve 7.5wt.% of gravimetric density and 7.0wt.% of volumetric density, while the cost of hydrogen should be reduced down to \$266 per kilogram.

3.1. Pressurised hydrogen gas

Hydrogen can be compressed and stored as pressurised gas in the cylinders, containers, or even in the underground caverns, with pressure up to 700 bar in suitable cylinders. High pressure gaseous hydrogen storage is currently the most popular and widely adopted method. As of October 2010, more than 80% of the total 215 hydrogen refuelling stations in operation worldwide adopt this high pressure gaseous storage method [77].

There are three major types of widely used high pressure hydrogen storage vessel, namely: stationary, vehicular, and bulk transportation [77]. Stationary storage is mainly used in hydrogen refuelling stations which requires large scale and low cost. For vehicular applications, it is preferable that the storage has high density, light weight and low cost that is suitable for on-board hydrogen supply system. Finally, for bulk transportation, which distributes hydrogen from producer to the end users, it is ideal that the storage vessels will have large capacity and light weight to reduce the delivery cost.

The major advantages of storing hydrogen as high pressure gas are the simplicity of the technology, and fast filling-releasing rate. However, the major drawback for such storage method is that the volumetric density does not increase proportionally to the pressure as a result of the real gas behaviour of the hydrogen [45], which is illustrated in Table 5. Meanwhile, it can also be seen from Table 5 that at 350 bar, the gravimetric density is 5.5wt.%, while at 700 bar, this density is even down to roughly 4.6wt.%. As a result, such storage is bulky and difficult to integrate within a vehicle. Early research indicated that in vehicular applications, for conventional passenger cars with 500 km driving range, the cost of large storage vessels are expensive due to the amount of strong materials required [78, 79]. There are efforts to identify low cost carbon fibre that can meet the required stress, strain and safety specifications for high-pressure storage tanks as well as satisfy the thickness constraints of the tank in order to meet volumetric capacity targets [80]. [80] also suggests two approaches to pursue for better gravimetric and volumetric storage capacities of compressed gas tanks. The first one is cryo-compressed tanks, which is either compressed cryogenic hydrogen or a combination of liquid hydrogen and high pressure hydrogen in the headspace. The second approach is developing conformable tanks, which is applicable to both conformable tank structure, e.g. internal structural supporting walls and internal cellular-type load bearing structures as well as materials-based storage technologies.

3.2. Liquefied hydrogen

Storing hydrogen in the liquid form can achieve higher density when compared with compressed hydrogen gas storage. Therefore, more energy can be stored per unit volume. Meanwhile, for low pressure liquid hydrogen storage systems, the cost can be reasonably low [81]. However, there is widespread criticism of the high cost and energy consumption for liquefaction. For instance, hydrogen has to be cooled down to 21K for liquefaction, and it is reported that the energy of over 30% of the lower heating value of hydrogen will be used for this process, which is much higher compared with the energy consumption in compression (around 15% in the latter case) [82]. The boil-off phenomenon is also another factor that will further reduce the efficiency. Due to the unavoidable heat input into the storage vessel, it is reported that 2 – 3% of evaporated hydrogen will be lost per day. For vehicular applications, loss of hydrogen due to boil-off should be minimised or eliminated. This is not only to achieve the maximum driving range, to reduce the refuelling frequency and cost, but also for improving the energy efficiency and safety, especially for vehicles parked in confined spaces like garages [80]. Meanwhile, other components, such as the insulation of the container to prevent hydrogen loss will increase the weight of the storage system as well.

Nevertheless, recent research indicated that incorporating with high-pressure capability into the cryogenic carbon-fibre composite tank design, i.e. the tank is filled with liquid hydrogen and can also be pressurised to 275 bar [83] or even 350 bar [81], this new storage system satisfied the critical DoE 2015 volumetric efficiency target [84]. The cryo-compressed design can also improve the degree of dormancy and reduce boil off lost [80].

3.3. Material-based storage

In this method, hydrogen atoms or molecules are tightly bound with other elements. It is perhaps the most promising hydrogen storage method as it is possible to store large amount of hydrogen within a relatively small volume. There are two basic bonding mechanisms for such material-based solid state storage [45]:

- Chemisorption (i.e., absorption): hydrogen molecules are dissociated into hydrogen atoms and integrated in the lattice of the materials. This method makes it possible to storage large quantities of hydrogen in small volume under low pressure and ambient temperature.
- Physisorption (i.e., adsorption): hydrogen atoms or molecules are attached to the surface of the materials

It is preferable that the storage material will have high gravimetric and volumetric capacity, reversibility of hydriding and dehydriding steps, favourable equilibrium temperature-pressure characteristics, adequate stability of the hydride formed and low sensitivity to impurities present in feed gas, as described in [85]. However, after years of research, a single material that possess all those features remains elusive.

3.3.1. Absorption

Hydrogen can react with metals like Li, Na, Mg, Ti, alloy or intermetallic compound (IMC) to form metal hydride (MH) [86, 87]. The reversible reaction of hydrogen gas with hydride-forming metal/alloy, or IMC to form metal hydride can be expressed as [86]:



where M is either a metal, an alloy or an IMC. Q is the heat generated during the forming of MH or the heat required for releasing hydrogen from MH. The major features of metal hydrides are listed in Table 6.

In general, MH offers simple design and operation, no moving parts, compactness, safety and reliability, and the possibility to consume waste industrial heat instead of electricity [86]. However, MH also suffers some shortages as well. For instance, although material such as Mg has the capability to store large quantities of hydrogen and is relatively inexpensive which is suitable for large scale applications, the reaction for pure magnesium is very slow and occurs only at high temperature and pressure [87]. Research has shown that MH cannot demonstrate satisfactory performance especially for commercial vehicular application [89].

Complex metal hydrides are another class of light weight hydrogen storage material [90]. The major difference between the complex and simple metal hydride is the formation of an ionic or covalent compound during absorption of hydrogen [91]. Metals like sodium, lithium and beryllium are the only elements lighter than magnesium and can also

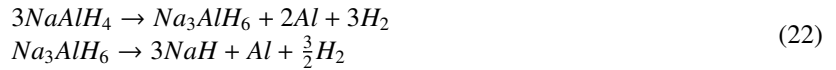
Table 6: Summary of metal hydride materials [88]

Materials	Maximum hydrogen content <i>wt%</i>	Decomposition temperature (K)	Comments
<i>NaH</i>	4.2	698	Good reversible kinetics
<i>MgH₂</i>	7.6	603	Poor reversibility and kinetics
<i>LiH</i>	12.6	~ 1000	Irreversible kinetics
<i>CaH₂</i>	4.8	873	Relatively good reversible kinetics
<i>AlH₃</i>	10.0	423	Production of <i>AlH₃</i> requires high pressure and other extreme conditions

form solid state compounds with hydrogen gas. They have the potential for higher gravimetric hydrogen capacities due to their light weight and number of atoms per metal atom [89], which normally is two [91]. There are intense research interest in developing low weight complex hydrides such as alanates, amides, imides and borohydrides.

Alanates are a family of compounds consisting of hydrogen and aluminium and are also known as 'aluminum-hydrides'. This group consists of sodium alanate, lithium alanate, magnesium alanate, potassium alanate, calcium alanate and others such as *Na₂LiAlH₆*, *K₂NaAlH₆*, *K₂LiAlH₆*, *LiMg(AlH₄)₃*, and *LiMgAlH₆* [89]. The alanates are easy to produce. Their features are listed in Table 7. Among them, *NaAlH₄* is the most popular material.

Hydrogen can be released from *NaAlH₄* from following two step reactions:

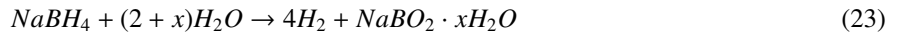


Furthermore, the produced *NaH* from second step can be further dissociated to release the remaining hydrogen. However, such process requires temperature higher than 450°C.

Alkali alanates suffer the requirement of high pressure for releasing hydrogen from the materials. Therefore, research focuses on using mixed alanates which contains more than one alkali or alkaline earth atom to retain high hydrogen storage capacity but at ambient condition, such as *Na₂LiAlH₆*, *K₂NaAlH₆*, *K₂LiAlH₆*, *LiMg(AlH₄)₃*, and *LiMgAlH₆* [89].

Borohydrides, also referred as tetrahydroborate, are a group of complex hydrides in which hydrogen is covalently bonded to the central atoms in the $(BH_4)^-$ complex anion. Borohydrides have been considered as promising hydrogen storage materials due to their higher gravimetric and volumetric hydrogen capacity. Several borohydrides exist, including sodium borohydride, lithium borohydride, magnesium borohydride, calcium borohydride, and other borohydrides having a general formula $M(BH_4)_n$ where M=Mn, Zn, Al, Be, Y, Dy, Gd, Zr, Rb, Cs and $n = 1, 2, 3, 4$ [89].

In borohydrides, hydrogen can be released from either a hydrolysis reaction (using sodium borohydride as an example):



or from the following reactions under certain temperature and pressure conditions (using magnesium borohydride as an example):



In the hydrolysis reaction, in order to generate hydrogen with less water consumption, a new technology called steam hydrolysis, which utilises steam instead of liquid water was proposed. It is reported that 95% of hydrogen evolution can be achieved without a catalyst [92]. The major features of borohydride are listed in Table 8.

In order to tailor the thermodynamic stability, multi cation borohydrides $MM'(BH_4)_n$, where *M* and *M'* have different electronegativities has been proposed [93]. Typical samples including *ZrLi(BH₄)₅* [94], *ZrLi₂(BH₄)₆* [94], *LiK(BH₄)₂*, *LiSc(BH₄)₄* [95, 96], *KSc(BH₄)₄* [97] and so on.

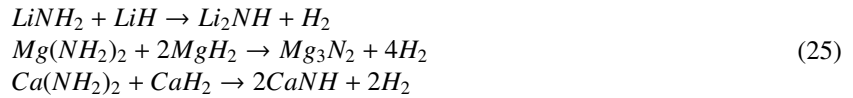
Last but not least, amides, $M(NH_2)_x$ and imides, $M(NH)_x$ are another group of materials that attracted global research interest due to their high storage capacity and low operation temperature. However, their poor absorption

Table 7: Features of alanates for hydride hydrogen storage [89]

Materials	Hydrogen capacity (wt%)	Dehydrogenation temperature (°C)	Dissociation enthalph ($\text{kJmol}^{-1}\text{H}_2$)
NaAlH_4	5.6	210-220 (1st step); >250 (2nd step)	37 (1st step); 47 (2nd step)
LiAlH_4	7.9	160-180 (1st step); 180-220 (2nd step)	-10 (1st step); 25 (2nd step)
$\text{Mg}(\text{AlH}_4)_2$	9.3	110-200 (1st step); 240-380 (2nd step)	41 (1st step); 76 (2nd step)
KAlH_4	5.7	300 (1st step); 340 (2nd step); 380 (3rd step)	55 (1st step); 70 (2nd step)
$\text{Ca}(\text{AlH}_4)_2$	5.9	127 (1st step); 250 (2nd step)	-7 (1st step); 28 (2nd step)
$\text{Na}_2\text{LiAlH}_6$	3.2	245	53.5 ± 1.2
K_2NaAlH_6	2.8	325	98

kinetics limit their practical application [89]. This group consists of materials such as lithium amide/imide, magnesium amide/imide, calcium amide/imide, and other amides/imides such as $\text{Li} - \text{Mg} - \text{N} - \text{H}$ and $\text{Li} - \text{Ca} - \text{N} - \text{H}$.

The overall decomposition reactions for lithium, magnesium and calcium amide/imide are



Absorption of hydrogen requires the thermal management to supply or remove the heat of reaction in order to split or recombine the hydrogen molecule and form chemical bonds with the material. Whether the heat can be recycled or reused becomes an important factor that will affect the overall efficiency of the system.

There are still challenges need to be considered in the future work [88, 89], such as:

- To reduce the cost and improve the storage capacity of hydrogen at low temperature and pressure
- To develop new novel processing routes to replace current lengthy and expensive process for material production
- To understand the physical and chemical processes of hydrogen storage at both atomic and molecular level
- To understand the structure, kinetic, thermodynamic and stabilities of the complex hydrides as well as their physical and chemical properties
- To achieve reasonable kinetics and reversibility of complex hydrides at low temperature
- To investigate the effect of size and curvature of nanomaterials for hydrogen storage.

3.3.2. Adsorption

Compared with metal hydrides which offer high volumetric capacities through dissociative absorption of hydrogen, high surface area absorbent materials offer the advantages of fast hydrogen kinetics and low hydrogen binding energies. In this physisorption process, the hydrogen gas molecule interacts with atoms at the surface of the material and the distance between the gas molecule and the surface diminished [91]. Hence, it potentially reduces the thermal management issues during charging and discharging of hydrogen [80]. Due to such weak interaction, the adsorption is only observed at low temperature.

For adsorption, the major problem is to provide light carrier materials with sufficient amount of bonding sites [45]. A number of materials can be used for adsorption, such as graphite, carbon nanotubes [98], C_{60} buckyballs, zeolites, metal organic frameworks, intercalation compounds and so on [99].

The big advantages of adsorption are the low operating pressure, the inexpensive material used, and the simple design of the storage system. However, major drawbacks including the requirement of low temperature and high pressure to storage hydrogen, together with low gravimetric and volumetric hydrogen density.

Table 8: Features of borohydrides for hydride hydrogen storage [89]

Materials	Hydrogen capacity (wt%)	Dehydrogenation temperature ($^{\circ}\text{C}$)	Dissociation enthalph ($\text{kJmol}^{-1}\text{H}_2$)
NaBH_4	10.8	400	-216.7 to -272.4
LiBH_4	13.4	380	-177.0
$\text{Mg}(\text{BH}_4)_2$	13.7	260-400	-39.3 to -57.0
$\text{Ca}(\text{BH}_4)_2$	9.6	350	32

4. Technologies in Electricity Generation Using Hydrogen

4.1. Fuel cells

A fuel cell is a device that conducts electrochemical reactions to convert chemical potential energy into electrical energy as well as heat energy as a by-product. A comprehensive overview of the fuel cell technologies is given in [100]. Hydrogen is normally used as a fuel in fuel cell systems. Oxygen, usually air, is feed into the fuel cell as oxidant. The oxidation of hydrogen takes place effectively in the fuel cell and water is the only by-product. Fuel cell systems can be used in a number of applications, such as automotive, backup power, combined heat and power (CHP), material handling and so on [101, 102]. Currently, there are six types of well established fuel cells on the market:

- Proton Exchange Membrane Fuel Cell (PEMFC)
- Direct Methanol Fuel Cell (DMFC)
- Alkaline Fuel Cell (AFC)
- Phosphoric Acid Fuel Cell (PAFC)
- Molten Carbonate Fuel Cell (MCFC)
- Solid Oxide Fuel Cell (SOFC)

However, there are still several different types of fuel cells under development, such as Direct Ammonia Fuel Cells [103], Direct Ethanol Fuel Cells [104, 105], Microbial Fuel Cells [106–109], Direct Carbon Fuel Cells [110], etc. The key specifications of major fuel cells are listed in Table 9.

PEMFC is a commonly used fuel cell type especially for portable or vehicular power supply. It can also be used for residential micro CHP, remote area power supplies, uninterruptible or backup power. Similar to PEM electrolyser, PEMFC has a solid polymer electrolyte membrane (e.g. NAFION) for proton conduction and platinum-based materials as catalyst. On the one hand, such membrane must be humidified continuously in order to maintain its conducting property, on the other, designers also need to make sure there is no flooding of the electrolyte [111]. In PEMFC, high purity hydrogen is required as the unit is sensitive to contaminants such as CO , sulfur species and ammonia. For instance, trace CO in the hydrogen-rich gas can adsorb on the surface of Pt and block the hydrogen oxidation reaction sites which dramatically reduces the activity of Pt in the anode and hence deteriorates the performance of PEMFC [112]. The cost of PEMFC is high because the use of expensive metal catalysts (platinum) at the electrodes, and the life time of PEMFC is relatively short. The advantages for PEMFC are low operating temperature, high power density, and ease of scale-up, but the major barriers for world-wide commercialisation are low durability and high cost [113]. Recently, there are research efforts in developing high temperature PEMFC, raising the operating temperature between 100°C and 200°C [114]. By using different membranes, when operating at high temperature, the amount of CO that adsorbs on the catalyst is reduced, and there is no need to humidify the hydrogen inlet gas. Therefore, CO poisoning and water management problems are mitigated [112]. A range of polymeric membranes were developed for high temperature PEMFC which can be catalogued into four groups: sulfonated aromatic hydrocarbon polymer membranes, inorganic-organic composite membranes, membranes of blend polymers, and acid-base polymer membranes, as reviewed in [115, 116]. There are also extensive research efforts on catalyst development. Either by developing Pt-based nanocatalysts to improve performance and durability [117], or replacing the expensive Pt/Pt-alloy catalysts, particularly by using Fe- and Co-based non-precious metal catalysts at the cathode of PEMFC to reduce the cost [118].

Table 9: Key specifications of major fuel cells (data gathered from [42])

FC type	Temperature (°C)	Reactions	Electrolyte	Efficiency (%)
PEMFC	60-140	Anode: $H_2 \rightarrow 2H^+ + 2e^-$ Cathode: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$	Polymer	55
DMFC	30-80	Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ Cathode: $\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$	Polymer	30
AFC	150-200	Anode: $H_2 + 2OH^- \rightarrow H_2O + 2e^-$ Cathode: $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$	Potassium hydroxide	60
PAFC	150-200	Anode: $H_2 \rightarrow 2H^+ + 2e^-$ Cathode: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$	Phosphoric acid	> 40
MCFC	600-700	Anode: $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$ Cathode: $\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$	Li/K/Na carbonate	45
SOFC (+)	200-700	Anode: $H_2 \rightarrow 2H^+ + 2e^-$ Cathode: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$	Barium cerate	40
Direct Ammonia	400-700	Anode: $2NH_3 \rightarrow N_2 + 6H^+ + 6e^-$ Cathode: $\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$	Barium cerate	40
SOFC (-)	1000	Anode: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$ Cathode: $\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$	Ytria-stabilized zirconia	40

Similar to alkaline electrolyzers, AFC uses a liquid alkaline solution, normally potassium hydroxide (KOH) as the electrolyte. The low cost, possibility for mass production and no dependency on expensive membrane electrolytes are the major advantages of AFC. Normally, fuel cleaning and periodic electrolyte replacing is required to remove the CO_2 as it will react with KOH to form carbonate which decreasing the electrolyte conductivity, oxygen solubility and electrode activity, and hence significantly downgrade the performance of AFC. Besides, the precipitated carbonate can also block the electrolyte pathways and electrode pores [119]. Historically, four different types of AFCs have been developed, and they all suffered from shortages such as difficulties in electrodes preparation, high degradation of the electrode, and hazardous for health due to use of asbestos for diaphragm [120].

Both MCFC and SOFC are operating at high temperature which makes them the best candidates for stationary power generation, as reviewed in [121] for the applications of SOFC. High operating temperature will not only increase the ionic conductivity but also increases the electrode reactions [122]. Depending on the ions that are present in the conducting electrolytes, SOFC has two different sub-types, named SOFC(-) where oxygen ions are conducting the electrolytes, and SOFC(+) where hydrogen protons are conducting the electrolytes. Unlike SOFC using a solid electrolyte, MCFC utilised a liquid electrolyte. Pure H_2 cannot directly feed into MCFC but mixtures of H_2 and CO . The disadvantage associated with MCFC and SOFC's high operating temperature is a long start-up time [111]. For example, start-up and shut-down operations of SOFC can take 12 hours or more. So SOFCs normally operate continuously, reducing the output when there is little or no demand [123]. To tackle this limitation, there are research efforts on developing micro-tubular SOFC (MT-SOFC) by reducing the cell size into micron scale in order to improve the thermal cycling tolerance, the start-up time and portable characteristics [124], or developing low temperature SOFC [122].

MCFCs have relatively low capital costs due to non-platinum catalysts and simple ancillary systems, but its life-time and power density are low [123]. The research and development of MCFC is actively carried out in US and Japan, as it is not been favorably supported in Europe [111].

Concentrated phosphoric acid is used in PAFC as the electrolyte. Although PAFC was the first commercially available fuel cell type, its market is still limited, due to several factors such as expense and the technology is unlikely to become much cheaper. PAFC is also less efficient and less powerful compared with other fuel cell types. The

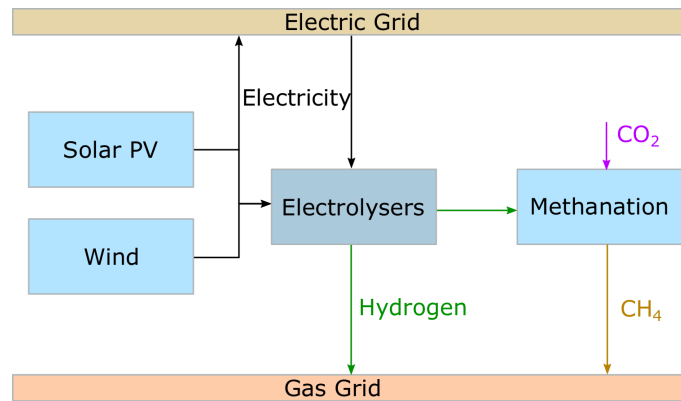


Figure 3: Principle of power-to-gas technology

majority of research and development activities for PAFC were carried out in US and Japan with US technology corporation UTC (United Technologies Corporation) being the global leader [111]. The majority of PAFCs are used in stationary combined heat and power applications [125].

DMFC directly converts methanol into electricity without the requirement of additional reformer. The applications of DMFC are mainly focused on mobile phones, laptops, electronic gadgets and other portable applications [126]. It also utilises a polymer electrolyte membrane as the electrolyte, and the operation of DMFC is similar to a PEMFC. Commonly used membranes in DMFC can be catalogued into five groups partially: fluorinated, perfluorinated ionomers, acidbase complexes, non-fluorinated ionomers, hydro carbon and aromatic polymers [127]. Two types of DMFC exists, named active DMFC and passive DMFC. In the passive DMFC, both reactants (methanol and oxygen) and products (CO_2 and water) are supplied or removed by passive means such as diffusion, natural convection and capillary action etc. As a result, the passive DMFC has compact and simple structure and low parasitive power losses [128–131]. DMFC has several advantages including light weight, compact size, long lifetime, higher volumetric energy density of liquid methanol than hydrogen, and ease of refueling [110, 132]. But it also suffers from various drawbacks. For example, cross-over of methanol through the membrane to the anode side results in the loss of fuel at the cathode side, together with other difficulties like water management, low power density, methanol concentration maintenance, etc [110, 133].

4.2. Power to gas

The intermittency together with the complexity of prediction of renewable energy such as wind and solar has significant impact on the electrical grid, causing problems such as creating power surges and shortages, requiring supplemental generation or storage for balancing, increasing the vulnerability of the existing power system, causing power quality problems such as voltage dips, frequency variations, and low power factor, etc as investigated in [134–137].

The concept of power-to-gas (P2G) is to feed electrolysers with cheap surplus renewable electricity to produce hydrogen and injecting this into the gas grid. There are two major routes, direct injection and methanation, as shown in Fig. 3.

The simplest way is to inject hydrogen directly into the natural gas grid. It possesses some advantages such as one step process, no further investment and energy lost, and no additional hydrogen storage required. However, there is research suggesting that the direct injection of significant quantities of hydrogen may have an influence on the thermodynamic and transportation properties of the natural gas as well as the natural gas pipeline and end use applications such as gas turbines and gas burners [138–142]. Some potential problems include hydrogen embrittlement for high pressure steel pipelines, reduction in gas grid capacity and efficiency due to high volume of hydrogen injection, and potential safety risk for end use applications such as flashback. Although there are suggestions that at Standard Temperature and Pressure the gas grid can cope with up to 17% of hydrogen by volume without any difficulties, there is also legislation in various countries that constrains the amount of hydrogen content in the natural gas grid. For example, a maximum 0.1% of hydrogen by volume is currently allowed in the UK gas grid.

For countries such as Italy, UK, US and Japan,[138] indications are that by injecting an amount of 1 *vol%* of hydrogen into the distributed natural gas on an average annual basis, the corresponding energy consumption will exceed 10% of total wind + solar production, which demonstrates a high possibility to mitigate the production instability of large wind farms. Recent research into the investigation of direct injection of renewable hydrogen gas to Great Britain's gas grid also confirms that significant reduction in both wind power curtailment and operating cost of the combined gas and electricity network can be achieved [143].

Alternatively, the hydrogen can react with CO_2 to generate other useful products. One well-known methanation process, also called the Sabatier reaction, involves reaction of CO_2 with H_2 over a metal catalyst to produce methane. The same process can also be used to convert CO to methane [144]. The reactions are expressed as:



The greatest advantage of methanation of hydrogen is that the synthesized methane can be fed directly into the gas distribution network without any limitations. Although the second reactant in the methanation process CO_2 can be separated from air, the related energy and economic effort is very high [145]. Hence, the methanation plants should be located close to a CO_2 source, such as fossil fuel power stations, industrial or biomass plants in order to get access to abundant of CO_2 with low economic and energy effort. So such systems can also recycle CO_2 emissions from existing CO_2 sources.

However, the disadvantages are also obvious. Due to the requirement of the additional step in the P2G chain, further investment on methanation plant and hydrogen storage is required, and such an additional step also causes further losses in energy and efficiency. After evaluating 41 realised and 7 planned P2G plants, [139] concluded that the design and sizing, control strategy and system integration of the P2G plants have great influence on their overall efficiency, reliability and economics.

The view of P2G technology is still controversial. There are supporters believe that P2G technology can solve the energy storage and grid congestion problems at the same time [146], but there are still researchers questioning that P2G does not seem to be an optimal storage system from economic and environmental perspective [147].

5. Conclusion

Along with the rapid development of renewable power generation, the impact of their inherent intermittency, fluctuation and difficulty in prediction on the existing electric grid attracts more and more concern. There is a need for flexibility within the system. Electricity storage is seem to be a solution for eliminate the curtailment, increase the penetration of renewable power generation, and provide better connection between demand and supply as well as other economic and technical benefits. Electricity storage is not a new technology. Currently, there are dozens of different storage methods in existence, from capacitor/supercapacitors, batteries, pumped-hydro, compressed air, flywheels, to superconducting magnetic energy storage, hydrogen and so on. Among them, hydrogen is believed to be a promising candidate not only for energy storage but also leads to a new hydrogen economy.

In this report, the key technologies used in hydrogen energy storage system are reviewed. Hydrogen can be produced from several different routes, either from fossil fuels, from nuclear power, or from renewable biomass and renewable electricity, using thermal, photonic, biochemical and electrical energy. At the current stage, the majority of hydrogen produced is from fossil fuels via well-established technologies such as steam reforming, gasification and partial oxidation, and it is been criticised for high energy consumption and carbon emission. Other routes such as production from biomass can mitigate the CO_2 emission and replace fossil fuels with sustainable biomass fuel. However, there is still a lot of work to be done before those technologies can be widely deployed. Producing hydrogen from water electrolysis is a clean and sustainable way for production especially when using renewable electricity.

The produced hydrogen can be stored in compressed gas form or in liquid form, which are quite commonly used in industry. To increase the gravimetric density of hydrogen storage, so it can be more suitable for vehicular applications, material based hydrogen storage has attracted a lot of research interest. Hydrogen atoms or molecules can be attached to the surface of the materials or the atoms can be integrated in the lattice of the materials. The effectiveness of the storage is strongly dependent on the development of the novel materials so that large amount of hydrogen can be stored and released at a reasonable temperature and pressure.

Finally, hydrogen can be used in fuel cell systems to combine with oxygen to generate electricity and heat, where water is the only by-product. Or, hydrogen can be directly blended into the natural gas grid with a limitation or via a methanation process to produce synthesis gas and injected into gas grid without any constraints. This so called power-to-gas technology provides the link between electricity grid and the gas grid, and provides additional energy storage capacity to relieve the electricity grid infrastructure which normally has less capacity and high cost compared with the natural gas grid.

Hydrogen technology has the potential to change our existing power infrastructure and even our lifestyle. However, to realise and fully unveil the potential and benefits of hydrogen economy, there are still a lot of challenges that needs intense effort from both academic and the industrial community.

Acknowledgement

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