Hydrogen Energy: Production, Storage and Application

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Abstract. With the global demand for sustainable energy rising, hydrogen energy has gained significant attention as a clean and efficient alternative. Fossil fuels are depleting and environmental impacts resulting from their combustion have driven humanity's quest for alternative energy sources. Hydrogen energy is a key choice due to its high energy density and eco-friendly attributes. This paper delves into the current status quo and prevailing technologies associated with hydrogen energy production, storage, and utilization. It scrutinizes dominant techniques such as water electrolysis and steam reforming, despite economic and safety hurdles. Storage strategies encompass compressed gas, liquid, and solid-state methods, each with unique characteristics and use cases. Mainstream hydrogen applications involve fuel cells, hydrogen combustion, and hydrogen-powered engines, demonstrating substantial potential for enhanced energy efficiency and reduced environmental pollution. Despite ongoing challenges in cost-effectiveness, safety, and technological maturity, hydrogen energy continues to hold considerable promise as a major energy source for the future.

Keywords: Hydrogen energy; renewable energy; hydrogen production; hydrogen storage.

1. Introduction

At present, fossil fuels provide most of the world's energy needs, but by the end of 2019, the world's proven oil reserves could only meet the production and living needs of human beings for about 50 years at the consumption level of that year and the coal reserves could not meet the long-term needs of human development [1]. At the same time, in the past 100 years, the burning of fossil fuels has caused environmental problems such as acid rain, smog, and global warming, and its harmful effects on humans and the environment are devastating. Therefore, it is urgent to quickly seek sustainable and renewable clean energy, and it has become a consensus in the global energy transition. Hydrogen energy is one of the popular energy options at present, it is a secondary energy source, is non-toxic, has a wide range of raw materials, and can be extracted from water, oil, gas, biofuels, and other substances, at the same time, hydrogen as an energy power generation will only generate pure water as a byproduct, and the calorific value is quite high; the same quality may offer three times more energy than gasoline combustion, and it is highly clean and efficient, thus it is regarded as the future energy.

Hydrogen energy also has obvious advantages over other clean energy sources, such as solar and wind energy, which have limited production capacity due to weather conditions and can only be stored and transported in the form of batteries, whereas hydrogen energy can be artificially adjusted and controlled, and then stored and transported via pipelines or liquid hydrogen storage tanks. The present uses of hydrogen energy are mostly for fuel cell power generation and fuel combustion in industrial processes to produce energy. However, the development of hydrogen energy also encounters many problems, such as high cost, insufficient preparation and storage technology, and insufficient safety. In this paper, the preparation, storage and application of hydrogen energy will be studied combined with the current development trend and dilemma of hydrogen energy, the main methods of hydrogen energy preparation and their principles, advantages and disadvantages, the technology, principles and materials of hydrogen energy storage, as well as the main methods and principles, advantages and disadvantages of hydrogen energy application will be introduced and analyzed, and some methods for future improvement will be provided.

2. Preparation of Hydrogen Energy

2.1. Hydrogen Preparation by Electrolysis of Water

In the cell, two electrodes are placed in the electrolyte and the power is turned on so that the current is conducted. When energized, water molecules gain electrons at the cathode to form hydrogen and lose electrons at the anode to produce oxygen, as shown in Fig. 1. The degree of ionization of water itself is low, but when there is a strong electrolyte dissolved in the water, such as KOH, polar water molecules will surround K^+, thus forming hydrated K^+, and at the same time, the charge of K^+ makes the water molecules have a polar direction, and under the action of direct current, hydrated K^+ migrates to the cathode, at this time, H^+ will first get electrons and undergo a reduction reaction to produce hydrogen [2].

There are two types of water electrolysis hydrogen production technology: acid water electrolysis hydrogen production and alkaline water electrolysis hydrogen production. The reaction formula for acid water electrolysis hydrogen production is:

Cathode response equation:

$$4H^{+}+4e^{-}\rightarrow 2H_2 \tag{1}$$

Anode response equation:

$$2H_2O-4e^{-}\rightarrow O_2+4H^{+} \tag{2}$$

Overall equation:

$$2H_2O=2H_2+O_2 \tag{3}$$

The reaction formula for alkaline water electrolysis to produce hydrogen is:

Cathode response equation:

$$4H_2O+4e^{-}\rightarrow 2H_2+4OH^{-} \tag{4}$$

Anode response equation:

$$4OH^{-}\rightarrow 2H_2O+O_2+4e^{-} \tag{5}$$

Overall equation:

$$2H_2O=2H_2+O_2 \tag{6}$$

Under the standard condition, the theoretical voltage driving water electrolysis is 1.23 V, but due to multiple obstacles from kinetics and resistance, a higher voltage is often required to achieve water electrolysis at appreciable currents [3].

Hydrogen production by water electrolysis has the advantages of low cost, no pollution, and easy access to raw materials, but its anode oxygen evolution reaction requires larger voltage, and its anode product oxygen is not only of low value but also forms an explosive and dangerous mixture with hydrogen [4].

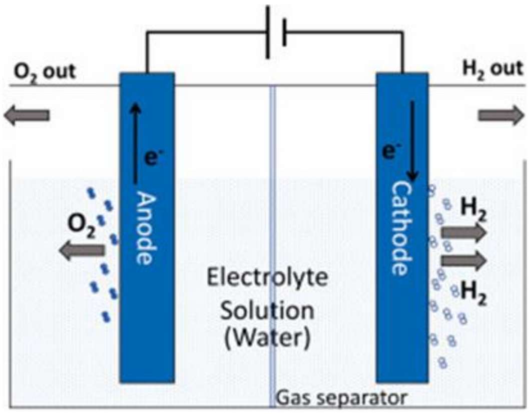

Fig. 1 Schematic diagram of hydrogen production by water electrolysis [5]

Because of the gap between reality and theory, it is extremely vital to utilize efficient catalysts to increase the efficiency of water electrolysis, and catalysts are usually separated into noble metal catalysts, transition metal catalysts, and non-metal catalysts. Among them, the precious metal catalyst is mainly platinum-based, although it has superior catalytic performance, the price is high, the reserves are scarce, and it is difficult to be used for large-scale industrial production. Because of the abundant reserves of transition metals and the strong adsorption of hydrogen, it is hoped that they will replace precious metals. However, the overall performance and use effect of single transition metals are not ideal, so transition metal alloying, heteroatom doping, and other methods are usually adopted, and the current transition metal catalysts are mainly transition metal alloys, transition metal sulfides, phosphides, borides and nitrides [6]. At present, non-metallic catalysts are mainly carbon-based materials.

2.2. Hydrogen Preparation by Reforming Steam

Steam reforming, the most used method of hydrogen production, is a process in which natural gas or liquid hydrocarbons are reacted with steam at high temperatures to produce hydrogen [7]. Steam reforming hydrogen production has low cost, high efficiency, and large hydrogen production, but it needs to treat exhaust gas and waste heat, and also needs a part of combustion as a heat source and has high requirements for catalysts.

Because the chemical structure of CH_4 is stable, it is reactive at high temperatures, and water vapor, which is one of the main raw materials, is cheap and easy to obtain, so natural gas water vapor conversion hydrogen production has become a commonly used natural gas hydrogen production method at home and abroad. The main process is to first pretreat natural gas with high-temperature hydrogenation and zinc oxide to remove organic sulfur and then reform it with water vapor at high temperature under the action of a nickel-based catalyst to produce reformed gas. The main reaction formula is:

$$CH_4+H_2O \rightarrow 3H_2+CO \quad \Delta H_{298}^{\Theta}=206.1 \text{ kJ/mol} \tag{7}$$

Secondly, the heat is recovered by the waste heat boiler to generate the water vapor required by the reformer, and the CO in the reforming gas is further converted to H_2 and CO_2 at medium temperature. The main reaction formula is:

$$CO+H_2O \rightarrow H_2+CO_2 \quad \Delta H_{298}^{\Theta}=-41.2 \text{ kJ/mol} \tag{8}$$

Finally, after the transformation reaction, the shift gas is condensed by a heat exchanger to remove the remaining water, and then the impurities are adsorbed by the pressure swing adsorption unit (PSA), and the product hydrogen is separated and purified. The technology is mature and reliable, and the block diagram of the process flow is shown in Fig. 2 [8].

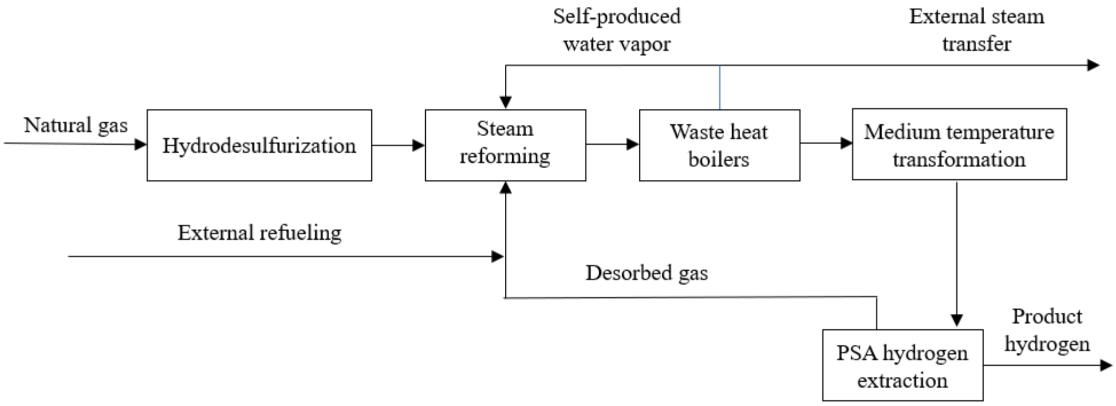

Fig. 2 Schematic diagram of natural gas water vapor conversion hydrogen production process [8]

2.3. Hydrogen Preparations by Alcohols

The major raw materials utilized in alcohol hydrogen production are methanol and ethanol, which are low-cost, practical for storage and transportation, and simple to get.

Methanol Lysis (SD):

$$CH_3OH=CO+2H_2 \tag{9}$$

Partial oxidation (POM):

$$CH_3OH+O_2=2CO_2+3H_2 \tag{10}$$

Steam Reforming (SMR):

$$CH_3OH+H_2O=CO_2+3H_2 \tag{11}$$

The above are several commonly used methods for methanol hydrogen production. The high hydrogen-to-carbon ratio of methanol favors the production of hydrogen and there are no chemical bonds between carbon elements, which greatly reduces the production of greenhouse gases [9].

Ethanol Steam Reforming (ESR):

$$C_2H_5OH+3H_2O=2CO_2+6H_2 \tag{12}$$

Partial Oxidation (POE):

$$2C_2H_5OH+30_2=2CO_2+6H_2 \tag{13}$$

Oxidized steam reforming (OSRE):

$$C_2H_5OH+(3-2x)H_2O+xO_2=(6-2x)H_2+2CO_2 \tag{14}$$

The above are some commonly used methods for ethanol to produce hydrogen.

3. Storage of Hydrogen Energy

3.1. Compressed Hydrogen Storage

Hydrogen is a gas with lower density and mass at room temperature and pressure but with a larger volume, resulting in relatively low storage efficiency. Compressed hydrogen storage compresses hydrogen to a higher pressure for more effective storage. In higher temperatures, particles have relatively more kinetic energy, resulting in a greater distance between particles, which reduces the density of hydrogen gas and makes it more difficult to compress. Conversely, hydrogen gas is denser and easier to compress in lower-temperature environments. Therefore, to achieve the highest storage efficiency, a lower-temperature storage environment should be provided for hydrogen gas.

3.1.1 Compression equipment

Compressing hydrogen requires specialized compression equipment, usually using a compressor or pump. These devices are capable of extracting and compressing hydrogen from low pressure to the desired high-pressure level. Compression equipment typically uses hydrogen compressors and electronic hydrogen pumps. The working process of the hydrogen compressor is divided into suction, compression, exhaust, and slag discharge. During the suction process, the intake valve of the compressor opens, and hydrogen enters the compressor from outside. The volume of hydrogen entering the compressor is larger and the pressure is lower; During the compression process, the intake valve is closed, and the piston or rotating mechanism inside the compressor works on the hydrogen gas, reducing the volume of hydrogen gas and reducing the molecular gap. The hydrogen pressure increases; When the hydrogen gas reaches the required pressure during the exhaust process, the exhaust valve opens and the hydrogen gas is pushed out of the compressor; The slag discharge process refers to the formation of filter residue during the compression of hydrogen gas by the compressor, which needs to be removed from the compression process at the slag discharge port. An electrochemical hydrogen pump is a device that uses electrochemical reactions to compress hydrogen gas. It uses electrochemical principles to convert hydrogen gas into hydrogen ions and compresses hydrogen gas by utilizing the movement of these ions. Electrochemical hydrogen pumps utilize electrochemical reactions in electrolyte solutions to compress hydrogen gas. This reaction involves the processes that break down water into hydrogen ions(H^+) and hydrogen(H^+). Electrochemical hydrogen pumps consist of at least two electrodes, typically the cathode and anode, typically made of conductive materials such as platinum or other precious metals. Electrolyte solution is the medium through which electrochemical reactions occur. A typical electrolyte may be a salt solution or an acidic solution. In the reaction, hydrogen gas is absorbed into the cathode and undergoes an electrochemical reaction on the surface of the cathode to produce hydrogen ions. These hydrogen ions then migrate towards the anode through the electrolyte solution. On the anode, hydrogen ions come into contact and react with hydrogen gas, releasing it into the container. This process is controlled by applying voltage, so the compression rate and ratio of hydrogen can be adjusted. Fig. 3 specifically shows the working principle of the electrochemical hydrogen pump.

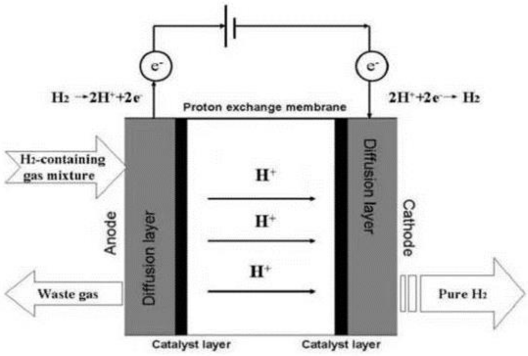

Fig. 3 Working principle of the electrochemical pump [10]

3.1.2 Storage container

Compressed hydrogen gas needs to be stored in high-pressure containers, which are usually sturdy and lightweight. There are currently four types of pressure vessels available for the storage of compressed hydrogen gas.

Type I is an all-metal pressure vessel. This type is the most conventional, economical, and largest hydrogen storage container with a capacity of approximately 3.0 lb/L. Aluminum or steel are commonly used in its construction and can withstand pressures up to 50 MPa. Type II material is coated with fiberglass composite material and is a steel pressure vessel. Type II vessels are 50% more expensive to manufacture than Type I vessels when made of composite materials instead of steel, but their quality is decreased by 30% to 40%. The highest pressure-bearing capacity is found in this kind of pressure vessel. Type III materials make up the pressure vessel with the metal liner and complete composite material coating. The majority of the structural load is supported by carbon fiber composite materials, which are sealed with aluminum lining plates. Approximately 5% of the mechanical load is supported by these metal lining plates. This kind of pressure vessel costs twice as much as Type II but has a working pressure of 45 MPa and a hydrogen carrying capacity of 0.75–1 lb/L, which is roughly half that of Type II. Type IV material is the lightest composite pressure vessel. Usually, high-density polyethylene (HDPE) and other polymers are used as lining plates, and carbon fiber or carbon glass composite materials are used to bear structural loads. Under pressure up to 100 MPa, but at a higher price. In addition, there is a type of pressure vessel (Type V) made entirely of composite materials and without liners, which was first developed in 2010. The container prepared with this material has a weight reduction of 20% compared to similar Type IV containers, and the allowable pressure is 1.37 MPa [11].

3.1.3 Safety

Compressed hydrogen storage involves high pressure; therefore, safety is a key issue. Storage devices need to have high security, ensuring their high strength and sealing, and preventing leakage or other security issues. In addition, various safety valves and detection devices are required in the system to ensure timely action in case of abnormal situations.

3.2. Liquid Hydrogen Storage

Liquid hydrogen storage cools hydrogen to a very low temperature, converting it into liquid form to increase storage density. Hydrogen is in a gaseous state at room temperature and can be converted into a liquid state by reducing temperature and increasing pressure. Liquid hydrogen typically needs to be stored at very low temperatures, typically close to absolute zero (-253 ℃ or -423 ℉), and the storage pressure for liquid hydrogen should also be controlled within the range of tens to hundreds of psi (pounds per square inch). At present, this method is mainly used in the aerospace field, with high storage costs and complex technical safety.

The design of hydrogen storage containers mainly considers three aspects: appearance, hydrogen storage materials, and safety. It is generally believed that the thermal leakage of hydrogen storage tanks is directly proportional to the specific surface area, so the shape of hydrogen storage tanks is mostly spherical and cylindrical with a smaller specific surface area. Spherical storage tanks have the smallest specific surface area and uniform stress distribution, but high manufacturing accuracy requirements and high prices. The production process of cylindrical storage tanks is simple and more widely used. Because hydrogen liquefaction can only be achieved through multiple throttling and expansion cycles, and there is a huge temperature difference with the outside world, the selected hydrogen storage material must have high insulation, and also consider the mechanical properties at low temperatures and possible Crisp phenomenon [12]. Common materials include high-strength metal alloys or composite materials, and the inner surface of the container may also be coated to reduce thermal radiation. These containers typically have a double arm structure, with a middle layer filled with vacuum or low-temperature insulation material to reduce heat conduction. Liquid hydrogen storage containers must be able to withstand high pressure and external impacts and have good safety performance to prevent leakage or explosion accidents. The container must be equipped with specially designed valves and fittings to ensure safe filling and discharge of liquid hydrogen gas. These components are usually made of low-temperature resistant materials and designed with sealing to prevent leakage. Liquid hydrogen storage containers are usually equipped with monitoring and control systems to monitor storage pressure, temperature, and liquid level, and ensure safe operation. These systems can promptly detect any abnormal situations and take corresponding measures.

3.3. Solid Hydrogen Storage

In addition to the two storage methods mentioned above, solid-state hydrogen storage is achieved by absorbing hydrogen atoms through physical adsorption or chemical reactions to produce metals or chemical cyanide (LiH, NaH, CaH_2, etc.). This technology is also widely recognized for its excellent hydrogen storage capacity, for example, palladium metal can store 900 times its volume of hydrogen at room temperature and pressure [5]. The main technical issues of this method are the high cost and complexity of hydrogen extraction reactions, as well as the need to optimize the temperature required for the reaction and the heat management of the storage structure [13]. There is another solid-state hydrogen storage method that physically adsorbs hydrogen through porous materials, but currently, this approach cannot meet the requirements in terms of hydrogen charging time [14].

4. Application of Hydrogen Energy

4.1. Hydrogen Fuel Cells

In essence, a hydrogen fuel cell is an energy converter that uses hydrogen energy, which is employed in cars, ships, and airplanes today since it is clean and very efficient. Proton exchange membrane fuel cells, of which hydrogen fuel cells are primarily a subclass, have a fundamental operation that may be broadly broken down into multiple phases, as illustrated in Figure 4, First, hydrogen and oxygen enter the anode and cathode of the battery, respectively, where hydrogen is decomposed into hydrogen ions and releases electrons under the action of the catalyst of the anode part, then the electrons generate current through the external circuit and provide electrical energy to external devices, and finally return to the cathode, while hydrogen ions pass through the proton exchange membrane to reach the cathode and undergo a reduction reaction. Currently, the most often utilized catalysts for reactions are platinum-based.

Although hydrogen fuel cells have many advantages, there are still many problems, such as high manufacturing costs, imperfect hydrogen storage systems, and battery life and durability that still need to be improved.

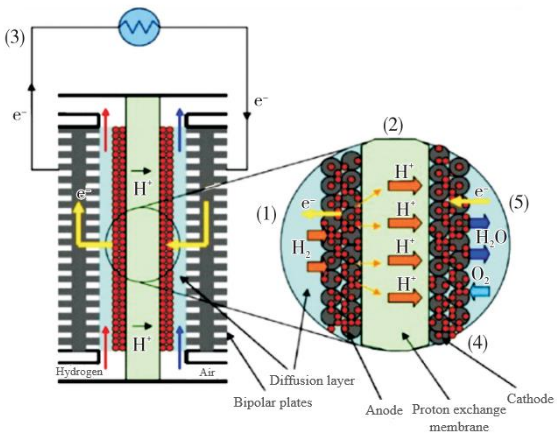

Fig. 4 The operating principle of hydrogen fuel cells [15]

4.2. Hydrogen Combustion

Due to its advantages of high calorific value, cleanliness, and fast flame propagation, the combustion of hydrogen has been intensively studied. Among them, hydrogen-doped combustion is one of the commonly used methods, which refers to the process of mixing hydrogen with other fuels (such as natural gas) and combustion, in power plants, the combination of hydrogen-doped combustion and gas turbines can improve power generation efficiency and effectively reduce carbon emissions. However, hydrogen has the characteristics of low density, wide flammability range, and low ignition energy [16], which greatly increases the possibility of backfire during combustion, so the anti-tempering ability of the fuel needs to be improved appropriately, and the NOx emissions generated at high temperatures need to be reduced, and the fuel combustion characteristics (such as flame temperature) and combustion stability that change after hydrogen doping also need to be specifically explored.

In addition, hydrogen-fueled engines also have a wide range of application prospects. It is an internal combustion engine fueled by hydrogen, which can not only be quickly refueled by filling liquid hydrogen compared with hydrogen fuel cells, but also has a higher power density, and the hydrogen-fueled gas turbine engine also has the characteristics of good starting performance, low fuel consumption, and high unit power [17].

The fuel supply system and ignition system of the hydrogen engine will be slightly different from that of the existing engine, but the structure and technology of the existing engine still need to be used to reduce additional costs as much as possible [18]. In addition, it is also feasible to use hydrogen fuel engines as a supplement to hydrogen fuel cells in vehicles. It should be noted that the phenomenon of hydrogen damage will cause damage and embrittlement of the metal materials of the engine, affecting the life and safety of the hydrogen fuel engine, so it is necessary to select the appropriate materials and carry out the appropriate material treatment in the design and manufacturing process.

5. Conclusion

This study critically evaluates the current status of hydrogen production, storage, and application processes, highlighting the mainstream methodologies and strategies employed in these sectors. Additionally, it highlights other methods that have advantages but are hindered by technical limitations. Water electrolysis and steam reforming, both common hydrogen production techniques, are discussed. However, both methods have drawbacks, including waste heat generation and explosion risks. Alcohol-based hydrogen production, particularly from methanol and ethanol, is considered a promising avenue because it is readily available, affordable, and environmentally friendly, and may eventually become the mainstay for hydrogen supply in the automotive sector and beyond. Regarding hydrogen storage, the paper identifies three primary modes: compressed gas storage where hydrogen is pressurized using specialized equipment and stored in metal or composite vessels; liquid hydrogen storage, requiring cryogenic temperatures and high-adiabatic materials to maintain liquid hydrogen, which is ideal for niche applications like aerospace but is costly and technically challenging.; and solid-state storage that integrates hydrogen into substances like metal hydrides via adsorption or chemical reactions, offering high-density storage though grappling with high costs, complex desorption processes, and thermal management optimization. In the field of hydrogen energy applications, fuel cells have made significant progress in the automotive, marine, and aviation sectors due to their high efficiency and zero-emission qualities. However, their widespread adoption is hindered by the high manufacturing costs and durability issues surrounding proton exchange membrane fuel cells. Hydrogen combustion offers significant opportunities, with improvements in power generation efficiency and carbon footprint reduction, but safety concerns tied to hydrogen's flammability must be addressed effectively. Hydrogen-fueled internal combustion engines exhibit rapid refueling times and high-power output, but they also need to address durability and safety concerns in materials and design. To conclude, this paper presents a comprehensive perspective on hydrogen energy, examining its advancements and constraints across all aspects of production and storage technology. Given its relative eco-friendliness and accessibility, hydrogen has emerged as the most promising form of energy to supplant fossil fuels as the principal energy carrier for human societies. Despite these obstacles, hydrogen's potential to serve as a cornerstone of future energy systems remains undiminished.

Author contribution

All the authors contributed equally, and their names were listed in alphabetical order.

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