Analysis Of the Current Situation and Prospective Study of Hydrogen Preparation and Storage

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Abstract. The research, development, and practical application of renewable energies are becoming a major trend with environmental problems such as increasingly serious global warming and the depletion of oil resources. Hydrogen is an ideal alternative energy source due to its cleanness and high combustion ratio. It is recognized as the most likely replacement for the existing coal and oil systems as the future energy base of the global economy. But as things stand, the hydrogen reserve technology and hydrogen storage technology at the current stage all have certain advantages and disadvantages. Based on this background, the study summarizes the current state of the art of hydrogen energy production technologies such as direct hydrogen production from fossil fuel, hydrogen production from electrolysis of water, hydrogen production from biomass, as well as four types of hydrogen storage methods, namely, high-pressure gaseous hydrogen storage, low-temperature liquid hydrogen storage, solid hydrogen storage, and organic liquid hydrogen storage, and analyzes the advantages and disadvantages of each technology. Among them, hydrogen production from electrolyzed water and bio-hydrogen production are the technologies with higher potential but still need to improve economic competitiveness. The high-pressure gaseous hydrogen storage technology can also be brought to market on a wide scale after cost reduction.

Keywords: Hydrogen energy, hydrogen preparation, hydrogen storage, development prospect.

1. Introduction

As people pay more attention to the living environment, petroleum fuels are gradually withdrawing from the stage of history, and replaced by a variety of clean and renewable new energy sources, such as solar energy, tidal energy, wind energy, nuclear energy, and so on. Hydrogen energy has a natural advantage over traditional fossil energy in that it has more than three times the calorific value and energy density; it has fewer environmental constraints and longer storage time than new energy sources such as solar energy, tidal energy, and wind energy. By all accounts, hydrogen energy is the most promising new energy source. A typical hydrogen energy chain includes hydrogen production, distribution and delivery, hydrogen storage, and final utilization. The energy chain for sustainable hydrogen energy consists of harvesting sunlight or other energy sources to produce hydrogen as an energy carrier, storing and distributing this energy carrier, and utilizing it in end-use devices centered on fuel cells or combustion to convert it into power [1]. However, for the current market, hydrogen production platforms at this stage are mainly based on fossil fuels, which are relatively inefficient in terms of energy efficiency and lead to significant greenhouse gas emissions [2]. The hydrogen energy industry chain is not yet fully mature, (For example, hydrogen storage is smaller in mass and volume than the energy storage density of gasoline hydrogen storage; on a mass basis, the highest hydrogen energy storage density can be achieved using liquid hydrogen storage, which is about 80% of gasoline storage, and on a volume basis, the highest hydrogen energy storage density can be achieved using a type of metal hydride storage, which is about 35% of gasoline storage, i.e., there is no hydrogen storage option High energy storage density in both mass and volume, which is a bigger problem in automotive applications where hydrogen is used as a fuel; it can leak from containment due to its low density and small molecular size; hydrogen can cause a number of material problems such as alloy embrittlement; and the cost of production of hydrogen as an energy carrier can be very high, especially when compared to the cost of current fossil fuels [3]. The fundamental reason is that the upstream preparation and midstream storage levels are yet to be perfected. According to the current hydrogen preparation method and hydrogen storage technology, this paper will carry out a series of researches on the main ways of hydrogen energy preparation, equipment, and principles involved in the preparation process, as well as the storage method at the end of the preparation, and make a prediction of the development orientation and trend of the hydrogen energy industry in the future.

2. Current Status of Research on the Production of Hydrogen

2.1. Direct Hydrogen Production from Fossil Energy

At present, the mainstream hydrogen production from fossil energy mainly includes coal gasification hydrogen production technology, natural gas steam reforming hydrogen production technology, methanol hydrogen production technology, etc., and China has the natural advantage of abundant coal resources, so the coal gasification hydrogen production technology is the main way of hydrogen production in China at the present stage [4]. The principle of coal gasification hydrogen production technology is to utilize the chemical energy of coal to produce hydrogen. The reaction is based on coal as the main raw material, which is fully reacted with oxygen and then reacted with water vapor. At high temperatures and high pressure, the coal is converted into a mixture of hydrogen and CO as the main components. After desulfurization and purification, the CO continues to be transformed with the steam reaction to generate CO2 and hydrogen, and finally purified by the way of transforming pressure, adsorption, etc., so as to obtain a certain degree of purity of the hydrogen gas [5]. Although hydrogen production by coal gasification can realize large-scale production by relying on the advantage of large coal resources in China, the cost of equipment still accounts for a large part of the investment cost, and a large amount of carbon dioxide is generated during the application of this technology [6].

Natural gas steam reforming technology for hydrogen production is based on natural gas extracted from the ground as the raw material, through a series of treatments (such as desulfurization, dechlorination, arsenic removal, etc.), and then reacted under a nickel catalyst. Natural gas hydrogen production is basically divided into four processes: raw gas pretreatment, water vapor conversion, medium and low temperature conversion process, and Pressure Swing Adsorption (PSA) hydrogen purification [6]. Hydrogen production from natural gas is less expensive, has low CO2 emissions and high hydrogen yield efficiency [4], but is limited by raw materials and the industry needs to be customized to natural gas-rich regions.

The production principle of methanol-to-hydrogen technology is to purify methane from biogas to produce methane, which is then used as a feedstock to produce hydrogen [4]. Its processes include pretreatment, catalytic reforming or syngas generation, water vapor displacement, methanation or gas cleaning. The methanol-to-hydrogen process is relatively simple and low-cost to operate, and convenient to transport, but the process route is long and complex [4], and the unit consumption is very high, which is also a waste of energy [6].

2.2. Hydrogen Production from Industrial by-Products

Hydrogen production from coke oven gas can effectively utilize hydrogen, carbon monoxide, and carbon dioxide in coal gas, and can also convert methane to hydrogen and carbon monoxide by heating during the reaction process [7]. Compared with hydrogen production from fossil fuels, hydrogen production from coke oven gas does not produce additional pollution and carbon emissions, but also has obvious advantages in terms of cost and other aspects [4]. However, the output of hydrogen is less pure, and the use of it still needs to go through a purification step.

The specific process of hydrogen production from chlor-alkali by-products is that the hydrogen discharged from the chlor-alkali system is alkaline washed and then cooled to remove a large amount of water, and then converged into the hydrogen main pipe, compressed and then de-chlorinated by the dechlorinator to remove chlorine, and then entered into the de-oxidizer to remove oxygen. This method can effectively solve the environmental problems caused by the trace chlorine in hydrogen along with the emission of large amounts of exhaust hydrogen, and save a lot of energy [8]. However, the purity is low and there are limitations in its use [9].

Propane dehydrogenation by-production and ethane cracking by-production technologies are still in the laboratory due to inefficiencies in capacity and the flammability of the raw materials.

2.3. Hydrogen Production from Electrolysis of Water

2.3.1 Direct electrolysis of water for hydrogen production

Hydrogen production by electrolysis of water is accomplished in an electrolyzer. The process of hydrogen production involves immersing a pair of electrodes in an electrolytic cell containing an electrolytic solution and applying a direct current, which breaks down the water into hydrogen and oxygen. With different types of electrolytes, hydrogen production from electrolyzed water can be categorized into alkaline electrolyzed water (ALK), proton exchange membrane (PEM), and solid oxide.

Alkaline water electrolysis technology uses inorganic ion exchange membranes or polymer membranes with hydroxide ion conductivity as the diaphragm material, which is a more mature technology in hydrogen production from electrolytic water. It is the right choice for today's megawatt-scale commercialized power with its low technology cost as well as high stability and durability. However, the corrosion problem and slow switching response of this technique have been a major drawback [10].

The core component of PEM water electrolysis is a thin perfluorosulfonic acid proton-conducting polymer membrane PEM. During the reaction, protons move to the cathode and a reduction reaction occurs resulting in the production of hydrogen gas. The compact design of the PEM water electrolyzer offers the advantages of high current density, fast response time, and the ability to produce high-purity hydrogen of up to 99.995%, making it extremely attractive for industrial use. However, the electrocatalyst used in PEM water electrolysis is a precious metal, which leads to the high cost of the technology, so the main challenge of PEM water electrolysis technology is to reduce the production cost while maintaining high efficiency. Most of the research directions at this stage are directed towards solving efficiency problems such as the relative size of the electrolyzer, operating intervals, output pressure, oxygen production, and water consumption [11]. To address the cost issue, Anion Exchange Membrane (AEM) water electrolysis technology has been developed, which is made of anionic conductive polymers to replace asbestos diaphragms. AEM water electrolysis combines the low cost of alkaline water electrolysis with the high efficiency of PEM water electrolysis to improve the overall electrolysis efficiency. However, AEM membranes are chemically and mechanically unstable, which greatly affects their service life.

Solid oxide water electrolysis technology is currently in the laboratory stage and has not been commercialized due to the high operating working temperature requirements and limited material selection. However, the technology exhibits extremely high ionic conductivity and hydrogen production efficiency, low power consumption, and does not require precious metals to act as catalysts [11], and with the development and breakthroughs in research and development technology, the technology will surely be widely used in the market.

2.3.2 Renewable energy technologies for hydrogen production from electrolyzed water

Renewable energy hydrogen production technology is the use of wind, solar, nuclear, and other renewable primary energy converted to electrical energy, and then the electrical energy into the hydrolysis tank, combined with electrolysis of water to hydrogen production technology will be electrolyzed into hydrogen and oxygen. This technology can better solve the problem of "abandoned light" and "abandoned power", but the construction and maintenance costs are extremely high, and the regional restrictions are large.

Wind-powered hydrogen production technology, i.e., the use of wind power to promote the rotation of wind blades, and then accelerate the rotation speed through the speed booster to promote the generator to generate electricity [10]. This technology can adjust the ratio of power generation for grid connection and electrolysis hydrogen production through an automatic control system, which effectively solves the problem of power generation waste. Hydrogen production from wind power can be further categorized into onshore electrolytic water production, offshore centralized electrolytic water production (constructing an electrical conversion network between the offshore generator and the offshore platform), and offshore distributed electrolytic water production (installing complete equipment at the bottom of the generator to directly empower the generator to produce hydrogen) [12]. So far, wind power hydrogen production technology still remains in the theoretical research and still faces many problems, such as highly adaptable wind turbines, power control, and regulation methods for high power fluctuations, high power hydrogen production equipment suitable for high power fluctuations, more efficient energy-saving technologies for hydrogen production, and integrated control of hydrogen production safety [13].

The principle of photovoltaic electrolysis to hydrogen technology is to use solar cells to convert solar energy into electricity. Solar collectors generally include trough, tower and dish, of which tower solar collectors have been put into use in actual production by virtue of the advantages of relatively low cost, simple tracking system, and strong wind resistance [14]. Solar energy is characterized by discontinuity and volatility. These challenges have been a major impediment to the progress of solar power generation for some time, and combining it with hydrogen production from electrolyzed water effectively avoids the problem of "abandonment of the electrical energy problem"(Refers to the phenomenon in which a photovoltaic system has to give up the electricity it generates due to the inability to send it out or store it in the process of generating electricity). As far as the current situation is concerned, it is difficult for solar cells to find a balance between the four aspects of cheapness, stability, efficiency, and environmental friendliness, and to find the optimal coupling between the cell and the electrolyzer, the competitiveness of photovoltaic electrolytic water-to-hydrogen technology may be further enhanced by continuous research development and the development of photovoltaic electrode materials [15].

Nuclear-to-hydrogen technology uses electricity from nuclear power plants to break down water into hydrogen and oxygen. Based on the electrolysis route, there are two types of cold water electrolysis and steam electrolysis. Cold water electrolysis is now available on a small scale and at a lower cost, whereas steam electrolysis for hydrogen production requires a reaction temperature of 600-1000 °C, with a theoretical energy consumption of one-third of that of cold water electrolysis and a higher efficiency [16]. Thermochemical decomposition of water is the use of thermal energy between 600 and 900 °C generated by Advanced Modular Reactors (AMRs) can be used to decompose water into hydrogen and oxygen with the use of chemical catalysts [17], but the low efficiency of this technology and the complex environment required for the reaction require further research and development.

2.4. Biomass-Based Hydrogen Production

Hydrogen production from biomass refers to the production of hydrogen from biomass using gasification or microbial-catalyzed deoxygenation after different pre-treatments, which are classified into thermochemical and biological methods [7]. Biomass pyrolysis and biomass gasification are the more mature technologies for thermochemical hydrogen production. The principle of hydrogen production from biomass pyrolysis is to obtain three kinds of products, namely, gas, liquid, and solid, by pyrolysis of biomass, and then convert the gas and liquid products into hydrogen by steam reforming and water-gas replacement technology, and the main research direction at present focuses on steam reforming [18]. Biomass gasification to hydrogen technology starts with heating the biomass to over 1000 K to get the gas-liquid-solid products, followed by steam reforming and water-gas replacement to get the hydrogen. Bioprocess hydrogen technology converts water molecules and organic substrates in biomass into hydrogen through the catalytic activity of two key enzymes--hydrogenase and nitrogenase. Common bio-based hydrogen technologies include direct photolysis, indirect photolysis, photo-fermentation, dark fermentation, light-dark coupled fermentation, and cell-free systems for hydrogen production. Hydrogen production from biomass has a positive impact on optimizing the structure of energy consumption, reducing environmental pollution, and combating climate change [10], which is a hot research topic in the field of hydrogen production today. However, at this stage, the low efficiency of the technology, high cost, low purity of the output hydrogen, and other factors greatly impede the large-scale industrial application of material hydrogen production. Therefore, the current mainstream research direction is to utilize genetic engineering techniques to obtain strains possessing higher hydrogen production efficiency as well as cheaper biomass feedstocks [19].

3. Current Status of Hydrogen Storage

3.1. High-Pressure Gaseous Hydrogen Storage

High-pressure gaseous hydrogen storage technology is based on the principle of compressing hydrogen at a high pressure of 6,000 to 10,000 psi, and storing the compressed, high-density hydrogen in a high-pressure gaseous hydrogen storage pressure vessel [20], which is currently the most mature and widely used hydrogen storage technology. The high-pressure gaseous hydrogen storage pressure vessel consists of an internal vessel, a shell, a support system, a pressure relief device, a control system, etc., of which the internal vessel is the main vessel [21]. At this stage, the pressure vessels that have been developed include all-metal pressure vessels (Type I), glass fiber composite clad steel vessels (Type II), all-composite clad and metal lined vessels (Type III), and all-composite vessels (Type IV). Type I to IV volumetric hydrogen storage densities gradually increase but at a higher cost [10], in addition to an all-composite, unlined pressure vessel (Type V), which was first developed in 2010 [22]. Containers prepared with this material have 20% less mass than similar Type IV containers and have an allowable pressure of 1.37 MPa. Although the current high-pressure gaseous hydrogen storage technology has been relatively mature, but in the high-pressure strong, high strength and low weight still need to strengthen research efforts, in addition, in terms of safety should also establish good corresponding high-pressure gaseous hydrogen storage standards and hydrogen storage pressure vessel standards, improve the risk assessment and safety monitoring of hydrogen storage pressure vessel [23].

3.2. Low-Temperature Liquid Hydrogen Storage

The principle of cryogenic liquid hydrogen storage is to liquefy hydrogen into liquid hydrogen at a temperature of -253 °C and then store it in a cryogenic adiabatic vacuum vessel [10]. Liquid hydrogen storage has obvious advantages over gaseous storage in terms of ease of transportation, high hydrogen storage density and high energy density (Liquid hydrogen is nearly a thousand times denser than H_2, which tends to be only about 60% of its liquid density at 90 MPa, and liquid hydrogen energy can reach 10.05 MJ/L, which is twice the energy of H_2 at 50 MPa.) [24]. From the perspective of energy storage density, this method has great prospects for development. However, the phenomenon of heat leakage loss in the process of hydrogen storage, accompanied by the natural volatilization of liquid hydrogen, has led to the strict requirements of low-temperature liquid hydrogen storage on the sealing of the container, and it is still difficult to realize large-scale industrial application [21].

3.3. Solid State Hydrogen Storage

Solid state hydrogen storage technology has high hydrogen storage capacity, does not require high pressure or insulated containers, and has no risk of explosion, making it a very desirable hydrogen storage technology. The main materials include hydrogen storage alloys, nanomaterials, etc. Solid state hydrogen storage is mainly categorized into hydrogen storage by physical adsorption and chemical hydrides. Physical adsorption is the adsorption of hydrogen by activated carbon, carbon nanotubes, carbon nanofibers carbon-based materials, as well as materials with microporous lattices, such as metal-organic frameworks (MOFs) and covalent organic skeletons (COFs), to capture and store hydrogen; and chemical hydride hydrogen storage is the use of metal hydride hydrogen storage

[23]. However, factors such as high cost and low hydrogen storage capacity have led to the fact that this technology cannot be applied on a large scale and remains in the laboratory stage, and its cutting-edge technological research is mainly invested in the development and utilization of new solid-state hydrogen storage materials and the optimization of its hydrogenation/dehydrogenation reaction [25].

3.4. Organic Liquid Hydrogen Storage

Organic liquid hydrogen storage technology consists of three main stages: hydrogenation of the storage medium (unsaturated liquid organics such as olefins, alkynes, or aromatic hydrocarbons) in the presence of a catalyst, storage, and transportation of the storage medium, and dehydrogenation [26]. The advantage of organic liquid hydrogen storage is that its mass hydrogen storage density is 5% to 10%, the storage capacity is large and the hydrogen storage material is liquid organic material, which can realize the storage and transportation at room temperature and pressure and long distance, convenient and safe [23]. However, its high cost and the immaturity of hydrogenation and dehydrogenation plant technology are the biggest problems for commercial use. At this stage, the research direction is mainly focused on reducing the energy consumption of hydrogen carrier dehydrogenation and the research of low-cost and efficient catalysts [25].

4. Conclusion

In the context of environmental pollution and resource depletion, the development of hydrogen energy is inevitable. Analysis that in the production of hydrogen, with the development of scientific and technological level, hydrolysis of electricity and wind power, photovoltaic combination, and biomass hydrogen ushered in a breakthrough in the technical level is just around the corner. While high-pressure gaseous hydrogen storage can soon be used in the transportation market such as hydrogen cars after solving the cost problem, with technological advances, organic liquid hydrogen storage with convenient and safe features has great potential for development and can realize large-scale storage. At present, the relationship between hydrogen production, energy efficiency, and low pollution has not yet reached a perfect balance, and the safety and transportation efficiency of hydrogen storage have yet to be resolved. It is analyzed that, with the rapid progress of science and technology, the electrolysis of water to produce hydrogen and bio-hydrogen will soon usher in a breakthrough, and the cost of high-pressure gaseous hydrogen storage problem is solved after the technology can also be widely used. Hydrogen energy, as a protagonist in the era of energy transition and carbon neutrality, is almost a major trend for hydrogen energy to become the main source of energy, and only by solving the problem of mobile hydrogen production and storage of hydrogen energy as soon as possible will we be able to fight the energy reform, which is a major battle belonging to the whole of mankind.

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