

Analysis on The Way of Product and Storage of Hydrogen

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Abstract. Nowadays, the over use of fossil fuel cause huge air pollution so people are trying to use a way, which cause less pollution, to produce energy more efficiently replacing fossil fuel. Among various new energy, hydrogen attracts attention due to its cleanliness and zero-carbon property. Following this trend of the increasing demand for hydrogen energy, there are more and more researches on hydrogen production and storage. In this paper, the advantages and disadvantages of several different mainstream hydrogen production and storage methods are compared based on their mechanism, economic benefit, etc. The future energy production and utilization are prospected by the evidences of advantages of production. The method of transporting hydrogen with highest efficiency is also predicted. Furthermore, the rough progress of using hydrogen energy and the attitude and newest technology used by different country for hydrogen energy in these few years is also include.

Keywords: PEM, SOEC, solid hydrogen storage.

1. Introduction

At present, the world energy development is in an important era, and the danger of fossil energy exhaustion is approaching. Since 2008, the deep-seated impact of the international financial crisis on the world economy has been complex and far from over [1]. There are signs of economic recovery, but it remains fragile. International oil prices are high and volatile, and the era of high oil prices has come. In the face of the new situation, countries have turned their attention to new energy, which has injected impetus into the development and utilization of new energy, and mankind will usher in the "spring of new energy." As it is currently in the transition stage from the third-generation energy period dominated by oil to the new energy period, the intermediary energy such as oil, coal and their processed products gasoline and gas are still the main energy in the fields of power generation, transportation and fuel, and hydrogen as a new generation of intermediary energy is currently only used in some special fields [2]. Coal, oil, natural gas and other fossil energy are the main body of energy consumption in today's society. With the continuous increase of total consumption, it is faced with the dilemma of decreasing reserves, increasing the difficulty of exploitation and increasing marginal production cost. The study believes that before 2020, global oil production will peak, natural gas production will also peak soon, and the ensuing supply shortage is bound to lead to a spike in global oil and gas prices. In the face of such an energy crisis, how should people cope [3]. For a long time, the extensive use of fossil fuels such as coal and oil may cause serious pollution to the global environment and even threaten human survival. At the same time, fossil fuels are a non-renewable energy source, and excessive development will deplete them. Therefore, the development and application of new alternative clean energy is the trend of The Times, and hydrogen energy, as one of the ideal clean energies, has attracted widespread attention. Some scientists believe that hydrogen energy is one of the most promising clean energy sources in the future energy structure, and will play an important role in the future energy field with its excellent performance [4]. As a highly efficient form of energy, hydrogen is becoming popular today. Not only is it environmentally friendly, but it is also an efficient way to transfer energy. Hydrogen is a flammable and explosive gas, but it is not as dangerous as people often think. Hydrogen is no more dangerous than natural gas, gasoline and propane, mainly because hydrogen has different physical and chemical properties than other combustible industrial gases. At room temperature and atmospheric pressure, hydrogen density is 0.0898kg/m³, about 1/4 air, small molecule, small viscosity (0.0101mPa·s), and large diffusion coefficient (0.634cm²/s), so it is easy to diffuse and leak, the diffusion rate is 3.8 times that of air,

resulting in the leakage rate of hydrogen through the same small slit at room temperature and low pressure is 1.26~2.8 times that of natural gas [5]. Internationally, the United States, the United Kingdom, Japan and other major developed countries in the world have also carried out a diversified layout in the field of hydrogen energy, and the United States currently relies on long-term hydrogen energy research to produce many leading technologies, and is widely used in hydrogen energy vehicles, chemical industry and other fields. By formulating industry policies, the United Kingdom strives to promote the application of hydrogen energy in heavy-duty equipment, petrochemical, energy and power, and strives to provide one-third of the country's energy supply by hydrogen energy in the future. Japan has long attached importance to the development of hydrogen energy, and plans to achieve carbon-free hydrogen production around 2040 through a series of technologies such as efficient fuel cells, while accumulating hydrogen energy to develop business models, iterating hydrogen energy efficient utilization technologies, and promoting hydrogen energy development. Furthermore, hydrogen also has some economical advantages, for example: Rapid ignition, wide flammable range when stirring with air, large ignition point and fast burning speed; It is part of a rich new energy source that is independent of fossil fuels; High calorific value: hydrogen has the highest calorific value of all fossil fuels, chemical fuels and biofuels, except for nuclear fuels; Low energy consumption: long-distance high-pressure transport can be interrupted, and long-distance and short-term pipelines can be used instead of hydrogen transport. Safety is relatively improved, reducing the loss of inefficient energy. But hydrogen is very active so the accident is easy to appear in transportation, and the method of product hydrogen is not efficient which makes the whole industrial chain shows less economically sustainable. The aim of the article is finding the way product and storage the hydrogen best fit the situation in real life nowadays.

2. The Production of Hydrogen

2.1. Basic theory

By the fast growth of demand of energy, scientists are trying to find another form of energy. Hydrogen is one of the directions. Totally, the production of hydrogen is electrolysis water. The basic principle is that water is converted by DC electricity into gaseous hydrogen and oxygen, which is the fuel cell reverse process as shown in fig.1. The United States is the first country in the world to take hydrogen energy and fuel cells as energy strategies. As early as 1970, the United States proposed a "hydrogen economy." The United States is a more mature hydrogen energy application in the world, and has the world's most hydrogen fuel cell forklift countries, the United States was once the biggest promoter of hydrogen energy industry. The United States is the first country in the world to propose the research and application of hydrogen energy, and the U.S. government has promulgated a number of policies and action plans to promote the development of hydrogen energy since 1990. In 2015, China successfully surpassed the United States to become the first country in the world to apply for biological hydrogen production patents. According to the International Energy Agency, China's annual hydrogen capacity once reached 33 million tons, making it the world's largest hydrogen energy producer, accounting for one-third of global hydrogen demand. In the United States, due to the game between various domestic political forces and group interests, the government is wavering in its hydrogen energy development plan. In 2003, the Bush administration invested 1.7 billion dollars in founding the Liberal Democratic Party. The CAR Hydrogen Fuel Development Plan proposes key development projects such as industrial hydrogen generation technology, hydrogen storage technology and hydrogen energy application. Last year, the Obama administration slashed spending on fuel cell and hydrogen energy programs at the U.S. Department of Energy, with the fiscal year 2011 budget funding of just \$137 million, down 21% from 2010. But corporate America has been keen on hydrogen [6].

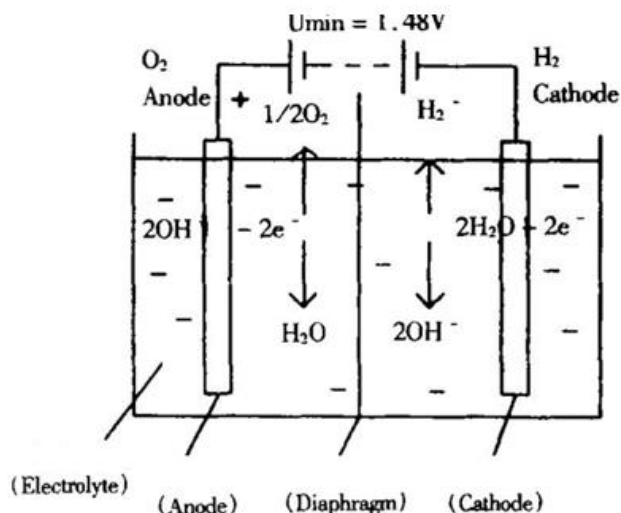


Figure 1. Hydrolysis of water [7]

2.2. Application of Hydrogen

Another subdivision can be the alkaline water electrolysis technology based on KOH, which uses NaOH aqueous solution as the electrolyte, such as using rock wool fabric as a diaphragm, to electrolyze water into hydrogen and oxygen under direct current. The principle of alkaline electrolysis is very simple. When direct current is applied to water, oxygen and hydrogen are separated from water, as shown in the equation. The technology of producing hydrogen gas through alkaline electrolysis of water is mature and inexpensive, but its efficiency is low. At present, the United States, Japan, South Korea, and Europe have identified electrolytic hydrogen production technology as the overall direction for future development, with a focus on expanding the scale of AE hydrogen production technology and industrialization of PEM hydrogen production technology, with a focus on large hydrogen refueling stations to meet the demand for hydrogen for transportation; The second step is to produce 10, 100, 250 MW PEM electrolyser to meet the demand for industrial hydrogen. The third step is to develop a PEM hydro-electrolysis hydrogen production system to meet the needs of large-scale hydrogen energy storage. Considering with the efficiency of the production, the SOEC become the most hopeful way of production in the future. Because conventional alkaline electrolysis of water to hydrogen requires a large amount of electric energy, energy conversion efficiency is low and cost is high, so its application is greatly limited. Compared with conventional water electrolysis, hydrogen production by electrolysis of water vapor at SOEC high temperature has the advantages of more efficient and environmentally friendly, and can be combined with various clean energy sources for the preparation of hydrogen, oxygen and other energy carriers [8]. The process of this technology is to apply a certain DC voltage to the electrodes on both sides of the SOEC at a higher temperature ($600-1000^{\circ}C$), and then decompose H_2O at the cathode to produce O_2^- , O_2^- through a dense solid oxide electrolyte layer to the anode, and the electron loss to obtain pure O_2 . The advantage of the process is that the less energy used, the function is reversible, and the SOEC cell is fed with water vapor, which, when added to carbon dioxide, produces syngas (a mixture of hydrogen and carbon monoxide), which is then further produced into synthetic fuels (electronic fuels such as diesel and jet fuel). Therefore, SOEC technology is expected to be widely used in carbon dioxide recovery, fuel production and compounds, which is also the EU's research and development focus in recent years. SOEC research has grown exponentially over the past decade. The United States, Denmark, Japan, Germany, the United Kingdom, etc. currently have relevant research, the focus of research is to develop new materials, improve performance, reduce material costs. The main purpose is to optimize the production process and prepare durable and efficient second-generation SOEC electrolytic cells. Domestic SOEC research is in its infancy, Tsinghua University has explored SOEC electrolysis efficiency, electrode polarization and cathodic optimization in recent years, in addition, University of Science and Technology of China and South China University of Technology have also conducted

relevant research on SOEC electrolysis of water [9]. In August 17, the Haldor Topsoe started to build the first industrialized SOEC factory.

3. The Storage of Hydrogen

Hydrogen is a fast gas at room temperature, which means it is prone to accidents because it can mix with air to form explosive mixtures. When exposed to high temperatures or an open flame, it will explode. Gases are lighter than air, and when used or stored indoors, air leaks can rise and remain on the roof, making its discharge difficult and causing explosions on Mars. Hydrogen reacts violently with halogens such as fluorine, chlorine and bromine, so that it needs additional storage conditions, for example, gaseous hydrogen storage, which generally uses hydrogen molecules to apply high pressure at intervals and store hydrogen in hydrogen storage tanks (generally high-pressure hydrogen storage tanks). So it is usually called high pressure gaseous hydrogen storage. The technical principle is to increase the density of hydrogen in hydrogen storage tanks by pressurizing hydrogen, thereby increasing the energy density of hydrogen in gas storage tanks, thus storing a large amount of hydrogen in a relatively small volume. Easy to transport and store. Although high pressure gaseous hydrogen storage has been widely used, but still faces many challenges, the weight of the current vehicle hydrogen storage bottle is too heavy and too large, compared with the traditional fuel vehicles, the vehicle mileage is insufficient, the hydrogen storage density of the cylinder still needs to continue to improve to apply to the long-distance endurance needs. The transportation efficiency of long tube trailer for hydrogen storage is low, which cannot fully meet the demand of hydrogen refueling station, and it is necessary to reduce the weight of gas cylinders and increase the transportation pressure. So, another form, liquid hydrogen storage in low temperature it belongs to physical storage and is a cryogenic hydrogen storage technology. After compression, hydrogen is cryogenic to 21K (about -253°C) below, so that it becomes liquid hydrogen, and then stored in a special low-temperature adiabatic liquid hydrogen tank, the density of up to 70.78kg/cm³, is about 850 times the density of hydrogen under standard conditions, the volume is large, suitable for large-scale, long-distance hydrogen energy storage and transportation. Due to the imperfect charging and isolation of liquid hydrogen storage, it is easy to cause high evaporation losses, resulting in higher storage costs and more complex safety technologies. Large-scale hydrogen liquefaction technology has matured commercial application models in the United States, Japan, Germany and other countries. Liquid hydrogen storage and transport account for about 70% of the hydrogen energy used in transport, and the transport cost of liquid hydrogen is 12.5-20.0% of that of high-pressure hydrogen. It has obvious economic advantages in mass transport. From the point of view of economic sustainability, it is worthwhile to use "she" (solid hydrogen storage), solid hydrogen storage refers to the storage of hydrogen in solid materials by physical and chemical adsorption of hydrogen. The physical adsorption mechanism refers to the reversible adsorption of hydrogen molecules on porous materials with a high specific surface area by van der Waal's forces. In the chemical adsorption mechanism, hydrogen normally binds to other elements through ions or covalent bonds to materials such as metal hydrides, which can absorb and release hydrogen reversibly under certain conditions. Compared to other hydrogen storage methods, the two main advantages of solid hydrogen storage are high density and good safety performance. Solid hydrogen storage tanks have a very high hydrogen storage density. Using the example of MgH₂ hydrogen storage, its volumetric hydrogen storage density can reach 106kg/m³, which under standard conditions corresponds to 119-fold the hydrogen density, 2.7-fold the high-pressure hydrogen storage at 70MPa and 1.5-fold the liquid hydrogen spoke. Magnesium-based hydrogen storage materials are the most promising type of hydrogen storage materials, because Mg is cheap, small density, and high hydrogen storage, and the theoretical hydrogen storage capacity can reach 7.6wt%. Elemental magnesium can react with hydrogen under high temperature conditions to generate MgH₂, but the enthalpy of pure magnesium to generate MgH₂ is large, and the kinetic performance of hydrogen absorption and discharge is poor, resulting in too stable hydride and increased hydrogen absorption and release temperature (usually above 300 °C), which limits the use

of magnesium-based hydrogen storage materials [10]. At present, the more studied hydrogen storage materials include metal hydrides, carbon nanotube materials, activated carbon structural materials, various silicate structural materials, complex hydrides, metal-organic compounds, among which metal hydrides are the most traditional, such as LaNi_5 , TiFe , etc., but the hydrogen storage capacity is low; Complex hydride hydrogen storage materials have become a hot spot in recent years with their high hydrogen storage capacity. Complex hydrides are formed by hydrogenation of hydrogen with metals or alloys under certain temperature and pressure conditions. Among them, the complex hydride containing Al–H bonds has a high hydrogen storage capacity, and some even reach more than 10% (mass fraction, the same below), such as LiAlH_4 reaches 10.5%, and the reversible hydrogen storage capacity meets the requirements of the US Department of Energy ($\geq 6.5\%$), and the development prospects are good [11].

4. Conclusion

With the end of the oil era, hydrogen energy will play a pivotal role in the new energy structure, therefore, in recent years, the United States, Japan, Germany and other developed countries in the application of hydrogen energy invested huge scientific research forces and funds, and developed a number of new technologies and products. In today's position, considering with the ecological sustainability, which means effectively utilizing resources to achieve a balance in economic and social development while meeting contemporary human survival needs, the SOEC could be the best way of produce hydrogen, and SHS has the most efficient way of storage, and it is safety compare with others so, it is the best way of storage. The largest problem of these technology is the cost of long run using, that, the profit may not high or even no profit by using SOEC to produce huge number of hydrogen or long-distance transportation by SHS

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