Research on the Hydrogen Production Technology

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Abstract. Hydrogen energy has attracted widespread attention because of its renewable and zero-emission characteristics. It is also a secondary energy source with broad development prospects, so the hydrogen energy industry is an emerging industry of strategic significance. In order to effectively promote the development of hydrogen energy industry, major countries in the world have attached great importance to the research, development and application of hydrogen energy technology, and its development and utilization technology has become an important direction of the new round of world energy technology reform. This paper mainly compares the three widely used methods of hydrogen production, namely, thermochemical recombination, electrolysis of water and photolysis of water, and analyzes the advantages and defects of each method, and lists the solutions to the different defects.

1. Introduction

Hydrogen energy is becoming the focus of energy revolution because of its rich, clean and efficient reserves. Hydrogen economy is considered as a new turning point of the world economy in the 21st century. According to the Research Report on the future development trend of hydrogen energy released by the international Hydrogen Energy Commission [1], it is estimated that by 2030, the number of fuel cell passenger cars will reach 10 million to 15 million. It is estimated that by 2050, the demand for hydrogen energy will be 10 times that of the present. From 2018 to 2020, the global hydrogen energy market will further expand, especially in Japan, the United States and Europe. Major countries have successively launched major hydrogen energy projects, and many innovations have been made in hydrogen production, hydrogen storage and hydrogenation.

The main ways of hydrogen production are thermochemical reforming, electrolytic water and photolysis water. According to the International Renewable Energy Agency (Irena), among all the hydrogen preparation methods in the world, the total heat produced by natural gas accounted for the highest proportion, reaching 48%. Hydrogen produced by petroleum gasification accounted for 30%. Hydrogen produced by coal gasification ranked third, accounting for 18%. Hydrogen production from electrolytic water accounted for only 4% [2]. At present, the chemical reforming of petrochemical fuels is the main way, but the fossil fuels with limited reserves cannot get rid of the dependence on traditional energy and will cause environmental pollution. Hydrogen production from electrolytic water is low-carbon and sustainable, but the efficiency is only 50-70%. Moreover, the production of hydrogen from electrolytic water needs to consume a lot of electric energy. High electricity price will raise the cost of hydrogen production, but the scale will be gradually expanded when the electricity price drops. Photolysis of water is the most ideal hydrogen production technology in theory, but it is still in the initial stage of research. Biological hydrogen production method is to decompose organic matter and biomass to produce hydrogen with the main mechanism of biological enzyme catalysis. Its main advantage is that it has a wide range of sources and no pollution, the reaction environment is normal temperature and
pressure, and the production cost is low, which completely subverts the traditional energy production process.

2. Hydrogen production by thermochemical recombination

Steam reforming, partial oxidation reforming and autothermal reforming are the three most widely used reforming technologies. Hydrogen is an energy carrier and thermochemically reconstituted hydrogen production is a sustainable and benign method of hydrogen production[3]. The concentration of hydrogen in steam reforming products is the highest and the reaction temperature is the lowest. However, the quality of the system is large, the start-up speed is slow, and the external heat source is needed. Therefore, it is suitable for the field of fixed hydrogen production. Since the structure of autothermal reforming system is relatively compact and the hydrogen concentration of the product is moderate, it is suitable for mobile hydrogen production such as automobiles, although the partial oxidation reforming reaction has the most compact system structure and fast start-up speed and the hydrogen concentration in the product is low. The above three reaction mechanisms are analyzed and the advantages and disadvantages of each are shown in Table 1.

| Technical Classification | Advantages | Disadvantages |
|--------------------------|------------|---------------|
| Steam reforming          | • Most experience in industrial applications • Oxygen is not required for the reaction. • Minimum reaction temperature • Highest H₂/CO ratio | • Highest air pollutant emissions • Larger system quality • External heat source required • Slow startup. |
| Partial oxidation reforming | • High sulfide tolerance • No external heat source required • The most compact system available • Fast system startup | • Lower H₂/CO ratios • Maximum reaction temperature • Prone to coking reactions • The reaction requires air or oxygen. • The reaction process generates too much heat. |
| Autothermal reforming   | • Moderate reaction temperature • No external heat source required • Higher H₂/CO ratios • Compact system construction | • Low level of technological maturity • The reaction requires air or oxygen. |

Methane steam reforming technology is the traditional main hydrogen production method and it is a kind of recombination technology. It has been used for more than 90 years since 1926 and has been continuously developed and improved. The natural gas reserves are rich, the methane reforming hydrogen production technology has large hydrogen production and low hydrogen production cost, so it has high commercial application value. The traditional methane hydrogen production technology is mature, some scholars have used plasma and catalyst coupling to produce hydrogen from methane, using the synergistic effect of the two to improve the reaction performance, and achieved good results [4].

Table 2 summarizes the results of the more representative studies of plasma technology in the field of methane to hydrogen. Compared to conventional methane-to-hydrogen technology, isomer technology enables rapid hydrogen production without catalysts. However, there was still a problem of carbon deposition on the catalyst. In addition, the electron density in the plasma region can be increased by adding carrier gas, thereby increasing the conversion of reactants and increasing the hydrogen production. Although high conversion and H₂ yield can be obtained by high temperature plasma, the
energy consumption is the highest and the hydrogen production is large, which can meet the industrial demand.

However, the high-temperature sintering, carbon deposition and deactivation of the catalyst still need to be solved, and catalyst optimization has become a breakthrough in this field. Plasma methane hydrogen production technology is still in the development stage, which can achieve rapid hydrogen production under mild conditions, which has guiding significance for small-scale hydrogen production, but has low hydrogen production and high energy consumption. The performance of hydrogen production can be improved to some extent by optimizing reaction conditions, coupling plasma with catalyst or injecting carrier gas, but it is still far from industrial application.

Table 2. Comparison of hydrogen production from plasma methane

| Hydrogen production method                  | Plasma type | raw materials    | CH4 Conversion rate % | Production of H2 | Hydrogen production efficiency |
|-------------------------------------------|-------------|------------------|-----------------------|------------------|--------------------------------|
| Steam reforming of plasma methane         | DBD         | H2O : CH4 = 2:1  | 42.0                  | Productivity: 41.7% | 0.19                           |
|                                           | Multi-stage ARC | CH4 : H2O = 42:10 | 36.0                  | Selectivity: 67%  | 8.13                           |
|                                           | MW          | H2O : CH4 = 3    | 95.3                  | Concentration: 71.3% |                               |
|                                           | MW          | Methane Hydrate  | 85.8                  | Selectivity: 42.1% | 0.36                           |
| Dry reforming of plasma methane           | Catalyze    | CO2 : CH4 = 1.05 | 83.2                  | Productivity: 38.7% | 5.97                           |
|                                           | DBD         | CH4 : CO2 = 1:1  | 2.7                   | Concentration: 22% |                               |
|                                           | MW          | CH4 : CO2 = 2:3  | 29.0                  | Selectivity: 80%  |                               |
| Plasma methane cracking for hydrogen production | Catalyze    | CH4 : AR = 1:10  | 91.1                  | production rate: 0.15g/h | 5.48                           |
|                                           | ARC         | CH4               | 47.0                  | selectivity: 97%  | 80.14                          |
|                                           | MW          | CH4               | 29.0                  | selectivity: 98.8% |                               |
| Plasma methane oxidation to hydrogen      | Catalyze    | O : C = 1.44     | 90.2                  | selectivity: 89.9% | 413.20                         |
| Hydrogen production from plasma methane autothermal reforming | Catalyze    | O : C = 1        | 83.6                  | selectivity: 58.8% |                               |
|                                           | ARC         | H2O:CH4=0.8      | 99.7                  | productivity: 93.7% |                               |

3. Hydrogen production by electrolysis of water

The basic principle of hydrogen production by electrolysis of water is that when enough voltage is applied at both ends of the electrode, the water molecules will oxidize at the anode to produce oxygen, and the reduction reaction at the cathode will produce hydrogen. Therefore, the electrolytic water reaction can be divided into two half reactions: anodic oxygen evolution reaction (OER) and cathodic hydrogen evolution reaction (HER). [5] Pure water, as a weak electrolyte, has low ionization degree and poor conductivity. In the process of hydrogen production from electrolytic water, some electrolytes which are easy to ionize are usually added to increase the conductivity of electrolyte. Alkaline electrolytes have strong hydrogen production effect and will not corrode electrodes and electrolyzers. KOH or NaOH solution with concentration of 20% - 30% is usually used as electrolyte.

According to the different electrolytes, the current hydrogen production technology of electrolytic water can be divided into three categories: alkaline electrolytic water hydrogen production technology (ALK), solid oxide electrolytic water hydrogen production technology (SOEC) and proton exchange membrane electrolysis water technology (PEM). Hydrogen production from alkaline electrolyzed water has been widely used because of its lowest manufacturing cost, the most mature structural framework, the longest stack life and the highest degree of commercialization. It is still the main research direction to reduce the energy loss, improve the electrolysis efficiency and further improve the structure of hydrogen production from alkaline electrolytic water. Research on efficient and stable catalysts can
overcome the kinetic energy barrier, thus increasing the reaction rate and reducing the overpotential. Table 3 shows a basic comparison of the three methods of hydrogen production from electrolyzed water.

### Table 3. Performance comparison of three types of water electrolysis technologies for hydrogen production

| Type of electrolysis cell | Alkaline electrolytic water hydrogen production technology (ALK) | Solid oxide electrolytic water hydrogen production technology (SOEC) | Proton exchange membrane electrolysis water technology (PEM) |
|--------------------------|---------------------------------------------------------------|-----------------------------------------------------------------|----------------------------------------------------------|
| Electrolytes             | 20% ~ 30% KOH or NaOH                                         | Y2O3/ZrO2                                                        | Commonly used NaFion                                      |
| Operating temperature    | 70 ~ 90                                                        | 700 ~ 1000                                                      | 70 ~ 80                                                   |
| Electrolytical efficiency| 60 ~ 75%                                                       | 85 ~ 100%                                                       | 70 ~ 90%                                                  |
| Energy consumption (Kw·h/Nm3) | 4.5 ~ 5.5                                                      | 2.6 ~ 3.6                                                       | 3.8 ~ 5.0                                                 |
| Life of the reactor      | Up to 120000h                                                  | —                                                              | 100,000 h has been reached                               |
| Electrolysis tank cost (USD/kW) | 400~600                                                        | 1000 ~ 1500                                                    | About 2000                                               |
| Characteristic           | Most mature highest level of commercial low cost              | Part of the electrical energy is replaced by thermal energy high conversion efficiency high temperature limits the choice of materials has not yet been industrialized | Renewable energy adaptability non-polluting high cost low industrialization |

At present, most of the hydrogen evolution process of electrolytic water mainly depends on high price, high cost. Due to the high cost of acid resistant platinum containing catalysts, the progress in cathodic hydrogen evolution reaction has been seriously restricted. The research direction has begun to shift to non-noble metal and non-metallic catalysts which are abundant in nature and have low price. In the future, hydrogen production from electrolytic water will focus on converting surplus power into hydrogen energy. Making good use of wind power and solar power generation to solve the intermittent problem of clean energy affected by day and night changes and climate factors is an important application field of hydrogen production from electrolytic water. From the current research and application situation, alkaline electrolyzed water research has been more thorough, also has certain application in industry. However, compared with alkaline electrolyzed water, acidic electrolyzed water is more popular. The next research will focus on three fields: electrocatalyst for oxygen evolution, electrode materials and diaphragm materials suitable for high-strength acid-base environment.

### 4. Hydrogen production by photolysis of water

It is considered to be an effective way to solve the problem of rapid consumption of fossil fuel and increasingly serious environmental pollution by using photocatalytic active materials. Combining the basic processes of solar energy conversion, including solar light harvesting, charge separation and surface catalytic reactions, an ideal material for solar hydrogen production should have several advantages, such as a narrow band gap for visible light response, long carrier diffusion length for efficient charge separation and excellent surface reaction kinetics for fast catalytic reactions. Since Fujishima and Honda first reported photocatalytic decomposition of water on TiO2 Electrode in 1972, semiconductor photocatalyst has attracted extensive attention. [6-9] In theory, TiO2 can decompose water by photocatalysis. When light irradiates the TiO2 semiconductor catalyst, after the catalyst absorbs the solar energy, the photogenerated electrons are generated in the valence band, and the electrons jump to the conduction band. At the same time, a hole is left in the valence band. However, the photogenerated hole in the valence band and the photogenerated electron in the conduction band do not recombine in a short time, and then H+ are reduced to H2 and O-2 are oxidized to O2. At present, there
are two factors restricting the practical application and economy of TiO2, on the one hand, due to the rapid recombination of photogenerated electrons and holes, the solar energy conversion efficiency of TiO2 photolysis water to hydrogen is too low. On the other hand, the band gap of TiO2 is very large (about 3eV), so it can only use the ultraviolet part of solar energy, which only accounts for 4% - 5% of the solar spectrum. In order to improve the photocatalytic performance of TiO2 under visible light irradiation, it is necessary to modify TiO2 to adjust its band gap. The modification of TiO2 includes metal doped TiO2, non-metal doped TiO2, semiconductor and TiO2 composite.

In recent years, the more studied modified metals of TiO2 are Pt, Au, Ag, Ni and Pd. By metal doping, additional doping energy levels can be introduced in the bandgap, thus lowering the energy barrier and inducing new optical absorption edges. TiO2 doped with noble metal ions can capture more visible light through the surface plasmon resonance effect, and the noble metal also acts as an electron acceptor and reactive center.

Compared with most metal ions, non-metallic doping is more efficient because the doping results in fewer charge complex centers and a narrower bandgap and is therefore more responsive to visible light. Xing et al [10] synthesized sulfur doped Porous Anatase TiO2 nanocolumns by a simple one-step thermal protection method. The hydrogen production efficiency of the TiO2 photocatalyst calcined at the optimum temperature was 163.9 μmol · h⁻¹ · G⁻¹. In this study, it was found that sulfur doped TiO2 can reduce the band gap energy, which facilitated the absorption of visible light, thus improving the photocatalytic performance of the catalyst.

In addition to ion doping-modified TiO2, TiO2 is compounded with other semiconductor materials, and the compounded TiO2 can obtain excellent multifunctional properties under the synergistic effect of the physical and chemical properties of multiple components. In addition, heterojunctions formed by coupling broadband-gap and narrowband-gap semiconductors can also have faster charge separation in visible light.

5. Conclusion

Hydrogen energy is an important carrier for building a multi-energy supply system based on clean energy in the future. Its development and utilization technology have become an important direction of a new round of world energy technology reform.

From the perspective of hydrogen production cost, the coal gasification hydrogen production cost is the lowest, followed by natural gas hydrogen production, and electrolytic water hydrogen production cost is the highest. At present, compared with the price of oil, the market of coal gasification and hydrogen production from natural gas has a profit margin. However, the economic cost of hydrogen production from electrolytic water is greater than the income, and government subsidies are still needed. Coal gasification hydrogen production technology is suitable for large mode preparation, low cost, wide space layout, abundant coal source, but high energy consumption, not environmental protection and high carbon emission. Hydrogen production from renewable sources has low energy consumption, environmental protection and low carbon emissions, but the cost of the whole life cycle and the resources available for hydrogen production, such as wind, light and water, cannot be steadily supplied. From the perspective of green development, the carbon emissions from coal gasification and hydrogen production from natural gas are relatively high. Using waste water, wind, light, nuclear and other renewable energy to produce hydrogen by electrolysis is more in line with the requirements of energy conservation and emission reduction and sustainable development. The three main factors driving the future development trend of hydrogen production are technology availability, cost controllability, and recyclability.

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