Design of Hydrogen Fuel Cell: Methods to Higher Efficiency

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Abstract. Since climate change has become a visible and significant issue, all people sharing the planet earth should take action to solve the difficulties. Hydrogen power is the alternative energy to replace traditional energy such as coal, gasoline and so on. Hydrogen energy has a few features being unique and irreplaceable, great economic benefit, environmentally friendly, etc. The research paper has mainly focused on the development and current circumstance of a specific energy form, the hydrogen fuel cell. In the following paper, the working principle and five concrete typically fuel cells, including the solid oxide fuel cell, proton exchange membrane fuel cell, direct methanol fuel cell, phosphoric acid fuel cell, as well as alkaline fuel cell, are recommended with their working performances, advantages and disadvantages. Furtherly, suggestions have been given based on the further development of the materials for different parts of the hydrogen fuel cell. This paper aims to provide a practical route for further hydrogen fuel cell development and promote hydrogen economy and clean energy usage.

Keywords: Hydrogen Fuel Cell, New Material, High-Efficiency Hydrogen Fuel Cell.

1. Introduction

Expanding population and developing industrialization are challenging the world's energy reserves. Over 50 percent of energy supplies come from fossil fuels extracted deeply from the crust. During the past 200 years, the enormous energy demand has caused tremendous stress and even threatened the planet. The over-mining and use of fossil fuels is the major cause of climate change. Studies have shown that traditional fossil energy sources reflect three significant problems. The first one is environmental pollution, which is caused by the burning of fossil fuels. It emits massive CO_2 and other greenhouse gases, which leads to extreme climate change. Furthermore, carbon emissions capture the heat inside the atmosphere, and an example proves the theory: In the United States, 75% of carbon emissions are attributed to burning fossil fuels, especially in the transportation and power-generating industries [1].

Secondly, greenhouse gas emissions, the surface temperature of the earth has risen by 0.7 degrees Celsius in the past decades. The burning of fossil fuels takes a significant portion of the source that impacts CO_2 emissions in the atmosphere. Finally, there is the issue of the supply of oil resources and economic security. Take China as an example, whose dependence on imported crude oil is as high as 95 percent, threatening China's economic security. China needs to reduce emissions and continue moving away from its dependence on traditional fossil energy sources, besides meeting the expectation of peak carbon dioxide emissions. According to the United Nations, China's carbon emissions reached 13.7 billion tons in 2018, an increase of 1.6 percent yearly, setting the priority goal to accomplish the Carbon Neutrality and lists of requirements. China will ultimately meet its CO_2 emission reduction goals and boost its use of non-fossil fuels in primary energy consumption to 20% by 2030. The hard work of lowering emissions is essential because it also pledged to achieve carbon neutrality by 2060 [2].

As a result, it is imperative to increase the proportion of non-fossil energy consumption, and hydrogen energy is a wise option with plenty of benefits. First, hydrogen energy is one of the most abundant elements known to be stored in the universe, characterized by its lightness, and constitutes 75 percent of the overall mass of the universe. At the same time, it ranks third in terms of energy reservation on earth, ensuring its sufficiency as an energy supply. The element hydrogen exists mainly in the form of water and is very easy to obtain as a raw material. In addition, hydrogen functions mainly in a redox reaction with oxygen, forming water and releasing chemical energy. Therefore, the whole process of energy production and consumption is waste-free and zero-pollution. With the development of hydrogen energy, hydrogen as the most suitable fuel has entered the process of high-speed development in recent years.

Hydrogen comes from water, and the product after use is still water, thus creating a closed loop and making it a sustainable project. The calorific value of hydrogen energy is 142KJ/g, which has the highest transformation efficiency among all energy sources—precisely, three times oil and four and a half times coal. Therefore, the production of energy by hydrogen is the greatest when people plan to consume the same mass of oil, coal, and hydrogen. Therefore, the characteristics of hydrogen are the most suitable and optimistic choice to meet both lightweight and economic requirements for automobiles, aerospace, and aviation. At this stage, the biggest competitor of hydrogen is lithium in the battery industry.

Meanwhile, the battery market has developed relatively mature. However, hydrogen energy has some unique advantages that traditional batteries cannot compare. For example, the conversion rate of hydrogen is much higher than traditional battery technology and almost functions in all kinds of operation circumstances, including extreme temperatures. Therefore, hydrogen energy is a feasible technology route to promoting global energy transition that has gradually become a popular topic worldwide. Additionally, not only the European, US, and Japanese governments lead the project's development but also many International Energy Agency. All human beings have a high expectation of hydrogen energy.

2. Hydrogen fuel cells

2.1. Advantages of hydrogen fuel cells

Hydrogen fuels have relatively high efficiency and clean output. Since fossil fuel consumption is the main source of carbon dioxide emissions and the efficiency of conventional processes is comparatively low because of the energy losses in several traditional mechanical cycles (Brayton cycle, Otto cycle), hydrogen fuel cell (HFC) can be regarded as an advanced technology with high efficiency and cleaner emission. Compared with traditional power generating systems, the fuel cell has high efficiency of 40-85%, while diesel has only about 35% and 29-42% for turbine generators [3]. The specific energy of hydrogen is the highest among all common kinds of fuels. It is about three times larger than diesel and liquid natural gas (about 120MJ/kg). Another advantage of HFC is the clean production. The most basic principle of the hydrogen fuel cell is oxygen delivered to the cathode and hydrogen to the anode, and then two reactants enter the main body of the fuel cell at a certain temperature and pressure to react and produce water. Based on the two main advantages, HFC is considered one of the future solutions to energy and environmental problems and is widely used in automobiles, uninterruptible power supplies (UPS), and distributed systems at present and in the coming decades.

HFC has other advantages, such as fast charging (within 5 minutes), no noise, and a long lifetime. However, to fully develop and apply this technology, many problems need to be overcome. The first and most important one is hydrogen extraction. Although hydrogen may be the most ubiquitous element in the world or even in the universe, H_2 is hard to be found in most cases. Therefore, it needs to be produced by water electrolysis or separated from oil and gas fuels. However, the two methods above may consume more energy than that obtained from the extracted hydrogen itself. Another issue is about safe storage and transportation since pure hydrogen is easy to burn and explode. All these problems come with extra costs.

2.2. Working principle of HFC

The electricity and heat are generated through the electrochemical reaction, which is the reverse of water electrolysis.

$$\mathrm{H_2(g) + 0.5O_2(g) \rightarrow H_2O + energy\ (electrical\ power + heat)} \tag{1}$$

Fuel cell types differ mostly due to variations in the electrolyte. However, anode, cathode, electrolyte, fuel, oxidant and external circuit are essential for every cell. The platinum catalyst at the anode oxidizes hydrogen, converting it into electrons and protons. Meanwhile, at the cathode, oxygen and protons combine to make water. The transport of electrons from the anode to the cathode through the external circuit also produces additional heat in addition to electricity. The ion-conducting electrolyte allows for the movement of protons and oxide ions. The working principle scheme of HFC is shown in Figure 1.

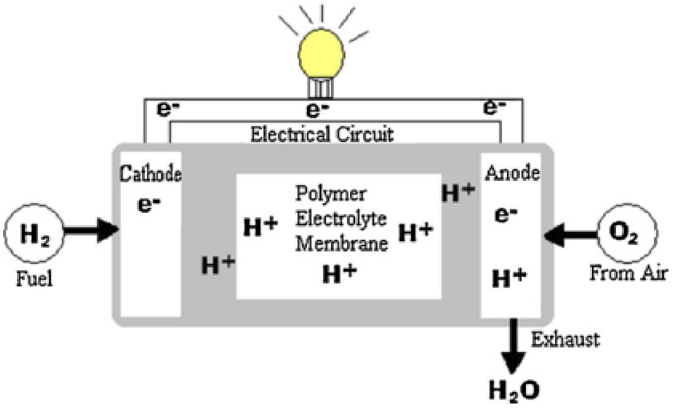

Figure 1. Working principle of an HFC [2]

3. Typical types of fuel cells

Based on the variations in fuel and electrolytes, there are many types of fuel cells. The next sections will present five primary types of fuel cells that are sufficient to review the past fuel cell and offer the possibility of achieving greater efficiency.

3.1. Solid oxide fuel cell (SOFC)

Operating at high temperatures, SOFC employs metallic oxide solid ceramic as the electrolyte. For SOFCs, the oxidizing agent is commonly a combination of hydrogen and carbon monoxide produced by internally converting hydrocarbon fuel and air [4, 5]. Material that has pure ionic conductivity and strong chemical and thermal stability is needed to be applied as the electrolyte for SOFCs. For example, Yttria stabilized zirconia (YSZ), a ceramic material that matches all the characteristics above and is commonly used [6].

Oxygen introduced to the cathode side gains electrons and turns into O^{2-} by the catalysis of the porous cathode surface material. Driven by the chemical potential, when O^{2-} encounters the solid electrolyte's contact with the anode, it combines with the fuel gases (H_2, CH_4) to produce water or other products. The lost electrons then go back through the external circuit to the cathode.

$$\text{Anode: } 2O^{2-}(s) + 2H_2(g) \rightarrow 2H_2O(g) + 4e^- \tag{2}$$

$$\text{Cathode: } O_2(g) + 4e^- \rightarrow 2O^{2-}(s) \tag{3}$$

Despite the common advantages of fuel cells, SOFCs have several characteristics: high adaptability of fuel, the ability to operate on multiple fuels, including carbon-based fuels; no need to use precious metal catalysts; all components are solid, and no management issues with leaks and corrosion; flexibility in size, building, and installation. All the points mentioned above make SOFCs suitable for distributed power generation systems and vehicle power sources. With high overall efficiency of up to 60% for a single loop, SOFC is widely applied in different areas, such as power generation, vehicles, thermoelectric reuse, and even space astronautics. It can be considered one of the future solutions to the energy problem.

However, long activating and cooling time, as well as the lifetime, may still limit the use of SOFC.

3.2. Proton exchange membrane fuel cell (PEMFC)

The most fundamental principle of HFC, which is the reversal of water electrolysis, is still followed by proton exchange membrane fuel cells. At the anode of the PEMFC, hydrogen is oxidized to produce protons and electrons. Electrons are pushed to flow from the anode to the cathode through the circuit to produce electrical power, while protons are forced to flow through the membrane and electrolyte solution to reach the cathode. Water is created at the cathode when protons and oxygen combine with electrons.

$$\text{Anode: } 2H_2(g) \rightarrow 4H^+ + 4e^- \tag{4}$$

$$\text{Cathode: } O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l) \tag{5}$$

Bipolar plates and a membrane electrode assembly make up most PEMFCs (MEA). On opposing sides of a ready proton exchange membrane, two carbon fiber paper electrodes are sprayed with Nafion solution and Pt catalyst to create the MEA, which is subsequently molded at a certain temperature and pressure. Graphite plate material, which has high density, high strength, no perforated air leakage, no deformation under high pressure, strong electrical and thermal conductivity, good electrode compatibility, and other properties, is frequently used to make bipolar plates.

PEMFC has several advantages: no limitation of the Carnot cycle and high energy converting rate since no burning is contained; it generates power without pollution. The power generation unit is modular, highly reliable, and easy to assemble and maintain; it works without noise. Therefore, PEMFC is a clean, efficient, and green option for power supply. With all these advantages, PEMFC is able to be used as a small-scale and mobile power source and is also expected to be the main solution for mobile equipment power sources and important building backup power.

3.3. Direct methanol fuel cell (DMFC)

Direct methanol fuel cell is an advanced type of PEMFC. It uses methanol as fuel instead of hydrogen. Thus, the working principle is almost the same as PEMFC. CH_3OH is converted into CO_2 at the anode, and oxygen is reduced to generate water at the cathode.

$$\text{Anode: } CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \tag{6}$$

$$\text{Cathode: } 1.5O_2 + 6e^- + 6H^+ \rightarrow 3H_2O \tag{7}$$

Platinum and platinum-adopted catalyst are used as the anode and cathode materials in DMFCs. Most PEMFCs employ trifluoroethane sulfonic acid as the electrolyte solution. However, methanol will permeate from the anode to the cathode as a result of trifluoroethane sulfonic acid. Electro-permeation and methanol diffusion are the causes of this phenomenon. Since methanol permeation leads to degradation of cathode performance, significant reduction of cell output power, and shortening of DMFC system lifetime, the development of proton exchange membranes with good performance and protection against methanol permeation is necessary to bring DMFC into further commercialization.

DMFC is a kind of low-temperature non-fuel flexible fuel cell. It was originally used in compact portable electronic gadgets such as laptops and mobile phones [7].

3.4. Phosphoric acid fuel cell (PAFC)

The phosphoric acid electrolyte used in phosphoric acid fuel cells is a transparent and colorless liquid that is also applied in medicines, detergents, food flavoring, and fertilizers. The working temperature is slightly higher than that in PEMFCs and AFCs, which is about 150-220ºC, and it leads to a faster reaction speed than PEMFCs have. The reactions at both anode and cathode are the same as PEMFC.

$$\text{Anode: } 2H_2 \rightarrow 4H^+ + 4e^-$$
$$\text{Cathode: } O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Electricity and heat are produced as a result of the movement of protons and electrons. The heat produced as a byproduct is often used to generate steam or heat water at atmospheric pressure. However, the steam might result in reforming processes and generate carbon monoxide near electrodes, which could have an impact on the PAFC's performance. The anode temperature should be raised to reduce CO. This gas will be desorbed at the cathode in a reverse electro-catalyst process at high temperatures.

PAFCs can be applied in two situations: cogeneration and power plants. Cogeneration is directly installing the PAFC near the users to provide electricity and heat, which is able to set capacity as needed without affecting the efficiency of the unit. As for the power plants, PAFCs can be used in both decentralized and central power plants with a capacity of 10-20MW and over 100MW. Compared with normal power plants, the PAFC plants are more efficient even at low generation loads and are easy to install for their template structure.

3.5. Alkaline fuel cell (AFC)

This kind of fuel cell is the first attempt in the field of fuel cell technology and uses an alkaline solution (KOH) as the electrolyte. The hydroxyl ions go through the electrolyte instead of protons.

$$\text{Anode: } \mathrm{H_2 + 2OH^- \rightarrow 2H_20 + 2e^-}$$

$$\text{Cathode: } \mathrm{0.5O_2 + H_2O + 2e^- \rightarrow 2OH^-}$$

AFCs usually perform at a temperature between 60 and 90ºC. With relatively low temperatures, it starts up very fast. AFC has a low power density which is about ten times lower than that of PEMFC; However, it may be employed in tiny stationary power generators since its production costs are the lowest of any type of fuel cell. AFC is also sensitive to carbon monoxide and other catalyst-contaminating contaminants. Additionally, the raw material must not include carbon dioxide since this gas might generate potassium carbonate, which impairs the operation of the cell when it reacts with potassium hydroxide electrolyte.

The use of AFCs to provide drinking water and electrical power to the shuttle flights for space applications was pioneered by NASA. They are now used in specialist transportation applications, forklift trucks, submarines, and boats.

4. Methods to improve HFC efficiency

Based on the various basic components of HFC, it can be divided into three parts to discuss the methods to improve energy efficiency: anode, cathode, and membrane.

4.1. Anode

The hydrogen oxidation reaction (HOR) at the anode is usually a fast process. However, it is still possible to raise energy efficiency by improving the material of the anode. According to the research of Cornell University, the nickel anode coated with nitrogen-doped carbon can catalyze the basic reactions in hydrogen fuel cells, which is significantly less expensive than the precious metals currently used [8]. The kinetics of the hydrogen oxidation reaction may be improved by the attempt of nitrogen-doped carbon coating as a protective layer, making the reaction quicker and more effective, which can speed up the adoption of hydrogen fuel cells.

4.2. Cathode

The sluggish pace of the four-electron oxygen reduction process (ORR) at the cathode, in contrast to the quick hydrogen oxidization at the anode, may be a significant factor limiting the efficiency of fuel cells. Pt/C catalysts are still effective ORR catalysts in HFC today. However, platinum is still expensive and poor at anti-toxic. The aggregation of the platinum particle during the long working cycle is also a problem. In that case, developing high activity, low-cost, and low/non-platinum ORR catalysts has become a research priority for hydrogen fuel cells.

Single-atom catalysts (SAC) are catalysts in which the active metal center is dispersed as a single atom in the carrier, maximizing the metal utilization and theoretically achieving 100% atom utilization. Due to the unique electronic structure of the metal active centers, they exhibit high catalytic activity and catalytic selectivity in ORR catalysts. Meanwhile, due to the diversity of active centers of single-atom catalysts, the diversity of ligand types and structures, and the interaction between active centers and substrates, these efficient modulation strategies are continuously explored, which significantly improve the ORR reaction activity. The characteristics of single-atom catalysts illustrate a promising future for HFCs cathode ORR. SAC materials may be split into two categories based on their value: SAC based on noble metals and SAC based on non-noble metals.

Regarding the noble metal-based SACs, the Pt/C catalysts exhibit superior performance but with high costs and low atomic utilization; however, reducing the Pt particle size until single atomic level dispersion maximizes the utilization of Pt atoms [9]. Ru is much cheaper than Pt, which is about 1/3 of the price of Pt, but has almost identical catalytic performance as Pt/C catalysts if synthesized properly. The noble metal-based SACs have the advantages of high stability and high activity; however, despite the high material efficiency with the adoption of the SAC catalyst, the cost of the noble metal remains high [10].

Thus, more recent research has been focused on designing non-noble metal-based SACs. As a matter of fact, common metals like Fe, Co, Ni, and Cu can also be applied in the catalysis of ORR. FeN_4 structure catalyst has high reactivity and low costs and performs a $775mW/cm^2$ maximum power density in H_2-O_2 fuel cells [10]; CoN_4 is also synthesized to replace Fe single-atom catalysts (to reduce Fenton reaction caused by Fe^{2+}/Fe^{3+} and H_2O_2, H_2O_2 is the production of two-electron side reactions) to avoid the negative effect of hydroxyl radicals [11]; Ni has similar catalytic effect as Pt, and Cu coordination compounds are naturally oxygen reduction catalysts.

4.3. Membrane

Membranes in HFC have the function of protons transportation and isolating electrons and other ions. The proton exchange membrane must have strong proton conductivity, good thermal and chemical stability, high mechanical strength, and durability for efficient and stable functioning. To fulfill the demands, sulfonated polymers are considered to be suitable materials, and the advanced research is based on introducing inorganic materials to hybridize or compound with other polymers [7]. The types of commonly used proton exchange membranes include perfluoro sulfonic acid PEM, partially fluorinated sulfonic acid PEM, and non-fluoropolymer PEM.

Perfluoro sulfonic acid (PFSA) PEM was first developed and produced by DuPont in the 1970s. With the main chain structure resembling PTFE and a short side chain containing a sulfonic acid group [12], the PFSA membrane might be the most extensively utilized proton exchange membrane due to its excellent stability and strong proton conductivity. However, there are still some problems that hinder the further development of the PFSA membrane. For example, readily deteriorates at high temperatures, has poor proton conductivity at low humidity, and is relatively expensive [12]. So, hybridization is needed to improve the performance of the membrane, for example, using expanded polytetrafluoroethylene (ePTFE) membrane to hybrid with PFSA [5], introducing inorganic materials (SiO_2, TiO_2, etc.), and introducing organic molecules with specific groups might be feasible methods. Applying ePTFE membrane can reduce the thickness of the membrane while it has the same level of performance but at fewer costs; SiO_2 and TiO_2 have good hygroscopicity to improve the performance of the membrane at high or low temperatures, and introducing certain organic groups can supply extra proton transfer channels to improve the proton transfer efficiency.

Due to the high cost of PFSA resin, researchers are working on the partially fluorinated sulfonic acid membrane. Using non-per fluorinated polymers as matrix materials, e.g., polytrifluorostyrene, polyvinylidene fluoride, to produce PEM.

It seems possible to use non-fluoropolymer as the material of PEM with former cases to study. Due to the limitations in cost, performance in high temperature and low humidity environments, and contamination issues in the production and disposal of fluoropolymers compounds, selecting nonfluorinated polymers for the preparation of proton exchange membranes has become a hot research topic. Considering the harsh working environment during the operation of hydrogen fuel cells, which requires greater mechanical strength, chemical and electrochemical stability, and heat resistance of the polymer matrix, aromatic polymers with benzene rings in the main chain are generally considered, and their proton conductivity is enhanced by sulfonation modification, such as sulfonated polyaryl ether sulfone, sulfonated polyether ether ketone, sulfonated polyimide, and polybenzimidazole.

5. Conclusion

Countries worldwide have invested special funds and expanded their workforce with material resources into the research of hydrogen energy to a different extent. In the case of China, specific projects prove that the development of hydrogen energy will be included as the national energy strategy in the coming decades so as among countries worldwide. Frankly, hydrogen energy in China has entered a historic moment. The study indicates that China has affluent storage of hydrogen energy and that these natural sources can be utilized wisely in the appropriate industry, which can boost the construction of industrialization, including the chemical and renewable energy industry. Therefore, how to convert and utilize these resources with the most sensible strategy may be a priority to consider within China. Thus, hydrogen energy will reach 10% of the total energy consumption by 2050.

Furthermore, it is also significant to diversify the ways of generating hydrogen energy to meet the green and recycling needs. As a result, people should no longer merely depend on natural gas and coal to generate energy. Instead, utilizing renewable energy sources like wind and sunshine is crucial for increasing energy capacity and lowering emissions from burning fossil fuels.

In addition, Germany, Japan, and the United States have made remarkable achievements in hydrogen energy. The advantages of hydrogen energy are ideally suited to Germany's energy needs. For example, the combustion process has only hydrogen dioxide as a byproduct, and no toxic gas is emitted, increasing the caloric value and playing a crucial role in environmental protection. Furthermore, the utilization of hydrogen energy evokes the idea for other industries that the applications can be so diversified and flexible because the difficulty of transporting hydrogen is way more accessible and more convenient than other traditional fossil fuels and chemical fuels.

In 2013, the Japanese government published a strategy stating that the development of hydrogen energy has been included in its national development strategy. Furthermore, they had started preliminary planning for the construction and use of hydrogen stations. Unlike Germany, Japan mainly aims that hydrogen energy can be integrated into daily life. In the United States, the development of hydrogen energy was deployed as early as 1994, focusing on the construction of hydrogen energy infrastructure and research. The progress in the United States has achieved groundbreaking results, especially between the decade from 2010 to 2020. Project in the US has gained strong support from the government, and many hydrogen energy experts have been trained from a technical point of view. For example, the solid fuel cell developed by fuel cell energy has been widely used in the automotive industry. Moreover, Air Products and Praxair are at the leading position within the industry, which has the core technology of hydrogen energy storage and transportation.

Finally, evidence from China and other countries suggests that hydrogen energy is a readily accessible secondary energy source. It is regarded as the primary study direction for the future clean energy studies due to its high efficiency, clean, zero carbon, and sustainable consumption properties.

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