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Current Situation and Development Trend of Fuel Cells

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Abstract

Clean and efficient hydrogen plays an important role in the new energy sources, and other energy sources can also be converted into easily stored hydrogen. Hydrogen fuel cell, the fuel cell that uses hydrogen as raw material, as one of the most promising new energy sources, has the characteristics of cleanliness and high efficiency. Fuel cell has great demand and application prospects in hydrogen energy automobile, factory and residential power supply and so on. It can even gradually replace the use of fossil fuels in the future and become an indispensable energy source for human life.

Keywords

Fuel cell, proton exchange membrane fuel cell, electrocatalysts, proton exchange membrane, bipolar plate.

1. Introduction

Fuel cell is an electrochemical device that converts the chemical energy in fuel and oxidant continuously and directly into electric energy. Fuel cell is completely different from ordinary battery in principle and structure. The active material of fuel cell is stored outside the battery. As long as fuel and oxide are continuously supplied, it can generate electricity, so the capacity of fuel cell is infinite. The capacity of the battery is limited. Once the active substance is used up, the life of the battery will be terminated. Fuel cell technology can provide clean, efficient and reliable power for any device that needs electricity. Fuel cells have replaced other energy supply facilities in some application areas and applied in portable, fixed and automotive fields, from battery chargers to home heating systems and automotive power sources. So far, fuel cells are the most widely used energy solutions [1].

2. Basic Principles of Fuel Cells

Fuel cell consists of cathode, anode, electrolyte diaphragm clamped between the two poles and the collector. Taking the hydrogen fuel cell as an example [2], the fuel is oxidized at the anode to produce H+ and electron (e).

$$H2 = 2H+ + 2e \tag{1}$$

H+ flows to the cathode through electrolyte, and the electroreduction reaction of oxidant occurs in the negative plate, resulting in water.

$$1/2O2- + 2H+ + 2e = H2O \tag{2}$$

The electrons form an electric current through an external circuit connecting the anode and cathode. The total reaction is as follows:

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$$H2 + 1/2O2 = H2O \tag{3}$$

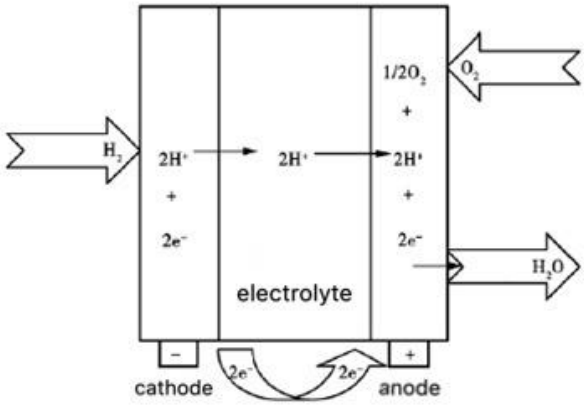

Figure 1. Schematic diagram of hydrogen fuel cell

3. Classification of Fuel Cells

According to the types of electrolytes, fuel cells can be divided into five categories, such as alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), solid oxide fuel cell (SOFC) and proton exchange membrane fuel cell (PEMFC). AFC, PEMFC and PAFC are low temperature fuel cells, while MCFC and SOFC are high temperature fuel cells.

For AFC, the problems of deterioration of electrolyte and control of water and heat balance need to be solved. For PAFC, the breakthroughs are expected in developing cheap catalyst, prolonging system life and reducing cost. For MCFC, working pressure and output current density is expected to be increased, while battery life should be prolonged and cost should be reduced. For SOFC, batteries junction is expected to be improved, what's more, developing heat-resistant materials, film electrolyte, realize low temperature operation are also important.

PEMFC is one of the most widely used and remarkable fuel cells, so we will emphatically introduce it in this paper.

4. Proton Exchange Membrane Fuel Cell (PEMFC)

In addition to the general characteristics of fuel cells, proton exchange membrane fuel cells (PEMFC) are characterized by fast start-up, long life, high specific power and specific energy. PEMFC has attracted great attention and has become a hot research topic nowadays. Electrocatalysts, proton exchange membranes, electrodes and bipolar plates are the important components of PEMFC, which have a significant impact on the performance and operation stability of PEMFC [3].

4.1. Electrocatalysts

The electrocatalyst of PEMFC is one of the key factors restricting its commercialization. Therefore, the research on PEMFC electrocatalyst has become the main content of PEMFC research. The catalysts used in PEMFC mainly include the following three categories. Firstly, it is the platinum catalyst. At present, PEMFC uses platinum catalysts supported on activated carbon, carbon black and graphite-carbon materials. Dispersion of platinum in different carriers to make composite electrode materials is an effective way to improve the utilization rate of platinum catalyst. Carbon nanotubes (CNTs) have great specific surface area and good conductivity, which is considered as a good catalyst carrier. Secondly, it is the platinum alloy catalyst. The hydrogen obtained from reforming hydrocarbons often contains impurities of CO, which poisons the catalyst and greatly reduces its catalytic capacity. Through the synergistic action of Pt and Ru, Pt-Ru catalyst has the ability of anti-toxicity to CO and maintains high

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performance of battery. Thirdly, it is the non-platinum electrocatalysts. Considering the high price of precious metal platinum, many studies are devoted to the research and development of non-platinum electrocatalysts. Transition metal macrocyclic oligomers can promote the decomposition of intermediate product H2O2 in ORR, which is conducive to the formation of water, making it a hotspot of research at one time. The transition metal N4 chelates supported on activated carbon have high activity. Transition metal macrocyclic compounds are inexpensive, and the main research direction in the future is to improve their stability and activity.

4.2. Proton Exchange Membrane

As the core material of proton exchange membrane fuel cell, proton exchange membrane (PEM) plays a selective role in conducting protons from cathode to anode, and at the same time it blocks fuel and oxidant. The performance of proton exchange membranes determines the performance of fuel cells.

Proton exchange membrane is the core component of PEMFC. It is a selective permeability membrane. Proton exchange membranes play a dual role in fuel cells, providing hydrogen ion channels as electrolytes and blocking bipolar reactions as media, such as hydrogen/oxygen or methanol/oxygen. The main technical requirements for proton exchange membranes are high proton conductivity, low gas permeability, good thermal, excellent chemical stability and high mechanical strength. At present, the most widely used proton exchange membrane is perfluorosulfonic acid membranes with C-F chain [4].

4.2.1. Perfluorosulfonic Acid Proton Exchange Membrane

At present, Nafion series membranes made by DuPont Company of the United States are widely used at home and abroad. The main material of Nafion series membranes is perfluorinated sulfonic acid ion exchange resin, which has a solid sulfonated fluorinated polymer hydrated sheet with similar structure to poly tetra fluoro ethylene. Its advantages are strong chemical stability, high mechanical strength and high conductivity at high humidity, high current density at low temperature and low proton conduction resistance. However, Perfluorosulfonic acid proton exchange membrane also have some shortcomings, such as higher temperature will lead to lower conductivity, chemical degradation of membranes at high temperature, difficult synthesis of monomers, high cost, difficult disposal of waste products, high price and methanol leakage when used in methanol fuel cells and so on.

4.2.2. Non-perfluorinated Proton Exchange Membranes

Non-perfluorination is mainly manifested in the use of substituted fluorides instead of fluororesins, or in the blending of fluorides with inorganic or other non-fluorides. For example, early polytrifluorostyrene sulfonic acid membranes can not meet the requirements of long-term use of fuel cells due to the poor mechanical strength and chemical stability. Subsequently, the Ballard Company of Canada improved the early polytrifluorostyrene sulfonic acid membranes and then get the BAM3G film. Its sulfonic acid content is low, and its working efficiency is high, the life of single battery can be increased to 15000 hours. What's more, its cost is much lower than that of Nafion film and Dow film, so it is more acceptable.

4.2.3. Organic/Inorganic Composite Membranes

In order to effectively reduce methanol permeation in direct methanol fuel cell membranes, inorganic substances were selected as the fillers. Inorganic materials have good solvent resistance and high temperature resistance, which can effectively inhibit the swelling of membrane materials and prevent methanol molecular penetration. For example, ZrP and SiO2 were filled into the micro-structure of Nafion membrane through ion exchange reaction to effectively reduce methanol leakage. Blending polymer materials with inorganic fillers to give full play to their respective strengths is one of the important ways to develop proton exchange membranes for batteries.

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4.2.4. Proton Exchange Membranes with Aromatic Polymers as Main Chains

Proton exchange membranes with aromatic polymers as main chains were prepared by using polymer materials with benzene ring structure in the main chains. The proton exchange membrane has the advantages of good thermal stability and resistance to electrochemical erosion. After a certain post-treatment process, sulfonic acid groups were introduced into the side chain structure to form proton exchange function. Common materials include polyether ether ketone (PEEK), polyether sulfone (PES), polyphenyl ether (PPO), and related derivatives. For example, Ph-SPEEKDK and ME-SPEEKDK are the most promising membrane materials with higher mechanical strength and dimensional stability than Nafion 117. The permeation rate of methanol in these two membranes is only 6% and 15% of Nafion 117, which shows excellent oxidation resistance in Fenton reagent.

In addition, phosphorus-containing polymer membranes have attracted considerable attention. The molecular structure of phosphorus-containing polymer membranes contains cross-linking phosphorus nitrogen bonds, which makes them have good mechanical and thermal stability. At the same time, the crosslinking structure limits the swelling of the polymer, making the permeability of methanol molecule much lower than that of Nafion membrane.

4.2.5. Proton Exchange Membrane for All-Vanadium Liquid Flow Batteries

Vanadium Redox battery (VRB) realizes the storage and release of electric energy by the mutual conversion of vanadium ions with different valences. By using the same elements to form a battery system, the cross-contamination caused by the infiltration of different kinds of active substances between positive and negative semi-batteries and the deterioration of battery performance are avoided in principle. All-vanadium liquid flow battery has obvious advantages in the following aspects. Firstly, it has large scale. The output power and storage capacity of all vanadium liquid flow battery are independent of each other. By changing the number of electrolytes in the storage tank, the large-scale energy storage needs can be met; by adjusting the number of single batteries in the stack and the electrode area, the rated discharge power requirements can be met. Secondly, it has long life. The positive and negative electrode reactions of batteries are completed in the liquid phase. The charging/discharging process only changes the state of vanadium ions in the solution. No external ions participate in the electrochemical reactions. The electrodes only play the role of transferring electrons and do not participate in the electrochemical reactions themselves. In theory, infinite and arbitrary charge-discharge cycles can be carried out, which greatly prolongs the service life of the battery. Thirdly, it is low cost. In the preparation of key battery materials, such as proton exchange membranes, conductive bipolar plates and other key battery materials, it achieves the large-scale and low-cost production through the realization of localization. All-vanadium liquid flow batteries avoid using precious metal catalysts and cost much less than chemical power sources such as fuel cells. They are suitable for applications of tens of kilowatt to several megawatt scales. Fourthly, it is high efficient. Because active substances in positive and negative half-cell electrolyte are stored in different storage tanks, self-discharge consumption in the process of electrolyte preservation is completely avoided. The energy efficiency of optimized battery system is as high as 80%.

Proton exchange membranes in all-vanadium flow batteries act as barriers to the diffusion of vanadium ions in positive and negative electrolytes, avoiding the energy loss caused by self-discharge of batteries, and forming the circuit in batteries through the transfer of hydrogen protons. Improving the proton transfer rate and minimizing the internal resistance of membrane batteries is one of the important means to improve the performance of liquid flow batteries. The proton exchange membranes for liquid-flow batteries should have the following characteristics. Firstly, they are low vanadium ion transmission, low cross-contamination, low self-discharge of batteries, and high energy efficiency. Secondly, they are high hydrogen proton transmittance, low membrane resistance and high voltage efficiency. Thirdly, they have certain

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mechanical strength, chemical corrosion resistance, electrochemical oxidation resistance and long cycle life. Fourthly, when the battery is charged or discharged, the water permeability is small, and the water balance between positive and negative electrolytes is maintained. Proton exchange membranes work in acidic oxidation environment under high gradient electric field, and their performance is directly affected by their operating conditions. Due to the complex transfer of multivalent vanadium ions in membrane and the hydration effect of ions in electrolyte, the relationship between the selective permeability and chemical stability of proton exchange membranes and the structure of membrane materials in liquid-flow battery storage system has not been studied comprehensively and thoroughly so far. Material preparation depends more on experience.

4.3. Bipolar Plate

In proton exchange membrane fuel cell, the role of bipolar plates is to conduct current, balance heat and provide the transmission path for the reaction gas. Bipolar plate materials should be corrosion resistant, low density, high strength, heat conductor, good conductor of electricity, easy to process and low cost. Graphite bipolar is the best material for bipolar plate. It has outstanding advantages of good conductivity, high chemical and electrochemical stability. Graphite bipolar plates include pure graphite bipolar plates, die-cast bipolar plates and expanded graphite bipolar plates. Pure graphite bipolar plate has high cost and processing cost. Carbon/polymer bipolar plates and metal bipolar plates have low cost and are suitable for mass production. However, metal bipolar plates have large weight, high contact resistance with electrodes, and are easy to cause ionic contamination on membranes and catalysts. The density of soft graphite is small, and the processing size is not easy to control accurately. Generally speaking, the most widely used bipolar plate is graphite/polymer composite material. On the one hand, this material has good conductivity and air tightness, on the other hand, it is lighter in weight, easier to process and much lower in cost than pure graphite plate.

5. Conclusion

Fuel cell technology has developed for more than 170 years, and has achieved great success in space planning, transportation and fixed applications. At present, there are many different types of fuel cell technologies, and over time, they have been developed and applied to various special applications. However, it is only in the last five years that the fuel cell industry has achieved commercial sales of some commodities. The advantage of fuel cells is that no other existing technology, such as internal combustion engines, can compare with them. Fuel cells can provide unique operating characteristics, such as low pollutant emissions, particularly efficient and reliable energy production, heating, cooling and power supply in some applications. Fuel cell applications can be divided into three main areas. Firstly, it is the portable fuel cells, including those designed to be mobile APU devices. Secondly, it is the fixed fuel cell power generation devices designed to provide electricity in fixed areas. Thirdly, fuel cells for vehicles that can provide driving power or improve the driving capacity of vehicles can be used. Therefore, we should advocate the development and application of fuel cells in the future [5].

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