Selection of Catalysts for Oxygen Reduction in Proton Exchange

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Abstract. Nowadays, the energy crisis is becoming more and more severe, and using fossil fuels widely has caused a large number of environmental problems, with the most severe impact being the greenhouse effect. At the same time, the problem of glacier melting has also been affecting our daily lives. In addition to the loss of habitat for a large number of animals and the impact on freshwater resources, the melting of glaciers is detrimental to the health of the human diet, among other issues. Due to their products' high energy density and lack of pollutants, hydrogen fuel cells have attracted a lot of interest. One of the main obstacles in the development of hydrogen fuel cells, while there are still many others as well, is the catalyst for the oxygen reduction process, which takes place in the cathode section of the hydrogen fuel cell's energy conversion core. Because the cathode oxygen reduction process is inactive and moves slowly, proton exchange membrane fuel cells (PEMFC) need to utilize a catalyst to speed up the reaction and increase efficiency even more. Proton exchange fuel cell catalysts may be broadly categorized into three groups: non-metal, non-precious metal, and precious metal catalysts. This article primarily examines, with examples, the benefits and drawbacks of several kinds of catalysts. In the review's conclusion, also discusses the challenges to their future development and the possibilities for PEMFC catalysts.

Keywords: PEMFC, catalysts, redox reactions.

1. Introduction

The need for energy keeps growing as society and technology advance, which accelerates energy use and exacerbates the energy dilemma. Fossil fuel consumption on a wide scale can also have a negative impact on the environment, with the greenhouse effect being the worst. The volume of water in the ocean keeps growing as a result of iceberg melting and the ongoing melting of the polar ice caps brought on by increasing temperatures, which raises the sea level. This also means that many islands will be submerged in the future and the amount of drinking water will gradually decrease. To protect the environment, mitigate the energy crisis and save nonrenewable resources, scientists have conducted extensive research to find ways to reduce pollution. Among them, a large amount of research is related to batteries, which are widely used in various fields and are important energy storage devices for renewable energy. As a result, other types of energy storage devices, including mechanical, chemical, and electromagnetic energy storage devices, have also been created. PEMFC has attracted widespread interest due to its high energy conversion efficiency, ultra-low pollution, and long lifespan. It is already being employed in domains including aerospace, aviation, automobiles, energy storage, and other industries, and is gradually encroaching on every industry. In the future, it may also involve applications in the rail transit industry [1]. PEMFC works on the fundamental tenet that an oxidation-reduction process between hydrogen and oxygen takes place on the electrode. Protons move through the proton exchange membrane and electrons flow to the cathode through an external circuit when hydrogen is split into protons and electrons by the action of a catalyst. At the same time, oxygen interacts with protons and electrons on the cathode side through the catalyst to form water. A current is created when electrons are transported from an external circuit to the anode and ions from the electrolyte to the cathode [2]. The anodic reaction of hydrogen-oxygen fuel cells is relatively rapid, but the core of energy conversion in the entire electrochemical process is the cathodic oxygen reduction reaction, which is limited by the activation energy barrier and has slow kinetics, greatly limiting the commercial development of fuel cells. To accelerate the chemical reactions inside the battery and improve the energy output efficiency that takes you to eat, a catalyst needs to be added

to PEMFC. A catalyst must be introduced to PEMFC to speed up the internal chemical processes and increase the battery's ability to produce electricity. To efficiently separate and transfer electrons and protons and to facilitate the chemical reaction between hydrogen and oxygen, the catalyst requires efficient proton transfer capacity. Metal, non-metal, and precious metal catalysts are different types of redox catalysts utilized in PEMFC. This article reviews and examines the benefits and drawbacks of several types of hydrogen fuel cell catalysts. The review of this paper serves as a resource for upcoming investigations on PEMFC catalysts.

2. Proton Exchange Membrane Fuel Cell (PEMFC)

Polymer membranes that can conduct ions are used as the electrolytes in proton exchange membrane batteries. On the electrodes, oxygen reduction processes between hydrogen and oxygen take place. Hydrogen protons may immediately flow through the proton exchange membrane and reach the cathode because proton exchange membranes can only conduct protons. In contrast, electrons must go through external circuits to reach the cathode. Direct current is generated during the process of electrons reaching the cathode. Proton exchange membrane batteries mainly consist of an electrode plate and a membrane electrode, wherein the membrane electrode includes a cathode, an anode, and a polymer electrolyte membrane. The electrode is generally a porous structure, consisting of two parts: a gas diffusion layer and a catalytic layer. Figure 1 shows the basic structure of PEMFC [3]. Due to its emissions being water or steam, it has the advantage of zero pollution, which is environmentally friendly. In addition, proton exchange membranes have high conversion efficiency, no mechanical vibration, and low noise characteristics. However, proton exchange membrane batteries still face many problems. The first challenge is in storing hydrogen gas. This type of battery uses hydrogen as its raw material, which means that special technologies and devices are needed to store hydrogen, resulting in high costs and more risks. Secondly, the acidic substances generated in the Proton exchange membrane fuel cell may cause electrochemical corrosion, which means that the service life of the equipment will be shortened. The most important point is that the cathodic partial oxygen reduction reaction is slow and requires a catalyst, as the catalysts being developed today have drawbacks that prevent their wider commercialization. After research, the types of catalysts are mainly divided into three categories and each has its advantages and disadvantages.

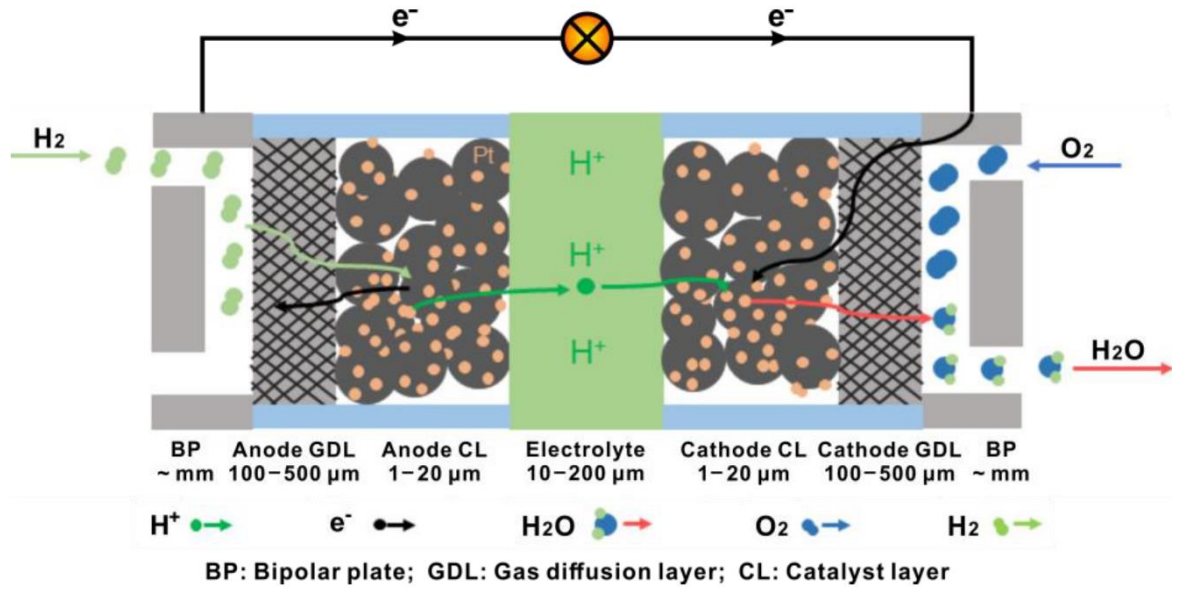


Figure 1. The Basic Structure of PEMFC [3]

3. Catalysts in PEMFC

3.1. Precious Metal Catalysts

Precious metal catalysts mainly include platinum, palladium, ruthenium, iridium, and osmium Pt is one of the most commonly used precious metal catalysts. Pt catalysts have high catalytic activity, strong selectivity, convenient catalyst production, and low usage. They can be optimized for catalytic performance through changes and improvements in manufacturing methods, as well as by compounding with other metals or active components of co-catalysts. It's widely used in various fields, capable of repeated regeneration and activation, with a long lifespan, and the metal palladium from waste catalysts can be recycled and reused. However, because there are so few platinum resources on Earth, there is an issue with expensive pricing, which will raise the cost of manufacturing. For this reason, the Pt/C catalyst is accessible. Pt nanoparticles supported on carbon and mixed with a Nafion ionomer were employed as the catalyst layer in fuel cells, thanks to pioneering work by Los Alamos National Laboratory on thin film catalyst layer synthesis [4]. Pt/C catalyst is relatively stable and highly conductive, and its preparation process is quite mature, which can be used commercially on a large scale. Due to the presence of activated carbon carriers, Pt/C has smaller particles. By reducing the average particle size of platinum particles, the catalytic active sites exposed per unit mass can be increased. However, Pt/C will eventually corrode, thus the key mitigation technique is to create corrosion-resistant materials to take the place of conventional carbon black carriers like TiO_2. However, Pt/C is also pricey. The Pt concentration may be decreased by alloying, which would lower the price of PEMFC and increase manufacturing efficiency. Additionally, platinum catalysts include platinum metals, which might potentially pollute the environment if not properly handled. However, the method of recycling and reuse can help address the issue and prevent environmental pollution. However, Pt also has many other problems such as scarce reserves, poor stability, poor methanol tolerance, and susceptibility to CO poisoning, thus meaning more research has to be done as some of them still don’t have solving methods.

3.2. Nonprecious Metal Catalysts

Non-precious transition metals are often converted into single-atom catalysts which form non-precious metal catalysts. Single-atom catalysts refer to the uniform distribution of metals in the form of single atoms on the carrier, which maximizes the utilization of metals. In theory, a 100% atomic utilization rate can be achieved. Due to the unique electronic structure of metal active centers, their high catalytic activity and selectivity can be demonstrated in ORR catalysts. Meanwhile, due to the diversity of its active centers, ligand types, and structures, as well as the interaction between active centers and substrates, these efficient regulatory strategies have been continuously explored, significantly improving the ORR reaction activity [5]. Among the many M-N-C single-atom catalysts, the FeN_4 structure is the favored single-atom catalyst by a wide range of researchers just because of its optimal reactivity close to the peak tip of the volcano diagram and low cost. A schematic diagram of FeN4 formation is shown in Figure 2 [6]. The iron single atom coordinated with the single atom of the FeN_4 structure is typically considered to be the true active site for the adsorption of O_2 and catalytic ORR kinetics and is commonly referred to as the catalytic active center for oxygen reduction reactions. As such, it is commonly considered to be a current research hotspot [7].

However, single-atom catalysts are susceptible to oxygen oxidation, causing the active components to decay, and the secondary reaction of two electrons will occur during the reaction process of single-atom catalysts, producing H_2O_2, triggering the Fenton reaction, resulting in the degradation of catalyst performance [8]. Single-atom catalysts also have a significant flaw. Small enough metal particles, down to the level of a single atom, will experience a rapid rise in specific surface area, which raises the free energy of the metal surface and might result in catalyst deactivation [9].

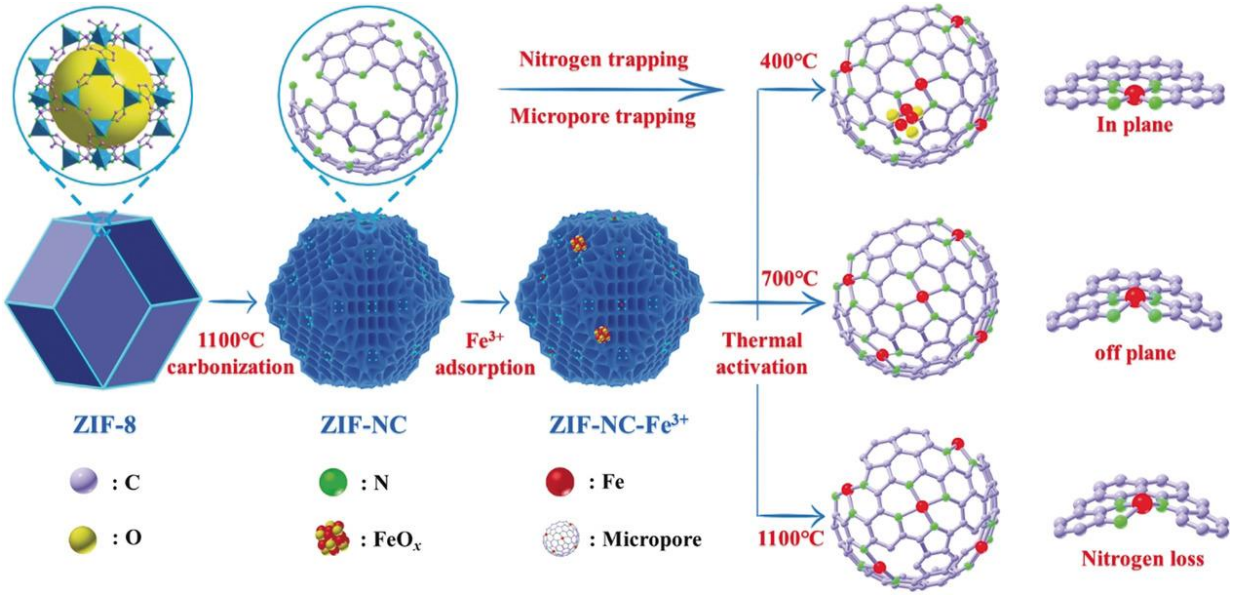


Figure 2. Schematic diagram of FeN4 formation [6]

3.3. Non-metallic Catalysts

Many scientists think that non-metallic catalysts, particularly platinum catalysts, will eventually be replaced by precious metal catalysts simply because they are less expensive than platinum catalysts, which lowers the cost of PEMFC. They are also more stable and have relatively high activity. In addition, Nonmetallic catalysts have a lot of advantages. First of all, it will not produce toxic and harmful exhaust emissions and is very environmentally friendly. Additionally, the catalytic temperature of non-metallic catalysts can reach over 1000 ℃, while traditional metal catalysts have poor temperature resistance and can often only be used below 300 ℃. However, it has a lot of problems. Non-metallic catalysts are not as stable as metal catalysts and are easily affected by oxidation, hydrolysis, and other factors, resulting in a decrease in catalytic performance. In addition, non-metallic catalysts have a shorter lifespan and can generally only be used a few times. Compared to conventional metal catalysts, non-metallic catalysts are less active and require a larger amount of catalyst to achieve the same catalytic effect, which leads to an increase in cost. Currently, the most researched are heteroatom-doped carbon materials. Apart from that, nitrogen-doped materials are one of the focuses of the research. Nitrogen-doped graphene, carbon nanotubes, and polymerized nitrogen are just a few of the nitrogen-doped materials that are currently being investigated. While nitrogen doping may significantly increase the thermal stability and ORR performance of carbon materials, the structure of carbon-based substrate materials will be harmed. If nitrogen doping is excessive, it will reduce the conductivity of the material and reduce the reaction performance to a certain extent. Therefore, the amount of nitrogen doping cannot be too high [10]. For nitrogen-doped materials, further optimization of catalyst performance requires directional control of doping types to provide strong support. Moreover, polymeric nitrogen materials have completely different structural characteristics from traditional heteroatomic carbon materials, and new applications of non-metallic oxygen reduction catalysts are expected to be explored. In addition, the ORR catalytic reaction mechanism of doped carbon materials still needs to be studied.

4. Conclusion

High energy conversion efficiency, rapid starting, and zero or low emissions are all advantages of PEMFC, a green energy technology. Catalysts are important in the design of PEMFC because they may speed up electrochemical processes and improve the effectiveness and durability of batteries. This article explores and contrasts the advantages and disadvantages of these three types of catalysts,

including precious metal, non-precious metal, and non-metallic catalysts, as they are employed to produce proton exchange membrane fuels.

At present, in addition to the high cost of precious metal catalysts, the catalysts in PEMFC also have many other problems, such as scarce reserves, poor methanol tolerance, and susceptibility to CO poisoning, which seriously hinder their large-scale commercial development. However, compared to precious metal catalysts, non-metallic catalysts, although relatively inexpensive, face issues such as susceptibility to oxygen oxidation and secondary reactions during the catalytic process. In addition, it has structural characteristics that are different from traditional heteroatomic carbon materials, which means it has the potential to explore new application fields. However, the doping amount of its chemical substances needs to be strictly controlled, and further optimization of catalyst performance requires directional control of the doping type to provide strong support. At the same time, further research is needed on their catalytic reaction mechanisms.

Nonprecious metal catalysts are the best choice for proton exchange membrane fuel cell catalysts due to their low cost, abundant resources, good ORR catalytic activity, and methanol resistance. They are also ideal for commercial development. However, much research will still be needed in the future to produce nonprecious metal catalysts for commercial use and to solve the issues caused by their quick oxidation and decay. Therefore, the further promotion and commercial development of PEMFC in the market still require large-scale research on the catalysts used in its cathode, exploring ways to reduce its decay rate and cost, and also exploring non-metallic catalysts, which have not yet been extensively studied. If the proton exchange membrane fuel cell is extensively adopted in daily life, it would significantly improve environmental protection and provide solutions to a number of societal issues, including the energy crisis. In addition, it will provide a healthy atmosphere for the inhabitants of the next generations. But there is still a long way to go on the protons exchange membrane fuel cell research trail, and it needs our further non-stop efforts to explore.

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