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Electrocatalytic Oxygen Reduction Reaction and Its Catalyst Selection and Development

Ming Wen, Man Liang, Jie Tan, Ao Wang*

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, China
**Corresponding author: aowang-scut@qq.com*

Abstract: *In the case of increasing energy demand year by year, traditional fossil fuels bear most of the global energy supply. However, due to their extremely limited reserves and the generation of harmful gases in the combustion process, people have to face energy crisis and serious environmental pollution. Therefore, new energy has come into people's vision, and oxygen reduction reaction, as an important field of electrochemical research, plays an important role in the development of these new energy. With the in-depth study of oxygen reduction reaction, seeking an ideal catalyst has become one of the important goals of people. In the important application fields of ORR reaction - fuel cell and metal air cell, due to its structural principle and the requirements of the operating environment, the selection of appropriate catalyst is particularly important, which is also one of the research focuses of scientists in recent years. So far, scientists are still working hard to develop a catalyst to meet the requirements of large-scale commercialization.*

Keywords: *Electrochemistry, Transition metal, Catalyst, ORR reaction*

1. Introduction

Traditional fossil fuels bear most of the world 's energy supply, but its reserves are limited, and a large number of harmful gases such as sulfur dioxide and nitrogen oxides are produced in the combustion process. The resulting energy crisis and environmental problems are threatening people 's production and life. Therefore, the development of clean and efficient renewable energy, such as hydrogen, solar energy, is the only way to achieve sustainable development. Electrochemical reactions play an increasingly important role in the development, storage and conversion of these new energy sources.

Among them, as an important field of electrochemical research, oxygen reduction reaction plays an important role in energy conversion devices (such as fuel cells and metal-air batteries). The key of these energy conversion technologies is the oxygen reduction catalytic reaction of cathode. The oxygen reduction catalyst with excellent performance helps to improve the energy conversion efficiency between chemical energy and electric energy. [1]

2. ORR Reaction Principle

ORR reaction is a complex multi-electron transfer process, which is divided into two-electron process and four-electron process. In the two-electron process, oxygen is reduced to HO_2^- or H_2O_2 after obtaining electrons in acidic or alkaline environment, and electrons are no longer obtained, and the final products are OH^- and O_2 or H_2O_2. four-electron process is more complex, can be divided into continuous four-electron process and direct four-electron process. [2]

In practice, there may be several reaction paths in the oxygen reduction reaction. Although HO_2^- or H_2O_2 generated by the two-electron process can reduce the activation energy of the reaction process, the reaction process is complex. The generated H_2O_2 not only reduces the energy output density, but also corrodes the battery pack. Therefore, the two-electron process is not conducive to the cathode ORR reaction of fuel cells, and the generation of intermediate transition products needs to be inhibited. The four-electron process steps are clear, and the main products are H_2O and OH^-. The conversion of oxygen into water can provide more energy output and the product has no negative impact on the reaction process. Therefore, the four-electron process is more beneficial to improve the output voltage and energy conversion efficiency of fuel cells.

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The theoretical steps and reduction potentials for ORR reactions in acidic and alkaline electrolytes via a four-electron process are as follows[3]:

Table 1: Theoretical steps and reduction potentials of ORR reaction in acidic and alkaline environments.

Direct four-electron process	Under acidic conditions	$O_2+4H^++4e^-\rightarrow 2H_2O$	E^0=1.229V
	Under alkaline conditions	$O_2+2H_2O+4e^-\rightarrow 4OH^-$	E^0=0.401V
Continuous four-electron process	Under acidic conditions	$O_2+2H^++2e^-\rightarrow 2H_2O_2$	E^0=0.670V
		$H_2O_2+2H^++2e^-\rightarrow 2H_2O$	E^0=1.277V
		$2H_2O_2\rightarrow 2H_2O+O_2$	
	Under alkaline conditions	$O_2+H_2O+2e^-\rightarrow HO_2^-+OH^-$	E^0=0.065V
		$HO_2^-+H_2O+2e^-\rightarrow 3OH^-$	E^0=0.867V
		$2HO_2^-\rightarrow 2OH^-+O_2$	

3. Application of ORR reaction

The two most important applications of ORR reaction are fuel cells and metal-air batteries. The performance of catalysts determines the performance of batteries.

3.1. Fuel cell

Fuel cell is a power generation technology that directly converts the chemical energy of fuel into electrical energy. The low-temperature fuel cell is described in detail below. Low temperature fuel cells can be divided into proton exchange membrane battery (PEMFC), direct methanol battery (DMFC) and alkaline battery (AFC). [4]

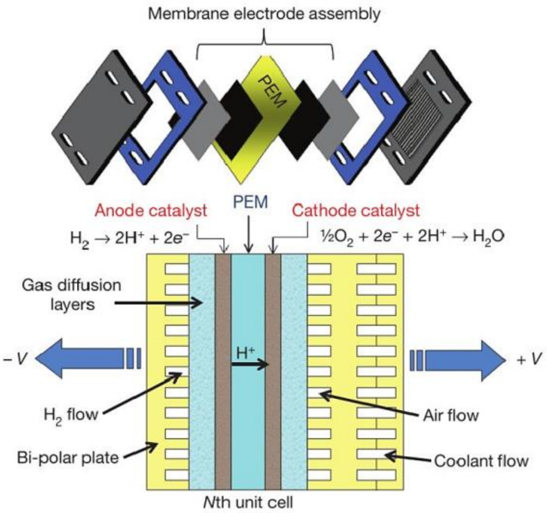

Figure 1: Fuel Cell Composition Diagram

Taking hydrogen fuel cell as an example, electrochemical reaction occurs on the membrane electrode assembly (MEA) electrode, and each electrode is connected to the solid polymer ion exchange membrane conducting protons. At present, the catalysts used in the positive and negative electrodes of the battery are Pt-based catalysts. ORR and hydroxide reactions occur on the surface of the catalysts, respectively. The product is only pure water, and heat is the only by-product. The porous gas diffusion layer transports reactants and product water between the flow field and the catalyst surface, and exchanges electrons between them. Fuel cell energy conversion efficiency is high, clean and pollution-free. Fuel cell MEA must consider three factors: cost, performance and durability. Cathode ORR is six or more orders of magnitude slower than anodic oxidation, limiting fuel cell performance, so almost all research and development are focused on improving cathode catalysts and electrodes. Most MEA catalysts currently used are based on Pt (loaded on carbon black carrier in the form of nanoparticles), and the high price of this rare precious metal has a decisive impact on the cost of the catalyst. The development of new ORR catalysts is of great significance to promote the large-scale commercialization of fuel cells.[5]

3.2. Metal-air battery

The structure principle of metal-air battery is similar to that of dry battery. The difference is that the positive material of metal-air battery comes from oxygen in the air. Such batteries have high energy density, safety and pollution-free. Various primary and rechargeable metal air batteries (zinc, aluminum, iron, lithium, potassium, sodium and magnesium) have attracted many people 's attention.

For rechargeable metal air batteries, lithium metal has the highest theoretical specific energy (5928 Wh k^{-1}) and higher battery voltage (2.96 V), but lithium metal is very unstable in the air. Magnesium and aluminum air batteries have serious self-corrosion in aqueous solution, which reduces the coulombic efficiency of the battery. These two batteries are not rechargeable and can only be used as primary batteries. Among these metals, zinc and iron have the most stable chemical properties, and zinc-air batteries have received more attention due to their higher energy density (1218 Wh k^{-1}) and battery voltage. Zinc-air batteries face many difficulties and challenges in the commercialization process.[6]

For anode zinc, the cycle performance of the battery is usually poor due to the high solubility of its discharge product (zincate) in alkaline electrolyte and its self-corrosion at the anode. After charging, zincate will not all return to the original position of the negative electrode surface, and eventually lead to electrode shape change or dendrite growth, which will also gradually reduce the cycle performance of the battery, or even more seriously make the battery short circuit. For the positive electrode, the ORR activity and stability of the air catalyst affect the power density and discharge capacity of the battery. So far, few catalysts can meet the needs of high activity and durability.

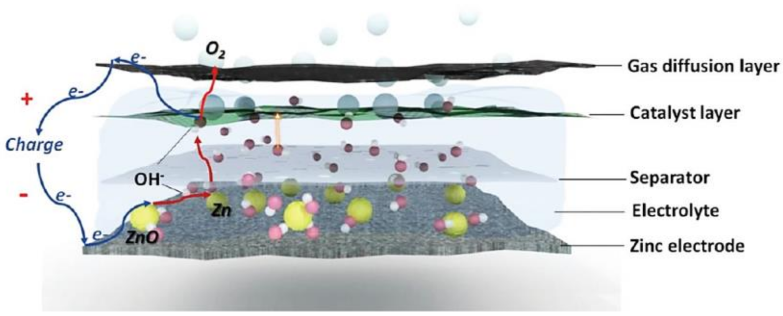

Figure 2: Composition diagram of zinc-air battery

4. Selection of catalysts

In recent years, with the deepening research on ORR, a large number of excellent ORR catalysts have emerged, but these catalysts have not yet reached the requirements of large-scale commercialization.[7] Usually, an ideal ORR catalyst must have the following characteristics:

1) High catalytic activity. The higher active catalyst can reduce the overpotential of oxygen reduction reaction, increase the current density per unit mass (area), and reduce the amount of catalyst, so as to reduce the cost.

2) Good stability. The long working environment of fuel cells and metal-air batteries requires that the catalyst must have good stability to ensure that the activity of the catalyst does not decrease significantly during operation, thereby improving the life of the battery.

3) High selectivity. Side reactions of two-electrons occur in the catalytic ORR process, which reduces the energy conversion efficiency of the battery. The highly selective catalyst can effectively promote the oxygen reduction process of four-electrons.

4) Low price, simple preparation process. The raw materials, preparation process and yield of the catalyst will affect the cost of the catalyst, and the cost of the catalyst plays a vital role in the commercial development of these two batteries.

5) Strong resistance to CO and methanol poisoning. In the fuel cell, the anode fuel such as CO and methanol will pass through the Fiaphth film to the cathode, poison the catalyst, and then reduce the catalytic activity of the catalyst. Therefore, good catalysts must have the ability to resist CO and methanol poisoning.

Traditional noble metal catalysts such as platinum and ruthenium have high catalytic activity, but they have the disadvantages of scarce resources, high cost and poor stability. This hinders their large-scale application. As an ideal substitute for noble metal catalysts, iron-related active site catalysts have attracted much attention due to their good ORR electrocatalytic activity and stability, abundant reserves and low manufacturing cost. A variety of iron-related active site catalysts for ORR have been reported, such as Fe-N-C and Fe-S-N sites.[8] So far, few catalysts can meet the needs of high activity and durability. The model constructed in the density functional theory calculation can theoretically reflect the structure, reaction interface and reaction path of the catalyst under realistic conditions. However, these models are usually highly idealized and fail to take into account some time-varying factors, such as the number of defects, various interface areas, electrolyte concentrations and pH values. Therefore, DFT calculation and simulation should be further studied to make the theoretical analysis closer to the actual reaction, which will help to accurately screen excellent ORR electrocatalysts with high performance and low cost. More importantly, there is still a long way to go to apply these high-performance ORR electrocatalysts to the actual equipment of metal-air batteries, and there is still much room for breakthrough in engineering applications.

5. Conclusion

Starting from the energy problems faced by the global society, we reviewed the research directions related to new energy and electrochemistry, namely, the ORR reaction catalysts. Firstly, the principle of ORR reaction and its main applications - fuel cells and metal air batteries are introduced. Secondly, the selection of suitable catalysts for ORR reaction which are currently in the research stage and have been put into large-scale commercial use is summarized. So far, the catalyst performance cannot fully meet the needs of practical applications, there is still a long way to go to apply the theoretical model to practice.

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