Research Progress on Oxygen Reduction Catalyst Materials for Proton Exchange Membrane Fuel Cells

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Abstract. The sustainable development of society gives rise to the increasing energy demand, making environmental pollution a problem that cannot be ignored. Among them, fuel cells are attracting attention as efficient and environmentally friendly. Proton exchange membrane fuel cells (PEMFCs) represent an advanced and eco-friendly energy conversion technology with substantial potential in transportation, distributed power generation, and other applications, while their performance can be remarkably impeded by the cathodic oxygen reduction reaction (ORR) which exhibits slow kinetics. Pt-based catalysts are the preferred materials for catalysis but are detrimental to the practical application of fuel cells due to their high cost and instability. Therefore, it is essential to develop stable and low-cost cathode catalysts. This paper reviews the advancements in cathode catalysts for PEMFCs, encompassing traditional platinum-based catalysts and their enhancement strategies, as well as the current status of emerging non-platinum-based catalysts. The paper also outlines future research directions for these cathode catalysts.

1 Introduction

Against the backdrop that energy demand grows rapidly and environmental problems deteriorate a lot, developing clean and renewable energy is of primary importance. Proton exchange membrane fuel cell (PEMFC) exhibits high energy conversion efficiency, high energy density, and environmental protection properties, capable of ensuring chemical energy is directly converted into electrical energy. It is widely used in vehicles (such as cars and airplanes), power generation stations, and military fields. However, the relevant cathodic oxygen reduction reaction (ORR) significantly affects fuel cells' overall performance because of the involvement of multiple proton-electron transfers and inherent slow kinetics. Although Pt-based catalysts exhibit excellent catalytic performance, their high cost, scarcity, and strict requirements for oxygen purity limit their applications. In terms of cost reduction, Deng et al. prepared an iron nanocatalyst encapsulated in pod-shaped carbon nanotubes, which can reduce the contact between the catalyst and air pollutants and also reduce the consumption of precious metals [1]. In addition, most PEMFCs use air as the raw material gas, and impurities such as SO_2 and NO_2 present in the air can easily poison the catalyst, significantly

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reducing the efficiency and service life of the fuel cell. Misz et al.summarized the impact of some pollutants in the air on PEMFC and found that a small amount of toxic substances can significantly reduce the performance of fuel cells [2]. Therefore, improving the anti-toxicity of catalysts, and ensuring their stability and activity, has become a key research direction at present. With the continuous advancement of PEMFC towards practical applications, researchers are required to pay more attention to anti-toxicity weakening and cost reduction while ensuring stability.

This article introduces several catalysts developed in recent years and explores the current problems, research directions, and corresponding solutions of traditional PEMFC oxygen reduction electrocatalysts to promote the development of PEMFC technology.

2 Cathodic reaction principles for PEMFC

PEMFCs have the function of generating electrical energy by the hydrogen-oxygen electrochemical reaction, enabling the transfer of electrons from the anode to the cathode relying on the ORR and the acquisition of electrical energy from fuel cells by external electrical appliances. Oxygen enters the fuel cell's cathode inlet and reaches the surface of the cathode catalyst through the gas diffusion layer, providing sufficient oxygen for the reaction. The hydrogen gas at the anode decomposes into protons and electrons, with the former reaching the cathode through the proton exchange membrane (PEM) and the latter flowing toward the cathode along the external circuit. When oxygen, protons, and electrons meet on the surface of the cathode catalyst, an oxygen reduction reaction occurs, producing water.

3 Pt-based catalysts

3.1 Traditional Pt-based catalysts

Platinum (Pt) has long been the preferred material for cathode catalysts in PEMFC relying on the outstanding catalytic activity towards ORR. Nevertheless, the scarcity of Pt resources results in high catalyst costs and insufficient stability under actual working conditions. In traditional Pt-based catalysts, excessive Pt dosage has greatly hindered their large-scale production applications. At the same time, Pt nanoparticles are loaded on carbon supports, which provides a larger specific surface area (SSA). However, corrosion is prone to occur at high potentials of carbon supports, and exposing more active sites also makes Pt-based catalysts susceptible to poisoning. Because the gas used for the cathode is usually air, rather than high-purity oxygen, pollutants such as SO_2 and NO_2 contained in the air will adsorb onto the surface of Pt-based catalysts, thereby reducing their catalytic activity. The problem of cathode catalyst poisoning can be solved from four perspectives: adding air filters, ozone treatment, electrochemical recovery, and developing new catalyst materials [3].

3.2 Pt-based alloy catalysts

Although Pt exhibits excellent catalytic performance in ORR, its scarce resources, high cost, and other issues greatly prevent PEMFCs from being applied. According to research, alloying Pt with other transition metals of Co and Nican improves the catalyst performance [4]. For example, Pt_3M (where M is another transition metal) alloy catalysts present improved catalytic mechanisms, thereby being well-concerned in the field of fuel cells. Alloying can adjust Pt atoms in terms of the electronic structure and optimize their ability to adsorb and dissociate oxygen molecules. For example, Pt-Ni alloy catalysts shift the d-band center of the

catalyst through the modulation of the ratio of Pt and Ni, thereby enhancing the catalytic activity. Zhou et al. added a small amount of Ag to PtCu and found an obvious improvement in the catalytic activity after adding Ag [5]. The current common method for preparing alloy catalysts is a solvothermal method, but this method has difficulties in removing organic residues when preparing end-capping agents, and the process flow is complex and costly [6]. Therefore, researchers are improving solvothermal methods (such as polyol methods) and exploring other preparation methods (such as electrodeposition and atomic layer deposition).

3.3 Pt-based core-shell catalysts

The Pt-based catalyst with a core-shell structure usually uses nonprecious metals (such as Co, Ni) as the core and Pt as the shell. The important reason why Pt-based catalysts with core-shell structure have attracted attention is not only because they can reduce the amount of Pt used, but also because there are two important adjustable interactions at the core-shell interface, namely strain effect and ligand effect, which can effectively improve the activity of electrocatalysts [7]. Upon the alloying of Pt with a transition metal, the electrons of the transition metal will interact with the electrons of Pt. If the electronegativity of the two is different, it will cause electron transfer, which will change the electron cloud density distribution of Pt atoms and thus affect their adsorption capacity for the reaction substrate. The strain effect originates from the change in the distance between atoms on the catalyst surface. Lattice distortion can occur because of the different sizes of atoms, resulting in strain. Under compressive strain, the d-band center of Pt presents a downward shift, reducing the adsorption energy for reaction intermediates and promoting the desorption of reaction products, thereby increasing the chemical reaction rate. Despite the role of the core-shell structure in remarkably decreasing the amount of Pt in PEMFCs, there are still some issues that need to be addressed, among which durability remains an important indicator to be considered. Regarding this, the Lv Yang team Pd3Au@Pt/C study was conducted on the C core-shell structure electrocatalyst, and it was concluded that adding a small amount of high redox potential precious metals to the original catalyst core can effectively enhance durability [8]. Although Pt-based core-shell catalysts have great advantages, there are still many shortcomings that need to be improved.

3.4 Pt-based single-atom catalysts

Pt-based single-atom catalysts refer to those in which a single Pt atom is uniformly distributed on a specific carrier. The smaller the radius of Pt particles, the higher their utilization rate. Single-atom catalysts can maximize the participation of active sites, therefore single-atom catalysts are currently developing into highly active electrochemical reaction catalysts. Liu et al. synthesized a Pt1/NBP catalyst using a low-temperature hydrothermal ethanol reduction method to develop an efficient ORR catalyst [9]. The catalyst was strongly selective for the 2-electron pathway of ORR. Further high-temperature heat treatment was performed to reconstruct the coordination environment for Pt atoms, forming a single-atom catalyst fixed with pyridine-N Pt1@Pt /NBP, thus obtaining an efficient 4-electron pathway [10]. Although single-atom Pt has a unique electronic structure and exhibits special catalytic activity and selectivity, it has great research potential. However, commonly used characterization methods make it difficult to verify the intrinsic relationship between single-atom size and its catalytic performance. Therefore, to study its reaction mechanism, it is necessary to develop new characterization methods.

4 Non-Pt-based catalysts

4.1 Transition metal nitrides

Transition metal nitrides exhibit excellent catalytic properties in oxygen reduction reactions. Specifically, Fe-N-C material has an initial potential approaching to Pt/C catalyst, and this catalytic property mainly results from the synergistic effect between nitrogen atoms and transition metals [11]. In the ORR reaction, nitrogen atoms can adsorb oxygen molecules, while transition metals promote the dissociation of oxygen molecules through electron transfer, forming adsorbed oxygen atoms that react with protons and electrons to generate water. By adjusting the electronic structure of transition metals, their adsorption and activation abilities can be optimized, thereby improving catalytic performance. Compared to ordinary C materials, adding N to the catalyst can activate more oxygen molecules, and the atomic radii of N and C are close, which can effectively solve the problem of lattice mismatch [12]. Therefore, the performance of nitrogen-doped carbon catalysts will be better than other catalysts. Jia et al. synthesized nitrogen-doped nanocages with porous self-supporting structures and found that they have dual catalytic effects, the ORR performance of which approaches that of commercial Pt/C [13]. According to research results, among nitrogen-doped carbon materials with different N configurations, pyridine-N has the best catalytic activity.

4.2 Transition metal chalcogenides

Transition metal chalcogenides are compounds composed of transition metal elements (Fe, Mo, Ni, etc.) and chalcogenides, divided into binary and ternary compounds, with Ru-based compounds being the main ones [14]. There are two structural types in ternary compounds: the Chevrel phase and the amorphous phase [15]. These compounds typically have a layered structure, with transition metal atoms and chalcogen atoms connected by chemical bonds within the layers, and weaker van der Waals forces interacting between the layers. This structure gives it a high SSA and rich active sites. For example, MoS_2 has high ORR activity in alkaline media, and its active sites are mainly distributed at the edge of MoS_2. By modifying and regulating the edge position, its catalytic performance can be improved. During the ORR process, metal atoms at the edge of transition metal chalcogenide can adsorb oxygen molecules, while sulfur atoms can alter metal atoms' electronic structure, promoting oxygen molecules to be activated.

4.3 Non-metal carbon-based catalysts

Despite the significant progress in Pt-based catalysts and non-noble metal catalysts, there are still shortcomings. Carbon-based materials exhibit certain catalytic activity in ORR reactions, such as graphene and carbon nanotubes. Carbon-based materials, with massive sources and low prices, can well resist methanol and remain stable in acidic and alkaline media. However, the catalytic activity of a single carbon material as a catalyst is not ideal. To solve this problem, its catalytic activity can be further improved by changing its porous structure or doping with heteroatoms [16]. Nitrogen-doped carbon materials are active, and doping nitrogen atoms can alter the carbon materials' electronic structure, introducing defect sites on their surfaces to be active sites for ORR. During ORR, nitrogen-doped carbon materials such as pyridine nitrogen and pyrrole nitrogen can adsorb oxygen molecules and activate them to generate water through electron transfer. Meanwhile, the pore structure of carbon materials also has a significant impact on ORR performance, and an appropriate pore structure can promote the diffusion and adsorption of reactants.

5 Conclusion

With the acceleration of social development, the contradiction between social development and the natural environment has become increasingly prominent. Therefore, developing new energy sources has become an urgent task, and PEMFCs, as a zero-pollution and zero-emission new energy source that uses hydrogen as fuel and water as a product, have enormous potential. However, there are still many issues to be addressed before its widespread application. Because most oxygen reduction catalysts currently rely on Pt, its scarce resources and high cost have primarily restricted the research progress of PEMFCs. Therefore, it is particularly important to enhance the performance of Pt-based catalysts and develop new non-Pt-based catalysts. This article summarizes the cathodic reaction principle of PEMFCs, explores the problems of traditional catalysts, and introduces the research directions of Pt-based catalysts (traditional Pt-based catalysts, Pt-based alloy catalysts, Pt-based core-shell catalysts, and Pt-based single-atom catalysts) and non-Pt-based catalysts (transition metal nitrides, transition metal chalcogenide, and Non-metal catalysts). The research summary is as follows: Further explore new cathode catalyst materials, especially high activity, high stability, and low-cost non-Pt-based catalysts; Conduct in-depth research on catalyst active sites and catalytic mechanisms to theoretically benefit catalyst design; Develop methods to more effectively prepare reusable catalysts, to meet the large-scale application needs of PEMFCs.

In summary, although Pt-based catalysts and non-Pt-based catalysts have made some progress in research, they still face many challenges. With the deepening of research and the development of technology, it is expected to develop new catalysts with high performance and cost-effectiveness for benefiting the achievement of the national carbon peak and carbon neutrality strategic goals.

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