Research progress of Pt-based electrocatalysts for the cathode of proton exchange membrane fuel cells

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Abstract: Research on advanced platinum (Pt)-based electrocatalysts has an important impact on proton exchange membrane fuel cells. This review introduces the current research progress of Pt-based electrocatalysts for oxygen reduction reaction (ORR) and puts forward the problems that need to be solved in future development.

1. Introduction
With the current rapid development of the world economy, the increasing demand for energy by mankind makes the climate and environmental problems more and more serious[1]. Traditional fossil energy has gradually been unable to meet people's requirements for environmental protection. The development of clean and efficient new energy is one of the main measures to deal with climate change. Hydrogen energy can be the main force in the field of new energy in the future due to its environmental protection, carbon-free, renewable and high energy characteristics. Among them, the hydrogen-oxygen fuel cell is a device that efficiently converts chemical energy into electrical energy[2]. However, due to the complex pathway of the cathode oxygen reduction reaction (ORR) and the slow reaction kinetics in the hydrogen-oxygen fuel cell, a highly active catalyst is required to ensure the reduction reaction of O₂ at the cathode³. Pt catalyst is one of the most commonly used electrocatalysts in the research and application of fuel cells because of its good activity and corrosion resistance. However, as a precious metal, Pt increases the production cost of fuel cells, and factors such as easy poisoning and poor durability limit its large-scale application. Most of the non-precious metal materials face factors such as poor corrosion resistance and insufficient activity, which are not easy to achieve large-scale use[4]. For this reason, Pt-based catalysts not only reduce the cost of raw materials due to the introduction of transition metals, but also improve the activity and durability of Pt by changing the original crystal structure of Pt[5]. This article summarizes several Pt-based catalyst performance improvement strategies from the perspective of catalyst composition and structure.

2. Research progress of Pt-based catalysts
Various effects in Pt-based catalysts are inseparable from the structure-activity relationship between Pt and transition metals. In order to further synthesize Pt-based catalysts with high performance and high stability, it is necessary to analyze the performance improvement strategies of Pt-based catalysts from
2.1 Reduce nanoparticle size
Generally, O₂ molecules complete the adsorption, catalytic reaction, and desorption processes on the surface of the electrocatalyst. The number of atoms on the surface of the traditional Pt monometallic catalyst particles is limited, and the internal atoms are not effectively used, resulting in a waste of Pt. For this reason, increasing the number of exposed active sites on the catalyst can increase the utilization of Pt atoms and reduce the Pt loading, which is an important measure to reduce the production cost of Pt-based catalysts[7]. Figure 1 shows the particle size decreases, the exposed active surface increases.

![Figure 1 Increase exposure to active surface](image_url)

As the size of Pt nanoparticles decreases, their specific surface area increases, and the proportion of Pt atoms exposed on the surface also increases. This means that under the condition of meeting the same catalytic activity, the amount of Pt used in the small-sized nanocatalyst is less[9]. However, if the size of nanoparticles is too small, the coordination number of the surface atoms will be over-unsaturated, and the surface energy will increase, which will cause problems such as agglomeration and difficult desorption of oxygen-containing intermediates[10]. Quinson[11] group adjusted the concentration of NaOH and H₂PtCl₆ to control the size of Pt nanoparticles, Pt nanoparticles with different diameters were prepared. The results show that the mass specific activity (MA) of the Pt catalyst with a particle size of 2.1 nm is about two times higher than that of the Pt catalyst with a particle size of 5.5 nm. It shows that reducing the particle size is beneficial to the improvement of catalyst activity to a certain extent.

2.2 Crystal face design
Increasing the number of active sites is not easy to achieve for large-size particle catalysts, so improving the catalytic activity on fixed active sites is another effective way to reduce Pt. In Pt-based catalysts, different crystal planes have different electrochemical activities, high-index crystal planes often exhibit high ORR activity, and low-index crystal planes are more thermodynamically stable. Usually in 0.1 M HClO₄ electrolyte, ORR activity is Pt(110) > Pt(111) > Pt(100)[2,12].

In electrocatalytic reactions, the performance of specific nanostructured catalysts is highly dependent on its crystallographic surface. Therefore, the shape control of nanostructured catalysts is the key to develop more effective ORR catalysts with selective exposure surfaces[13]. Liao[14] PtCu₅@Pt₃Cu@Pt nanoclusters were prepared, the surface of which were (331), (332) and (221) high-index crystal planes formed by (111) platforms and (110) edges, with abundant thorn branches. In 0.1 M HClO₄, PtCu₅@Pt₃Cu@Pt nanoclusters showed excellent ORR mass specific activity and area specific activity. In addition, MA lost only 8% after 5000 cycles in the accelerated durability test (ADT), which is much lower than Pt/C (27%).

2.3 Synthetic ordered structure
In the process of synthesizing Pt-M alloy, due to the existence of the diffusion barrier, Pt and M in the
commonly prepared Pt-M alloy are randomly distributed to form a disordered solid solution. Although disordered Pt-M alloys can enhance the electrocatalytic performance of materials, they are prone to catalyst degradation due to leaching of non-precious metals. Use component control, heat treatment and other means to change its original crystal phase, transforming it from a disordered structure to an ordered structure, that is, intermetallic phase compound material. Therefore, ordered Pt-M alloys are thermodynamically stable and generally exhibit higher durability than Pt-M\[15\]. The arrangement of atoms in the Pt-M alloy will also affect its surface structure, causing changes in the binding energy of the catalyst surface and the reactants or intermediate products during the catalytic reaction, which ultimately affects its catalytic performance. 

Zhao\[16\] group synthesised the L1₀-PtZn intermetallic structure. The L1₀-PtZn catalyst exhibits high ORR activity that MA is 0.926 A mg⁻¹ and SA is 1.13 mA cm⁻², which are 5.4 and 4.0 times that of commercial Pt/C, respectively. Maintaining good stability that it’s half-wave potential (E½) only lost 11 mV after 30,000 cycles, while the commercial Pt/C E½ decreased by 24 mV. This is due to the formation of ordered L1₀-PtZn. The enhanced bonding of Pt and Zn stabilizes the Zn atoms, thereby improving the structural stability of the fuel cell during operation\[16, 17\]. This indicates that the regulation of the order of atoms in the nanocrystalline phase structure has a significant impact on its catalytic performance.

2.4 Interface design of Pt-based electrical catalysts

ORR catalysts with ordered structure have great prospects in improving stability and activity. At the same time, by adjusting the structure and composition of the Pt-based catalyst, a heterogeneous nanostructure is formed, and a two-phase interface is formed at the boundary of different phases. This interface has a balanced effect on the adsorption and desorption of the intermediate product of the catalytic reaction on the catalyst, and at the same time has an important effect on the transport process of the intermediate product, electrons and adsorbate\[18\]. Figure 2 shows the schematic illustration of the typical bimetal based interfaces. For instance, Su\[19\] deposited PtPdCu nanocrystals on the carbon support to construct the Pt-C interface. The electrochemical activity test results show that the E½ (0.93 V vs. RHE) of PtPdCu/C is higher than that of Pt/C (0.86 V vs. RHE). This is due to the ligand effect on the interface between Pt and C, which makes the chemical bonding between the d orbital of Pt and the p orbital of C at the atomic level change the electronic structure of the active site of Pt, thereby promoting O₂ on the interface. Adsorption enhances the catalytic activity. Therefore, the design of catalyst interface hybridization is a feasible strategy for the preparation of efficient and stable alloy catalysts.

![Figure 2 Schematic illustration showing of the typical bimetal based interfaces](image)
3. Conclusion and Prospect of Pt-based ORR Electro catalyst

For fuel cells, the electrocatalyst with high activity and stability determines its application value, and the good electrocatalytic performance of the catalyst is inseparable from the regulation of structure and composition. The Pt-based electrocatalyst formed by Pt-doped non-precious metal materials has the characteristics of high activity, good stability and reduced Pt consumption, which makes it widely researched and applied. Although non-precious metal catalysts get rid of the fuel cell's dependence on Pt to achieve the goal of reducing costs, with the continuous in-depth research on Pt-based catalysts, more and more excellent Pt-based catalysts have been developed. This shows that Pt-based catalysts still occupy an important position in fuel cell research and application.

However, the current research and application still face the following challenges: On the one hand, although Pt-based catalysts have lower Pt loading and higher catalytic activity than pure Pt catalysts, due to technical limitations, some Pt atoms are still unused. In the research process, it is necessary to further improve the catalyst structure and develop low-Pt catalysts to meet the requirements of industrialization cost; on the other hand, as the framework of the catalyst active material, the carrier must not only have a larger specific surface area to expose more active material particles, but also have good electrical conductivity and structural stability. At present, the most widely used carriers are carbon materials and metal oxides. In battery systems, carbon carriers face the problem of being degraded, while metal oxides have poor conductivity. Therefore, the development of Pt-based electrocatalysts still has a long way to go.

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