

Research progress on platinum catalysts for hydrogen-oxygen fuel cells

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Abstract. In recent years, China's fuel cell technology and industry have developed rapidly. However, the high-cost problem caused by the extensive use of Pt-based catalysts remains one of the most important factors restricting its development. As an important component of hydrogen-oxygen fuel cells, platinum-based catalysts are crucial for promoting their application in this field. The development and research of Pt-based catalysts with higher catalytic efficiency are of great significance for promoting the development of fuel cell technology and industry. In this review, some feasible strategies for improving the performance of Pt-based catalysts were summarized based on reducing platinum usage. In addition, the methods and mechanisms of each strategy in enhancing catalytic activity and reducing the amount of platinum catalyst were discussed in detail. At the same time, the shortcomings and challenges faced by this type of catalyst were pointed out, and the future research and application of this type of catalyst were discussed.

1 Introduction

The global energy crisis and climate change have become pressing issues in recent decades. As our reliance on fossil fuels continues to grow, projections suggest that oil and gas reserves could be depleted by 2042 and coal by 2112. This situation highlights the urgent need to explore alternative energy sources to reduce our dependence on fossil fuels for energy and transportation. Among potential solutions, energy-efficient and environmentally friendly fuel cells are emerging as viable alternatives for portable, mobile, and stationary power applications [1]. Hydrogen fuel cells, in particular, are notable for their high theoretical energy density, zero pollution, and high efficiency, making them a focal point of research. In hydrogen-oxygen fuel cells, catalysts are critical for driving the oxidation of hydrogen and the reduction of oxygen at the electrodes. These catalysts are crucial in influencing the activation polarization of hydrogen fuel cells and are therefore essential materials. Selecting suitable catalysts requires ensuring high resistance to temperature and corrosion under operational conditions. Currently, platinum (Pt) supported on carbon (Pt/C) is the most widely used catalyst. However, the high cost of platinum necessitates the development of more cost-effective alternatives.

This review examines recent advancements in platinum catalysts for hydrogen-oxygen fuel cells and explores strategies to enhance performance while reducing platinum usage.

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2 Mechanism of ORR and HER

Currently, platinum (Pt) is the most effective electrocatalyst in fuel cells and promotes key reactions in hydrogen-oxygen fuel cells. In these batteries, the anodic reaction is hydrogen oxidation (HOR), while the cathodic reaction is oxygen reduction (ORR). The ORR process can be divided into two main paths. [2] The first method is to partially reduce oxygen to hydrogen peroxide (H₂O₂) or superoxide (HO₂) via a two-electron path. But this approach has its lower potential and stronger oxidation performance, which is not very beneficial and can also damage the catalyst. The second approach is to completely reduce oxygen to water (H₂O) or hydroxide (OH) through a four-electron process, which is usually preferred. [3] The four-electron ORR pathway differs in acidic and alkaline solvents. This difference is influenced by the fact that the protons required for oxygen reduction come from water and hydrogen ions in solvents. Furthermore, the mechanism of O-O bond cleavage can be divided into two categories: association and dissociation [4]. In acidic solvents, these mechanisms can be described by the following reactions: [5]

1. $O_2 + M^* + H^+ + e^- \rightarrow M\text{-OOH}$
2. $M\text{-OOH} + H_2O \rightarrow M\text{-OH} + H^+ + e^-$
3. $M\text{-OH} + H_2O \rightarrow M^* + H^+ + e^-$

Dissociative Pathway:

1. $O_2 + 2M^* \rightarrow 2M\text{-O}$
2. $2H^+ + 2e^- \rightarrow 2M\text{-OH}$
3. $2H_2O \rightarrow 2M^* + 2H^+ + 2e^-$

In basic solvents, the mechanisms are:

Associative Pathway:

1. $O_2 + M^* + H_2O + e^- \rightarrow M\text{-OOH} + OH^-$
2. $M\text{-OOH} + H_2O + e^- \rightarrow M\text{-OH} + OH^-$
3. $M\text{-OH} + OH^- \rightarrow M^* + H_2O$

Dissociative Pathway:

1. $O_2 + 2M^* \rightarrow 2M\text{-O}$
2. $2H_2O + 2e^- \rightarrow 2M\text{-OH} + 2OH^-$
3. $2OH^- \rightarrow M^* + H_2O$

Here, M* represents the catalytic active site.

The dual functional mechanism in the hydrogen oxidation reaction (HOR) is the reaction between adsorbed hydrogen (Had) and adsorbed hydroxide (OHad), which desorbs to form water. The activity of HOR is positively correlated with the gas affinity of the catalyst. Therefore, the HOR activity can be improved by adding materials that are prone to forming OHad on the catalyst surface.

3 Electrocatalyst for ORR and HOR

In hydrogen fuel cells, the oxidation of hydrogen and the reduction of oxygen at the electrodes are primarily controlled by catalysts. These catalysts significantly impact the activation polarization, overall performance, and fuel economy of hydrogen fuel cell vehicles. Selecting appropriate catalysts involves ensuring high temperature and corrosion resistance. The commonly used catalyst is Pt/C.

However, Pt/C faces issues such as Pt particle dissolution, migration, and agglomeration over time, which reduces its active surface area and fails to meet the strength requirements of carbon carriers. As a precious metal, Pt is often used in small particle sizes to enhance performance and minimize usage. Despite this, nano-sized Pt particles have high surface free energy and weak interactions with carbon carriers, leading to particle migration and

agglomeration. Smaller Pt particles tend to oxidize, diffuse as Pt ions, and deposit on larger particles, which then grow and agglomerate.

3.1 Pt-based catalysts with special morphologies

Research has shown that the design of platinum-based catalysts with unique morphologies is a very effective strategy for controlling the amount of platinum used. In special forms of wave catalysts, the specific surface area and the atomic utilization efficiency of the catalyst have been improved. Research has shown that the active sites of catalysts lie on the surface of the catalyst and Pt atoms in nanoparticles usually do not participate in the reaction, resulting in low utilization of Pt. Therefore, in order to improve the utilization rate of Pt, we can design some special forms of catalysts that expose more active sites on the catalyst surface. To achieve this goal, special morphologies such as facets with high refractive index (HIF), nanowires (NW), and hollow structures were synthesized. In addition, three-dimensional structured nanomaterials typically have a large specific surface area, which can provide more active sites for reactant molecules. Therefore, the three-dimensional structure can effectively improve the mass transfer and gas diffusion on the alloy surface, thereby enhancing the electrocatalytic performance. The construction of nanomaterials with three-dimensional structures can usually form crystal planes with high refractive index with special structures and other crystal planes with special structural features on the material surface, thereby significantly improving catalyst activity.

In 2014, Stamenkovic et al. reported for the first time on a platinum-based catalyst with a three-dimensional skeletal structure. This catalyst has a high specific surface and is rich in crystal planes with a high refractive index. The mass-specific activity of Pt can reach 5.7A/mg-Pt, which is more than 20-times that of the widely used Pt/C catalyst, making research on three-dimensional skeleton Pt based catalysts in the field of electrocatalysis ever hotter [6]. Traditionally, the utilization efficiency of Pt can be improved by reducing the size of Pt-based catalyst particles. However, catalysts can clump strongly during use. The three-dimensional nanoframework has unique structural advantages. First, it has a highly open three-dimensional structure, a higher specific surface area, a higher density of active sites and a more complete contact with reactant molecules, which can accelerate the reaction. Secondly, its structure is more stable and can withstand harsh reaction environments. Therefore, three-dimensional metal nano scaffolding can effectively improve the activity and stability of catalysts and reduce the amount of precious metal Pt used.

The synthesis of noble metal Pt-based nano frameworks is mainly based on the following two strategies: (1) selective deposition and etching of active sites; (2) Dealloying of hollow or bi (poly) metal nanocrystals. In general, the synthesis mechanism includes an electric displacement reaction, an oxidation etching, diffusion of internal atoms, or a combination thereof.

Pt-based catalysts with three-dimensional special morphology are a kind of highly efficient electrocatalysts with great development in recent years, in terms of material preparation technology, activity and structure characterization, and mechanism exploration. A lot of research work has been carried out and many important results have been achieved. Several important preparation methods have been formed, and some basic understanding of its activity and mechanism has been obtained. However, this type of catalyst still has the following problems:

The preparation process is complex, which leads to the fact that the current research mainly stays at the stage of micro-preparation in the laboratory, and it is necessary to further explore a simple, repeatable and easy-to-scale preparation technology;

At present, the research on this kind of catalyst is still at the level of rotating disk electrodes, and there is almost no report on the application of this kind of catalyst in single fuel cell;

The current 3D Pt-based catalyst model can not well reflect the real reaction conditions of the catalyst, so it is necessary to establish a theoretical calculation model closer to the real environment as soon as possible and develop a new and efficient theoretical calculation method.

The understanding of the structure formation mechanism and catalytic mechanism of these catalysts is still insufficient.

Future research should focus on exploring and developing new preparation technologies; The formation mechanism of the special morphology of the catalyst and the catalytic mechanism were studied by means of advanced technologies such as in-situ technology. The performance and practical application prospects of these catalysts in fuel cells were studied[7].

3.2 Pt-based alloy catalysts

Pt-based alloy catalysts are gaining attention due to their reduced platinum (Pt) usage and enhanced properties. By incorporating foreign atoms into the Pt lattice, alloying modifies the catalyst's electronic structure, affecting the adsorption energy of intermediates and potentially creating dual-function mechanisms. This synergistic effect between surface and electronic structure often results in improved catalytic activity [8,9]. When only Pt is used for catalysis, the significant decrease in Pt utilization efficiency is due to the electrocatalytic oxidation of intermediates (such as CO) on the Pt surface, which occupies the catalytic active sites. The oxidation of desorption and adsorption intermediates can be improved by adding a second metal. Adding a second metal to the catalyst will re expose the active sites, thus improving the reaction kinetics. In addition, the catalytic activity of Pt and the tolerance of CO can be improved through electronic or synergistic effects, thereby promoting interactions between other catalyst components.

In Pt based core-shell structures, common noble metal core elements are Pd, Au, Ag, Ru, and Ir, among which Au and Pd/Pt are more typical for intermetallic alloying. Au exhibits high catalytic activity in nanoscale reactions. Au@Pt Nanocatalysts can exhibit synergistic catalytic effects by changing the surface adsorption force to alter the structure of Pt electron bands. Platinum based catalysts can effectively improve their electrocatalytic activity and stability, as well as enhance their CO resistance through synergistic catalysis. In addition to precious metal alloys, extensive research has been conducted to prepare inexpensive and efficient PEMFC catalysts. By alloying Pt with other single metals, the use of Pt can be reduced and catalytic performance can be improved. Reducing the usage of Pt while ensuring good electrocatalytic activity is an urgent problem to be solved.

Alloying Pt with non precious metal elements such as Co, Ni, Cu, Fe, Sr, Gd, and Mg can improve catalytic efficiency and reduce costs. In addition, the atomic utilization efficiency of Pt can be improved by integrating with other metals. Co/Pt and Cu/Pt catalysts are mainly prepared by two methods: one is to first synthesize elemental nuclei, and then coat the surface of the nuclei with a Pt shell layer. According to the synthesis method of elemental nuclei, it can be further divided into hydrogen thermal reduction, sodium borohydride reduction, electrodeposition, and solvothermal methods; Another method is to form PtCo and PtCu alloys with internal Co or Cu enrichment and surface Pt enrichment through acid treatment, heat treatment, and electrochemical treatment Co@Pt and Cu@Pt Core shell structure [10].

3.3 Pt-based atomic-level-dispersed catalysts

In heterogeneous catalysis, nanoparticle size and shape significantly impact activity and selectivity. Reducing nanoparticles to sub-nanometer scales increases the number of uncoordinated metal atoms available as active sites, optimizing catalyst utilization. The comparison between experimental results and theoretical calculations can be made through a simplified model of an ideal atomic-level dispersed catalyst.

Cluster catalysts are a type of catalyst consisting of several metal atoms or clusters that are normally formed from several metal atoms connected by coordination bonds or direct bonds. The main carrier for the production of cluster catalysts is usually made of carbon-containing materials, such as graphene doped with N, S, P, B, F, porous carbon, soot, carbon nanotubes, etc. These heteroatoms form stable precious metal precursors during wet chemical synthesis due to anchoring effects, and then cluster/carbon composite catalysts are obtained through reduction methods. Cluster catalysts have high catalytic activity and selectivity, which can effectively catalyze molecular conversion reactions while avoiding problems such as excessive sintering of the catalyst. Compared to conventional single-atom catalysts, cluster catalysts have richer electronic structures and surface reaction sites and thus exhibit higher catalytic activity and selectivity. Researchers have developed a highly stable and highly dispersed surface catalyst that firmly anchors 1.8 \pm 0.6nm Pt nanoparticles to a porous 3D carbon carrier through a combination of electrochemical methods and extrusion. Changing the reaction temperature and ligand type during the experimental process can precisely regulate the composition, structure, and atomic number of noble metal clusters at the atomic level.

Metal nanoclusters are a new type of nanomaterial that can obtain atomic level precise structures. They have many advantages such as easy synthesis, strong designability, clear geometric/electronic structure information, and easy regulation of catalytic active sites. They can not only help us understand the structural transformation laws of metal materials, but also be applied to the precise design and construction of catalyst model molecules. Studying the fundamental correlation between catalytic kinetics and surface sealing of metal nanoparticles is crucial, but it remains challenging at present. Researchers have designed a unique 1.7nm Pt nanocluster catalytic system and found that the activity and selectivity of electrocatalytic ORR can be affected by surface caps [11]. In addition, Pt cluster catalysts with different atomic numbers (clusters Pt7, Pt10, and Pt11) have been discovered in the application of ORR. These Pt cluster catalysts not only exhibit similar catalytic activity on ORR, but also have catalytic activity comparable to traditional Pt nanoparticle catalysts. Thermodynamic instability is an inherent problem of metal nanoclusters in catalytic applications. In high-temperature catalytic reactions, metal nanoclusters are prone to rapid deactivation due to particle sintering and growth. Liang et al. found in their study that when sulfur is doped into a carbon matrix, it can effectively stabilize 1nm metal nanoclusters and prevent them from undergoing thermal sintering at high temperatures up to 700°C. Through spectral characterization and DFT calculations, it can be seen that due to the thermally stable and strong metal sulfur bond, the adhesion strength at the metal/S-C interface is enhanced, which greatly suppresses the particle sintering of metal nanoclusters by delaying the diffusion of metal atoms and the migration of nanoparticles. In addition, the prepared Pt nanocluster catalyst exhibits excellent propylene selectivity and stability in the high-temperature propane dehydrogenation to propylene reaction, supported on sulfur doped carbon (S-C) Pt nanocluster catalyst.

Efforts to reduce platinum-based catalysts, enhance power density (catalytic activity), and optimize membrane electrode assembly (MEA) preparation remain crucial for lowering the commercial cost of hydrogen fuel cell systems.

4 Challenge and future

Significant progress has been made in the research of precious metal platinum-based catalysts in the past few years. The several different structures of platinum catalysts mentioned in this article can significantly improve the activity and stability of half-reactions, but there are still some doubts about whether these catalysts can achieve stable performance in fuel cells. To further advance the development of platinum-based catalysts, it is still necessary to address many issues that arise when using platinum-based catalysts in fuel cells. Platinum-based catalysts are an important component of fuel cells, and improving the utilization rate and reducing costs of platinum catalysts are crucial for the commercialization of fuel cells. In the future, platinum catalysts can be studied by optimizing catalyst structures and simplifying synthesis routes to meet the requirements of fuel cells. In the future, the use of platinum can be reduced by exploring highly dispersed catalyst supports, further improving the catalytic performance and stability of the catalyst. In addition, further research can be conducted on the electrocatalytic mechanism of platinum-based catalysts through a combination of theoretical analysis and experimental analysis. Building efficient fuel cell catalysts with good CO tolerance is also essential. Finally, the development of innovative technologies plays an irreplaceable role in researching catalysts with high power, strong stability, and strong environmental adaptability.

5 Conclusion

Hydrogen-oxygen fuel cells represent a promising energy technology with vast application potential. As fossil fuel resources dwindle, hydrogen emerges as a sustainable and inexhaustible energy source. Notably, hydrogen can be produced from renewable energy sources, positioning hydrogen-oxygen fuel cells as a cornerstone for sustainable development.

One of the significant advantages of these fuel cells is their emission profile: they produce only water vapor, avoiding harmful pollutants such as carbon dioxide and nitrogen oxides. This characteristic is crucial for mitigating greenhouse gas emissions and protecting our atmosphere.

However, the widespread adoption of hydrogen-oxygen fuel cells faces challenges, particularly regarding catalysts. Most current catalysts rely on platinum, whose scarcity and high cost pose significant hurdles. This article explores several proposed strategies to enhance platinum-based catalysts by reducing platinum usage while improving overall performance.

Despite progress in the development of platinum-based catalysts, critical issues remain. Reducing platinum content and enhancing power density are vital for decreasing the production costs of hydrogen-oxygen fuel cells. With ongoing technological advancements, the high-performance, cost-effective catalysts will emerge that can significantly enhance the performance and economic viability of hydrogen-oxygen fuel cells across various applications.

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