Research Advances on Electrocatalysts for Oxygen Reduction Reaction in Fuel Cells

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Abstract: Nowadays, fuel cells have attracted much attention because they produce almost no carbon dioxide and air pollutants, help reduce greenhouse gas emissions and air pollution, and mitigate climate change. Among them, seeking electrocatalysts for the oxygen reduction reaction (ORR) is a top priority. This article aims to introduce platinum group metals, transition metal compounds, and carbon-based non-noble metal electrocatalysts with novel nanostructures. At the same time, it summarizes the research progress of various electrocatalysts in recent years. The optimization strategies of catalytic processes are reviewed and their development prospects are prospected. In addition, problems existing in the research on oxygen reduction electrocatalysts are summarized. In the future, these contents can help researchers develop new catalysts and electrolyte materials, optimize manufacturing processes, enhance system integration, study fuel cells for portable and large-scale applications, explore hydrogen production and storage technologies, and integrate fuel cells with smart grids and distributed Integrated energy systems.

1 INTRODUCTION

In today's society, energy consumption is increasing, and concurrently, the issue of environmental degradation is progressively intensifying. Consequently, the advancement of alternative and renewable energy sources has ascended to an imperative priority status. A fuel cell typically comprises three components: a cathode, an anode, and an electrolyte. It uses hydrogen, methanol, ethanol and other fuels to react with oxygen to produce electrical energy and water. In a fuel cell, it can be divided into ORR and Hydrogen Oxidation Reaction (HOR) are direct reactions that occur at the cathode and anode, respectively. ORR refers to a sequence of reactions involving oxygen that transpire within an electrochemical system, in which oxygen accepts electrons and chemically reacts with water or other substances. HOR refers to a series of reactions that occur with water in an electrochemical system in which water molecules lose electrons and form hydroxides or other products with protons. In fuel cells, the hydrogen oxidation reaction usually refers to the reaction of hydrogen gas at the anode, in which the hydrogen molecule loses electrons and combines with protons to form water.

Compared with traditional internal combustion engines, its advantages are more obvious. In practical applications, the electrical energy conversion efficiency of fuel cells is usually between 40% and 60%. However, traditional internal combustion engines convert the thermal energy generated by fuel combustion into mechanical energy, which is then converted into mechanical energy through a generator. Electric energy has low efficiency, only 20%~40%. More importantly, fuel cells have a lower environmental impact. However, the slow kinetic factor in the fuel cell results in a low oxygen reduction reaction efficiency on the cathode, which in turn is affected by the O=O bond energy (498 kJ/mol). Even though platinum and its alloys have been validated as the preeminent electrocatalysts for oxygen reduction, their exorbitant cost and the complexities associated with their preparation impede their large-scale utilization. Hence, it is urgent to find a new cathode electrocatalyst capable of supplanting the traditional platinum-group metal-based counterparts, and non-precious metal (NPM)-based oxygen reduction electrocatalyst has emerged as an exceptional alternative. The purpose of this paper is to introduce platinum group metals, transition metal compounds and carbon-based non-noble metal electrocatalysts

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with new nanostructures. Strategies for optimizing the catalytic process are also reviewed, and finally their development prospects are prospected. In addition, the existing problems in the research of oxygen reduction electrocatalysts are summarized.

2 ORR ELECTROCATALYTIC MECHANISM

The mechanism of ORR mainly includes the following steps. Firstly, O_2 molecules become attached to the catalytic surface, engaging with the active site on the surface to form adsorbed oxygen (O_{ads}). Adsorbed oxygen (O_{ads}) accepts electrons and is converted into peroxy intermediates (OOH^-). Secondly, the peroxy intermediate (OOH^-) further accepts electrons and protons and is reduced to water (H_2O).

The influence of catalysts on ORR is mainly reflected in increasing the reaction rate and reducing the activation energy. Excellent ORR catalysts should have high active site density and catalytic activity, and can reduce the energy loss of reaction. Current challenges include issues such as catalyst stability, cost and durability. In response to these challenges, researchers are seeking to design more efficient and stable catalysts and explore novel materials and structural designs.

2.1 Dynamic Influencing Factors

The adsorption/desorption of oxygen-containing intermediates, e.g. O_2^*, $^*O$, $^*OH$, $^*OOH$ and $HOOH^*$ on the catalyst surface is a key factor affecting ORR kinetics (Nørskov et al., 2004). $O_2 \rightarrow O_2^*$ (The adsorption process of O_2) as the initial step of the reaction determines the subsequent reaction process, and the initial potential of the reaction is determined by the adsorption/desorption of $^*OH$ (at high potential), and the effective number of active centers is determined by the adsorption amount of $^*OH$. More importantly, the adsorption of the catalyst to the intermediate can directly affect the catalytic activity, too weak adsorption strength will hinder the proton/electron movement, too strong adsorption strength will cause desorption.

2.2 Promotion Mechanism of Catalyst Performance

By adjusting the diameter and shape of the catalyst particles, the exposure degree of the active site of the catalyst and oxidation reaction can be increased, so as to increase the specific surface area of the catalyst, so as to improve the performance of the ORR. The synthesis of core-shell structured catalysts and the choice of catalyst support possessing comparatively expansive specific surface areas can markedly enhance catalytic efficacy. Simultaneously, modulating the electronic structure of Pt induces a downward shift in the D-band center, thereby altering the binding energy between the catalyst and aerobic species. Appropriately tuning this binding energy can thereby bolster catalyst activity at its fundamental source.

2.3 Inhibition and Strategies for Stability Enhancement

The decline in the activity stability of Pt catalyst can be attributed to two primary factors: Initially, the dissolution, aggregation, and dispersion of Pt particles result in the depletion of active constituents. Secondly, corrosion of the carbon carrier attenuates the interaction between catalytic particles and the carrier. The stability of catalyst activity can be achieved through the fabrication of Pt-transition metal alloys and intermetallic compounds. Nevertheless, Pt electrode will generate PtO after a long period of operation, thereby overlaying the original active sites. Alternatively, the oxidation/dissolution of other metals resulted in the thickening of the Pt layer and subsequent reduction in activity. Hence, when selecting various carriers to enhance catalyst activity, the corrosion resistance of the carrier stands as a pivotal consideration.

Based on the above, the search for a carrier with high corrosion resistance is essentially to extend the service life and reduce costs. Previous studies have shown that the oxidation of Pt on the catalyst's surface will cause Pt to corrode and then chemically dissolve. Therefore, in order to avoid that, it is an effective means to cover the surface with a layer of oxygen-bound substances. However, there is also the possibility of electrochemical dissolution acting directly on the unmasked Pt nanoparticles and thus degrading the catalyst. Research in this area shows that the quality of Pt does not change within the working potential range of 0-0.8V vs. RHE. However, in order to prevent Pt from being interfered by oxidation factors, under highly acidic conditions and the working potential is greater than 0-0.8V vs. RHE, the quality of Pt was found to decrease significantly (Liu et al., 2010 & Rinaldo et al., 2010). It can be seen that if you want to enhance stability, you must optimize the size and crystal structure of Pt, because the thermodynamic properties of tiny particles are inherently unstable, and at the same time, the surface energy is relatively high, making them easier to aggregate. Not only that, the carbon corrosion phenomenon caused by high potential is also not conducive to maintaining the Pt/C system. Although increasing the size has the potential to reduce ECSA and catalyst activity because it results in a lower surface-to-volume ratio, economic considerations require sacrificing some activity to extend the operational longevity of the catalyst. The following related research is conducted based on the principle of developing multi-dimensional Pt nanostructures. Compared with conventional isotropic nanoparticles, this complex structure remains more stable. Among them, adding metals with higher oxidation potential to improve the stability of Pt is one of the most promising methods. For example, attaching Au particles to the surface of Pt, after 30,000 potential cycles, the catalyst still maintains good stability and almost no decay (Zhang et al., 2007). In addition, you can also consider using a protective coating, which can effectively prevent the non-precious metals inside from being corroded by the environment. However, protective coatings, especially carbon coatings under high-temperature conditions, will inhibit the exchange process between reactants and active sites.

Although the size and structure of the catalyst are optimized, its stability is still limited. Therefore, there is an urgent need to find other methods to solve the above problems, and alloying is one of them. The alloy has stronger dissolution resistance and is relatively cheap. Alloying can improve durability, but it will still be accompanied by corrosion of the metal, which will cause particles to overflow, leading to redeposition and aggregation problems. This phenomenon was found on the PtAu surface of the PtAuCo catalyst, with only 25% loss after 100,000 potential cycles (Tan et al., 2015). Such excellent stability is attributed to the self-healing mechanism of Au to fine-tune the surface electronic structure. Isolated Au with low surface energy can improve the stability of the PtAu surface, thereby mitigating the corrosion and dissolution process of Co (Sasaki et al., 2012).

3 ELECTROCATALYSTS

Electrocatalysts are capable of diminishing the activation energy associated with electrochemical reactions, thereby augmenting the rate of these reactions. In addition, it can improve the efficiency of electrochemical reactions, resulting in higher product output at the same voltage or current. Moreover, some electrocatalysts can promote certain reaction pathways, thereby improving product selectivity and reducing the occurrence of side reactions.

3.1 Platinum Group Metals

The platinum group metals have the characteristics of high melting point, high density, good corrosion resistance, catalytic performance and oxidation resistance, so they are excellent choices for use as electrocatalysts. Platinum group metal electrocatalysts mainly include platinum-based alloys and core-shell structures. The former option has the potential to diminish the utilization of the precious metal platinum and concurrently mitigate the likelihood of catalyst poisoning. The central layer of the latter consists of base metals, while the outer layer comprises platinum. Employed as an electrocatalyst, it exhibits traits such as minimal Pt loading, exceptional endurance, and commendable cost-effectiveness.

3.1.1 Pt Alloy

While Pt exhibits highly efficacious catalytic activity for ORR, its limited abundance and expensive nature have emerged as primary obstacles impeding the advancement of fuel cell technology. Therefore, the use of platinum-based binary alloy or ternary alloy electrocatalyst constitutes an efficacious method to improve both the activity and stability of ORR. Pt-based alloys serve to curtail the consumption of Pt elements while concurrently mitigating the likelihood of catalyst poisoning occurrences, and improving the catalytic efficiency of ORR. Employing the soft template method, Yang et al. successfully engineered Pt-Co nanowire networks that serve as electrocatalysts for ORR (Yang et al., 2016). Tang et al. synthesized ultrafine Pt nanoparticles, doped with minute amounts of Co and modified them on carbon black carrier via modified ethylene glycol reduction and chemical etching techniques (Tang et al., 2019). The uniform distribution of Pt-Co nanoparticles was successfully achieved without the addition of extra surfactants, leading to enhanced catalytic efficacy and stability of the Pt-Co nanoparticles.

3.1.2 Pt-Based Core-Shell Structure

While the fabrication of alloy-type catalysts helps to minimize the financial expenditure of catalysts, the potential loss of metal atoms through dissolution during continuous operation may diminish the catalytic activity of the catalyst. Core-shell Pt-based catalysts exhibit attributes such as low Pt loading, cost-effectiveness, and high durability, thus showcasing broad prospects for application. Core-shell Pt-based catalysts typically consist of two components: the core layer is mainly composed of non-precious metals, while the shell primarily comprises precious metals. The non-precious metal core layer is wrapped by a Pt layer of precious metal. By establishing a thin Pt shell encapsulating the core, the exposed surface area of platinum particles can be effectively augmented, thereby significantly improving the utilization rate of platinum. Owing to the electronic interaction between the core and shell, the existence of different metal clusters accelerates the oxidation of Pt, thus alleviating the dissolution and loss of Pt particles at high electric potential.

G.M.Leteba et al. synthesized binary Pt-Ni nanoparticles via a co-pyrolysis approach and optimized the synthesis parameters, consequently yielding a substantial enhancement in catalytic performance (Leteba et al., 2020). F. Zhou et al. successfully synthesized Pt/C catalyst possessing a core-shell architecture via an one-step self-assembled calcination process (Zhou et al., 2020). In this procedure, commercial platinum carbon underwent treatment with isopropyl alcohol and Nafion. The commercial platinum carbon underwent combustion and decomposition in a nitrogen atmosphere, resulting in the formation of a porous coating devoid of sulfonate. The results show that there is a thin porous layer between Pt particles and Nafion, which effectively improves the performance of the catalyst without affecting the electrical conductivity and oxygen conduction rate.

3.1.3 Pt-Based Nano-Structure

In recent years, researchers have devoted themselves to designing and preparing different Pt nanostructures, including 1D nanowires, 2D nanoplates, and 3D nanoframes. The above-mentioned nanostructures serve to effectively augment the utilization rate of Pt, thereby improving catalytic performance, accelerating electron transfer, and exposing more active sites, shown as Figure 1. It is worth noting that such nanostructures are anisotropic and have stronger crystallinity, allowing the catalyst to remain active for a longer period of time. Ultra-long and ultra-thin platinum nanowires not only facilitate the unimpeded conveyance of electrons, but can also serve as the basic material for forming 2D nanoplates and 3D nanoframes because these nanowires are malleable. Moreover, this will have a more stable structure and larger space, which will help the stable transfer of electrons.

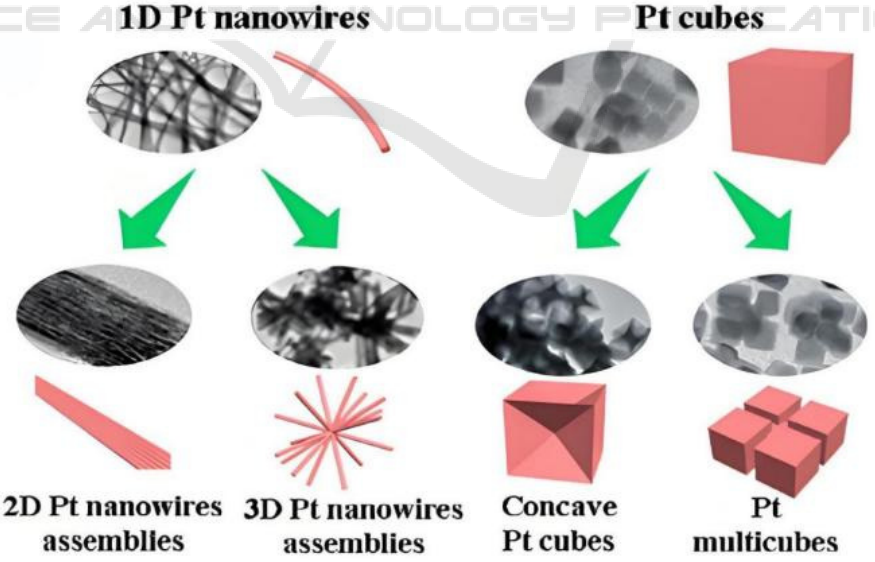

Figure 1: Structure control of Pt catalysts (Huang et al., 2021)

3.2 Transition Metal Electrocatalysts

Nowadays, Pt-based electrocatalysts have been commonly used in ORR, with pronounced initialization and robust half-wave potential. However, it confronts challenges such as elevated costs and limited stability. Consequently, there is an imperative necessity to identify cost-effective non-noble metal catalysts (NPMC) to replace them. Transition metal catalysts are cheap, have high catalytic activity, and have better controllability, thereby achieving precise control of the reaction. More importantly, it has better stability and can maintain its catalytic activity for a long time under reaction conditions, extending the service life of the catalyst.

3.2.1 Carbides

To find a catalyst at a lower cost, metal carbide materials such as tungsten carbide (WC) were initially evaluated. Tungsten carbide possesses surface electronic properties akin to those of metal Pt and is naturally occurring in various formations.

At present, the vast majority of research focuses on its application as an anode electrocatalyst, and has demonstrated exceptional catalytic performance. However, the stability of WC is affected when it encounters acids and high concentrations of oxygen. Therefore, it seems difficult to realize the pristine WC material as an ORR electrocatalyst and utilize it in fuel cell cathodes without changing its composition and structure.

Recently, Yu and his team conducted unbiased structure searches and first-principles calculations for the 2D TiC_2, VC_2, NbC_2, TaC_2 and MoC_2 to comprehensively investigate the electrocatalytic properties (Yu, Zhou and Sun, 2020). Owing to their excellent conductivity, these materials can facilitate rapid charge transfer kinetics in catalytic reactions.

3.2.2 Oxides

Oxides have better stability in acidic, alkaline and oxidising environments than transition metal carbides. As well as demonstrating certain ORR activity in alkaline solutions, however, enhancing their ORR performance remains a formidable challenge. Due to the altered atomic coordination environment and electronic structure of the metal oxides, a certain strain is generated on the catalyst surface, which leads to a significant increase in its adsorption capacity with ORR intermediates. Of these, manganese oxide has garnered considerable interest on account of its cost-effectiveness, environmental protection, polyvalent states and diverse crystal structures. Previous studies have shown that MnO_x activity follows a trend as $Mn_5O_8 < Mn_3O_4 < Mn_2O_3$. This shows that the MnO_x catalyst performance changes with its different crystalline morphology (Chu et al., 2014). Thus, Zhang et al. adopted the method of calcination of manganese glycolate to synthesize Mn_3O_4 with manganese defects. In Mn_3O_4, the change in electronic structure makes it a better conductor. Moreover, Wang and his team prepared a new 3D oriented monolithic integrated electrode. The electrode consists of Fe_3O_4 cores and N-doped C shell composite nanostructure (Wang et al., 2020). Owing to its judicious pore architecture and N-Fe synergy, as well as the optimized combination of metal species modification of the N species catalytic site, the material exhibits considerable ORR activity in acidic solutions.

3.3 Carbon-Based Electrocatalysts

A carbon-based electrocatalyst is a catalyst composed of carbon-based materials that is used to promote electrochemical reactions. The carbon nanotubes, graphene, carbon black, and porous carbon have good electrical conductivity, chemical stability and structural tunability. Compared with transition metal electrocatalysts, carbon-based electrocatalysts have lower raw material costs; they do not contain heavy metal elements and are environmentally friendly.

3.3.1 Metal-Organic Framework Carbon Materials (MOFs)

MOFs represent a novel class of microporous materials, constructed from the assembly of metallic ions and organic linker molecules. The intrinsic porosity of MOFs endows the resulting carbonaceous materials with a wealth of pores and elevated specific surface areas, facilitating enhanced mass transport capabilities and, consequently, manifesting superior electrocatalytic properties (Kalaj et al., 2020). Qiao and colleagues employed a method of dissolve-induced heteronucleation to create layered ordered porous carbon on a polystyrene sphere (PS) template, which was subsequently carbonized to yield a material doped with atomically dispersed FeN_4 (FeN_4/HOPC). Following this, they developed Fe-doped ordered macroporous/microporous ZIF-8 (referred to as OMSFe-ZIF-8) (Xu et al., 2020).

In comparison to monometallic MOFs, bimetallic MOFs exhibit enhanced catalytic performance due to synergistic effects between the incorporated metallic species, thereby demonstrating superior activity. Han et al. successfully prepared a new type of binary Co-Ni sites by pyrolysis of MOFs containing dopamine (DPA) coating. These sites are atomically dispersedly embedded into N-doped hollow carbon nanotubes, showing a highly reactive single-atom dispersed state. At the same time, the synergistic catalytic effect of the bimetallic Co-Ni sites reduces the energy barrier of the reaction and accelerates the reaction. the reaction kinetics. Consequently, it exhibits exceptional ORR performance similar to Pt/C (Han et al., 2019).

4 CONCLUSION AND OUTLOOK

This article comprehensively reviews the research progress of Pt noble metal, transition metal and carbon-based material ORR electrocatalysts and reviews strategies to optimize the catalytic process. Although the ORR mechanism of some materials has been extensively studied, for most emerging materials, the mechanism of ORR remains incompletely elucidated. Therefore, it's urgent to have an in-depth comprehension of the mechanism. Although the overall scientific research strength is increasing, the physical characterization methods are becoming more and more perfect. Some ideal catalysts can be prepared and constructed accurately by in-situ characterization techniques, but there are still some limitations in the study of these catalysts in the field of theoretical calculation. Therefore, in the future, it is necessary to further improve the research capabilities by combining theoretical calculations and experiments on Pt-based catalysts, and explore the ability to operate within a wider pH range. Efficiently working ORR electrocatalyst. All things considered, designing a robust, efficient and eco-friendly electrocatalyst is the current challenge that needs to be solved.

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