Advances in ORR Metal and Non-metal Catalysts at the Anode of PEMFCs

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Abstract. Proton exchange membrane fuel cells (PEMFCs) are distinguished by their high efficiency, zero emissions, high power density, and rapid start-up capability. But here’ s the problem: the cathodic oxygen reduction reaction (ORR) is really slow, and that seriously holds back the overall performance of PEMFCs and their ability to be used commercially. Since ORR catalysts are the key materials that control how fast this reaction goes, they’ve become a major focus of research all over the world. This review systematicly shows the latest progress in ORR catalysts for PEMFCs. First of all, briefly explain the basic reaction mechanisms of ORR in acidic media, as well as the key indicators for evaluating performance. Then, show details about the strategies to improve their performance, like adjusting the electronic structure, designing their morphology and pore structure, engineering interfaces, and optimizing their synthesis process. Finally, current challenges like poor long-term stability and high costs for large-scale production are analysed in the review. Besides, list and analyse the future research directions and prospects for industrial application. All in all, this work aims to provide a timely, systematic reference to help with the rational design, development, and application of high-performance ORR catalysts for PEMFCs.

1 Introduction

A lot of consumption of fossil fuels has emerged as a critical global challenge, largely driven by conventional vehicles that rely on petroleum‑ based fuels and emit substantial amounts of greenhouse gases such as carbon dioxide. This urgent environmental and energy‑ security context has accelerated the global transition toward sustainable energy systems.

Hydrogen energy, envisioned as a cornerstone of the future hydrogen economy, offers a clean and efficient alternative. Proton exchange membrane fuel cells (PEMFCs), often described as the fifth‑ generation fuel cell originally pioneered by General Electric, have gained prominence as a key enabler of hydrogen‑ powered mobility [1]. PEMFCs generate electricity through the electrochemical reaction of hydrogen and oxygen, producing only water and heat as by‑ products, thereby offering a truly zero‑ emission power solution. In recent years, power density, efficiency, durability, and operational lifetime of PEMFC

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systems are improved by researches and studies. A PEMFC usually have four essential components: the proton exchange membrane, the catalyst layers, the gas diffusion layers and so on.

Among these, Cathode of oxygen reduction reaction is the main electrochemical process which can determine overall cell performance. However, ORR has a problem of slow kinetics, so the use of efficient catalysts is highly necessary. Platinum-based noble-metal catalysts are currently the benchmark due to its high activity and stability. Now, their high cost and scarcity become major barriers to the widespread commercialization of PEMFCs. Therefore, developing highly active, durable, and cost-effective alternatives to platinum generally become central research in the field.

This review aims to systematically examine the current state of ORR catalyst research for PEMFCs. It will cover the fundamental reaction mechanisms, established performance evaluation protocols, categories and recent advances in catalyst materials, strategic approaches for performance modulation, advanced characterization and computational tools, as well as potential challenges and future development. By integrating these aspects, this work intends to provide a coherent blueprint for the continued development of high-performance ORR catalysts and their integration into next-generation PEMFC systems.

2 Basic theories and performance evaluation systems of ORR

2.1 Principle of the ORR

The oxygen reduction reaction is the critical cathodic process in proton exchange membrane fuel cells, involving the stepwise reduction of oxygen molecules to water via the acceptance of electrons and protons at the catalyst surface. This reaction mainly happens in one of two ways: either a direct $4e^-$ process, or a $2e^-$ process that's not as efficient and involves peroxide intermediates. In acidic media, the ideal $4e^-$ reaction is written as follows. How efficient this process depends on two key things: breaking the O=O bond, and the simultaneous transfer of protons and electrons. Platinum-based catalysts work really well because they have the ideal binding strength to oxygen and oxygen-containing intermediates—this greatly lowers the reaction energy barrier and makes the reaction go faster. On the platinum-based catalyst surface, the ORR usually starts with O_2 adsorbing onto the active sites. Then, it gets reduced by one electron to form a superoxide-like species (*OOH). This intermediate then goes through more proton-electron transfers. There is a key point where the reaction splits, deciding its selectivity: if it continues along the $4e^-$ process, it leads straight to water. But if *OOH desorbs too early, or gets further reduced, it takes the $2e^-$ process instead, producing H_2O_2 as a by-product. Finally, the H_2O that's made desorbs, and the active site is ready to be used again. The overall activity depends on a mix of factors: the catalyst's electronic structure, the electrolyte's properties (like pH and ion concentration), and interfacial properties between catalyst and electrolyte.

2.2 Key performance metrics for ORR catalysts

Setting up a complete set of performance metrics for ORR catalysts is very significant since it helps with their reasonable development and comparison. After all, their properties directly affect how efficient PEMFCs are, how long they last, and whether they can be used commercially. These metrics can be divided into four main categories.

2.2.1 Electrocatalytic activity

In previous researches, researchers usually measure electrocatalytic activity using parameters like onset potential, half-wave potential, and limiting current density. To assess electrocatalytic activity in prior research, key parameters including half-wave potential, onset potential, and limiting current density were commonly employed. These parameters clearly show the behavior of the catalyst in starting and sustaining the ORR reaction-even under low-overpotential and high-reaction-rate conditions.

2.2.2 Stability and durability

Stability and durability are really crucial for the long-term use of the catalyst. Researchers usually test it with accelerated stress tests, such as continuous potential cycling in cyclic voltammetry, or steady-state tests like chronoamperometry and chronopotentiometry. The key thing researchers look at is the behavior of the catalyst in holding up electrochemical surface area, activity, and structural integrity under simulated actual operating conditions.

2.2.3 Selectivity

Selectivity means that the catalyst prefers the $4e^-$ reaction process that is more efficient, rather than the $2e^-$ process that produces hydrogen H_2O_2. The rotating ring-disk electrode (RRDE) enables the assessment of catalyst selectivity by quantifying the H_2O_2 generated during the reaction via the ring current.

2.3 Structural characterization techniques for ORR catalysts

Structural characterization mainly uses five key techniques. First, the scanning range of Fourier Transform Infrared Spectroscopy can reach from 4000 to 400 centimeters^{-1} and helps identify the surface functional groups of carbon nanotubes. Second, researchers usually use X-ray diffraction to obtain crystal structures, particle sizes, and lattice parameters. Third, transmission electron microscopy is used to observe nanoparticle dispersion, size, and core-shell structures. Fourth, scanning electron microscopy shows us the surface morphology. Fifth, X-ray photoelectron spectroscopy is used to analyse elemental composition of the surface and oxidation state of metals [2].

3 Classification and research progress of ORR catalysts

Given that the reaction kinetics of the ORR at the cathode of PEMFCs is relatively slow, the development of efficient electrocatalysts has attracted considerable attention. Based on their composition, ORR catalysts are typically classified as: noble-metal-based, non-noble-metal-based, and metal-free. Each type exhibits distinct advantages and limitations in terms of mobility and durability. This section focuses on the recent developments in these three categories.

3.1 Noble metal-based catalysts

Among various noble-metal-based catalysts, the Pt and their derivatives are most widely used and thoroughly studied in PEMFCs. It demonstrates an excellent activity and chemical stability in acidic environments [3]. However, noble metals have a high cost, driving the research efforts to reduce their usage and maintaining catalytic activity ate the same time.

3.1.1 Pt-based single-metal catalyst

Pt-based monometallic catalysts are earliest studied and applied in ORR catalysts. It has an optimal binding strength to oxygen and oxygen-containing intermediates (*O, *OH, *OOH) [4]. This can help attract oxygen molecules to its surface and breaking O-O double bonds, so pure Pt nanoparticles supported on carbon materials can help promote the desirable four-electron reaction pathway [3]: $O_2+4H^++4e^-\rightarrow H_2O$ and avoid producing byproduct hydrogen peroxide.

Meanwhile, Pt-based catalysts also have some defects. Firstly, utilization of Pt-atom is relatively very low since ORR reaction can only occur on the surface of Pt, which limits their efficiency. Secondly, Pt belongs to noble metal that has a high cost, so it is difficult to achieve large-scale production and commercial application.

To resolve these issues, existing researches focus on controlling the size, structure, and dispersion of Pt nanoparticles [5]. For instance, nanostructures such as Pt nanowires, nano frames, and ultrafine nanoparticles have been developed to increase the electrochemical surface area. Additionally, catalyst durability can be improved by mixing optimizing carbon with enhanced corrosion resistance and stronger metal – support interactions.

3.1.2 Pt-based alloy catalysts

T The widespread adoption of PEMFCs is limited by two primary challenges: the sluggish kinetics of the ORR and the prohibitive cost of platinum-based catalysts. Therefore, in order to solve these problems, the strategy of alloying Pt with transition metals, rare-earth elements, or constructing high-entropy alloys has become pivotal for enhancing activity, reducing Pt loading, and improving durability [6, 7].

Binary Pt-based alloys show a remarkable performance. Kim et al. reported a carbon layer-protected face-centered tetragonal-PtFe catalyst synthesized via a one-step method, achieving a mass activity of 848 A g^{-1} at 0.9 V and maintaining stability over 30000 cycles, far exceeding the 2025 U.S. DOE target [8]. For high-temperature PEMFCs, Lin et al. developed PtCe alloys, where electron transfer from Ce to Pt mitigates phosphoric acid poisoning, delivering a peak power density of 605 mW cm^{-2} with only 31.6% loss after 30000 cycles [6].

Ternary alloys offer synergistic advantages beyond binary systems. Fang et al. reported that a PtNiFe/C catalyst, when annealed at 800 °C, achieved an impressive peak power density of 1.21 W cm^{-2} a 130% improvement over commercial Pt/C-which they attributed to thermal-treatment-induced lattice shrinkage [9]. He et al. identified PtTiNi, PtTiCu, and PtTiV through combinatorial screening, showing 6-10 times higher activity than pure Pt, highlighting stabilizing role of Ti [9].

High-entropy alloys leverage the "cocktail effect" and lattice distortion for enhanced performance. Shen et al. summarized that Pt-based HEAs prepared via carbothermal shock achieve mass activities 10-15 times higher than Pt/C, with exceptional durability [7]. Despite these advances, several key obstacles remain, such as transition metal leaching, nanoparticle agglomeration [8], and the performance gap between rotating disk electrode (RDE) and membrane electrode assembly (MEA) measurements [7].

In summary, Pt-based alloy catalysts offer effective solutions to key limitations of PEMFC catalysts. Through tailored compositions and synthesis methods, their performance meets or exceeds DOE targets. Future research should focus on scaling up synthesis processes, optimizing MEA integration, and developing corrosion-resistant supports to accelerate commercialization [7, 10].

3.1.3 Other noble metal catalysts

Besides Pt, other noble metals such as Pd have potential to be developed as alternatives for ORR catalysts. Pd-based catalysts are particularly attractive since they have lower cost and electronic structure similar to Pt. These catalysts exhibit moderate activity in alkaline environments but generally show lower activity than Pt‑based systems in the acidic conditions required for PEMFCs. Overall, the comprehensive catalytic efficiency and durability of non-Pt noble-metal catalysts still need to improve to approach lag Pt‑based systems.

3.2 Non-noble metal-based ORR catalysts

Regarded as an alternative for Pt-based catalysts, non-noble metal-based ORR catalysts have been attractive due to its abundance and low cost comparing to Pt-based catalysts. In recent years, their activity and stability have been improved through adjusting their structure, especially M-N-C system.

3.2.1 Transition metal-based catalysts

Among transition metal-based ORR catalysts, Fe-N-C and Co-N-C are currently the most attractive and promising systems [11, 12]. They mainly use iron, cobalt, manganese, and their related compounds to with nitrogen and carbon materials to form active structures.

In these materials, transition metal atoms are anchored within the carbon framework to create active sites [13]. This structure can promote the four‑electron reaction pathway similar to Pt‑based catalysts and provide an optimal binding strength for oxygen and oxygen‑containing intermediates, as a result, achieving high efficiency. In alkaline media, some transition‑metal‑based catalysts can reach catalytic activities similar to those of Pt‑based catalysts.

However, in acidic environment required for PEMFCs, transition-metal-based ORR catalysts arouses problems such as activity degradation under acidic conditions, which currently limits their commercial application.

3.3 Carbon-based non-noble-metal ORR catalysts

Carbon-based non-noble-metal catalysts for the oxygen reduction reaction (ORR) have become promising alternatives to expensive Pt-based materials. These systems are on the basis of conductive carbon substrates like graphite, carbon nanotubes, and porous carbon. They are modified through heteroatom doping strategies. By introducing non-metallic elements such as nitrogen, sulfur, or phosphorus into the carbon lattice, the intrinsic electronic structure and charge distribution of the carbon surface can be effectively modulated. This structural regulation enhances oxygen adsorption and activation, and therefore can improve the overall ORR kinetics.

Among various doped carbon catalysts, nitrogen-doped carbon materials have been the most intensively investigated. Different nitrogen configurations, like pyridinic N and graphitic N, are seen as key active sites responsible for high ORR performance. Such catalysts display remarkable advantages including abundant resources, low cost, excellent electrical conductivity, and strong chemical stability, making them highly competitive in alkaline electrolytes.

For example, Qu et al. prepared nitrogen-doped graphene by annealing graphene oxide in an ammonia atmosphere. The catalyst exhibited an onset potential of approximately −0.19 V (*vs.* Ag/AgCl), a simulating an electric current density comparable to that of commercial platinum/carbon materials [14]. Further analysis verified that pyridinic and graphitic nitrogen species were closely related with the enhanced catalytic activity.

Nevertheless, compared with metal-containing catalysts, purely carbon-based catalysts generally exhibit lower ORR activity in acidic environments and struggle to match the performance of noble-metal catalysts [11]. Therefore, the rational design of active sites and further improvement of catalytic activity and stability still represent major challenges in this field.

The synthesis of carbon-based non-noble-metal ORR catalysts heavily relies on controllable preparation strategies, which directly determine their structure and catalytic performance. Common methods include in-situ doping, post- treatment doping, template-assisted carbonization, and high-temperature pyrolysis. In-situ doping achieves uniform heteroatom introduction by directly pyrolyzing heteroatom- rich precursors such as polymers, biomass, and metal-organic frameworks (MOFs). Post-treatment doping modifies pre-synthesized carbon materials by annealing in reactive atmospheres like NH_3, allowing flexible heteroatom incorporation. To create porous carbon materials with high specific surface area and efficient transport channels, the template method—employing either hard or soft templates-is widely adopted.

Pyrolysis temperature, heating rate, and reaction atmosphere greatly affect the content and configuration of active sites. By optimizing these synthetic parameters, the electronic structure and surface properties of carbon supports can become efficiently regulated. Reasonable preparation design not only increases the density of accessible active sites but also improves electron transfer and oxygen diffusion. In this way, the ORR activity and stability of carbon-based non-noble-metal catalysts can become effectively enhanced, making them more competitive in practical energy conversion devices.

4 Conclusion

Current ORR catalysts for PEMFCs face three major challenges. First of all, noble-metal-based catalysts are constrained by high cost, low atomic utilization, and issues such as transition-metal leaching and particle agglomeration in alloy systems. Then, non-noble-metal and metal-free catalysts don’ t have enough activity or stability in acidic media, so they can’ t really compete with Pt-based catalysts in terms of performance. What’ s more, scalable production is still expensive. There’ s also a performance gap between the results got from lab-scale tests and how these catalysts work when integrated into membrane-electrode-assemblies (MEAs). On top of that, they don’t hold up well under complex operating conditions.

ORR is the main limiting factor for PEMFCs-if one wants to commercialize them, developing high-performance ORR catalysts is absolutely key. Pt-based noble metal catalysts are still the standard for acidic ORR. Strategies like nanostructuring and alloying have helped boost their activity and durability, while also reducing dosage of platinum. But the high cost and metal leaching problems are still there, holding them back.

Non-noble metal catalysts-especially M-N-C ones-and metal-free catalysts are cheaper alternatives, and they work well in alkaline media. But their activity and stability in acidic media are still not good enough to meet the needs of practical use.

Now, the field also has other issues. For example, scalable production is still costly, and there’s a big difference between the performance that were observed in lab tests and how these catalysts perform in real MEA applications. For future research, researchers should focus on a few key areas: advancing high-entropy alloy and single-atom Pt catalysts, optimizing the structure of non-noble metal catalysts, combining AI with in-situ characterization techniques, and developing green synthesis methods.

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

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