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Oxygen Reduction Reaction Catalysts for PEMFCs: Mechanisms, Classification and Optimization Strategies

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Abstract. Proton exchange membrane fuel cells (PEMFCs) are a central technology for the efficient utilization of hydrogen energy, but their performance is fundamentally limited by the sluggish kinetics and high overpotential of the cathode oxygen reduction reaction (ORR). Moreover, the currently used platinum-based catalysts are expensive, suffer from resource scarcity, and are readily poisoned, all of which impede the commercialization of PEMFCs. Hence, this paper provides a thorough review of the reaction mechanisms of ORR. The text first clearly and logically distinguishes four-electron from two-electron pathways and discusses their relevance to fuel cells, then naturally proceeds to summarize and compare the classification, design strategies, and synthesis methods of precious metal and non-precious metal catalysts. More importantly, it systematically presents the key strategies for improving ORR catalyst performance from three well-defined dimensions: microstructure regulation, development of low-platinum/non-precious metal substitutes, and surface engineering/doping modification. Following this, current challenges are analyzed, and future directions are suggested with clear theoretical and technical implications for designing high-performance, low-cost, and highly stable ORR catalysts.

1 Introduction

Achieving global carbon neutrality goals requires hydrogen energy to play a major role as a decarbonization carrier, proton exchange membrane fuel cells (PEMFCs) are central to efficient hydrogen utilization, but their performance is fundamentally limited by the slow kinetics and high overpotential of the cathode oxygen reduction reaction (ORR). Platinum-based catalysts currently used for ORR exhibit exceptional catalytic activity, yet their high cost, scarcity, and tendency to be poisoned by impurities such as carbon monoxide (CO) [1] have all been longstanding and serious barriers to the commercialization of PEMFCs.

Since the existing limitations are well recognized, the current literature on this topic can reasonably and clearly be divided into three distinct directions: first, the precise control of microstructures such as single atoms, double atoms, or nanoclusters to optimize the spatial distribution and electronic properties of active sites, hence improving catalytic reaction

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kinetics [2]. Second, the design of alternative catalysts based on low-platinum alloys or non-precious metals (including transition metal-nitrogen-carbon materials, metal oxides) to minimize platinum dependence and lower costs. Third, the use of surface engineering and doping strategies to modulate the surface composition and lattice structure of catalysts, thereby enhancing their resistance to poisoning and long-term stability [3].

The paper first gives a clear, logical review of the fundamental reaction mechanisms of the ORR, then proceeds to introduce the classification of mainstream ORR catalysts along with their design and synthesis methods, after which it naturally and systematically summarizes the major design and optimization strategies for ORR catalysts, namely microstructure regulation, alternative material development, and surface modification.

The article first reviews the present status and problems of ORR catalysts in practical applications, then logically proceeds to discuss major future challenges and development opportunities, before systematically addressing the balance between catalytic activity, durability, and cost from the viewpoints of material design and reaction mechanisms. Thus, it provides solid theoretical foundations and concrete technical suggestions for the large-scale commercialization of PEMFC technology.

2 A study of the mechanism

Since the ORR reaction mechanism consists of several well-defined steps, it is natural and reasonable to classify the currently prevailing, widely accepted reaction mechanisms in electrocatalysis according to their electron transfer pathways and the adsorption modes of reaction intermediates [4].

2.1 A discussion of four-electron and two-electron reaction pathways

Since the ORR can be reasonably classified according to the number of electrons transferred in the reaction, it is customary to divide the ORR into four-electron and two-electron reduction pathways.

Because the four-electron pathway involves the direct reduction of oxygen molecules to water or hydroxide ions on the catalyst surface by a sequential proton–electron coupling transfer process, it has exceptionally high thermodynamic efficiency and therefore is regarded as the ideal reaction mechanism for fuel cells and metal–air batteries.

Since the two-electron reaction pathway involves only two electrons being transferred and mainly produces hydrogen peroxide or hydroperoxide ion, it utilizes energy less efficiently and can also lead to chemical corrosion of the catalyst and membrane materials; therefore, in PEMFCs, the key goal of ORR catalyst design is to suppress the two-electron pathway and promote the four-electron pathway.

2.2 An introduction to the associative mechanism and the dissociative mechanism.

From the consideration of the adsorption mode of reaction intermediates, it is natural and convenient to classify the ORR into two basic types: the associative mechanism and the dissociative mechanism.

In the associative mechanism, the molecule first adsorbs on the active sites of the catalyst surface in an end-on or side-on fashion to form molecularly adsorbed oxygen species, then undergoes the first proton–electron coupling transfer step to form the essential reaction intermediate *OOH, with the O–O bond still intact at this stage. Both theoretical calculations and experimental data support this sequence.

The formation of *OOH usually involves a high activation energy, hence it is the rate-determining step in the ORR process, after which *OOH undergoes O–O bond cleavage to produce *O and *OH intermediates, which then convert to *OH and the final products via successive proton–electron transfer steps. Because this mechanism does not require O–O bond cleavage during the initial adsorption phase, its energy barrier is relatively low, making it much more universally applicable in low-to-medium temperature electrocatalytic systems. Consequently, it is now widely and firmly accepted that the association mechanism is the dominant reaction pathway for ORR in non-precious metal catalysts, M–N–C catalysts, and single-atom catalyst systems.

Since the dissociation mechanism generally takes place on metal surfaces with a strong adsorption affinity for oxygen molecules, and noble metal catalysts such as Pt and Pd are the best known examples, it is reasonable to describe the mechanism as follows: the molecule adsorbs on the catalyst surface and undergoes direct O–O bond cleavage to form two atomic-state adsorbed oxygen species (2O*), which then proceed through separate proton–electron transfer steps.

Because the formation of *OH proceeds stepwise and eventually leads to water formation, and since direct O–O bond cleavage requires a very high activation energy, the dissociation mechanism is generally thermodynamically and kinetically viable only on catalysts with strong metal–oxygen interactions. Therefore, it does not occur readily in non-precious metal or low-coordination active site systems.

3 Mainstream ORR catalyst classification

3.1 Precious metal catalysts

Metal-based catalysts, especially those based on platinum (Pt) and its alloys, have long been accepted as the performance benchmark for oxygen reduction reactions (ORR), and the reason for their outstanding catalytic activity is well understood: they achieve near-optimal regulation of the adsorption energies of key oxygen intermediates (*OOH, *O, and*OH). By the Sabatier principle, the Pt surface neither overly binds nor repels oxygen species, hence the low reaction energy barrier and excellent kinetic performance in the four-electron reduction pathway. More importantly, density functional theory (DFT) studies have rigorously established that the relative position of Pt's d-band center with respect to the Fermi level directly controls its chemical adsorption strength toward oxygen intermediates, making this the clear electronic structural basis for Pt's high intrinsic activity.

Since the activity and stability of individual Pt nanoparticles in practical catalytic systems are intimately governed by particle size effects, crystal plane exposure, and surface reconstruction behavior, it is well established that different crystal planes (Pt(111), Pt(100), and Pt(110)) have distinct adsorption capacities for *OH, with the Pt(111) plane generally showing the highest ORR activity and selectivity. Therefore, crystal plane regulation and morphology engineering have naturally become two of the most important strategies for improving precious metal catalytic performance: designing nanocubes, nanooctahedra, or high-index crystal plane structures to precisely control the reactive sites.

Since reducing Pt loading and increasing its mass activity are important goals, the research community has quite naturally shifted from single-metal systems to multi-component alloying strategies, and Pt–M(M = Co, Ni, Fe, Cu, etc.) alloy catalysts provide an excellent example of how strain and coordination effects can synergistically modulate Pt's electronic structure: subsurface transition metals cause Pt–Pt bond length compression, which shifts the Pt d-band center downward, thereby weakening *OH adsorption strength and accelerating the late-stage reaction kinetics. More importantly, core–shell structures with

Pt-rich surfaces combine high activity with exceptional durability, making them a clear and highly promising direction for designing precious-metal ORR catalysts.

3.2 Non-precious metal catalysts

Non-Precious metal catalysts are universally recognized as the most promising candidates for the large-scale application of the oxygen reduction reaction (ORR) because they are abundant, inexpensive, and have highly tunable structures. Among various types of precious metal catalysts, those based on transition metal–nitrogen–carbon (M–N–C, M = Fe, Co, Mn, etc.) systems have made the most significant and systematic advances in recent years, with their ORR activity in alkaline media already approaching or exceeding that of commercial Pt/C catalysts. More importantly, both experimental and theoretical studies have convincingly established that atomically dispersed metal–nitrogen coordination structures such as $Fe–N_4$ or $Co–N_4$ are the primary active sites. The unique coordination environment and electronic structure of these sites make them exceptionally suitable for O_2 adsorption and activation.

Since from an electronic point of view the catalytic performance of non-precious metal active sites is governed by the valence state, spin state, and electronic coupling of the metal center with surrounding nitrogen coordination atoms, density functional theory calculations have clearly shown that $M–N_4$ sites can efficiently tune the adsorption energies of important oxygen intermediates such as *OOH.

By controlling the filling of metal d orbitals with *O, and*OH, this approach lowers reaction energy barriers and therefore favors the four-electron reduction pathway. More importantly, unlike precious metal surfaces where activity is mainly governed by metal–metal interactions, non-precious metal catalysts have activity that is intimately tied to their local coordination structures and the electronic conductivity of the supporting carbon framework, which makes the structure–performance relationship much richer and more tunable.

Non-precious metal ORR catalysts are usually prepared by high-temperature pyrolysis methods, and therefore it is natural and accurate to describe their synthesis as follows: metal precursors, nitrogen-containing organic ligands, and carbon sources are carbonized under inert or weakly reducing atmospheres, with metal atoms being directly and uniformly anchored in nitrogen-doped carbon matrices to form stable $M–N_x$ coordination structures.

Although non-precious metal catalysts have clear advantages in cost and tunability, their practical application is hindered by two fundamental problems: first, M–N–C catalysts in acidic media are susceptible to metal center dissolution and coordination structure breakdown, hence their activity decays rapidly. Second, under high potentials or strong oxidation conditions, the carbon support can corrode, which directly compromises the stability of the active sites.

4 Strategies for enhancing ORR catalyst performance

4.1 Microstructural control

Since microstructural control is fundamental to improving catalytic activity and atomic utilization, it is logical and effective to regulate active metal atoms into single atoms, double atoms, or nanoclusters in order to optimize the geometric and electronic environments of active sites. Single-atom catalysts(SACs) achieve almost 100% atomic utilization by forming stable $M–N_4$ or $M–N_2$ C_2 sites with isolated metal atoms coordinated to nitrogen or carbon atoms.

The text presents a clear and concise way to discuss the precise control of the adsorption energies of *OOH,*O, and*OH species, and then naturally leads into the main result: a single-atom catalyst anchored on a double-vacancy defect in graphene shows excellent synergistic regulation of the electronic structure and catalytic activity by nitrogen-boron co-coordination. As a result, the Co-N_2 B_2 , Pd-N_2 B_2 ， and Pt-N_2 B_2 structures exhibit greatly enhanced ORR activity with overpotentials as low as 0.46 – 0.58 V.

The present discussion begins with the level of noble metal platinum surfaces (0.45 V), but it is immediately and appropriately noted that insufficient consideration of solvation effects and dynamic interfacial processes limits the generalizability of the results to practical systems [5]. Binary or bimetallic synergistic sites are shown to utilize metal–metal electronic coupling and cooperative interactions to lower the O–O bond activation energy and thus improve multi-electron transfer efficiency [6]. Nanocluster structures combine high active site density with precise control over the catalyst's electronic structure via modulation of size and exposed crystal planes, therefore achieving an excellent balance between activity and stability [7]. Consequently, careful control of metal species dispersion, coordination environment, and support pore structure can lead to significantly enhanced catalytic performance [8].

4.2 Development of low-platinum alloys and non-precious metal catalysts

Because reducing precious metal consumption and lowering costs are important goals, researchers have made significant efforts in developing low-platinum alloys and non-precious metal-based catalysts: Low-platinum alloys such as Pt–Co, Pt–Ni modulate Pt's d-band centers via strain and coordination effects, thereby optimizing the intermediate adsorption energy and thus improving both mass activity and four-electron reduction selectivity. Non-precious metal catalysts are most commonly represented by transition metal–nitrogen–carbon (M–N–C) materials.

Transition metal oxides, hydroxides, and their composites can be studied in the context of atomically dispersed M–N–C sites, which allow precise control of electronic structures and therefore greatly enhance O_2 activation and *OOH intermediate formation efficiency. Importantly, recent work has shown that FeN_4 sites anchored on different carbon supports (graphene, armchair-type, and zigzag-type carbon nanotubes) exhibit different behavior depending on the carbon support structure and relative orientation of the FeN_4 fragments.

The Fe in FeN_4 supported on zigzag CNTs does not merely affect the activity of the metal center but actually activates adjacent carbon dimer(C_2)sites as independent catalytic centers [9]. Therefore, Fe in FeN_4 supported on zigzag CNTs has lower electropositivity and weaker O_2 adsorption, and most importantly, its CO adsorption is endothermic($\Delta G>0$), which makes it inherently CO tolerant. In sharp contrast, Fe centers on armchair CNTs and graphene are prone to irreversible CO poisoning.

Because the armchair-type CNTs have a C_2 site adjacent to FeN_4 that acts as an independent catalytic site for ORR owing to its enhanced π-bond character, this site exhibits an overpotential lower than that of the metal center itself. All the systems considered prefer the 4-electron pathway in the reaction mechanism. More importantly, the present work provides a clear, atomic-scale analysis of the intermediate stability, leading naturally to the conclusion about the rational design of the support structure.

The orientation of the metal center can be used to synergistically optimize both the activity and anti-poisoning capability of Fe-N-C catalysts, thereby naturally leading to the discovery of the catalytic potential of non-metallic C_2 sites, which in turn provides a clear path for designing highly stable, anti-poisoning non-precious metal catalysts. More importantly, oxide and hydroxide materials facilitate electron transfer via variable-valent metal centers, resulting in excellent ORR activity in alkaline media. Combining multiple metals or tuning electronic structures allows non-precious metal systems to achieve an optimal balance among cost, stability, and activity.

4.3 Surface engineering and doping modification

Face engineering and doping modification are two well-established and effective ways to tune the electronic structure, active site exposure, and interfacial properties of a catalyst, and indeed, doping heteroatoms (e. g., N, B, S, P) or introducing surface defects allows precise control over the charge distribution and spin density of carbon supports or metal centers, which in turn optimizes the adsorption energy and reaction pathways for oxygen intermediates. Notably, phosphorus (P) and sulfur (S) have shown excellent performance in this regard.

Doping allows very effective control over pathway selectivity in oxygen reduction reactions (ORR) for nitrogen-doped hollow mesoporous carbon spheres (N-HMCS), and hence it has been clearly established that introducing P to form N, P-HMCS increases the proportion of graphitic N and generates electron-rich C-P bond domains, which weaken the adsorption of the *OOH intermediate and promote its desorption to form H_2O_2, thereby dominating the $2e^-$ pathway.

The introduction of sulfur (to form N, S-HMCS) increases the pyridinic nitrogen content and generates electron-deficient C-S bond domains, therefore enhancing *OOH adsorption and facilitating O-O bond cleavage, which in turn favors the $4e^-$ pathway. More importantly, DFT calculations clearly and unambiguously show that the adsorption energy of*OOH on the C-P bond (-0.45 eV) is much lower than that on the C-S bond (-0.77 eV), perfectly matching the experimental selectivity [10].

Because strategies such as surface coating, oxidation treatment, and crystal plane exposure control can be used to optimally modify the catalyst's surface composition and lattice structure, they are very effective in enhancing corrosion resistance, suppressing metal agglomeration or dissolution, and therefore improving long-term stability. More recently, MOF-derived carbon supports and high-index crystal plane control have been extensively applied to modulate surface structures for synergistic optimization of activity and durability.

4.4 Analysis of the problems and future prospects

Although precious metal catalysts have excellent performance, their high cost and scarcity of resources are formidable problems, so non-precious metal catalysts based on M–N–C materials show great substitution potential in alkaline media, but further breakthroughs are required in stability, active site density, and mass transfer efficiency in acidic environments.

Future research should combine in situ characterization with theoretical calculations to clearly determine the dynamic evolution and deactivation mechanisms of active sites under complex conditions, and at the same time, develop novel non-precious metal and non-platinum group metal catalysts — a broad class including multi-component alloys, intermetallic compounds, and carbon-based metal-free catalysts—a major research goal. With concerted efforts across disciplines and strong industry-academia-research collaborations, breakthroughs in ORR catalyst activity, stability, and cost are within reach, which will directly accelerate the commercialization of PEMFC technology.

5 Conclusion

Since ORR catalysts are fundamental to PEMFC performance, cost, and durability, the literature already has notable achievements in microstructure regulation, low-platinum/non-precious metal substitution, and surface engineering, but it is also clear that cost, stability, and durability in acidic media remain major challenges. Therefore, future work should promote multidisciplinary collaboration and strengthen industry-academia-research partnerships to develop high-performance, low-cost, and highly stable catalysts, thereby accelerating fuel cell commercialization.

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