

Design Progress of Advanced Carbon Materials in Oxygen Reduction Electrocatalysis

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Abstract

The oxygen reduction reaction (ORR) was the kinetic bottleneck in energy devices such as fuel cells and metal-air batteries. Carbon-based catalysts were considered promising alternatives to noble-metal catalysts because low cost, structural tunability, and corrosion resistance were achieved. However, the nature of the active sites and the mechanisms governing durability were not fully clarified. In this work, recent progress in mechanistic studies and material design of carbon-based ORR catalysts was systematically reviewed. The catalysts were discussed by material category, including pristine carbon, defect-rich and hierarchical porous carbon, heteroatom-doped carbon, and carbon-supported single- and dual-atom catalysts (SACs/DACs). For each category, the relationships among active-site structure, electronic properties, and catalytic performance were summarized, and key structure-activity trends were identified. Practical design rules were extracted from reported studies. Active-site engineering strategies were emphasized, such as the construction of M-N₄ motifs and synergistic Fe-Co dual-atom centers. In addition, multiscale pore architectures were highlighted because mass transport was improved through hierarchical channels. Durability challenges were further analyzed under conditions that were relevant to real devices. Design considerations were provided for operation at high current density and in complex electrolyte environments, where carbon corrosion, metal leaching, and interface degradation were often accelerated. Interfacial engineering was also discussed as a route to stabilize active centers and to maintain efficient charge and reactant transport. Overall, the conclusions are generally applicable: ORR activity is governed by the local coordination and electronic structure of carbon-based active sites, and stability is determined by coupled chemical and transport processes at the catalyst-electrolyte interface. This review aims to bridge mechanistic understanding and engineering-oriented design, and to promote the translation of carbon-based ORR catalysts from fundamental research to practical application.

Keywords: oxygen reduction reaction; electrocatalyst; carbon materials; stability mechanism; interfacial engineering

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I. Introduction

The oxygen reduction reaction (ORR) is a key process in many energy conversion systems, such as fuel cells, metal-air batteries, and other electrochemical energy devices [1]. The reaction kinetics of ORR are generally slow, especially in acidic or alkaline environments, making efficient catalysts essential to enhance the reaction rate [2]. Although platinum and its alloys are widely used in ORR, their high cost, scarcity, and limited durability hinder their application in large-scale energy systems [3].

In recent years, carbon-based catalysts have emerged as promising alternatives to precious metal catalysts due to their low cost, excellent conductivity, and structural tunability [4]. The research focus has gradually shifted from using carbon merely as a support to designing carbon as the active center itself. Key strategies include heteroatom doping, defect engineering, and pore structure control. The introduction of heteroatoms such as N, B, S, and P can effectively modify the charge distribution and spin density of the carbon framework, creating more active sites for adsorption and activation. Meanwhile, edge defects, vacancies, and topological distortions can alter the local electronic states and improve reaction kinetics. Additionally, constructing hierarchical pore structures and high specific surface areas not only increases the number of exposed active sites but also promotes mass transfer of reactants and desorption of intermediates, thereby enhancing catalytic activity, selectivity, and stability.

Against this backdrop, establishing a clear relationship between macroscopic structure and microscopic electronic properties, and achieving precise control over active site preparation, have become key challenges for the practical application of high-performance carbon-based catalysts. In ORR, the activity of carbon-based catalysts mainly depends on their surface structure, electronic structure, and their interaction with reactants, which has become a major focus in catalyst design [5, 6].

This review first outlines several types of carbon-based catalysts and how structural design can

improve their catalytic performance. It highlights the advantages and challenges in structural design within ORR systems. Furthermore, it systematically summarizes recent advances in carbon-based electrocatalysts for ORR. The discussion focuses on structural design, electronic structure regulation, and their impact on ORR catalytic performance. Finally, it points out existing challenges and future research directions.

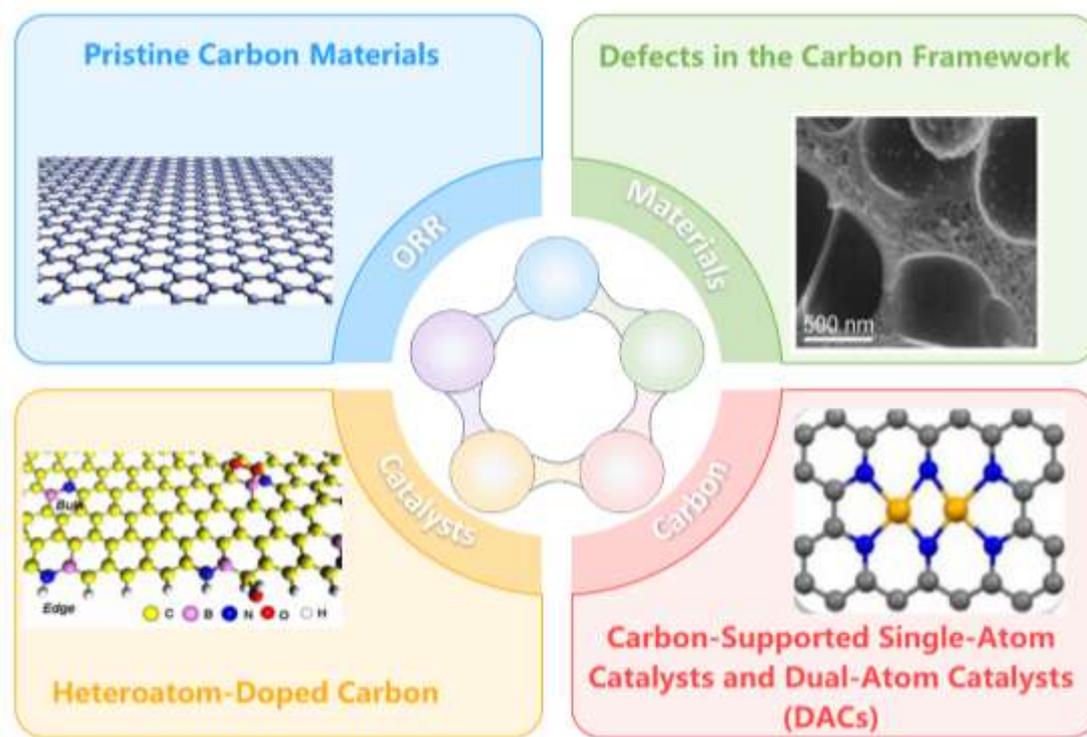


Fig. 1. Schematic illustrations of several common structures of carbon-based electrocatalysts.

II. The structural features and limitations of pure carbon materials in the oxygen reduction reaction

The oxygen reduction reaction (ORR) primarily follows two pathways: the 4-electron path ($O_2 \rightarrow 4 OH^-$ or $2 H_2O$) and the 2-electron path ($O_2 \rightarrow H_2O_2$). The reaction's overpotential (η) is largely determined by the free energy changes during the adsorption, transformation, and desorption of key intermediates such as O, OH, and OOH^* . If these intermediates bind too strongly or too weakly, the overall catalytic rate can be limited.

Due to their high conductivity, stability, and structural tunability, pristine carbon materials—such as graphene, carbon nanotubes, and activated carbon—are widely studied as electrocatalyst supports for the ORR. Graphene, with its two-dimensional sp^2 -hybridized carbon network and fully conjugated π -electron system, is even considered an ideal model carbon material. However, when used as the main catalytic component, pristine graphene typically shows negligible ORR activity. This limited catalytic performance stems primarily from its perfect basal-plane structure. In an ideal graphene lattice, all carbon atoms are fully coordinated, forming a delocalized π -electron system that interacts only weakly with oxygen molecules and ORR intermediates. The lack of unsaturated carbon atoms, structural defects, or electronic perturbations leads to insufficient adsorption strength for key intermediates like O_2 , OOH , and OH, thereby hindering reaction kinetics. Systematic experiments by J.-H. Zhong et al. showed that the density of states near the Dirac point of perfect monolayer graphene approaches zero, resulting in extremely low electrochemical activity. Their work demonstrated a strong correlation between graphene's electrochemical activity and its defect density—introducing defects can significantly enhance catalytic performance, which directly supports the theory that intact graphene surfaces lack active sites [8]. After introducing defects (such as vacancies or 5-/7-membered-ring distortions), the adsorption free energies ΔG_{O^*} and ΔG_{OOH^*} clearly decrease, improving activity. Yuan et al. provided a straightforward comparison between the “perfect basal structure with full coordination and a delocalized π system” and the “likely higher reactivity of edge/defect sites” [9]. Their study explicitly noted that the basal plane is a 2D conjugated sp^2 network, while edges contain dangling bonds/terminal groups. The report highlighted that “edge performance is significantly stronger than that of the basal plane,” confirming the conclusion that “the ideal π -conjugated basal plane has weak ability to adsorb/activate O_2 ” (Figs. 3a, 3b).

Furthermore, experimental evidence indicates that the apparent electrocatalytic activity often reported for graphene-based materials may originate from trace metal impurities rather than the intrinsic carbon framework [10]. When ultra-pure graphene is used and metal contaminants are carefully removed, data show that pristine graphene exhibits almost no activity for ORR and other electrochemical reactions (e.g., the hydrogen evolution reaction, HER). In contrast, graphene samples containing trace transition metals (e.g., iron or nickel at ppm levels) display significant electrochemical responses, clearly indicating that these metal species dominate the observed catalytic behavior. This finding convincingly demonstrates that an intact π -conjugated graphene network lacks effective intrinsic active sites.

Metal contamination can also be unintentionally introduced during graphene synthesis and processing. In particular, chemical vapor deposition (CVD) growth on metal substrates followed by transfer steps can leave residual metal species embedded in or adsorbed onto the graphene lattice. The work of Ambrosi et al. provides direct evidence that “transfer steps readily introduce metal impurities and alter electrochemical properties” [13]. These residual metals can act as highly active ORR sites, leading to misinterpretations of so-called “metal-free” carbon catalysis. Such effects underscore the necessity of stringent impurity control when evaluating the intrinsic activity of pristine carbon materials (Fig. 3c).

Similar limitations exist in other pure carbon structures. Although carbon nanotubes possess excellent conductivity and mechanical strength, their pristine graphitic sidewalls offer limited intrinsic

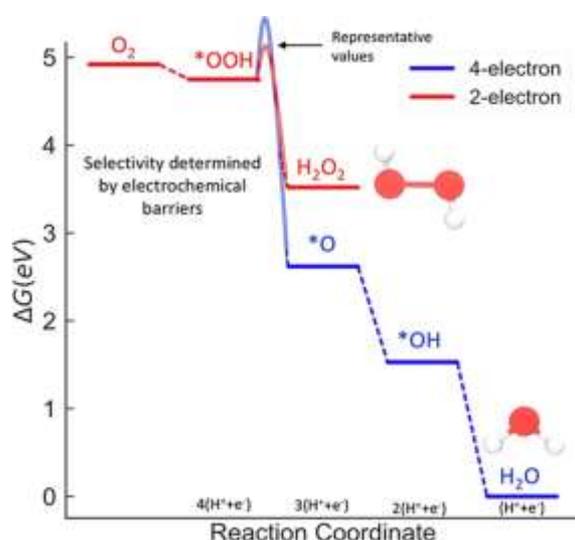
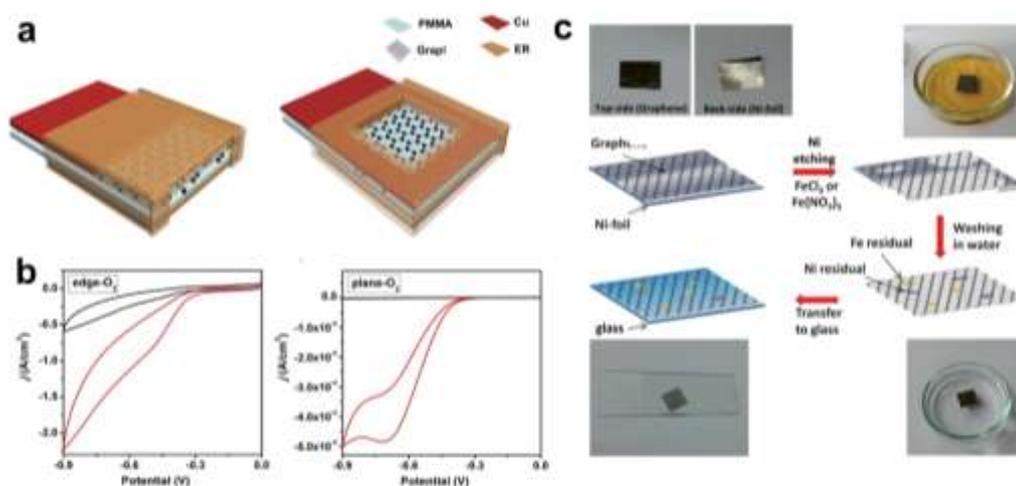


Fig 2. Free-energy diagrams for the four-electron and two-electron oxygen reduction pathways [7].



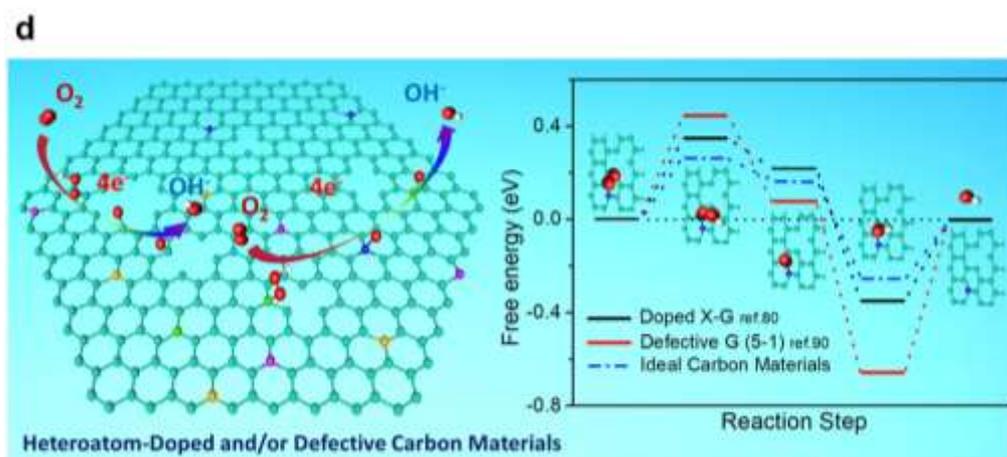


Fig 3. Structural limitations of pristine carbon materials in ORR and “engineered active-site” strategies(a) Schematic illustration of the basal plane and edge regions of monolayer graphene and the corresponding electrode configurations.(b) Comparison of the electrochemical responses of O_2 on graphene edge and basal-plane electrodes, showing the intrinsically low ORR activity on the basal plane and the higher electrocatalytic reactivity at edges/defects.(c) Schematic of possible introduction of residual metals (e.g., Fe/Ni/Cu) during the growth of CVD graphene on metal substrates and the subsequent transfer process [11].(d) Overall roadmap for constructing active centers capable of adsorbing and activating O_2 /ORR intermediates via structural engineering approaches such as defect creation, heteroatom doping, and edge/curvature modulation [12].

ORR activity. Experimental studies show that the ORR performance of carbon-nanotube-based materials is mainly associated with surface defects, edge sites, or oxygen-containing functional groups introduced through oxidation/post-treatment, rather than the intact carbon lattice itself. Likewise, activated carbon has a high specific surface area and abundant pore structure, which are beneficial for mass transport; however, without deliberate structural modification, its intrinsic ORR activity remains quite limited. Only after creating defects or performing chemical activation does activated carbon exhibit significantly enhanced electrocatalytic performance.

In summary, pristine carbon materials possess excellent physical properties but generally lack well-defined intrinsic active sites for efficient ORR. To make ideal carbon frameworks catalytic, structural engineering strategies—such as introducing defects, heteroatom doping, or curvature/edge modulation—are required to create active centers capable of effectively adsorbing and activating oxygen molecules. “Engineered carbon materials” (e.g., doped or defect-modified) represent an important direction for improving their catalytic performance.

III. Defect Engineering Strategies for Carbon Materials

After recognizing that pristine carbon lattices lack inherent active sites for oxygen reduction, defect engineering has emerged as a key strategy to activate carbon frameworks for ORR. Carbon defects—including vacancies, edge sites, topological defects, and curvature-induced distortions—break the perfect sp^2 conjugation in ideal carbon networks and generate localized electronic states that can serve as catalytic active centers. Common approaches to enhance the activity of carbon-based catalysts involve introducing structural defects (such as vacancies, 5-/7-membered-ring distortions, and edge sites) or creating high-surface-area, porous architectures. These defects not only increase the density of active sites but also modify the electronic structure of the support, thereby strengthening adsorption of O_2 and intermediates like OH^* and OOH^* . Sites at defect regions exhibit lower ΔG values compared to perfect graphene, leading to improved ORR activity [14]. Porous structures also enhance electrolyte diffusion pathways, helping catalysts achieve higher current densities in experiments (Fig. 3d). For example, H. Xia et al. found that the coupling between carbon vacancies and adjacent pentagonal structures significantly increases charge-transfer efficiency and effectively lowers the energy barrier for ORR. This synergistic effect substantially enhances catalytic performance over that of a simple pentagonal structure [15]. Similarly, G. P. Chen et al. demonstrated that carbon catalysts containing pentagonal rings show significantly boosted ORR activity due to spin localization effects in pentagonal rings. The singly occupied molecular orbital (SOMO) structure with low-energy π -orbitals effectively promotes oxygen adsorption [16].

Introducing heteroatoms (such as N, B, P, S, F) or metal dopants into the carbon network is a powerful way to fine-tune its electronic structure. Taking nitrogen-doped graphene as an example, nitrogen atoms donate extra electrons to the carbon framework, enhance its ability to support active sites, and strengthen interactions

with O_2 or OH^* , ultimately boosting catalytic activity [17]. Other dopants like B, P, and S have also been shown to alter the carbon lattice's electron density, hole characteristics, and adsorption behavior [18]. By adding heteroatoms, the electronic structure of the carbon network is rearranged, which in turn affects how oxygen molecules are adsorbed and activated. When the dopant introduces a suitable electron density, the barriers for O_2 adsorption and OOH^* conversion are lowered—a key factor for improving ORR performance. Research by X.-B. Ding et al. confirmed that doping carbon materials with multiple non-metal heteroatoms can significantly enhance catalytic activity. Theoretical calculations reveal that sulfur (S) and phosphorus (P) doping generate more active sites, promote the formation of the peroxo-type intermediate (OOH^*), regulate the adsorption energies of oxygen-containing intermediates, and lower the thermodynamic limiting potential [19]. When nitrogen atoms are bonded to two carbon atoms, the resulting active catalytic sites can match the performance of nitrogen-doped graphene catalysts. This demonstrates that heteroatom doping modifies the adsorption mode of O_2 by inducing charge transfer [20]. In recent years, single-atom catalysts (SACs) have become a cutting-edge topic in catalysis due to their atom-scale active sites, ultra-high atomic utilization, and tunable electronic structures. A typical example is the M–N–C structure, where metal atoms (e.g., Fe, Co, Ni) are anchored in a nitrogen-doped carbon network, forming M–N₄ active centers. Peng Zhang et al. developed a highly efficient hierarchical porous Fe single-atom catalyst with Fe atoms densely situated in micropores and mesopores. It achieved a half-wave potential of 0.94 V and a turnover frequency of $5.99 e^- 1 s^- 1 site^- 1$ at 0.80 V. Theoretical simulations revealed that structural heterogeneity induces optimization: mesoporous Fe–N₄

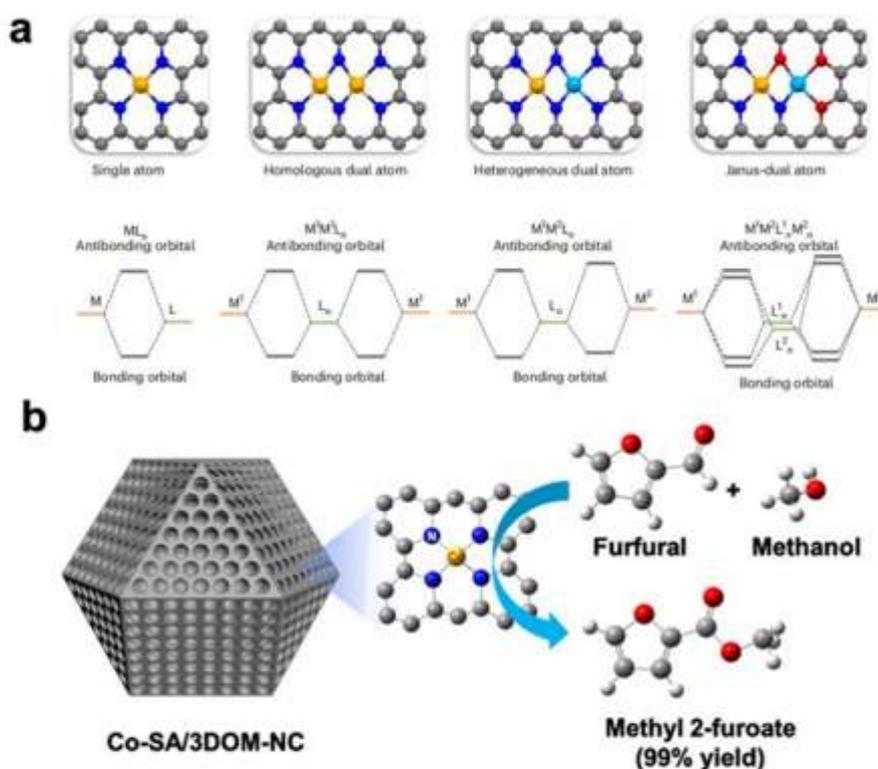


Fig 4. Electrochemical performance of the prepared catalysts.(a) LSV curves of the prepared catalysts in 0.1 M KOH.(b) Alkaline kinetic current density (J_k) at 0.90 V and the half-wave potential ($E_{1/2}$) of the catalysts.(c) Alkaline accelerated durability test (ADT) of Fe-SAs-HP.(d) Comparison of the alkaline ORR performance of Fe-SAs-HP with previously reported catalysts.(e) Polarization curves of the prepared catalysts with different pore structures measured using the GDE method.(f) Potential–current density plots of the prepared catalysts from (e) on a logarithmic current scale [21].

sites act as the real active centers, benefiting from long-range electronic regulation by nearby microporous sites. This work sheds light on the dynamic evolution of iron in porous structures and provides a pathway for designing efficient catalysts for practical applications. Dual-atom catalysts (DACs) go a step further by introducing synergy between two metal atoms, improving the balance between adsorption and desorption, and thus boosting catalytic activity. Bimetallic active centers on

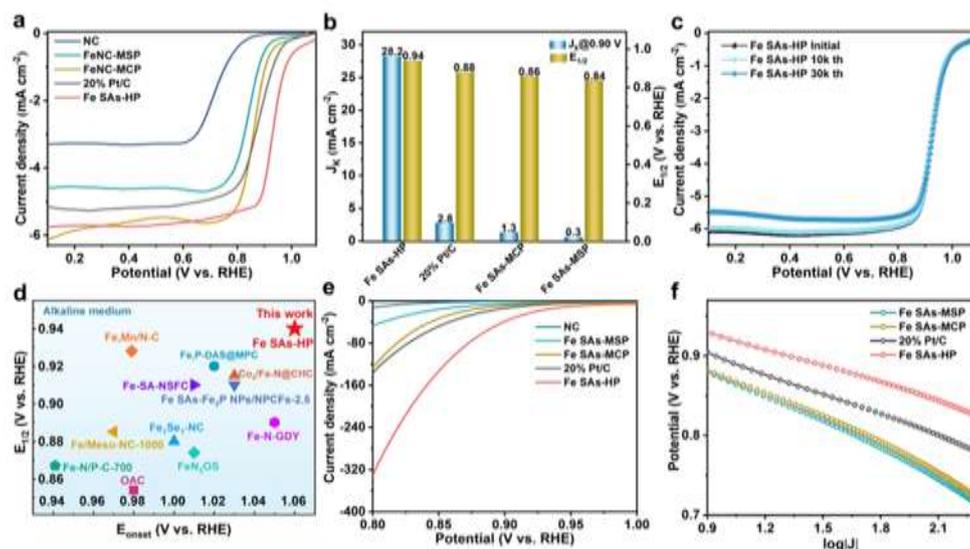


Fig 5. (a) Schematic illustration of the Janus dual-atom catalyst structure. (b) Schematic illustration of the ordered macroporous carbon support structure.

carbon supports can further lower the overpotential (η). For carbon-supported SAC/DAC systems, factors such as structure, coordination environment, and carrier interactions are decisive for catalytic performance. Bing Tang et al. prepared a Janus-type dual-atom catalyst that clearly shows the precise coordination environment of the two metal sites. This catalyst contains paired Fe–Co atoms coordinated by nitrogen and oxygen atoms, linked by bridging nitrogen and oxygen atoms (FeCo–N₃O₃@C). The Janus FeCo–N₃O₃@C quaternary dimer is a stable and highly efficient bifunctional catalyst for both the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) [22].

Hierarchical pore structures refer to materials that contain pores of different sizes, typically including micropores (diameter < 2 nm), mesopores (diameter 2–50 nm), and macropores (diameter > 50 nm). Each pore-size range plays a distinct role in meeting different functional needs. Carbon-based materials with hierarchical pores, thanks to their unique pore distribution and tunable pore structures, can significantly improve catalytic performance. In oxygen reduction reaction (ORR), for example, hierarchical pore structures enhance the transport of reactants and improve the exposure of active sites, leading to higher catalytic efficiency (Fig. 5b).

Different categories of carbon-based materials offer distinct advantages: Pure carbon provides a robust supporting platform. Defective/porous carbon enhances catalytic potential by creating activated sites. Doped carbon tunes electronic structure to strengthen adsorption and activation. Carbon-supported SAC/DAC enables efficient catalysis through well-defined active centers.

For ORR, these structural features directly influence electronic structure analysis and catalytic mechanisms. When discussing the mechanism of carbon-based catalysts for ORR, precise analysis will be conducted based on these structural systems.

Based on the structural features described above [23] [24], designing high-performance carbon-based catalysts focuses on two main areas:

(1) Engineering active sites at the atomic scale:

The key here is precisely tailoring the local environment around the active sites. Studies show that creating dual-atom sites (such as Fe–Co pairs) can strongly influence electronic interactions between the metal atoms. This tunes the d-band center effectively, significantly boosting the adsorption of reaction intermediates and overcoming limitations of single-atom active sites [25]. In addition, heteroatom doping (e.g., with pyridinic or graphitic nitrogen) can adjust the electron density of the sp²-hybridized carbon framework, creating intrinsic non-metal active centers. [26]

(2) Engineering the carbon support at nano- and micro-scales:

Even with highly active sites, catalysts cannot perform well if those sites are trapped inside micropores and cannot be reached by reactants. That's why building a three-dimensional interconnected pore network is crucial. An ideal architecture works like this:

Macropores (> 50 nm) act as "express lanes" for fast transport of reactants.

Mesopores (2–50 nm) promote ion diffusion through the particles.

Micropores (< 2 nm) provide a huge surface area to host a high density of active sites.

This structure ensures both high accessibility of the active sites and continuous pathways for electron conduction. [27]

IV. Challenges for Carbon-Based Catalysts

For carbon-based catalysts, improving activity in theory is important, but stability is equally critical. These catalysts face serious stability issues at high current densities or in complex electrolyte environments. The degradation of the carbon support in the cathode catalyst layer is a major durability problem in PEMFCs, and electrochemical oxidation from carbon corrosion is a key reason for this degradation. Corrosion of the carbon support leads to loss of electrode porosity and collapse of the pore structure, which in turn causes thinning of the catalyst layer, changes in ion distribution, and increased contact resistance. Second, performance degradation at high current densities: at industrial-level current densities, carbon-based catalysts typically show poor durability. While heteroatom doping can improve catalytic performance, dopants in the carbon material gradually leach out during long-term testing at high current densities, leading to performance decline. This is mainly because the doped carbon structures undergo hydrogenation and reconstruction, making it difficult for dopants to remain stable. For example, Y. Guo, J. et al. systematically discussed how metal–support interactions (MSIs) play a key role in determining the stability and performance of supported catalysts. The study introduces the concept of covalent metal–support interaction (CMSI), referring to covalent bonding between individual metal atoms and the support surface. By quantifying these interactions, the stability of the catalyst can be predicted. L. He, C. et al. emphasize that strong bonds must form between individual atoms and the support to prevent single atoms from clustering. Studies show that MSIs not only affect the stability of single atoms but also change the nature of the binding sites and the reactions they can catalyze. At industrial current densities, carbon-based catalysts usually exhibit poor durability. Although heteroatom doping can boost catalytic performance, dopants gradually leach out during long-term, high-current testing, leading to performance decay. Additionally, issues like catalyst support corrosion, migration of active sites, and particle agglomeration need close attention in industrial applications. Moving carbon-based catalysts into practical devices (like fuel cells, metal–air batteries, and water electrolyzers) also requires considering cost, use of renewable materials, and environmentally friendly recycling. Carbon materials themselves are low-cost and structurally tunable, but if the preparation process is too complex or the active-site density is too low, their cost-effectiveness can suffer. M. Gong, A. et al. reported a Co–N/C catalyst with a high cobalt content (3 wt%). Extended X-ray absorption fine structure analysis confirmed the structure of the cobalt–tetrapyrroline–N–C catalyst. Quantified via a nitrite-stripping method, the catalyst showed excellent ORR activity in a rotating ring–disk electrode setup, achieving a half-wave potential of 0.76 V at a low loading of 0.2 mg cm⁻² and a mass activity of 3.5 A g⁻¹ at 0.80 V. Single-cell H₂/O₂ PEMFC tests delivered a peak power density exceeding 1.3 W cm⁻² under H₂–air conditions. At 0.60 V, the output current reached 0.54 A cm⁻². Although iron-based catalysts can have higher turnover frequencies, the optimized Co–N/C catalyst achieved fuel-cell performance similar to Fe–N/C, highlighting the key role of active-site density in overall activity and stability [28-39].

V. Conclusion and Outlook

Focusing on the kinetic bottlenecks of the oxygen reduction reaction in fuel cells and metal–air batteries, this review organizes the research progress in transitioning carbon-based electrocatalysts from "carbon as a support" to "carbon as an active center." It summarizes the design logic and practical guidelines for the structure–electronic–catalytic performance relationship. While pristine carbon materials possess limited intrinsic activity, defect engineering—through vacancies, edges, or topological distortions—can introduce localized electronic states, enhance adsorption of key intermediates, and improve reaction kinetics. Heteroatom doping, on the other hand, tunes charge distribution and spin density to create sites that more readily adsorb and activate oxygen molecules. When combined with hierarchical pore structures for mass transport, these strategies offer a promising path toward balanced performance. Looking ahead, future efforts should focus on establishing quantifiable structure–property relationships that link macroscopic architectures with microscopic electronic structures, enabling precise control and reproducible fabrication of active sites. At the same time, addressing stability challenges—such as carbon corrosion, dopant leaching, and site migration/agglomeration—under industrial-level current densities and complex electrolyte environments is critical. Cost-effectiveness and sustainable recyclability must also be considered to advance carbon-based catalysts from mechanistic

understanding toward practical application.

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