

Rational design of carbon-based metal-free electrocatalyst architectures for selective oxygen reduction reaction: From structure–performance correlations to predictive strategies

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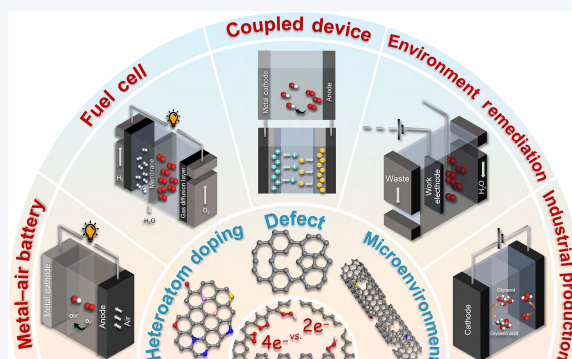


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ABSTRACT: The escalating energy crisis and environmental pollution necessitate the development of clean energy technologies and remediation strategies, wherein the oxygen reduction reaction (ORR) plays a dual role. It is central to the efficiency of fuel cells and metal–air batteries and enables the green electrosynthesis of hydrogen peroxide (H₂O₂). However, the intrinsic competition between these pathways limits practical applications: The four-electron (4e[−]) pathway requires suppression of H₂O₂ byproduct, while the two-electron (2e[−]) pathway demands avoidance of O–O bond cleavage for high H₂O₂ selectivity. Carbon-based metal-free electrocatalysts (CMFECs) have emerged as promising candidates for regulating

ORR selectivity due to their low cost, structural tunability, and excellent stability. This review focuses on the rational design of these catalysts through multiscale structural engineering, systematically discussing three primary strategies: heteroatom doping, defect engineering, and microenvironment modulation of active sites. We first elucidate the mechanistic origins of ORR activity and selectivity, introducing key theoretical descriptors based on the adsorption free energies of intermediates *OH and *OOH (ΔG_{OH} and ΔG_{OOH}). Subsequently, we provide an in-depth analysis of how specific structural motifs—such as pyridinic nitrogen, pentagonal defects, and hierarchical pores—modulate the local electronic structure and mass transport to govern reaction pathways. By integrating theoretical calculations with *in-situ* characterization, we aim to establish clear structure–performance relationships, shifting catalyst design from empirical trial-and-error toward rational paradigms. Finally, we highlight the frontier applications of these catalysts in energy storage, H₂O₂ production, and *in-situ* environmental remediation. Current challenges and future directions, including advanced characterization, multiscale simulations, and machine-learning-assisted design, are also discussed.

KEYWORDS: electrocatalytic oxygen reduction reaction, activity and selectivity, carbon-based metal-free electrocatalysts, structural engineering, structure–performance relationship



1 Introduction

Against the backdrop of increasingly severe global energy crisis and

environmental pollution, the development of clean energy technologies and environmental remediation strategies has become crucial for addressing sustainable development challenges [1]. The electrocatalytic oxygen reduction reaction (ORR), which proceeds via four-electron (4e[−]) or two-electron (2e[−]) mechanisms, plays a pivotal role in renewable energy conversion technologies and several important chemical processes [2, 3]. It is generally accepted that the ORR proceeds via two distinct pathways: the 4e[−] and the 2e[−] pathways. The 4e[−] pathway, producing water as the final product, exhibits higher energy efficiency by utilizing more

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electrons per oxygen (O_2) molecule. This pathway is central to energy conversion and storage devices, such as fuel cells and metal–air batteries, serving as the core of high-efficiency energy conversion technologies [4, 5]. In contrast, the $2e^-$ pathway selectively generates H_2O_2 , providing a green oxidant for advanced oxidation processes and representing a key component in environmentally benign pollution control technologies [6]. Therefore, gaining an in-depth understanding and enabling the rational design of electrocatalytic ORR processes are of great significance for collaboratively addressing energy crises and environmental challenges.

However, despite its considerable application potential across various fields, the ORR involves complex reaction pathways. Mechanistic studies still face numerous challenges, which hinder further research and practical utilization of the ORR [7]. The selectivity between $4e^-$ and $2e^-$ reaction pathways significantly hinders the high-quality application of the two pathways in their respective fields [8]. The $2e^-$ and $4e^-$ pathways are always competitive reactions: On the one hand, in membrane fuel cells and metal–air batteries, the $2e^-$ pathway not only acts as a parasitic reaction that reduces energy conversion efficiency, but the H_2O_2 generated can also corrode the device, adversely affecting its operational lifetime [9]. On the other hand, during the electrochemical synthesis of H_2O_2 via the ORR, the $4e^-$ pathway conversely serves as a side reaction that lowers the Faradaic efficiency (FE), thereby hindering the efficient production of H_2O_2 [10]. To address these challenges, researchers have devoted extensive efforts to developing high-performance catalysts aimed at improving reaction selectivity and steering the reaction toward oriented, efficient, and stable progress [11].

It is widely accepted that the ORR activity primarily stems from the efficient adsorption and activation of oxygen molecules at active sites, while the selectivity between the $2e^-$ and $4e^-$ pathways originates from the capability of the catalyst to activate and cleave the O–O bond in molecular O_2 [43]. Taking acidic conditions as an example, when O_2 is adsorbed on an active site in the Pauling mode, it combines with one proton and one electron to form the $^*\text{OOH}$ reactive intermediate. If the bonding strength between the active site and the oxygen atom is sufficiently high, the O–O bond tends to cleave. The detached OH radical then combines with a proton and an electron to form H_2O , while the remaining $^*\text{O}$ undergoes two further proton–electron transfer steps to produce another H_2O , thereby completing the $4e^-$ ORR [44]. In contrast, if the bonding strength between the active site and oxygen is moderate, the O–O bond remains intact. Instead, the $^*\text{OOH}$ intermediate accepts one proton and one electron to yield H_2O_2 , completing the $2e^-$ ORR [45].

Given the nearly constant linear scaling relations between the adsorption free energies of different oxygenated intermediates (e.g., $^*\text{OOH}$ and $^*\text{OH}$), it is feasible to evaluate the overall reaction activity using the adsorption energy of a representative intermediate (such as $^*\text{OH}$ or $^*\text{OOH}$) [46, 47]. Based on this theoretical framework, Nørskov and co-workers successfully constructed a volcano plot for ORR activity using the adsorption free energy of $^*\text{OH}$ (ΔG_{OH}) as a general descriptor [48]. This plot not only visually presents the activity limitation of the $4e^-$ pathway but also provides a consistent explanation for the selectivity tendency between the $2e^-$ and $4e^-$ pathways. Subsequently, Siahrostami et al. established for the first time the adsorption free energy of $^*\text{OOH}$ (ΔG_{OOH}) as a universal descriptor for quantitatively describing the

catalytic activity of the $2e^-$ ORR, thereby enriching the evaluation system [49].

For decades, noble metals, such as platinum (Pt) and their alloys, have been regarded as the benchmark for the ORR catalysts due to their exceptional activity [50], while certain alloys (e.g., Pt–Hg systems) have also been explored for the $2e^-$ pathway [49]. However, their high cost poses a significant barrier to large-scale commercial application [51]. Non-precious metal catalysts have emerged as promising alternatives and have achieved remarkable progress [52, 53], whereas their practical use is often limited by insufficient long-term stability [54]. In contrast, carbon-based metal-free electrocatalysts (CMFECs) have attracted widespread research interest owing to their low cost and excellent stability [55]. Nonetheless, the structural robustness of carbon substrates (e.g., graphene) entails chemical inertness, which inherently restricts their intrinsic catalytic activity [24].

To enhance the catalytic activity of CMFECs, progressive evolutions on structural modulation are achieved through strategies, such as heteroatom doping, defect introduction, and microenvironment engineering [56, 57], which are illustrated as a timeline chart as shown in Fig. 1. These approaches represent key origins of catalytic activity in metal-free carbon-based materials, and are widely adopted for ameliorating catalytic performance [58]. In 2009, Dai and co-workers reported nitrogen-doped carbon nanotubes (NCNTs) exhibiting $4e^-$ ORR activity comparable to that of 20% Pt/C, which unleashed a wave of research interest in applying CMFECs to electrocatalytic ORR [12]. Similarly, Cui and co-workers enhanced the selectivity of the $2e^-$ ORR from approximately 60% to 90% by introducing oxygen atoms into carbon nanotubes, successfully extending the doping strategy to the $2e^-$ pathway [35]. As research deepened, the advantages of CMFECs—including facile tunability, easy accessibility, low cost, and excellent stability—have been increasingly recognized, making them highly attractive in the field of electrocatalytic ORR. Beyond doping strategies, defect engineering has also been widely employed in the development of CMFECs [55, 59]. For instance, Yao and co-workers demonstrated that 585 and 7557 defects in undoped defective graphene (DG) play a critical catalytic role in the $4e^-$ ORR [19]. Meanwhile, Zhang et al. confirmed the catalytic contribution of pentagonal zigzag sites toward the $2e^-$ ORR [40]. In recent years, research focus has expanded beyond the active sites themselves to include the precise engineering of their local microenvironment [60]. Xia et al., for example, modified the intrinsic environment of pentagonal defects by introducing phosphorus and sulfur atoms, which boosted the $4e^-$ pathway selectivity to nearly 100% and increased the kinetic current density (j_k) by 19.7 times compared to the original pentagonal carbon ($2.55 \text{ mA}\cdot\text{cm}^{-2}$) [61]. In contrast, Chen and co-workers achieved a high H_2O_2 production rate of $25 \text{ mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ in a flow cell by topologically doping thiophene-sulfur into vertically aligned cylindrical ordered mesoporous carbon [42]. The curved thiophene-sulfur topology was shown to induce charge redistribution around the active centers, which translates into enhanced catalytic performance.

Despite significant progress in the development of CMFECs, precise control over the activity and selectivity of electrocatalysts for ORR remains challenging [62]. On the one hand, due to limitations in synthetic methods, it is extremely difficult to introduce a single and well-defined structural motif into carbon materials, which hampers the establishment of clear structure–performance relationships [63]. Moreover, structural characterization typically hinges on spectral deconvolution (e.g., X-ray photoelectron

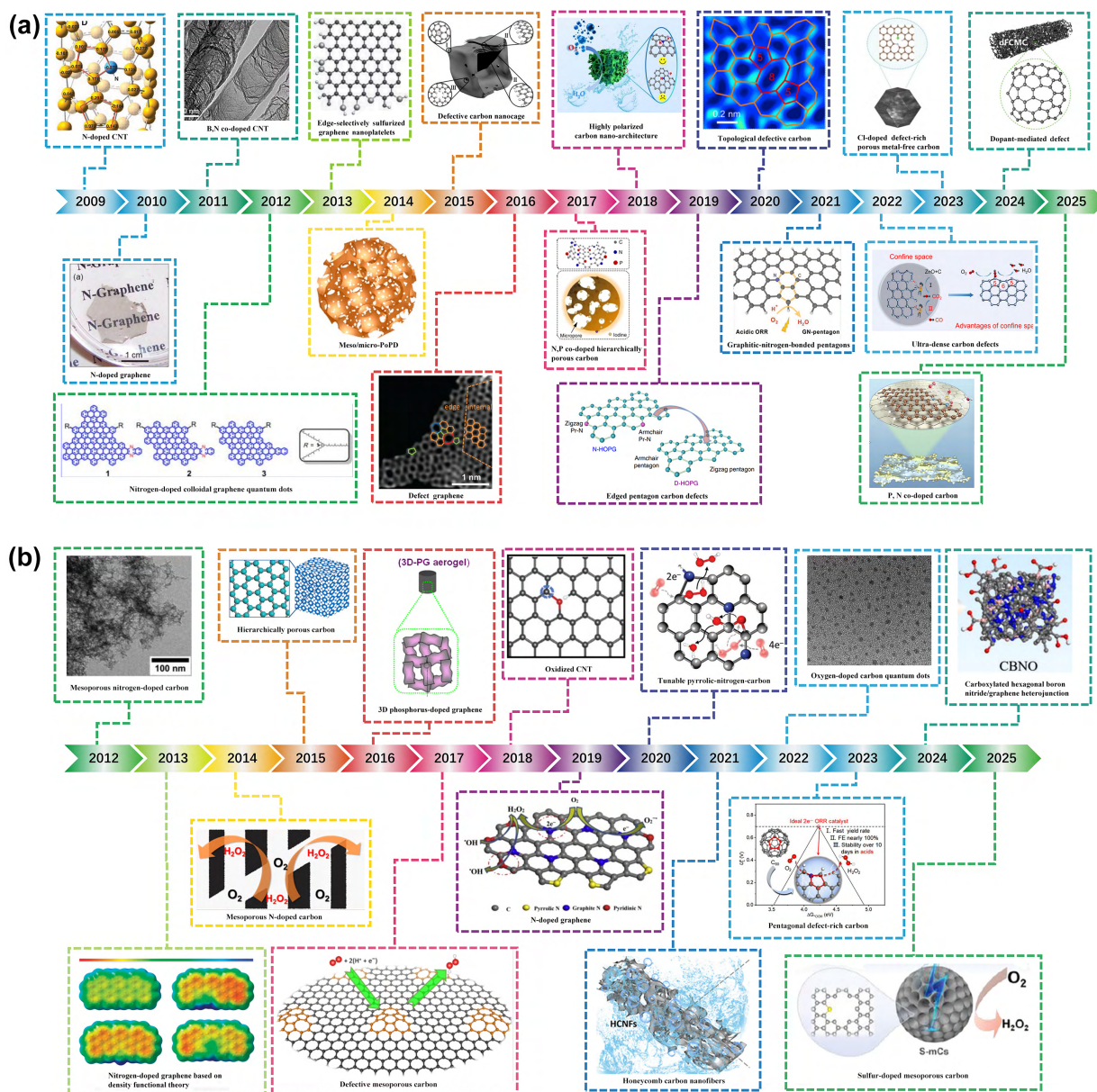


Figure 1 Timelines of milestone research discoveries/findings in CMFECs for (a) 4e⁻ ORR [12–28] and (b) 2e⁻ ORR [29–42]. (a) Reproduced with permission from Ref. [12], © American Association for the Advancement of Science 2009. Reproduced with permission from Ref. [13], © American Chemical Society 2010. Reproduced with permission from Ref. [14], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2011. Reproduced with permission from Ref. [15], © American Chemical Society 2012. Reproduced with permission from Ref. [16], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2013. Reproduced with permission from Ref. [17], © Macmillan Publishers Limited 2014. Reproduced with permission from Ref. [18], © American Chemical Society 2015. Reproduced with permission from Ref. [19], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2016. Reproduced with permission from Ref. [20], © Lu, K. et al. 2017. Reproduced with permission from Ref. [21], © Elsevier Ltd. 2018. Reproduced with permission from Ref. [22], © Jia, Y. et al. 2019. Reproduced with permission from Ref. [23], © Elsevier Inc. 2020. Reproduced with permission from Ref. [24], © Wiley-VCH GmbH 2021. Reproduced with permission from Ref. [25], © Elsevier Inc. 2022. Reproduced with permission from Ref. [26], © Wiley-VCH GmbH 2023. Reproduced with permission from Ref. [27], © Wiley-VCH GmbH 2024. Reproduced with permission from Ref. [28], © The Royal Society of Chemistry 2025. (b) Reproduced with permission from Ref. [29], © American Chemical Society 2012. Reproduced with permission from Ref. [30], © the Owner Societies 2013. Reproduced with permission from Ref. [31], © American Chemical Society 2014. Reproduced with permission from Ref. [32], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2015. Reproduced with permission from Ref. [33], © Elsevier B.V. 2016. Reproduced with permission from Ref. [34], © American Chemical Society 2017. Reproduced with permission from Ref. [35], © Macmillan Publishers Limited 2018. Reproduced with permission from Ref. [36], © Elsevier B.V. 2019. Reproduced with permission from Ref. [37], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2020. Reproduced with permission from Ref. [38], © Wiley-VCH GmbH 2021. Reproduced with permission from Ref. [39], © The Royal Society of Chemistry 2022. Reproduced with permission from Ref. [40], © American Chemical Society 2023. Reproduced with permission from Ref. [41], © Wiley-VCH GmbH 2023. Reproduced with permission from Ref. [42], © Wiley-VCH GmbH 2025.

spectroscopy (XPS) and Raman); nevertheless, operator-dependent variability in data interpretation complicates rational catalyst design and reproducible engineering of catalyst structures [64]. On the other hand, the field still exhibits a reliance on empirically driven

trial-and-error methods [65]. This approach not only consumes considerable time and resources but also struggles to meet the rapid development needs of the field [66]. Therefore, shifting from a trial-and-error mode toward rational design has become an inevitable

trend in the advancement of CMFECs. Specifically, at the experimental level, structure–performance relationships should be established by integrating reported precedents with advanced characterization techniques. At the theoretical level, computational tools, such as density functional theory (DFT) and finite element analysis, can be employed to start from the reaction mechanism and structural optimization, and use specific descriptors as evaluation criteria to validate the rationality of catalyst structural designs. Building on this, combining experimental results with theoretical calculations can form an integrated framework to guide catalyst development, thereby enabling the design of efficient and synthetically feasible pathways. Moreover, with the vigorous growth of artificial intelligence (AI) and the deep integration of machine learning (ML) techniques, their application to the rational design of catalysts can enable high-throughput screening of catalyst candidates, significantly enhancing the efficiency and focus of research and development.

Based on the aforementioned background and the accumulated work of our group in recent years, this review will adopt a chemistry-oriented perspective, focusing on the precise construction of atomic-level structures in CMFECs. With the regulation of the electron-transfer pathway in the ORR as the central thread, we will discuss how characteristic structures govern ORR selectivity and establish the structure–selectivity relationships (Fig. 2). The review first systematically introduces the mechanistic origins of ORR selectivity, activity, and stability, along with reaction pathway competition, and then demonstrates how these aspects are elucidated by integrating theoretical descriptors, *in-situ* characterization, and ML. It will then systematically categorize existing CMFECs according to three key design strategies: doping, defect engineering, and microenvironment modulation of active sites. By critically analyzing their performance metrics and structural characterization data, and integrating theoretical simulations and descriptor-based analysis, we aim to promote a deeper fusion of experiment and theory, thereby constructing a rational design framework for high-performance CMFECs. Furthermore, this article will comprehensively summarize recent advances in the practical industrial applications of CMFECs,

highlighting the real-world value of electrocatalytic ORR. Finally, we will outline the current challenges and future development directions for CMFECs.

2 Mechanistic understanding of ORR selectivity, activity, and stability

In recent years, CMFECs have achieved significant progress in the field of the ORR, with their performance approaching that of some benchmark noble-metal systems [67]. However, the further development of CMFECs still largely relies on traditional trial-and-error screening, which is limited by low throughput and long experimental cycles, and lacks efficient and directed guidance toward rational design. This has become a key bottleneck hindering breakthroughs in performance and the advancement of practical applications [68].

To break through this bottleneck, clarifying reaction mechanisms at the atomic scale and establishing clear structure–activity relationships have become critical prerequisites for achieving rational catalyst design [69]. This requires an in-depth understanding of the true structure of active sites, the rate-determining steps of reaction pathways, and the adsorption behavior of key intermediates, as well as the identification and unification of effective descriptors to guide material design [70, 71]. Accordingly, the subsequent sections of this article will first systematically analyze the possible pathways and mechanisms of the ORR, aiming to lay a solid theoretical foundation for the rational design of CMFECs.

2.1 Mechanisms for four-electron ORR

In the ORR, achieving an efficient $4e^-$ pathway is crucial for enhancing the energy conversion efficiency of relevant devices. The $4e^-$ ORR can be simplified into the following elementary reaction steps, which belong to the associative pathway:

Acidic conditions/electrolytes

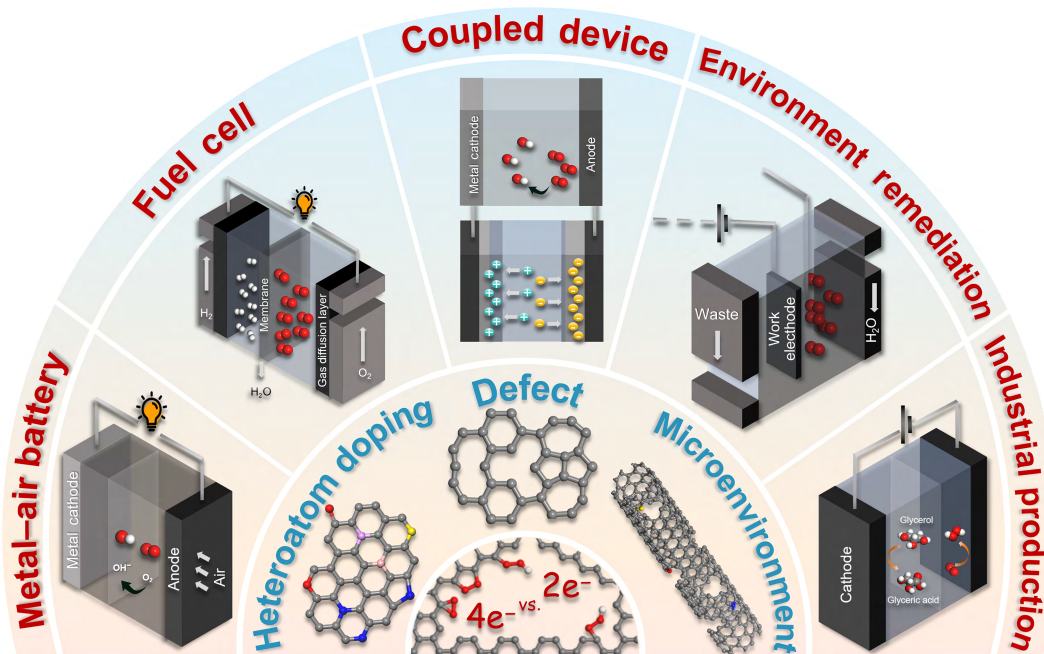
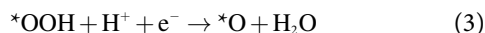


Figure 2 Schematic of rational design strategies for CMFECs architectures towards selective $4e^-/2e^-$ ORR.



Alkaline conditions/electrolytes



Here, * represents the active site. On the one hand, the selectivity of this process primarily depends on the performance of the catalyst to activate and cleave the O–O bond in molecular O₂ [72]. Ideally, the catalyst surface should facilitate O₂ adsorption, proton-coupled electron transfer, and O–O bond cleavage, ultimately leading to the formation of H₂O or OH[−], rather than yielding by-products, such as H₂O₂ via the 2e[−] pathway. Thus, the selectivity toward the 4e[−] pathway is fundamentally governed by the kinetics of O–O bond dissociation and the bonding strength of the adsorbed intermediates. On the other hand, the overall activity of the ORR involves more complex multi-step adsorption–desorption equilibria and charge-transfer processes [73]. The initial step relies on the efficient adsorption and activation of O₂ at the active sites, which entails the favorable electron population of antibonding orbitals for O–O bond weakening. The progression of subsequent steps, especially at high overpotentials, is often limited by the adsorption strengths of oxygenated intermediates, such as *OOH, *O, and *OH. Among these, the desorption of water as the terminal step—if sluggish—can lead to site blocking and hinder continuous reaction

turnover. Therefore, an efficient ORR catalyst must simultaneously optimize O₂ adsorption and activation, moderate binding energies of adsorbed intermediates, and ensure timely desorption of product molecules, thereby unifying high selectivity toward the 4e[−] pathway with high catalytic activity.

Although the 4e[−] ORR has been relatively well understood, optimizing its catalytic efficiency has long faced a fundamental challenge: establishing a universal descriptor capable of accurately measuring and predicting catalyst activity [74]. This complexity arises from the multi-step electron-transfer nature of the ORR. As early as the beginning of the twentieth century, Sabatier proposed the “adsorption–activation–desorption” model, which qualitatively revealed a volcano-type relationship between catalyst activity and the adsorption strength of intermediates, thereby pointing toward a basic direction for the rational design of catalysts [75].

Furthermore, the research conducted by Nørskov and his team provided key theoretical and methodological advances toward quantifying and generalizing this problem. Their proposed computational hydrogen electrode (CHE) model established a standard thermodynamic framework for calculating the free energy of electrochemical reactions based on DFT calculations, thereby making it possible to predict catalytic activity from first principles [76]. Koper discovered nearly constant linear scaling relations between the adsorption free energies of different oxygenated intermediates (e.g., *OOH and *OH) (Fig. 3(a)) [46]. This implies that when the adsorption strength of one intermediate on the catalyst surface is tuned, the adsorption behavior of other intermediates is inevitably altered in a correlated manner. Consequently, optimizing only a single elementary reaction step faces a theoretical limitation—A finding that essentially quantifies and deepens the Sabatier principle within the context of ORR systems. Building upon this scaling relation, Nørskov and co-workers successfully constructed a volcano plot for ORR activity using the ΔG_{OH} as a unified descriptor (Fig. 3(b)) [48]. The horizontal axis of the volcano plot represents the reaction descriptor, which corresponds to the binding strength between adsorbed intermediates and the active site, typically expressed as adsorption energy or Gibbs free energy. This axis essentially reflects the intrinsic electronic structure of the catalyst. A binding strength that is too strong inhibits desorption of intermediates, whereas one that is too weak hampers reactant activation. The vertical axis represents the catalytic activity metric, commonly defined by the limiting potential (U_L) at which all elementary steps become thermodynamically spontaneous. For the ORR, a higher U_L

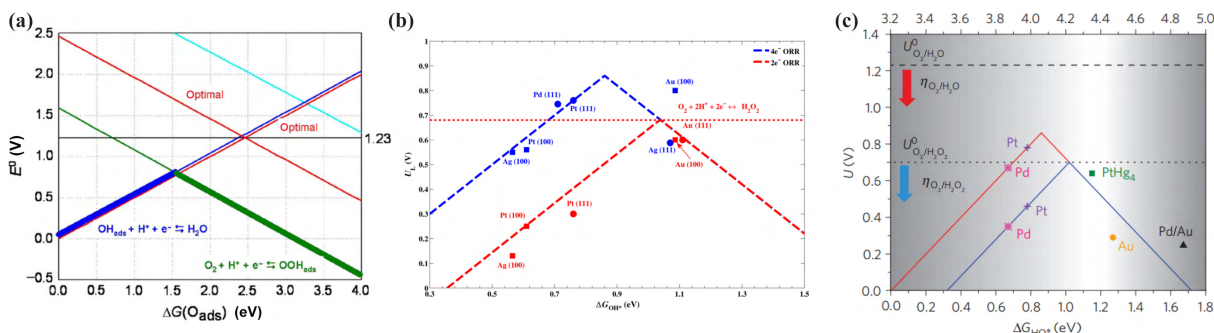
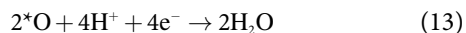


Figure 3 Development and application of volcano plots in electrocatalytic ORR. (a) Plot of the equilibrium potentials of reaction $* \text{OOH} + \text{H}^+ + \text{e}^- \rightleftharpoons 2* \text{OH}$ and $* \text{OOH} + \text{H}^+ + \text{e}^- \rightleftharpoons 2* \text{OH}$ as a function of the free binding energy of oxygen. Reproduced with permission from Ref. [46], © Elsevier B.V. 2010. (b) Activity volcanoes for the 2e[−] and 4e[−] reduction of oxygen are shown in red and blue. Reproduced with permission from Ref. [48], © American Chemical Society 2012. (c) Theoretically calculated oxygen reduction volcano plot for the two-electron (blue) and four-electron (red) reduction of O₂, with the limiting potential plotted as a function of ΔG_{OH} (lower horizontal axis) and ΔG_{OOH} (upper horizontal axis). Reproduced with permission from Ref. [49], © Macmillan Publishers Limited 2013.

corresponds to a lower overpotential, indicating superior catalytic performance. A catalyst positioned closer to the peak of the volcano plot signifies that its adsorption energy approaches the optimal value. The ΔG_{OH} descriptor successfully correlates experimental activity data across different metal crystal facets, transforming Sabatier's qualitative model into a quantitative predictive framework. This advancement provides a solid theoretical foundation and a universal tool for the rational design of ORR catalysts.

Although this method was originally developed for metal-based catalysts, its core principle is equally applicable to CMFECs. Jiao et al. were the first to extend this methodology to metal-free systems [58]. Through a systematic investigation of the relationship between experimental electrocatalytic oxygen reduction performance and theoretically calculated free energies of adsorbed intermediates for a series of non-metal element-doped graphene materials, their work highlighted the critical role of adsorption energy in describing the activity of CMFECs. Similarly, Wissam A. Saidi employed the adsorption energy of intermediate species (ΔE_{OH}) to characterize the ORR catalytic activity of nitrogen-doped graphene quantum dots [77]. By utilizing scaling relations between adsorption energies, they successfully correlated ΔE_{OH} with the reaction free energy, thereby predicting and explaining the overpotential and activity trends of CMFECs in the ORR. This adsorption-energy-based evaluation framework continues to be widely adopted in related research to this day.

In addition, there is another route known as dissociative pathway



The occurrence of this pathway is often closely linked to the adsorption mode of the molecular oxygen: When oxygen is adsorbed via the Griffiths model or the Yeager mode, direct cleavage of the O–O bond tends to occur; in contrast, under the Pauling adsorption mode, the ORR typically proceeds through the aforementioned sequential proton-coupled electron transfer steps.

Current understanding of this pathway remains debated: Some researchers contend that the end-on oxygen configuration exhibits higher efficiency than the bridge-adsorption configuration and accelerates the reaction progression, which holds significant implications for catalyst design and performance [78]. Others maintain that this specific adsorption mode facilitates direct cleavage of the O–O bond, bypassing the formation of the $*\text{OOH}$ intermediate and thereby avoiding the risk of H_2O_2 generation. This fundamentally enhances reaction selectivity, while the more efficient reaction steps contribute to accelerated reaction kinetics [79].

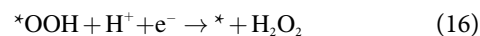
Beyond the thermodynamic descriptors discussed above, the adsorption geometry of O_2 on the catalyst surface profoundly influences the 4e^- pathway selectivity. Three adsorption modes are generally recognized: end-on (Pauling model), side-on (Griffiths model), and bridge (Yeager model). The key difference lies in the coordination number: Pauling model involves a single carbon active site (single-site binding), whereas both the Griffiths and Yeager models involve dual-site binding between O_2 and two

adjacent carbon atoms (or carbon–heteroatom pairs). This dual-site interaction enables efficient back-donation of electrons from the catalyst into the π^* orbitals of O_2 , significantly weakening the O–O bond and lowering the dissociation barrier. Consequently, dual-site adsorption intrinsically favors the 4e^- pathway, whereas the single-site Pauling mode often leads to sequential proton–electron transfer with higher overpotential. Recent studies have demonstrated that specific structural motifs can induce this favorable dual-site adsorption in CMFECs. For instance, nitrogen doping in carbon nanotubes creates positively charged carbon pairs that enable a transition from Pauling-type to Yeager-type binding [12]. Similarly, P=O ligands in P, N-co-doped carbon materials modulate the charge and spin states of adjacent carbon atoms, promoting bridge-type O_2 chemisorption [28]. Topological defects, such as Stone–Wales defects, also generate diatomic active sites that favor dual-site binding [80]. These examples highlight a crucial design principle: For efficient 4e^- ORR, CMFECs should be rationally engineered to create dual-site binding motifs that facilitate O–O bond cleavage, shifting the adsorption mode from single-site Pauling to dual-site Griffiths or Yeager [81].

2.2 Mechanisms for two-electron ORR

In the ORR, achieving a selective and efficient 2e^- pathway is central to the direct electrosynthesis of H_2O_2 —an important green chemical in the industries. The 2e^- ORR pathway can be simplified into the following elementary reaction steps:

Acidic conditions/electrolytes



Alkaline conditions/electrolytes



In the 2e^- ORR, achieving high selectivity toward H_2O_2 generation hinges on the precise tuning of the adsorption energy of the key intermediate $*\text{OOH}$ [82]. An ideal catalyst must exhibit a moderate $*\text{OOH}$ binding strength: If the adsorption is too weak, the O_2 molecule cannot be effectively activated and protonated; if the adsorption strength is too strong, $*\text{OOH}$ tends to undergo O–O bond cleavage rather than desorption as H_2O_2 , leading to further reduction into $*\text{O}$ and $*\text{OH}$ and triggering the parasitic 4e^- pathway. Therefore, balancing catalytic activity and selectivity fundamentally depends on the ability of catalysts to promote O_2 activation while enabling efficient $*\text{OOH}$ desorption.

Despite the existence of scaling relations, the difference in reaction pathways makes $*\text{OOH}$ a more suitable descriptor for reflecting the catalytic activity of the 2e^- ORR. In 2013, Siahrostami et al. provided a key theoretical framework and descriptor to address the aforementioned challenge [49]. They pointed out that selectively suppressing O–O bond cleavage is crucial for steering the 2e^- pathway, and for the first time established the $\Delta G_{*\text{OOH}}$ as a

universal descriptor for quantitatively describing the catalytic activity of the $2e^-$ ORR (Fig. 3(c)). By constructing a volcano-shaped activity plot using ΔG_{OOH} as the variable, their study clearly illustrated the optimal range balancing activity and selectivity, and successfully predicted and experimentally validated the high performance of Pt–Hg alloy catalysts based on this principle. Similarly, this descriptor framework is not limited to metal-based catalysts. Its physical essence—That is, optimizing the adsorption behavior of key intermediates by tuning the electronic and geometric structure of active sites—also provides an important theoretical tool for understanding and designing non-metal catalysts, such as CMFECs [83]. Up to now, ΔG_{OOH} remains one of the central metrics for the rational design and screening of efficient electrocatalysts for H_2O_2 synthesis.

2.3 Analysis of stability and inactivation mechanisms

Currently, carbon-based metal-doped catalysts, typified by Pt/C catalysts, are commonly employed in methanol fuel cell devices. However, they often suffer from poisoning of active sites by CO generated from the incomplete oxidation of methanol, while the dissolution of metal atoms also compromises their long-term stability. In contrast, CMFECs do not exhibit strong adsorption of CO at active sites, nor are they subject to the dissolution of dopant atoms. Consequently, they demonstrate favorable adaptability in addressing the aforementioned challenges. Nevertheless, the stability of carbon-based metal-free catalysts remains constrained by multiple factors.

The carbon oxidation reaction (COR) exerts a non-negligible corrosive effect on the carbon framework. Although existing studies have largely focused on metal-doped carbon-based systems, the corrosion behavior of the carbon framework in these systems still provides important reference value for carbon-based metal-free catalysts. For $4e^-$ ORR catalysts applied in fuel cells, the start-up/shut-down process can cause transient elevation of the cathode potential to above 1.5 V, significantly accelerating COR [84]. Defect sites on the carbon framework surface are oxidized at high potentials and detach in the form of CO/CO₂, leading to collapse of the graphitic structure and irreversible loss of electrochemical active surface area [85]. Although the duration of each high-potential exposure is short, the damage from carbon corrosion accumulates over time; the catalyst layer markedly degrades after repeated cycles, shortening the electrode lifetime. Moreover, hydrogen peroxide and other reactive oxygen species can chemically attack unsaturated bonds and defects in carbon materials, continuously weakening the carbon framework even under conventional potential conditions [86].

The Nakamura group systematically investigated the stability of nitrogen-doped carbon (NC) materials during acidic ORR [87]. They found that pyridinic (pyri) N (Py-N) readily undergoes protonation due to its delocalized lone pair electrons, forming a pyri-NH⁺ structure that directly passivates the active centers. In contrast, graphitic N (G-N), which lacks lone pair electrons, exhibits significant inertness. To address this non-covalent deactivation mechanism, the group innovatively designed a dual-microenvironment system combining “hydrophobic isolation” and “proton conduction”: A cage-like porous carbon framework with a hydrophobic backbone suppresses water molecule access to the pyridinic N centers, while an embedded ionic-liquid-modified proton conductor ensures the supply of H⁺, thereby effectively mitigating the performance decay induced by protonation.

Furthermore, anion adsorption can block active catalytic sites and alter the surface properties of carbon catalysts or supports, subsequently affecting key attributes, such as hydrophobicity and electronic conductivity, ultimately impairing mass transport and electron transfer processes, which are crucial for efficient ORR. Consequently, these changes exacerbate performance degradation over time. Hu et al. developed a Cl-pentagonal-rich defective carbon (PDC) catalyst; unmodified defective carbon suffers from strong Cl⁻ adsorption due to local positive charges, leading to poisoning [88]. By modulating the electronic structure via chlorine doping, Cl⁻ blocking was significantly alleviated, enabling high H_2O_2 selectivity and long-term stability at industrial current densities.

In addition to heteroatom-based active sites, defect structures also widely exhibit catalytic activity. However, these defects face stability challenges as they readily react with oxygen, water, or moisture, losing activity during ORR or storage. Manage et al. found that defective vacancies on the carbon matrix surface undergo severe oxidation when exposed to air, with oxygen content increasing as aging time lengthens [89]. This indicates that oxidation of defect active sites during atmospheric aging is a major factor responsible for the activity decline of defective carbon catalysts. Unfortunately, research on the stabilization of defects in carbon materials remains very limited.

In CMFECs, pore architecture significantly influences mass transport: micropores maximize active surface area, mesopores facilitate oxygen diffusion, and macropores promote water expulsion, thereby mitigating pore blockage by water. However, an unbalanced pore structure—for example, excessive micropores or insufficient meso-/macropores—can exacerbate water retention. When water accumulates within micropores, reactant transport to the three-phase reaction interface is restricted, mass transport efficiency decreases, and catalyst activity declines. Du et al. directly demonstrated using finite element analysis that meso-/microporous-dominated structures exhibit higher flow velocities and shorter product residence times than microporous structures, effectively avoiding local water accumulation and significantly enhancing mass transfer efficiency [42]. In terms of surface wettability modulation, Dong et al. prepared carbon nanofibers with honeycomb carbon nanofibers (HCNFBs) [38]. The surface oxygen functional groups create a super-hydrophilic chemical microenvironment, while the interconnected hollow nanocavities form a “hydrophilic and oxygen-rich” three-phase interface. This configuration not only ensures adequate electrolyte infiltration but also promotes oxygen enrichment and rapid product desorption, thereby fundamentally preventing the failure of catalytic sites caused by micropore flooding.

2.4 In-situ characterization techniques

In the field of electrocatalytic ORR, the widely discussed and established structure–performance relationships are often based on static characterization of the catalyst as an electrode material prior to electrochemical testing. However, during the actual electrochemical process, these carefully designed active sites cannot be guaranteed to remain structurally stable [90]. More critically, if the catalyst structure evolves into a new “genuine” active site that differs from its initial state during the catalytic reaction, it poses a significant challenge to the in-depth understanding of the electrocatalytic ORR mechanism. Therefore, in studies on CMFECs for ORR, researchers have employed various *in-situ* characterization techniques to probe the catalyst structure, active

sites, and reaction pathways, enabling monitoring of the active site structure under real reaction conditions.

Fourier transform infrared (FTIR) spectroscopy is a common tool for analyzing molecular structures and chemical bonds, while *in-situ* FTIR can track in real time the changes in surface functional groups of the catalyst during ORR. Among these, surface-enhanced infrared reflection absorption spectroscopy (SEIRAS) can detect intermediates, such as superoxide anions, and is particularly suitable for carbon-based materials (with signal enhancement via a metal thin film). For example, Zhao et al. used *in-situ* attenuated total reflection SEIRAS (ATR-SEIRAS) to monitor the dynamic evolution of adsorbed species on the surface of a P, N-co-doped carbon catalyst during ORR [28]. They observed the appearance of a characteristic peak of P=O ligands, a continuous red shift of the O–O bond vibration, and the intensity attenuation of the *OOH intermediate peak, directly revealing the real-time process of O₂ switching from end-on adsorption to bridge-type adsorption. Similarly, Xia et al. utilized this technique to directly observe the complete evolution of characteristic peaks of *O₂, *OOH, and HOOH on the P/S-doped carbon surface, which gradually intensified as the potential shifted negatively (1.0 → 0.70 V), clearly presenting the continuous reaction pathway of O₂ adsorption/activation → protonation to *OOH → further conversion to HOOH [61]. More importantly, by integrating the peak area ratio of *OOH to O₂, *in-situ* FTIR revealed the promoting effect of P/S co-doping on the hydrogenation step of O₂—a piece of kinetic information completely inaccessible by conventional static characterization.

Raman spectroscopy can provide detailed information about the catalyst structure, adsorbates, and reaction intermediates. *In-situ* Raman spectroscopy can dynamically track the evolution of the catalyst surface structure as a function of applied potential. Wu et al. used *in-situ* Raman spectroscopy to monitor the evolution of *OOH intermediates and oxygen-containing functional groups on an oxygen-modified DG-30 (O-DG-30) catalyst during ORR [91]. Similarly, our team investigated the ORR process on defective graphite using *in-situ* electrochemical surface-enhanced Raman spectroscopy (EC-SERS) [92]. As the potential decreased, the Raman peak at 713 cm⁻¹ attributed to *OOH gradually weakened, while the peak at 1038 cm⁻¹ attributed to *OH continuously intensified. This trade-off in transient intermediates directly indicates that *OOH is rapidly reduced and converted to *OH, while *OH accumulates on the surface and is difficult to desorb, suggesting that *OH desorption is the rate-determining step, thereby providing key evidence for understanding the catalytic mechanism.

XPS is used to analyze the surface elemental composition and the local bonding environment of carbon atoms. Conventional *ex-situ* XPS can distinguish different nitrogen doping configurations, such as pyridinic N and graphitic N. For instance, Guo et al. found that pyridinic N is key to ORR activity, decreasing after the reaction with the formation of pyridonic N. However, *ex-situ* XPS cannot preserve the surface chemistry under real reaction conditions, and short-lived intermediates tend to disappear [93]. Morallón et al. used synchrotron-based near-ambient pressure XPS (NAP-XPS) to characterize nitrogen-doped carbon electrocatalysts *in-situ* under potential control, successfully capturing the transient N–C–O intermediate and revealing the dynamic evolution of edge graphitic nitrogen and its adjacent carbon atoms under different potentials and pH conditions [94].

The combination of these *in-situ* and *ex-situ* techniques provides a solid experimental basis for unraveling the ORR active centers, intermediate evolution, and reaction pathways of CMFECs.

2.5 Basic principle for machine learning

Although DFT calculations have been widely employed in catalyst screening and the exploration of novel materials, they are computationally intensive and time-consuming, making it difficult to comprehensively analyze complex catalytic systems [95]. ML, with its ability to uncover hidden patterns from multi-source data, offers significant advantages in the fields of materials and catalysis research [96]. By integrating high-throughput experiments, first-principles calculations, and literature data, ML can establish predictive models and guide experimental design [97].

2.5.1 High-throughput screening

Traditional development of electrocatalysts relies on trial-and-error experiments and DFT calculations, which suffer from low efficiency and high cost [98]. By integrating ML with high-throughput DFT calculations, public material databases, and interpretable algorithms, it is possible to systematically reveal the quantitative relationships between material structure and catalytic activity, thereby enabling efficient screening of candidate catalysts [99]. Specifically, structural and electronic features (e.g., bond length and electronegativity) extracted from DFT results are used as descriptors. The resulting ML models can rapidly predict fundamental parameters, such as adsorption energy and reaction energy, significantly improving screening efficiency and accelerating the rational design of advanced catalysts [100].

Under this strategy, researchers have achieved a series of advances using various approaches. For example, Yang et al. combined random forest ML with DFT calculations to automatically identify the system's free energy and the number of valence electrons as key catalytic descriptors from multi-dimensional physicochemical features [101]. This work revealed the origin of the bifunctional activity of non-metal single-atom catalysts, overcoming the limitations of traditional linear scaling relationships, and subsequently enabled high-throughput screening of catalysts, leading to the development of non-metal-doped single-atom bifunctional (oxygen evolution reaction (OER)/ORR) catalysts. Similarly, Zhu et al. employed ML potentials to accelerate screening and DFT calculations, automatically identifying the lowest-energy *OOH intermediate adsorption site from hundreds of candidate adsorption configurations [102]. They elucidated the intrinsic mechanism by which the sp²/sp³ hybridization ratio and oxygen content jointly govern the selectivity toward hydrogen peroxide in carbon materials, breaking through the conventional understanding based solely on heteroatom-doped active sites. On this basis, they efficiently identified the optimal design window for CMFECs and proposed a design strategy for non-metal two-electron oxygen reduction catalysts based on a carbon-oxygen framework. Furthermore, Lv et al. utilized extreme gradient boosting (XGB) ML together with DFT calculations to automatically screen the atomic charge (Q) as the key descriptor from multi-dimensional physicochemical features of catalytic sites and their local environments (e.g., atomic charge, bond length, and hybridization state) [103]. They clarified the structural origin of the bifunctional oxygen reduction and hydrogen evolution activities of β-graphyne/graphdiyne nanoribbons, overcoming the shortcomings of traditional linear scaling relationships based on a

single descriptor. Accordingly, they performed high-throughput screening of catalysts with different edge configurations and nitrogen doping patterns, developing non-metal-doped carbon-based bifunctional (ORR/hydrogen evolution reaction (HER)) electrocatalysts. Collectively, these studies demonstrate the broad applicability of ML-enabled high-throughput screening across various catalytic systems.

2.5.2 Revealing reaction mechanisms and optimizing structure–performance relationships

In addition to accelerating screening, ML can also reveal key physicochemical principles in catalytic processes. Integrating ML into catalyst design enables efficient exploration of catalytic mechanisms around active sites at a level of accuracy approaching that of DFT calculations. By leveraging feature importance analysis (e.g., first ionization energy difference and Bader charge) and interpretable methods, such as least absolute shrinkage and selection operator (LASSO), compact and physically meaningful descriptors can be extracted from complex feature spaces.

For example, Zhu et al. combined an orthogonal material library with interpretable ML methods to automatically identify the sp^2/sp^3 hybridization ratio and moderate oxygen content as key catalytic descriptors from the multi-dimensional data of standardized catalyst passports [97]. This work revealed the true origin of the structure–performance relationship of CMFECs for electrochemical H_2O_2 generation, breaking the limitations of traditional active site assumptions and simplified DFT models. Consequently, they achieved precise control over the hybridization state of the carbon framework and the surface oxygen functionality, establishing a new data-driven paradigm for optimizing structure–activity relationships. In another study, He et al. employed ML models, such as random forest and XGB-ML, together with Shapley value analysis to automatically identify mesopore size, carbonization temperature, and exogenous doping method as key catalytic descriptors from multi-dimensional preparation and structural features [104]. They elucidated the structure–performance relationship for selectivity regulation of biomass-derived carbon catalysts in the two-electron oxygen reduction reaction, overcoming the limitations of traditional trial-and-error methods in optimizing complex parameter spaces. On this basis, they achieved efficient design and targeted synthesis of catalysts, developing boron-doped biomass-derived carbon bifunctional electrocatalysts for H_2O_2 synthesis and near-neutral zinc–air batteries. These works demonstrate that interpretable ML can not only reveal catalytic mechanisms but also provide clear directions for experimental optimization.

However, existing ML models still face challenges, such as insufficient physical interpretability due to the “black box” problem and a tendency to overfit under small-sample conditions. Further breakthroughs are urgently needed in the development of efficient, computable, and interpretable material descriptors [96, 105].

3 Rational structural design of CMFECs

In the rational design of CMFECs, the activity and selectivity are fundamentally governed by the adsorption mode and strength of key reaction intermediates on the catalyst surface [28, 88]. These adsorption properties are directly determined by the electronic structure characteristics of the active sites. Therefore, targeted modulation of the intrinsic electronic structure of materials represents the essential pathway for optimizing their catalytic

performance, which can be achieved through strategies, such as heteroatom doping, defect engineering, and microenvironment engineering of active centers. These strategies enable fine-tuning of key parameters, such as local charge distribution around active sites, density of states near the Fermi level (e.g., the d-band center for transition metals or the p-band center for carbon-based materials), and spin polarization [92, 106]. Such electronic-level adjustments directly modify the orbital coupling and electron transfer capability between the surface and reaction intermediates, thereby precisely regulating the adsorption configuration and binding strength of intermediates. This electronic-scale control determines both the selectivity of reaction pathways and the energy barriers of elementary steps, forming the microscopic physical foundation of catalytic performance.

In addition, the macroscopic morphology and hierarchical pore structure of CMFECs govern mass transport during the reaction process [38, 107]. By designing high specific surface area, appropriate pore size distribution, and open pore-channel networks, the diffusion of reactants (e.g., O_2) toward active sites, the maintenance of interfacial concentrations, and the timely desorption of products (e.g., H_2O_2) can be effectively promoted. Such structural engineering significantly reduces mass transport resistance, prevents the shielding of active sites and local concentration polarization, and ensures that the intrinsic catalytic activity can be fully realized even at high current densities. This represents a critical engineering aspect for achieving high-performance catalytic systems.

3.1 Heteroatom-induced active sites

The introduction of heteroatoms can alter the charge distribution and spin density of CMFECs, modulating the adsorption strength and bonding mode of active sites toward key reaction intermediates, thereby influencing the pathway and catalytic activity of the ORR [12, 108]. However, it remains unclear which specific structural features favor the $2e^-$ pathway and which promote the $4e^-$ pathway. In the following sections, we will separately review relevant studies, aiming to clarify the structural characteristics of CMFECs that govern the selectivity between the two ORR pathways.

3.1.1 Heteroatoms favorable for triggering four-electron ORR

Nitrogen heteroatoms are the typical dopants in CMFECs for the pursuit of high-performance $4e^-$ ORR. In 2009, Dai et al. first reported a metal-free carbon-based catalyst that outperformed commercial platinum-based catalysts [12]. The authors prepared NCNTs, which exhibited a limiting current density (j_L) four times higher than that of platinum-based catalysts while also demonstrating superior selectivity and stability. The carbon atoms adjacent to nitrogen heteroatoms, where charge redistribution occurs due to the electronegativity difference between carbon and nitrogen, were identified as active sites. This assignment was supported by multiple lines of evidence: electrochemical purification ruled out residual Fe catalysts, control experiments with nitrogen-free CNTs confirmed the essential role of N, and DFT calculations revealed the positive charge density on adjacent carbon atoms. This modification effectively alters the adsorption mode of oxygen and influences the pathway of the ORR (Fig. 4(a)). This work sparked widespread interest in using heteroatom doping to enhance the performance of metal-free carbon-based catalysts [109].

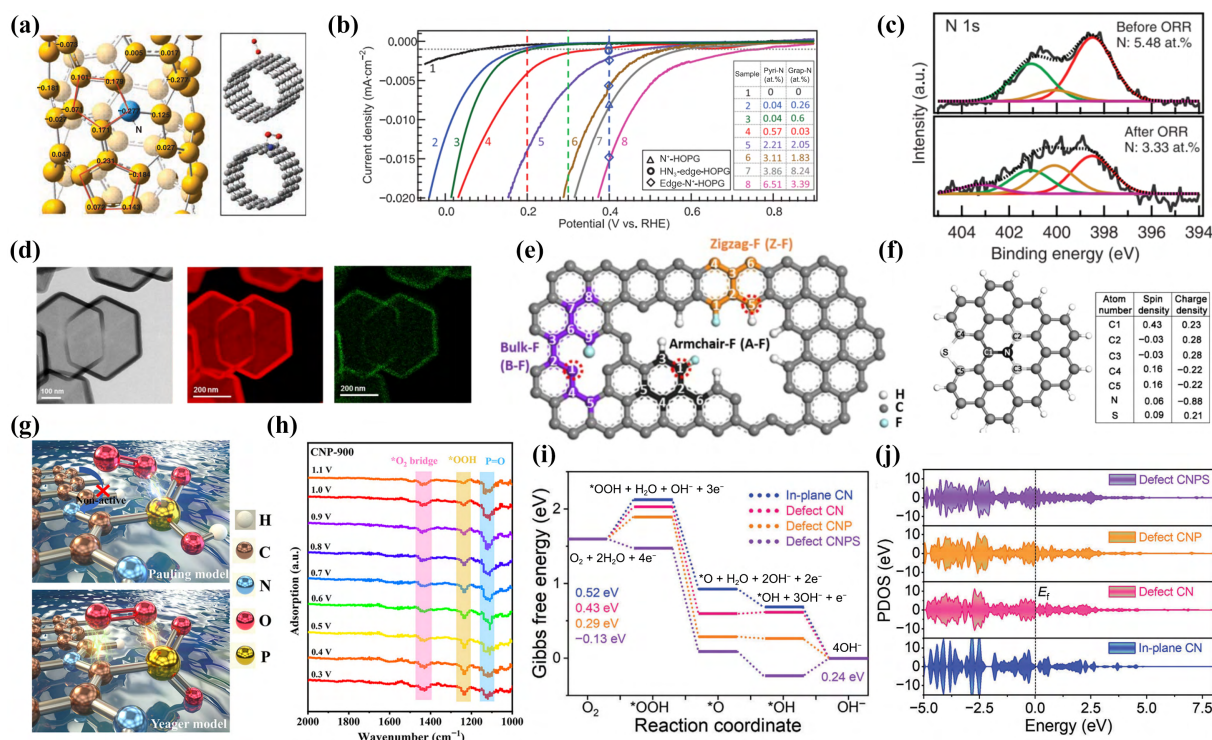


Figure 4 Heteroatom doping strategy for CMFECs towards 4e⁻ ORR. (a) Calculated charge density distribution for the NCNTs and schematic representations of possible adsorption modes of an oxygen molecule at the carbon nanotube (CCNTs) (top) and NCNTs (bottom). Reproduced with permission from Ref. [12], © American Association for the Advancement of Science 2009. (b) ORR results obtained for the model catalysts with different N concentrations and (c) N 1s XPS spectra of the N-HOPG model catalyst before and after ORR. Reproduced with permission from Ref. [93], © American Association for the Advancement of Science 2016. (d) Elemental mapping images using energy-filtered TEM (EF-TEM) of 850S: carbon (red) and sulfur (green). Reproduced with permission from Ref. [112], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2018. (e) The scheme that depicts the structures of armchair-F (A-F), bulk-F (B-F), and zigzag-F (Z-F). Reproduced with permission from Ref. [113], © Elsevier B.V. 2020. (f) Spin and charge density of graphene network (gray) dual-doped by N (black) and S (white). Reproduced with permission from Ref. [108], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2012. (g) Schematic representation of the P=O ligand-induced activation toward O₂ adsorption: Pauling model and Yeager model, and (h) *in-situ* ATR-SEIRAS testing for CNP-900 at various potentials (vs. RHE) in O₂-saturated 0.1 M phosphate-buffered saline (PBS). Reproduced with permission from Ref. [28], © The Royal Society of Chemistry 2025. (i) Free energy diagrams of ORR processes occurring on the four models at the equilibrium potential ($U = 0$ V) and (j) the calculated PDOS of C 2p orbitals of different models. Reproduced with permission from Ref. [115], © Wiley-VCH Verlag GmbH 2025.

Although nitrogen-doped CMFECs exhibit excellent catalytic activity, the diverse configurations of nitrogen atoms—such as pyridinic N, pyrrolic N, graphitic N, and oxidized N—hinder the clear identification of active sites, posing challenges for the precise development of efficient ORR catalysts via nitrogen doping strategies [77]. To overcome this difficulty, Guo et al. prepared a series of model catalysts based on highly oriented pyrolytic graphite (HOPG), each dominated by either pyridinic N, graphitic N, or edge-rich structures, along with a pristine HOPG reference [93]. Electrochemical tests revealed that the pyridinic N-dominated model catalyst showed significantly higher ORR activity under acidic conditions, whereas the nitrogen-free model exhibited much lower activity. Moreover, the ORR activity correlated linearly with the concentration of pyridinic N but showed no clear dependence on the graphitic N content (Fig. 4(b)). This linear correlation, observed across different sample preparation methods, provides strong evidence that pyridinic N—rather than graphitic N or other structural factors—is the direct determinant of ORR activity. XPS and CO₂ adsorption experiments confirmed that pyridinic N creates Lewis basic sites on the HOPG surface, which facilitates the adsorption of O₂ molecules (Fig. 4(c)). Building on these insights, the authors synthesized pyridinic N-doped graphene nanosheets (GNS), which demonstrated an onset potential (E_o) of 0.91 V and a current density of 1.4 mA cm⁻² at 0.5 V, further validating the

proposed mechanism. This work has provided important guidance for subsequent studies on nitrogen-doped carbon materials. For example, Zheng et al. derived nitrogen-doped carbon spheres from covalent triazine polymers (CTPs) [110]. The preserved pyridinic N within the triazine ring structure provided abundant active sites. A zinc-air battery using the N-doped carbon spheres as the cathode material achieved a peak power density (P_{max}) of 148 mW cm⁻², outperforming the commercial Pt/C catalyst (123 mW cm⁻²).

Not only does nitrogen doping significantly enhance the ORR performance of CMFECs, but other heteroatoms, such as sulfur, phosphorus, and fluorine, also exhibit considerable potential for improving ORR performance. Wu et al. prepared a phosphorus-doped carbon aerogel that exhibits outstanding ORR performance with an onset potential of -0.13 V vs. Ag/AgCl and a limiting current density of -6.01 mA cm⁻² in 0.1 M KOH [111]. This remarkable performance fundamentally stems from the dual modulation of both the electronic structure and the microscopic morphology of the carbon matrix induced by phosphorus doping. On the one hand, the lower electronegativity of phosphorus increases the electron density of adjacent carbon atoms, creating negatively charged active sites that facilitate the adsorption and activation of oxygen molecules. On the other hand, the relatively large atomic radius of phosphorus (107 pm) significantly distorts the carbon skeleton, increases edge exposure and defects, and

provides active carbon sites with asymmetric spin density, thereby further optimizing the local electronic environment of carbon and promoting the $4e^-$ reaction pathway. The assignment of these active sites is substantiated by XPS evidence of P–C bonding and Raman results showing an increased intensity ratio (I_D/I_G) with higher P content. In addition, Shin et al. embedded sulfur atoms into the carbon framework via Sonogashira coupling using zeolitic imidazolate framework-8 (ZIF-8) as a template (Fig. 4(d)) [112]. With comparable morphology, porosity, and carbon chemical state (verified by transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET), XPS, and near-edge X-ray absorption fine structure (NEXAFS)), they convincingly identified sulfur species as the active sites. A positive correlation was observed between sulfur content and kinetic current density, with the catalyst exhibiting an electron transfer number (n) close to 4. The study revealed that the relatively low electronegativity of sulfur induces local charge redistribution in the carbon lattice, and the transfer of its lone-pair electrons into the carbon layers increases the density of states near the Fermi level, thereby reducing the energy barrier for oxygen adsorption. Afterward, Chang et al. prepared fluorine-doped carbon nanosheets using polyvinylidene fluoride (PVDF) as the carbon/fluorine source and NaCl as a template (Fig. 4(e)) [113]. The high electronegativity of fluorine (3.98) polarizes the carbon skeleton, forming semi-ionic C–F bonds (binding energy of 689.8 eV). XPS and DFT analyses identify the semi-ionic C–F bonds at armchair edges as the dominant active sites, where the resulting charge density on adjacent carbon atoms promotes O_2 adsorption and activation. This bonding state significantly enhances the charge density of carbon atoms adjacent to fluorine, promoting O_2 adsorption and activation.

Although single-heteroatom doping has improved the performance of CMFECs, it remains limited to achieving performance enhancement with only one type of heteroatom [56]. Consequently, the co-doping strategy has broadened the horizons for the development of CMFECs. Introducing multiple heteroatoms enables fine-tuning of the charge distribution, band structure, and other properties of carbon materials. Moreover, due to the synergistic interactions between different heteroatoms, such co-doping systems often exhibit a “ $1 + 1 > 2$ ” effect, significantly outperforming their single-heteroatom-doped counterparts in ORR process [114]. Liang et al. prepared sulfur and nitrogen co-doped mesoporous graphene (N–S–G) [108]. The n for N–S–G ranged between 3.3 and 3.6, and its current density reached $52 \text{ mA}\cdot\text{cm}^{-2}$ at -0.8 V , which is twice that of Pt/C. Combined experimental and DFT evidence confirms that this outstanding activity originates from the synergistic effect between the altered charge distribution around N–C sites and the spin density redistribution induced by orbital mismatch between S and C atoms (Fig. 4(f)). In addition, Zhao et al. synthesized a P/N co-doped carbon catalyst (CNP-900) via a molten-salt-mediated method, which demonstrated superior selectivity and activity compared to Pt/C [28]. *In-situ* infrared spectroscopy and DFT calculations revealed that P=O ligands modulate the charge and spin state of carbon sites, promoting the transition of O_2 adsorption from an end-on to a bridge configuration and thereby lowering the O–O bond cleavage energy barrier (Figs. 4(g) and 4(h)). Meanwhile, nitrogen atoms enhance the $4e^-$ pathway selectivity and stability of the catalyst. Similarly, Xu et al. developed N/P/S tri-doped carbon nanofibers [115]. In this system, nitrogen atoms withdraw electrons from the carbon skeleton, forming electron-rich regions that enhance oxygen

adsorption and improve the electrical conductivity of the carbon layers to facilitate electron transfer. The size mismatch of phosphorus atoms induces lattice strain, creating edge-active sites and exposing more active centers. The hybridization between sulfur 3p and carbon 2p orbitals adjusts the electronic spin density distribution, accelerating the rate-determining step. The consistency between XPS-detected N/P/S species and DFT-calculated free energy barriers substantiates the assignment of active sites. As revealed by the free energy diagrams in Fig. 4(i), the tri-doped configuration exhibits the lowest Gibbs free energy barrier for the rate-determining step, indicating thermodynamically favored ORR kinetics. Furthermore, the projected density of states (PDOS) analysis in Fig. 4(j) demonstrates that N/P/S tri-doping optimizes the electronic states near the Fermi level, enhancing charge transfer and conductivity to synergistically boost overall catalytic activity. The synergistic interplay among these three heteroatoms results in nearly 100% selectivity toward the $4e^-$ pathway and catalytic activity even surpassing that of Pt/C.

3.1.2 Heteroatoms favorable for triggering two-electron ORR

In contrast to the $4e^-$ pathway, the $2e^-$ pathway is historically regarded as a parasitic reaction that hindered efficient electron utilization [9]. However, the high electrical energy conversion efficiency and inherent clean-energy attributes have positioned electrocatalytic ORR for H_2O_2 production as a compelling alternative to revolutionize the existing H_2O_2 industry [116]. Generally, nitrogen atoms are regarded as highly efficient active sites that promote the $4e^-$ ORR pathway [56]. However, Peng et al. discovered the route can be switched by constructing a bipyrrrolic nitrogen configuration on a graphene/mesoporous carbon composite [106]. The resulting material (P-NMG-10) exhibited high H_2O_2 selectivity ($\sim 91\%$) and remarkable production rate ($30 \text{ mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) with a Faradaic efficiency of 80%. By modeling four nitrogen configurations—pyrrolic N, bipyrrrolic N, pyridinic N, and graphitic N—the authors simulated the reaction pathways and energy barriers (Fig. 5(a)). The bipyrrrolic nitrogen site exhibited a near-zero overpotential for the $2e^-$ ORR pathway. Furthermore, using the slow-growth approach, they estimated the reaction barrier for the $2e^-$ ORR pathway to be 0.54 eV , which is significantly lower than that of the $4e^-$ ORR pathway (0.92 eV) (Fig. 5(b)). The consistency between experimental quantification of pyrrolic N by XPS/X-ray absorption near-edge structure (XANES) and theoretical calculations strongly supports the assignment of bipyrrrolic nitrogen as the active site. This elucidates the mechanism by which such nitrogen configurations reduce the energy barrier of the $2e^-$ ORR process.

Oxygen-containing functional groups are generally considered to exhibit catalytic activity towards the $2e^-$ ORR [117]. Cui and colleagues introduced oxygen functional groups into carbon nanotubes via surface oxidation [35]. Compared to untreated nanotubes, the overpotential was reduced by approximately 130 mV , and the selectivity toward H_2O_2 increased from 60% to 90%. Theoretical calculations indicated that ether groups on the basal plane and carboxyl groups at the edges of graphene exhibited high activity (Figs. 5(c) and 5(d)). Oxygen doping modifies the electronic structure and surface properties of the CMFECs, promoting oxygen adsorption and reduction, thereby creating efficient active sites for ORR. Similarly, Wu et al. prepared a series of oxygen-DG samples with varied defect densities (Figs. 5(e) and 5(f)) [91]. Among them, O-DG-30 showed the highest Faradaic

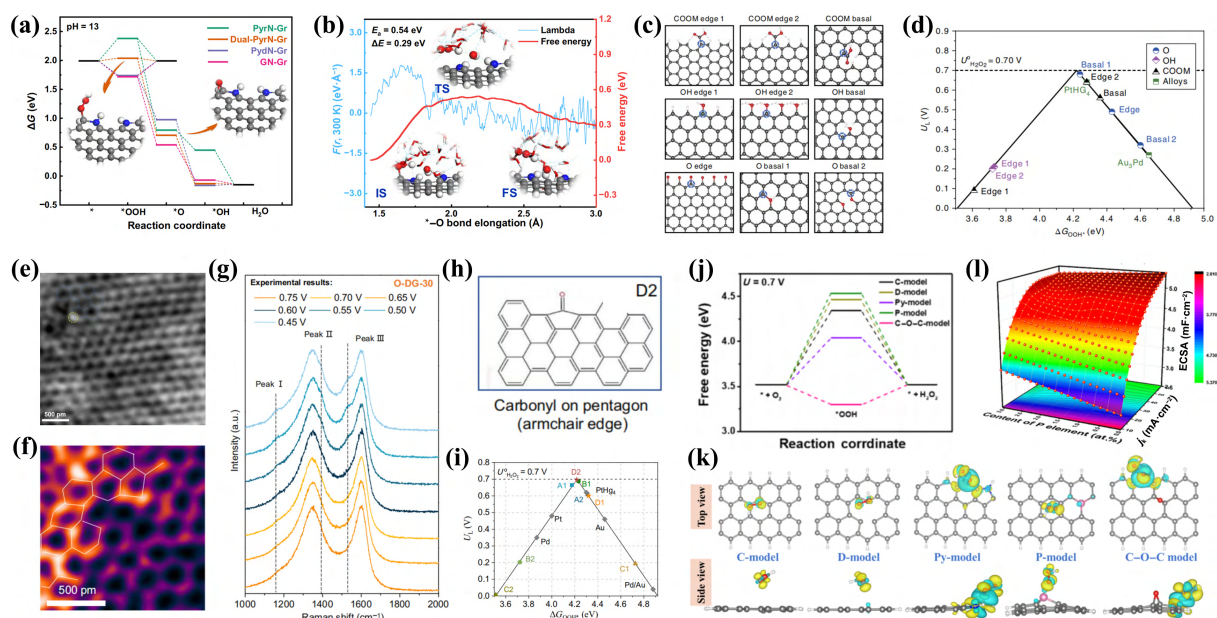


Figure 5 Heteroatom doping strategy for CMFECs towards $2e^-$ ORR. (a) Free energy profile of $2e^-$ and $4e^-$ ORR pathways at the equilibrium potentials of 0.7 V vs. RHE on different N-doped graphene models and (b) C–O bond cleavage for the $2e^-$ ORR pathways. The initial state, transition state, and final state structures are denoted as IS, TS, and FS. Blue, gray, red, and white spheres represent the N, C, O, and H atoms. Reproduced with permission from Ref. [106], © Peng, W. et al. 2023. (c) Different oxygen functional group type configurations were examined in this study. The carbon atoms denoted by a blue circle are the active sites under investigation ($M = H$ and Na), and (d) calculated $2e^-$ (solid black) ORR-related volcano plot for the electro-reduction of oxygen to H_2O_2 displayed with the limiting potential plotted as a function of ΔG_{OOH} . The equilibrium potential for the $2e^-$ ORR is shown as the dashed black line. The green squares display the activities of Pt–Hg and Pd–Au alloys, and the result for the OH basal configuration is out of the range. Reproduced with permission from Ref. [35], © Macmillan Publishers Limited 2018. (e) Integrated differential phase contrast scanning TEM (iDPC-STEM) image of O-DG-30 with partial defective domain and major perfect domain, (f) coloring and magnifying iDPC-STEM image of O-DG-30 in defective domain, (g) *in-situ* Raman spectra of O-DG-30 on flow cell in O_2 -saturated 0.1 M KOH (three new peaks were observed with the decrease of applied potentials), (h) the atomic structures of the examined O-groups on pentagon defect sites, and (i) theoretical activity volcano plot. Horizontal dashed line corresponds to the thermodynamic equilibrium potential for $2e^-$ ORR (the standard thermodynamic equilibrium potential ($U_{H_2O_2}^\circ$) = 0.70 V). Reproduced with permission from Ref. [91], © Wu, Q. L. et al. 2023. (j) Free energy profiles for the $2e^-$ ORR to H_2O_2 at the potential of $U = 0.7$ V, (k) charge density difference (CDD) of different structural units interacting with the OOH intermediate, where the isosurface is set to be 0.002 e-Bohr $^{-3}$. Yellow and cyan parts represent the enriched and deficient charges, and (l) the relationship between j_0 , efficient electrochemical surface area (ECSA), and content of P element. Reproduced with permission from Ref. [121], © American Chemical Society 2024.

efficiency for H_2O_2 production (98.38%) and a generation rate of 41.45 mg·cm $^{-2}$ ·h $^{-1}$ at 0.2 V vs. reversible hydrogen electrode (RHE). *In-situ* infrared and Raman spectroscopy were employed to monitor the dynamic evolution of oxygen-containing groups during electrocatalysis, confirming the critical role of pentagon-defect carbonyl groups in the process (Fig. 5(g)). Theoretical calculations revealed that pentagon-defect carbonyl groups are positioned near the peak of the activity volcano plot, demonstrating exceptional thermodynamic advantages (Figs. 5(h) and 5(i)).

Due to its high electronegativity, fluorine atoms demonstrate outstanding performance in modulating electronic structures [118]. Xiang et al. fabricated F, S-co-doped nanofibers via an electrospinning process [119]. The resulting F/S dual-doped metal-free carbon fibers (FS-CFs) catalyst exhibited an H_2O_2 selectivity of 99.1% at an onset potential of 0.814 V vs. RHE and achieved a H_2O_2 partial current density of 1.44 mA·cm $^{-2}$ at 0.6 V vs. RHE. DFT calculations further revealed that the dual doping of fluorine and sulfur significantly reduces the reaction energy barrier and enhances the catalytic activity through charge redistribution and electronic spin-state modulation.

The co-doping strategy is equally applicable to the $2e^-$ pathway [120]. For instance, our group achieved efficient regulation of the $2e^-$ ORR pathway through synergistic doping with N, O, and P [121]. Pyrrolic nitrogen enhances the onset potential of the reaction. Stepwise diagrams and volcano plots reveal that the C–O–C

configuration exhibits the lowest overpotential for the $2e^-$ ORR, indicating optimal thermodynamic activity (Fig. 5(j)). Differential charge density analysis visually demonstrates the binding capability of each site toward key reaction intermediates (Fig. 5(k)). Moreover, phosphorus doping improves electron transfer and intermediate transport kinetics (Fig. 5(l)). The synergistic interplay of these three elements results in a high H_2O_2 production rate of up to 16.32 mg·cm $^{-2}$ ·h $^{-1}$. Similarly, Zhang et al. developed a N, O, S-tridoped porous carbon derived from feathers [83]. In this system, pyrrolic nitrogen acts as an electron donor, contributing lone-pair electrons to the conjugated carbon matrix, which significantly enhances the nucleophilicity of adjacent carbon atoms and promotes O_2 adsorption and activation. Cyclic ether and carbonyl groups directly participate in stabilizing the *OOH intermediate through inductive effects and hydrogen-bonding interactions. Meanwhile, sulfur introduces topological strain and carbon-framework defects, accelerating proton transfer. These assignments are substantiated by combined XPS, *in-situ* FT-IR, and DFT calculations, collectively confirming the active sites.

To achieve precise regulation of the $2e^-$ ORR pathway, the rational design of dual-heteroatom-doped carbon catalysts has emerged as an effective strategy for balancing intermediate adsorption energetics and structural stability. For instance, Yu et al. developed a N, F-co-doped carbon catalyst (NFC) through a denitrogenation-fluorination cascade [122]. Fluorine selectively

passivates the unstable pyrrolic and pyridinic nitrogen sites within the nitrogen-doped carbon framework by forming semionic C–F bonds, thereby reconstructing the local coordination environment and defect state distribution. This active-site assignment is supported by DFT-calculated formation energies and validated by XPS and N K-edge XANES. This structural modulation, on the one hand, leverages the strong electron-withdrawing effect of fluorine to reduce the positive charge density on adjacent carbon atoms, optimizing the $^*\text{OOH}$ adsorption free energy toward the thermodynamically ideal value. On the other hand, the residual graphitic nitrogen preserves the integrity of the π -conjugated network, which synergizes with the fluorine-induced reduction in work function and the formation of localized in-plane electric fields to collectively facilitate interfacial electron transfer and reaction kinetics. As a result, this synergistic electronic modulation between nitrogen and fluorine endows the catalyst with nearly 100% H_2O_2 selectivity in the potential range between 0.5 and 0.65 V vs. RHE, and maintains over 95% selectivity across a wide potential window from 0.01 to 0.65 V vs. RHE.

To sum up, in the rational design of CMFECs, heteroatom doping serves as a fundamental strategy to break the inherent inertness of carbon substrates by introducing atoms with distinct structural and electronic properties, enabling precise modulation of the local electronic environment. This approach is the primary origin of ORR activity and pathway selectivity in carbon materials. Different heteroatoms modify the charge distribution, spin density, and orbital energy levels of the carbon framework in specific ways, thereby distinctly influencing the adsorption energies of key reaction intermediates.

Pyridinic nitrogen is currently the most well-defined efficient active center for the $4e^-$ pathway. Its higher electronegativity compared to carbon induces charge redistribution in adjacent carbon atoms, creating Lewis basic sites that significantly promote oxygen adsorption and O–O bond cleavage. Experimental studies have consistently shown a linear positive correlation between ORR activity and pyridinic nitrogen concentration. In contrast, pyrrolic nitrogen has been reported in several studies to favor the $2e^-$ ORR. This behavior is attributed to the five-membered ring structure of pyrrolic nitrogen and the participation of its lone-pair electrons in the conjugated system, which induces localized modulation of the charge distribution on adjacent carbon atoms. Such modulation moderately weakens the adsorption strength of the $^*\text{OOH}$ intermediate, thereby suppressing undesired O–O bond cleavage. However, the roles of other nitrogen configurations in the ORR remain poorly understood. Phosphorus, with its lower electronegativity, also induces charge redistribution around neighboring carbon atoms. Furthermore, its larger atomic radius and tendency toward sp^3 hybridization disrupt the planar sp^2 graphitic structure, introducing structural defects and strain that mitigate the catalytic inertness of the carbon matrix.

Oxygen-containing functional groups—particularly carbonyl groups at pentagon defects, ether groups, and edge carboxyl groups—are widely recognized as highly selective active sites for the $2e^-$ pathway. They optimize the adsorption and stabilization of the $^*\text{OOH}$ intermediate by altering the electronic structure and surface properties of the carbon material, offering significant thermodynamic advantages that greatly enhance selectivity toward H_2O_2 production. Interestingly, pyrrolic nitrogen has also been reported to exhibit catalytic activity for the $2e^-$ ORR.

The pathway selectivity induced by heteroatoms, such as sulfur

and fluorine, exhibits notable “configuration sensitivity” and “environment dependency”. For instance, sulfur and fluorine atoms can promote O–O bond cleavage (favoring the $4e^-$ pathway) by modulating charge/spin density, yet under specific doping environments, they may also facilitate H_2O_2 generation (favoring the $2e^-$ pathway) by optimizing electron transfer and intermediate adsorption. This ambiguity highlights the complexity inherent in the function of individual elements.

The core value of co-doping strategies lies in leveraging synergistic interactions between elements to achieve “cooperative enhancement” of the desired reaction pathway and “nonlinear improvement” in overall performance. For example, N, S co-doping synergistically promotes the $4e^-$ process through combined charge rearrangement and spin density modulation, while N, O, P, or F, S co-doping precisely optimizes the $2e^-$ pathway by jointly regulating electron supply, proton transfer, and intermediate stability. It is important to note, however, that while such strategies enable exceptional catalyst performance, the complex composition of these materials poses significant challenges for precisely tracing and elucidating the underlying mechanisms.

3.2 Defect engineering

In addition to heteroatom doping, which constitutes a crucial factor in designing active centers for electrocatalytic ORR, constructing rational defect structures is another key strategy for enhancing the intrinsic activity of catalysts [19]. By modulating defect density and defect type, the electronic structure and surface properties of CMFECs can be significantly optimized, thereby improving their catalytic performance in ORR and other electrochemical reactions [123].

3.2.1 Defect engineering for four-electron ORR

Similar to heteroatom-doped CMFECs, the undoped defective ones can also exhibit excellent ORR activity, with these defects sometimes even outperforming heteroatom-doped carbon electrocatalysts. For instance, Yao and co-workers reported a “pure” carbon material (PC-I8-950) without any elemental doping by high-temperature pyrolysis of a zinc-based metal–organic framework (MOF, IRMOF-8) [124], where the authors proposed a “defect-driven” ORR mechanism distinct from conventional heteroatom doping: In the complete absence of dopants, the high activity originates from carbon-framework defects introduced during the removal of zinc atoms in the carbonization process (Fig. 6(a)). In alkaline medium, this material showed an ORR onset potential (-0.06 V vs. Ag/AgCl) comparable to that of commercial Pt/C, high $4e^-$ selectivity, and outstanding stability as well as methanol tolerance (Fig. 6(b)). The assignment of defects as active sites is evidenced by the pronounced Raman D-band, XPS confirmation of no residual Zn or heteroatoms, and the poor ORR activity of defect-poor XC-72. These defects promote O_2 adsorption and optimize the reaction pathway by modulating local charge and spin density, thereby enabling an efficient $4e^-$ transfer process. This study opened a new chapter in understanding the intrinsic catalytic activity of CMFECs.

Furthermore, the edge structures over basal-plane structures are found to hold superior catalytic ORR performance. For example, Wang and co-workers prepared an edge-rich graphite material (G100-BM-96) via a ball-milling method [125]. This material exhibited outstanding ORR performance in 0.1 M KOH electrolyte: Its onset potential shifted significantly positively compared to

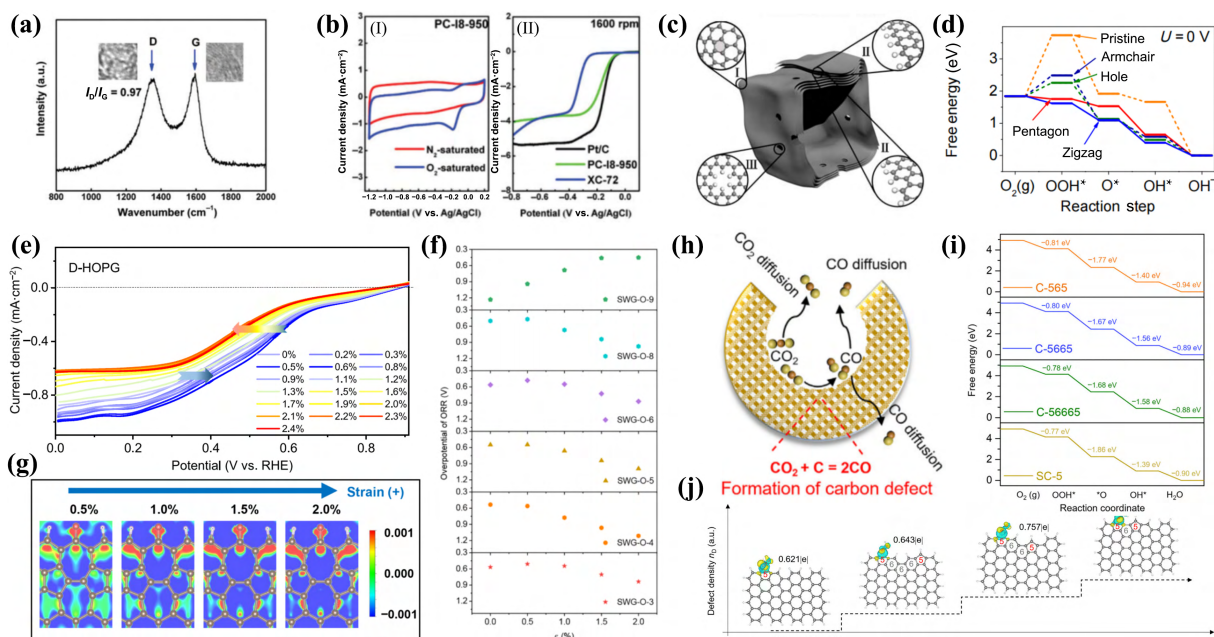


Figure 6 Defect engineering for CMFECs towards $4e^-$ ORR. (a) Raman spectra of PC-I8-950 and cyclic voltammetry (CV) curve of PC-Zn-950 sample in 0.1 M KOH solution. (b) Linear sweep voltammogram (LSV) curves at 1600 rpm of PC-Zn-950, Pt/C, and XC-72 catalysts. Reproduced with permission from Ref. [124], © The Royal Society of Chemistry 2012. (c) Schematic structural characters of the carbon nanocages. I, II, and III represent three typical defective locations, i.e., the corner, the broken fringe, and the hole. (d) Free energy diagrams for ORR activities of different defects. Reproduced with permission from Ref. [18], © American Chemical Society 2015. (e) ORR polarization curves of D-HOPG under different ϵ from 0.0% to 2.4% in 0.1 M KOH. (f) The relationship between strain and overpotential for Stone–Wales graphene (SWG)–O sites, and (g) variation of charge density distribution with strain in the SWG–O structure. Red and blue stand for the increase and decrease of charge density compared to the initial state. Reproduced with permission from Ref. [92], © American Chemical Society 2025. (h) Diagram of CO_2 gas diffusion on carbon cavity and relevant redox reaction at pyrolytic process, (i) free energy diagram SC-5, C-56665, C-5665, and C-565 models at potential of 0 V, and (j) the electron density corresponding to adsorbed $^*\text{OOH}$ on SC-5, C-56665, C-5665, and C-565 sites. Reproduced with permission from Ref. [25], © Elsevier Inc. 2022.

pristine graphite, and its kinetic current density reached $2.15 \text{ mA}\cdot\text{cm}^{-2}$ at -0.4 V vs. saturated calomel electrode (SCE), which is 8.6 times higher than that of pristine graphite ($0.25 \text{ mA}\cdot\text{cm}^{-2}$). This enhancement is attributed to the abundant edge defects introduced by ball-milling, which greatly increased the edge density (the I_D/I_G ratio rose from 0.19 to 1.12). Theoretical calculations revealed that these edge carbon atoms possess higher local charge density. Such a distinct electronic structure optimizes the adsorption of ORR intermediates, thereby significantly boosting the catalytic activity. Micro-droplet electrochemical experiments provided direct, visual evidence for this “edge-high-activity” mechanism by comparing the activity of edge and basal sites on the same graphite crystal.

In addition, topological defects, including zigzag-edge carbons and armchair-type pentagon defects, are recognized as the primary ORR active sites. Srinivas et al. introduced topological defects into pure nanocarbon to synthesize defect-rich mesoporous carbon nanoribbons (NR-900) [126], which exhibited a diffusion-limited current density of $5.13 \text{ mA}\cdot\text{cm}^{-2}$ and a n close to 4. Notably, its double-layer capacitance (C_{dl}) value reached $38.66 \text{ mF}\cdot\text{cm}^{-3}$, significantly higher than that of other control samples, indicating a larger electrochemical active surface area and more exposed catalytic sites. DFT calculations identified that zigzag-edge defects exhibited a low free-energy requirement, especially during the $^*\text{OH}$ removal step (0.43 eV), effectively promoting $^*\text{OH}$ desorption and enhancing ORR efficiency. Armchair-type pentagon defects located at pore edges showed a low energy barrier for O_2 adsorption and $^*\text{OOH}$ formation (0.64 eV), thereby improving the onset potential. These two types of defects synergistically enhanced the overall catalytic performance.

Hu and colleagues prepared a defective carbon nanocage (CNC-700) with topological pentagon defects, which demonstrated a high onset potential of about 0.11 V vs. normal hydrogen electrode (NHE) in 0.1 M KOH [18]. The introduced defects disrupted the π -conjugation integrity, leading to charge redistribution around the defective sites and activating the carbonyl π -electrons (Fig. 6(c)). Meanwhile, zigzag-edge defects, possessing unpaired π -electrons, facilitated electron transfer to O_2 and the formation of $^*\text{OOH}$. DFT calculations showed that the free-energy diagrams for ORR on these defect sites exhibited a stepwise downward trend, indicating thermodynamic favorability (Fig. 6(d)). Annealing experiments under argon to heal edge defects resulted in retained catalytic activity, experimentally confirming the theoretical prediction that pentagon defects contribute significantly to the catalytic performance. Similarly, Li et al. reported a defect-engineering strategy based on fullerene-derived carbon, successfully constructing a pentagon-defect-rich carbon electrocatalyst (dFCMC) via a nitrogen-doping followed by de-doping process [27]. This material displayed excellent ORR performance in alkaline media, with a half-wave potential ($E_{1/2}$) as high as 0.834 V , close to that of commercial Pt/C, and high $4e^-$ selectivity ($n = 4.01$). Combined theoretical and experimental studies revealed that the intrinsic pentagon defects in the precursor significantly altered the preferred sites for nitrogen doping, shifting them from edges to the basal plane and thus substantially increasing the doping level. More importantly, during the de-doping process, graphitic nitrogen located within pentagons was more readily removed than nitrogen in hexagonal rings, generating a new pentagon–heptagon–pentagon (5–7–5) topological defect structure. The assignment of the 5–7–5 structure as the active site is strongly evidenced by the

correlation between experimental pentagon enrichment and theoretical free-energy diagrams, which identify specific sites of the 5–7–5 structure with high spin density and favorable *OH formation barrier. This structure served as an efficient ORR active center by modulating the charge and spin density distribution of adjacent carbon atoms, effectively promoting O₂ adsorption and O–O bond cleavage. The reaction followed a 4e[−] pathway, reducing the energy barrier of the rate-determining step (*OH formation) and facilitating efficient ORR.

Beyond conventional chemical approaches, the catalytic activity of CMFECs can also be efficiently modulated through convenient mechanical stimuli. Wang group systematically investigated the effect of intrinsic mechanical strain on the ORR performance of HOPG by constructing a platform capable of applying continuous and controllable strain [92]. For pristine HOPG, ORR activity showed only minor variations within the strain range between 1.0% and 2.0%, with a maximum current density increase of about 9.7% observed under approximately 0.8% compressive strain. In contrast, in-plane defect-rich HOPG (D-HOPG) exhibited a pronounced strain-enhancement effect: Applying about 0.6% tensile strain (ϵ) in alkaline electrolyte increased the ORR current density at 0.5 V vs. RHE by approximately 35.0%, and this effect remained consistent in both acidic and alkaline environments (Fig. 6(e)). Mechanistic studies revealed that Stone–Wales defects serve as the key strain-responsive active centers (Fig. 6(f)). The assignment is strongly supported by the convergence of *in-situ* spectroscopies, DFT calculations, and strain-controlled electrochemistry. A tensile strain of around 0.5% optimizes the charge distribution of adjacent carbon atoms, modulates the adsorption energy of intermediates, such as *OOH and *OH, and shifts the rate-determining step from *OH desorption to *OOH adsorption, thereby lowering the reaction barrier and enhancing the efficiency of the 4e[−] ORR pathway (Fig. 6(g)). This work elucidates, at the atomic scale, the mechanism by which mechanical strain activates inert sites in CMFECs through local electronic structure modulation, providing a theoretical and experimental foundation for the development of carbon-based mechano-electrocatalysis.

Topological defects have made outstanding contributions to enhancing the catalytic activity of CMFECs, while sp³-hybridized carbon can also significantly improve the ORR performance [127]. Cao et al. prepared a nitrogen-doped carbon catalyst rich in sp³-hybridized carbon [128]. XANES analysis revealed an increased fraction of sp³-carbon, which disrupts the π -conjugation of the carbon framework. This alteration in the electronic structure of the carbon material activates inherently inert carbon atoms. The structural disordering and short-range disruption induced by sp³-carbon led to charge redistribution around the defects, endowing neighboring carbon atoms with higher reactivity. This enhanced reactivity facilitates more efficient adsorption and activation of oxygen molecules (O₂) and promotes subsequent reduction steps. The identification of sp³-hybridized defects as active sites is substantiated by multiple complementary techniques, including XPS, Raman, XANES, and DFT calculations.

In addition to defect type and configuration, defect density also plays a crucial role in determining catalytic activity. Yao and colleagues reported an interfacial self-corrosion strategy to successfully prepare a higher defect density porous carbon (HDPC) material [25]. Through a thermochemical redox reaction between ZnO quantum dots and the generated CO₂ gas within confined carbon cavities, the removal and reconstruction of carbon atoms

could be precisely controlled, resulting in an ultra-high density of carbon defects (Fig. 6(h)). The synthesized HDPC catalyst exhibited a defect density as high as $2.46 \times 10^{13} \text{ cm}^{-2}$. In 0.1 M KOH and 0.1 M HClO₄ electrolytes, the half-wave potentials of HDPC reached 0.90 and 0.75 V, respectively, both surpassing those of commercial Pt/C. Experimental results and DFT calculations jointly indicated that both the density and spatial proximity of carbon defects significantly influence ORR activity. Free energy diagrams and Bader charge analysis revealed that high-density, neighboring defect sites optimize the adsorption energy of intermediates and enhance charge transfer through a “proximity effect”, leading to outstanding ORR performance (Figs. 6(i) and 6(j)). Moreover, finite element method (FEM) simulations were employed to study the diffusion and transformation of CO₂ within the carbon cavities, verifying the critical role of confined space in the formation of carbon defects.

The performance of pure-carbon catalysts is highly dependent on the balance between graphitic structure (high conductivity) and defect structure (abundant active sites). Our group utilized a dual-molten-salt chemical treatment method to prepare heteroatom-free graphite/defect heterostructured carbon nanosheets, which simultaneously possess efficient charge transport and rich active sites [129]. Structure–property relationship studies reveal a strong correlation between the proportion of pentagon defects and electrochemical activity. Furthermore, *in-situ* Raman spectroscopy observed strong interaction between pentagon defects and intermediates (e.g., *OOH), providing direct evidence that pentagon rings serve as the active sites, while the graphite structure dynamically participates in the ORR process along with potential changes. The sample with an optimal graphite-to-defect ratio exhibited the lowest charge-transfer resistance, demonstrating excellent synergy between graphite and defects, and ultimately achieved a high turnover frequency (TOF) value of 4.672 electrons·site^{−1}·s^{−1} and an electron transfer number close to 4. In another study by our group, we identified a clear threshold relationship between edge-defect density and conductivity in carbon catalysts: When conductivity exceeds approximately 70 S·m^{−1}, increasing edge density significantly enhances ORR activity (positive shift in half-wave potential and increased limiting current); however, when conductivity falls below this threshold (e.g., 44.6 S·m^{−1}), the ORR activity declines with the defective edging degree, indicating that a conductive network is essential for edge-site activity [130]. Edge sites promote O₂ adsorption and O–O bond cleavage via their unsaturated dangling bonds and high local density of states, thereby favoring the 4e[−] pathway.

3.2.2 Defect engineering for two-electron ORR

Similar to heteroatom-based active sites, defect structures can function as catalytic centers not only for driving the 4e[−] ORR pathway but also for promoting the 2e[−] pathway, posing a significant challenge for the rational design of defective carbon materials with tailored selectivity for either 2e[−] or 4e[−] ORR. In contrast to the earlier discussion on pentagon defects favoring the 4e[−] pathway, Zhang et al. reported a CMFEC rich in pentagon defects for H₂O₂ production [40]. Although nitrogen atoms were also introduced, the E_0 showed a positive correlation with the D3/G band ratio, confirming the dominant contribution of defects to the activity (Fig. 7(a)). Electron paramagnetic resonance (EPR), aberration-corrected-STEM, Raman D3/G ratio, and DFT calculations collectively identify pentagon defects adjacent to

graphitic N as the active sites. The curvature distortion of the carbon skeleton induced by pentagonal defects results in asymmetric electron distribution and enhanced local charge density, enabling precise modulation of the adsorption strength of $^*\text{OOH}$ (Fig. 7(b)). High H_2O_2 selectivity ($\sim 98\%$) was maintained over a broad potential range between 0 and 0.6 V. In a related study, Deng et al. achieved controlled H_2O_2 generation via pentagon defects by tuning the applied potential [131]. DFT-calculated $^*\text{OOH}$ adsorption energies and free energy diagrams across multiple defect configurations corroborate this active-site assignment. They proposed an “active site saturation” theory: At low overpotentials ($E > 0.65$ V), $4e^-$ ORR sites become saturated due to slow intermediate desorption, allowing $2e^-$ sites to participate and favoring H_2O_2 formation. In their system, vacancy defects were found to promote the $4e^-$ pathway, while edge-located pentagon defects facilitated the $2e^-$ pathway (Figs. 7(c) and 7(d)). Interestingly, interfacial electric field could be effectively tuned by the construction of carbon defects. Su et al. employed a defect-modification strategy by leveraging the surface dipole difference between dopamine molecules and defective carbon sites [132]. Through non-covalent electrostatic interactions, an interfacial electric field was formed, redistributing the electron density around carbon active sites and inhibiting O–O bond cleavage. Although oxygen dopant was present in the material, *in-situ* infrared spectroscopy confirmed that carbon defects served as the active centers (Fig. 7(e)). The resulting catalyst exhibited excellent $2e^-$ ORR activity, with Faradaic efficiency $> 95\%$ (0.4–0.7 V vs. RHE) in 0.1 M KOH and an H_2O_2 production rate of $1.8 \text{ mol}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ (accumulated concentration of $105 \text{ mmol} \cdot \text{L}^{-1}$ over 12 h).

The unique electronic structure of sp^3 -hybridized carbon is recognized to effectively stabilize the $^*\text{OOH}$ intermediate and consequently improve $2e^-$ ORR selectivity. For example, Ni et al. prepared oxygen-functionalized carbon quantum dots (CQDs) and observed that although electron-withdrawing groups, such as aldehydes, increased the C 1s binding energy of sp^3 -carbon, the catalytic performance did not directly correlate with oxygen content [116]. Instead, a strong positive correlation ($R^2 > 0.95$) was found between sp^3 -carbon content and H_2O_2 selectivity (Fig. 7(f)). The strong electron-withdrawing nature of sp^3 -carbon weakens the tendency for O–O bond cleavage in $^*\text{OOH}$, suppressing the $4e^-$ pathway and optimizing its adsorption energy. DFT calculations yielded $\Delta G_{^*\text{OOH}} = 4.70 \text{ eV}$, close to the theoretical optimum (4.22 eV) (Fig. 7(g)).

Beyond directly utilizing the intrinsic activity of defect sites, introducing secondary structures that themselves lack catalytic activity can serve as modifiers to tune defect performance and enhance overall catalytic properties. Hu et al. prepared a chlorine-doped, pentagon-defect-rich carbon catalyst (Cl-PDC) using fullerene as a precursor via a molten-salt-assisted strategy [88]. Under simulated seawater conditions (0.5 M NaCl), Cl-PDC showed a significantly more positive onset potential than undoped PDC, indicating enhanced ORR performance due to chlorine doping. Over a wide potential range between 0.2 and 0.5 V vs. RHE, H_2O_2 selectivity exceeded 90%, accompanied by the lowest Tafel slope ($64 \text{ mV} \cdot \text{dec}^{-1}$) and the largest electrochemical active surface area. The improvement in activity and selectivity originated from the precise anchoring of chlorine atoms, which modified the electronic structure of pentagon defects. The high electronegativity

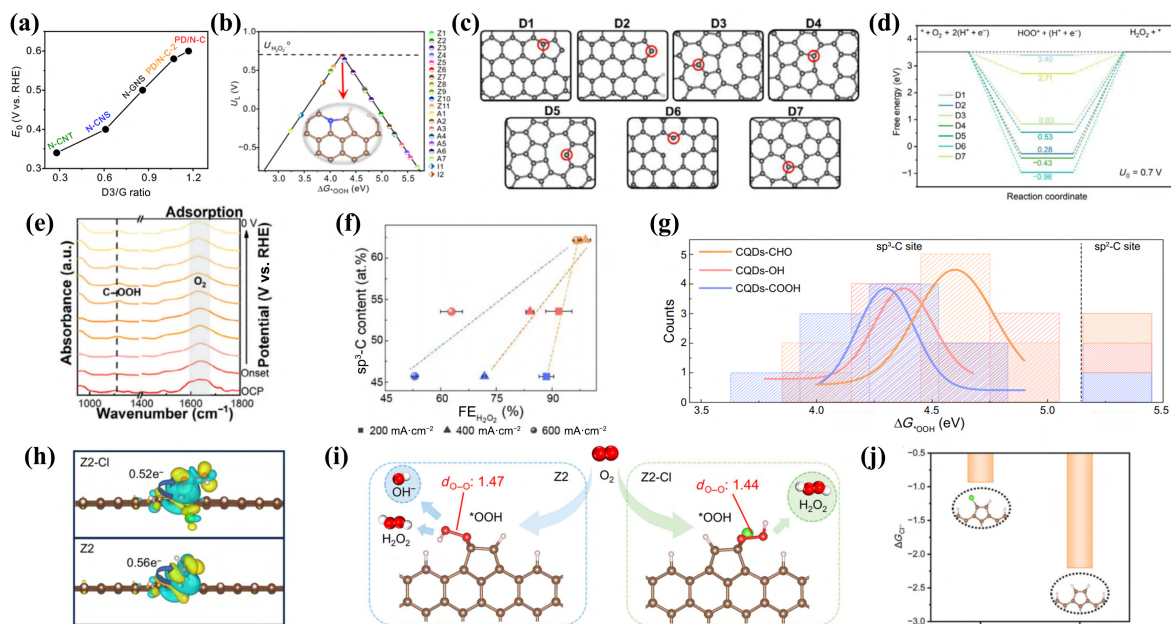


Figure 7 Defect engineering for carbocatalysts towards $2e^-$ ORR. (a) E_0 as a function of the D3/G ratio of N-CNT, N-doped carbon nanospheres (N-CNS), N-GNS, pentagonal defect-rich NC nanomaterial (PD/N-C)-2, and PD/N-C and (b) volcano plot between U_1 and $\Delta G_{^*\text{OOH}}$ for $2e^-$ ORR. Reproduced with permission from Ref. [40], © American Chemical Society 2023. (c) Atomic configurations of the various defect models and (d) free energy diagram of different carbon sites for $2e^-$ ORR at the potential of 0.7 V. Reproduced with permission from Ref. [131], © Deng, Z. P. et al. 2025. (e) *Operando*-FTIR spectra recorded during electrosynthesis of H_2O_2 in O_2 -saturated 0.01 M KOH solution. Reproduced with permission from Ref. [132], © Wiley-VCH GmbH 2023. (f) Atomic content of sp^3 -carbon at industrially relevant current densities as a function of H_2O_2 selectivity for CQDs and (g) distribution of $\Delta G_{^*\text{OOH}}$ on three CQDs, highlighting differences between sp^2 -C and sp^3 -C adsorption sites. The statistical distributions of $\Delta G_{^*\text{OOH}}$ are obtained from the calculation of sp^3 -C sites on three CQDs. Reproduced with permission from Ref. [116], © Ni, B. X. et al. 2025. (h) The charge density before and after interacting with $^*\text{OOH}$ of Z2-Cl and Z2; the isosurface is set as $0.005e^-$ per Å; yellow and cyan represent positive and negative charges, (i) catalytic mechanism of O_2 reduction on Z2 and Z2-Cl, and (j) the adsorption energy of Z2-Cl and Z2 for Cl^- . Reproduced with permission from Ref. [88], © Wiley-VCH GmbH 2025.

of chlorine (3.16) induced charge redistribution in the carbon skeleton, reducing the charge transfer at the active site from $0.56e^-$ (undoped) to $0.52e^-$ (Fig. 7(h)), thereby weakening the adsorption strength of *OOH and optimizing the adsorption energy of pentagon defects for key intermediates. Mechanistic analysis further reveals that chlorine doping shortens the O–O bond length of the *OOH intermediate from 1.47 Å (Z2) to 1.44 Å (Z2-Cl), indicating moderated O_2 activation that prevents excessive O–O bond cleavage and thus favors the $2e^-$ ORR pathway (Fig. 7(i)). Moreover, the reduced positive charge at active sites due to chlorine doping increased the adsorption energy of Cl^- from -2.202 eV (undoped) to -0.931 eV (Fig. 7(j)), significantly mitigating chloride poisoning in seawater.

In summary, the defect-active sites can be categorized as follows:

Defects that favor the $4e^-$ ORR primarily include edge defects (e.g., zig-zag edges), topological defects (e.g., pentagon–heptagon structures), and high-density neighboring defects. These defects enhance O_2 adsorption, facilitate O–O bond cleavage, and optimize the desorption kinetics of intermediates, such as *OH , by modulating local charge and spin density. Furthermore, the full expression of their catalytic performance often relies on synergistic support from a highly conductive graphitic network and responsiveness to mechanical strain, collectively promoting an efficient and stable $4e^-$ transfer pathway.

In contrast, defect conducive to the $2e^-$ ORR focuses on suppressing O–O bond cleavage and stabilizing the *OOH intermediate to achieve high selectivity toward H_2O_2 production. Defects with such tendency mainly include certain pentagon defects, sp^3 -hybridized carbon defects, as well as defect structures modified by doping (e.g., chlorine) or interfacial electric fields. These defects reconstruct the local electronic structure and optimize the adsorption mode of O_2 toward an end-on configuration, thereby promoting the formation of the *OOH intermediate. In terms of reaction energetics, the $\Delta G_{^*OOH}$ on these defect sites is tuned close to the thermodynamic ideal value, stabilizing this intermediate and inhibiting its further O–O bond cleavage and reduction. Moreover, electronic modulation introduced via doping or interfacial engineering (e.g., highly electronegative chlorine atoms) can further reduce charge transfer at the active site, weaken the adsorption strength of *OOH , and facilitate *OOH desorption as H_2O_2 . Consequently, such microenvironments work synergistically at both electronic and kinetic levels to effectively steer the ORR along the $2e^-$ pathway.

It is noteworthy that certain defects, such as pentagon defects, exhibit a dual catalytic nature—They can promote either the $4e^-$ pathway or a highly selective $2e^-$ process. This apparent contradiction stems partly from limitations in characterization: Current identification of defects largely relies on deconvolution of Raman spectra, where overlapping peaks from different defect types and subjective interpretation can affect accurate defect assignment. Notably, difficulties in precise control over defect structures during synthesis introduce ambiguity in attributing intrinsic catalytic properties. Additionally, the local microenvironment—including the arrangement of neighboring defects, heteroatom doping, strain state, and the nature of the conductive substrate—can significantly influence the catalytic behavior of defects, which may also explain the divergent selectivity observed for pentagon defects. This complexity underscores the need for more advanced characterization techniques and precisely controlled synthesis methods to fully unravel the structure–activity relationships of

defect sites, thereby enabling the rational design of CMFECs with tailored ORR selectivity.

3.3 Active-site microenvironment engineering

Research on the intrinsic activity of active sites in CMFECs has become increasingly in-depth. However, the activity of the electrocatalytic ORR process is not solely determined by the intrinsic activity of the active sites but is also closely related to the microenvironment surrounding them. The term “active-site microenvironment” proposed in this review refers to the localized structure within a finite scale surrounding the active site (such as doped atoms or defects), which constitutes an inherent structural attribute of the catalyst itself.

It is important to note that the term “microenvironment” frequently appears in the context of single-atom catalysts, where it typically refers to the coordinating atoms surrounding the metal active center. This concept differs from the “microenvironment” discussed in this article. In the present context, microenvironment pertains to the localized structural and electronic environment of active sites within the carbon matrix itself, including factors like adjacent functional groups, defect arrangements, charge distribution, and interfacial interactions that collectively modulate the adsorption behavior and reaction pathway of intermediates. This distinction underscores the need for precise terminology when describing catalytic systems across different material classes [133].

Distinct from isolated heteroatom sites or defect structures, the “active-site microenvironment” itself is generally not considered catalytically active. Instead, it enhances the catalytic capability of the active center, facilitates the full expression of its activity, and functions in a manner analogous to a “catalytic promoter”. In the following sections, we will focus on three categories of microenvironment: (1) Atomic-scale chemical environment: This refers to the adjacent heteroatom configurations around the active center, which directly influence its electronic structure, including charge density and spin state. (2) Topological and surface configuration: This encompasses the carbon-based topology supporting the active site (e.g., topological defects and curvature) and the local fine structure of the surface (e.g., edges and wrinkles), along with the resulting strain effects. (3) Morphological and mesoscale spatial structure: This involves the pore architecture or morphological features surrounding the active site, which affect reactant mass transport and intermediate stabilization through spatial confinement.

This conceptual framework aims to treat the catalytic active region as an integrated “active system” or “cascade system”, moving beyond the traditional focus on isolated atoms or functional groups. It emphasizes a synergistic analysis that considers both the global and local aspects of the catalytic system [134].

3.3.1 Microenvironment engineering for four-electron ORR

The charge distribution around an active site is a critical component of its microenvironment, and modulating the local charge environment serves as an important strategy for constructing an effective active center. For instance, Zhang et al. synthesized a nitrogen/sulfur-co-doped hierarchical porous carbon nanoreactor with ultra-high surface areas (NSC_{HSA}) using ZIF-8 as a precursor via an etching-doping pyrolysis strategy [135]. In both alkaline (0.1 M KOH) and acidic (0.5 M H_2SO_4) electrolytes, the NSC_{HSA} exhibited significantly more positive half-wave potentials

(0.952 and 0.754 V vs. RHE, respectively) compared to undoped and singly-doped samples. It maintained an electron transfer number close to 4 over a wide potential range, along with low Tafel slopes (88 and 84 mV·dec⁻¹). This performance enhancement originated from the atomic-scale microenvironment engineering of the carbon active sites. The two heteroatoms were not doped in isolation but formed an S–C–N configuration around the carbon atom, altering its electron cloud distribution. This assignment of S–C–N as the genuine active site is substantiated by *in-situ* XPS, Raman, ATR-SEIRAS, and DFT calculations. Furthermore, under ORR working potentials, the initial S–C–N structure reversibly transformed into an pre-adsorbed oxygen (O_{pre})–S–C–N configuration. This dynamic evolution further regulated the electron density of the carbon active center, optimizing charge transfer from 1.24e⁻ (in NC) to 1.39e⁻ (in O_{pre}–S–C–N) (Figs. 8(a)–8(c)). This adjustment weakened the adsorption strength of oxygen intermediates and reduced the energy barrier for the conversion of *O to *OH (from 1.03 to 0.69 eV) (Fig. 8(d)). When applied in an aluminum–air battery (AAB), the catalyst enabled a high-power density (265 mW·cm⁻²) and energy density (4152 Wh·kg⁻¹).

Although studies have shown that the intrinsic catalytic activity of graphitic nitrogen for the 4e⁻ ORR remains debated, this does not preclude its role as an effective microenvironmental modulator that enhances the catalytic performance of active sites [93]. Chen et al. synthesized a hierarchically porous S, N-doped carbon nanoflower (H-SNF) [107]. In 0.1 M KOH solution, H-SNF

exhibited an onset potential of 0.97 V and a half-wave potential of 0.81 V vs. RHE, with a *n* close to 4. A zinc–air battery based on H-SNF delivered a high open-circuit voltage (OCV) of 1.40 V and a peak power density of 161.4 mW·cm⁻². Combined XPS, NEXAFS, and DFT calculations provided robust evidence that pyridinic N serves as the primary active site for O₂ activation, whereas graphitic N acts as a catalytic promoter. In this system, graphitic nitrogen does not serve as an independent catalytic site but acts as a “catalytic promoter” that optimizes the reaction pathway by modulating the microenvironment of the primary active center—pyridinic nitrogen (Fig. 8(e)). The introduction of graphitic nitrogen alters the electronic structure around pyridinic nitrogen sites, weakening their overly strong adsorption toward oxygen intermediates and thereby enhancing the desorption and transfer efficiency of *OOH. While pyridinic nitrogen acts as the main active site responsible for rapid O₂ activation and *OOH formation, graphitic nitrogen, though incapable of catalyzing ORR alone, accepts the post-cleavage intermediates (O/OH) generated after O–O bond scission. This cooperative arrangement prevents the accumulation of intermediates on the active sites, mitigating site poisoning. By avoiding excessive *OOH buildup at the oxygen-adsorption sites, this structure accelerates mass transport and enables an efficient 4e⁻ ORR process.

Existing studies have demonstrated the catalytic potential of pentagon defects for the ORR, indicating that modulating the microenvironment of these pentagon defects represents a viable strategy for further enhancing their performance [136]. Xia et al.

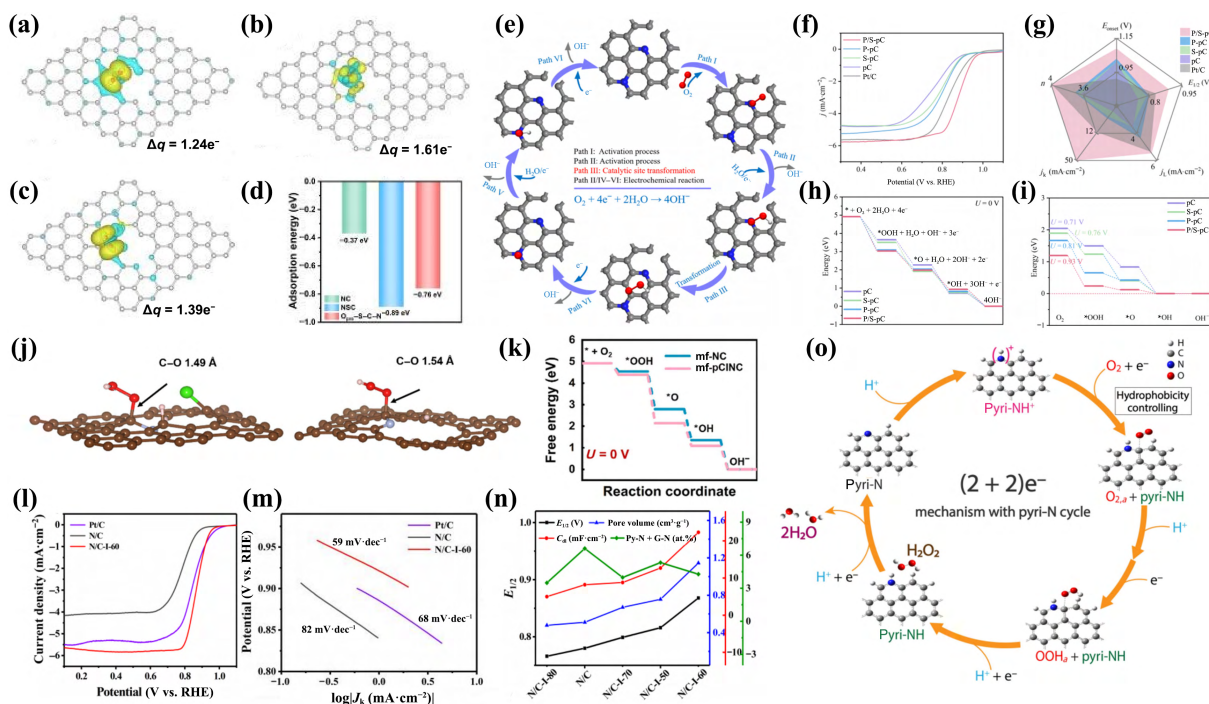


Figure 8 Active-site microenvironment engineering for CMFEs towards 4e⁻ ORR. ((a)–(c)) Charge transfer between various models (charge accumulation and consumption in yellow and cyan) and (d) adsorption energy of O₂ on NC, NSC, and O_{pre}–S–C–N. Reproduced with permission from Ref. [135], © The Royal Society of Chemistry 2026. (e) Schematic diagram of the synergistic catalytic ORR mechanism on both G-N and pyridinic N sites. Reproduced with permission from Ref. [107], © Chen, C. L. et al. 2025. (f) LSV curves of the resultant catalysts and Pt/C in 0.1 M KOH, (g) plots of *E*_{onset}, *E*_{1/2}, *j*_{0.8V}, *j*_k (@0.80 V vs. RHE), and *n*, (h) the ORR trends under 1.23 V, and (i) estimated onset potentials. Reproduced with permission from Ref. [61], © American Chemical Society 2025. (j) Side view of the metal-free porous electrocatalyst doped with Cl (mf-pCINC) electrocatalyst and the mf-NC electrocatalyst adsorbed with *OOH, and (k) Gibbs free energy of the ORR intermediates on the mf-pCINC and the mf-NC electrocatalysts at 1.23 V vs. RHE. Reproduced with permission from Ref. [26], © Wiley-VCH GmbH 2023. (l) LSV curves of Pt/C, N/C-I-60, and N/C, (m) Tafel slopes of ORR on Pt/C, N/C-I-60, and N/C, and (n) the changing trend of *E*_{1/2}, pore volume, *C*_{st}, and Py-N + G-N content in N/C and N/C-I-T (*T* indicates the temperature). Reproduced with permission from Ref. [137], © 2022 Elsevier B.V. (o) Schematic pathway for the ORR over nitrogen-doped carbon materials with pyridinic N. Reproduced with permission from Ref. [87], © Wiley-VCH GmbH 2022.

prepared a P/S-co-coordinated pentagon-defect carbon catalyst (P/S-pC) [61]. The kinetic current density reached $50.14 \text{ mA}\cdot\text{cm}^{-2}$ at 0.80 V vs. RHE, which is 19.7 times that of pristine pentagon-defect carbon ($2.55 \text{ mA}\cdot\text{cm}^{-2}$) and 4.2 times that of commercial Pt/C ($11.83 \text{ mA}\cdot\text{cm}^{-2}$), with nearly 100% selectivity for the $4e^-$ pathway (Figs. 8(f) and 8(g)). XPS, high-angle annular dark-field (HAADF)-STEM mapping, and DFT calculations collectively confirm that P and S atoms occupy specific meta positions of pentagonal carbon, unambiguously identifying the active sites. This remarkable enhancement stems from atom-level deconstruction design of the pentagon-defect site: P and S atoms were deliberately positioned at specific meta-sites of the pentagon carbon defect, fundamentally reconstructing the local chemical microenvironment of the active center. The rational tuning of the pentagon-defect microenvironment by the P/S pair enables asynchronous optimization of O_2 adsorption and OH desorption (Figs. 8(h) and 8(i)). On the one hand, the precise anchoring of low-electronegativity P/S atoms induces charge redistribution in the pentagon defect, increasing the nucleophilicity of the defective carbon site and promoting $^*\text{O}_2$ adsorption and activation. On the other hand, coupling between the $3p$ orbitals of P/S and the $2p$ orbitals of carbon shifts the p -band center from near the Fermi level down to -1.5 eV . This downward shift weakens the adsorption strength of $^*\text{OH}$. A zinc-air battery using P/S-pC as the cathode catalyst outperformed the Pt/C-based system in all key metrics: Peak power density reached $204.9 \text{ mW}\cdot\text{cm}^{-2}$ ($1.5\times$ that of Pt/C at $137.7 \text{ mW}\cdot\text{cm}^{-2}$), and specific capacity achieved $797.5 \text{ mAh}\cdot\text{g}_{\text{Zn}}^{-1}$ (97.3% of the theoretical value).

Similarly, Feng et al. introduced chlorine heteroatoms and sp^3 -hybridized carbon to modulate the activity of nitrogen-doped carbon catalysts [26]. They first identified the carbon atom adjacent to nitrogen in CMFECs as the core ORR active center, and then revealed that the performance improvement primarily originates from precise regulation of the atomic-scale microenvironment jointly constructed by sp^3 -hybridized carbon defects and chlorine doping. In this microenvironment, sp^3 -carbon defects disrupt the π -conjugation continuity of the graphite network, leading to localized electron distribution around neighboring nitrogen atoms. Simultaneously, chlorine atoms, due to their high electronegativity, synergize with sp^3 -carbon to induce directional electron transfer from nitrogen atoms to the adjacent carbon active center. This assignment of N-adjacent carbon as the active site is strongly evidenced by combined XPS, Raman, XANES, and DFT calculations, which consistently show Cl/ sp^3 -induced electronic modulation and reduced OOH adsorption barrier. Ultimately, this microenvironment engineering effectively optimizes the electronic structure of the active site. Bader charge analysis indicated electron transfer from the catalyst surface to $^*\text{OOH}$, shortening the C–O bond length ($1.49 \text{ \AA}$) and strengthening adsorption (Fig. 8(j)). This significantly reduced the adsorption energy barrier for the key intermediate $^*\text{OOH}$ (from 0.85 to 0.70 eV) (Fig. 8(k)), thereby greatly enhancing the intrinsic ORR activity of the material.

Hierarchical porous structures, which integrate pores of different scales, provide an ideal microenvironment for active centers by efficiently exposing sites, accelerating mass transport, and stabilizing local concentrations. This represents an important direction for improving catalyst performance. Su et al. employed a template-free iodine-vapor-assisted pyrolysis strategy to prepare a coral-like nitrogen-doped carbon material (N/C) with a hierarchical porous structure [137]. N/C-I-60 exhibited a half-wave potential of 0.868 V , a limiting current density of $5.84 \text{ mA}\cdot\text{cm}^{-2}$, and a Tafel slope of $59 \text{ mV}\cdot\text{dec}^{-1}$, demonstrating excellent catalytic activity and fast

reaction kinetics (Figs. 8(l) and 8(m)). The hierarchical porous structure played a key role in mass transport: Micropores provide a high specific surface area, exposing numerous pyridinic N sites (Fig. 8(n)). XPS, SCN^- poisoning, and acid washing tests confirm that pyridinic N serves as the primary active site while ruling out any catalytic contribution from residual Zn species. Mesopores ($2\text{--}50 \text{ nm}$) serve as fast channels for mass exchange, accelerating the diffusion of O_2 and electrolyte, and macropores act as “electrolyte reservoirs”, buffering local concentration fluctuations and ensuring a steady and continuous supply of reactants.

Beyond the regulation of the local environment of active centers through heteroatom doping, defect engineering, and pore architecture, recent research has revealed that the “docking” behavior of electrolyte cations in sub-nanopores ($< 1 \text{ nm}$) of carbon cathodes constitutes another important class of microenvironment modulation mechanism [138]. By combining constant-voltage reactive molecular dynamics simulations with electrochemical experiments, Cs^+ , K^+ , and Na^+ are demonstrated to exhibit different degrees of dehydration upon entering sub-nanopores: Cs^+ is almost completely dehydrated, whereas Na^+ carries approximately three water molecules. This difference leads to varying extents of local charge redistribution, with Cs^+ inducing the largest charge fluctuation on carbon atoms after docking, thereby significantly enhancing O_2 adsorption and O–O bond cleavage ability—a critical step for the $4e^-$ ORR pathway. Experimental results confirm that the Cs^+ system possesses the highest capacitance and an electron transfer number close to 4, whereas the Na^+ system shows the poorest performance. This finding establishes, for the first time, a direct correlation between the classical Hofmeister series and $4e^-$ ORR selectivity, and highlights that sub-nanopores not only serve as confined spaces for O_2 but also function as active sites for ion-electrode charge coupling.

The microenvironment at the reaction interface also constrains the enhancement of catalytic activity. Constructing a rational morphological structure to regulate the hydrophilicity/hydrophobicity of the catalyst surface is conducive to the full activity expression of the active sites [139]. Nakamura and colleagues addressed the issue of decreased ORR activity in nitrogen-doped carbon materials under acidic conditions—caused by the hydration of pyridinic N sites (pyri-NH^+)—by innovatively proposing and constructing a dual-microenvironment system characterized by “hydrophobic isolation + proton conduction” (Fig. 8(o)) [87]. Using a NaCl-template method, they prepared nitrogen-doped graphene with cage-like pores, where the macroscopic hydrophobic structure inhibits water contact with the active centers, thereby mitigating the poisoning effect of hydration. The assignment of pyridinic N as the active site is strongly supported by a combination of complementary techniques, including electron probe micro-analysis (EPMA), confocal fluorescence microscopy, Boehm titration, and direct electrochemical detection of trapped O_2 , collectively providing robust and self-consistent evidence. Simultaneously, SiO_2 particles coated with an ionic liquid were introduced as embedded proton conductors, establishing efficient proton-transport channels within the hydrophobic environment to ensure the supply of H^+ required for the reaction. This design ultimately achieved an onset potential as high as 0.86 V and a half-wave potential of 0.75 V vs. RHE.

3.3.2 Microenvironment engineering for two-electron ORR

Modulating the electronic structure of active sites to optimize

intermediate adsorption behavior represents a fundamental approach for tailoring the microenvironment and enhancing catalytic activity. Song et al. constructed a carboxylated hexagonal boron nitride/graphene (h-BN/G) heterojunction (CBNO) catalyst using commercial activated carbon (AC) as a carrier (Fig. 9(a)) [41]. Multiple characterizations (XPS, NEXAFS, *in-situ* Raman) and DFT calculations consistently identify the carboxylated h-BN/G heterojunction as the genuine active site. This catalyst exhibited excellent $2e^-$ ORR performance in a neutral electrolyte (0.1 M Na_2SO_4): H_2O_2 selectivity > 95%, an onset potential of 0.67 V vs. RHE, and an H_2O_2 production rate of $13.4 \text{ mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ with a Faradaic efficiency exceeding 90%. This significant enhancement originates from the precise construction of a carboxyl-functionalized microenvironment at the heterojunction periphery. The chemical bonding of $-\text{COOH}$ groups with the heterojunction regulates the charge distribution and proton transport pathways around the active centers, effectively stabilizing the adsorption of the key intermediate $^*\text{OOH}$ (Fig. 9(b)). This microenvironment engineering lowers the energy barrier for the rate-determining step ($\text{HOOH}^* \rightarrow \text{H}_2\text{O}_2$) from 1.34 eV (non-carboxylated) to 0.62 eV and switches the electron transfer number from 2.55 to nearly 2, thereby enabling efficient H_2O_2 production (Fig. 9(c)).

In addition to rationally adjusting charge distribution, designing appropriate pore structures to serve as microenvironments for efficient mass exchange is also a promising strategy [140]. Du et al.

prepared a hierarchically porous carbon that creates an ideal pore-channel microenvironment for active centers, effectively improving mass transport efficiency and the exchange of substances at active sites [141]. In this system, macropores serve as primary channels for gas diffusion, mesopores provide a high specific surface area to expose abundant active sites, and micropores regulate intermediate adsorption through confinement effects. The synergistic action of this hierarchical pore architecture significantly enhances oxygen mass transfer and facilitates rapid desorption of the product H_2O_2 , thereby effectively suppressing product accumulation and decomposition. Finite element analysis demonstrates that the introduction of hierarchical porosity substantially improves mass transport kinetics, with meso-/macroporous structures exhibiting a considerable increase in flow velocity relative to microporous counterparts (Fig. 9(d)). This indicates that the hierarchical porous structure effectively reduces the residence time of H_2O_2 and inhibits its further reduction due to slow desorption. Such structural microenvironment engineering allows the full expression of catalytic site activity, enabling the catalyst to achieve an H_2O_2 production rate as high as $17.3 \text{ mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ at an industrial-level current density ($200 \text{ mA}\cdot\text{cm}^{-2}$) while maintaining stable operation for over 100 h. Crucially, Du et al. confirmed the N/O dual-doped sites as the genuine active centers via XPS, *in-situ* ATR-SEIRAS, and DFT-calculated OOH adsorption free energy. This work provides a key example of microenvironment engineering for efficient and stable electrosynthesis of H_2O_2 .

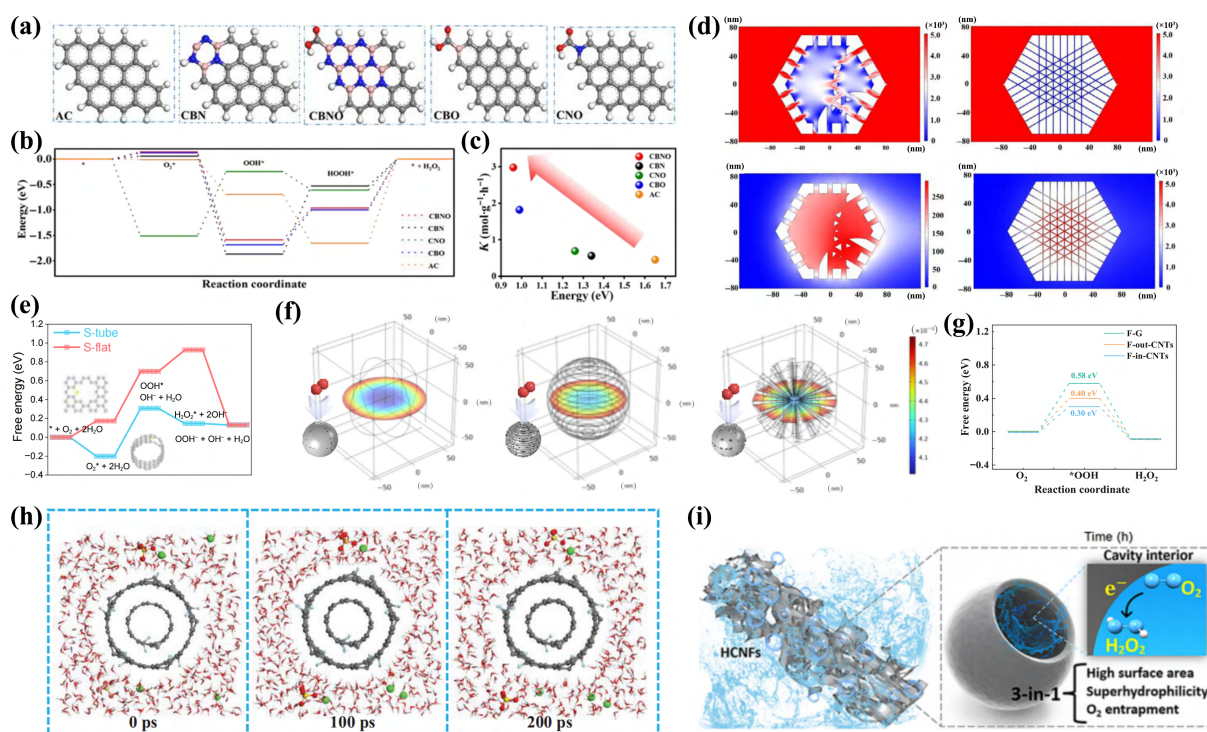


Figure 9 Active-site microenvironment engineering for CMFECs towards $2e^-$ ORR. (a) Schematic configuration models of representative CBNO, CBN, CNO, CBO, and AC fragments. The carbon, nitrogen, boron, and oxygen atoms are represented by gray, blue, pink, and red spheres, (b) free energy profiles of CBNO, CBN, CNO, CBO, and AC models during H_2O_2 electrosynthesis via $2e^-$ pathway, and (c) the relationship of the energy barriers in the rate-determining step and production rates of CBNO, CBN, CNO, CBO, and AC. Reproduced with permission from Ref. [41], © Wiley-VCH GmbH 2023. (d) Velocity field models with different structures: meso/macropore-dominated and micropore-dominated systems. (upper panel) (colors represent corresponding numerical values) and Surface H_2O_2 concentration models with different structures: meso/macropore-dominated and micropore-dominated systems (lower panel). (colors represent corresponding numerical values). Reproduced with permission from Ref. [141], © Wiley-VCH GmbH 2025. (e) Free energy diagrams for $2e^-$ ORR reduction and (f) spatial distribution of O_2 concentration over different pore structures. Reproduced with permission from Ref. [42], © Wiley-VCH GmbH 2025. (g) Free energy profiles of O_2 reduction at 0.7 V versus RHE and (h) representative periodic modeling for proton distribution on F-CNTs surface at 0.05 M H_2SO_4 under -1.0 V versus RHE (H, F atoms, S atoms, and H atoms are in green, cyan, red, yellow, and white). Reproduced with permission from Ref. [143], © Wiley-VCH GmbH 2025. (i) 3-in-1 effect of HCNFs promotes O_2 -to- H_2O_2 conversion. Reproduced with permission from Ref. [38], © Wiley-VCH GmbH 2021.

The morphology of CMFECs also plays an important role in the microenvironment of ORR process. Sun et al. synthesized a hollow mesoporous carbon bowl co-doped with S, N, and O [142]. COMSOL simulations and morphology comparison prove that the hollow bowl structure optimizes mass transport. DFT calculations and control experiments verify that S/N/O defects lower the OOH free energy barrier as the $2e^-$ ORR active sites. Under pulsed-potential conditions in an H-type electrolytic cell, the catalyst achieved an H_2O_2 production rate of $55.6 \text{ mg}\cdot\text{h}^{-1}\cdot\text{mg}_{\text{cat}}^{-1}$ while maintaining a Faradaic efficiency above 94.6%. Carbon defects together with sulfur and pyrrolic nitrogen constitute a cascade of active centers for the $2e^-$ ORR, while carboxyl groups and the hollow carbon bowl structure synergistically regulate the microenvironment of the active centers from both electronic and spatial perspectives. The hollow carbon bowl optimizes the mass-transport microenvironment at the spatial-structural level: The unique spatial confinement effect of the bowl-shaped cavity and the mesoporous walls accelerate the diffusion of O_2 and H_2O to the active sites and promptly remove generated OH^- and H_2O_2 , alleviating local concentration polarization and pH rise, thus allowing the active centers to operate continuously and efficiently. Furthermore, the pulsed potential dynamically modulates the electrode-surface microenvironment by periodically varying the applied potential, reducing the accumulation of OH^- at the electrode surface and promoting rapid substance exchange on the catalyst surface. These effects work synergistically to accelerate the formation kinetics of the *OOH intermediate, thereby enhancing the H_2O_2 production rate.

Rational microenvironment design has shown excellent performance in independently optimizing electron transfer and mass transport, which naturally inspires researchers to explore integrated microenvironments that can boost both efficiencies at the same time. Chen and co-workers proposed a hierarchical catalytic system design strategy [42]. In this system, thiophene-sulfur atoms serve as the core active sites, the unique carbon substrate topology (a sp^2/sp^3 -hybridized network) surrounding them functions as the electronic microenvironment, and a vertically ordered cylindrical mesoporous carbon sphere array provides the spatial-structural microenvironment. This active-site assignment is strongly supported by multiple pieces of evidence: *In-situ* Raman/FTIR capture of OOH, DFT-derived free energy profiles, and comparative adsorption energy calculations on S-doped vs. undoped carbons. Within this architecture, sulfur atoms induce charge redistribution in the surrounding carbon framework, creating electron-deficient regions that optimize the adsorption of the *OOH intermediate (Fig. 9(e)), thermodynamically enabling H_2O_2 selectivity > 99%. Concurrently, the ordered mesoporous channels supporting the S-C active centers significantly enhance O_2 diffusion and H_2O_2 desorption, improving reaction kinetics (Fig. 9(f)). This synergistic microenvironment design enabled the catalyst to achieve an H_2O_2 production rate of $25 \text{ mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ in a flow cell, alongside excellent electrochemical stability.

Although the excessive accumulation of OH^- in alkaline electrolytes can hinder efficient ORR progress, in acidic electrolytes, a suitable localized alkaline microenvironment is actually beneficial for suppressing the HER or the further reduction of H_2O_2 . Zhu et al. prepared fluorine-doped carbon nanotubes (F-CNTs) for highly efficient electrosynthesis of H_2O_2 under acidic conditions [143]. During this process, fluorine atoms play a dual role: Firstly, their strong electronegativity modulates the electronic structure of

adjacent carbon atoms, altering the electronic microenvironment and causing a significant upward shift in the p-band center of the carbon atoms. This optimizes the adsorption energy for the key *OOH intermediate, thereby activating the fluorine-adjacent carbon atoms as highly efficient intrinsic carbon active sites (Fig. 9(g)). XPS, Raman, *in-situ* ATR-SEIRAS, and DFT calculations collectively provide strong evidence for this assignment of active sites. Secondly, fluorine doping on the outer walls imparts superhydrophobicity to the material, while inner-wall doping enhances the confinement effect. Together, they synergistically create a dynamically stable localized alkaline microenvironment at the electrode surface within the strongly acidic bulk solution (Fig. 9(h)). This microenvironment effectively suppresses excessive proton supply, while the optimized active sites significantly lower the formation energy barrier for *OOH . The synergy between these two aspects leads to outstanding catalytic performance: In 0.05 M H_2SO_4 solution, F-CNTs achieved a Faradaic efficiency of 99.2%–95.6% and an H_2O_2 production rate of 351.5 – $606.6 \text{ mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ at current densities of 600 – $1000 \text{ mA}\cdot\text{cm}^{-2}$.

Rational regulation of catalyst surface wettability also plays a crucial role in catalytic ORR process. Dong et al. employed an electrospinning process to prepare carbon nanofibers (HCNFs), achieving a breakthrough in the performance of $2e^-$ ORR for H_2O_2 synthesis [38]. The fiber skeleton exhibits a honeycomb-like architecture composed of interconnected open hollow nanocavities. In 0.1 M KOH, HCNFs demonstrated an H_2O_2 selectivity of 97.3%, and flow-cell tests revealed an H_2O_2 production rate of $6.37 \text{ mmol}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$. The activity originates from two complementary aspects: On the one hand, active sites comprising topological defects at carbon edges and sp^3 -hybridized carbon defects. *In-situ* Raman spectroscopy identified the D_1 defect as the dominant active site, and DFT calculations further revealed the synergistic effect between carbon edges and topological defects, providing robust evidence for the assignment of active sites. Moreover, the construction of a honeycombed porous structure that serves as a structural microenvironment to efficiently trap and enrich oxygen, while surface oxygen functional groups create a super-hydrophilic chemical microenvironment, ensuring effective wetting and mass transport at the reaction interface (Fig. 9(i)). This deep integration of “active sites” and a “hydrophilic oxygen-enrichment microenvironment” collectively establishes an extensive, efficient three-phase interface throughout the catalyst, thereby synergistically optimizing the catalytic process at both atomic and mesoscopic scales, ultimately leading to the outstanding H_2O_2 production performance.

Beyond the intrinsic structural microenvironment discussed above, external factors originating from electrode fabrication and the electrolyte environment also profoundly influence the ORR performance of CMFECs. On the one hand, polymeric ionomers, such as Nafion, commonly used as binders and proton conductors in practical electrodes, modulate the local proton transport and mass transfer around active sites [144]. However, not an inherent part of the carbon catalyst, rational optimization of such interfacial layers can significantly affect the accessibility and stability of active sites. On the other hand, solvation effects—i.e., the interaction between oxygenated intermediates and surrounding water molecules via hydrogen bonding—play an equally critical role in governing the adsorption energetics of *OOH and *OH [145]. Explicit solvation models in DFT calculations have demonstrated that neglecting these solvent interactions leads to overestimated

overpotentials and, in some cases, misidentification of active sites. Together, these external microenvironmental considerations bridge the gap between idealized catalyst designs and realistic operating conditions, and they represent important yet often overlooked dimensions in the rational design of high-performance ORR catalysts.

In summary, the modulation of the active-site microenvironment primarily operates at three levels: First, the atomic-scale chemical environment, which directly tailors the electronic structure by adjusting the composition of neighboring coordinating atoms; second, the topological and surface configuration, which introduces geometric and strain effects through defects, curvature, and edge structures of the carbon basal plane; and third, the integrated structural features of morphology, pore architecture, electrolyte microenvironment, and contact interface, which optimize mass transport and confinement through designed channels, three-dimensional morphology, and interfacial configuration. These three types of microenvironments work synergistically to form an integrated “active system”, emphasizing systematic optimization from local regulation to overall performance. These strategies have all been employed in the construction of CMFECs; however, their specific design principles and operative mechanisms differ when promoting the $2e^-$ versus the $4e^-$ ORR pathways:

In the $4e^-$ ORR, the approaches focus on facilitating O–O bond cleavage and completing the multi-step proton–electron transfer. For instance, electronic regulation aims to enhance O_2 adsorption and activation, and through the construction of a “host–promoter” synergistic active-center system, optimize the adsorption strength of a series of intermediates, such as *OOH , *O , and *OH , thereby avoiding site poisoning. Spatial structure design strives to achieve efficient mass transport of reactants and water molecules while

maintaining a high density of active sites, often via hierarchical pore synergy. Interfacial microenvironment engineering frequently involves creating a dual structure of “hydrophobic isolation + proton conduction” to protect active centers from hydration-induced poisoning while ensuring a continuous supply of reaction protons.

In contrast, for the $2e^-$ ORR, the core objective is to stabilize the *OOH intermediate and promote its rapid desorption as H_2O_2 . Accordingly, the emphasis of electronic regulation shifts toward tuning the adsorption strength of *OOH on the active site to a moderate range—sufficient for its effective formation yet preventing its over-hydrogenation and further reduction. Spatial structure design places greater stress on constructing channels (e.g., ordered mesopores) that favor rapid O_2 diffusion and immediate H_2O_2 desorption, thereby minimizing product retention and decomposition. Interfacial microenvironment engineering is more flexible: It may create a localized alkaline microenvironment within an acidic bulk to suppress further reduction of H_2O_2 , or adjust surface wettability to optimize the three-phase interface and mass-transfer efficiency.

We have correlated the active-site structures of the catalysts with DFT-calculated adsorption energetics and summarized the $2e^-$ and $4e^-$ ORR catalysts separately. Figure 10(a) presents a theoretical activity volcano plot for representative $2e^-$ ORR CMFECs discussed in this review, correlating the calculated U_L with $\Delta G_{^*OOH}$. This directly visualizes how different active-site structures modulate *OOH adsorption strength to achieve optimal $2e^-$ selectivity. Figure 10(b) shows the calculated U_L values for representative $4e^-$ ORR CMFECs, illustrating how various structural designs enhance O–O bond cleavage and promote the $4e^-$ pathway. To more clearly elucidate the relationship between key structural factors and ORR performance, Fig. 10(c) provides a schematic weighting diagram

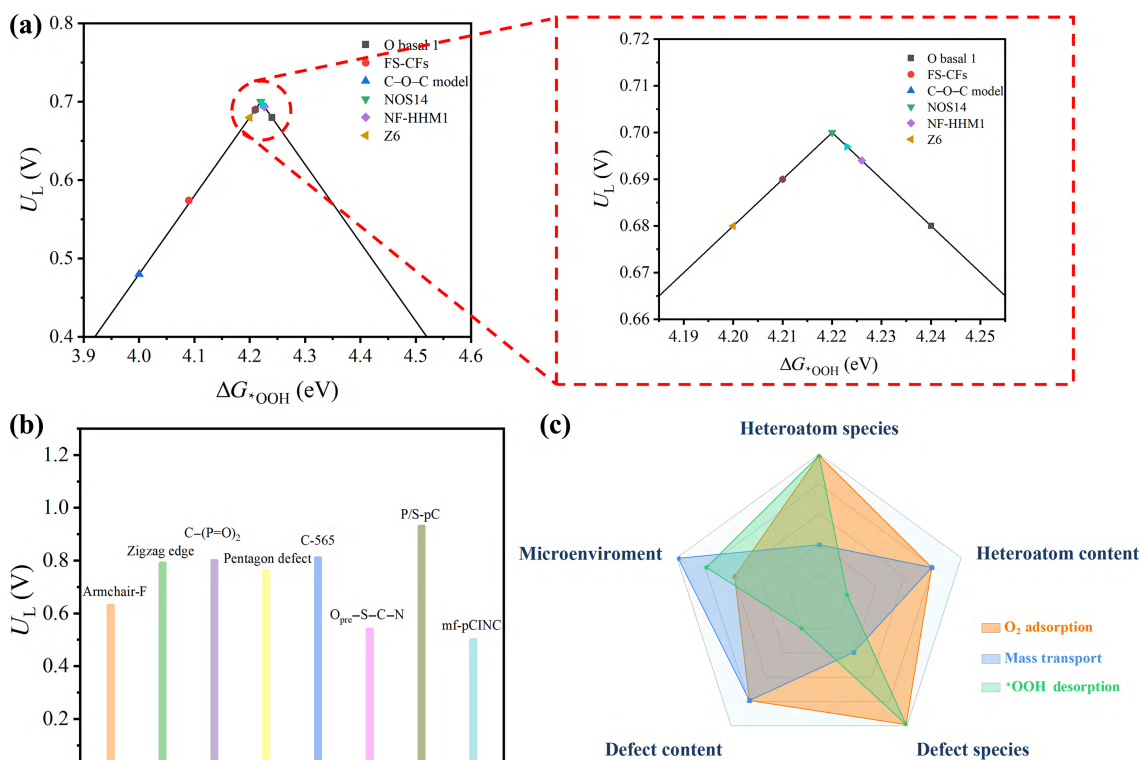


Figure 10 (a) Theoretical activity volcano plot for part of mentioned $2e^-$ ORR CMFECs. (b) Calculated U_L values for part of mentioned $4e^-$ ORR CMFECs. (c) Weighting of structural factors on the ORR catalytic activity of CMFECs.

that systematically deconvolutes the relative contributions of active site species, active site content, and microenvironment engineering to the overall catalytic activity and selectivity. This figure could somehow serve as a “decision map” which could help researchers to quickly understand which structural features favor $4e^-$ versus $2e^-$ pathways, directly addressing the need for a predictive design framework. Heteroatoms and defects typically serve as active sites for the ORR, and their species exert a significant influence on the adsorption behavior of O_2 and the bond-breaking pathways of reaction intermediates, directly dictating the activity and selectivity of the catalyst. However, the modification of the carbon substrate by heteroatoms/defects constitutes atomic-scale localized modulation, which can hardly exert a substantial impact on the macroscopic-scale mass transport processes of reactants/products. It is worth noting that specific heteroatoms may indirectly modulate wettability or local pH by altering surface polarity, thereby facilitating, to some extent, the transport of reactants to the catalyst surface or the desorption of products from the active sites, playing an auxiliary role in mass transfer.

A sufficient number of active sites facilitates the efficient adsorption and activation of reactants, thereby enhancing catalytic activity. Furthermore, a high content of active sites can maintain an interfacial concentration gradient through rapid reactant consumption, promoting mass transport to the catalyst surface. However, although an increased content of active sites is generally considered beneficial for reaction efficiency, not all heteroatoms/defects can be distributed on the catalyst surface to fully participate in the reaction. Active sites that are not effectively exposed are unable to deliver their anticipated catalytic performance. This implies that catalyst activity does not exhibit a consistently stable enhancement with increasing heteroatom/defect content, indicating a limited correlation between this factor and the overall ORR process. Moreover, bond-breaking behavior is primarily governed by the electronic structure and geometric configuration of the active center; reports on modulating intermediate bond-breaking processes by simply controlling the content of active sites remain scarce.

In recent years, numerous outstanding studies have achieved remarkable improvements in catalyst performance through active site microenvironment engineering. This strategy impacts the ORR process from two perspectives: charge transport and mass transport. Its application is manifested in the precise regulation of active site structures and the construction of tailored morphologies and pore architectures within the local environment of the active sites. On the one hand, structural fine-tuning of heteroatom/defect sites (e.g., introducing ligands and tailoring the local topology) can further optimize the electronic structure, promoting reactant adsorption/activation and intermediate bond cleavage. On the other hand, constructing rational morphologies and pore structures can significantly reduce the diffusion resistance of O_2 , shorten mass transfer pathways, ensure a stable three-phase interface, and expose more active sites embedded within the bulk, thereby enhancing active site utilization. Furthermore, Tables 1 and 2 provide a comprehensive summary of representative CMFECs for the $4e^-$ and $2e^-$ ORR, respectively. These tables are organized around the central structure–selectivity correlation, with active-site identity as the primary entry, which could serve as a supplementary “decision map” to quickly grasp the key structural features favoring $4e^-$ versus $2e^-$ pathways. For each catalyst, we document the onset potential, half-wave potential (for $4e^-$) or Faradaic efficiency (for $2e^-$), electron transfer number, and long-term stability, alongside the key

structural features responsible for the observed performance. This compilation enables a direct comparison of catalyst performance under standardized metrics and reinforces the design principles derived from the mechanistic and computational analyses presented earlier. Since the fundamental selectivity tendencies—strong O–O bond cleavage for the $4e^-$ pathway and optimal *OOH adsorption for the $2e^-$ pathway—are inherent to the respective reaction mechanisms; these thermodynamic descriptors are not repeated in the tables, allowing the focus to remain on experimentally accessible performance indicators relevant to practical applications.

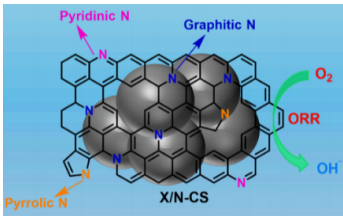
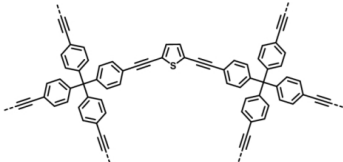
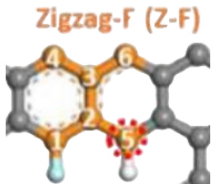
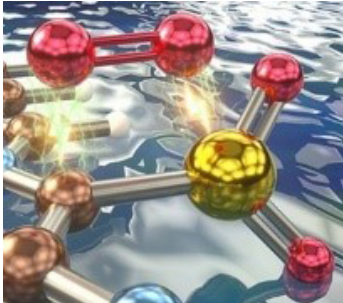
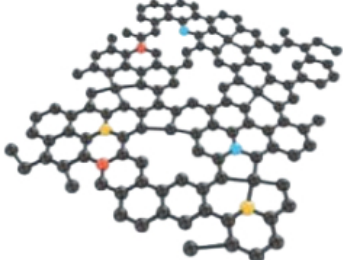
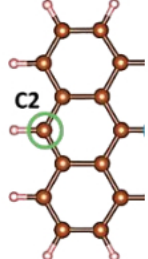
4 Coupling ORR with emerging applications

From a mechanistic perspective, the suitability of ORR for diverse applications originates from its unique thermodynamic and kinetic characteristics. Thermodynamically and kinetically, the $4e^-$ pathway (standard electrode potential (E^0) = 1.23 V vs. RHE) offers a high thermodynamic driving force, enabling efficient energy conversion in fuel cells and metal–air batteries, whereas the $2e^-$ pathway (E^0 = 0.70 V vs. RHE in acid) provides a milder potential window that favors selective H_2O_2 generation. Kinetically, the competition between the two pathways is governed by the $\Delta G_{^*OOH}$: Strong *OOH binding promotes O–O bond cleavage ($4e^-$), while moderate binding favors *OOH desorption as H_2O_2 ($2e^-$). This mechanistic framework directly translates into practical advantages—spontaneous or low-energy coupling with anodic reactions via favorable thermodynamics, and *in-situ* H_2O_2 synthesis without chemical inputs via kinetic selectivity—thereby bridging fundamental electrochemistry with real-world applications.

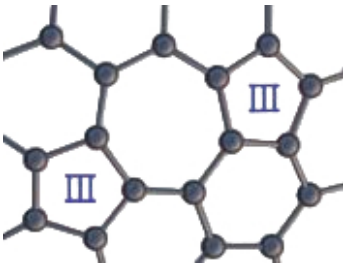
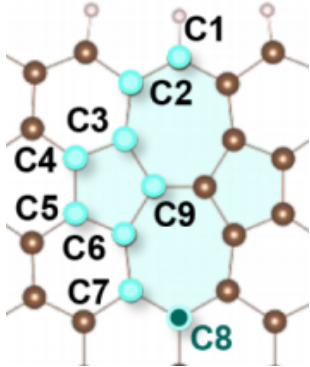
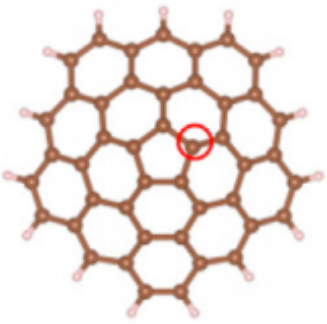
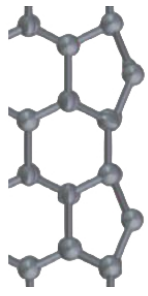
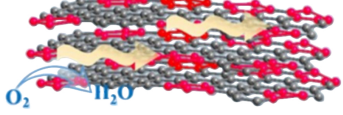
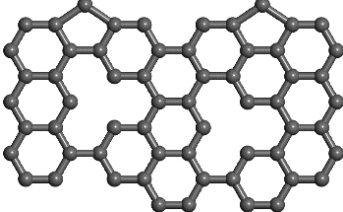
Before delving into the specific applications, it is essential to establish a consistent framework for evaluating catalyst performance. The field of electrocatalytic ORR encompasses a wide array of testing configurations, from fundamental half-cell studies to full device integrations, each employing distinct figures of merit. To facilitate a direct and coherent comparison of CMFEC performance across these varied applications, we present Table 3 as a standardized guide. This table codifies the primary and supplementary performance indicators, their common units, and their significance for each application type. By unifying these criteria, we aim to provide a clear benchmark for researchers transitioning catalysts from mechanistic understanding to practical implementation, thereby highlighting the key metrics that define success at each development stage.

In recent years, translating research outcomes into commercial and industrial applications has become a critical direction of technological development [73]. This trend imposes more explicit requirements on the application of ORR. Although the emergence of the rotating ring-disk electrode (RRDE) has facilitated rapid standardized comparisons among different catalysts, the measured performance—particularly selectivity and yield—cannot be directly extrapolated to practical large-scale reactors (e.g., gas diffusion electrode (GDE) flow cells) due to the small reaction area and distinct mass transport conditions (forced convection, rapid product removal) [146]. This hinders the translation of scientific findings into practical applications. In view of this, it is necessary to design devices that more closely mimic real operating conditions and to develop corresponding application scenarios. This chapter shifts the perspective from laboratory-based catalyst development to industrial/commercial applications, systematically summarizing the recent research progress on CMFECs.

Table 1 Summary of key structural characterizations for 4e⁻ ORR toward energy storage

Strategy	Active sites	Specific type of active site	Onset potential	Half-wave potential	Electron transfer number	Stability	References
	Pyridinic N		1.01 V vs. RHE	0.865 V vs. RHE	3.87–3.98	97.2% current retention after 10 h	[110]
	P atoms		−0.13 V vs. Ag/AgCl	~ −0.22 V vs. Ag/AgCl	3.69–3.78	Half-wave potential loss of 36 mV after 2000 cycles	[111]
	S atoms		~ 0.84 V vs. RHE	—	~ 4	> 90% current retention after 20,000 s	[112]
Heteroatom-induced active sites	Edged F atoms		0.973 V vs. RHE	0.847 V vs. RHE	3.6–3.9	—	[113]
	P atoms adjacent C atoms and P atoms		~ 0.94 V vs. RHE	0.77 V vs. RHE	~ 4.0	Half-wave potential decay of 13 mV after 10,000 cycles	[28]
	Pyridinic N, graphitic N, and P, S atoms		—	0.86 V vs. RHE	~ 4	Half-wave potential decay of 10 mV after 10,000 cycles	[115]
Defect engineering	Zigzag edge defects and pentagonal defects		1.015 V vs. RHE	0.837 V vs. RHE	~ 4	Half-wave potential decay of 16 mV after 5000 cycles	[126]

(Continued)

Strategy	Active sites	Specific type of active site	Onset potential	Half-wave potential	Electron transfer number	Stability	References
	5-7-5 ring defects		—	0.834 V vs. RHE	~ 4.01	93.4% current retention after 12 h of testing	[27]
	Stone-Wales defects (activated by strain)		~ 0.68 V vs. RHE	~ 0.57 V vs. RHE	~ 4	—	[92]
	sp ³ -hybridized carbon defects		0.967 V vs. RHE	0.85 V vs. RHE	~ 4.0	Negligible decay after 10,000 cycles	[128]
	C-565 ring defects		~ 0.98 V vs. RHE	0.90 V vs. RHE	~ 4.0	< 5% decay after 10 h	[25]
	Pentagonal defects		—	0.891 V vs. RHE	~ 4.0	Negligible overpotential degradation after 300 h of charge-discharge cycling	[129]
	N/S-doped carbon edges		0.92 V vs. RHE	0.78 V vs. RHE	~ 3.85	90% current retention after 30,000 s of testing	[130]

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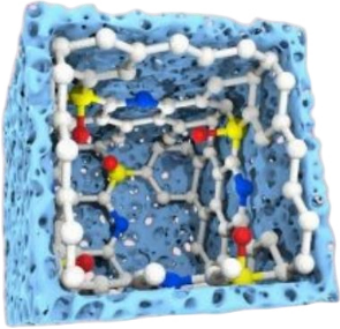
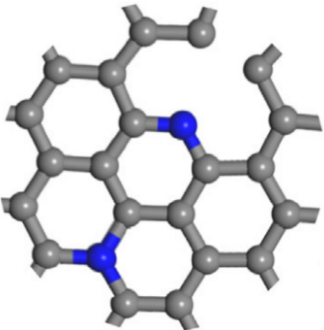
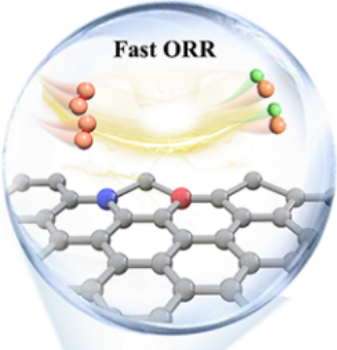
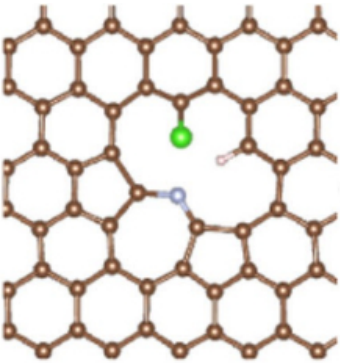
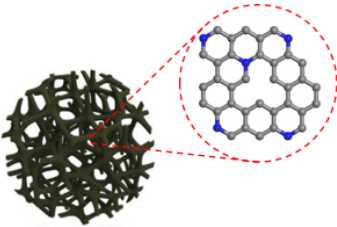
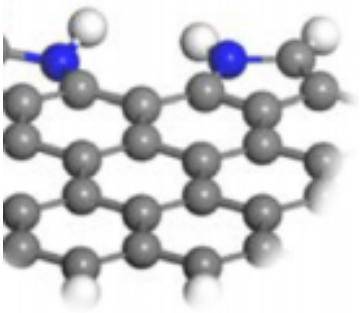
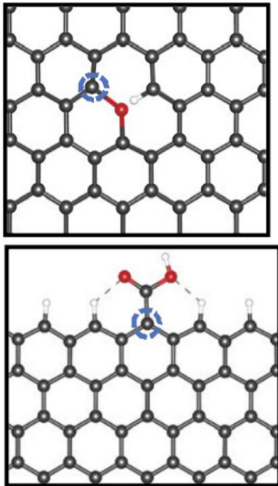
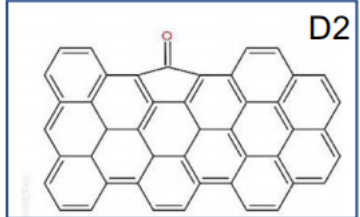
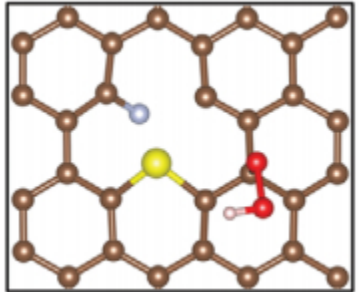
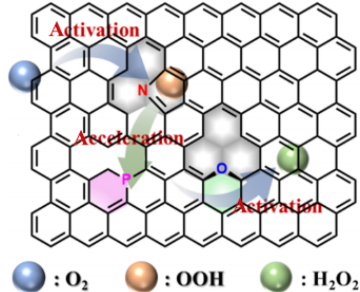
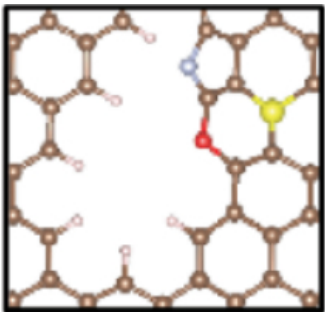
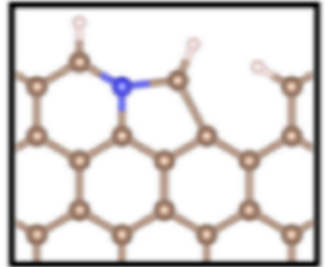
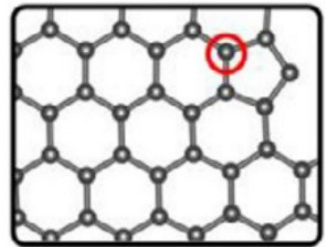
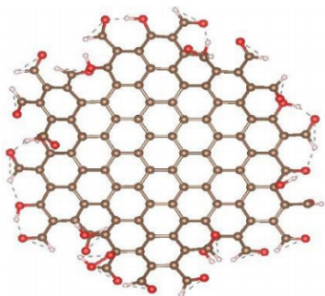
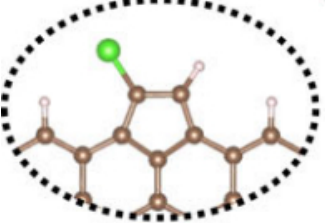
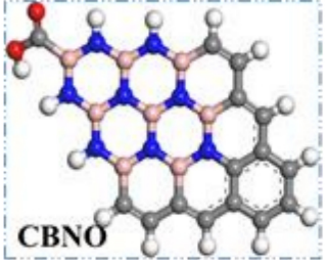
Strategy	Active sites	Specific type of active site	Onset potential	Half-wave potential	Electron transfer number	Stability	References
	S-C-N/O _{pre} -S-C-N		1.14 (0.1 M KOH); 0.887 (0.5 M H ₂ SO ₄) V vs. RHE	0.952 (alkaline)/ 0.754 (acidic)	~ 4.0	Current decay of only 6.9% (0.1 M KOH)/ 7.2% decay (0.5 M H ₂ SO ₄) after 24 h	[135]
	Pyridinic N/graphitic N pairs		0.97 V vs. RHE	0.81 V vs. RHE	3.45	95% current retention after 15,000 s	[107]
Active-site microenvironment engineering	P/S-coordinated pentagonal carbon		1.12 V vs. RHE	0.89 V vs. RHE	4	Half-wave potential decay of 13 mV after 20,000 cycles; 6.2% loss after 30 h	[61]
	N-adjacent carbon modulated by sp ³ -C and Cl		1.02 V vs. RHE	0.91 V vs. RHE	~ 4	Negligible half-wave potential decay after 100,000 cycles (0.1 M KOH) and 10,000 cycles ((0.5 M H ₂ SO ₄))	[26]
	Pyridinic N, graphitic N, carbon defects, and hierarchical porous structures		—	0.868 V vs. RHE	3.92	4% current loss after 15,000 s	[137]

Table 2 Summary of key structural characterizations for 2e⁻ ORR toward H₂O₂ production

Strategy	Active sites	Specific type of active site	Onset potential	Selectivity	H ₂ O ₂ yield	Stability	References
Heteroatom-induced active sites	Bipyrrolic N		~ 0.64 V vs. RHE	~ 91%	30 mol·g ⁻¹ ·h ⁻¹	Stable current over 24 h	[106]
	C–O–C and –COOH functional groups		~ 0.75 V vs. RHE	~ 90% (0.1 M KOH)/ ~ 85% (PBS)	1975 mg·L ⁻¹ (30 min)	No significant decay over 10 h	[35]
	Carbonyl groups connected to five-membered rings		0.9 V vs. RHE	98.38%	41.45 mg·cm ⁻² ·h ⁻¹	Faradaic efficiency remained at ~ 92% over 10 h	[91]
	Thiophene S, F atom		0.814 V vs. RHE	99.1% (0.1 M KOH)/84.1% (0.1 M H ₂ SO ₄)	—	Stable structure in acid (0.1 M H ₂ SO ₄)	[119]
	N, P, O atom		—	92.6%	16.32 mg·cm ⁻² ·h ⁻¹	90.2% selectivity retained after 10 h	[121]

(Continued)

Strategy	Active sites	Specific type of active site	Onset potential	Selectivity	H ₂ O ₂ yield	Stability	References
Defect engineering	Synergistic N, O, S doping + defect structure		~ 0.75 (0.1 M HClO ₄); ~ 0.80 (3.5 wt.% NaCl) V vs. RHE	95% (0.1 M HClO ₄) 90% (3.5 wt.% NaCl)	4187 mg·L ⁻¹ ·h ⁻¹ (0.1 M HClO ₄) (flow cell)	Continuous operation > 12 h (flow cell)	[83]
	Pentagon defects		0.60 V vs. RHE	80%–98%	2923 mg·L ⁻¹ ·h ⁻¹ (flow cell)	Continuous operation for 10 days under air without decay	[40]
	Edge-defect		0.86 V vs. RHE	> 95%	5600 mg·day ⁻¹ (flow cell)	200 h	[131]
	sp ³ -C adjacent to -CHO		—	99.03%	3.0 μmol·s ⁻¹ ·cm ⁻²	> 100 h	[116]
	Pentagonal defects adjacent to Cl atom		—	> 90%	74.61 mol·g ⁻¹ ·h ⁻¹ (flow cell)	> 400 h, FE > 95%	[88]
	Active-site microenvironment engineering	Carboxylated h-BN/G heterojunction 	0.67 V vs. RHE	> 95%	13,400 mmol·g ⁻¹ ·h ⁻¹ (flow cell)/ 2890 mmol·g ⁻¹ ·h ⁻¹ (H-type)	Stable for 24 h	[41]

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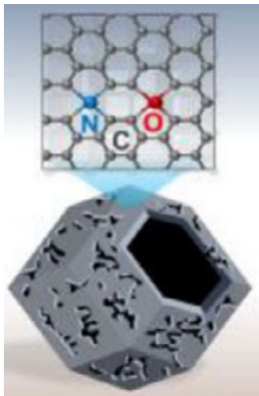
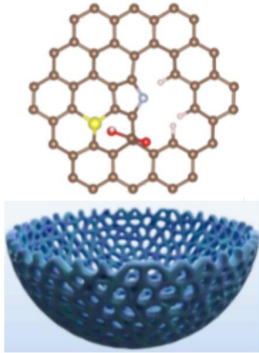
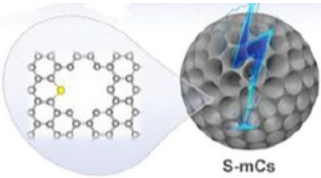
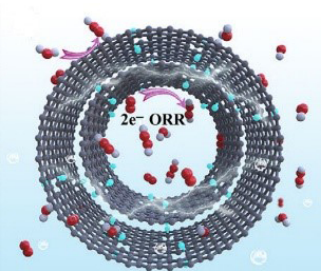
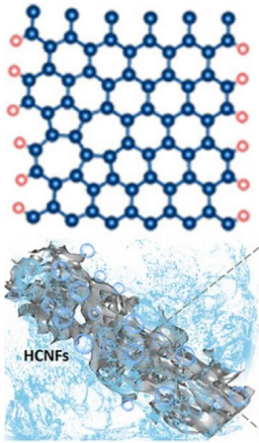
Strategy	Active sites	Specific type of active site	Onset potential	Selectivity	H ₂ O ₂ yield	Stability	References
	N/O atom and hierarchically porous		~ 0.6 V vs. RHE	> 90%	17.3 mol·g ⁻¹ ·h ⁻¹ (flow cell)	FE > 80% over 100 h	[141]
	Pyrrolic N, C=O, defect sites, and mesoporous carbon bowl structure		0.77 V vs. RHE	91.9%	55.6 (pulsed electrolysis, H-cell)	FE > 93.1% over 10 cycles	[142]
	S atom vertical mesoporous structure		0.66 V vs. RHE	> 99%	25 mol·g _{cat} ⁻¹ ·h ⁻¹ (flow cell)	> 48 h (RRDE), 24 h (flow cell)	[42]
	F atom and tuned carbon nanotube		—	95.6%–99.2%	351.5–606.6 mg·cm ⁻² ·h ⁻¹ (dual-chamber flow cell)	Stable for 30 h	[143]
	sp ³ -carbon, edge topological defects, and honeycomb-like architecture		> 0.70 V vs. RHE	97.3%	6.37 mmol·L ⁻¹ ·h ⁻¹ @0.50 V (alkaline, flow cell)	Stable current over 12 h, structure and performance retained	[38]

Table 3 Standardized key performance indicators for CMFECs across different applications

Application category	Specific device/pathway	Primary performance indicators	Supplementary indicators	Key purpose of the indicators
Fundamental 4e ⁻ ORR	RRDE test	$E_{1/2}$ (V vs. RHE); n	E_0 (V vs. RHE); j_k (mA·cm ⁻²); Tafel slope (mV·dec ⁻¹)	Evaluate the intrinsic activity and selectivity of the catalyst for the 4-electron water-producing pathway
Fundamental 2e ⁻ ORR	RRDE test	H ₂ O ₂ selectivity (FE (%)); H ₂ O ₂ production rate (mol·g _{cat} ⁻¹ ·h ⁻¹ or mg·cm ⁻² ·h ⁻¹)	E_0 (V vs. RHE); stability (h)	Quantify the efficiency of the catalyst for selective H ₂ O ₂ electrosynthesis
Metal–air batteries	Zn–air, Al–air, Mg–air batteries	P_{max} (mW·cm ⁻²); specific capacity (mAh·g _{Zn} ⁻¹ or mAh·g _{Al} ⁻¹); cycling stability/service life (h or cycles)	OCV (V); discharge/charge voltage gap (V)	Demonstrate the performance of the catalyst in a practical energy conversion and storage device
Fuel cells	PEMFC/AEMFC	Peak areal power density (mW·cm ⁻² or W·cm ⁻²); long-term durability (voltage decay rate over hundreds of hours)	Peak mass power density (W·g ⁻¹); cell voltage at a given current density (e.g., 0.8 A·cm ⁻²)	Assess the catalyst's viability under realistic H ₂ /O ₂ or H ₂ /air operating conditions
H ₂ O ₂ <i>in-situ</i> applications	Electro-Fenton, pulp bleaching, disinfection	Pollutant degradation efficiency (%); k (min ⁻¹); FE (%)	Energy consumption (kWh·order ⁻¹ ·m ⁻³)	Showcase the practical effectiveness of the electrogenerated H ₂ O ₂ in downstream processes
Coupled systems	Paired electrolysis, self-powered devices	Overall system voltage/energy saving (% vs. OER); co-product yield rate (e.g., for glyceric acid); desalination capacity (mg·g ⁻¹); Faradaic efficiency for both anodic and cathodic products (%)	Faradaic efficiency for both anodic and cathodic products (%)	Highlight the techno-economic and energy-efficiency advantages of the integrated system

4.1 Applications based on four-electron ORR

4e⁻ ORR catalysts are designed to achieve efficient and complete reduction of oxygen, serving as the core of high-energy-conversion-efficiency systems, such as fuel cells and metal–air batteries. It is projected that by 2035, the number of fuel cell vehicles in China could reach as high as approximately 8.84 million units [147]. This broad market prospect is driving oxygen reduction technology further toward commercialization. At the level of application testing, researchers are no longer satisfied with laboratory-scale data obtained from RRDE measurements; instead, they prefer to load the catalyst onto GDEs as cathodes, assemble them into membrane fuel cells or metal–air batteries, and conduct rigorous evaluations of the battery modules under diverse testing conditions, such as temperature variations and mechanical deformation, in order to meet the performance and stability requirements of practical applications.

4.1.1 Metal–air batteries

Lithium–air batteries, with their ultra-high energy density, are regarded as a candidate for next-generation high-performance energy storage devices. However, their practical application faces challenges, such as poor cycling performance, safety concerns, and stability issues [148]. Li et al. successfully induced the formation of a large-area amorphous Li₂O₂ film through a synergistic strategy of heteroatom co-doping and spatial confinement, significantly enhancing the overall performance of a Li–O₂ battery: The battery achieved a high specific capacity of 23,778 mAh·g⁻¹ at a current density of 200 mA·g⁻¹, with an initial first-cycle Coulombic efficiency of ~87.8% [149]. Under a limited capacity of 500 mAh·g⁻¹ at 300 mA·g⁻¹, the battery could cycle for 320 h, showing good cycling stability. Furthermore, the electrode maintained high capacity and low polarization over a wide current density range (50–1000 mA·g⁻¹), exhibiting remarkable rate capability and electrochemical reversibility.

AABs possess advantages, such as high theoretical energy density (8100 Wh·kg⁻¹), abundant raw materials, low cost, safety, environmental friendliness, and simple structure, making them ideal candidates for backup power and traction batteries [150].

Zhang et al. applied a developed CMFEC to an aluminum–air battery, achieving a peak power density of 265 mW·cm⁻² (surpassing the 212 mW·cm⁻² of Pt/C), an energy density as high as 4152 Wh·kg⁻¹, and a specific capacity of 2806 mAh·g⁻¹ (compared to 2170 mAh·g⁻¹ for Pt/C) (Figs. 11(a) and 11(b)) [135]. After a 160 h cycling test, the voltage retention remained > 96% with negligible performance degradation, and the rate capability was excellent. Similarly, Yu et al. also developed an aluminum–air battery whose performance comprehensively exceeded that of Pt/C [151]. The open-circuit voltage reached 1.85 V, and the maximum power density was 344.3 mW·cm⁻². At a high current density of 200 mA·cm⁻², the discharge voltage was 1.28 V, demonstrating low polarization characteristics and broad application prospects.

Magnesium–air batteries offer high safety, abundant resources, a high theoretical specific energy density (6800 Wh·kg⁻¹), and long service life. However, there is room for further optimization regarding magnesium activity and air electrode stability [152]. Su et al. employed their prepared coral-like nitrogen-doped carbon (N/C-I-60) as the cathode catalyst to assemble a magnesium–air battery using 2 M NaCl as the electrolyte, which exhibited outstanding performance: Its peak power density reached 123 mW·cm⁻² (at 0.73 V), significantly superior to the 100 mW·cm⁻² (at 0.72 V) of a commercial Pt/C catalyst under the same conditions; for the ORR, the half-wave potential was 0.868 V vs. RHE, and it predominantly followed the 4e⁻ transfer pathway [137]. More notably, after a 15,000 s potentiostatic test, the battery retained over 96% of its current, demonstrating exceptional long-term operational stability. These performance improvements are primarily attributed to the unique hierarchical porous structure dominated by meso-/macropores, which effectively promotes oxygen mass transport and active site exposure, endowing this metal-free carbon material with significant potential to replace precious metal catalysts in practical magnesium–air battery systems.

Zinc–air batteries, as a typical representative of new green battery systems, are considered efficient rechargeable energy devices due to their high theoretical specific capacity, intrinsic safety, and stable performance [46]. Su et al. prepared a nitrogen–boron–fluorine tri-doped carbon material as the air-cathode catalyst for a zinc–air battery, achieving a peak power density of 147 mW·cm⁻², far

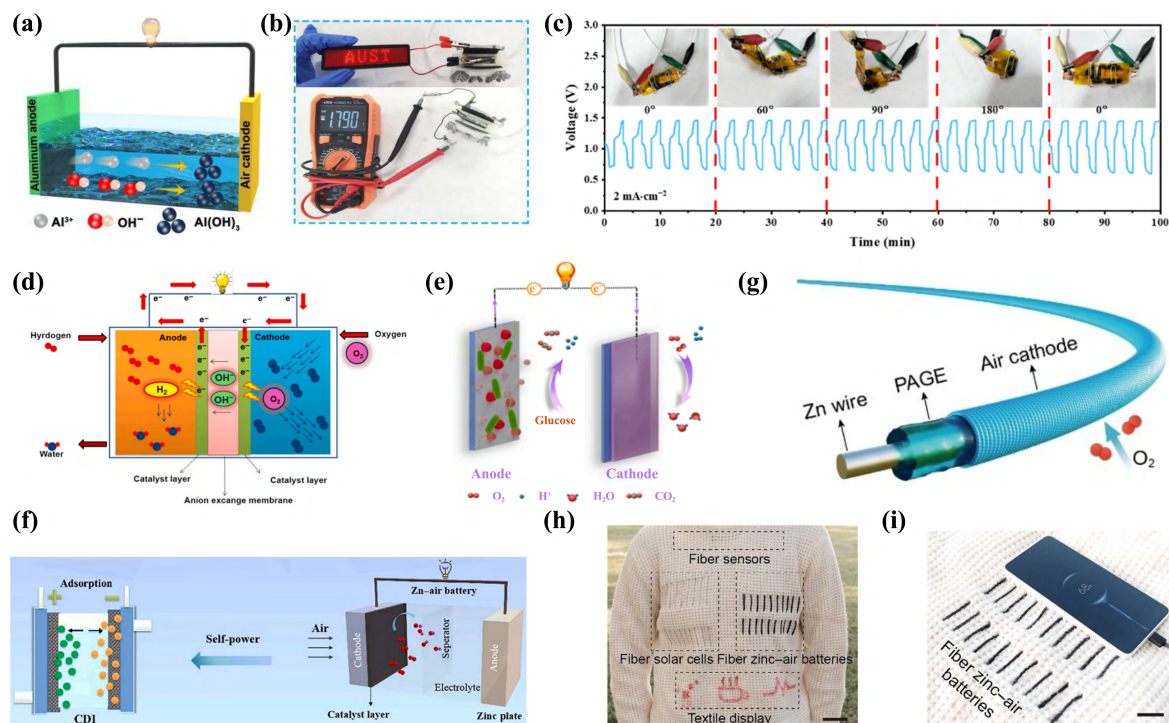


Figure 11 Application of CMFECs in 4e⁻ ORR. (a) Structural schematic of AABs and (b) photographs of a 1 V LED powered by AABs and their open circuit potentials (OCPs). Reproduced with permission from Ref. [135], © The Royal Society of Chemistry 2026. (c) Charge/discharge curves of GDHfCN-based flexible zinc-air batteries under different bending angles. Reproduced with permission from Ref. [129], © American Chemical Society 2024. (d) Schematic diagram for AEMFCs measurement. Reproduced with permission from Ref. [158], © Elsevier Ltd. 2025. (e) Schematic illustration of SC-MFCs. Reproduced with permission from Ref. [161], © Elsevier B.V. 2024. (f) Schematic diagram of capacitive deionization driven by a zinc-air battery. Reproduced with permission from Ref. [162], © Elsevier B.V. 2022. (g) Schematic of fiber zinc-air batteries, (h) photograph of a sweater integrated with fiber zinc-air batteries, fiber solar cells, luminescent fibers, and fiber sensors. Scale bar, 4 cm. (i) Demonstration of a cell phone being charged with self-powered electronic textiles. Scale bar, 2 cm. Reproduced with permission from Ref. [164], © Wiley-VCH GmbH 2024.

exceeding that of a Pt/C-based battery (117 mW·cm⁻²) [153]. It operated stably for 100 h (approximately 300 cycles) at a current density of 5 mA·cm⁻² with negligible voltage decay, whereas the Pt/C-based battery failed after only 49 h. Its open-circuit voltage (1.47 V) was higher than that of the Pt/C-based battery, and it could power 40 light-emitting diode (LED) beads, demonstrating its high output capability and practicality. A zinc-air battery assembled by our group using graphitic/defective heteroatom-free carbon nanosheet (GDHfCN) as the air cathode exhibited a high open-circuit voltage of 1.46 V at a current density of 0.1 mA·cm⁻² and a peak power density of 202.4 mW·cm⁻², significantly surpassing the 96.5 mW·cm⁻² of a commercial Pt/C catalyst [129]. This battery maintained a voltage above 1.0 V even at a high current density of 50 mA·cm⁻², with a discharge specific capacity of 571.0 mAh·g⁻¹, higher than the 537.0 mAh·g⁻¹ of the Pt/C-based battery. During long-term cycling at 5 mA·cm⁻², the battery showed almost no overpotential increase over 300 h, indicating excellent cycling stability. Furthermore, a flexible battery based on this material delivered an output voltage of 1.14 V at 0.1 mA·cm⁻² and maintained 0.93 V even at the relatively high current density of 5 mA·cm⁻² (Fig. 11(c)). During bending tests, the voltage fluctuation was minimal at different bending angles (0°, 60°, 90°, and 180°), and the electrical performance fully recovered upon returning to the flat state, demonstrating good electrode flexibility and interfacial stability.

4.1.2 Fuel cells

Proton exchange membrane fuel cells (PEMFCs) have attracted

widespread attention due to their environmental friendliness, high efficiency, and stability. However, their commercialization has been severely hindered by the sluggish kinetics of the cathode ORR [154]. Xue et al. employed a zigzag-edge graphene nanoribbon/carbon nanotube composite catalyst as the cathode in a PEMFC [155]. Operated with H₂/O₂ as the reactant gases, it achieved a peak mass power density of 520 W·g⁻¹ and an areal power density of 161 mW·cm⁻², outperforming most non-precious metal catalysts. More importantly, this catalyst demonstrated excellent stability during a long-term potentiostatic test at 0.5 V, with a current decay rate significantly lower than that of typical Fe/N-C catalysts.

In recent years, anion exchange membrane fuel cells (AEMFCs) have gained increasing attention from researchers. Compared to PEMFCs, AEMFCs offer advantages, such as higher catalytic activity and faster ORR kinetics in alkaline environments, making them a current focus in fuel cell research [156, 157]. Ravichandran et al. developed a lignin-derived nitrogen- and oxygen-co-doped defective carbon catalyst (LNOC-900) as the cathode catalyst for an AEMFC, which exhibited outstanding overall performance (Fig. 11(d)) [158]. At a working voltage of 0.8 V, it achieved a high current density of 3.30 A·cm⁻² and delivered a peak power density of 1.05 W·cm⁻², surpassing the performance of commercial PtRu/C and most reported metal-based materials. After 10,000 cycles over a wide potential range (0.6–1.0 V vs. RHE), negligible decay was observed for the half-wave potential. Furthermore, it retained 96.2% of its initial current after 15,000 s of continuous operation at a constant potential of 0.6 V, demonstrating excellent electrochemical stability and structural durability. Similarly, Yang et al. employed

NDPC-1000 as the cathode material in an AEMFC, which showed remarkable electrochemical output and operational stability [159]. Operated with H_2/O_2 as the reactant gases, the cell achieved a peak power density of $913 \text{ mW}\cdot\text{cm}^{-2}$, approaching the performance level of some noble-metal and single-atom iron-based catalysts. In long-term durability tests, the cell voltage decayed by only about 25% after 100 h of continuous operation at a current density of $0.25 \text{ A}\cdot\text{cm}^{-2}$, and by about 22% after 60 h at $0.5 \text{ A}\cdot\text{cm}^{-2}$. This stability is significantly superior to that of single-atom Fe-based catalysts (e.g., SA-Fe/NG), which suffer from noticeable degradation due to metal leaching. Moreover, operated with H_2 /air as the reactant gases, the cell still achieved a peak power density of $597 \text{ mW}\cdot\text{cm}^{-2}$.

Microbial fuel cell (MFC) technology has gradually become a research hotspot in the field of clean energy due to its unique environmental benefits and energy conversion advantages, offering an innovative solution to address the dual challenges of environment and energy [160]. Sun et al. developed a phosphorus and nitrogen-co-doped metal-free porous carbon catalyst (AB-N-P), which demonstrated outstanding comprehensive performance in electricity generation and wastewater treatment in single-chamber MFCs (SC-MFCs) (Fig. 11(e)) [161]. The SC-MFCs equipped with AB-N-P cathodes achieved a maximum power density of $896.4 \text{ mW}\cdot\text{m}^{-2}$, representing an increase of over 66% compared to commercial Pt/C cathodes ($538.2 \text{ mW}\cdot\text{m}^{-2}$). Simultaneously, the chemical oxygen demand (COD) removal efficiency reached 93.5%, with a Coulombic efficiency of approximately 30%. During long-term operation, the cell output voltage remained stable at around 0.55 V for over 1000 h. Furthermore, the catalyst exhibited superior ORR activity (half-wave potential of 0.832 vs. 0.806 V for Pt/C) and excellent glucose tolerance in neutral electrolyte.

4.1.3 Coupling devices

CMFECs demonstrate impressive application potential in energy storage systems based on the $4e^-$ ORR. These stable power supply systems can not only be coupled with other devices to form integrated “energy-environment/industry” systems but also provide new energy options for remote areas disconnected from the grid. Cao et al. designed a bifunctional nitrogen-doped porous carbon/graphene composite, which exhibited excellent performance in both zinc-air batteries and capacitive deionization (CDI) applications (Fig. 11(f)) [162]. As a cathode for zinc-air batteries, the material showed good ORR activity with a half-wave potential of 0.725 V. The assembled battery achieved an open-circuit voltage of approximately 1.4 V and high-power output capability, enabling it to stably drive downstream processes. Simultaneously, as a CDI electrode, benefiting from a high specific surface area of $1426.32 \text{ m}^2\cdot\text{g}^{-1}$ and a hierarchical porous structure, it delivered a high desalination capacity of $15.59 \text{ mg}\cdot\text{g}^{-1}$ for a $250 \text{ mg}\cdot\text{L}^{-1}$ NaCl solution at a working voltage of 1.4 V, along with excellent cycling stability. Notably, our group also systematically integrated an efficient ORR catalyst with a CDI device to construct a self-powered desalination system directly driven by a zinc-air battery, highlighting the potential of ORR in synergistic energy conversion and water treatment applications [163]. In this system, the zinc-air battery assembled with nitrogen-doped porous carbon exhibited outstanding electrochemical performance, including an open-circuit voltage of 1.443 V, a peak power density of $149.6 \text{ mW}\cdot\text{cm}^{-2}$, a specific capacity of $804.4 \text{ mAh}\cdot\text{g}^{-1}$, and stable cycling for over 240 h at $5 \text{ mA}\cdot\text{cm}^{-2}$. This battery, serving as an independent power

source, could directly drive a CDI device constructed from the same material without connection to an external grid. Regarding CDI performance, the system achieved a desalination capacity of $32.58 \text{ mg}\cdot\text{g}^{-1}$ at a working voltage of 1.6 V; when powered by the matched zinc-air battery, it still maintained a stable adsorption capacity of $27.8 \text{ mg}\cdot\text{g}^{-1}$ over 6 h, comparable to its performance under direct current power supply. This integrated design not only confirms the feasibility of CMFECs-derived materials for dual-functional energy storage and desalination applications but also provides an important reference for developing compact, sustainable, and self-powered off-grid water-energy cogeneration systems.

Fiber-shaped zinc-air batteries, characterized by their lightweight nature, high theoretical energy density ($> 1000 \text{ Wh}\cdot\text{kg}^{-1}$), and intrinsic safety, represent an ideal flexible power source for wearable electronics. Yang et al. enhanced both the reversibility of the zinc anode and the reaction kinetics of the air cathode by designing an integrated polydopamine-based gel electrolyte (PAGE), enabling the fiber battery to maintain a high energy efficiency of 95% and a long cycle life of 40 h even under bending conditions (Fig. 11(g)) [164]. Such a battery can be integrated into textiles and work synergistically with fiber-shaped solar cells, sensors, and light-emitting devices to perform functions, such as charging mobile phones and monitoring physiological indicators in real time, demonstrating broad application prospects as an efficient, durable, and flexible energy-supply unit in future smart wearable systems (Figs. 11(h) and 11(i)).

4.2 Applications based on two-electron ORR

Compared with the broad application potential of the $4e^-$ ORR in the energy sector, the $2e^-$ ORR has attracted extensive attention due to its unique prospects in green chemical synthesis. As an environmentally friendly alternative, electrocatalytic $2e^-$ ORR enables the green on-site generation of H_2O_2 , promising to replace the traditional anthraquinone process, which suffers from high energy consumption and severe pollution [165]. However, laboratory-scale production based on a RRDE falls far short of actual market demand, prompting researchers to develop platforms suitable for industrial production and application.

Unlike the centralized production of H_2O_2 via the anthraquinone process, electrocatalytic synthesis offers the technological foundation for distributed production and on-demand application, thereby promoting the development of device miniaturization and on-site utilization [166]. Researchers have loaded catalysts onto GDEs as cathodes and employed H-type electrolytic cells or flow cells as reactors, achieving both accumulative and continuous production of H_2O_2 . By coupling such a system with processes, such as organic wastewater treatment or pulp bleaching, on-site environmental remediation and pulp bleaching can be realized [167]. Furthermore, based on the design concept of half-cell reactions, selecting an appropriate anodic half-reaction to couple with the cathodic oxygen reduction reaction enables simultaneous H_2O_2 generation and value-added chemical synthesis under non-biased or low-biased conditions, thereby reducing energy consumption while improving overall economic benefits, demonstrating great promise for the electrosynthesis economy.

4.2.1 H_2O_2 production

Although the anthraquinone process is currently used for large-scale H_2O_2 production in industry, it suffers from significant

drawbacks due to its high demand for organic solvents and complex procedures. Moreover, the obtained H_2O_2 must be concentrated to ~ 70 wt.% to reduce transportation costs, posing dual environmental and safety challenges [168]. As an alternative, electrochemical production of H_2O_2 via 2e^- ORR route presents great potential due to the environmental benign, low cost, and excellent security. Du et al. applied N/O-doped hierarchically porous carbon nanosheets (N/O-HPCNs) as the cathode for the ORR. This catalyst maintained H_2O_2 selectivity $> 90\%$ over a potential range between 0.05 and 0.6 V vs. RHE in alkaline electrolyte (0.1 M KOH). In a flow-cell setup simulating practical production, N/O-HPCNs achieved an H_2O_2 production rate of $17.3 \text{ mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ at an industrial-level current density of $200 \text{ mA}\cdot\text{cm}^{-2}$, with a corresponding Faradaic efficiency as high as 92.8%. Even after continuous operation for 100 h, the Faradaic efficiency remained above 80%, demonstrating excellent long-term operational stability [141]. The same group also reported an outstanding 2e^- ORR system based on sulfur-doped mesoporous carbon spheres (S-mC) for H_2O_2 electrosynthesis [42]. The catalyst exhibited nearly 100% H_2O_2 selectivity in 0.1 M KOH, with high activity maintained at a current density of $-3.5 \text{ mA}\cdot\text{cm}^{-2}$. In a more practical flow-cell device, S-mC achieved a current density of $185 \text{ mA}\cdot\text{cm}^{-2}$ at 0.2 V vs. RHE, corresponding to an H_2O_2 production rate of $25 \text{ mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ and a Faradaic efficiency exceeding 95%. The performance remained stable over 24 h of continuous operation, showing excellent operational durability.

The H_2O_2 produced via the 2e^- ORR in acidic media can be directly utilized in existing acidic wastewater treatment and Fenton-oxidation systems without additional pH adjustment, significantly reducing process integration costs and energy consumption. Furthermore, H_2O_2 generated under acidic conditions is more stable, effectively avoiding its decomposition in neutral/alkaline environments. This enhances the usable concentration of the product while ensuring high Faradaic efficiency, improving feasibility for storage, transportation, or *in-situ* use. Ni et al. established a 2e^- ORR system based on aldehyde-functionalized CQDs (CQDs-CHO), achieving highly efficient H_2O_2 electrosynthesis under industrial-relevant conditions in acidic medium (0.05 M H_2SO_4) [116]. In an electrolyzer employing a proton-conducting solid-state electrolyte (SSE), CQDs-CHO achieved a Faradaic efficiency of 99.03% at a current density of $400 \text{ mA}\cdot\text{cm}^{-2}$, corresponding to an H_2O_2 generation rate of $3.0 \mu\text{mol}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$ (Fig. 12(a)). Stable operation for over 100 h at $100 \text{ mA}\cdot\text{cm}^{-2}$ was demonstrated, with the Faradaic efficiency maintained above 90%. The system was further validated in a scaled-up device with an effective electrode area of 100 cm^2 , achieving a Faradaic efficiency of 83.2% and an H_2O_2 production rate of $82.9 \mu\text{mol}\cdot\text{s}^{-1}$ under circulating acidic electrolyte conditions. These results not only prove that CMFECs can simultaneously achieve high selectivity, high current density, and long-term stability under acidic conditions but also provide crucial technical support for developing on-site, on-demand electrosynthesis systems that directly produce acidic H_2O_2 solutions.

Seawater electrosynthesis of H_2O_2 is a frontier research topic in green chemistry, showing significant potential for marine environmental remediation and resource utilization. Hu et al. employed Cl-PDC as a cathode in a simulated seawater system, achieving a remarkably high H_2O_2 production rate of $74.61 \text{ mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ at an industrial-level current density of $800 \text{ mA}\cdot\text{cm}^{-2}$, with a Faradaic efficiency close to 100% [88]. The

system maintained over 95% efficiency and structural stability after 400 h of continuous operation, demonstrating excellent resistance to chloride-ion corrosion. Furthermore, the system performed well in real seawater, maintaining a Faradaic efficiency above 98% at $500 \text{ mA}\cdot\text{cm}^{-2}$. The generated H_2O_2 could be used immediately for marine environmental remediation, achieving near-complete inactivation of marine bacteria (e.g., *Vibrio parahaemolyticus*) within 90 s and efficiently degrading organic dyes and antibiotic pollutants within 2–10 min (Fig. 12(b)).

However, given the wide variation in testing conditions across different studies (e.g., flow cells vs. H-cells, acidic/neutral/alkaline electrolytes), the reported catalytic performance of CMFECs is often not directly comparable. To facilitate fair and efficient cross-comparison while reducing redundant effort, we encourage researchers to adopt standardized reporting practices for 2e^- ORR. At a minimum, we recommend reporting Faradaic efficiency (%), mass- or area-normalized H_2O_2 production rate ($\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ or $\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$), onset potential (V vs. RHE), and long-term stability (h), along with explicit specification of the cell configuration and electrolyte composition. Such normalization will enable the community to build reliable structure–performance correlations and accelerate the rational design of high-performance CMFECs.

4.2.2 In-situ applications

Electrocatalytic ORR for H_2O_2 synthesis overcomes the inherent limitations of centralized anthraquinone-process production related to storage, transportation, safety, and energy consumption, giving rise to a series of *in-situ* application models. This strategy of directly coupling synthesis devices with usage scenarios not only eliminates the risks and costs associated with high-concentration storage and long-distance transport, but also provides unprecedented flexibility and process intensification possibilities for environmental remediation, green chemical engineering, and advanced manufacturing through precise spatiotemporal control.

The persistent contamination of antibiotics in the environment poses a serious threat to aquatic ecosystems, making the development of efficient, green technologies for remediating antibiotic residues in water an urgent and critical challenge [169]. The metal-free electro-Fenton system with a nitrogen-doped cathode constructed by Liu et al. exhibited outstanding degradation efficacy against pollutants (Fig. 12(c)) [170]. Under optimal conditions, the system achieved complete degradation of sulfamethazine (SMZ) with an initial concentration of $50 \text{ mg}\cdot\text{L}^{-1}$ within 60 min, with a pseudo-first-order kinetic constant as high as 0.0963 min^{-1} . The system demonstrated good broad-spectrum degradation capability, achieving degradation rates of 100%, 97.1%, 95.4%, 92.8%, and 86.4% for five sulfonamide antibiotics (SMZ, sulfamethoxazole (SMX), sulfadiazine (SDZ), sulfathiazole (STZ), and sulfadimethoxine (SDM)) within 60 min, with total organic carbon removal (mineralization) rates reaching 73.8%–86.9%. In practical water matrices, the system maintained high degradation rates of 87.9%–96.4% for SMZ in mixed samples of lake water, river water, and tap water. The system exhibited excellent stability: After six consecutive cycles of use, the SMZ degradation rate remained at 94.6%, and the active sites on the electrode surface were well preserved. Similarly, Chan et al. prepared a P-PBC-4 cathode that exhibited excellent performance in tetracycline (TC) degradation [171]. Using P-PBC-4 as the cathode achieved 99% TC removal within 30 min, with a degradation rate constant (k) as high as 0.1322 min^{-1} . Its degradation efficiency was 7.2 and 4.0 times that of

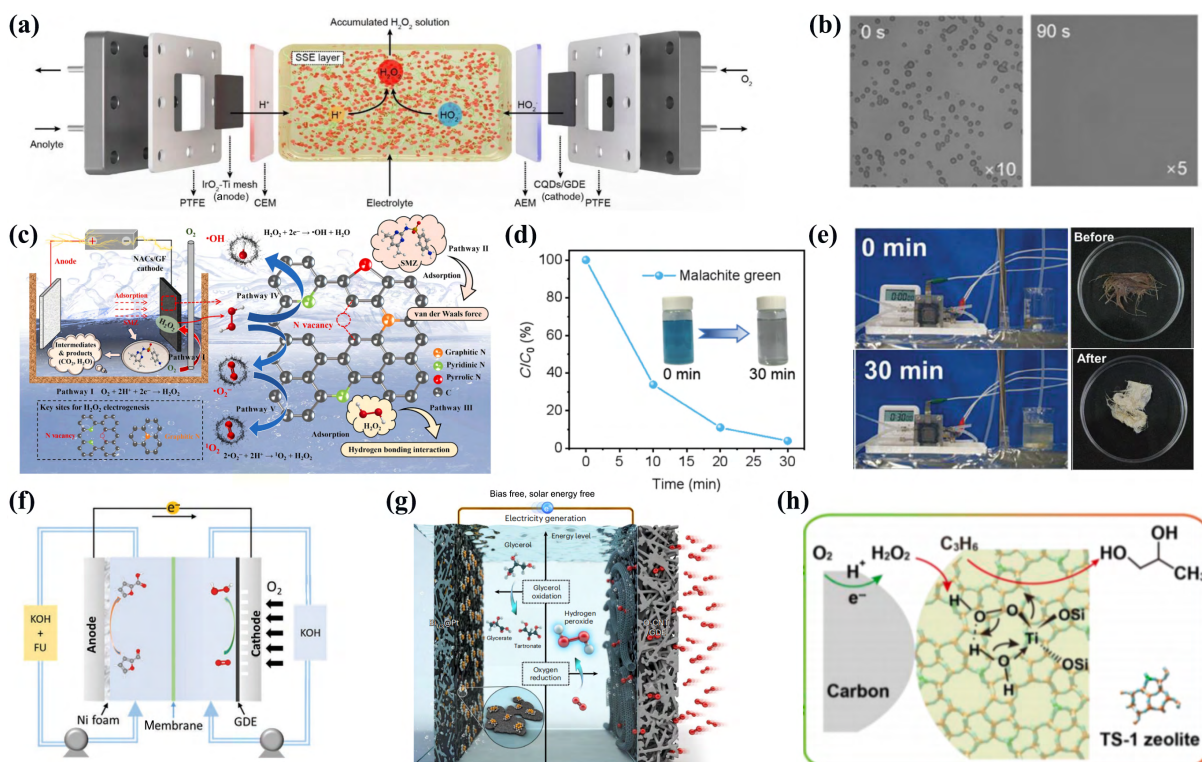


Figure 12 Application of CMFECs in $2e^-$ ORR. (a) Schematic of H_2O_2 electrosynthesis over CQDs-cast gas diffusion electrodes via a solid-state electrolyte reactor. Reproduced with permission from Ref. [116], © Ni, B. X. et al. 2025. (b) Charge-coupled device (CCD) images of overnight bacterial culture plates taken at different time intervals during electrolysis. Reproduced with permission from Ref. [88], © Wiley-VCH GmbH 2025. (c) Degradation mechanism of metal-free electro-Fenton system with nitrogen-doped cathode. Reproduced with permission from Ref. [170], © Elsevier B.V. 2024. (d) Degradation curve of MG and the corresponding optical picture (inset). Reproduced with permission from Ref. [172], © Tsinghua University Press 2023. (e) Bleaching device and comparison of the pulp before and after bleaching treatments. Reproduced with permission from Ref. [132], © Wiley-VCH GmbH 2023. (f) Scheme of the flow cell coupling electrochemical furfural oxidation and H_2O_2 generation. Reproduced with permission from Ref. [37], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2020. (g) Schematic illustration of the system demonstrating unassisted glycerol oxidation and oxygen reduction. Reproduced with permission from Ref. [173], © Oh, D. et al. 2025. (h) Schematic diagram of propylene oxidation on the C-O/TS-1 catalyst via electrocatalysis coupled with thermocatalysis. Reproduced with permission from Ref. [174], © Liu, X. C. et al. 2023.

catalysts prepared by single acid-etching and single salt-etching, respectively, and outperformed most reported electrocatalytic systems. It maintained high degradation efficiency across a wide pH range (3–11) and in various real water matrices, such as lake water, tap water, and seawater. The catalytic performance showed no significant decay after five consecutive cycles, demonstrating excellent operational stability.

While addressing water pollution caused by antibiotic abuse in the medical field, wastewater containing dyes discharged from the textile and printing industry also requires significant attention. Shen et al. prepared a boron-doped defective nanocarbon (B-DC) electrocatalyst, which, in addition to efficient H_2O_2 electrosynthesis (production rate: $247 \text{ mg} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$ and Faradaic efficiency $\sim 100\%$), demonstrated excellent rapid pollutant degradation performance in a Fenton-like system [172]. Experiments showed that solutions of malachite green (MG) and methylene blue could be completely decolorized within a very short time, and the catalyst maintained stable performance over 10 h of continuous operation (Fig. 12(d)). This high degradation capability originates from the synergistic effect between the unique hierarchical porous structure (specific surface area $320 \text{ m}^2 \cdot \text{g}^{-1}$) and boron doping-topological pentagon defects. This synergy not only optimizes the activity and selectivity for H_2O_2 electrosynthesis but also provides an efficient oxidant source and stable catalytic interface for advanced oxidation degradation of organic pollutants. Recently, our group

demonstrated an excellent catalytic degradation performance of rhodamine B (RhB) pollutant based on a N, P, O tri-doped carbon-based composite catalyst [121]. Experimental results showed that under an applied bias of only 0.3 V (vs. RHE), the catalyst efficiently catalyzed the $2e^-$ ORR pathway, generating H_2O_2 *in-situ* and driving a Fenton-like reaction, thereby achieving highly efficient degradation of RhB: a degradation rate of 95% within 120 min, which remained at 94.3% after three consecutive cycles. Furthermore, the catalyst demonstrated superior environmental adaptability and structural stability, maintaining Faradaic efficiencies of approximately 80% and 60% in neutral and weakly acidic electrolytes, respectively.

Currently, electrocatalytic ORR for H_2O_2 production is gradually approaching industrial levels, laying a solid foundation for its industrial application in fields, such as pulp bleaching. Compared to traditional chlorine-containing bleaching agents, H_2O_2 bleaching is milder, better preserves fiber strength, and reduces pulp strength loss. Secondly, the whiteness stability of paper after H_2O_2 bleaching is high, with less tendency for yellowing. Most importantly, its final decomposition products are only water and oxygen, fundamentally avoiding the generation of toxic pollutants, such as adsorbable organic halides (AOX), making it a recognized green bleaching technology. Su et al. prepared a catalyst using a defect-modification strategy that exhibited excellent $2e^-$ catalytic activity, with a Faradaic efficiency $> 95\%$ (0.4–0.7 V vs. RHE) in 0.1 M KOH and an H_2O_2

production rate of $1.8 \text{ mol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ (accumulated concentration of $105 \text{ mmol} \cdot \text{L}^{-1}$ over 12 h) [132]. The authors produced H_2O_2 using a self-made flow cell with a Faradaic efficiency exceeding 85%. Without additional purification steps, the produced H_2O_2 could be directly used for pulp treatment, successfully bleaching brown pulp (mixed paper mulberry pulp) to pure white within 30 min (Fig. 12(e)). This process significantly outperforms traditional bleaching methods, greatly shortening the treatment time.

4.2.3 Chemical industrial progress coupling

Although the development of highly selective 2e^- ORR catalysts has laid a solid material foundation for efficient and green electrochemical synthesis of H_2O_2 , the overall energy efficiency and economics of the system remain limited by the high overpotential and low-value output of the coupled anodic OER. Consequently, research focus is shifting towards designing coupled anode reactions to replace OER and construct synergistic electrolysis systems. By integrating the anodic reaction with the selective oxidation of biomass-derived molecules, high-value-added biochemicals (such as aldehydes, carboxylic acids, and pharmaceutical intermediates) can be directionally synthesized. This strategy not only greatly lowers the overall energy consumption of the reaction but also realizes the dual-channel co-conversion of renewable electricity and biomass into high-value chemicals. In doing so, it may provide a new route for the next generation of efficient and cost-effective electrosynthesis systems. Accordingly, Li et al. employed nitrogen-rich few-layer graphene (N-FLG) as a highly selective cathode for H_2O_2 electrosynthesis, coupled with the electrooxidation of the biomass-derived platform molecule furfural to 2-furoic acid at the anode [37] (Fig. 12(f)). In this integrated flow-cell device, the system required a low cell voltage of only 1.8 V to simultaneously achieve a high H_2O_2 production rate ($9.66 \text{ mol} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$) at the cathode and efficient synthesis of 2-furoic acid ($2.076 \text{ mol} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) at the anode, significantly reducing overall energy consumption and enabling the co-production of dual-channel high-value products. This work highlights that precise coupling of ORR with specific anode reactions can effectively break through the limitations of traditional electrosynthesis modes, not only greatly improving process economics, but also providing a technologically promising paradigm for driving green chemical synthesis and biomass valorization using renewable electricity.

Furthermore, Oh et al. constructed a spontaneous (galvanic) electrochemical system that requires no external electrical or solar energy input [173]. This was achieved by coupling the cathodic 2e^- ORR (producing H_2O_2) with the anodic glycerol oxidation reaction (GOR, producing glyceric acid), utilizing the thermodynamic potential difference between the two reactions to drive the overall process (Fig. 12(g)). The key to this system was the development of anode and cathode catalysts with onset potentials close to their theoretical values, enabling spontaneous glycerol oxidation and oxygen reduction. Without any external energy input, this device simultaneously achieved a high H_2O_2 generation rate ($8.475 \mu\text{mol} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$) and selective synthesis of high-value-added glyceric acid (74% selectivity), while also generating a net output of electrical power. This achievement marks a transition for ORR-coupled systems from traditional “energy-saving” electrosynthesis towards a novel “energy-producing” co-production paradigm for chemical products—a “chemical-product fuel cell” capable of generating electricity. It provides a revolutionary technological

prototype for integrated green chemical production and clean energy supply in off-grid scenarios, greatly expanding the practical application scope and economic value of electrosynthesis.

While exploring strategies to enhance the practical value of ORR, the coupling of cathode and anode reactions has shown significant advantages. A further development trend involves the tight spatial and temporal integration of the cathodic ORR with downstream chemical conversion processes to construct integrated electrically-driven synthesis systems. For example, Liu et al. designed a tandem-reaction cathode featuring “electrocatalytic generation + thermocatalytic consumption”: An oxygen-doped carbon catalyst efficiently performed 2e^- ORR for *in-situ* H_2O_2 synthesis, while titanium-silicalite (TS-1) zeolite catalysts with excellent selective oxidation performance were physically mixed with it to co-construct a composite cathode layer [174]. In this system, the electro-generated H_2O_2 did not require separation or storage but was immediately consumed on adjacent zeolite active sites to catalyze the epoxidation and hydration of propylene, converting it into the high-value-added product propylene glycol with high selectivity (79.7%) (Fig. 12(h)). The utilization efficiency of H_2O_2 reached 47.6%. This work transcends the simple pairing mode of cathode and anode reactions. Its core application value lies in ingeniously balancing electron conduction and mass transport of reactants (H_2O_2 , O_2 , propylene) by optimizing the structure and composition of the catalytic layer (e.g., the mass ratio of conductive phase to catalytic phase). This enabled continuous, efficient electrosynthesis from basic chemical feedstocks to fine chemicals under mild conditions (40°C). Such a design provides a prototype for developing modular, continuous flow electrochemical synthesis reactors that require no intermediate separation, significantly enhancing atom economy and process efficiency. It also points towards a highly engineerable technological pathway for directly embedding ORR technology into existing chemical production chains to achieve the valorization of bulk chemicals like light olefins.

5 Summary and outlook

Driven by the growing demand for energy conversion and green chemical processes, research on ORR catalysts continues to attract widespread attention. The 4e^- pathway is central to achieving efficient energy conversion in zinc–air batteries and fuel cells, while the 2e^- pathway enables the direct electrosynthesis of industrially valuable H_2O_2 , offering a clean and efficient alternative to traditional chemical processes. In recent years, CMFECs have made significant progress in this field. Through multiple strategies, such as heteroatom doping, defect engineering, and microenvironment modulation, researchers have achieved fine-tuning of material electronic structures and spatial configurations at the atomic scale. This has not only substantially enhanced catalytic activity and selectivity but also deepened the understanding of active site nature and reaction mechanisms, propelling catalyst design from empirical exploration into a new stage of rational design.

However, this field still faces a series of critical challenges (Fig. 13). At the mechanistic level, there is an urgent need for theoretical models and *in-situ* dynamic characterization techniques that better mimic realistic electrochemical environments. Such tools are essential for clarifying reaction pathways and the dynamic evolution of active sites under complex interfacial conditions. Regarding material synthesis, achieving precise control over the

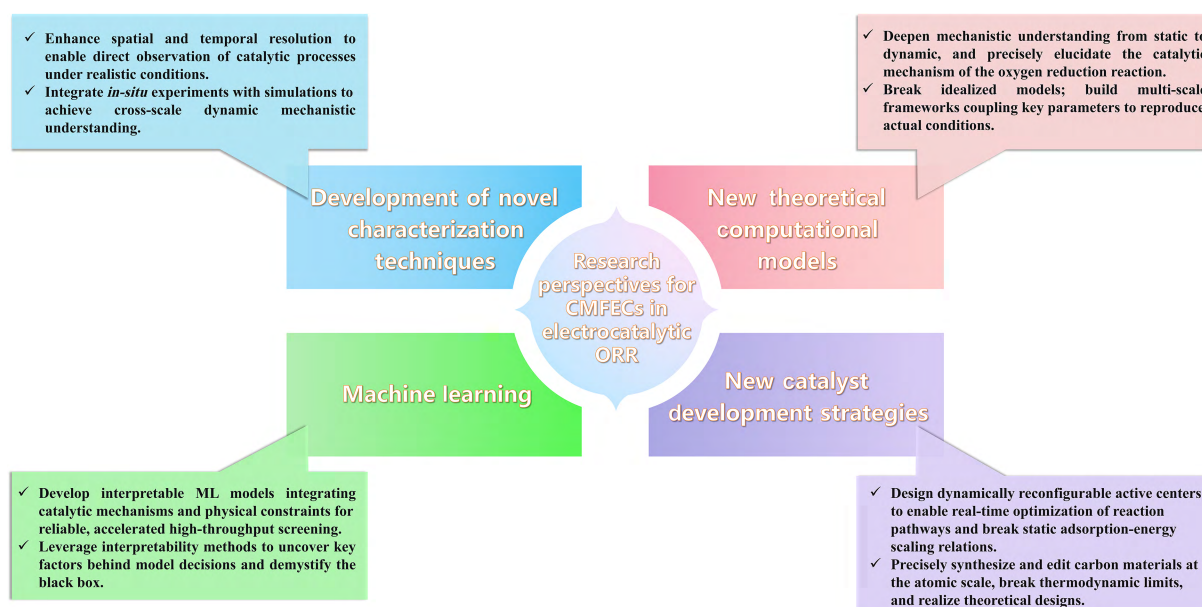


Figure 13 Research perspectives for CMFECs in electrocatalytic ORR.

type, density, and spatial distribution of active sites remains a bottleneck in preparing high-performance catalysts. Furthermore, bridging the gap between high-performance catalysts in the laboratory and their practical application requires addressing a series of engineering and scientific problems, including mass-transport optimization at high current densities, structural stability under long-term operating conditions, and scalable device integration. Solving these challenges demands deep integration of theory and experiment, multidisciplinary collaboration, and sustained research investment, ultimately driving ORR catalytic technology toward maturity and widespread application.

5.1 Development of novel characterization techniques

As rational catalyst design and controlled synthesis technologies continue to advance, the understanding of ORR performance and mechanisms needs to progress towards higher spatial and temporal resolution. In this endeavor, developing more advanced characterization techniques for elucidating material structure, combined with *in-situ* characterization—which enables real-time probing of catalyst structure and interfacial processes under reaction conditions—has become a key means to reveal the true catalytic environment and dynamic mechanisms.

Utilizing *in-situ* spectroscopy (e.g., *in-situ* infrared, Raman spectroscopy, atomic force microscopy, and transmission electron microscopy) allows direct observation of catalyst surface morphology, lattice structure, and the dynamic evolution of intermediate species under operating potentials, thereby providing direct evidence for reaction pathways and rate-determining steps. Furthermore, high-resolution surface analysis techniques (e.g., X-ray photoelectron spectroscopy and scanning electron microscopy) can precisely analyze the surface composition, chemical states, and atomic coordination structure of catalysts, offering crucial information for identifying active centers and their evolution during reactions. By integrating multiscale, multi-modal *in-situ* characterization platforms and combining them with computational simulations, it is promising to achieve a holistic dynamic analysis spanning from atomic-scale active sites to macroscopic device behavior. This will advance ORR catalyst

research from static description to a new stage of dynamic mechanistic understanding, providing a solid foundation for the rational design and performance optimization of catalysts.

5.2 New theoretical computational models

Theoretical computation has become a core tool for gaining deep insights into the catalytic mechanisms of ORR and guiding the rational design of CMFECs. Using first-principles methods, such as DFT calculations, researchers can systematically analyze the electronic structure of catalysts, the adsorption behavior of key intermediates, and the kinetic energy barriers of elementary reaction steps at the electronic and atomic levels. This microscopic understanding forms the theoretical basis for establishing structure–activity relationships and identifying core activity descriptors, providing key guidance for the targeted design of high-performance catalysts.

Currently, the application of theoretical computation in this field is mainly manifested in several key directions. First, by systematically calculating the adsorption free energies of intermediates on different material surfaces, it is possible to efficiently predict active sites and construct volcano-shaped activity trend plots, thereby indicating the most promising material systems for experimental synthesis. Second, the calculation can precisely reveal detailed processes involving electron transfer, proton coupling, and chemical bond reorganization along reaction pathways, providing a microscopic picture for elucidating selectivity-control mechanisms. Importantly, a deeply synergistic and iteratively optimized research paradigm has formed between theoretical computation and experimental studies. Theoretical models can predict the structure and performance of novel active sites, guiding experimental synthetic strategies; meanwhile, advanced characterization techniques provide critical feedback—such as electronic structure information, spectroscopic evidence of intermediates, and kinetic data—for validating and calibrating computational models. For instance, intermediate species observed via *in-situ* spectroscopic experiments can be directly compared with computed vibrational frequencies or adsorption configurations, allowing for model parameter

adjustments and enhanced prediction reliability. This closed-loop research mode of “computational pre-screening → experimental validation → mechanistic refinement → re-design” is continuously driving breakthroughs in catalyst performance.

It must be noted that a gap remains between theoretical computational models and practical electrochemical environments. Conventional models, based on idealized surfaces and simplified environments, often struggle to fully incorporate factors, such as the electric field effects within the electrode–electrolyte interface double layer, dynamic evolution of local pH during reaction, spatial confinement effects from carrier topology, and the influence of macroscopic mass transport. These neglected environmental factors frequently lead to discrepancies between theoretically predicted adsorption energies/reaction pathways and experimental observations. With the ongoing innovation of computational methods, developing multiscale simulation frameworks that integrate first-principles calculations, continuity models, and macroscopic transport analysis will be key to bridging this “environmental gap” between theory and experiment. By more accurately reproducing the complex environment of real reaction interfaces, such cross-scale models hold promise for achieving more reliable predictions of catalyst performance, thereby advancing ORR catalyst research from empirical exploration towards genuine rational design and performance breakthroughs [175].

5.3 Machine learning

ML is playing an increasingly important role in the rational design of ORR catalysts, primarily due to its unique capabilities in handling high-dimensional data, identifying complex non-linear relationships, and accelerating high-throughput screening. By establishing quantitative structure–activity relationships between material structure, electronic properties, and catalytic performance, ML can effectively predict key descriptors (e.g., intermediate adsorption energies), thereby guiding the design and optimization of active sites. Furthermore, its deep integration with first-principles calculations has formed an iterative research paradigm of “computational data generation → ML prediction → experimental validation and feedback”, significantly enhancing the efficiency and focus of catalyst development.

However, the widespread application of this approach also raises concerns regarding model reliability and physical interpretability. Since ML models, especially complex neural networks, are often treated as “black boxes”, their predictions may lack a clear physicochemical foundation, leading to significant deviations when extrapolating beyond the training dataset or applying them to real, complex electrochemical environments. This limitation often stems from the dependence of the adopted model on the quality and coverage of the training data, as well as insufficient characterization of the dynamic interfacial micro-mechanisms of catalytic reactions.

Future research needs to focus on enhancing model transparency and physical consistency. On the one hand, closer integration of ML with catalytic theory should be promoted by developing “physics-informed ML” models that incorporate mechanistically-informed features and constraints. On the other hand, emphasis should be placed on the systematic accumulation of high-quality, multiscale experimental and computational data, alongside the development of explainable AI methods to uncover the key factors behind model decisions. This will transform the powerful predictive capability of ML into a deeper understanding of catalytic science and a more reliable capacity for rational design.

5.4 New catalyst development strategies

In the progression toward rational design of CMFECs, a methodological framework has been systematically established, encompassing the modulation of electronic structure via heteroatom doping, the construction of active sites through defect engineering, and the optimization of interfacial mass transport and stability via microenvironment engineering. To transcend current optimization paradigms, frontier exploration is gradually shifting towards probing deeper scientific principles related to the intrinsic dynamic properties and complex electronic behaviors of catalysts.

Future breakthrough designs may lie in the understanding and control of non-equilibrium processes and collective quantum effects within materials. Specifically, designing active centers within the carbon skeleton that possess dynamically reconfigurable properties—undergoing controllable changes in valence state or coordination under electrochemical potential—holds promise for real-time optimization of reaction pathways and breaking the limitations imposed by static adsorption-energy scaling relations. In-depth exploration of long-range electronic synergistic effects induced by periodic defects or heterostructures may provide new mechanisms for holistically regulating the rate and selectivity of multi-electron transfer reactions. Moreover, precisely constructed carbon nanocavities at the molecular scale could exert decisive influence on the configuration and stability of key reaction intermediates through physical confinement and interfacial electrostatic effects, thereby enabling advanced control over reaction pathways.

Realizing these design concepts, which go beyond traditional static structures, fundamentally relies on a revolutionary advancement in the ability to precisely synthesize and “edit” carbon materials at the atomic scale. This requires the development of frontier synthetic science capable of crossing thermodynamic equilibrium limits and precisely manipulating carbon-atom bonding and assembly within complex energy fields, thereby translating theoretically conceived intricate catalyst structures into reality.

Data availability

Not applicable.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

R. Z. G.: Writing – original draft, investigation. S. H. Z.: Data curation, validation. X. Q. H.: visualization. J. L. Z.: Methodology. Q. Y.: Supervision, funding acquisition, writing – review & editing. Z. C. X.: Conceptualization, funding acquisition, writing – review &

editing. S. L. Z.: Funding acquisition, supervision. All authors have approved the final manuscript.

Use of AI statement

During the preparation of this work, the authors used DeepSeek and ChatGPT in order to correct grammar and improve language fluency. After using these tools, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

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