



From single-atom to multi-metallic composite systems: Rational design and mechanistic insights of metal-nitrogen-carbon catalysts for oxygen reduction reaction

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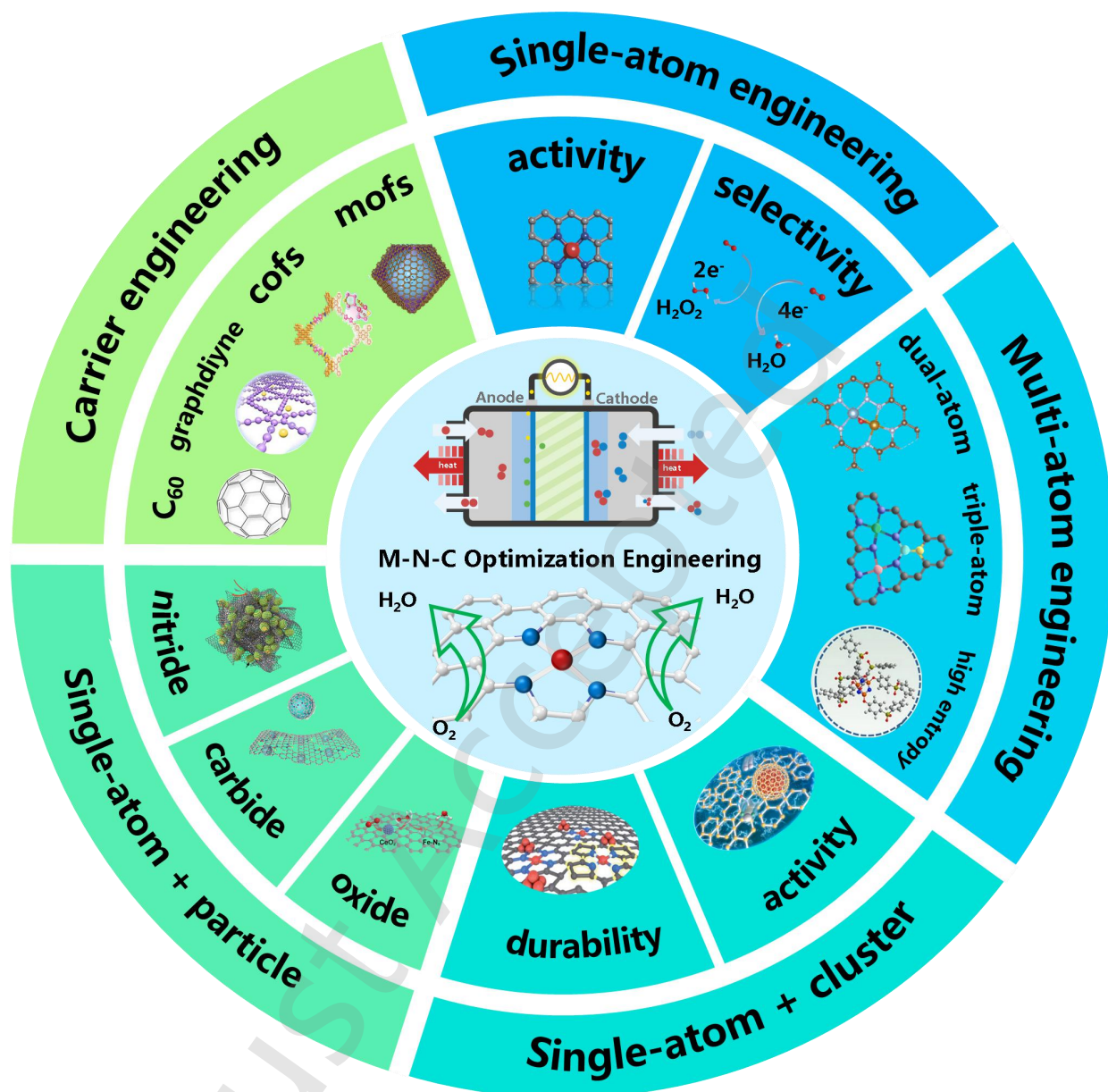
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This review systematically traces the evolution of metal-nitrogen-carbon (M-N-C) catalysts in the oxygen reduction reaction (ORR), highlighting the progression from single-atom active sites to composite optimization strategies involving clusters, particles, and carriers, with the aim of providing valuable insights for developing high-performance M-N-C catalysts.

From single-atom to multi-metallic composite systems: Rational design and mechanistic insights of metal-nitrogen-carbon catalysts for oxygen reduction reaction

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ABSTRACT

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Atomically dispersed M-N-C catalysts have been demonstrated as one of the most promising non-precious metal catalysts for proton exchange membrane fuel cells (PEMFCs) and zinc-air batteries (ZABs), owing to their excellent performance in the oxygen reduction reaction (ORR). To date, diverse M-N-C catalysts have been developed for the ORR. This review comprehensively summarizes the optimization strategies for M-N-C catalysts, progressing from single-atom catalysts to composite structures, including dual-atom sites, multi-atom sites, and architectures integrated with clusters and particles. Furthermore, it explores the differences in activity and stability among various types of M-N-C catalysts and analyzes their potential for transition from laboratory to industry, highlighting key considerations in this process. Finally, the review emphasizes persisting challenges and proposes three critical aspects warranting further attention in the future development of M-N-C catalysts, aiming to provide constructive perspectives for the sustainable advancement of clean energy technologies.

Keywords: M-N-C catalysts, oxygen reduction reaction (ORR), proton exchange membrane fuel cells (PEMFCs), zinc-air batteries (ZABs)

1 Introduction

The escalating depletion of fossil fuels has precipitated a crisis of environmental degradation and energy security, garnering urgent global attention. Advanced energy conversion devices, such as proton exchange membrane fuel cells (PEMFCs) and zinc-air batteries (ZABs), are recognized as promising candidates to replace fossil fuels owing to their high energy efficiency, sustainability, and environmental friendliness [1]. They not only reduce greenhouse gas emissions but also address the energy conversion requirements for diverse applications such as portable electronics, electric vehicles, and smart devices [2]. The oxygen reduction reaction (ORR) serves as the core electrochemical process in both PEMFCs and ZABs [3]. Its kinetic rate and reaction pathway selectivity determine the output power density, cycle life, and economic feasibility of these energy conversion devices [4, 5]. The ORR exhibits complex kinetic characteristics in both acidic and alkaline media due to the involvement of multi-proton transfer pathways and the generation of multiple oxygen-containing intermediates [6]. The inherently sluggish kinetics and the competitive two-electron pathway (producing H_2O_2 as a byproduct) necessitate efficient catalysts to accelerate the reaction. Pt-based catalysts, endowed with excellent oxygen-intermediate adsorption/desorption capabilities owing to their appropriate d-band center, have long dominated commercial applications [7]. While Pt-based catalysts remain the highest mass activity ORR catalysts, their practical implementation encounters multiple barriers including the geographical concentration of Pt reserves (80% controlled by South Africa and Russia), prohibitively high costs and insufficient durability under operating conditions all of which hinder large-scale application [8].

These challenges have driven the exploration of non-precious metal catalysts [9, 10]. In 2017, Ballard Power Systems and Japan's Nisshinbo jointly launched the world's first commercial PEMFCs

product FCgen-Micro utilizing non-precious metal catalysts [11]. This breakthrough has been recognized as a significant milestone in the fuel cell industry, marking the transition of non-precious metal catalysts from laboratory research to commercial-scale applications. The use of non-precious metal catalysts in PEMFCs to replace Pt-based catalysts can effectively reduce the cost of membrane electrode assemblies. To this end, the U.S. Department of Energy (DOE) has established 2025 targets for non-precious metal catalysts, specifying that these catalysts must achieve a current density of $44 \text{ mA} \cdot \text{cm}^{-2}$ @ 0.9 V in MEA, exhibit durability of over 5000 hours in accelerated stress testing with $\leq 30\%$ voltage decay, while reducing fuel cell system cost to below \$10/kW [12]. These targets aim to decrease the reliance on Pt materials in PEMFCs, thereby lowering system costs and enhancing the popularity of PEMFCs.

In the development of non-precious metal catalysts, M-N-C catalysts represent the most promising achievement. These catalysts feature transition metals (e.g., Fe, Co, Ni) as active centers coordinated with nitrogen atoms to form M-N_x structures [13]. Through the electronic modulation effect of the M-N_x coordination, M-N-C catalysts exhibit high intrinsic activity, enabling them to achieve performance levels comparable to Pt-based catalysts [14, 15]. These M-N-C catalysts align with sustainable development goals, as they utilize transition metals abundantly available on Earth, thereby mitigating the resource constraints to Pt-based catalysts. The emergence of M-N-C catalysts has opened up a high-performance and eco-friendly technological pathway for scaling up clean energy applications.

Over the past decade, M-N-C catalysts with diverse configurations and excellent ORR performance have been extensively reported (Table 1) [16–18]. Research efforts have predominantly focused on microstructural optimization, such as the regulation of metal-active sites, the optimization

of nitrogen coordination environments, and the design of hierarchical porous carbon frameworks, to enhance M-N-C catalysts' intrinsic ORR activity and durability. While these atomic-level engineering strategies have markedly improved the intrinsic catalytic activity, the gap between laboratory-scale research and industrial implementation remains unresolved due to multiple challenges: i) The actual catalytic mechanisms at atomic-scale active sites remain controversial, as single characterization techniques inadequately elucidate reaction pathways [19]. ii) M-N-C catalysts (e.g., Fe-N-C) suffer from metal leaching under harsh acid conditions, reducing operational stability [20]. iii) Due to differences in transport interfaces, a significant discrepancy exists between the laboratory-scale rotating disk electrode (RDE) test and the membrane electrode assembly (MEA) performance [21]. Furthermore, the lack of sustainable synthesis methods and the absence of standardized stability evaluation frameworks have hindered technology development.

Given these challenges, this work systematically reviews the development of M-N-C catalysts for the 4-electron oxygen reduction reaction (ORR), with a focus on atomic-scale active-site engineering and stability enhancement strategies. The discussion begins with the fundamental mechanisms of the ORR, and is followed by a comprehensive analysis of M-N-C catalysts categorized into three key aspects: i) The past: early explorations of M-N-C catalysts. This discussion focuses on early studies of M-N-C catalysts and their feasibility for ORR applications, laying the groundwork for subsequent advancements. ii) The present: advanced M-N-C catalyst design. Here, recent progress in M-N-C catalyst optimization is reviewed including methods for tuning atomic coordination structures, support engineering, and composite engineering. Variations in activity and stability among different M-N-C catalysts are provided, with an assessment of their potential for transitioning from laboratory research to industrial implementation. Key challenges and

Catalysts	$E_{1/2}$	Peak power density in			Refs.
	(V vs. RHE)	Durability in RDE	PEMFCs	Durability in PEMFCs	
Fe(<i>t</i> Co)-N-C	0.8 V (0.1 M HClO ₄)	maintain 92.5% after 40,000s	0.89 W·cm ⁻² 1.5 bar, H ₂ -O ₂	current density loss 11% after 60 h under H ₂ -air, 0.5 V	[22]
Fe _n @Fe-N _{pyrr} -C	0.81 V (0.1 M HClO ₄)	loss 3 mV after 10k cycles	0.8 W·cm ⁻² 2.0 bar, H ₂ -O ₂	current density loss 24.5% after 100 h under H ₂ -O ₂ , 0.5 V	[23]
FeRu-DACs	0.82 V (0.1 M HClO ₄)	loss 15 mV after 30k cycles	1.73 W·cm ⁻² 2.5 bar, H ₂ -air	current density loss 97.5% after 50 h under H ₂ -air, 0.6 V	[24]
Fe/Co-B-NC	0.85 V (0.1 M HClO ₄)	maintain 90.4% after 50 h	1.5 W·cm ⁻² 1.5bar, H ₂ -O ₂	current density loss 30% after 36 h under H ₂ -O ₂ , 0.67 V	[25]
FeN ₃ Sey	0.89 V (0.1 M HClO ₄)	loss 10 mV after 10k cycles	0.72 W·cm ⁻² 1.0 bar, H ₂ -O ₂	current density loss 6% after 100 h under H ₂ -O ₂ , 0.5 V	[26]
Fe/Ce-N-C	0.79 V (0.1 M HClO ₄)	loss 13 mV after 20k cycles	0.82 W·cm ⁻² 1.0 bar, H ₂ -O ₂	$P_{\max}$ loss 21% after 30k cycles under 1.0 bar, H ₂ -air	[27]
Fe, Cu Das-NC	0.8 V (0.1 M HClO ₄)	maintain 84.2% after 50,000 s	0.88 W·cm ⁻² 2.0 bar, H ₂ -O ₂	current density loss 8.3% after 20 h under H ₂ -O ₂ , 0.6 V	[28]
Fe _{AC} -N-SC	0.82 V (0.1 M HClO ₄)	loss 12 mV after 10k cycles	1.1 W·cm ⁻² 1.5 bar, H ₂ -O ₂	$P_{\max}$ loss 39% after 30k cycles under 1.0bar, H ₂ -air	[29]
Cr(acac)-NC-650	0.74 V (0.1 M HClO ₄)	loss 8 mV after 30k cycles	0.39 mW·cm ⁻² 1.5 bar, H ₂ -O ₂	current density loss 50% after 25 h under H ₂ -air, 0.5 V	[20]
FeAl-RNC	0.83 V (0.1 M HClO ₄)	loss 16 mV after 10k cycles	1.05 W·cm ⁻² 1.5 bar, H ₂ -O ₂	current density loss 7% after 100 h under H ₂ -O ₂ , 0.7 V	[30]
700 CO ₂ Fe-NC	0.83 V (0.1 M HClO ₄)	maintain 93% after 20,000 s	1.11 W·cm ⁻² 1 bar, H ₂ -O ₂	current density loss 53.5% after 25h under H ₂ -air, 0.5 V	[31]
Fe-S-NC/Fe ₃ C	0.80 V (0.1 M HClO ₄)	maintain 26% after 12 h	0.84 W·cm ⁻² 1.5 bar, H ₂ -O ₂	current density loss 51% after 68 h under H ₂ -O ₂ , 0.67 V	[32]
Fe-N-C-B	0.83 V (0.1 M HClO ₄)	maintain 95% after 100 h	0.7 W·cm ⁻² 1 bar, H ₂ -air	current density loss 53.5% after 500 h under H ₂ -air, 0.5 V	[33]
Fe-N-C _{CVM}	0.8 V	loss 1 mV after 30k	0.45 W·cm ⁻²	$P_{\max}$ loss 15% after 100 h	[34]

considerations in this process are also highlighted. iii) The Future: research priorities. In the final section, future directions for M-N-C catalyst development are proposed. This review advocates for the integrated design of multi-scale, highly active, and robust M-N-C catalysts, and offers insights for the rational development of cost-effective, high-performance ORR electrocatalysts.

Table 1 Performance of M-N-C catalysts in acidic RDE and PEMFCs over the past decade

	(0.1 M HClO ₄)	cycles	1.0 bar, H ₂ -air	under H ₂ -O ₂ , 0.5 V	
FeCoN ₅ P ₁	0.82 V (0.1 M HClO ₄)	loss 15 mV after 10k cycles	1.02 W·cm ⁻² 1 bar, H ₂ -O ₂	current density loss 60% after 25 h under H ₂ -air, 0.5 V	[35]
Co(mim)-NC(1.0)	0.86 V (0.1 M HClO ₄)	loss 8 mV after 10k cycles	0.64 W·cm ⁻² 1 bar, H ₂ -O ₂	current density loss 20% after 100 h under H ₂ -air, 0.7 V	[2]
Fe-Zr/N/C	0.872 V (0.1 M HClO ₄)	maintain 95.44% after 48,000 s	1.2 W·cm ⁻² 2 bar, H ₂ -O ₂	voltage loss 60% after 100 h under H ₂ -O ₂ , 1 A·cm ⁻²	[36]

2 Fundamental mechanisms of the oxygen reduction reaction

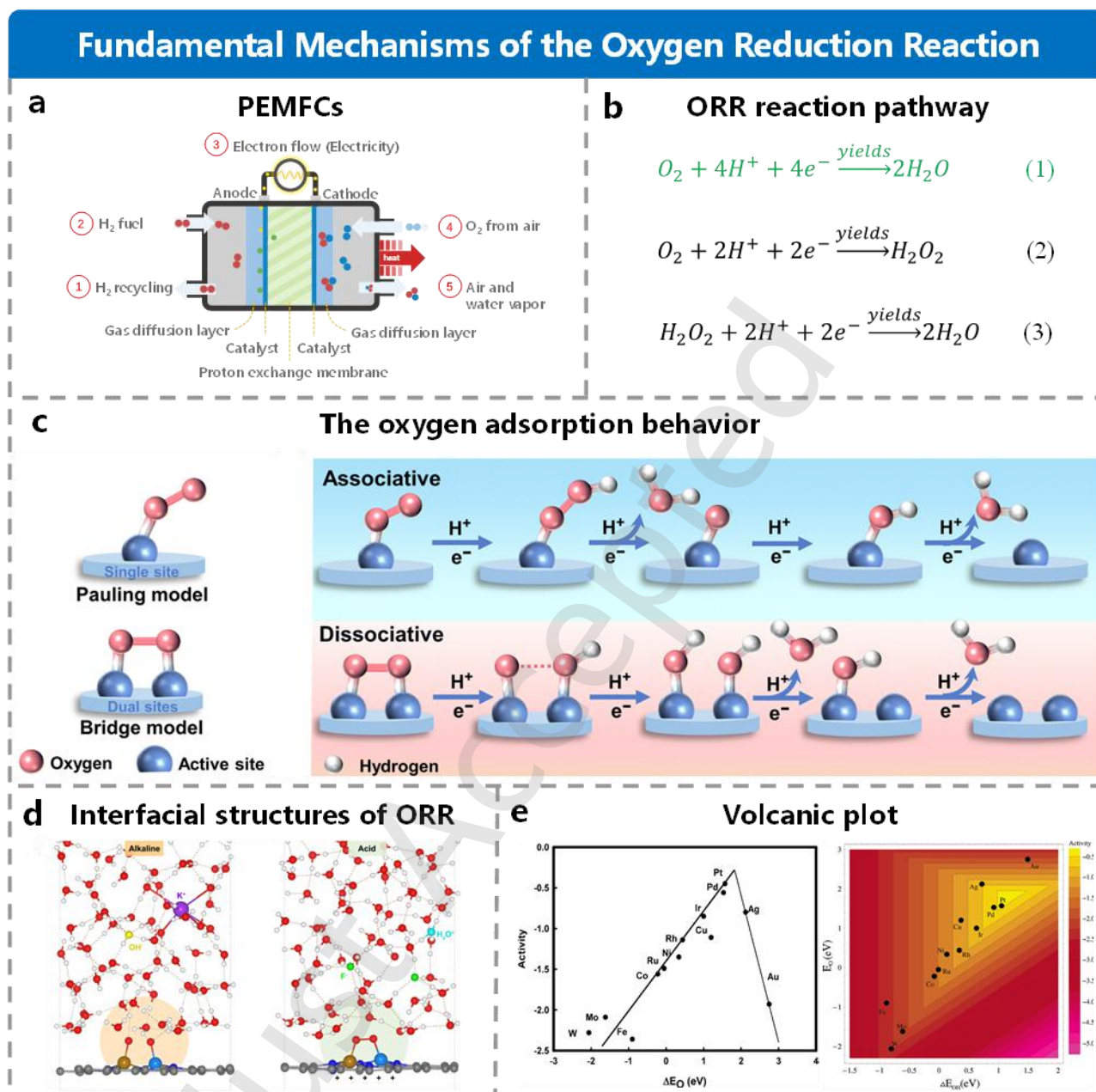


Figure 1 (a) Schematic diagram of the working principle of PEMFCs. (b) 4-electron (Eq. (1)) and 2-electron (Eqs. (2) and (3)) reaction pathways for the ORR. (c) The oxygen adsorption behavior. Reproduced with permission from Ref. [37], © Royal Society of Chemistry 2024. (d) The arrangement of water molecules in acidic and alkaline media. Reproduced with permission from Ref. [38], © Li, P. et al. 2023. (e) Volcanic plot. Reproduced with permission from Ref. [39], © American Chemical Society 2004.

The ORR involves a multi-step proton transfer mechanism with diverse reaction intermediates (Figure 1(a)) [40]. As early as 2004, Nørskov and coworkers proposed possible intermediate species and reaction pathways during the ORR through density functional theory (DFT) calculations [39]. Fundamentally, this reaction entails the stepwise reduction of O_2 to H_2O or H_2O_2 via proton transfer processes on catalyst surfaces. The specific pathway is determined by the properties of the catalyst and the reaction conditions (e.g., pH, composition of the catalyst) [41]. Two primary reaction mechanisms are currently recognized: the four-electron ($4e^-$) pathway (Eq. (1)) and the two-electron ($2e^-$) pathways (Eqs. (2) and (3)), as illustrated in Figure 1(b). Among these, the direct $4e^-$ pathway converting O_2 to H_2O is considered ideal for the ORR applications, as the $4e^-$ pathway provides higher efficiency and excellent energy conversion compared to the $2e^-$ pathway [42].

The $4e^-$ pathway typically proceeds via associative or dissociative mechanisms, with their relative dominance determined by the adsorption behavior of O_2 at active sites (Figure 1(c)) [43, 44]. When O_2 is adsorbed onto the active site via a single oxygen atom, with the other oxygen atom moving away from the active site, this configuration is termed the Pauling or Griffiths model [45]. This configuration favors the associative mechanism [46]. In this pathway, O_2 undergoes sequential electron and proton transfers, forming intermediates such as $*OOH$ and $*O$, which are ultimately reduced to H_2O . Conversely, when both oxygen atoms of O_2 simultaneously adsorb to active sites, this configuration is termed the bridge model [47]. This configuration favors the dissociative mechanism, where the O-O bond rapidly breaks upon adsorption, yielding two separate oxygen atoms that are independently reduced to H_2O [48]. Compared to the associative pathway, the dissociative mechanism accelerates the kinetics of the ORR by cleaving O_2 early, thereby simplifying

subsequent reduction steps [37, 46]. Pt-based catalysts follow a dissociative pathway. Their unique electronic and geometric structures enable O₂ adsorption via the bridge model, driving efficient 4e⁻ reduction through the dissociative pathway and resulting in excellent ORR performance [49]. In the 2e⁻ pathway, O₂ initially gains two electrons to form H₂O₂ as an intermediate [50], which subsequently accepts two additional electrons to undergo further reduction to H₂O. This 2e⁻ pathway is predominantly observed in catalysts with weak O-O bond dissociation capabilities [51].

During the ORR process, catalytic activity in alkaline media generally surpasses that in acidic environments. According to Chen et al. [38], significant differences exist in the surface charge states of electrodes under acidic and alkaline conditions (Figure 1(d)). Under acidic conditions, the electrode surface becomes positively charged, while under alkaline conditions, it remains uncharged. Due to the absence of surface charge in alkaline conditions, the water molecules are orientated disorderly, enabling the formation of hydrogen bonds with adsorbed oxygen species. These hydrogen bonds promote proton transfer, thereby accelerating the ORR kinetics. Conversely, in acidic environments, the positively charged electrode surface induces ordered alignment of interfacial water molecules (oxygen atoms facing downward). This ordered configuration prevents hydrogen bonding with adsorbed oxygen species. Consequently, the ORR process must overcome kinetic barriers to change the water molecules for hydrogen bond formation. This requirement leads to additional energy consumption, thus resulting in sluggish reaction kinetics in acid condition. Li et al. propose that the O₂ → HOO* step dominates the reaction rate of the ORR [52]. In acidic medium, the presence of abundant H⁺ ions enhances the stability of HOO*, thereby hindering the bond-breaking process. Conversely, under alkaline conditions, the scarcity of H⁺ reduces HOO* stability, allowing the O-O bond-breaking step to proceed more readily. Consequently, higher ORR activity is observed

in alkaline media.

The ORR reaction rate is also determined by the adsorption strength of oxygen-containing species at the catalyst's active sites, a phenomenon explained by the volcano plot activity theory (Figure 1(e)) [39]. The binding energy of oxygen intermediates (*O, *OH, *OOH) to the metal active sites must be moderate—neither too strong nor too weak. Noble metal platinum is located at the peak of the volcano curve due to its near-optimal adsorption strength for *OOH intermediates, aligning with thermodynamic requirements [39]. The M-N-C catalyst exhibits Pt-like catalytic activity by engineering the metal's d-band center position [53]. Therefore, the turnover frequency (TOF) of M-N-C catalysts can be comparable to that of Pt-based catalyst. However, the mass activity of M-N-C catalysts continues to be significantly lower than of Pt-based catalysts due to the far lower site density of the former vs. latter [54].

Although the volcano plot theory provides guidance for catalyst design, the comprehensive performance of catalysts under practical operating conditions must also consider challenges such as metal dissolution, support corrosion, and three-phase interfacial mass transfer [55–57]. The mass transport resistance at the three-phase interface is governed by the catalyst layer structure, the properties of the ionomer, and the architecture of the gas diffusion layer (GDL), among other factors [58]. This resistance can be mitigated by enhancing the exposure of active sites, optimizing the architecture of the catalyst layer and GDL, and regulating humidity conditions [59–61]. The issue of metal dissolution is particularly prominent in non-noble metal catalysts [62]. Taking Fe-based catalysts as an example, dissolved Fe^{2+} ions generate reactive oxygen species (ROS) via the Fenton reaction ($\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{*OH} + \text{OH}^-$) in acidic environments. These ROS attack Fe active sites, leading to Fe leaching [63]. Additionally, at high potentials carbon oxidation can occur (e.g., C

+ H₂O → CO↑ + 2H⁺ + 2e⁻) causing structural collapse [64, 65]. Schuhmann et al. employed modified differential electrochemical mass spectrometry to monitor carbon corrosion processes in real-time [64]. They observed that C-O-C bonds undergo hydrolytic cleavage at high potentials (>1.0 V vs. RHE), producing CO and H₂O. Although normal operating potentials will be 0.6–0.8 V, during startup shut down events in stacks the cathode potential can reach >> 1 V. While system mitigation strategies for this failure mode exist, some degree of carbon stability is always required for commercial products. Therefore, developing durable M-N-C catalysts for practical applications is of high importance.

3 The past: Early explorations of M-N-C catalysts

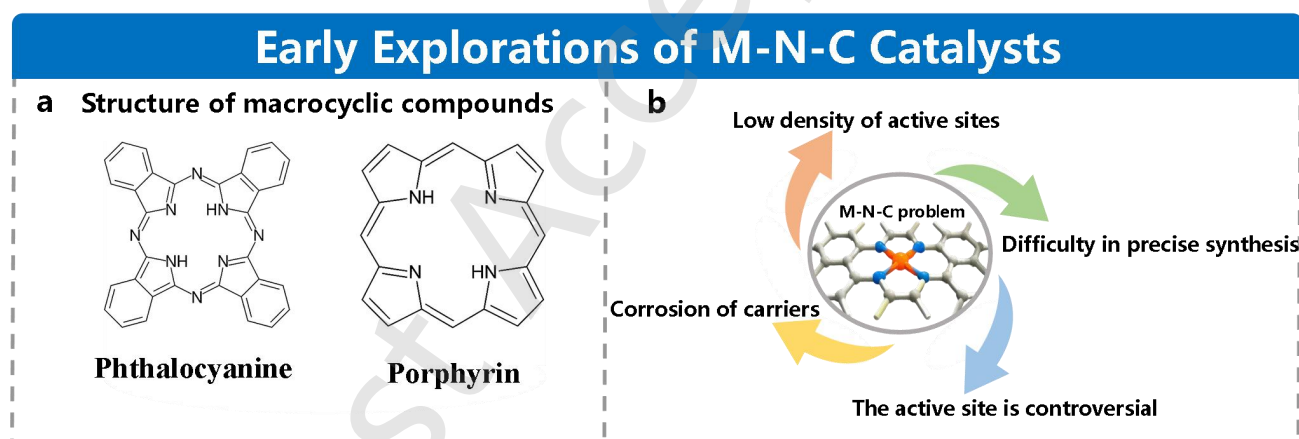


Figure 2 (a) Structure of macrocycle compounds. (b) Challenges of M-N-C catalysts.

3.1 Pioneering transition metal compounds

The period from the 1960s to the 1980s represents the initial exploratory phase of M-N-C catalyst research. Researchers conducted systematic investigations into the precursors of M-N-C—metal macrocyclic compounds such as phthalocyanines and porphyrins [66]. These metal macrocyclic compounds demonstrated significant potential in the ORR applications due to their unique conjugated macrocyclic structures and strong coordination capability with transition metals (e.g., Fe,

Co, Ni). Phthalocyanines and porphyrins are two major classes of macrocyclic compounds (Figure 2(a)). Porphyrins consist of four pyrrole rings interconnected by methine bridges ($-\text{CH}=\text{}$), typically coordinating with central metal ions to form biomolecules like heme and chlorophyll. Porphyrins are widely present in nature (e.g., iron porphyrin, cobalt porphyrin) and participate in biocatalytic processes [67]. Phthalocyanines are conjugated macrocycles formed by four isoindole units linked via nitrogen atoms, which stabilize through metal ion coordination (e.g., iron phthalocyanine, copper phthalocyanine). Most phthalocyanines are synthetically derived. In 1964, Jasinski et al. reported groundbreaking research on the ORR activity of cobalt phthalocyanine (CoPc) [68]. They constructed a test system using nickel, platinum, and copper benzylamine electrodes with potassium hydroxide electrolyte, providing the first evidence that CoPc could act as an ORR catalyst in alkaline media. They proposed that the Co^{2+} metal center served as the catalytic active site. Subsequently in 1984, the Yeager group employed RDE techniques to confirm the 4e^- reaction pathway of CoPc and extended this discovery to other metals [69]. These foundation studies laid the groundwork for subsequent M-N-C catalysts research.

3.2 Emergence of M-N-C catalysts

With the rapid development of fuel cell technology, the performance requirements for ORR cathode catalysts grew more demanding [70]. Simple metal macrocyclic compounds could no longer meet the requirements for PEMFCs and thus researchers began exploring the potential of alternative materials [71]. Specifically, M-N-C catalysts have attracted scientists' attention due to their high conductivity and highly tunable chemical properties [72]. In his pioneering work on Fe-N-C catalysts, Dodelet et al. synthesized electrocatalysts via pyrolysis of iron acetate and nitrogen precursors (e.g., NH_3) supported on perylene tetracarboxylic dianhydride [73]. Time-of-flight secondary ion mass

spectrometry (ToF-SIMS) and electrochemical tests demonstrated that the ORR activity exhibited a strong correlation with the characteristic FeN_2C_4^+ secondary ion signal, identified as an active site formed at high temperatures. In their subsequent study, pyrolysis of precursors at varying temperatures (400–1000 °C) revealed that FeN_4C_8^+ sites predominantly formed at lower temperatures, while FeN_2C_4^+ sites became dominant at higher temperatures [74]. The FeN_2/C sites demonstrated significantly higher activity than the FeN_4/C sites. This discovery substantially refined the understanding of structure-activity relationships in diverse M-N-C catalysts. The M-N_x coordination environment in M-N-C catalysts closely resembles that of macrocyclic compounds. Both M-N-C and macrocyclic compounds feature a central metal atom coordinated to nitrogen and carbon atoms. However, M-N-C catalysts do not merely replicate the structure of macrocyclic compounds; instead, they are engineered through materials science methods to enhance and optimize precursor structures, creating configurations analogous to macrocyclic compounds [75]. Among various M-N-C synthesis methods, the pyrolysis method has emerged as the dominant technique due to its simplicity [76]. This process involves high-temperature pyrolysis of precursors containing metal, nitrogen, and carbon, forming active sites where metal atoms coordinate with nitrogen-doped carbon support (e.g., Fe-N₄, Co-N₄). The strong metal-nitrogen bonds formed at high temperatures significantly enhance activity, allowing M-N-C catalysts to exhibit Pt-like TOF even in acidic environments [77, 78]. Compared to metal macrocyclic compounds, M-N-C catalysts exhibit the following advantages: i) M-N-C catalysts are typically synthesized from porous precursors [79]. These porous precursors provide abundant pore structures, effectively offering anchoring sites for metal active centers and sufficient space for O₂ reactions. ii) The abundance of carbon defects in M-N-C catalysts provides effective anchoring sites for metal atoms, thereby generating catalytically

active centers [80]. Studies have shown that nitrogen atoms in M-N-C can modify the charge distribution of the carbon skeleton, enhancing the adsorption and activation capabilities of oxygen molecules on the surface of the catalysts [81]. For example, Wang et al. demonstrated that sp-hybridized nitrogen-doped graphdiyne induces a positive charge on adjacent carbon atoms, significantly strengthening O₂ adsorption and activation, achieving the ORR activity close to that of Pt/C catalysts [82]. iii) Traditional porphyrin or phthalocyanine compounds exhibit poor conductivity. In contrast, M-N-C catalysts greatly improve the graphitization degree of the carbon support through precursor pyrolysis [83]. The compact carbon framework provides efficient electron transport pathways for the ORR, which is essential for the excellent ORR activity of M-N-C catalysts [84]. Among various M-N-C catalysts, Fe-N-C catalysts demonstrate excellent ORR activity due to their enhanced ability to promote O₂ adsorption and activation. Lalande et al. confirmed that when Fe and N are coordinated, they exhibit a synergistic effect during active site formation, improving the ORR reaction kinetics [85]. The Fe-N-C catalyst they prepared exhibited a voltage of 0.4 V at 1.5 A·cm⁻² under H₂-O₂. With a deepening understanding of M-N-C catalysts, researchers have gradually shifted toward tailoring metal centers. Efforts are underway to combine other transition metals (e.g., Mn, Ni, Cu) with nitrogen-doped carbon support to further optimize the ORR kinetics [86, 87].

3.3 Challenges in early development

Although M-N-C catalysts demonstrated promising potential for the ORR, they encountered significant challenges in their early development stages (Figure 2(b)), primarily due to the following reasons: i) A low density of active sites. Most M-N-C catalysts have metal contents below 3% [88], which severely restricts their mass activity and thus practical viability because this necessitates high loadings (and thus thick layers) resulting in high mass transport losses when tested in MEA. ii)

Difficulty in precisely synthesizing atomic-level $M-N_x$ active sites. Inconsistent coordination numbers between metal and nitrogen atoms result in heterogeneous active site types, complicating the characterization and analysis of these catalysts [89]. The uneven distribution of active nitrogen configurations (e.g., pyridinic N, graphitic N) in M-N-C materials also leads to limited catalytic efficiency [90]. iii) Carbon supports corrosion. M-N-C catalysts typically consist of metal species hosted on carbon supports. During the long-term ORR cycling or under high potentials, carbon will undergo oxidative corrosion, causing structural collapse of the metal-anchoring sites [91]. Furthermore, when M-N-C catalysts are utilized in PEMFCs cathode catalyst layers, carbon corrosion destroys the porous structure of the catalytic layer, leading to significantly increased mass transfer resistance [92]. iv) Elucidation of the active sites remain challenging. Due to limitations in early characterization techniques, researchers faced significant challenges in determining the structural features of active sites at the microscopic scale. Some studies attributed catalytic activity to $M-N_x$ coordination structures, given their resemblance to the metal macrocyclic compounds [93]. Others proposed that defects or edge sites in nitrogen-doped carbon materials themselves act as the ORR active sites [82]. Consequently, controversies surrounding the M-N-C active centers remain unresolved.

4` The present: advanced M-N-C catalyst design

To date, atomically dispersed M-N-C catalysts have exhibited remarkable progress in the field of the ORR catalysts [94–97]. These catalysts achieve nearly 100% atomic utilization efficiency. Such high atomic utilization efficiency enables turnover frequencies comparable to platinum-based catalysts. This advancement paves the way for the sustainable development of PEMFCs.

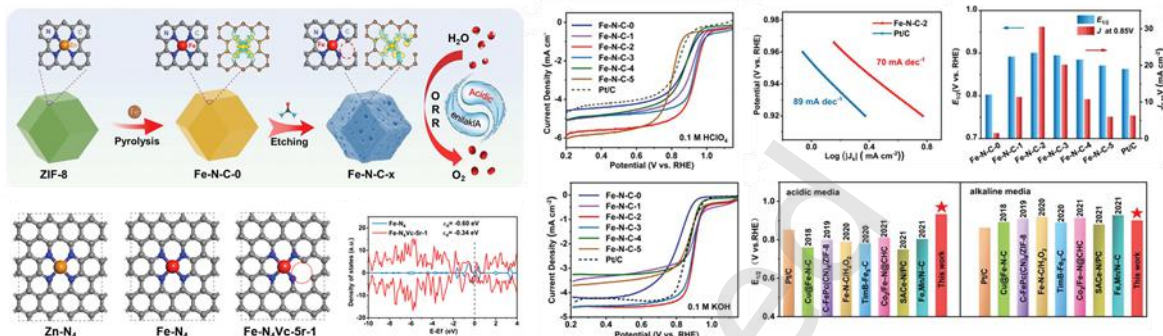
4.1 Engineering of single-atom active sites

In the field of the ORR catalysts, the most common M-N-C catalysts is Fe-N-C. Fe atoms are embedded in nitrogen-doped carbon support in a planar square coordination configuration, forming unique Fe-N₄ active centers [98, 99]. Their appropriate d-band electronic structure significantly regulates the adsorption strength of oxygen intermediates, exhibiting the ORR performance comparable to Pt-based catalysts.

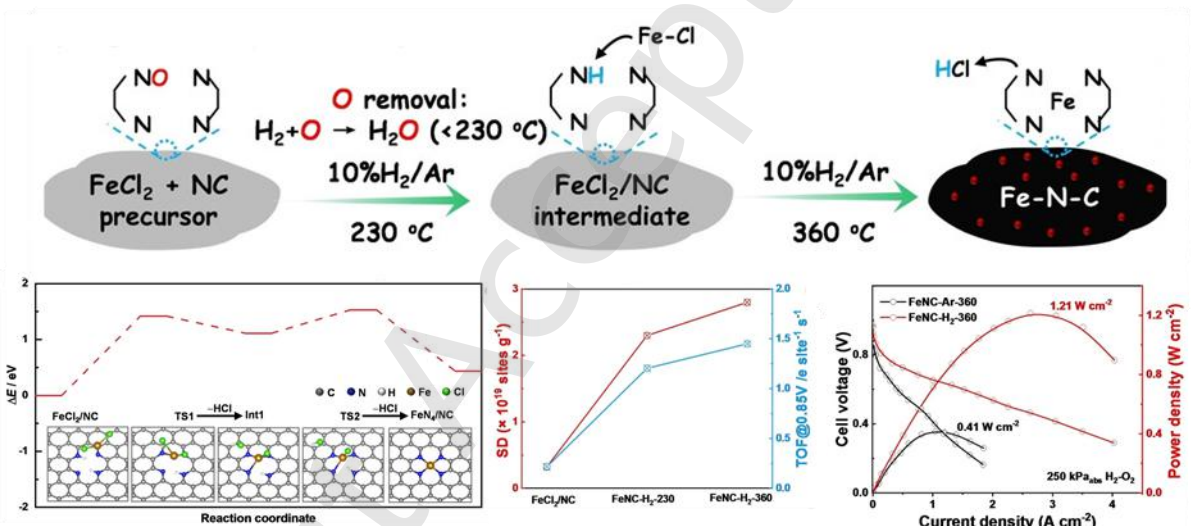
Engineering of Single-Atom Active Sites

Activity optimization

a. Improvements in TOF

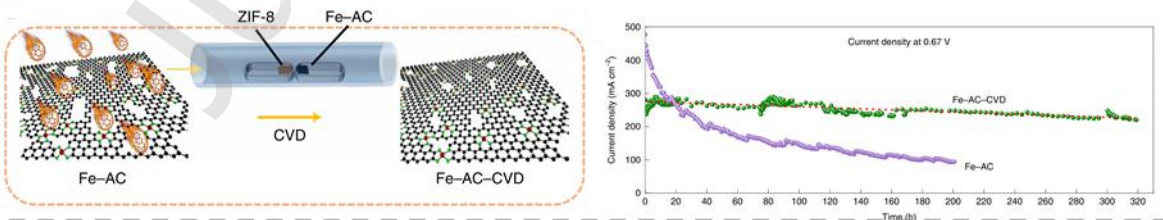


b. Increasing site density



Durability optimization

c. Increasing the proportion of S2 sites



d. Metals with low fenton reaction activity

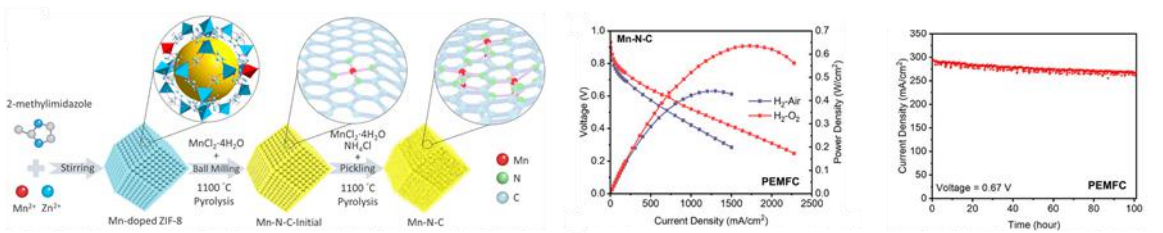


Figure 3 (a) Guo et al.'s method for enhancing the intrinsic activity of Fe-N-C and DFT computational structure. Reproduced with permission from Ref. [100], © Tu, H. L. et al. Advanced Science published by Wiley-VCH GmbH 2023. (b). Sun's research group's method for enhancing Fe loading and its DFT results and PEMFCs performance. Reproduced with permission from Ref. [101], © Wiley-VCH GmbH 2024. (c) Wu et al.'s approach to enhancing S₂ sites and the resultant performance data. Reproduced with permission from Ref. [102], © Liu, S. W. et al. under exclusive licence to Springer Nature Limited 2022. (d) Synthesis flowchart and performance of Mn-N-C Catalysts. Reproduced with permission from Ref. [103], © Wiley-VCH GmbH 2025.

4.1.1 Synthesis of single-atom M-N-C catalysts

Numerous methods have been developed for synthesizing single-atom catalysts, including the impregnation method, spatial confinement method, and atomic layer deposition method [30]. The impregnation method involves immersing porous supports in low-concentration metal precursor solutions to achieve single-atom dispersion. This method is widely adopted due to its simplicity and ease of operation [104]. The spatial confinement method represents an improved version of impregnation method, where additional physical barriers (e.g., SiO₂, AlO₄) are introduced to suppress metal agglomeration [36]. This modification enables a high degree of atomic dispersion. Notably, precursors such as MOFs and COFs inherently possess spatial confinement effects, where metal species can be confined within their porous frameworks to achieve atomic dispersion. Finally, the atomic layer deposition method employs advanced thin-film growth techniques to deposit single atoms on support surfaces with precision [105]. While this approach achieves excellent atomic-level control, it demands sophisticated instrumentation. The primary challenge for all of these methods lies in synthesizing catalysts with high metal loading and atomic dispersion, which still requires

substantial research efforts to overcome.

4.1.2 Activity optimization of single atom M-N-C catalysts

In PEMFCs or ZABs applications, the mass activity of the catalyst is the most critical metric of activity since this dictates the loading and thus the cost and thickness of the catalyst layer. The mass activity can be defined in several ways, but for the purposes of this discussion, we will consider it the product of TOF (reaction/site/s) and site density (sites/g or sites/cm²).

4.1.2.1 Improvements in TOF

The intrinsic activity can be quantified by the TOF, which directly reflects the number of reactions occurring per active site per unit time. The TOF is primarily dependent on the electronic structure and local coordination environment of the active sites [101]. The TOF of conventional Fe-N-C catalysts typically ranges around 1 e[−]·site^{−1}·s^{−1} (at 0.80 V vs. RHE). Enhancing the TOF of M-N-C catalysts can be achieved by engineering the electronic structure of active center, which is attainable through modulation of both the metal center and coordinating atoms. This is because the ORR involves complex multi-electron transfer steps. The configuration of the active center along with the type of coordinating atoms, collectively influence the electronic structure of the metal center (particularly the d-band center position) and its adsorption strength toward key reaction intermediates. Liu et al. treated an Fe-N-C catalyst with ammonium iodide (NH₄I) vapor, obtaining an iodine-doped Fe-N-C catalyst [106]. This catalyst achieved a TOF of 3.71 e[−]·site^{−1}·s^{−1} (at 0.8 V vs. RHE), representing a ~3-fold enhancement over the pristine Fe-N-C catalyst. However, the oxidation potential of I[−] is low (0.62 V vs. RHE), while the operating environment of MEA typically operates at ≥0.7 V. This could lead to catalyst instability. As expected, when applied in ZABs, this catalyst

operated for only 500 h at a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$. Wan et al. transformed the active center from the conventional planar Fe-N_4 structure to a $\text{Fe-N}_3\text{O}_2$ configuration by increasing the oxygen coordination number [107]. Their catalyst achieved a TOF of $3.65 \text{ e}\cdot\text{site}^{-1}\cdot\text{s}^{-1}$, representing a 2.8-fold enhancement over traditional Fe-N_4 sites. Significantly, this work pioneered the use of electron occupancy as a descriptor, establishing a linear proportionality between the electron occupancy of Fe single-atom catalysts and ORR activity. This breakthrough provides valuable insights for designing single-atom electrocatalysts. Beyond the two aforementioned methods, the TOF of M-N-C catalysts can be enhanced by creating defects near the active center. Defect generation near active center causes redistribution of electron density in M-N_x structures and induces asymmetric electronic states. Such asymmetric electronic configurations at active sites may facilitate the ORR. Guo et al. enhanced the TOF by creating defects near Fe-N_4 sites (Figure 3(a)) [100]. The authors partially substituted Zn in ZIF-8 with Fe to form Fe-N_4 coordination structures. Simultaneously, urea etching introduced carbon vacancies near Fe-N_4 sites, breaking the electronic symmetry of Fe. DFT calculations revealed that the adjacent carbon vacancies optimized the d-band center of Fe, thereby improving the TOF of catalyst. The authors propose a strategy for enhancing the TOF by modulating adjacent carbon defects at the active site, highlighting the critical role of these carbon defects in boosting the TOF of single-atom catalysts and thus offering insights for designing high-performance catalysts.

However, these strategies face inherent limitations that warrant critical consideration. Defect engineering (Guo et al.) relies on fragile carbon vacancies susceptible to oxidation under harsh electrochemical conditions, potentially compromising long-term stability. While heteroatom doping (Liu et al.) significantly enhances TOF, the thermodynamic instability of metal atoms in practical

MEAs must be addressed – irreversible catalyst deactivation occurs when operating voltages exceed their oxidation potential. Although oxygen coordination tuning (Wan et al.) achieves excellent TOF, the Fe-N₃O₂ configuration requires complex support preparation processes. Future efforts must concurrently optimize catalyst TOF and address MEA integration challenges to bridge the gap between lab-grade and industrial-grade catalysts.

4.1.2.2 Increasing site density

As stated, the mass activity of M-N-C catalysts also depends on the density of active sites.[108] Typically, the metal loading in M-N-C catalysts is below 3 wt.% [109–111]. A high density of active sites increases the probability of contact with O₂, thereby accelerating the reduction of O₂ to H₂O. The density of active sites is determined by the amount of metal precursor added, the degree of metal precursor dispersion, and the pyrolysis atmosphere, among other factors [112]. For instance, Sun's group demonstrated that introducing carboxylates during ZIF-8 synthesis significantly enhances the Fe concentration through coordination interactions. Acetate ions preferentially anchored on the ZIF-8 surface as binding sites, which subsequently coordinated Fe ions. The resultant catalyst exhibited a peak power density of 1.33 W·cm⁻² when tested in an MEA under H₂/O₂ and high Fe loading content of 3.5 wt.%. The catalyst they prepared reaches an active site density of 14 μmol·g⁻¹, which is higher than conventional Fe-N-C catalysts (8 μmol·g⁻¹). This strategy demonstrated universality, with formate, oxalate, and tartrate systems also achieving Fe loadings exceeding 1 wt.%, surpassing the 0.55 wt.% value observed in carboxylate-free Fe-N-C counterparts. This catalyst achieves a mass activity of 0.005 A·mg⁻¹_{catalyst} (at 0.85 V). However, even assuming identical TOF to 20 wt.% Pt/C, its mass activity remains lower than Pt/C (0.038 A·mg⁻¹_{catalysts}) [113]. In their subsequent study, Sun et al. reported that supplying hydrogen at low temperatures could promote the formation of Fe-N₄ active

centers [101]. The prepared catalyst achieved an Fe content as high as 8.3 wt.% which translates to an active site density of 2.80×10^{19} sites·g⁻¹. Through TPD and *in situ* XPS analyses, they discovered that hydrogen effectively removed N-O bonds, Fe-O bonds, and Cl⁻ from Fe precursors, facilitating the formation of dense Fe-N₄ structures. The catalyst exhibited a peak power density of 1.21 W·cm⁻² when tested in an MEA under H₂-O₂ (Figure 3(b)). Comparative analysis of Sun's two studies reveals that while one catalyst contains 3.5 wt.% Fe and the other carries 8 wt.% (representing a 2× increase in Fe loading), the MEA performance of the higher-loading catalyst does not show a proportional enhancement. This demonstrates that simply increasing Fe content may not effectively improve MEA performance, and highlights the challenge that currently faces the research community in attempting to increase site density. The decisive factor lies in the density of high-activity Fe sites – some Fe inevitably exists as low-activity species (e.g., Fe-N₁, Fe-N₃, or Fe-N₅) [114]. These low-activity Fe species exhibit varying ORR activities depending on their distinct coordination environments. In terms of activity levels, the general trend is Fe-N₄ ≈ Fe-N₅ > Fe-N₃ > Fe-N₁. Specifically: Fe-N₄, the most extensively studied active site, features a planar square configuration that provides optimal adsorption strength for O₂. [115] Fe-N₅ introduces an additional nitrogen atom, which fine-tunes the electron density of the Fe center [116]. However, the higher coordination number weakens its ability to donate electrons to the antibonding orbitals of O₂ and can lead to strong adsorption of intermediates (such as *OH). Consequently, its activity is slightly lower than that of Fe-N₄. Fe-N₃ and Fe-N₁ have fewer coordinating atoms, resulting in higher electron density at the Fe center [114]. This causes strong binding with intermediates, hindering subsequent ORR steps. Additionally, their coordination structures exhibit poorer stability and are prone to collapse during the ORR. Future research must prioritize synthesizing catalysts with homogeneous distributions of highly active iron

sites. Examples of catalysts with relatively high metal loading are listed in Table 2. While not a perfect correlation, the data in Table 2 does indicate that progress is being made in terms of site density, as there is a clear positive relationship between metal loadings and activity. This is shown in Figure S1 in the ESM which plots the half wave potential vs. metal loading for the samples tested in acid (Figure. S1(a) in the ESM) and alkaline (Figure. S1(b) in the ESM), with both showing a clear positive correlation. Figures S1(c) and S1(d) in the ESM compare the measured and calculated change in overpotential vs. metal wt.% loadings for samples tested in KOH, and acid, respectively. These calculations are based on standard Butler-Volmer kinetics [117] (Eq. (1)).

$$\eta_2 - \eta_1 = \frac{RT}{\alpha F} \ln \left(\frac{\text{Loading}_1}{\text{Loading}_2} \right) \quad (1)$$

Equation (1): Butler-Volmer equation, with the parameters explicitly defined: $\alpha = 1$ (transfer coefficient), $F = 96485 \text{ C}\cdot\text{mol}^{-1}$ (Faraday constant), $R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ (gas constant), $T = 298 \text{ K}$ (temperature).

Table 2 Recent advances in high metal-loading catalysts and RDE performance over the past 5 years

Catalysts	Metal loadings	Performance ($E_{1/2}$)	Refs.
FeSA-SeNC-meso/microporous	18.3 wt. %	0.895 V, 0.1 M KOH, 1600rpm	[118]
Fe-N-C-PDBA	12.8 wt. %	0.914 V, 0.1 M KOH, 1600rpm	[119]
Fe, Co SAs-PNCF	9.8 wt. %	0.89 V, 0.1 M KOH, 1600rpm	[120]
Fe-N-C SA/HCF	4.8 wt. %	0.802 V, 0.1 M KOH, 1600rpm	[121]
CS-Fe-E	3.87 wt. %	0.831 V, 0.1 M KOH, 1600rpm	[122]
FeNC-H ₂ -360	8.3 wt. %	0.851 V, 0.1 M H ₂ SO ₄ , 900rpm	[101]
Fe-N ₄ -C	7 wt. %	0.815 V, 0.5 M H ₂ SO ₄ , 900rpm	[123]
Fe-N-C/MS-450	4.7 wt. %	0.815 V, 0.1 M H ₂ SO ₄ , 900rpm	[124]
Fe/N/C(4Mmlm)-OAc	3.49 wt. %	0.82 V, 0.1 M H ₂ SO ₄ , 900rpm	[125]
Fe@MNC-OAc	2.55 wt. %	0.8 V, 0.1 M HClO ₄ , 900rpm	[126]

Table 2 and Figure S1 in the ESM show that higher metal content does not always lead to excellent ORR activity. This highlights two critical requirements: i) dispersion of metals as single atoms on the carbon support: taking Fe-N-C as an example, increasing the Fe content might in principle raise the density of active sites. However, loading too much Fe promotes migration of Fe atoms to form particles. These particles generally show much lower ORR activity than isolated single-atom sites (e.g., Fe-N₄). Thus, ensuring metal dispersion as single atoms is essential. ii) high intrinsic ORR activity per single-atom site: Even when Fe is successfully maintained as dispersed single atoms, their individual activity is not uniform. During catalyst preparation, structures with less or more coordination atoms (e.g., Fe-N₂, Fe-N₆) may form. These configurations can exhibit overly strong or weak binding strength toward oxygen-containing intermediates (*O, *OH, *OOH), leading

to lower intrinsic activity compared to ideal single-atom sites (e.g., Fe-N₄). Therefore, ensuring high intrinsic activity per single-atom center is vital.

4.1.3 Durability optimization of single-atom M-N-C catalysts

M-N-C catalysts, especially Fe-N-C, undergo rapid performance degradation during constant potential and CV cycling tests. This is primarily attributed to Fenton reactions. However, for years, the M-N-C community has frequently reported cycling tests conducted under N₂ (following test protocols established by the Pt group metals community) to claim superior stability over Pt group metals. This approach is misleading—as N₂ conditions cannot generate H₂O₂, it fails to probe the catalyst's true degradation pathways. Studies indicate that Fe-N-C coordination primarily consists of pyrrolic-type Fe-N₄ (denoted as S1 sites) and pyridinic-type Fe-N₄ (denoted as S2 sites) [127]. S1 sites exhibit higher intrinsic ORR activity but undergo irreversible conversion to inactive Fe₂O₃ during ORR. In contrast, S2 sites demonstrate significantly greater resistance to dissolution, conferring higher stability, albeit with relatively lower ORR activity. Therefore, the ratio of S1 to S2 sites is crucial. Consequently, strategies for enhancing the durability of Fe-N-C catalysts focus on two main aspects: i) increasing the proportion of S2 sites, and ii) improving the stability of S1 sites. To improve Fe-N-C stability, the Wu group employed an approach where a catalyst containing a high density of S1 sites was first prepared (Figure 3(c)) [102]. Subsequently, nitrogen-doped carbon thin layers were deposited via chemical vapor deposition, leading to the formation of a substantial proportion of S2 sites. This modified catalyst exhibited exceptional stability in MEA accelerated stress tests, retaining 85% of its initial current density after 320 h of operation under H₂-air at 0.67 V. The primary drawback of this approach, however, was the catalyst's relatively low initial activity

(current density: $280 \text{ mA} \cdot \text{cm}^{-2}$ under H_2 -air, 0.67 V, 1.5 bar); a point that was later acknowledged in their subsequent work [128]. This phenomenon was attributed to the extensive conversion of S1 sites into S2 sites. To address this, they incorporated small amounts of H_2 during the preparation of the Fe-N-C catalyst [128]. This modification resulted in a significantly enhanced current density of $400 \text{ mA} \cdot \text{cm}^{-2}$ (under H_2 -air, 0.67 V, 1.5 bar). Unfortunately, this improvement in activity came at the expense of stability (conversion of S2 sites into S1 sites), with the catalyst retaining only 50% of its initial current density after 200 h of operation under H_2 -air at 0.67 V. Consequently, it is evident that achieving a balance between the activity and stability of Fe-N-C catalysts poses a significant challenge.

In another approach, numerous researchers are exploring alternative metal elements such as Mn-N-C and Co-N-C catalysts. These catalysts offer enhanced durability due to their lower tendency toward Fenton reactions, despite exhibiting significantly lower activity compared to Fe-based catalysts. For example, Shao et al. investigated Mn-N-C catalysts, observing only an 18% current density loss after 100 h of testing in a PEMFCs (under H_2 -air, 0.67 V, 1 bar) (Figure 3(d)). Wu et al. studied Co-N-C catalysts, reporting only a 20% current density decrease after the same test duration, significantly outperforming an Fe-N-C catalyst which suffered a 46.8% decrease (under H_2 -air, 0.7 V, 1 bar) [2].

In summary, M-N-C catalysts have demonstrated excellent TOF through precise regulation of atomic-level coordination environments, but are still quite limited in terms of site density (and thus mass activity). This challenge has been acknowledged for the past several years but has yet to be overcome [129]. Here, it must again be mentioned that although M-N-C catalysts are much lower cost than PGM catalysts, it is naïve to think that mass activity therefore has little meaning. This is

because the mass activity also directly impacts also the thickness of the catalyst layer that must be coated in a real-world MEA, and as the thickness of the cathode increases so too do the mass transport losses which ultimately prevent M-N-C-based MEA from reaching the high current densities necessary for any high-power applications. Furthermore, while promising advances in terms of stability have been achieved, this must be put into the context of commercial applications which typically require > 20,000 h of lifetime. Thus, there is still much work to be done in this area.

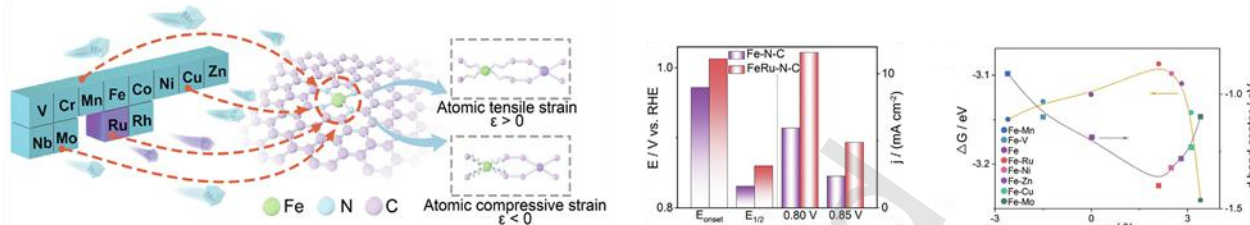
4.2 Engineering of dual-atom active sites

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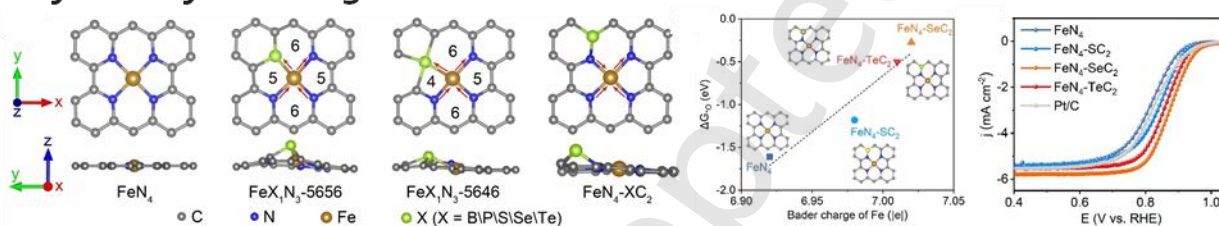
Engineering of Dual-Atom Active Sites

Activity optimization

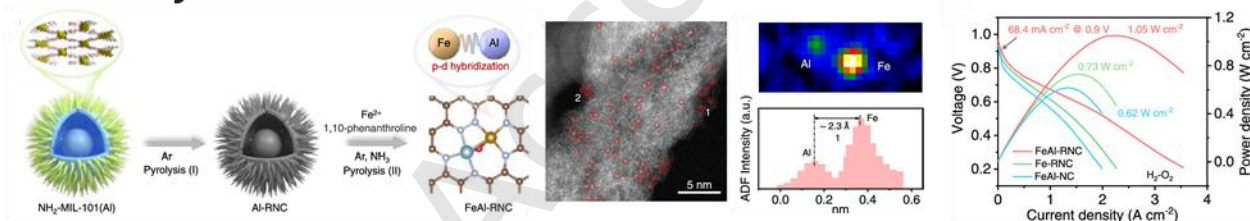
a. Modulation of atomic strain



b. Symmetry-breaking

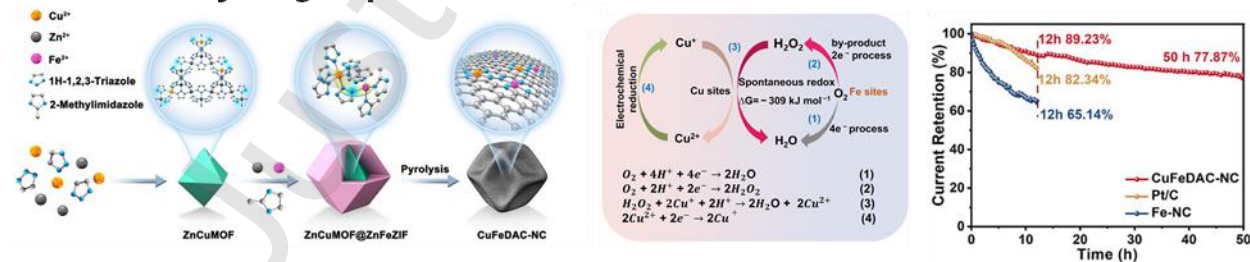


c. Orbital hybridization



Durability optimization

d. Eliminate hydrogen peroxide



e. Elevate the protonation energy barrier

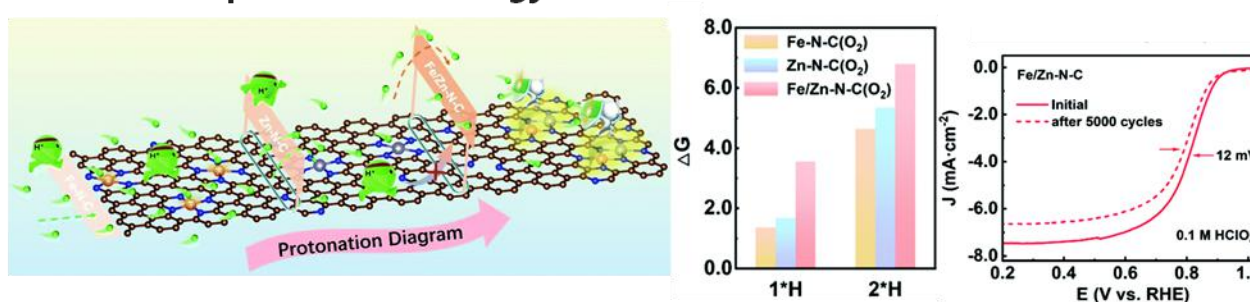


Figure 4 (a) The Fe-Ru diatomic schematic diagram, the ORR performance, and DFT calculation

results. Reproduced with permission from Ref. [130], © Elsevier Inc. 2024. (b) Configuration, DFT calculation results, and the ORR performance of Fe based catalysts with different symmetries. Reproduced with permission from Ref. [131], © Cao, Y. H. et al. *Angewandte Chemie, International Edition* published by Wiley-VCH GmbH 2025. (c) Synthesis schematic diagram of FeAl-RNC, AC-TEM images, and performance diagrams of PEMFCs. Reproduced with permission from Ref. [30], © American Chemical Society, 2024. (d) Schematic diagram, mechanism diagram, and the ORR performance of Fe-Cu bimetallic catalyst. Reproduced with permission from Ref. [132], © Wiley-VCH GmbH 2025. (e) Schematic diagram, DFT calculation results, and the ORR performance of Fe-Zn bimetallic catalyst. Reproduced with permission from Ref. [133], © Royal Society of Chemistry 2022.

With in-depth research on M-N-C catalysts, researchers have discovered that active sites composed of two metal atoms exhibit distinct catalytic properties compared to single-atom sites, particularly in terms of the synergistic effects between the two metal atoms (Table 3) [134, 135]. The interaction between two metal atoms influences their d-orbital electronic structures [30]. In some diatomic M-N-C catalysts, the presence of metal-metal bonds induces electron redistribution, thereby altering the oxidation states and electron cloud density of the active centers [136]. Additionally, electronic interactions (e.g., charge transfer) among multiple atoms can adjust the d-band center position to optimize the adsorption strength of intermediates [137].

4.2.1 Synthesis of dual-atom M-N-C catalysts

Generally, the challenge in synthesizing diatomic catalysts is achieving precise control over the interatomic distance between the two metal centers [138]. Many research groups attempt to control the distance by changing the dosage of metal precursors [139, 140]. However, excessive addition of

metal precursors often leads to the formation of metal nanoparticles rather than single-atom. Conversely, insufficient precursor dosage results in increased distances between metal atoms [138]. To achieve controllable synthesis of dual-atom catalysts, Sun et al. developed a selective etching and metal ion adsorption strategy [141]. First, the authors selectively etched specific carbon atoms in single-atom catalysts using hydrogen peroxide, generating defect sites near the original single-atom sites. These etched vacancies, characterized by low adsorption energy and strong interactions, enable precise anchoring of a second metal atom adjacent to the original single atom. Using this method, the authors constructed a series of dual-atom sites (e.g., Fe-Zn, Co-Fe, Co-Ni, and Co-Cu) with an interatomic distance controlled at 0.23 nm. Building on the concept of precise spatial control, Zhao et al. reported an alternative approach utilizing molecular bridging and vacancy generation [142]. In this approach, the Fe precursor was initially anchored onto a carbon support via electrostatic interactions. After high-temperature treatment, isolated single-atom sites were first formed. Subsequently, melamine was employed to bridge adjacent Fe single atoms, where the negative charges on N atoms interacted with the positive charges of Fe^{3+} ions. During the secondary high-temperature annealing process, the nitrogen precursor released NH_3 gas, which etched the carbon support to generate adjacent vacancies. These vacancies then captured the second Fe^{3+} ion, ultimately forming a well-defined Fe-N₂-Fe configuration. This methodology demonstrated broad applicability, enabling the synthesis of various M-N₂-M-type dual-atom catalysts (e.g., Co-N₂-Co).

4.2.2 Activity optimization of dual-atom M-N-C catalysts

4.2.2.1 Improvements in TOF

The introduction of a second atom into single-atom catalysts enhances the TOF via synergistic effects between the dual atoms [143, 144]. This TOF improvement stems from diatomic interactions

(e.g., strain effects and orbital hybridization effects) that modulate the adsorption strength of oxygen-containing intermediates and the cleavage energy barrier of O=O bonds [28]. Taking Fe-N-C as an example, Li et al. introduced Ru atoms to Fe-N₄ sites, forming Fe-Ru diatomic pairs (Figure 4(a)) [130]. The authors found that Ru atoms induce moderate tensile strain on Fe sites, leading to an increased Fe-N bond length. DFT and *in situ* FT-IR spectroscopy demonstrated that this strained environment causes a downshift of the Fe d-band center, promoting greater electron occupancy in antibonding orbitals. This weakens the Fe-*OH interaction and accelerates *OH desorption, ultimately enhancing the ORR kinetics. This work reveals that strain engineering can boost the TOF of dual-atom catalysts, but whether such strain effects extend to other metal elements still requires further validation in diverse catalysts.

The quasi-planar D_{4h} symmetry of Fe-N₄ coordination results in inadequate adsorption of oxygen-containing intermediates [145–147]. This planar symmetry prevents Fe-N₄ sites from meeting the optimal adsorption strength for intermediates required by the Sabatier principle, leading to limited ORR activity. Therefore, to regulate the adsorption-desorption of reaction intermediates, many research groups have attempted to break the planar symmetry of Fe-N₄ sites by introducing heteroatoms at adjacent positions, though achieving precise control remains challenging. Wang et al. synthesized an Fe-based catalyst with an asymmetric coordination structure (Fe-N₃-S-OH) [148], where the Fe atom is coordinated with three nitrogen atoms, one sulfur atom, and an axial hydroxyl group (-OH), forming a Fe-N₃-S-OH configuration. This asymmetric coordination breaks the symmetry of the conventional Fe-N₄ sites, consequently enhancing its TOF. Zheng et al. constructed various asymmetric Fe-based models (e.g., FeX₁N₃ and FeN₄-XC₂, where X = B, P, S, Se, or Te) through DFT calculations (Figure 4(b)). They revealed that the catalyst with Se doping in the second

coordination shell ($\text{FeN}_4\text{-SeC}_2$) possesses an optimal asymmetry degree, which was theoretically predicted to exhibit the highest ORR activity. Experimentally synthesized $\text{FeN}_4\text{-SeC}_2$ delivered a TOF value of $0.033 \text{ e}\cdot\text{site}^{-1}\cdot\text{s}^{-1}$ at 0.8 V vs. RHE which is 1.7 times higher than that of Fe-N_4 ($0.005 \text{ e}\cdot\text{site}^{-1}\cdot\text{s}^{-1}$). Their work demonstrates that leveraging DFT guidance to accelerate the development of catalysts with high TOF constitutes an efficient pathway, as it dramatically shortens the catalyst development timeline. Wang and Zheng's studies confirm that breaking the planar symmetry of Fe-N_4 sites enhances TOF. However, judging by TOF values, the improvement via asymmetry strategies remains limited. Precise engineering of the degree of active-site asymmetry constitutes a critical unresolved challenge.

Beyond enhancing activity by breaking the planar symmetry of M-N_x sites, introducing secondary metals for orbital hybridization offers another pathway for TOF improvement. In transition metal systems, incompletely filled d-orbitals and unpaired d/p electrons can induce d-d orbital hybridization and d-p orbital hybridization, respectively [149, 150]. Under the narrow energy levels and high electron density of states near the Fermi level, orbital hybridization optimizes the adsorption strength of reaction intermediates at active sites through antibonding orbital electron filling effects, thereby significantly boosting catalytic activity [151]. However, d-d orbital hybridization has limited capacity to modulate band gaps and electronic structures. Excessive d-d hybridization may lead to overly strong chemisorption of intermediates on the catalyst surface, causing active site passivation and hindering electron transfer pathways, which ultimately inhibits catalytic processes [152]. To address this, p-block and d-block elements can be introduced into M-N-C for orbital hybridization to regulate oxygen-containing intermediate adsorption. Wang et al. implemented a p-d orbital hybridization strategy by introducing Al atoms into Fe-N_4 sites (Figure

4(c)) [30]. The strong p-d hybridization between Al and Fe creates an asymmetric electron distribution with moderate adsorption strength for oxygen intermediates, enhancing the intrinsic ORR activity. The catalyst they prepared achieves a mass activity of $17.1 \text{ mA} \cdot \text{mg}^{-1}$ at 0.9 V in PEMFCs under $\text{H}_2\text{-O}_2$, outperforming conventional Fe-N-C catalysts ($10.3 \text{ mA} \cdot \text{mg}^{-1}$). Chen et al. also reported a d-p orbital hybridization strategy [143]. They embedded asymmetric Fe-Sn diatomic sites into a two-dimensional nanosheet. XAFS and HRTEM analyses confirmed a FeSn dimeric structure with an interatomic distance of 2.6 Å. This optimal distance enables interactions between Fe and Sn. Simultaneously, strong p-d hybridization between p-block Sn and d-block Fe triggers electron delocalization at Fe sites and reduces the energy barrier for *OH protonation, thereby improving the ORR activity. When applied in ZABs, this catalyst delivers a peak power density of $265.5 \text{ mW} \cdot \text{cm}^{-2}$, exceeding that of commercial Pt/C catalysts ($186.1 \text{ mW} \cdot \text{cm}^{-2}$). Wang and Chen's studies demonstrate the feasibility of enhancing TOF through d-p orbital hybridization strategies. However, p-d orbital hybridization is sensitive to the uniformity of metal precursor mixing, it imposes stringent requirements on catalyst preparation processes. Additionally, the impact of the interatomic distance between p-block and d-block elements on catalyst activity remains a problem requiring rigorous analysis.

One obvious objective of dual-atom catalysts is the potential ability to form dual-center adsorption sites. These dual-center sites enable O_2 to adsorb in a bridge model between the two metal atoms [153]. The dual-atom active centers synergistically cleave the O-O bond, simplifying the four-electron ORR pathway. Wang's group constructed an Fe-Ru-N₆ atomic configuration by introducing Ru atoms near Fe atoms [37]. *In situ* Raman and *in situ* FT-IR spectroscopy confirmed that this coordination structure allows two O atoms to adsorb on Fe and Ru active sites separately.

Importantly, the authors observed no formation of *OOH intermediates during the ORR process. They proposed that the catalyst follows a bridge adsorption model. Based on this model, the catalyst achieving a high power density of $1.152 \text{ W} \cdot \text{cm}^{-2}$ under $\text{H}_2\text{-O}_2$. Research by Wang demonstrated that dual-atom centers significantly enhance the activity via a bridging adsorption mechanism. However, this mechanism hinges critically on optimal interatomic distances. Current synthetic approaches remain challenged in precisely controlling interatomic distances, necessitating further development of controllable preparation methods for diatomic sites.

4.2.2.2 Increasing site density

Some researchers have found that introducing a second metal into M-N-C catalysts can enhance the density of active sites per unit area. On one hand, the introduced second metal can form additional active sites, effectively increasing the site density. On the other hand, the electronic interaction between distinct metals can modulate the electronic structure of the primary metal centers, rendering previously inactive atoms into active atoms [154]. Chi et al. incorporated Zr atoms into Fe-N-C to prepare Fe-Zr-N-C catalysts [36]. Compared to Fe-N-C, a new peak emerged at 397.4 eV in the N1s XPS spectra of Fe-Zr-N-C. The authors speculated that, in addition to traditional Fe-N_x sites, Zr-N_x active sites also exist in the Fe-Zr-N-C catalyst. This feature significantly increases the number of active sites. The authors used nitrite (NO_2^-) poisoning and electrochemical stripping methods to determine the number of active sites. While active sites for M-N-C catalysts are much more difficult to characterize than for Pt/C, the authors were able to make a reasonable estimate by comparing the CV charge before and after poisoning with NO_2^- . This method assumes that the NO_2^- will selectively bind to the M-N_x active sites, rendering them electrochemically inert. Through this study, it was determined that the Fe/Zr-N-C catalysts possessed a higher density of active sites ($46.48 \text{ C} \cdot \text{g}^{-1}$) vs.

the Fe-N-C catalysts ($21.55 \text{ C} \cdot \text{g}^{-1}$). This ratio ($46.48/21.55$) matches the metal ratio ($1.08 \text{ wt.}\%/0.55 \text{ wt.}\%$) between the two catalysts. This suggests atomically dispersed (or at least equally agglomerated) metals for both the single and dual element one. Notably, when applying the modified Butler-Volmer equation ($\eta_2 - \eta_1 = RT/(\alpha F) \times \ln(\text{Loading}_1/\text{Loading}_2)$) to calculate the overpotential difference, the experimental overpotential (-0.052) difference between Fe/Zr-N-C and Fe-N-C was found to be larger in magnitude than the theoretically predicted (-0.022) difference. This discrepancy indicates the presence of a synergistic effect between Zr and Fe—an interaction that enhances the TOF of the Fe active sites. In addition, Tan et al. prepared an Fe-Mn dual-atom catalyst [155]. The authors employed NO_2^- poisoning and electrochemical stripping methods to detect the active site density (SD). The results revealed SD values of $5.423 \times 10^{18} \text{ e} \cdot \text{sites} \cdot \text{g}^{-1}$ for Fe-N-C, $5.782 \times 10^{18} \text{ e} \cdot \text{sites} \cdot \text{g}^{-1}$ for Mn-N-C, and $9.169 \times 10^{18} \text{ e} \cdot \text{sites} \cdot \text{g}^{-1}$ for Fe-Mn-N-C. This enhancement was attributed by the authors to the synergistic effect of multiple catalytically active sites formed by Fe and Mn doping, which increased the active site density. Notably, comparing the SD values of these three catalysts shows that the SD value of Fe-Mn-N-C is nearly equivalent to the combined SD of (Fe-N-C + Mn-N-C). Based on the LSV curves measured by the authors, the half-wave potential of Mn-N-C (0.87 V in 0.1 M KOH at 900 rpm) is closely comparable to that of commercial Pt/C (0.88 V). Considering both the SD values and the half-wave potential, it is plausible that Mn-N_x sites can also catalyze the ORR.

4.2.3 Durability optimization of dual-atom M-N-C catalysts

The incorporation of a second atom into single-atom catalysts to construct dual-atom sites enables the formation of a more stabilized coordination environment, thereby enhancing the stability of the catalyst [156]. For this reason, two key advantages vs. single-atom catalysts emerge: i) compared

with single-atom catalysts, dual-atom catalysts feature metal-metal interactions that enhance the bond strength through electron transfer, thereby inhibiting metal leaching [157]; ii) these interactions facilitate the four-electron pathway in the ORR, minimizing hydrogen peroxide generation [158]. For example, Sun et al. introduced Mn atoms into Fe-N-C catalysts [159]. XAFS and HAADF-STEM confirmed the atomically dispersed Fe-Mn-N₆ active sites. Mn atom reduced H₂O₂ production and showed low reactivity in Fenton reactions, thereby minimizing Fe²⁺ oxidation and carbon support corrosion. This catalyst successfully enhanced the stability in PEMFCs, a result that retained 84.3% of its initial current density after a 25 h durability test at 0.6 V under H₂-O₂. Yang et al. reported a Fe-Cu dual-atom catalyst, where the Fe site facilitates efficient the 4-electron ORR, while the adjacent Cu site reduces the reaction byproduct H₂O₂ into H₂O via a 2-electron pathway (Figure 4(d)) [132]. This catalyst not only minimized the generation of free radicals but also suppressed Fenton-induced carbon corrosion and metal site leaching, thereby enhancing the durability of the catalyst. The catalyst only decays by 12 mV after 10,000 cycles between 0.6 and 1.0 V in 0.1 M HClO₄ under O₂-saturated condition. The authors conducted testing under O₂-saturated conditions, which is highly valuable. When assessing the stability of non-precious metal catalysts, it is crucial to pay attention to the test conditions: Pt-based catalysts can be examined in N₂ atmosphere using potential cycling between 0.6–1.0 V to evaluate their dissolution mechanism which is accelerated each time the Pt cycles between and oxidized/reduced state in situ analysis of scan rate effects on Pt dissolution under potential cycling using a channel flow double electrode [160], b) platinum electro-dissolution in acidic media upon potential cycling). Since the formation of PtO is dependent on the availability of water and not O₂ ($\text{Pt} + \text{H}_2\text{O} \rightarrow \text{PtOH} + \text{H}^+ + \text{e}^-$; $\text{PtOH} \rightarrow \text{PtO}_2 + \text{H}^+ + \text{e}^-$), this mechanism is relatively independent of the gas environment. In contrast, evaluating

non-precious metal catalysts must strictly be performed in an O_2 -saturated conditions, as their degradation is predominantly caused by H_2O_2 , a byproduct of the ORR. Under N_2 atmosphere, no Faradaic reaction (and thus H_2O_2 generation) can occur. Consequently, assessing non-precious metal catalysts under an inert N_2 atmosphere will severely underestimate their true degradation rate, and for these catalysts, potentiostatic testing under an O_2 purged environment at fuel cell relevant potentials (~ 0.6 – 0.8 V) is a more valuable stress test. Wang's group designed a Fe-Zn dual-atom catalyst, in which the Zn-N bonds serve as sacrificial bonds that preferentially break during the reaction, thereby protecting the FeN_4 active centers and enhancing structural stability (Figure 4(e)) [133]. After 5000 cycles of cyclic voltammetry testing between 0.25 and 1.0 V in a 0.1M $HClO_4$ electrolyte saturated with O_2 , the catalyst exhibited a minimal half-wave potential loss of 12 mV, demonstrating significantly enhanced durability compared to Fe-N-C catalyst (loss 28 mV). The studies by the teams of Sun, Yang, and Wang provide strategies for enhancing stability in dual-atom catalysts by suppressing Fenton reactions and scavenging free radicals, demonstrating the advantage of dual-atom catalysts in boosting catalytic stability.

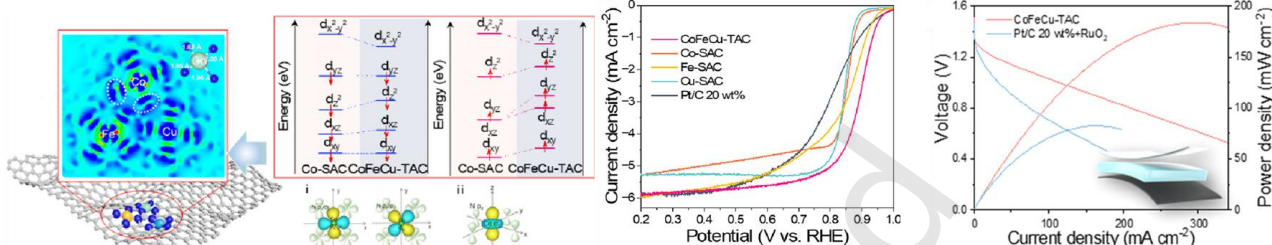
Table 3 The performance of dual atom catalysts in RDE under O₂-saturated over the past 5 years

Catalysts	Performance ($E_{1/2}$)	Durability	Refs.
D-FeCo-Das-N-C	0.927 V, 0.1 M KOH, 1600rpm	loss 5.8% current density after 100 h	[161]
Fe ₁ Se ₁ -NC	0.88 V, 0.1 M KOH, 1600rpm	loss 13 mV after 5k cycles	[162]
FePc Nanorods	0.91 V, 0.1 M KOH, 1600rpm	loss 20 mV after 5k cycles	[163]
ZnCuN ₆ /C	0.89 V, 0.1 M KOH, 1600rpm	loss 36 mV after 5k cycles	[164]
FeMn-N-C	0.92 V, 0.1 M KOH, 900rpm	loss 9 mV after 30k cycles	[165]
FeSn-C ₂ N	0.914 V, 0.1 M KOH, 1600rpm	loss 13 mV after 10k cycles	[143]
FeCo-NC-3	0.86 V, 0.1 M KOH, 900rpm	loss 9 mV after 10k cycles	[166]
FeAl-RNC	0.83 V, 0.5 M H ₂ SO ₄ , 1600rpm	loss 16 mV after 10k cycles	[30]
(Au-Co)DO-NPs	0.82 V, 0.1 M HClO ₄ , 900rpm	loss 15 mV after 30k cycles	[167]
FeRu-N-C	0.86 V, 0.1 M HClO ₄ , 900rpm	loss 17 mV after 50k cycles	[130]
Cu, Fe/N-C	0.757 V, 0.1 M HClO ₄ , 900rpm	loss 15 mV after 5k cycles	[168]
Co-Se-N-C-2	0.764 V, 0.5 M H ₂ SO ₄ , 900rpm	loss 5% current density after 15,000 s	[169]
CoMn/NC	0.82 V, 0.5 M H ₂ SO ₄ , 900rpm	loss 3.1% current density after 86,400 s	[170]
Mn-Fe/p-DC-900	0.8 V, 0.5 M H ₂ SO ₄ , 900rpm	loss 20 mV after 5k cycles	[171]

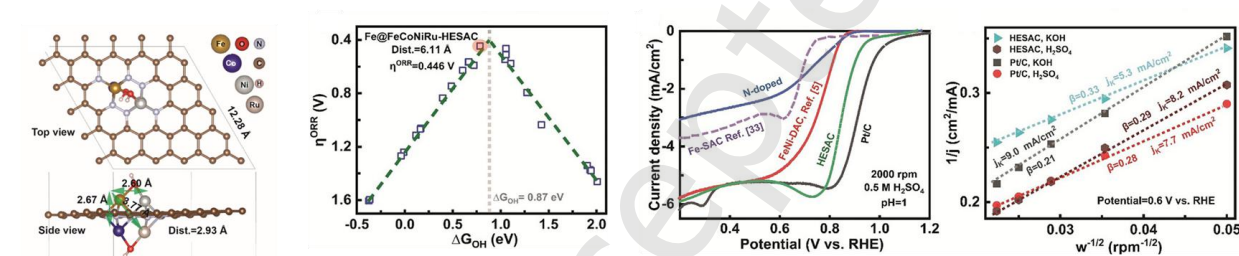
4.3 Engineering of multi-atom active site

Engineering of Multi-Atom Active Sites

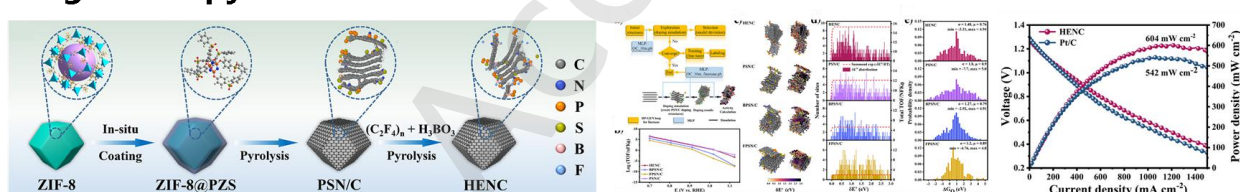
a. Triatomic active site



b. Four-atom active site

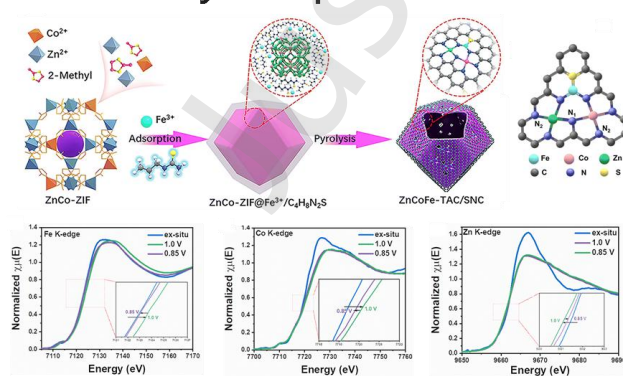


c. High-entropy atom active site



Elucidating the role of each-atom

d. In situ X-ray Absorption Fine Structure



e. In situ Raman spectroscopy

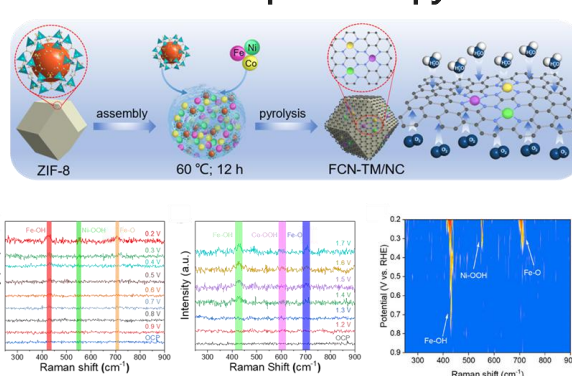


Figure 5 (a) DFT calculation results, the ORR performance, and power density of FrCoCu triatomic catalyst for zinc air battery. Reproduced with permission from Ref. [172], © American Chemical Society 2023. (b) DFT calculation results and the ORR performance of FeCoNiRu four-atom catalyst.

Reproduced with permission from Ref. [173], © Tamtaji, M. et al. *Advanced Science* published by Wiley-VCH GmbH 2024. (c) Synthesis schematic diagram, performance diagrams, and DFT results of the FBSP-NC catalyst. Reproduced with permission from Ref. [174], © Wiley-VCH GmbH 2025. (d) Synthesis schematic diagram of the ZnFeCo triatomic catalyst and *in situ* XAFS diagrams. Reproduced with permission. Reproduced with permission from Ref. [175], © Royal Society of Chemistry 2024. (e) Schematic diagram of FeCoNi triatomic catalyst and operando Raman spectroscopy diagrams. Reproduced with permission from Ref. [176], © Wiley-VCH GmbH 2025.

Beyond dual-atom catalysts, some research groups have introduced three or more metal atoms into M-N-C catalysts to further optimize the electronic structures of active sites [172]. Multi-atom configurations can create abundant coordination microenvironments (e.g., linear, triangular) [175, 176]. These atomic configurations alter the electronic distribution of active centers through geometric effects, enabling precise regulation of the adsorption/desorption behaviors of the ORR intermediates [177]. Additionally, diverse metal atoms can cooperatively accelerate the O₂ to H₂O reduction process, enhance proton transfer, and promote O-O bond cleavage, thereby boosting the ORR reaction efficiency [178].

4.3.1 Synthesis of multi-atom M-N-C catalysts

Synthesis of multi-atomic catalysts is highly challenging in the ORR. To date, numerous methods have been developed for the precise synthesis of single-atom and dual atom M-N-C catalysts. However, strategies for the precise synthesis of M-N-C catalysts incorporating three or more metal atoms remain scarce. This is primarily attributed to: i) With increasing number of metal atoms, the interatomic interactions (e.g., metal-metal bonding) intensify, leading to a sharp increase in surface free energy. During high-temperature synthesis, this facilitates facile migration and agglomeration of

atoms into particles or clusters. ii) Compared to single-atom and diatomic M-N-C catalysts, it is difficult to simultaneously coordinate three or more metal atoms in a homogeneous configuration with uniformity. To address the challenge of synthesizing catalysts with multiple, highly dispersed metal atoms, Tian et al. reported a novel “moveable-type printing” strategy [179]. The authors designed metal-specific templates, then transferred metal atoms from these templates to a carbon support, enabling the fabrication of highly dispersed multi-atom catalysts. Based on this strategy, they successfully demonstrated the synthesis of high-entropy single-atom catalysts incorporating 11 distinct metallic elements.

4.3.2 Multi-atom M-N-C catalysts

The stable and high ORR performance of multi-atomic catalysts should be attributed to abundant active sites and the synergistic interplay between diverse active sites. For example, Zeng et al. reported a triatomic catalyst comprising Co, Fe, and Cu atoms (Figure 5(a)) [172]. The incorporation of Fe and Cu atoms disrupted the local symmetry of the CoN₄ configuration, inducing variations in Co-N bond lengths. Bader charge analysis revealed an enhanced electron density at the Co active sites, which promoted O₂ activation. When integrated as a cathode in ZABs, this catalyst achieved a peak power density of 208 mW·cm⁻² higher than the Pt/C (90 mW·cm⁻²). It should be noted that the authors' Pt/C benchmark underperformed the standard benchmark (150 mW·cm⁻²) [180], but even taking this benchmark value, it does appear the authors were successful in improving the overall performance. Zhu et al. developed a catalyst incorporating four metal atoms (Fe, Co, Ni, Ru) through the integration of DFT and machine learning (Figure 5(b)) [173]. The synergistic effects between the Fe sites and Co, Ni, and Ru effectively weaken the adsorption of *OH intermediates, thereby accelerating the ORR kinetics. The aforementioned studies demonstrate the catalytic efficacy of

varying atomic configurations on the ORR. Multi-atomic catalysts create diverse coordination structures that synergistically accelerate the rate-determining steps of the ORR. Considering the multi-step proton transfer process of the ORR, some groups have employed high-entropy atomic systems. These systems introduce five or more elements into M-N-C catalysts. The multi-element synergistic effects simultaneously tune O₂ adsorption strength, accelerate proton transfer and optimize intermediate desorption, thereby alleviating rate-limiting caused by single-site constraints [181, 182]. Wen et al. constructed a high-entropy single-atom catalyst with five elements (B, F, P, S, N) (Figure 5(c)) [174]. N, P, and S served as primary active sites to regulate the carbon support's electronic structure and promote *O₂ intermediate formation. B and F enhanced structural stability and suppressed P-induced carbon layer exfoliation. Zheng et al. reported a catalyst composed of Fe, Mn, Co, Ni, and Cu [183]. The high-entropy metal configuration disrupts the π -electron symmetry of the carbon support, thereby accelerating the ORR.

4.3.3 Elucidating the role of each-atom

While multi-atom active sites integrate the mass transfer properties of multiple metals and change intermediate adsorption/desorption, incorporating multiple atoms inevitably complicates the catalytic system. The individual catalytic roles of each metal center in the ORR remain ambiguous [184]. Clarifying these roles is critical. Therefore, it is necessary to employ state-of-the-art instruments to determine the catalytic role of individual atoms. The structure of a catalyst in its non-working state often differs from its structure under actual catalytic reaction conditions. *In situ* XAFS is capable of directly probing the valence state and coordination environment of the active sites that catalyze the ORR at different potentials. Li et al. employed *in situ* XAFS techniques to elucidate the mechanistic role of ZnCoFe triatomic metal catalyst (Figure 5(d)) [175]. The *in situ* XAFS analysis revealed that

the absorption edge of Co shifted toward lower energy as the potential decreased, while Fe exhibited a similar trend in absorption edge shift but with a smaller magnitude, indicating that Co served as the primary catalytic site and Fe acted as a secondary catalytic site. For Zn atom, the absorption edge shifted toward lower energy at 1.0 V, suggesting a decrease in its oxidation state. When the potential was adjusted to 0.85 V, the oxidation state of Zn returned to a higher level. This observation demonstrates that Zn functions as an electron modulator, optimizing the electronic states of Co and Fe through electron transfer during the catalytic process. *In situ* Raman spectroscopy enables the real-time detection of key reaction intermediates adsorbed on the catalyst surface under working conditions; this represents its most critical role in ORR research. Analyzing changes in the intensity and position of characteristic Raman peaks provides insights into the coverage of adsorbed intermediates and the nature of the primary active sites on the catalyst. Liu et al. employed *in situ* Raman spectroscopy and *in situ* XAFS to probe the roles of each atom [176]. They synthesized a FeCoNi single-atom catalyst (Figure 5(e)). *In situ* Raman spectroscopy showed increasing signals at 433 cm^{-1} (Fe-OH) and 700 cm^{-1} (Fe-O) as the potential decreased, confirming Fe's dominance in oxygen intermediate adsorption. The absence of Co/Ni-related peaks suggested their roles as co-catalytic sites. *In situ* XAFS further demonstrated Fe's reduced oxidation state (absorption edge shift to lower energies) as the potential dropped from 0.8 to 0.6 V, proving that Fe acts as the main active site participating in the ORR. The aforementioned studies demonstrate the feasibility of employing *in situ* XAFS and Raman techniques to pinpoint catalytic mechanisms at atomic sites. Future research should focus on integrating these approaches with DFT to elucidate the interaction mechanisms within multi-atomic catalysts. Aberration-corrected scanning transmission electron microscopy (AC-STEM) is widely employed to characterize atomically dispersed catalysts. However,

it's crucial to recognize that AC-STEM exhibits inherent limitations in resolving structures of multi-atomic catalysts, primarily due to its imaging mechanism and intrinsic atomic characteristics of the catalysts. When multiple atoms adopt asymmetric configurations (e.g., triangular geometry), they are prone to misinterpretation as nanoclusters in AC-TEM images. Furthermore, AC-TEM struggles to distinguish atoms with similar atomic masses (e.g., Fe vs. Co) via contrast intensity. Collectively, these factors constrain the structural identification of multi-atomic catalysts using AC-TEM.

4.4 Synergistic engineering of cluster and single-atom

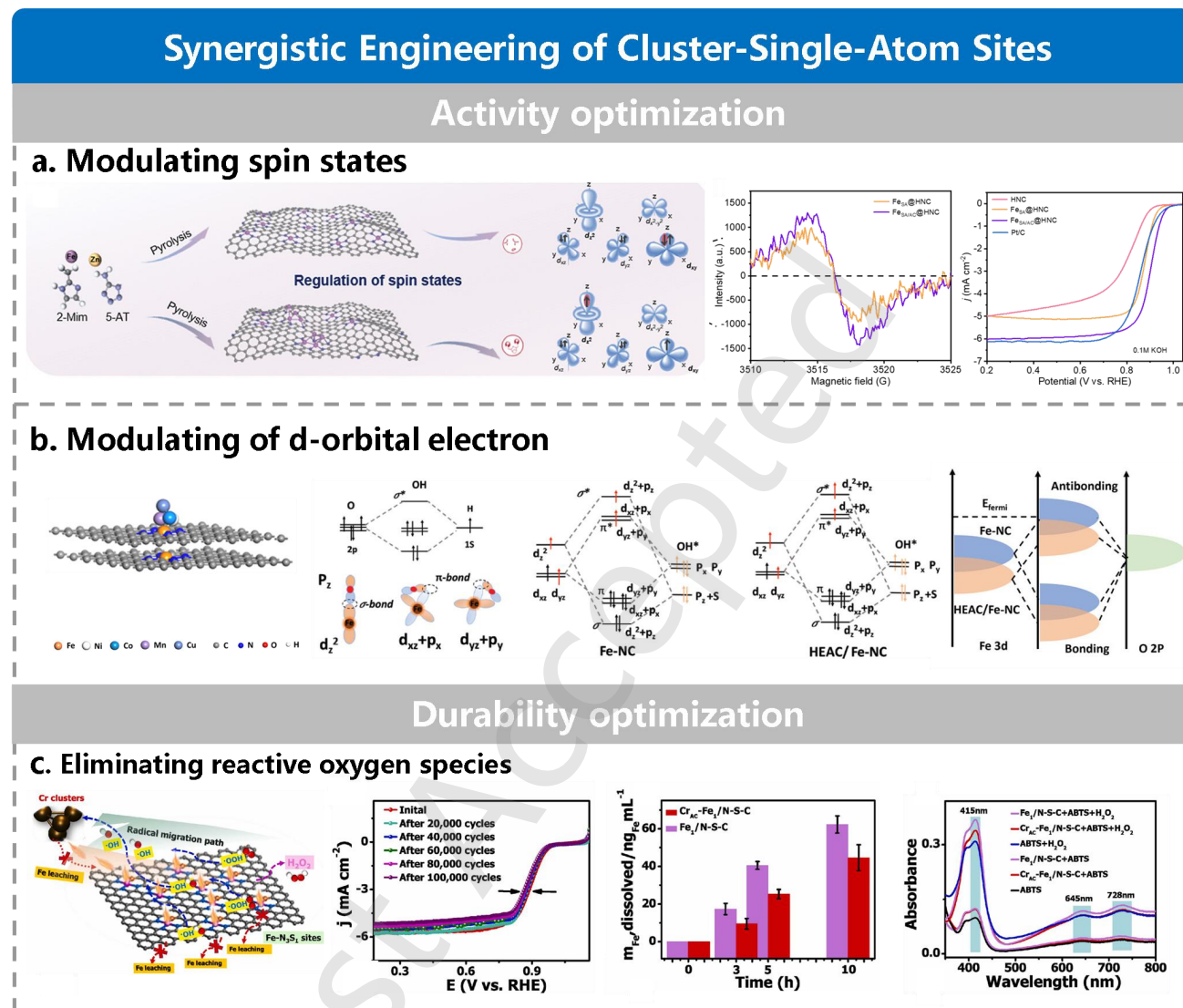


Figure 6 (a) Synthesis schematic diagram, electron paramagnetic resonance, and ORR performance diagrams of $\text{Fe}_{\text{SA}}/\text{AC}@\text{HNC}$. Reproduced with permission from Ref. [185], © Wiley-VCH GmbH 2024. (b) Schematic diagram of d-orbital electron modulation in Fe-N_4 by high-entropy clusters and *in situ* Raman spectroscopy analysis. Reproduced with permission from Ref. [186], © Wiley-VCH GmbH 2024. (c) synthesis schematic diagram, UV-vis spectra, Fenton-like reactivity test diagrams, and performance diagrams of $\text{Cr}_{\text{AC}}\text{-Fe}_{\text{SA}}/\text{N-S-C}$. Reproduced with permission from Ref. [187], © Elsevier B.V. 2023.

4.4.1 Synthesis of cluster-single-atom M-N-C catalysts

The controllable synthesis of clusters is important. Cluster formation depends on temperature and metal precursor concentration [188]. Temperature critically influences cluster structure: as temperature rises, increased atomic thermal motion induces internal vibrations, leading to clusters structural rearrangement or decomposition [189]. Studies show that higher synthesis temperatures promote small clusters merging into larger ones [190]. Metal loading is another key factor, as excessive precursors favor nanoparticle formation. Insufficient loading, however, yields sparse atoms that are unsuitable for forming clusters [191]. To address these problems, Xia group developed a chelation strategy for synthesizing Fe single-atom/cluster catalysts [192]. By chelating tannic acid with Fe^{3+} to form a hydrogel, they controlled active site types (single atoms, clusters, nanoparticles) via tannic acid dosage adjustments. With increasing tannic acid content, Fe atoms are more readily dispersed and stabilized as single atoms. In contrast, lower tannic acid ratios result in insufficient chelation of Fe precursors, leading to aggregation during pyrolysis and the formation of larger Fe nanoparticles. When tannic acid is present at a moderate ratio, it forms clusters approximately 2 nm in size. Xu et al. developed a controllable synthesis of Cu clusters via underpotential deposition on a sulfur-nitrogen co-doped support [193]. By tailoring the deposition potential and duration, the authors enabled preferential nucleation of Cu at sulfur sites, followed by the growth of small-sized clusters (~1 nm).

4.4.2 Activity optimization of cluster-single-atom M-N-C catalysts

4.4.2.1 Improvements in TOF

4.4.2.1.1 Modulating spin states

Clusters are aggregates composed of several atoms.[188] Their sizes lie between individual atoms

and macroscopic crystals. Unlike the isolated metal sites in single-atom catalysts, the multi-metallic coordination environment in clusters enhances the TOF through metal-metal synergistic effect [194]. This synergistic effect stems from electronic coupling between adjacent metal sites, which optimizes the adsorption energy barriers of key intermediates (*OOH/*O species) [195]. The clusters can modulate the electronic density of adjacent single atoms through interfacial charge transfer, thereby optimizing the spin state of the M-N-C metal centers to enhance catalytic activity [196]. The Wang group reported a Fe-N₄ catalyst integrated with Fe atomic clusters (Figure 6(a)) [185]. By introducing Fe clusters adjacent to the Fe-N₄ sites, the spin state of Fe-N₄ was modulated from low-spin to high-spin configuration, effectively weakening *OH adsorption and improving the TOF. Guo et al. reported a catalyst composed of Fe single atoms and Pd clusters [197]. The electronic interaction between the Pd clusters and the Fe single atoms induced a transition in the spin state of Fe from low-spin to intermediate-spin. This transition facilitated a shift in the ORR pathway from the associative to the dissociative mechanism, thereby improving the TOF. While the works by Wang and Guo demonstrate that cluster-single atom interactions can modulate spin states to enhance the TOF, it must be noted that spin states vary dynamically variation under electrochemical operating conditions, with different spin configurations exhibiting differential contributions to activity. Consequently, future studies necessitate operando characterization techniques to resolve the real-time impact of spin states on ORR performance.

4.4.2.1.2 Modulating of d-orbital electron

The introduction of atomic clusters into single-atom catalysts can modulate the d-orbital electronic structure of the single-atom active centers through synergistic effects, thus improving the TOF. For example, Zheng et al. fabricated a catalyst composed of Te clusters and Fe atoms [198]. They

discovered that when the Te clusters contain two or more atoms, the 5p orbitals of the Te clusters couple with the 3d orbitals of Fe, modulating the electronic states of Fe's d-orbitals. This interaction reduces the overly strong adsorption of Fe on intermediate species, thereby improving the TOF. The authors achieve d-orbital electron modulation of Fe single atoms through Te clusters. However, under acidic conditions, the Te species can be oxidized to H_2TeO_3 , resulting in catalyst degradation. As expected, when the authors employed this catalyst in the cathode of a ZAB, it operated for only 20 hours at a current density of $20 \text{ mA} \cdot \text{cm}^{-2}$. Yang et al. integrated Fe single atoms with FeCoNiCuMn high-entropy atomic clusters (Figure 6(b)) [186]. The introduction of atomic clusters induced rehybridization of the Fe 3d orbitals, which led to increased electron occupancy in antibonding states during OH^* adsorption. This electronic modulation weakened the Fe- OH^* bonding strength, thereby facilitating OH^* desorption and accelerating the rate-determining step of the ORR. Similarly, Tamtagi et al. developed a high-entropy cluster (Co, Ni, Cu, Rh) on N-doped graphene with Fe- N_4 sites [199]. DFT calculations suggested Fe- N_4 as active sites, while the CoNiCuRh cluster acted as an electronic modulator via intermetallic interactions, thereby enhancing the catalyst's TOF. The studies by both Yang and Tamtagi introduce high-entropy atomic clusters into single-atom systems, collectively demonstrating the strong capability of high-entropy materials in modulating d-orbital electrons.

4.4.3 Durability optimization of cluster-single-atom M-N-C catalysts

4.4.3.1 Eliminating reactive oxygen species

Fe-N-C catalysts exhibit significant activity decay during 5000–30,000 CV cycles under O_2 -saturated conditions [200]. This degradation likely stems from ROS generated via the 2-electron ORR pathway, which attack the Fe active centers and induce Fe leaching [201]. Consequently, suppressing ROS

generation becomes imperative to preserve catalytic stability. Some metal clusters can also eliminate ROS generated during the ORR via strong atom-cluster bonding, preventing active site degradation. Guo et al. incorporated Cr clusters near Fe-N₄ sites (Figure 6(c)) [187]. Fenton-like reactivity tests demonstrated that Cr clusters scavenged *in situ*-generated ROS and delayed Fe ion leaching. After 100,000 CV cycles between 0.6 and 1.0 V in 0.1 M KOH under O₂-saturated conditions, the activity loss was negligible. Guo's team developed an effective strategy to enhance catalyst stability. The Cr clusters effectively scavenge reactive oxygen species generated during electrochemical processes, directly mitigating oxidative attack on iron active centers and inhibiting Fe leaching, thereby providing a viable pathway for developing durable ORR catalysts.

4.5 Synergistic engineering of particles-single-atom sites

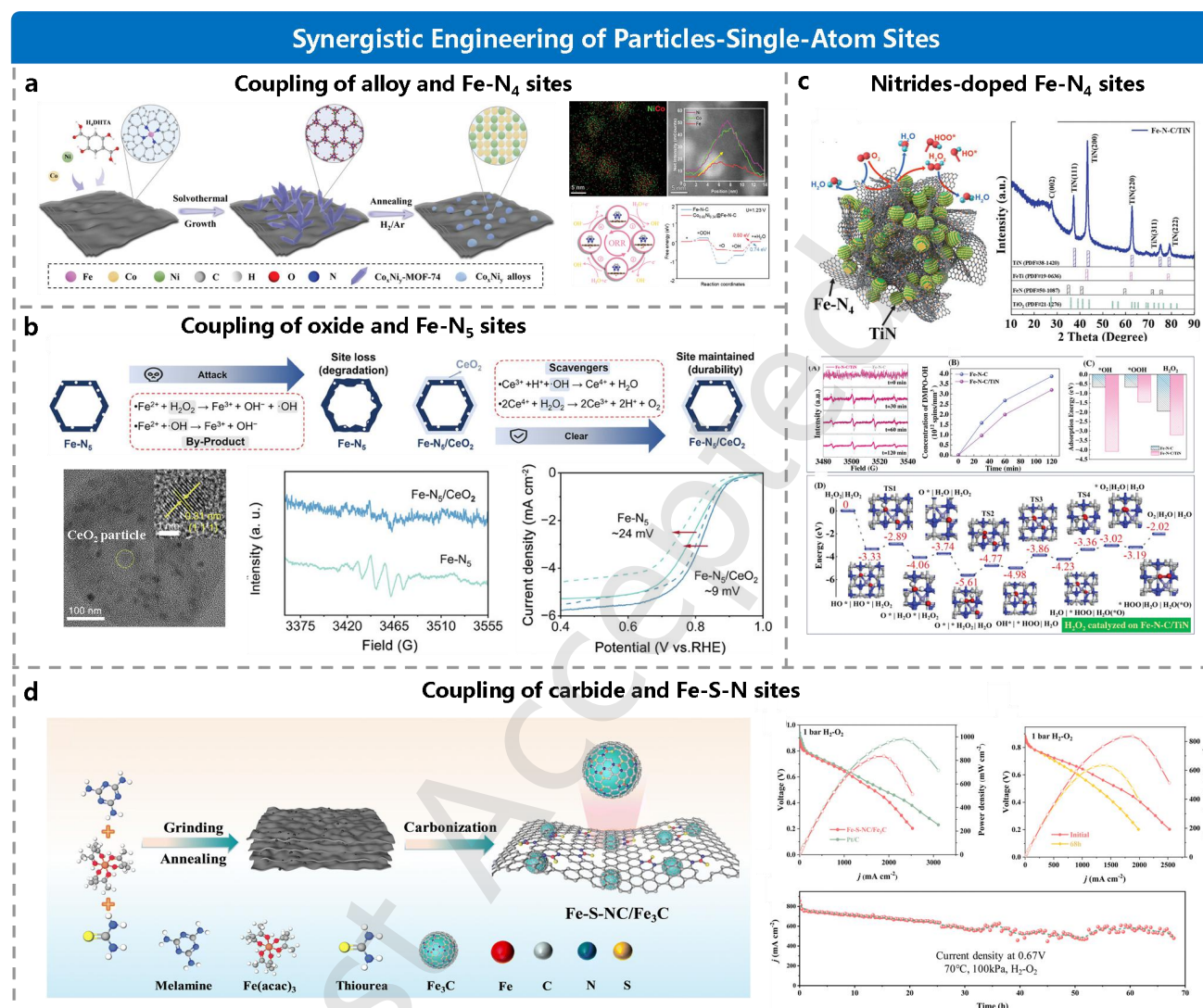


Figure 7 (a) Schematic diagrams, electron microscopy images, and DFT free energy barrier diagrams of the CoNi alloy-composite Fe-N-C catalyst. Reproduced with permission from Ref. [202], © Wiley-VCH GmbH 2024. (b) Schematic diagrams, electron microscopy images, electron spin resonance (ESR) spectra, and durability test results of the CeO₂-composite Fe-N₅ catalyst. Reproduced with permission from Ref. [203], © Wiley-VCH GmbH 2025. (c) Schematic diagrams, XRD patterns, and DFT-calculated adsorption energy profiles of free radicals on the surface of the TiN/Fe-N-C composite catalyst. Reproduced with permission from Ref. [204], © Wiley-VCH GmbH

2024. (d) Schematic diagrams and MEA performance of the Fe-S-NC/Fe₃C catalyst. Reproduced with permission from Ref. [32], © the Royal Society of Chemistry 2024.

Particles (e.g., alloys, intermetallic compounds, metal oxides and sulfides) exhibit excellent performance compared to single/dual-atom catalysts under specific conditions, owing to their tailored electronic structures and geometric configurations [205–207]. These materials regulate the adsorption behavior of oxygen intermediates at active sites through their lattice configuration and interface engineering.[208] Additionally, particles can be synthesized via solution-based or low-temperature pyrolysis methods, which are relatively simple processes.

4.5.1 Synthesis of particle-single-atom M-N-C catalysts

In the field of ORR catalysis, the most widely utilized particles include alloys, carbides, nitrides, and oxides. The general approach to synthesizing alloy-single-atom composite structures involves first anchoring single atoms on a carbon support, followed by mixing two or more metal precursors on the single-atom-loaded support, and finally reducing the precursors at elevated temperatures to form an alloy [202]. Critical considerations during alloy synthesis include controlling the pyrolysis temperature, as excessively high temperatures may lead to oversized alloy particles, which reduce the electrochemically active surface area. Some research groups also employ liquid-phase reduction for alloy synthesis, where two or more metal precursors are reduced by agents such as NaBH₄ and ascorbic acid to form alloy [209]. For carbide catalyst synthesis, high-temperature reactions are typically employed to combine metal precursors with carbon sources, forming stable metal-carbon bonds [32]. Common methods include carbothermal reduction, chemical vapor deposition, and sol-gel processes. Key factors involve precise control of temperature and the carbon-to-metal ratio, as insufficient temperatures may leave residual oxide impurities, while excessive temperatures risk

particle sintering. In contrast, synthesizing nitrides requires introducing additional nitrogen sources (e.g., an ammonia atmosphere) during precursor pyrolysis. The ammonia-pyrolysis method, which involves high-temperature treatment under ammonia flow to form stable metal-nitrogen bonds, is widely adopted. Current challenges lie in achieving nitride products with high purity and uniform composition [208]. Oxide synthesis is relatively straightforward, as oxygen-containing species (e.g., water molecules, oxygen functional groups in precursors, or trace oxygen in calcination atmospheres) inherently present during catalyst preparation can oxidize metal precursors [210]. By adjusting precursor concentrations and calcination atmospheres, oxides can be synthesized.

4.5.2 Coupling alloys and single-atom

Among various particles, alloys have attracted significant attention [211]. Alloys are solid solutions formed by two or more metallic elements through melting or chemical synthesis, where atoms randomly occupy lattice sites, resulting in disordered structures [212]. Coupling alloys with M-N-C can modulate the d-band center of single-atom active sites via electronic synergy and geometric effects between different metals [213], thus optimizing intermediate adsorption strength [214]. Yang et al. loaded high-electronegativity Co/Ni alloys onto Fe-N-C carbon supports (Figure 7(a)) [202]. The Co/Ni alloys connected to Fe via Co/Ni-N bonds. The authors found that electron transfer occurs from the Co/Ni alloy to Fe-N-C due to their electronegativity difference. Similarly, Zhong et al. loaded Fe/Co alloys onto carbon supports containing abundant Fe and Co single atoms [209]. The hybridization between the d-orbitals of Fe/Co in single atoms/alloys and the p-orbitals of N/C atoms accelerated $^*OH$ desorption. A notable feature of this work was the encapsulation of Fe/Co alloys within carbon layers containing metal sites. The carbon coating acted as a protective barrier against metal leaching, while the electronic interaction between single atoms and alloys enhanced charge

transport. The porous carbon structure further facilitated reactant diffusion, improving electrocatalytic efficiency.

4.5.3 Coupling compounds and single-atom

Metal oxides (e.g., Co_3O_4 , MnO_2), carbide (e.g., Fe_3C , WC), and nitrides (e.g., MnN , CoN) are also promising the ORR-active compounds. Some groups have integrated these materials into M-N-C catalysts. Surface O, S, or N vacancies in these compounds disrupt lattice periodicity, providing additional anchoring sites for single atoms [215]. Single-atom-particle synergy further enhances the ORR performance. Yang et al. in situ grew CeO_2 nanoparticles on hollow-structured Fe-N₅ sites (Figure 7(b)) [203]. The Fe-N₅ sites adopted a unique five-coordinated configuration via axial bonding with the fifth N atom. This structure shifted the spin state of Fe from high to low, optimizing oxygen intermediate adsorption and reducing reaction barriers. ESR spectroscopy revealed that CeO_2 decomposed harmful H_2O_2 and quenched $\cdot\text{OH}$ radicals through $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox cycling, mitigating Fe-N₅ site corrosion. Feng et al. synthesized TiN-doped Fe-N-C via a sol-gel method (Figure 7(c)) [204]. The interconnected Fe-N-C/TiN network scavenged reactive radicals while maintaining a high ORR activity. The H_2O_2 yield of Fe-N-C/TiN was suppressed below 4%, four-fold lower than Fe-N-C. After 30,000 CV cycles between 0.6 and 1.0 V in 0.1 M HClO_4 under O_2 -saturated conditions, the half-wave potential decayed by 15 mV. Dang et al. have synthesized a composite catalyst of Fe-S-N-C carbon layers and ultrasmall Fe_3C nanoparticles via in situ S-doping (Figure 7(d)) [32]. This structure features an Fe_3C core tightly encapsulated by an Fe-S-N-C carbon shell. The curved carbon layers significantly increased the exposure density of Fe-S-N-C active sites by enlarging the specific surface area and surface curvature. Strong electronic interactions between Fe and S atoms anchored the Fe_3C , enabling operation at 0.67 V for 68 h. However, the current density

decreased by over 40%, highlighting opportunities to improve the catalyst's durability for commercial applications [30, 102].

In summary, introducing particles into M-N-C catalysts can enhance the ORR performance via particle-single-atom synergistic effects. These particles optimize the electronic structure of single-atom sites to regulate intermediate adsorption and create heterointerfaces to improve activity.

4.6 Support engineering

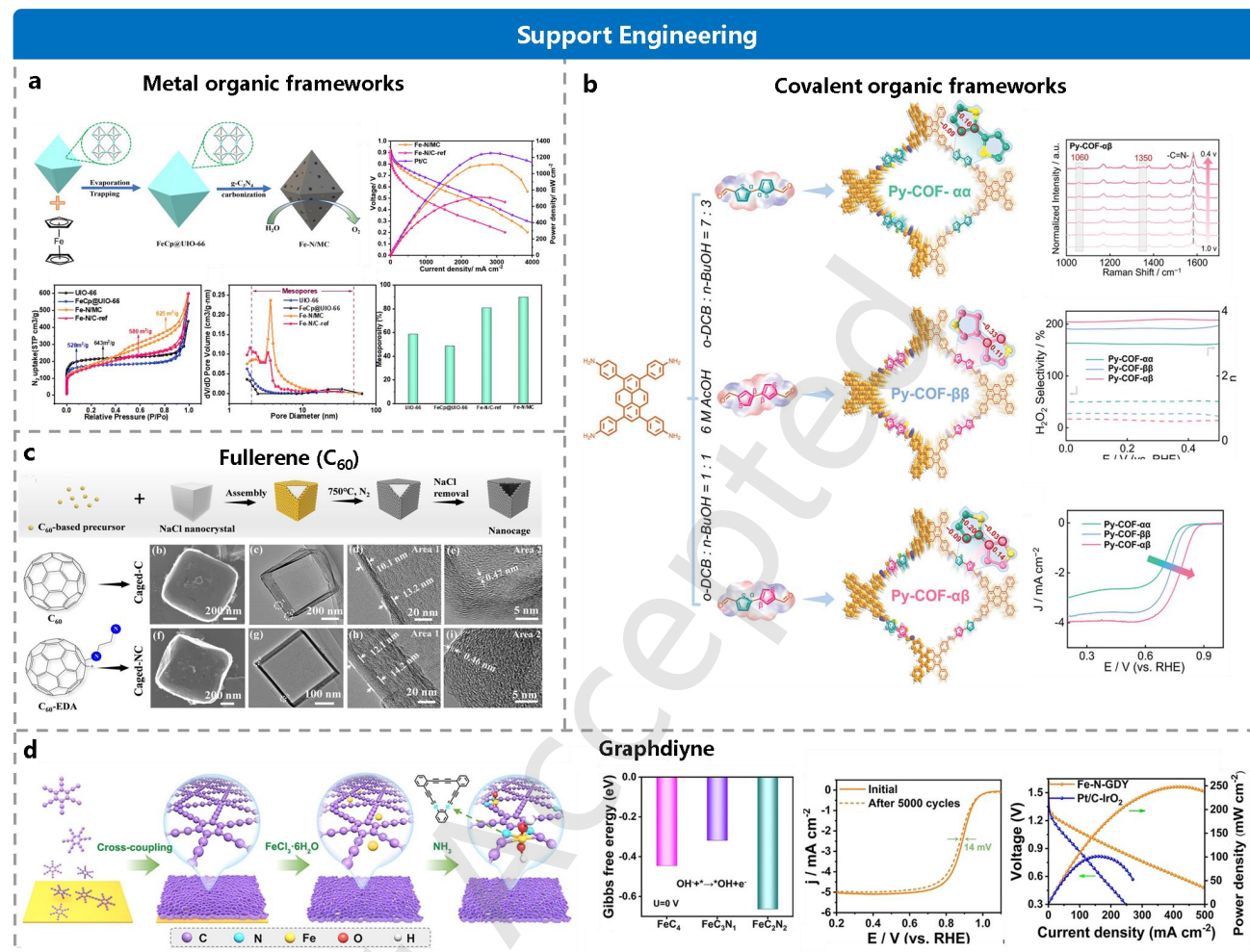


Figure 8 (a) Schematic diagram and BET and PEMFC performance of Fe-N-C catalyst derived from UIO-66. Reproduced with permission from Ref. [79], © the Royal Society of Chemistry 2023. (b) The Raman spectra, and the ORR performance plots of COFs with different bithiophene substitution positions. Reproduced with permission from Ref. [216], © Wiley-VCH GmbH 2025. (c) Schematic illustration of a cage-like cubic carbon catalyst rich in pentagonal structures. Reproduced with permission from Ref. [217], © Wiley-VCH GmbH 2024. (d) DFT calculation, RDE durability and PEMFCs performance of the Fe-N-C catalyst loaded on Graphdiyne support. Reproduced with permission from Ref. [218], © Wiley-VCH GmbH 2022.

The support not only serves as a physical anchoring platform for metal but also participates in

catalytic processes through electron conduction and chemical bonding [219]. It is feasible to optimize the spatial distribution of active sites and mass transfer kinetics through precise design of the properties of M-N-C supports. An ideal support should possess the following characteristics: i) dispersing and stabilizing metal sites. The support suppresses metal agglomeration during electrochemical processes via spatial constraints [220]. ii) high specific surface area. This enhances triple-phase interface mass transfer efficiency and provides reaction channel for O₂ [221]. Additionally, support with high specific surface area can more effectively anchor metal atoms, forming active centers [222]. iii) support-metal synergistic effects. The support can modulate the electronic structure of metal active centers through the support-metal synergistic effect, thereby enhancing the ORR kinetics [223]. As early as 2009, Gong et al. discovered that nitrogen-doped carbon nanotube supports act as effective metal-free ORR catalysts [224]. Subsequently, researchers have conducted in-depth explorations of M-N-C supports.

4.6.1 Metal organic frameworks

Metal organic frameworks (MOFs) are porous materials formed by coordination bonds between metal ions and organic ligands [225]. MOFs can be categorized into various types such as zeolitic imidazolate frameworks (ZIFs), materials of institute Lavoisier (MILs), porous coordination networks (PCNs), and isoreticular metal organic frameworks (IRMOFs). In the field of the ORR catalysts, MOFs have been extensively utilized due to their ultrahigh surface area and highly tunable structures [130]. Many M-N-C catalysts employ MOF-derived materials as their supports. Therefore, the catalytic activity is determined by the design of MOF precursors. By tailoring the structure of MOFs, the active sites can be provided with sufficient reaction space, which enhances mass transfer and optimizes the exposure of active centers [226]. Li et al. fabricated a ZIF-8-derived Fe-N-C

catalyst via strategic etching of specific crystal facets of ZIF-8, which created a defective structure [227]. This catalyst enhanced the accessibility of active sites to oxygen, thereby improving the ORR kinetics. In 0.1 M HClO₄, the catalyst exhibited an exceptional half-wave potential of 0.89 V higher than of the Fe-N-C (0.71 V). Notably, the Fe contents of these two catalysts are nearly identical (1.8 wt.% and 1.7 wt.%), which further demonstrates the high mass transport efficiency enabled by their defective structure. However, it should be clarified that the authors' limiting current densities are slightly lower than those of the normal value (4.2 mA·cm⁻²) (their catalyst: 3.5 mA·cm⁻²; reference sample Fe-N-C: 3.3 mA·cm⁻²). Dang et al. developed a Fe-N-C catalyst derived from UIO-66 (Figure 8(a)) [79]. The high mesopore ratio (> 80%) and large specific surface area (1240 m²·g⁻¹) of the catalyst facilitated oxygen molecule diffusion, thereby enhancing the utilization efficiency of active sites. MOF-derived carbon supports often suffer from aggregation at high temperatures, which reduces the exposure of active sites. In another work from Dang et al., this challenge was addressed by integrating carbon nanotubes into a ZIF-67-derived porous carbon support [181]. The introduced carbon nanotubes significantly enhanced the dispersion of ZIF-67-derived carbon frameworks, thereby maximizing the accessibility of active sites. The curvature of the support plays a critical role in modulating metal-support interactions and tailoring the electronic structure of metal sites. High-curvature surfaces could generate strain on active sites, which alters the adsorption strength of oxygen-containing intermediates on active sites. Kang et al. discovered that adjusting the curvature of ZIF-8 could regulate the activity of M-N-C catalysts. By modulating the ZIF-8's curvature, they achieved a shortened Fe-N bond length and spatially redistributed the electron density around Fe sites. The optimized catalyst exhibited a half-wave potential of 0.926 V in 0.1M KOH [228]. Zhao et al. developed ZIF-8 with high-curvature surfaces, which effectively lowers the d-band center of Fe,

thereby weakening the adsorption of OH* intermediates [229]. The resulting catalyst exhibits a high half-wave potential of 0.85 V in 0.1 M HClO₄. MOF-derived M-N-C catalysts demonstrate excellent promise for the ORR. The intrinsic metal and nitrogen within MOFs enable convenient one-step pyrolysis synthesis of such catalysts. However, the low production yield of MOFs remains a critical challenge that must be addressed.

4.6.2 Covalent organic frameworks

Covalent organic frameworks (COFs) are crystalline porous materials constructed from lightweight organic units linked by covalent bonds. These materials have garnered attention for their well-ordered pore architectures and customizable functionalities [230]. Long et al. synthesized a thiophene-based COF using 2,3-asymmetrically substituted bithiophene units (Figure 8(b)) [216]. *Operando* Raman revealed that asymmetric substitution induced charge redistribution and optimized oxygen intermediate adsorption. Yan et al. designed a fully conjugated 2D COF catalyst [231]. By employing an interlayer polymerization strategy, polythiophene chains were introduced into the COF nanochannels to form interlayer conjugated bridges, effectively avoiding pore blockage issues caused by conventional intrapore polymerization. However, the MEA in this work exhibited subpar performance, delivering merely 176 mW·cm⁻² as the peak power density in AEMFC (H₂-O₂, 1 bar). This value is significantly lower than that of the commercial 60 wt.% Pt-Ru/C benchmark (1500 mW·cm⁻², H₂-O₂, 1 bar). [232] Xu et al. engineered COFs with mixed nitrogen types (imine-N, pyridinic-N, phenazine-N) [233]. The authors discovered that incorporating different nitrogen atoms enables tunable interactions with water molecules. Among the synthesized COFs, the COF containing pyridinic N atoms exhibited the highest activity. COFs offer the advantages of atomically tunable metal sites and pore architectures. However, the development of COFs remains immature,

and their performance in MEA falls substantially short of commercialization benchmarks (peak power density: $800 \text{ mW} \cdot \text{cm}^{-2}$ under H_2 -air, 1 bar) [113].

4.6.3 Fullerene

Fullerene (C_{60}) is a spherical molecule composed of 60 carbon atoms arranged in a soccer ball-like structure [234]. As a carbon allotrope, C_{60} has been widely utilized as a support for M-N-C catalysts in the ORR. The highly delocalized π -electrons of C_{60} could facilitate proton transfer during the ORR process, thereby enhancing the reaction kinetics [235]. Kong et al. synthesized an Fe-N-C catalyst by integrating C_{60} with FePc through π - π interactions [236]. The closed C_{60} structure, via π -electron coupling with FePc, induced charge redistribution at the Fe- N_4 active sites, effectively reducing the energy barrier of the rate-determining step in the ORR. It should be noted that although their half-wave potential reaches as high as 0.91 V (in 0.1 M KOH, 1600 rpm), this value lacks reference significance. This is because at 1600 rpm, the limiting current density of Pt/C is only $5 \text{ mA} \cdot \text{cm}^{-2}$, significantly lower than the normal value ($6 \text{ mA} \cdot \text{cm}^{-2}$). Nakamura et al. synthesized cage-like cubic carbon catalysts with pentagon-rich structures using C_{60} and NaCl templates (Figure 8(c)) [217]. The pentagon defects induce localized high-spin electrons, which enhances the ORR activity of the catalyst. These studies collectively demonstrate that C_{60} , with its unique soccer ball-like structure and highly delocalized π -electron system, serves as an excellent support for M-N-C catalysts. Despite its unique electronic properties, fullerene also exhibits limitations. Fullerene solids consist of discrete, globular molecules packed together. The molecules are held together by weak van der Waals forces. As a result, this structure hinders efficient electron transport between the individual molecules, leading to lower electrical conductivity compared to materials like graphene. Consequently, while fullerene possess advantageous intrinsic electronic characteristics, the hindered intermolecular

electron transport inherent in its molecular crystal structure presents a significant limitation for its application in MEA.

4.6.4 Graphdiyne

Graphdiyne, a carbon allotrope, consists of benzene rings interconnected via diacetylenic ($\text{-C}\equiv\text{C-}$) [237]. Owing to the conjugated π -electron system of the diyne bonds, it exhibits exceptional electron transport capabilities [238]. Traditional Fe-N-C catalysts typically anchor Fe single atoms at defect sites on carbon supports. However, these carbon defects directly lead to lower electrical conductivity and weaker structural stability [239]. Therefore, Huang et al. reported a catalyst with Fe atoms anchored on the surface of graphdiyne [240]. Acetylene bonds (sp-C) can directly anchor metal atoms without introducing defects. The strong interaction between graphdiyne and Fe enables high ORR activity. To further enhance the structural stability of Fe-N bonds, they utilized NH_3 annealing treatment to substitute sp-C atoms with nitrogen, forming sp-N sites (Figure 8(d)) [218]. The adsorption energy calculations of Fe on graphdiyne demonstrate that Fe atoms preferentially anchor at sp-N -doped acetylene sites, thereby forming stable Fe-N coordination sites. The above studies have demonstrated that Fe/N co-doped graphdiyne exhibits high ORR activity. However, Li et al. raised doubts about whether Fe serves as the primary active site [241]. To address this, they performed DFT calculations to evaluate the adsorption free energies of the ORR intermediates on different atomic configurations. Their results revealed that Fe sites exhibited excessively strong intermediate binding, resulting in a high overpotential of 1.06 V (This overpotential value is derived from DFT calculations performed by the authors). In contrast, carbon sites on adjacent acetylene chains displayed moderate binding strength, achieving a significantly lower overpotential of 0.43 V, thereby identifying these C sites as the optimal active centers.

Significant progress has been made in support modulation engineering, yet achieving atomic-level regulation of defect density, heteroatom distribution, and pore architecture in supports remains challenging. Furthermore, the evolution of interfacial electronic properties between the support and active sites during the ORR requires in-depth investigation via operando characterization techniques.

4.7 Understanding the activity of different M-N-C catalysts

The differences in the ORR activity among various types of M-N-C catalysts primarily stem from variations in their atomic configurations, active site architectures, and adsorption/desorption kinetics of reaction intermediates, ultimately influencing the rate-determining step of the ORR.

4.7.1 Single-atom catalysts

The advantage of single-atom catalysts lies in their isolated dispersion of metal atoms on supports, where all metal atoms are fully exposed as active sites [242]. The intrinsic activity of single-atom sites primarily stems from their M-N_x coordination structures, with the metal center serving as the crucial determinant of catalytic performance. The metal type directly governs the adsorption strength of ORR intermediates, constituting the primary factor in regulating M-N-C activity [243]. The hybridization degree between the d-orbitals of different metals and nitrogen atoms determines the metal's d-band center, which in turn determines the activity of M-N-C catalysts [244]. An upward shift of the d-band center enhances intermediate adsorption but may impede desorption, whereas a downward shift weakens adsorption but could hinder O-O bond cleavage. An optimal d-band center position slightly below the Fermi level enables intermediate adsorption energies to approach the peak of the volcano plot. Furthermore, the oxidation state of the metal center significantly influences the ORR kinetics. For instance, in Fe-N-C catalysts, Fe²⁺ facilitates O₂ activation and O-O bond

dissociation, while Fe^{3+} may induce overly strong intermediate adsorption, thereby reducing desorption rates [77].

However, the single-atom active sites impose inherent limitations. The multi-electron ORR process requires sequential reaction steps, yet the absence of adjacent sites in single-atom configurations hinders synergistic effects, resulting in elevated energy barriers for O-O bond cleavage. Additionally, the restricted tunability of adsorption strength for ORR intermediates on single-metal centers may drive the activity away from the volcano plot optimum, as intermediates could be either over- or under-adsorbed.

4.7.2 Multi-atom M-N-C catalysts

Introducing additional metal to form multi-metal active centers represents a viable strategy to improve the intrinsic activity of single-atom sites. Compared to single-atom sites, the enhanced activity of multi-metal centers primarily originates from metal-metal interactions [245]. The incorporation of secondary metals induces charge transfer between metal atoms, which modulates the d-band center of the primary metal, thereby optimizing intermediate adsorption and avoiding the suboptimal adsorption strength ("too strong" or "too weak") characteristic of single-metal sites [246].

For instance, in Fe-N-C catalysts, when Fe bonds with another metal, electrons flow freely between the two metals. This charge redistribution alters the charge density at Fe sites, optimizing the d-band center or spin state of Fe and ultimately lowering the energy barrier of the rate-determining step. Furthermore, multi-metal sites enable simultaneous co-adsorption of both oxygen atoms of an O_2 molecule, shifting the ORR pathway from associative to dissociative. This mechanism circumvents the linear Sabatier relationship constraints typical of single-metal sites, accelerating the ORR kinetics.

4.7.3 Composite M-N-C catalysts of single-atoms and clusters

The enhanced activity of single-atom/cluster composite structures originates from charge transfer between single-atom and adjacent clusters [247]. When clusters approach single atoms, electron migration occurs due to differences in electron cloud density. This electronic effect modulates the d-band center of single atoms, optimizing their adsorption energy for reaction intermediates and thereby lowering the energy barriers of key steps in processes like the ORR. For instance, Che et al. demonstrated that introducing Fe clusters near Fe single atoms induced significant charge redistribution, substantially boosting catalytic activity [248].

The composite structure exhibits high activity because clusters can establish synergistic catalytic pathways with single-atom sites. This synergy overcomes the inherent Sabatier activity limitations of single-atom catalysts, leading to overall catalytic enhancement. Additionally, clusters modify the support environment, strengthening the anchoring of single atoms and mitigating their agglomeration or leaching during the ORR [249]. Wei et al. systematically compared the ORR contributions of single-atom catalysts, pure clusters, and their composite structures [250]. Their experiments revealed that the coexistence of single atoms and clusters significantly improves the adsorption and desorption behaviors of oxygen-containing intermediates during the ORR.

4.7.4 Composite M-N-C catalysts of single-atoms and particle

The enhanced ORR catalytic activity of single-atom/particle composites structure stems from interfacial electron transfer between particles and single atoms, which modifies the electronic environment of the single-atom sites [251]. Studies indicate that nanoparticles can act as electron donors to improve the electrocatalytic ability of single atoms, thereby optimizing the adsorption strength of single atoms toward oxygen-containing intermediates. For example, Guo et al.

demonstrated that incorporating ultrasmall Fe₃C nanoparticles adjacent to Fe-N₄ sites modulated the electronic structure of Fe centers [252]. This modification strengthened O₂ adsorption at Fe-N₄ sites and lowered the free energy barrier, ultimately enhancing ORR activity.

Additionally, defect vacancies on particle surfaces possess unsaturated coordination environments, exhibiting distinct intermediate adsorption capabilities compared to single atoms [253]. These vacancies serve as auxiliary active centers for synergistic catalysis with single-atom sites. In such cooperative systems, defect vacancies function as “secondary active centers” that preferentially capture and pre-activate oxygen molecules, while neighboring single-atom sites catalyze subsequent intermediate conversion. This synergy reduces energy barriers for reactant adsorption, intermediate conversion, and product desorption, collectively boosting the ORR performance. Zhu et al. exemplified this mechanism by constructing a cooperative system of Pt nanoparticles and Mn single atoms [254]. Here, Mn single atoms served as auxiliary sites, where strong electronic polarization through Mn-Pt bonds synergistically promoted O₂ dissociation on Pt nanoparticles, accelerating the overall ORR process.

4.8 The stability of M-N-C catalysts

Despite significant advances in ORR activity achieved by various M-N-C catalysts, their long-term stability under acidic conditions and high electrode potentials remains a critical challenge in the scientific community. The primary degradation mechanisms of M-N-C catalysts include: i) metal leaching, ii) corrosion of carbon supports, and iii) poisoning by contaminants.

4.8.1 Metal leaching

In M-N-C catalysts, the metal leaching is essentially the electrochemical corrosion process of the metal centers under electrochemical conditions. This leads to the metal being unable to be anchored

on the carbon support, ultimately resulting in metal leaching.

This issue stems from the inherent structural defects of the catalyst and the harsh environment of the ORR process. Under the ORR process, metal atoms are anchored to the carbon support via M-N_x coordination bonds. However, under high potentials (>0.9 V vs. RHE) or sustained attack from aggressive oxidative intermediates (such as H₂O₂ and *OOH), the valence state of the metal atoms changes [2]. This leads to a decrease in the bond energy of the M-N_x. When the M-N_x bond energy becomes insufficient to resist this attack, the metal atoms gradually leach from the carbon support and dissolve into the electrolyte as ions. Therefore, preventing the metal leaching is crucial. For example, Peng et al. introduced Mn atoms into Fe-N-C. Acting as an electron donor, Mn enhances the electron density around Fe, thereby strengthening the Fe-N bond energy and resulting in improved catalyst stability [165]. Utilizing non-iron elements as the metal center represents another viable approach. Employing metals with low Fenton activity, such as Co, Mn, or Cr, effectively suppresses the Fenton reaction at its source. This constitutes an effective strategy, even though their ORR activity is inferior to that of Fe. Further research suggests that demetalation of Fe-N-C catalysts begins below potentials of 0.7–0.8 V, primarily originating from inactive Fe species that do not participate in the ORR [255]. While the dissolution of these inactive iron species itself may not cause significant ORR activity loss, the released Fe^{2+/3+} can still trigger detrimental effects within the MEA. Therefore, removing the inactive Fe species prior to MEA assembly is likely critical for the successful implementation of Fe-N-C catalysts in PEMFCs. Conventionally, acid washing is employed to remove inactive iron particles (e.g., metallic iron, iron oxides, iron carbides) and is considered effective. However, this method struggles to eliminate carbon-encapsulated inactive Fe particles. To address this limitation, Jaouen and coworkers proposed two distinct strategies [256]: i)

Synthesis-stage particle minimization: They employed dry ball-milling to homogeneously mix precursors (Fe salt, 1,10-phenanthroline, ZIF-8), thereby circumventing local iron enrichment associated with wet impregnation methods. ii) Post-synthesis particle removal: Conducting 100 CV cycles in Ar-saturated 0.1 M HClO₄ using a potential range of 1.0 to 0.0 V vs. RHE and a scan rate of 100 mV·s⁻¹. While approach i) has practical importance for commercialization of M-N-C catalyst, approach ii) is clearly not a viable commercial approach and was thus used purely for the purpose of improving mechanistic understanding.

4.8.2 Corrosion of carbon supports

The carbon support is susceptible to electrochemical corrosion at high potentials ($\sim > 1$ V), leading to structural collapse of the support [257]. Since most M-N_x active sites reside within micropores, the collapse of the support exposes the metal active sites originally embedded within these micropores to the electrolyte, accelerating their dissolution. Therefore, highly graphitized carbon supports can be employed in M-N-C catalysts to mitigate corrosion. The primary reasons are: i) enhanced structural stability: highly graphitized carbon supports, characterized by its ordered structure, possesses stronger sp² bonds, making it more resistant to oxidation and thereby slowing corrosion [258]. In contrast, disordered carbon structures contain numerous defects and edge sites. While these sites exhibit higher reactivity, they are significantly more prone to oxidation. ii) improved electrical conductivity: highly graphitized supports offer excellent electrical conductivity. This facilitates rapid electron transfer, reducing localized high current densities that can cause electrochemical corrosion [259]. However, in the design of M-N-C catalysts, achieving highly stable carbon supports typically necessitates a compromise in catalytic activity. To attain superior oxidation and corrosion resistance, carbon supports must undergo high-temperature treatment to eliminate structural defects. This

reduction in defects translates to fewer anchoring sites for M-N_x moieties. Consequently, the pursuit of high stability—via highly graphitized, low-defect carbon supports—usually entails a decline in active site density. Therefore, an optimal balance must be struck between the graphitization and defect levels of the supports to endow the catalyst with enhanced durability while maintaining excellent activity.

4.8.3 Poisoning by contaminants

Contaminants degrade catalyst stability by occupying active sites through physical adsorption or chemical bonding, disrupting the electronic structure of the active sites, and triggering metal dissolution [260]. The catalyst poisoning process is typically irreversible; once poisoning occurs, the catalyst's activity becomes permanently degraded. Common contaminants include Cl⁻, SO₄²⁻, and H₂O₂. These species adsorb electrostatically onto the active sites. This alters the electronic density of states of the active sites and blocks the adsorption of O₂ at the M-N_x sites, leading to activity decay [261]. Therefore, minimizing the generation of contaminants or implementing their source removal at the source is crucial.

Clusters (e.g., Co, Fe) exhibit strong adsorption capabilities for contaminants. Introducing such clusters onto M-N-C catalysts can enhance stability by adsorbing contaminants. For example, Deng et al. introduced Co clusters around Co single atoms [262]. Owing to the strong adsorption affinity of Co clusters for Cl⁻, the catalyst's stability was significantly enhanced. Oxides possess free radical scavenging capabilities, with CeO₂ being widely recognized. CeO₂ exhibits catalase-like activity analogous to superoxide dismutase, enabling it to scavenge superoxide anion radicals by converting them into O₂ and H₂O, thereby mitigating catalyst poisoning. In a previous study, the Yamauchi group incorporated CeO₂ onto Fe-N-C. Due to CeO₂'s radical scavenging mechanism, the reactive

oxygen species generated by Fe-N-C were rapidly eliminated [263]. Consequently, the catalyst demonstrated exceptional stability in ZABs. However, it should be noted that, in terms of tolerance towards environmental pollutants, non-precious metal catalysts (such as Fe-N-C) exhibit significant advantages over traditional platinum group metal catalysts. This is primarily demonstrated in their resistance to sulfur-containing species, notably sulfur dioxide (SO_2): Pt-based catalysts are highly sensitive to even low concentrations of SO_2 , experiencing a marked decrease in activity. In contrast, Fe-N-C catalysts can maintain relatively stable ORR activity under exposure to SO_2 at higher concentrations. This superior tolerance is considered an advantage for the future practical application of non-precious metal catalysts.

4.9 Scale preparation and industrial application

The scalable production of M-N-C catalysts relies on reliable and stable manufacturing processes. To date, numerous synthesis methods for M-N-C catalysts have been developed in laboratories, such as impregnation, ball milling, atomic layer deposition, and high-temperature pyrolysis [81]. While laboratory-scale synthesis allows for precise control over reaction conditions to achieve controllable catalyst fabrication, industrial-scale production faces challenges. Issues including inhomogeneous precursor mixing and metal agglomeration during large-batch processing result in reduced active site density and non-uniform distribution, significantly diminishing catalytic performance.

Commercial production must prioritize cost-effectiveness and stability [264, 265]. The catalyst manufacturing process should avoid excessive complexity, and the overall synthesis route must feature low energy consumption, short production cycles, and environmental friendliness. Currently, most laboratory synthesis routes are unsuitable for industrial-scale manufacturing. Scaling up catalyst production often leads to difficulties in controlling active site types and causes significant

batch-to-batch quality variations [266]. Consequently, the performance of these catalysts in fuel cell falls below that observed under ideal laboratory conditions. Therefore, the key to industrial production lies in the large-scale, efficient, and low-cost preparation of catalysts.

4.9.1 Uniformity of active sites

Controlling the uniformity of active sites constitutes a central challenge in the large-scale preparation of M-N-C catalysts, directly determining their industrial applicability [267]. During mass production of M-N-C catalysts, achieving uniform dispersion of metal atoms remains particularly challenging. Addressing the homogeneous distribution of active sites is therefore critically necessary. To resolve this issue, spray drying and impregnation methods have shown potential for industrial-scale synthesis of M-N-C catalysts with uniformly dispersed active sites.

The spray drying method involves atomizing a mixed solution of metal precursors and a support into micrometer-sized droplets, followed by rapid drying in a hot gas stream to form particles [268]. This method offers high production efficiency, enables highly uniform dispersion of metals, and is suitable for large-scale preparation of M-N-C catalysts. For instance, Zheng et al. developed an N-, P-, and Fe-co-doped ORR catalyst using a spray drying process [269]. They combined tetraethyl orthosilicate with egg white for spray drying, followed by etching to obtain the catalyst without requiring high-temperature pyrolysis. The resulting catalyst achieved a maximum power density of $225 \text{ mW} \cdot \text{cm}^{-2}$ in ZABs.

Compared to spray drying methods, the impregnation method has been widely adopted due to its fewer process steps and strong controllability. The standard procedure for impregnation involves precursor impregnation, solution adsorption, drying, and calcination. With simple equipment requirements, this method enables large-scale production through batch processing of supports and

can be easily integrated into existing industrial systems. In impregnation, the uniformity of active sites depends on the homogeneous distribution of metal precursors and nitrogen sources on the support, which in turn relies on the physicochemical compatibility between the support and the metal salt solution [270]. As the support for adsorbing metal precursors, the support must exhibit strictly standardized pore structure, mechanical strength, and surface chemical properties to ensure consistent distribution of the metal solution within its channels. Consequently, supports typically require pretreatment before impregnation, such as modulating the physicochemical properties of the support surface through surface modification or high-temperature calcination, thereby enhancing the adsorption efficiency of metal precursors [271]. The concentration of the metal salt solution determines the metal loading of the catalyst. The concentration must neither be excessively high nor too low. If the concentration is excessively high, precursors tend to form nanoparticles instead of single-atom sites during pyrolysis due to localized supersaturation, leading to a loss of active surface area. Conversely, excessively low concentrations, while favoring single-atom dispersion, fail to achieve the metal loading per unit area required for industrial applications. Therefore, precise regulation of the metal solutions properties is critical.

4.9.2 Remove impurities

The removal and detection of impurities and by-products are critical metrics in the scalable production of M-N-C catalysts. The synthesis of M-N-C catalysts typically involves the mixing of metal sources, nitrogen sources, and carbon sources. Metal salts and organic polymers, when used as precursors, may decompose incompletely during high-temperature pyrolysis, leaving residual metal ions or undegraded organic residues [77]. These residual metal impurities can compete with primary metals and nitrogen atoms for coordination, thereby reducing active site density. In large-scale

production, impurity control constitutes a core aspect of catalyst preparation, divided into pre-treatment and post-treatment processes. For pre-treatment, high-purity metal sources are generally selected to minimize impurity introduction, as this approach reduces the likelihood of side reactions and prevent impurities from competing with active components for coordination. Post-treatment often involves multi-stage washing techniques, such as ultrasonic cleaning and high-pressure water rinsing, to remove impurities after catalyst synthesis. Beyond impurity minimization, robust impurity detection methods are essential, primarily utilizing ICP-OES/MS for quantitative analysis of metal impurity content.

To regulate the morphology of such catalysts, certain preparation methods require the introduction of templating agents. However, these approaches inevitably lead to residual impurities on the catalyst surface, which may block pores or poison active sites, thereby degrading catalytic activity. Developing appropriate detemplation techniques is therefore essential. Template removal typically involves etching with strong acids or bases such as hydrofluoric acid, sulfuric acid, or potassium hydroxide. While effective, these reagents pose environmental and safety challenges, necessitating careful selection of etching agents. Gianola et al. investigated the efficacy of different reagents—hydrofluoric acid, sodium hydroxide, hydrochloric acid, and an acid-free Teflon-based process—for template removal [272]. Their experiments demonstrated that hydrofluoric acid effectively eliminates silica and metal impurities but has adverse environmental impacts. In comparison, the NaOH + HCl method combines optimal template removal efficiency with minimized environmental hazards.

The development of self-templating methods represents an ideal strategy for synthesizing M-N-C catalysts. In self-sacrificial templating methods, the templating agent is integrated with

precursors, enabling in situ generation of active sites and simultaneous template removal through pyrolysis, oxidation, or chemical etching, thereby eliminating the need for additional template introduction and removal steps. For example, MOFs can serve dual roles as both templates and active component precursors. Upon thermal decomposition, MOFs form porous structures, bypassing the multi-step template preparation, loading, and removal processes inherent in conventional templating methods. This significantly simplifies the workflow and reduces material costs. Xu et al. developed a self-sacrificial templating approach to synthesize Fe-N-C catalysts [273]. They created composite microspheres via hydrogen-bond-driven self-assembly of melamine and cyanuric acid. These microspheres acted simultaneously as sacrificial templates and nitrogen sources. Subsequently, Fe³⁺ chelated with polydopamine was uniformly coated onto the microspheres under alkaline conditions. The obtained catalyst delivers a power density of 187 mW·cm⁻² in ZABs, exceeding that of Pt/C (101 mW·cm⁻²). It should be clarified that the Pt/C performance achieved in this work is below the typical reported values (>150 mW·cm⁻²) [143, 274, 275].

4.9.3 Equipment requirements

Current laboratory-scale synthesis routes for M-N-C catalysts predominantly rely on high-temperature pyrolysis at 800–1200 °C to form M-N_x active sites. This is because metal and nitrogen atoms must overcome a significant activation energy barrier to form stable M-N_x coordination structures. Consequently, uniform temperature distribution within equipment is critical during large-scale synthesis of M-N-C catalysts. Uneven heat transfer in the equipment results in inconsistent distribution and quantity of active sites in the synthesized catalysts. This imposes stringent requirements on the thermal uniformity of large-scale production equipment, as only equipment with highly uniform heat conduction can yield catalysts with balanced performance. For

the large-scale production of high-quality catalysts, the development of low-temperature synthesis methods for M-N-C catalysts has emerged as a promising approach. This method simultaneously reduces equipment requirements and lowers energy consumption. For instance, Sun et al. developed a low-temperature pyrolysis process for Fe-N-C catalyst preparation [101]. By introducing trace hydrogen during synthesis, they achieved high-performance catalysts at a reduced pyrolysis temperature of 360 °C. Given the complexity of pyrolysis in precisely controlling atomic configurations, substantial efforts have focused on pyrolysis-free synthesis methods, which could drastically reduce the enormous energy demands associated with high-temperature processing, particularly in large-scale synthesis. Consequently, Xiang et al. developed a pyrolysis-free and scalable synthesis method for catalysts using COFs [276]. They prepared highly active catalysts by assembling COFs with carbon nanotubes via a simple one-pot method at room temperature. Owing to this strategy, the synthesized catalysts enable large-scale production with a per-batch capacity exceeding 1 kg. This work significantly reduces the energy consumption associated with high-temperature processing.

5 The future: research priorities

Significant progress has been made in M-N-C catalysts for the ORR, demonstrating promising potential in both catalytic activity and selectivity. However, substantial challenges remain to be overcome before large-scale commercial implementation, particularly regarding the replacement of Pt in critical target applications. Future research should prioritize the following key directions:

i) Approaches to increase site density. Although most M-N-C catalysts exhibit excellent performance in RDE tests, their overall performance in MEA remains unsatisfactory. This is primarily attributed to the lower density of accessible active sites than the level required for practical

applications, resulting in mass activity far inferior to that of Pt/C. Table 4 compares the mass activity of M-N-C catalysts and commercial Pt/C over the past five years, showing an $\sim 20 \times$ difference in mass activity between conventional Pt/C and some recent M-N-C catalysts. Even if we normalize to the total weight of the Pt/C in Table 4 (only 20 wt.% Pt), the mass activity of the Pt/C is still $\sim 4\text{--}5 \times$ higher than that of the M-N-C catalysts. A corollary of this is that catalyst layers prepared from M-N-C catalysts must therefore be coated at $4\text{--}5 \times$ higher loadings to achieve the same activity as Pt/C. This explains why M-N-C based catalyst layers are typically 80–100 microns thick vs. ~ 20 micron thick for the 20 wt.% Pt/C layers [277, 278]. It should be noted that this difference in catalyst layer thickness is further exacerbated when comparing against 50 wt.% Pt/C layers which are then closer to 8–10 microns thick. This excessive thickness of M-N-C based designs impedes the diffusion of the reactants (oxygen and protons) and results in significant mass transport losses. Consequently, the overall MEA performance falls short of expectations based on RDE results. Therefore, researchers should focus on enhancing the active site density to reduce catalyst loading and ultimately address mass transport issues for M-N-C catalysts within MEAs.

Table 4 Comparison of mass activities between M-N-C catalysts and Pt/C in MEA over the past five years

Catalysts	Mass activity (at 0.9 V in MEA)	Refs.
Johnson Matthey 20 wt.% Pt/C	200 mA·mg _{Pt} ⁻¹ (H ₂ -air, 1.5 bar)	[113]
Fe-N-C-FG	12.8 mA·mg ⁻¹ (H ₂ -O ₂ , 1.5 bar)	[128]
Feg-NC/Phen	11.5 mA·mg ⁻¹ (H ₂ -O ₂ , 1.5 bar)	[279]
Fe-NC ^A -DCDA	10.2 mA·mg ⁻¹ (H ₂ -O ₂ , 1.0 bar)	[123]
Fe-AC-CVD	8.3 mA·mg ⁻¹ (H ₂ -O ₂ , 1.5 bar)	[102]
KJ-Fe/N/Carbon	8.0 mA·mg ⁻¹ (H ₂ -O ₂ , 1.5 bar)	[280]

Fe-MOF100 nm	7.9 mA · mg ⁻¹ (H ₂ -O ₂ , 1.0 bar)	[281]
FeNC-H ₂ -360	7.4 mA · mg ⁻¹ (H ₂ -O ₂ , 2.5 bar)	[101]
Sur-FeN ₄ -HPC	6.0 mA · mg ⁻¹ (H ₂ -O ₂ , 1.5 bar)	[282]
TPI@Z8(SiO ₂)-650-C	5.5 mA · mg ⁻¹ (H ₂ -O ₂ , 1.5 bar)	[109]

ii) Getting the community to move towards useful testing. Currently adopted stability testing protocols for some non-precious metal catalysts (e.g., via RDE or MEA) involve potential cycling between 0.6 and 1.0 V under a N₂ atmosphere. This approach is not only ineffective but also impedes progress in the field by masking the real limitations of these catalysts concerning stability. By testing in such ways, we only serve to trick ourselves into believing we have made great progress (e.g., “only 10 mA · cm⁻² loss at 0.8 V after 10k cycles in MEA”). Here, we recommend that MEA testing—particularly for non-precious metal catalysts—adhere to standardized protocols [283]. Current MEA stability assessments typically employ three methods: i) constant-current testing, ii) constant-potential testing, and iii) cyclic voltammetry (CV) cycling. Regardless of the methodology employed, all tests must be performed in O₂-containing atmospheres to simulate real-world fuel cell operating conditions. We recommend evaluating catalyst stability via the CV testing method reported by Zelenay et al [283]: Square-wave cycling (0.60 V → OCV, 3 s per step), continuing for up to 30,000 cycles or until the open-circuit voltage drops to 0.80 V, while monitoring the current density loss (≤ 30 mV loss at 0.80 A · cm⁻²) and current density at 0.8 V (≥ 0.3 A · cm⁻²) in H₂-air fuel cells. Minimizing H₂O₂ production is critical; however, particular attention should be given to the reliability of experiments determining H₂O₂ yield. It should be noted that efforts in this direction have also been hampered by the approach commonly taken in literature of using very high loadings

of M-N-C catalysts for RDE testing (typically $> 0.2 \text{ mg} \cdot \text{cm}^{-2}$). When using thick catalyst layers, nearly all non-precious metal catalysts exhibit low measured H_2O_2 content, even if they are in fact generating significant amounts of H_2O_2 . Therefore, it is better to use lower loadings for RRDE testing ($\sim 0.1 \text{ mg} \cdot \text{cm}^{-2}$) similar to what is used for Pt/C testing. The goal is not merely to detect low H_2O_2 generation, but to actually generate small amounts of H_2O_2 , and determining how successful we have been in this regard requires the use of lower RDE loadings than have typically been used by the M-N-C community.

iii) Focus on backup power applications. Backup power systems impose less stringent power density requirements than automotive motive applications, while also accommodating larger equipment footprints without the need for rigorous miniaturization. Furthermore, the inherent tolerance of non-precious metal catalysts toward airborne contaminants (e.g., CO/SO_2) enables reductions in air filtration system costs, whereas Pt-based catalysts necessitate sophisticated (and costly) high-precision filtration systems [284]. These advantages provide M-N-C catalysts with excellent performance compatibility and cost competitiveness in backup power applications, establishing a more viable commercialization pathway.

6 Conclusions

Over the course of half a century of development, M-N-C catalysts have evolved from macrocyclic precursors to atomic-scale architectures—spanning single-atom, dual-atom, multi-atom, and cluster/particle-integrated systems—demonstrating significant potential as Pt-alternatives for the ORR in sustainable energy technologies like PEMFCs and ZABs. This review systematically summarizes this progression, highlighting rational design strategies to enhance both activity and stability. We further identify key challenges hindering large-scale applications. Finally, targeted

recommendations are provided to steer future research towards higher efficiency, stability, and reliability. In summary, M-N-C catalysts offer new pathways for energy conversion technologies. With deeper mechanistic understanding, they hold promise for broader application in PEMFCs and ZABs, advancing progress toward sustainable development goals.

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Declaration of conflicting interest

The authors declare no conflicting interests regarding the content of this article.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Supplementary Materials. Additional data related to this paper may be requested from the corresponding author upon request.

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From single-atom to multi-metallic composite systems: Rational design and mechanistic insights of metal-nitrogen-carbon catalysts for oxygen reduction reaction

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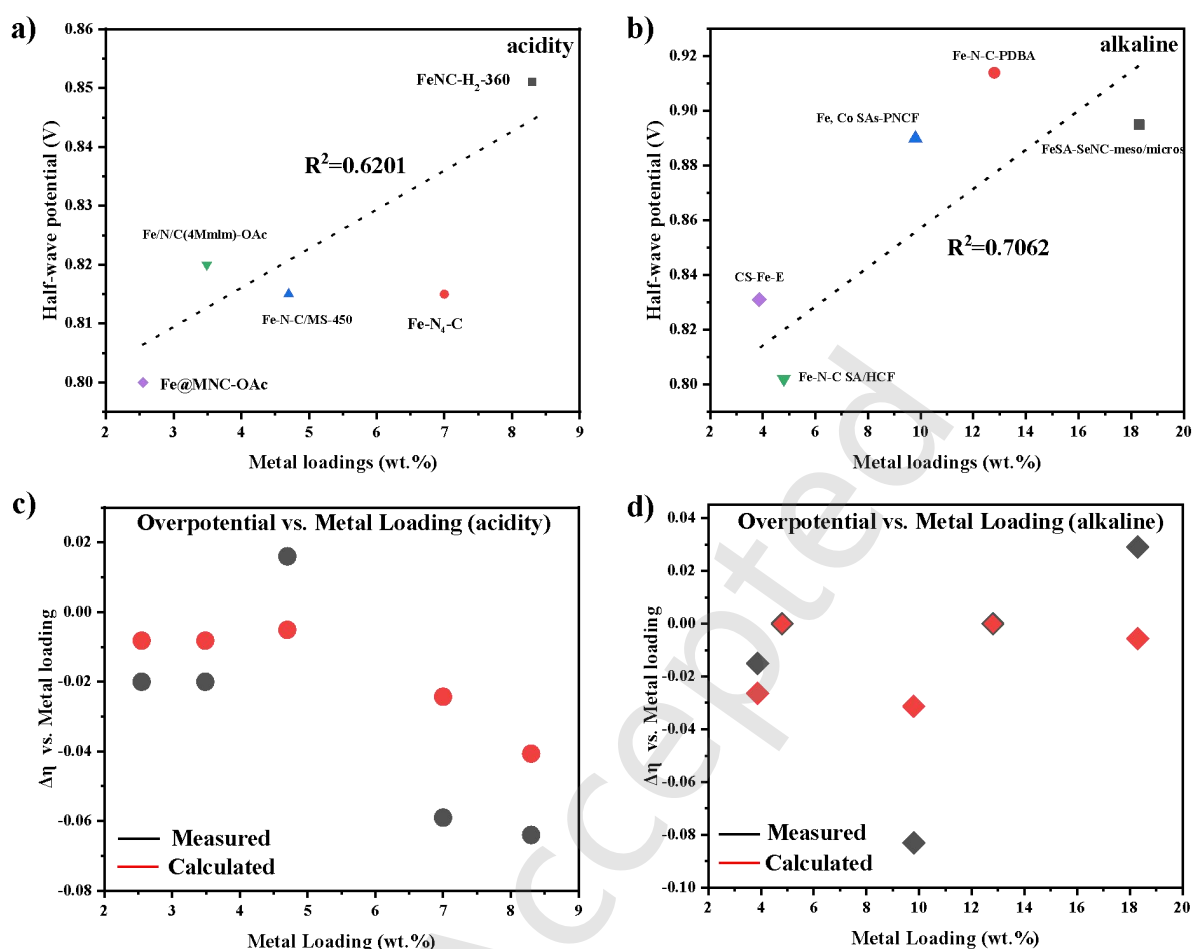


Figure S1. Half-wave potential vs. metal loading under a) acidic and b) alkaline conditions. It can be seen that in both cases, there is a clear correlation between increased halfwave potential (lower overpotential) and metal loading. Figs. (c) and (d) show the relationship between the overpotential and the metal loading in acid and base, respectively.

For the analysis in Figs (c) and (d), the reference point was whichever catalyst had the lowest metal loading (Fe@MNC-OAc at 2.55 wt. % in acid and CS-Fe-E at 3.87 wt. % in KOH).[1, 2] The estimated change in overpotential was calculated based on standard Butler-Volmer kinetics, using Equation S1:

$$\eta_2 - \eta_1 = \frac{RT}{\alpha F} \ln \frac{\text{Loading}_1}{\text{Loading}_2}$$

Equation S1. standard Butler-Volmer kinetics

Use this ref for the equation: *Modern Electrochemistry 2A Fundamentals of Electrodics*. J. Bockris, A. Reddy and M. Gamboa-Aldeco. Publisher: Kluwer Academic/Plenum Publishers 2000 Second Edition edn.

Where R is the gas constant ($R = 8.314159$), T is temperature in Kelvin, α is the transfer coefficient (assumed here to be 1), and F is Faraday's constant ($F = 96485$ C/mol). Loading 1 represents the reference catalyst metal wt.% and Loading 2 represents the metal wt.% of the catalyst being compared against the reference. This simple relationship was then used to estimate the reduction in overpotential (more active catalyst) that would be achieved if all of the Fe sites were atomically dispersed (or at least, equally agglomerated) and had the same TOF. The values from this estimate are compared directly against the measured values reported in Table 2 of the manuscript in Figs. (c) and (d). While clearly not a perfect fit, given the variety of factors which impact this analysis (not least of which is the attempt to compare data among many different labs) the correlation is nonetheless obvious and provides strong evidence that increasing metal loadings has been a successful approach to increasing the site density (and mass activity) of M-N-C catalysts.

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