Engineering local coordination environments and site densities for high-performance Fe-N-C oxygen reduction reaction electrocatalysis

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Abstract
Fe-N-C catalysts represent very promising cathode catalysts for polymer electrolyte fuel cells, owing to their outstanding activity for the oxygen reduction reaction (ORR), especially in alkaline media. In this review, we summarize recent advances in the design and synthesis of Fe-N-C catalysts rich in highly dispersed FeNₓ active sites. Special emphasis is placed on emerging strategies for tuning the electronic structure of the Fe atoms to enhance the ORR activity, and also maximizing the surface concentration of FeNₓ sites that are catalytically accessible during ORR. While great progress has been made over the past 5 years in the development of Fe-N-C catalyst for ORR, significant technical obstacles still need to be overcome to enable the large-scale application of Fe-N-C materials as cathode catalysts in real-world fuel cells.

KEYWORDS
Fe-N-C, local coordination environment, oxygen reduction reaction, site density
Polymer electrolyte fuel cells (PEFCs) are clean energy conversion technology that use hydrogen fuel to generate electricity. PEFCs are increasingly being used in transportation, portable or stationary power generation, and emergency backup power systems.\(^1\,2\) Oxygen reduction reaction (ORR) at the cathode of PEFCs is kinetically sluggish,\(^3\) which typically needs Pt-based catalysts to drive the reaction at technically reasonable rates. Electro catalyst cost currently comprises approximately 40% of the total cost of PEFCs (US $40 kW\(^{-1}\)). Thus, to lower the costs and achieve large-scale production, it is crucial to minimize or eliminate the use of platinum or platinum group metals (PGM) as ORR catalysts (and also hydrogen oxidation catalysts) in PEFCs. Approaches currently being pursued to achieve this goal include (1) alloying Pt group metals with other transition metals to increase the specific activity of Pt\(^4\,5\), and (2) developing PGM-free catalysts with high ORR performance, for example, first-row transition metal catalysts, especially metal single-atom catalysts supported on N-doped carbon supports (M-N-C).\(^6\,8\)

Among PGM-free catalysts, Fe-N-C catalysts (i.e., iron and nitrogen co-doped carbons) represent the state-of-the-art ORR catalysts in both alkaline and acid electrolytes.\(^9\) Some Fe-N-C catalysts, now exhibit ORR activities approaching those of PGM catalysts at a fraction of the materials cost, thus showing the potential for large-scale commercial applications.\(^10\,11\) The development of artificial Fe-based ORR catalyst was inspired by the iron-heme-copper active center in cytochrome \(c\) oxidase, an enzyme that catalyzes oxygen reduction in both prokaryotes and mitochondria.\(^12\) The synthesis of Fe-N-C catalysts generally involves the pyrolysis of sources containing nitrogen, carbon, and iron at high temperatures (\(>600\,^\circ\text{C}\)).\(^7\,13\) However, the nature of the ORR active site in most Fe-N-C catalysts remained somewhat controversial until quite recently. Initially, it was proposed that supported Fe nanoparticles were the active site for ORR, though more recent research suggests that isolated FeN\(_4\) moieties are more active. Fe-N-C materials free from metallic Fe nanoparticles\(^14\,15\) demonstrate outstanding ORR activity and durability, with the active Fe determined to exist in a porphyrin-like N coordination environment (FeN\(_4\)) using advanced physical methods, including Mössbauer spectroscopy, X-ray absorption spectroscopy (XAS), and high-angle annular dark-field scanning transmission electron microscope. Density functional theory calculations (DFT) added further evidence that FeN\(_4\) sites were indeed very active sites for ORR.\(^14\,16\,22\) Although deeper knowledge is emerging about the true active site of Fe-N-C material for ORR (i.e., porphyrin-like iron single-atom sites), the ORR performance of Fe-N-C materials remains generally inferior to commercial Pt/C catalysts.\(^23\,24\) Generally, the overall performance of a catalyst is determined by the intrinsic activity of active sites and the site density (SD) of active sites. The insufficient activity of Fe-N-C materials is currently limited by (1) insufficient intrinsic activity (or turnover frequency [TOF]) due to the too strong FeN\(_4\) adsorption of ORR intermediates, and (2) low SD of accessible FeN\(_4\) active sites, with most of the FeN\(_4\) sites buried in the carbon matrix or inside the deep pores inaccessible for ORR.

In this review, we aim to summarize recent advances in the design of high-performance Fe-N-C electrocatalysts with high TOFs or/and high SD for ORR. Regarding the development of FeN\(_4\) sites with a higher TOF, we first explore prior knowledge relating to ORR on Fe-N-C materials, with particular emphasis placed on reaction mechanisms. Approaches for the modulation of the properties of the central iron atom in Fe-N-C materials and thus ORR activity are then explored. For porous Fe-N-C materials with a high SD, synthetic strategies used to engineer porous N-doped carbon supports to allow better utilization of FeN\(_4\) active sites are discussed. Finally, perspectives
on the challenges and future prospects of Fe-N-C electrocatalysts for PEFCs are given.

2 | CONTROL OVER FEN<sub>x</sub> ACTIVE SITES IN FE-N-C MATERIALS

2.1 | Reactivity descriptors of M-N-C materials for ORR

ORR involves two possible reaction pathways, a two-electron pathway with H<sub>2</sub>O<sub>2</sub> as the main product and a four-electron pathway to produce H<sub>2</sub>O.\textsuperscript{25-27} H<sub>2</sub>O<sub>2</sub> can be damaging to fuel cell systems, thus the two-electron pathway is expected to be avoided. Hence, metal, N co-doped carbon (M-N-C) catalysts need to be fabricated that selectively drive the desirable four-electron pathway.\textsuperscript{28} There are two mechanisms proposed in the four-electron pathway, denoted as the associative or dissociative mechanisms.\textsuperscript{29} Considering the relatively high oxygen dissociation barrier on MN<sub>4</sub> sites, the associative mechanism is more typical for M-N-C materials.\textsuperscript{30} The simplified associative ORR mechanism is described by Equations (1)–(5) in basic media or Equations (6)–(10) in acidic media. Generally, the O<sub>2</sub> molecule is first adsorbed on the catalyst surface to form activated O<sub>2</sub>*<sup>+</sup>, followed by the successive addition of four electrons and four protons (H<sup>+</sup>) over four steps, with the reaction proceeding via OOH*, O*, and OH* intermediates.

In basic media:

\[
\begin{align*}
O_2(g) + * &\rightarrow O_2^*(\Delta G_1), \\
O_2^* + H_2O(l) + e^- &\rightarrow OOH^* + OH^*(\Delta G_2), \\
OOH^* + e^- &\rightarrow O^* + OH^*(\Delta G_3), \\
O^* + H_2O(l) + e^- &\rightarrow OH^* + OH^*(\Delta G_4), \\
OH^* + e^- &\rightarrow OH^- + *(\Delta G_5).
\end{align*}
\]

In acidic media:

\[
\begin{align*}
O_2(g) + * &\rightarrow O_2^*(\Delta G_1), \\
O_2^* + H^+ + e^- &\rightarrow OOH^*(\Delta G_2), \\
OOH^* + H^+ + e^- &\rightarrow O^* + H_2O(l)(\Delta G_3), \\
O^* + H^+ + e^- &\rightarrow OH^*(\Delta G_4), \\
OH^* + H^+ + e^- &\rightarrow H_2O(l) + *(\Delta G_5).
\end{align*}
\]

Here, “*” represents the catalytic active site. The adsorption free energy (\(\Delta G_{ads}\)) for the formation of the intermediates serves as an indicator of the reaction barriers that control overall ORR kinetics. The intermediate with the highest adsorption free energy is the rate-determining step for ORR. According to Sabatier’s principle,\textsuperscript{31} the optimum catalyst for a reaction will be that with intermediate binding energy for the key intermediate(s). Catalysts with weaker or stronger adsorption energies than the optimum for the ORR intermediates will result in lower ORR activity. Aside from the direct chemisorption of desolvated O<sub>2</sub> molecules to initiate the ORR, the hydroxyl species (OH<sub>ads</sub>) are also involved to interact with solvated O<sub>2</sub> molecules through noncovalent hydrogen bonding forces, which reproduces hydroxide intermediates (i.e., HO<sub>2</sub><sup>-</sup> anions).\textsuperscript{32} For the ORR in alkaline electrolyte, the as-formed HO<sub>2</sub><sup>-</sup> anions can be easily reduced to the four-electron-pathway products, due to the efficient hydrogen peroxide reduction reaction process. In contrast, the hydrogen peroxide reduction reaction in the acid electrolyte is kinetically slow to immediately reduce the HO<sub>2</sub><sup>-</sup> anions. This mechanism changeover thus results in the lower Tafel slopes and the more facile ORR processes in alkaline electrolyte.\textsuperscript{24}

Zagal et al.\textsuperscript{33} established a linear correlation between the M\textsuperscript{III}/M\textsuperscript{II} redox potential of MN<sub>4</sub> moieties (in macrocyclic complexes) and the M-O<sub>2</sub> binding energies during ORR (Figure 1A). Thus, the M\textsuperscript{III}/M\textsuperscript{II} redox potential of MN<sub>4</sub> moiety is a reactivity descriptor for ORR. For MN<sub>4</sub> catalysts adsorbed on pyrolytic graphite (i.e., M-N-C materials), a volcano plot relationship was established between the ORR activity and M-O<sub>2</sub> binding energies (Figure 1B). To optimize the ORR activity of M-N-C materials, the M\textsuperscript{III}/M\textsuperscript{II} redox potential ought to occur in a suitable window. For example, O<sub>2</sub> adsorption on FeN<sub>4</sub> centers is situated in the strong binding side of the maximum in Figure 1B. If a weaker Fe-O<sub>2</sub> binding energy was achievable from modified FeN<sub>x</sub> coordination, the ORR performance is expected to be improved. Optimization of the electronic properties of Fe centers to achieve O<sub>2</sub> binding energy near the apex in the ORR activity volcano plot is a prudent strategy for maximizing ORR activity. Approaches include (1) substitution of the metal center, which is the key factor in determining the M\textsuperscript{III}/M\textsuperscript{II} redox potential and thus the binding energy of central metal sites to ORR intermediates. However, FeN<sub>4</sub> is near-optimal for ORR; (2) alternation of FeN<sub>x</sub> structures, that is, the coordination number of the metal atom (e.g., FeN<sub>5</sub>, FeN<sub>3</sub>, FeN<sub>2</sub>) as well as the type of nearest neighbor configuration, which can modulate the electronic structure of central metal (e.g., replacing N with different electron donors such as S, P, or B, or introducing axial ligands on the metal site); (3) doping the carbon matrix with electron-donating or electron-withdrawing heteroatoms, which also affects the
electronic structure and charge transfer abilities of the central metal to some extent.

2.2 | The nature of FeN\(_4\) sites in Fe-N-C materials

To date, Fe-N-C materials afford the highest ORR activity among M-N-C materials, wherein the FeN\(_x\) sites are regarded as the active sites for ORR. XAS is a powerful technique for probing the local coordination environment of FeN\(_x\) sites. In most of the reported Fe-N-C materials, the central Fe atoms are coordinated by four nitrogen atoms with an Fe-N bonding distance around 2.0 Å (Figure 2A,B), closed to that of iron(II) phthalocyanine (FePc, 1.96 Å).\(^{14,17,22,34}\) X-ray absorption near-edge structure (XANES), which involves the study of absorption edge positions and spectrum shapes, is sensitive to the valence states and local coordination geometry of the central metal atom sites in M-N-C catalysts. By comparing the experimental Fe K-edge XANES spectra of Fe-N-C materials and calculated XANES spectra for model structures (Figure 2C,D), Jaouen et al.\(^{14}\) established that a pyridinic-N coordinated Fe\(_2\)N\(_{12}\) moiety could closely reproduce the Fe K-edge XANES spectrum of an Fe-N-C catalyst (Fe\(_{0.5}\), 0.5 wt% of Fe atoms in the precursor). Surendranath et al.\(^{35}\) discovered that the fingerprint peak positions in the Fe K-edge XANES spectrum of a typical Fe-N-C material closely resembled those of the pyridinic hexazacyclophane macrocycle, [(phen\(_2\)N\(_2\))Fe]\(_2\)O (Figure 2E,F). These analyses suggest that the FeN\(_x\) sites in Fe-N-C material possess pyridinic-N coordination. It should be pointed out at this point that XAS provides an average overall detected Fe sites with most samples, likely possessing a diverse local FeN\(_x\) coordination. Also, the local coordination environment of FeN\(_x\) sites in Fe-N-C materials will also vary slightly between different research groups (even when the same synthesis method is used), making the pinpointing of the best local FeN\(_x\) coordination for ORR more challenging.

In situ Fe K-edge XANES experiments were conducted to gain a deeper understanding of the potential-dependent behavior of FeN\(_x\) sites during ORR. At an applied potential of 0.2–1.0 V versus reversible hydrogen electrode (RHE), the absorption edge of Fe\(_{0.5}\) XANES spectra steadily shifted to higher photon energies (-Figure 2G), indicating an increase in the oxidation state of the Fe centers from +2 to +3.\(^{36}\) The same XANES spectrum changes were observed in both O\(_2\)-saturated and N\(_2\)-saturated electrolytes (Figure 2H), implying a potentially dependent behavior of the central Fe atoms during ORR (i.e., with the adsorption of O\(_2\) or oxygen intermediates having only a minor effect). The potentially dependent behavior of Fe-N-C materials has been confirmed by a number of in situ XAS studies.\(^{17,22,38}\) Mukerjee et al.\(^{37}\) found that different Fe-N-C materials prepared by different methods (Figure 2I) had a range of Fe–N bond distances and different Fe\(^{3+}/\text{Fe}^{2+}\) redox potentials, suggesting that the Fe bonding configuration was important. A Fe-N-C catalyst, with the central Fe\(^{2+}\) atoms initially out of N\(_4\) planes, underwent a significant change with potential sweeping, with the iron atom moving into the N\(_4\) plane with Fe\(^{3+}\) formation, as evidenced by the decreased Fe–N bond distances and higher Fe\(^{3+}/\text{Fe}^{2+}\) redox potential. Fe-N-C catalysts with a high Fe\(^{3+}/\text{Fe}^{2+}\) redox potential of Fe-N-C catalyst generally show good ORR performance.

2.3 | Effect of FeN\(_x\) configuration

A diversity of FeN\(_x\) sites can exist in Fe-N-C materials, differing in their location in the carbon matrix and local
Piotr et al. first proposed that the edge-hosted FeN4 sites were the main contributor to the high ORR performance of the Fe-N-C materials developed in their group. HAADF-STEM (Figure 3A) revealed directly atomically dispersed Fe atoms positioned at exposed carbon basal-plane edges and steps in the Fe-N-C material. In a 1.0 bar H2-air fuel cell test, the edge-hosted Fe-N-C material delivered the same current densities in the kinetic region of cathode operation (>0.75 V), as a fuel cell constructed with a Pt/C cathode (0.1 mgPt/cm²) (Figure 3B). Further studies indicated that the edge-hosted FeN4 sites were more likely to be formed on the margin of the pores in the carbon matrix (Figure 3C). DFT calculations also added further evidence for the high activity of edge-hosted FeN4 sites. As shown in Figure 3C, the binding of O2* and OOH*
was endothermic on the bulk-hosted FeN4 model (Figure 3D), while all steps were exothermic and downhill on the other three edge-hosted FeN4 models. This indicates optimized adsorption/desorption energies for ORR intermediates on the edge-hosted FeN4 site.

Additionally, the geometry of FeN4 sites changes in Fe-N-C materials as a function of the pyrolysis temperature used in their synthesis. Wu et al. found that the central Fe atom in FeN4 sites gradually moved away from the N4 plane with increasing pyrolysis temperatures up to 1100°C (Figure 3E). The geometry changes in the FeN4 site resulted in the shortening of Fe–N bonding distances in Fe K-edge R-space EXAFS plots as the pyrolysis temperature increased (Figure 3F). The small degree of Fe–N bond contraction allowed greater charge transfer from the Fe atom to the adjacent N atoms, and
weaker adsorption of ORR intermediates by the central Fe atoms (Figure 3G). For the Fe-N-C obtained at 700°C, its out-of-plane FeN₄ sites with a small degree of Fe–N bond contraction that were identified as sites with optimal ORR performance (Onset potential \[E_{\text{onset}}\] of 0.98 V vs. RHE, half-wave potential \[E_{1/2}\] of 0.84 V vs. RHE, 0.5 M \(\text{H}_2\text{SO}_4\)), even though contraction strain about FeN₄ is not energetically favorable for the catalyst. The N coordination number can also be varied to form defective MNₓ (\(x = 2, 3, \text{ or } 5\)) sites, leading to central metals with different electronic structures and different ORR activities.\(^{20,44-47}\) However, it remains unclear whether FeNₓ (\(x = 2, 3, \text{ or } 5\)) structure with nitrogen vacancies or excess nitrogen relative to the traditional FeN₄ coordination can enhance ORR activity.

### 2.4 | Synergistic effect of heteroatom dopants

Heteroatom dopants can be introduced into Fe-N-C materials via directly substituting the neighboring atoms of the central metals in the FeN₄ moieties,\(^{48,49}\) or alternatively by randomly introducing atoms within the carbon skeleton.\(^{50,51}\) Heteroatom doping induces charge redistribution at the central metal by (1) acting as a coordination atom or (2) modulating the long-range electronic structure of the support. This modulation results from the different atomic size and electronegativity of heteroatom dopants compared to the N and C atoms typically in Fe-N-C materials. The variability (i.e., general lack of control) of heteroatom doping in Fe-N-C materials often makes it challenging to establish a direct relationship between heteroatom doping effects and ORR activity.

Several works have demonstrated that introducing S or P dopants into Fe-N-C materials is beneficial for ORR.\(^{49,50,52-56}\) For Fe-N-C materials, the introduction of electron-donating S or P dopants in the carbon support imparts more negative charge on the N atoms and less positive charge on the central Fe atoms, thus weakening the binding energy of Fe centers toward ORR intermediates. This promotes the release of \(\text{OH}^+\) from central Fe sites in the last electron transfer step of ORR, thus accelerating the overall ORR process. Li et al.\(^{51}\) demonstrated that co-doping S and P was more effective in lowering the positive charge on central Fe sites than P-doping or S-doping alone. According to the DFT calculation of Bader charge on the central Fe sites, the S, P co-doped Fe-N-C material had the lowest binding energy for

![Figure 4](image-url)

**Figure 4** (A) Linear relationship between \(\text{OH}^+\) binding energy and Bader charge of central Fe atom in a FeN₄ site, P-doped FeN₄ site, and S,P co-doped FeN₄ site. (B) Free energy diagram of the oxygen reduction reaction (ORR) on a FeN₄ site, P-doped FeN₄ site, and S,P co-doped FeN₄ site. (C) Kinetic current density \((J_k)\) and half-wave potential \((E_{1/2})\) for Fe-SAs/NPS-HC and the control samples. Reproduced with permission: Copyright 2018, Springer Nature.\(^{51}\) (D) Effect of the amount of charge transfer from the S-doped functional groups to the d-band center of the Fe site, and the relationship between the adsorption energy of various intermediates and the d-band center of Fe site. (E) Plot for the kinetic activity of ORR catalysts as a function of the electron-donating/withdrawing properties of a Fe-N-C material incorporating S dopants, and the corresponding ORR activities. Reproduced with permission: Copyright 2019, American Chemical Society.\(^{57}\)
OH* among the three sites (Figure 4A,B), thus offering the best ORR performance (Figure 4C). This work highlighted the contributions of heteroatom dopants located adjacent to the FeN₄ sites. Chen et al.⁴⁸ reported that P dopants neighboring the central Fe atoms (Fe₅P sites) can directly modulate the electronic structure of Fe atoms to enable a new ORR reaction pathway, that is, two O₂ molecules adsorbing on different sides of the planar Fe₅P unit. Lee et al.⁵⁷ studied the effect of withdrawing/donating S dopants on the Fe site in Fe-N-C materials. DFT results (Figure 4D) indicated that oxidized sulfur atoms can decrease the d-band center of iron by withdrawing electrons, leading to the weaker adsorption of ORR intermediates, and thus facilitating ORR. This was supported by a volcano plot (Figure 4E) established between ORR activity and the ratio of oxidized S and thiophene-like S, where an increased content of oxidized S increased ORR activity, while more thiophene-S species lowered ORR activity. Other factors like the sulfur content also influence the ORR performance of S-doped M-N-C materials. Too high sulfur content results in carbon materials with poor conductivity and lower performance.⁵⁹ Thus, many different factors need to be considered when attempting to utilize the S-doping effect for improved ORR activity.

### 2.5 Synergy of dual metal sites

In addition to modification of the atoms neighboring the central metals, the central metals themselves can also be varied in number, from single metal sites to dual metal sites located adjacently on the N-doped carbon support. Such dual metal sites not only possess porphyrin-like coordination geometries but also benefit from synergistic effects arising from metal–metal interactions and charge polarization similar to metal alloys. The d-d orbital hybridization between adjacent metal sites, different from p-d orbital hybridization between metals and coordinating heteroatoms (N, S, P), offers a novel way of modulating the electronic structure of both metals. Furthermore, both metal sites can serve as active centers during ORR, leading to new reaction pathways with lower reaction barriers. Various dual metal sites have been reported with enhanced ORR performance, including Fe-Co,⁶⁰–⁶² Fe-Mn,⁶⁴,⁶⁵ and Fe-Fe.⁶⁶

As a representative example, consider Fe-Co dual-atom sites (FeCoN₅) as a new type of active site with optimized structure for ORR.⁶⁵ In situ Fe K-edge XAS results (Figure 5A,B) demonstrated that Fe²⁺ site was the dominant iron state in the FeCoN₅ catalyst up to 0.8 V, whereas almost negligible Fe²⁺ was found for the FeN₄ catalyst at 0.4 V. This indicates that the FeCoN₅ catalyst had a higher Fe³⁺/Fe²⁺ redox potential than FeN₄ sites during ORR. Also, instead of adopting an end-on O₂ adsorption configuration at the Fe single-atom sites, the binuclear site of FeCoN₅ catalyst promoted a bridging-cis O₂ adsorption configuration, making the O–O bond easier to cleave (Figure 5C). These advantages resulted in FeCoN₅ being a much more active catalyst site than FeN₄ sites, displaying an E_{onset} of only 1.02 V and an E_{1/2} of 0.86 V (vs. RHE) in 0.1 M HClO₄ (Figure 5D). Zhang et al.⁶⁵ reported that the neighboring MnN₄ sites can activate the spin state of Fe¹¹¹ sites, that is, changing from the low spin state (t₂g₅e₅⁰) to intermediate spin state (t₂g₄ e₅⁰). As evidenced by the magnetic susceptibility results (Figure 5E,F), the effective magnetic moment for Fe,Mn/N-C and Fe/N-C was 3.75 µ_{eff} and 2.16 µ_{eff} thus corresponding to the number of unpaired d electron (n) of Fe¹¹¹ Ion to be 1 and 0, respectively. The one e₉ electron filling of the central Fe sites in Fe,Mn/N-C allows the penetration of the antibonding π-orbital of O₂ easily, thereby delivering an E_{1/2} of 0.804 and 0.928 V versus RHE in 0.1 M HClO₄ and 0.1 M KOH, respectively.

### 3 Improving site densities of FeN₄ sites in Fe-N-C materials

The pyrolysis synthesis of Fe-N-C materials involves the simultaneous formation of iron single-atom active sites (and sometimes nanoparticles also) and the N-doped carbon support. As demonstrated by the examples above, the activity of atomically dispersed Fe sites for ORR is closely linked to the chemical (iron coordination environment) and structural properties (microporosity) of the support, both of which control FeN₄ dispersion and active site accessibility. Carbons with high specific surface area and pore volumes enable better dispersion of iron single metal sites, avoiding the undesirable aggregation of the active iron in the form of iron nanoparticles or iron-carbide species.⁶⁷ Also, the utilization of FeN₄ sites during ORR is greatly influenced by the location of FeN₄ sites in the carbon support. It is intuitive that FeN₄ moieties on or near the external surface of the carbons will be more accessible for ORR. While those buried deep in the carbon matrix will have limited activity.⁹³,⁹⁴ Thus, it is crucial to engineer Fe-N-C materials with a high density of exposed surface FeN₄ sites.

### 3.1 Quantification of the SD of FeN₄ site

The quantification of FeN₄ sites can be achieved using various methods, including Mössbauer spectroscopy, CO-
chemisorption, and nitrite electrochemical reductive stripping. Mössbauer spectroscopy provides bulk qualitative and quantitative information on the different Fe species in Fe-N-C catalysts. For example, the Fe$_{1.0}$ catalyst developed by Jaouen et al.\textsuperscript{14} was identified to contain six distinct iron species, including square-planar Fe(II)N$_4$ coordination (D1 and D2) and metallic Fe species (Fe$_2$N, α-Fe, β-Fe, and Fe$_x$C) (Figure 6A). The content of D1 and D2 in Fe-N-C catalyst can be regarded as the total content of FeN$_4$ sites in a Fe-N-C catalyst.

CO-chemisorption involves the physical adsorption of one CO molecule per MN$_4$ site (M = Fe, Co, Mn) on the surface of Fe-N-C catalyst, typically at an inert gas atmosphere at temperatures of 400–600°C.\textsuperscript{23} As shown in

![Figure 5](image-url)
FIGURE 6  (A) Mössbauer spectroscopy data for Fe$_{1.0}$ (A Fe-N-C catalyst with 1.0 wt% of Fe atoms used in the precursor). Reproduced with permission: Copyright 2015, Springer Nature.14 (B) CO pulse chemisorption profiles for N-C, Fe-N-C-2HT-1AL, Fe-N-C-3HT-2AL, (Fe,Mn)-N-C-3HT-2AL, and Mn-N-C-3HT-2AL. (C) CO uptake versus ORR catalyst mass activity $I_m$ at 0.8 V in 0.1 M HClO$_4$. Reproduced with permission: Copyright 2015, Springer Nature.23 (D) The adsorption and stripping process of nitrite (NO$_2^-$) on the FeN$_4$ site. (E) ORR CV curves, wide range baseline scan (avoiding nitrite reduction area), and narrow baseline scan in the nitrite reductive stripping region for Fe-N-C catalyst before, during, and after nitrite adsorption. Reproduced with permission: Copyright 2016, Springer Nature.24 Comparison of (F) surface FeN$_4$ site density (SD) values and (G) turnover frequencies (TOFs) at 0.80 V$_{RHE}$ of four Fe-N-C catalysts obtained using CO-chemisorption and nitrite electrochemical reductive stripping. The site density-ORR turnover frequency maps (SD-TOF ORR reactivity maps) achieved from (H) nitrite electrochemical reductive stripping. Reproduced with permission: Copyright 2020, The Royal Society of Chemistry.68
Figure 6B, there was no CO adsorption on the metal-free-N-C material, whereas CO uptake was observed in the Fe-N-C and Mn-N-C materials. The mass-based surface site density (MSD) of MN₄ sites was calculated through the amount of CO adsorption uptake:

$$\text{MSD} = n_{\text{CO}} \times 10^{-6} \times N_A.$$  

where $n_{\text{CO}}$ (nmol/mg) is the molar CO uptake and $N_A$ is the Avogadro’s constant. Further, a linear correlation established between the CO adsorption uptake ($n_{\text{CO}}$) and ORR mass activity ($I_m$, mA/cm²) at 0.8 V versus RHE (Figure 6C), which allows the TOF to be calculated, that is,

$$\text{TOF}_{\text{CO}}(0.8V)[s^{-1}] = \frac{I_m}{F \times n_{\text{CO}}}$$

where $F$ is the Faraday constant.

Nitrite electrochemical reductive stripping (Figure 6D) is based on the chemi-adsorption of one NO molecule per FeN₄ site (the NO is obtained by decomposition of NO₂⁻), followed by the five electron reduction of one adsorbed NO per FeN₄ site under electrochemical conditions.²⁴ Before, during, and after the NO₂⁻ poisoning experiments, CV curves of Fe-N-C catalyst are collected in an O₂-saturated 0.5 M acetate buffer over the ORR region and nitrite reductive stripping region (Figure 6E). Electrochemical nitrite reduction stripping charge on Fe(II)N₄ sites ($Q_{\text{strip}}$) is determined from the difference between the poisoned CV curve and the unpoisoned CV baseline. The MSD of the FeN₄ site was calculated using the following equation:

$$\text{MSD} \left[ \text{molsitesg}^{-1} \right] = \frac{Q_{\text{strip}} [\text{Cmol}^{-1}]}{n_{\text{strip}} F [\text{Cmol}^{-1}]}.$$  

where $Q_{\text{strip}}$ is the excess charge associated with the stripping peak; $n_{\text{strip}}$ is the number of electrons associated with the reduction of one adsorbed nitrosyl per site. Based on the difference of the kinetic current between the poisoned and unpoisoned Fe-N-C catalysts, the mean TOF can be calculated as follow:

$$\text{TOF}(0.8V)[s^{-1}] = \frac{\Delta I_k [\text{A/g}]}{F [\text{As/mol}] \times \text{MSD}[\text{mol/g}]}.$$  

where $\Delta I_k$ is the difference in the kinetic current at 0.8 V versus RHE.

Primbs et al.⁶⁸ found that the SD values achieved by CO-chemisorption were generally higher than those from nitrite electrochemical reductive stripping experiments (Figure 6F,G). This is explained by the fact that the surface FeN₄ sites deep inside micropores are electrochemically inaccessible for NO₂⁻/NO molecules, while such sites are still accessible for CO gas in dry Fe-N-C catalysts. Further, the SD-TOF descriptor maps established from both methods (Figure 6H) showed that the micropore-rich Fe-N-C catalyst can accommodate abundant FeN₄ sites with a large SD, but with a low TOF. Conversely, surface FeN₄ sites in mesoporous Fe-N-C catalysts allow ORR to proceed very efficiently with a high TOF, but with a low SD. These results motivate the engineering of novel carbon supports with optimal micropore and meso/macropore structures, to allow a high dispersion of FeN₄ sites and facile reactant/product transport during ORR, respectively.

### 3.2 Control over the metal organic frameworks (MOF) precursors for Fe-N-C synthesis

Introducing physical structure into the carbon support of Fe-N-C catalysts starts with the precursor, then continues through the pyrolysis process.²⁹ For MOF templates, the pore structure and size of the pristine MOFs have a large influence on the pore structure of the final carbon materials, thus affecting their ORR performance. Jaouen et al.⁷⁰ (-Figure 7A) systematically studied the correlation between the ORR activity of ZIF-derived Fe-N-C materials and the cavity size of the ZIF precursors. Increasing the cavity size in ZIF precursors from 1.16 to 18.00 Å favored a better dispersion of Fe sites, and a higher specific surface area in the resulting Fe-N-C materials, thereby delivering higher ORR activity. A ZIF precursor with a cavity size of 18.00 Å, afforded the Fe-N-C material with the highest ORR activity (cf. the more commonly used ZIF-8 with a cavity size of 11.10 Å). Wu et al.⁷¹ demonstrated that the crystal size of the Fe-doped ZIF precursors (50–1000 nm) (Figure 7B) was largely retained in the carbonized Fe-N-C materials, with the smaller size ZIF crystals yielding Fe,N co-doped carbon nanoparticles with larger exposed external surface areas for catalyzing the ORR. However, when the size of the Fe-doped ZIF precursor was reduced to only 20 nm, the resulting Fe,N co-doped carbon nanoparticles were susceptible to aggregation during pyrolysis, thus burying active sites and reducing interparticle porosity (which negatively affected ORR performance). Fe-doped ZIF crystals with a size of 50 nm were determined to be optimal, with the derived Fe-ZIF (50 nm) catalyst offering the highest electrochemical surface area (~550 m²/g) and ORR $E_{1/2}$ of 0.85 V versus RHE in 0.5 mol/L H₂SO₄ electrolyte. Wu et al.⁷² further demonstrated that the combination of large ZIF precursors (100 nm) and smaller supported ZIF nanoparticles (30 nm) was effective in preventing the aggregation of smaller ZIF nanoparticles, thus leading to the Fe-N-C carbon products with highly exposed external surface areas for efficient ORR ($E_{1/2}$ of 0.86 V vs. RHE in 0.5 mol/L H₂SO₄ electrolyte, Figure 7C). The size of ZIF nanoparticles also has a great impact on the electron
transport when the derived Fe-N-C materials were being constructed into devices, with the smaller sized ZIF nanoparticles affording a faster electron transport (Figure 7D,E). The homogenous distribution of site-isolated Fe atoms in Fe-N-C materials is essential for achieving high ORR activity and catalyst durability. Wu et al. varied the amount of Fe (0–9 at%) in the ZIF-8 precursors, with 1.5 Fe-ZIF (i.e., containing 1.5 at% Fe in ZIF precursor) being optimal for achieving a high loading of FeN₄ sites (Figure 7F). From CO-chemisorption experiments, the maximum mass-based site density (MSDₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑявление (A) Linear relationship between the specific pore volume in a pristine zeolitic imidazolate framework (ZIF) and the ORR activity of the resulting carbon material. Reproduced with permission: Copyright 2016, American Chemical Society. (B) The relationship between the crystal size of ZIF precursors, surface area, and ORR activity. Reproduced with permission: Copyright 2017, American Chemical Society. (C) HAADF-STEM images for a 55% 100 @30 catalyst. Reproduced with permission: Copyright 2020, Elsevier. (D) TEM images and the schematic charge transport of Fe-N-C materials derived from ZIF nanoparticles with different sizes. Reproduced with permission: Copyright 2019, WILEY-VCH. (F) Mössbauer spectroscopy data for 1.5 Fe-ZIF. (G) ORR LSV curves for Fe-N-C catalysts with different Fe contents in O₂-saturated 0.5 M H₂SO₄. (H) Fuel cell performance for 1.5 Fe-ZIF under 1 bar H₂-O₂ condition. Reproduced with permission: Copyright 2019, The Royal Society of Chemistry.

The homogenous distribution of site-isolated Fe atoms in Fe-N-C materials is essential for achieving high ORR activity and catalyst durability. Wu et al. varied the amount of Fe (0–9 at%) in the ZIF-8 precursors, with 1.5 Fe-ZIF (i.e., containing 1.5 at% Fe in ZIF precursor) being optimal for achieving a high loading of FeN₄ sites (Figure 7F). From CO-chemisorption experiments, the maximum mass-based site density (MSDₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑ_e�⁾⁻¹ and 2.1 e⁻ s⁻¹ site⁻¹, respectively. As a result, the 1.5 Fe-ZIF displayed a high $E_{1/2}$ of 0.88 V versus RHE in O₂-saturated 0.5 M H₂SO₄ electrolyte (Figure 7G). Under 1 bar H₂-O₂ fuel cell, the 1.5Fe-ZIF cathode electrocatalyst delivered a current density of 0.044 A/cm² at 0.87 V, only 30 mV lower than the U.S. DOE activity target (0.90 V) (Figure 7H).

3.3 | Pore-forming templates

To improve the utilization of FeN₄ sites in the Fe-N-C catalysts, the mesoporous-SiO₂ protection strategy has proved effective in minimizing the aggregation and fusion of carbon nanoparticles during high-
FIGURE 8  (See caption on next page)
FIGURE 9  (A) Scheme for the synthesis of FeNC-CVD-750 via a CVD pyrolysis process. Reproduced with permission: Copyright 2020, ChemRxiv.99 (B) Schematic illustration of the evolution process of Fe ions to FeO$_4$ sites and finally FeN$_4$ sites on N-doped carbon. (C) Fe K-edge XANES spectra, (D) Fourier-transformed Fe K-edge EXAFS spectra, and (E) first derivative of the Fe K-edge XANES spectra of FeCl$_2$-NC-T ($T=25^\circ-1000^\circ$C). Reproduced with permission: Copyright 2019, American Chemical Society.101 (F) CV curves of FeNC-CVD-750 and N-C catalysts in an Ar-saturated 0.5 M H$_2$SO$_4$ electrolyte. (G) Fe K-edge XANES spectra of FeNC-CVD-750 collected in O$_2$-saturated 0.5 M H$_2$SO$_4$ at applied potentials of 0.9–0.5 V. (H) Correlation between the fraction of Fe$^{3+}$ species and the applied potentials. Reproduced with permission: Copyright 2020, ChemRxiv.99

FIGURE 8  (A) Scheme for the synthesis of Co,N-CNF using a mesoporous-SiO$_2$ protection strategy. Reproduced with permission: Copyright 2015, WILEY-VCH.78 (B) Scheme for the synthesis of TPI@Z8(SiO$_2$)-650-C with a mesoporous-SiO$_2$ protection strategy. (C) TEM images for TPI@Z8-650-C and TPI@Z8(SiO$_2$)-650-C. (D) Tafel plot for determination of the ORR activity for TPI@Z8(SiO$_2$)-650-C at 0.9 V$_{IR-free}$ measured under 1 bar H$_2$O$_2$. (E) Correlation between the Fe content and the site density of surface FeN$_4$ site; a correlation between the Fe content and the Fe utilization. (F) Correlation between the site density of surface FeN$_4$ site and the fuel cell current density achieved at the voltages of 0.6 V and 0.8 V$_{IR-free}$. Reproduced with permission: Copyright 2019, Springer Nature.80 ORR, oxygen reduction reaction
temperature pyrolysis treatments. Following the mesoporous-SiO2-protective strategy developed by Zhang et al.78 (Figure 8A), Shui et al.79 synthesized a TPI@Z8(SiO2)-650-C product with a concave morphology, which showed an external surface area increase of about 32%, relative to the dense morphology of SiO2-free TPI@Z8-650-C (Figure 8B,C). Due to the high-density exposed active FeN4 sites (57 μmol/g), the TPI@Z8(SiO2)-650-C catalyst achieved a current density of 22 mA/cm2 at 0.9 V_{\text{IR-free}} and 47 mA/cm2 at 0.88 V_{\text{IR-free}} during 1.0 bar H2-O2 fuel cells tests (Figure 8D), reaching the 2018 DOE Target for PGM-free catalysts (44 mA/cm2 at 0.88 V_{\text{IR-free}}). Correlation between the Fe content and the SD of FeN4 sites, as well as the SD of FeN4 sites and the ORR activity, were further explored. As shown in Figure 8E, an increase in the Fe content leads to an increase in the SD of FeN4 sites, reaching saturation of 57 μmol/g for TPI@Z8(SiO2)-650-C at a Fe loading approaching 3 wt %. However, the Fe utilization dropped as the Fe loading increased, then leveled off at approximately 11%. Results conclusively demonstrate that an increased SD of FeN4 sites leads to an increased ORR performance (Figure 8F).

Traditional templates (SiO2,79,81,82 PVP,83 F127,84 etc.) have been widely applied to introduce mesopores into carbon supports. Feng et al.79 prepared a hierarchically porous Fe-N-C material (SA-Fe-NHPC) by pyrolysis of a complex of ZnCl2, FeCl3, and 2, 6-diaminopyridine around SiO2 colloids (12 nm). The SA-Fe-NHPC with the optimal Zn2+/Fe3+ molar ratio possessed a high Fe single atom loading of approximately 1.0 wt% and abundant mesopores (12 nm), where the Zn atoms served as the barriers to prevent the aggregation of Fe atoms to form nanoparticles. Due to the densely exposed FeN4 sites, the SA-Fe-NHPC exhibited a high E1/2 of 0.93 V in 0.1 mol/L KOH. In addition to creating pores, SiO2 nanoparticles are also capable of minimizing the aggregation of Fe atoms to form nanoparticles during high-temperature pyrolysis. Jiang et al.55 demonstrated that during the pyrolysis of an Fe-containing porphyrin-MOF, PCN-222(Fe), the presence of SiO2 nanoparticles in the mesopores (3.2 nm) enabled the generation of Fe-N-C material with a very high Fe loading of 3.46 wt%. This was attributed to the formation of a thermally stable Fe/SiO2 interface, which increased the migration energy barrier of Fe atoms and prevented the aggregation of Fe nanoparticles.

Molten salts (e.g., NaCl,36–40 ZnCl2,91 KCl,92 or a combination thereof33–47) are efficient pore-forming agents. The interplay between the melting temperature (T_{\text{melt}}) of molten salts and the decomposition temperature of organic precursors is the key to the modulation of the porosity of the resulting carbon products. For example, Wei et al.98 used a mixture of ZnCl2 (T_{\text{melt}} = 390°C) and KCl (T_{\text{melt}} = 749°C) to create a “semi-closed” liquid environment over a wide

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**TABLE 1** Performance comparison of various Fe-N-C materials for ORR in alkaline solution

| Catalyst | MN_x site | Metal loading | BET SA (m²/g) | E_{onset} (V) | E_{1/2} (V) | E_{1/2} loss after CV cycles (0.6–1.0 V) |
|----------|-----------|---------------|---------------|--------------|-------------|-----------------------------------------|
| Fe SAs-N/C-2040 | Edge FeN4 | 0.200 wt% | 1393 | 1.000 | 0.909 | 10,000 cycles, no E_{1/2} loss |
| Fe/N-G-SAC43 | FeN4 | 0.670 wt% | 532 | 0.980 | 0.890 | 10,000 cycles, 3 mV |
| Fe-SAs/NPS-HC51 | FeN4 on S,N-doped carbon | 1.540 wt% | – | 0.960 | 0.912 | 5000 cycles, 5 mV |
| Fe-N/P-C-70044 | FeN4P | 1.030 at% | 828 | 0.941 | 0.867 | 10,000 cycles, no E_{1/2} loss |
| Fe-SAs/NSC49 | FeN4 on S,N-doped carbon | 0.870 wt% | 547 | 1.000 | 0.870 | 5000 cycles, no E_{1/2} loss |
| FeCl1N4/CNS50 | FeN4Cl | 1.500 wt% | – | 1.020 | 0.921 | 10,000 cycles, 8 mV |
| Fe-ISA/SNC53 | FeN2N2 | 0.947 wt% | – | 0.980 | 0.896 | 15,000 cycles, no E_{1/2} loss |
| m-FeSNC56 | FeN2 | 0.550 wt% | 1483 | 0.950 | 0.904 | 5000 cycles, 4 mV |
| Fe-NSDC54 | FeN3S | 0.320 at% | 1534 | 0.920 | 0.840 | – |
| FeCo-ISAs/CN60 | FeN4 and CoN4 | 0.964 wt% 0.218 wt% | – | 0.995 | 0.920 | 5000 cycles, no E_{1/2} loss |
| Commercial Pt/C79 | 20 wt% | – | 1.000 | 0.850 | – |

Abbreviation: ORR, oxygen reduction reaction.
temperature range of 390–923°C for the carbonization of a Fe-containing poly(o-phenylenediamine) precursor. The continuous molten reaction environment created the salts yielded Fe-N-C materials with high porosity, high mass yield, and high N content, thus delivering an $E_{1/2}$ of 0.803 and 0.918 versus RHE in acid and alkaline electrolytes, respectively.

### 3.4 On-surface deposition of FeN₄ sites

Aside from efforts to engineer porosity in the carbon support (typically N-doped carbon support), controlling the location of FeN₄ sites is important. Unlike the direct pyrolysis of Fe-containing carbon-based precursors, the chemical vapor deposition (CVD) method involves the evaporation of a metal precursor then depositing it onto a substrate (Figure 9A). The generated metal-containing vapor carried by an inert gas flow to a downstream location where it is deposited onto the substrate (typically an N-doped carbon), leading to the creation of MN₄ sites. This CVD method successfully prevented the undesirable migration and aggregation of metal atoms, which inevitably occurs in the traditional high-temperature pyrolysis processes when the metal loading is more than 1 wt%. The evolution of Fe ions into FeN₄ sites on N-doped carbon was investigated by in situ XAS experiments (Figure 9B).

#### TABLE 2 Performance comparison of various Fe-N-C materials for ORR in acid solution

| Catalyst                      | MNₓ site   | Metal loading | BET SA (m²/g) | $E_{\text{onset}}$(V) | $E_{\text{1/2}}$(V) | $E_{\text{1/2}}$ loss after CV cycles (0.6–1.0 V) |
|-------------------------------|------------|---------------|---------------|-----------------------|---------------------|-------------------------------------------------|
| Fe-N-C-950                    | Reduced FeN₄ | 0.320 wt%     | 1498          | 0.920                 | 0.780               | 10,000 cycles, 12 mV                             |
| Fe₄N₄/GM                      | Edge FeN₄  | 0.960 at%     | 1070          | 0.900                 | 0.800               | –                                               |
| ZIF-NC-0.5Fe-700               | FeN₄ with contraction | 1.120 wt%     | 396           | 0.980                 | 0.840               | 30,000 cycles, 31 mV                             |
| Fe-N-C-60                     | Edge FeN₄  | –             | 387.1         | 0.950                 | 0.800               | 5000 cycles, no $E_{1/2}$ loss                   |
| 5% Fe-N/C                     | Fe₃Nₓ     | 0.390 at%     | 1036          | 0.860                 | 0.735               | –                                               |
| FeNC-S-MSUFC-2                | FeN₄ on S,N doped carbon | 0.045 at%     | 1180          | 0.850                 | 0.730               | 3000 cycles, no $E_{1/2}$ loss                   |
| (Fe,Co)/N-C                   | Fe₃Nₓ,CoN₄ | –             | –             | 1.060                 | 0.863               | 50,000 cycles, no $E_{1/2}$ loss                 |
| Fe/Co-N-C                     | FeN₄,CoN₄ | –             | 807.6         | 1.000                 | 0.850               | 10,000 cycles, 20 mV                             |
| Fe₂-N-C                       | Fe₂N₆     | 0.380 wt%     | 1090          | 0.950                 | 0.780               | 20,000 cycles, 20 mV                             |
| FeCo₉₃                      | FeCoN₅     | 1.060 wt% 1.120 wt% | –             | 1.000                 | 0.860               | 5000 cycles, 13 mV                               |
| 1.5Fe-ZIF                     | FeN₄      | 2.140 wt%     | 556           | 0.980                 | 0.880               | 40,000 cycles, 30 mV                             |
| Fe-ZIF-50 nm                  | FeN₄      | 0.450 at%     | 614           | 0.980                 | 0.850               | 10,000 cycles, 20 mV                             |
| 55@100@30                    | FeN₄      | 0.380 at%     | 651           | 0.950                 | 0.860               | 30,000 cycles 30.8 mV                            |
| FeSA-G                       | FeN₄      | 7.700 wt%     | 670.8         | 0.950                 | 0.804               | 5000 cycles, 20 mV                               |
| TP[@28(SiO₂)-650-C]          | FeN₄      | 3.010 wt%     | 1648          | 0.930                 | 0.823               | $i-t$ at 0.5 V for 10000 s                       |
| SA-Fe-NHPC                   | FeN₄      | 1.120 wt%     | 1327          | 0.850                 | 0.760               | –                                               |
| Fe₄N₄/HOPC-c-1000             | FeN₄      | 0.330 at%     | 1483          | 0.900                 | 0.800               | –                                               |
| Fe₆Nₓ-N/C                    | FeN₄      | 3.460 wt%     | 1615          | 0.950                 | 0.800               | 20,000 cycles, 5 mV                              |
| FeNC-CVD-750                  | FeN₄      | 2 wt%         | 807           | 0.950                 | 0.850               | –                                               |
| 0.17CVD/Fe-NC-kat            | FeN₄      | 0.280 at%     | 216           | 0.963                 | 0.835               | 50,000 cycles, 35 mV                             |
| Fe₂-Zs-C                     | FeN₄O     | 3 wt%         | 1265          | 0.902                 | 0.805               | 10,000 s 17 mV                                   |
| H-Fe₄N₄-C                    | FeN₄      | 1.200 wt%     | 917           | 0.950                 | 0.770               | –                                               |
| Commercial Pt/C              | FeN₄      | 20 wt%        | 1000          | 0.860                 |                     | –                                               |

Abbreviation: ORR, oxygen reduction reaction.
TABLE 3  Performance comparison of Fe-N-C catalysts in H₂-O₂ fuel cells and H₂-air fuel cells

| Catalyst          | \(P_{\text{max}}\) (W/cm²) 1 bar H₂-O₂ | \(P_{\text{max}}\) (W/cm²) 1 bar H₂-air | Current density (A/cm²) 1 bar H₂-O₂ | Current retention after durability tests 1 bar H₂-O₂ |
|-------------------|--------------------------------------|----------------------------------------|------------------------------------|----------------------------------------------------------|
| FeN₄/GM⁴¹         | 0.74 (30 psi)                        | 0.430                                  | –                                  | –                                                        |
| ZIF-NC-0.5Fe-700¹⁹ | 0.73                                 | 0.320                                  | 0.030@0.9 V_{IR-free}                | 72%, 0.85 V, 50 h                                        |
| Fe₇ₓN₄₋ₓC-60¹²     | 0.74                                 | –                                      | –                                  | –                                                        |
| (Fe,Co)/N-C⁵⁹     | 0.85                                 | 0.505                                  | –                                  | ~100%, 0.6 A/cm², 100 h                                  |
| 55%100@30²       | 0.75                                 | 0.340                                  | 0.035@0.9 V_{IR-free}                | –                                                        |
| TPI@Z8(SiO₂)-650-C³⁰ | 1.18 (2.5 bar)                      | 0.420                                  | 0.022@0.9 V_{IR-free}                | 20%, 0.5 V, 50 h                                        |
| Fe₇ₓN₄₋ₓHOPC-100₀³¹ | 0.69                                 | 0.420                                  | 0.750@0.6 V_{IR-free}                | 53%, 0.7 V, 100 h                                       |
| Fe₇ₓN₄₋ₓC⁸⁵     | 0.68                                 | –                                      | 0.463@0.8 V_{IR-free}                | 50%, 0.5 V, 20 h                                        |
| 1.5Fe-ZIF¹¹       | 0.67                                 | 0.360                                  | 0.044@0.87 V_{IR-free}               | 48%, 0.7 V, 118 h                                       |
| FeNC-CVD-750⁹⁹   | –                                    | 0.370                                  | 0.033@0.9 V_{IR-free}                | –                                                        |
| 0.17CVD/Fe-NC-kat¹⁰² | 0.70                               | 0.320                                  | 0.027@0.9 V_{IR-free}                | 60%, 0.7 V, 100 h                                       |
| Fe₂-Z8-C¹⁰³       | 1.14 (2.5 bar)                       | –                                      | 0.035@0.9 V_{IR-free}                | 14%, 0.5 V, 50 h                                        |
| H-Fe₇ₓN₄₋ₓC¹⁰⁴   | 0.71                                 | 0.220                                  | 1.550@0.43 V_{IR-free}               | –                                                        |
| Fe SAs/N-C¹⁰⁵     | 0.75                                 | 0.350                                  | –                                  | –                                                        |
| 2025 DOE Target   | –                                    | –                                      | 0.044@0.9 V_{IR-free}                | –                                                        |

area of Fe³⁺/Fe²⁺ redox peaks (Figure 9F), the SD of FeN₄ site in FeNC-CVD-750 was determined to be 2 × 10²⁰ sites·g⁻¹.⁹⁹ Remarkably, the FeN₄ content with respect to the total Fe sites was approximately 90%, and with the accessible FeN₄ sites measured with respect to the total FeN₄ sites being 100%. Further, the Fe³⁺/Fe²⁺ redox potential determined from in situ XAS was consistent with that observed in the CV curve (Figure 9G,H), consistent with an abundance of accessible FeN₄ sites in FeNC-CVD-750. Due to the high ratio of FeN₄ sites and accessible FeN₄ sites, the FeNC-CVD-750 catalyst exhibited a high ORR \(E_{1/2}\) of 0.85 V in 0.5 M H₂SO₄ electrolyte. When used as cathode catalyst in 1 bar H₂-O₂ fuel cell, the catalyst delivered a high current density of 33 mA·cm⁻² at 0.90 V_{IR-free}. Wu et al.¹⁰² demonstrated that the CVD method allowed a gas-solid reaction between 2-methylimidazole vapors and a Fe-containing ZnO solid, generating a new MOF topology, that is, \(kat\) phase. Compared to ZIF-8, the new \(kat\) phase featured narrower pores, thus assisting the confinement of Fe atoms to achieve a high density of FeN₄ sites (26 µmol/g).

4  CONCLUSIONS AND PERSPECTIVES

In this review, different strategies for synthesizing high-performance Fe-N-C electrocatalysts for ORR were summarized. We explored two key aspects, (1) improving the intrinsic activity of FeNₓ active sites by tailoring the Fe coordination, and (2) increasing the SD of accessible FeN₄ active sites through engineering porous carbon supports. With a view toward the future discovery of new types of FeNₓ active sites, we examined additional approaches for tuning the activity of Fe active sites, such as the introduction of heteroatom dopants in the carbon matrix, or the construction of dual-atom sites, both of which have shown to be effective in enhancing ORR activity. Current research relating to Fe-N-C catalysts for ORR aims to increase SD of accessible FeN₄ active sites, which involves a judicious selection of pyrolysis precursor, or the introduction of pore-forming agents ahead of FeN₄ site formation. As summarized in Tables 1–3, a diverse range of Fe-N-C electrocatalysts have recently been reported that demonstrate exceptional ORR activities, exceeding that of commercial Pt/C in alkaline electrolytes, and approaching that of Pt/C in acid electrolytes. However, there remains a performance gap (operational stability at high current densities) between Fe-N-C electrocatalysts and PGM electrocatalysts in practical applications of the fuel cell, with the 2025 DOE Target for PGM-free electrocatalysts still proving challenging to achieve. Below we offer our perspectives regarding the future directions of Fe-N-C electrocatalysts for ORR:

(1) The gap between the designed new FeNₓ sites and the experimentally achieved FeNₓ sites remains an issue.
First, the complex pyrolysis synthetic processes inevitably lead to the resulting FeN\textsubscript{x} sites with diverse coordination, which means the constructed new FeN\textsubscript{x} sites with high TOFs often exist in a low ratio among all the detected FeN\textsubscript{x} sites. Aside from using precursors with well-defined structures (e.g., metal organic frameworks or covalent organic frameworks), developing a facile low-temperature synthetic method is critical to preserve the designed structure in the final Fe-N-C product. Also, new FeN\textsubscript{x} sites can be engineered by more precisely controlled carbon structures (e.g., four-member, five-member, or seven-member carbon ring). Second, the structural identification of the iron centers as well as the neighboring few atoms (e.g., N and C) is essential but limited so far. Currently, atomic-resolution HAADF-STEM seems to be the only technique directly probing the Fe single atoms, as well as the supported carbon revealing graphene honeycomb lattice. Fe coordination models established from Fe K-edge XANES and EXAFS fittings should be presented/viewed with caution since such results represent the average of all detected metal atoms, whereas for most N-doped carbon-supported catalysts a diverse array of metal coordination might exist. The oxidation states/spin states of Fe atoms serve as a useful indicator of the average electronic states of central Fe sites, which require hard XAS analyses (Fe K-edge) and Mössbauer spectroscopy for the bulk Fe analysis, and soft XAS (Fe L-edge), XPS for near-surface region analyses. Ideally, such analyses would be performed under both in situ and ex situ conditions to allow the true working state of the FeN\textsubscript{x} sites to be probed. 

(2) Achieving Fe-N-C materials with high total Fe loadings (e.g., more than 3 wt\%) as well as high FeN\textsubscript{x} utilization (e.g., more than 50%) is still a challenge. To further improve SD and TOF of FeN\textsubscript{4} active sites, attention can be paid to the rational design of carbon supports comprising abundant surface micropores and mesopores in which surface micropores are capable of the accommodation of FeN\textsubscript{4} active sites with high SD, While mesopores afford the external surfaces, with high TOF for fast mass transport of ORR intermediates. Also, quantification of the SD and TOF of FeN\textsubscript{4} active sites and establishing correlations between the SD and TOF of FeN\textsubscript{x} active sites in porous Fe-N-C materials are important (to date, only a few works cover this important aspect). The SD-TOF maps allow meaningful performance comparison of different Fe-N-C catalysts for ORR, and inform the future design of carbons with optimal micro/meso/macro-porous architectures, allowing both a high surface FeN\textsubscript{x} SD and easy transport of reactants (i.e., O\textsubscript{2} and H\textsuperscript{+}) to such sites.

(3) The intrinsic activity and SD of FeN\textsubscript{x} sites are closely linked to each other and work collectively to boost the ORR performance of Fe-N-C electrocatalysts. However, few studies took both factors into consideration. The combined strategies for constructing porous carbon supports as well as controlling over the central Fe coordination could be feasible. We also believe one Fe-N-C electrocatalyst comprising both high intrinsic activity of advanced FeN\textsubscript{x} sites and high SD could be realized by the in-depth study of surface FeN\textsubscript{x} sites with the modified electronic structures induced by the pores, defects, and surface functional groups.

(4) The integration of Fe-N-C electrocatalysts into the membrane electrode assembly of real fuel cells needs more work. Under rotating disk electrode (RDE) tests and fuel cell tests, huge activity and stability differences can arise. These differences relate to ORR processes in practical fuel cells being much more complicated and thermally/mechanically demanding, involving three-phase transport, heat/water management, high-potentials at startup/shutdown, etc. More knowledge/methodologies need to be achieved/established from transferring RDE ORR into fuel cell conditions. For example: (1) How does the adsorption/desorption behavior of FeN\textsubscript{4} sites to ORR intermediates change as a function of O\textsubscript{2} pressure? (2) How to quantify the SD of FeN\textsubscript{4} sites under fuel cell testing conditions?

In summary, Fe-N-C materials rich in FeN\textsubscript{x} sites hold great promise as cathode catalysts in PEFCs. Over the last 5 years, enormous progress has been made in the synthesis and performance testing of Fe-N-C catalysts for the ORR, with the best-performing catalysts being comparable to Pt/C in both acid and alkaline media (in alkaline media, Fe-N-C catalysts frequently outperform Pt/C). Recent work has highlighted the key role of the porosity of the carbon support in controlling the maximum FeN\textsubscript{4} loading and SD of catalytic accessible active sites for ORR. The main challenge ahead for researchers is a successful integration of Fe-N-C catalysts into practical fuel cells.

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CONFLICT OF INTEREST
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