

Atomically dispersed transition-metal electrocatalysts for oxygen reduction reaction in fuel cells: activity versus stability

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Abstract | Polymer electrolyte fuel cells (PEFCs) operating on clean and sustainable hydrogen represent potentially the most attractive solution for clean transportation. However, PEFCs must first overcome the high-cost challenge, primarily related to the use of considerable amounts of platinum group metal (PGM) catalysts, especially for catalyzing the very slow oxygen reduction reaction (ORR) at the cathode. The most attractive path in that regard is a complete replacement of precious metal catalysts by PGM-free materials with similar or better performance. A noteworthy progress has been achieved in the field of PGM-free electrocatalysis in the past decade, with numerous promising catalysts proposed, their performance improved, and fundamental mechanistic insights offered. However, the best-performing catalysts do not yet meet the requirements of practical systems. One significant hurdle in catalyst discovery is relying heavily on empirical rather than rational design-based approaches. This Perspective article focuses on the most promising PGM-free ORR catalysts based on atomically dispersed, nitrogen-coordinated single-atom metal sites (M-N-C catalysts). We specifically concentrate on the active site structure and critical factors governing catalytic activity and performance durability. We propose potentially effective strategies for improving performance by controlling the catalyst structure at atomic, meso-, and nanoscales. We highlight the importance of overcoming often observed activity-stability trade-offs and the significance of advanced modelling for the rational design of catalysts.

Introduction

Developing clean and sustainable hydrogen technologies is crucial for global efforts aimed at decarbonizing most emission-heavy industry sectors, minimizing climate changes, and eventually realizing a carbon-neutral economy¹. Of several available technologies, low-temperature polymer electrolyte fuel cells (PEFCs) for automotive applications have drawn by far the most attention as an essential strategy for assuring energy and environmental sustainability². They offer high-power density, low weight, compact size, fast start-up, and quick response to the power demand,³ all critically important for the electrochemical conversion of chemical energy of hydrogen into electricity in automotive power systems, in particular in medium- and heavy-duty transportation. However, the large-scale advent of PEFCs continues to be limited by the prohibitive cost of platinum-group metal (PGM) catalysts, mainly for the notoriously sluggish oxygen reduction reaction (ORR) at the cathode⁴. Besides the long-lasting efforts in Pt thrifting, the most attractive path toward overcoming the cost barrier has been the development of PGM-free catalysts⁵.

Following the discovery in the 1960's of the macrocyclic molecular catalysts containing well-defined, ORR-active MN₄ moieties, the most significant progress has been achieved *via* the

development of M-N-C catalysts (M: Fe, Co, Mn, etc.) obtained in a high-temperature process (above 700 °C)⁶⁻⁸. By now, these catalysts have shown by far the highest ORR activity and stability in the challenging acidic environment of the PEFC cathode, much superior to other explored PGM-free formulations such as metal-free carbons, carbides, sulphides, and oxides⁹. The performance of M-N-C catalysts has been continuously improved thanks to continuous modifications to the atomic active-site structures and surrounding carbon morphologies¹⁰.

Recent advances in the spectroscopic and microscopic characterization techniques have allowed to correlate the measured ORR activity of M-N-C catalysts with the presence of atomically dispersed, nitrogen-coordinated transition metal sites¹¹⁻¹⁴. Of numerous M-N-C materials, Fe-based catalysts have consistently shown the highest activity attributed to single-atom metal sites coordinated by four nitrogen ligands, which are in turn linked to carbon atoms in carbon planes^{12,15}. However, the activity and stability (performance durability) of different catalysts vary widely, depending primarily on the synthesis details such as the type of Fe, N, and C precursors, thermal activation conditions, and types of a template or support used¹⁶. The synthesis conditions are crucial to achieving the right coordination environment of the single-atom metal sites and coordination environment next to active sites that together determine the ORR performance¹⁷. The catalyst nanostructures and morphologies also impact the surface concentration of active sites, as well as the catalyst porosity, which in turn directly affects the mass transport and crucially important properties of the catalyst-ionomer interface^{18,19}.

The high performance of recent Fe-N-C catalysts has been at least partially attributed to the use of zeolitic imidazolate framework (ZIF)-8 precursors and the formation of a unique 3D metal-organic framework (MOF) structure capable of hosting metal-precursor species *via* chemical doping, adsorption, and encapsulation⁹. During the subsequent high-temperature treatment, the Fe species are gradually converted into single-atom Fe sites *via* coordination with N atoms to yield the active sites, such as the often proposed FeN₄ moieties, bound to microporous carbon formed during the simultaneous carbonization of ZIF-8 precursor¹⁷. The first principles density-functional theory (DFT) calculations have provided some explanation of the experimental observations and allowed for predicting the ORR activity of FeN₄ sites expressed in terms of the limiting potentials and calculated activation barriers for O-O bond scission²⁰. Among others, the predictions include the Fe-N bond lengths, local coordination environment, carbon structure, energetics of O₂, and reaction intermediates that are optimal for the ORR kinetics²¹⁻²⁴.

While at high loadings in the PEFC cathode (*ca.* 4 mg cm⁻²) the performance of Fe-N-C catalysts is close to that of Pt/C catalysts when used at low loadings, acceptable from the cost point of view (*ca.* 0.1 mg_{Pt} cm⁻²), their stability during the ORR is insufficient, likely due to the demetallation of the N-coordinated Fe sites and corrosion of the surrounding carbon. To address the stability challenge, the focus of Fe-N-C catalyst development has shifted, at least in part, to degradation mechanisms and exploring effective strategies for creating FeN₄ sites with enhanced stability while maintaining adequate activity. Recent *operando* ORR and fuel cell studies have suggested that pyridinic-N-coordinated single Fe sites better resist demetallation during the ORR than the pyrrolic-N-coordinated sites but are less active due to O₂ overbinding^{25,26}. Breaking the apparent activity-stability trade-off in the design of Fe-N-C catalysts represents an essential challenge of PGM-free electrocatalysis²⁷.

Tuning the electronic properties and structure of the single-atom metal sites by regulating the metal coordination sphere is paramount for controlling the reaction pathways and catalytic properties^{28,29}. In this context, the currently prevailing highly simplified approaches used in theoretical studies are yet to provide unambiguous insights into the ORR mechanism under the

actual fuel cell conditions²³. For example, it is still unclear how the MN₄ coordination, bonding, local carbon structure, and immediate chemical/electrochemical environment affect the catalytic activity, four-electron selectivity, and stability^{30,31}. The primary mechanisms of catalyst degradation during the ORR at the atomic level are not fully understood either³².

The development of M-N-C catalysts has been almost exclusively empirical rather than model-based design. A comprehensive and innovative approach is required to ensure further progress in PGM-free electrocatalysis. The approach needs to complementarily combine computational materials science—including artificial intelligence (AI) and machine learning (ML) methods, as well as electrochemical descriptors—judicious materials synthesis, *operando* atomic-level characterization, and high-fidelity property measurements for exploring optimal catalyst structures and morphologies at multiple lengths, from atomic/molecular to nanoscale.

In this Perspective article, we critically assess the current understanding of the nature of presumed ORR active sites in M-N-C catalysts and their formation mechanism during the high-temperature activation step. We also analyse correlations between the atomic structure and coordination environment of the active sites and their activity and stability as an important steppingstone on the path to a rational design of catalysts. Finally, we outline the pathway and future directions towards achieving simultaneous improvements in M-N-C catalyst activity and performance durability using combined experiment-theory approaches, stressing the critical importance of the input from theory.

Elucidation of active site structures

Identification of active sites: from metal-free carbons to atomically dispersed transition metal sites. In the early days of the development of PGM-free catalysts, the lack of control over the chemistry and structure of M-N-C materials during the pyrolysis resulted in the formation of various metal species, *e.g.*, metal oxides/carbides or metal clusters³³, making identification of the actual active sites very challenging^{34,35}. Pyridinic and graphitic nitrogen atoms with excess valence electrons were proposed to simultaneously modify the electronic properties and structure of carbon planes, therefore forming active ORR catalytic sites^{16,36,37}. This hypothesis was supported by extensive DFT studies^{38,39}. However, the often-unavoidable presence of trace transition-metal contaminants in the catalyst precursors ultimately cast doubt on the claims of ORR activity of the metal-free catalysts, not only in the acidic but even in the alkaline media⁴⁰⁻⁴².

More recently, the development of highly active catalysts, exclusively containing single-atom metal sites, allowed to directly correlate the metal content and catalytic activity, highlighting the importance of metal sites in catalysts^{12,43}. Advanced characterization techniques, including high-resolution electron microscopy, X-ray absorption spectroscopy, and Mössbauer spectroscopy, allow for direct insight into the chemical nature, local atomic-level structure, and coordination environment of the likely active sites, such as the already mentioned nitrogen-coordinated transition-metal atoms (**Figures 1a and 1b**)⁴⁴⁻⁴⁶. DFT calculations then allow further to estimate their possible activity, selectivity for the four-electron ORR, stability, as well as predict the ORR pathway^{17,47} as a function of the metal, its coordination environment, and geometry at an atomic level^{13,14,48-50}. Among others, the first principles DFT calculations have predicted that the most favourable pathway (**Figure 1c**) should involve O₂ chemisorption at the FeN₄ site, followed by the first protonation step to form OOH, O–O bond scission to generate O and OH, and then the second protonation step to yield H₂O, the ultimate and desirable reaction product in acidic media. In line with experimental observations, DFT calculations have also projected that ORR should occur at the FeN₄ site at a more positive potential and lower activation energy of the O–O bond scission

than at CoN_4 and MnN_4 sites¹⁷. Among the possible elemental steps, the OOH dissociation has been predicted to be the rate-determining step (RDS)⁵¹. More recently, a new constant-potential hybrid solvation-dynamic model has been developed, aimed at simulating electrochemical kinetics at the solid-liquid interfaces⁵². According to that model, the RDS is the replacement of adsorbed water on Fe sites by O_2 molecule. Interestingly, the corresponding activation barrier is counterintuitively predicted in this model to decrease with decreasing electrode potential. This can be explained by stronger Fe– O_2 binding and weaker Fe– H_2O binding at lower potentials due to O_2 gaining electrons and H_2O donating electrons to the catalyst. The ongoing RDS debate reflects difficulties in theoretically describing the ORR mechanism, further complicated by the need to account for the effects of solvation and electrode potential.

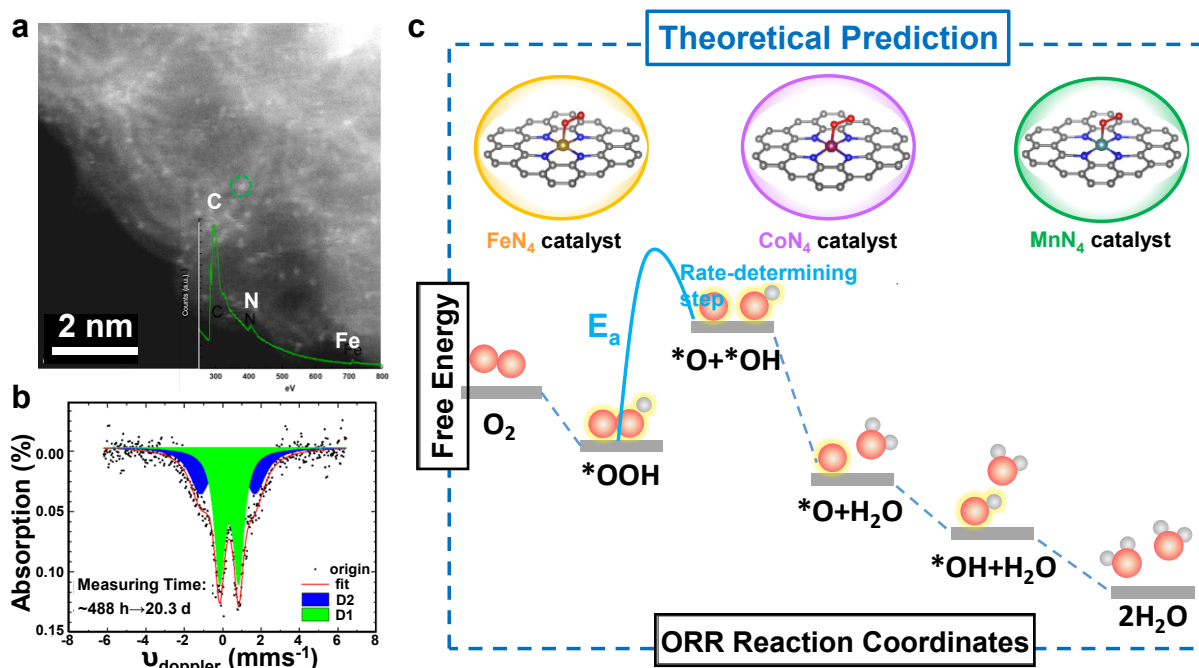


Figure 1. Atomically dispersed, nitrogen-coordinated metal sites in Fe-N-C catalysts. (a) Advanced scanning transition electron microscopy/electron energy loss spectroscopy (STEM/EELS) verification of the atomic dispersion of metal sites and their colocation with N and C atoms. (b) Mössbauer spectroscopy evidence of atomic dispersion of Fe and nitrogen coordination of Fe atoms in two different forms (D1 and D2) reproduced with permission from REF.¹², copyright 2017 American Chemical Society. (c) DFT calculations of possible elemental steps of the ORR on atomically dispersed and nitrogen-coordinated metal sites (e.g., Fe, Co, and Mn) reproduced with permission from REF.¹⁷, copyright 2019 American Chemical Society.

Active site formation. Single-atom metal sites in heat-treated M-N-C catalysts are generally more active than metal sites in molecular catalysts containing MN_4 moieties^{53,54}. During the traditional M-N-C synthesis, the active site creation at high temperatures is complex because the formation of M–N bonds is accompanied by carbonization and nitrogen doping⁵⁵. Designing model systems is desirable to decouple the effect of all these complex phenomena and allow to exclusively study Fe–N formation at various temperatures. In a recent work^{56,57}, ZIF-8 was selected as a precursor for designing a model N-doped carbon (N-C) active-site host system by heat-treating ZIF-8 nanocrystals at 1100 °C in argon (Ar) atmosphere. The purpose was to reveal the M–N bond

formation in M-N-C catalysts. The N-C material had a high content of defects and nitrogen-rich hierarchical carbon structure, as well as a considerable content of micro- and mesopores resulting in a high specific surface area of ca. 1000 m² g⁻¹. These properties allowed the N-C material to act as an effective host for atomically dispersed metal sites (e.g., Fe, Mn, or Co). The sites were generated via chemisorption and encapsulation that occurred both outside and inside the N-C phase. The N-doped carbon is thermally stable, maintaining its structure and N-dopant content during the subsequent heat treatments at temperatures as high as 1200 °C, required to activate Fe-N bonds. This allowed for tuning the temperature-dependent formation of M-N bonds without the interference from other processes, such as carbonization and nitrogen loss. The structural properties, revealed via advanced spectroscopic characterization, could then be further linked to catalyst activity, selectivity, and stability⁵⁷. Therefore, The N-doped carbon model system with well-defined chemistry and structure helped to unearth the mechanisms of MN₄ formation and establish structure-property correlations.

Similarly to Fe ions, other metal ions, e.g., Co, Mn, and Ni, can be adsorbed by the N-C host, followed by controlled thermal activation to form stable and active M-N bonds instead of modifying carbon structures and nitrogen dopants^{56,58-61}. Structural advanced characterization techniques, e.g., X-ray absorption spectroscopy (XAS) methods and scanning transition electron microscopy combined with electron energy loss spectroscopy (STEM/EELS), provide insights into the formation mechanism of M-N bonds as a function of the heat-treatment temperature. Electrochemical measurements further correlate the intrinsic catalytic properties with the M-N bond structure.

A significant discovery was that active Fe-N bonds could form at 400 °C⁵⁷, at a temperature much lower than typically required (> 800 °C) for achieving high ORR activity. Such high temperatures are crucial for forming nitrogen-doped carbon to host metal sites, but not necessary for generating the FeN₄ sites themselves^{15,62,63}. The highest ORR activity was observed at a higher heating temperature of 700 °C, likely due to the shortening of the Fe-N bond, according to XAS data. Theoretical calculations suggested that Fe-N bond shortening by ca. 2% should help optimize the O₂ adsorption strength, favouring subsequent O-O bond-breaking during the ORR. For Co-N bonds, this critical transition occurs at 700 °C and becomes optimal at 900 °C⁵⁶, i.e., at higher temperatures than for the Fe-N bond formation. These differences in optimum heat-treatment temperatures may also explain the higher resistance of the CoN₄ site to demetallation. Summarizing, the formation of M-N bonds even appears to be the origin of the ORR activity, even at relatively low temperatures. In contrast, the compressive structural strain of M-N bonds and their shortening at higher temperatures is the key to further activity (and stability) enhancements.

Effect of local atomic structure and coordination environment. Local carbon structure. Modifications to the carbon structure and coordination environment next to MN₄, the most likely active site, seem to directly impact activity and stability^{15,33}. Instead of a relatively compact CoN₄ configuration in the polyaniline-derived Co-N-C catalysts, the more complex CoN₂₊₂ configuration dominates in the ZIF-8-derived Co-N-C catalysts^{64,65}, resulting in much enhanced ORR activity and better 4e⁻ selectivity. DFT calculations suggest that the free-energy change for individual ORR steps at the CoN₂₊₂ site (a CoN₄ moiety bridging over two adjacent zigzag graphitic edges) turns negative, i.e., the reaction becomes exergonic at a potential of 0.73 V. The latter value is more positive than 0.67 V calculated for the conventional CoN₄ site, thus making the reaction at the CoN₂₊₂ site thermodynamically favourable⁶⁴. It is worth noting that the activation energy for the OOH dissociation is lower at the CoN₂₊₂ site (0.69 eV) than at the CoN₄

site (1.11 eV)⁶⁴, making it also kinetically favourable. The effects of defective local carbon structures have been studied for the analogous Fe-based sites, revealing similar ORR activity enhancement^{12,22}.

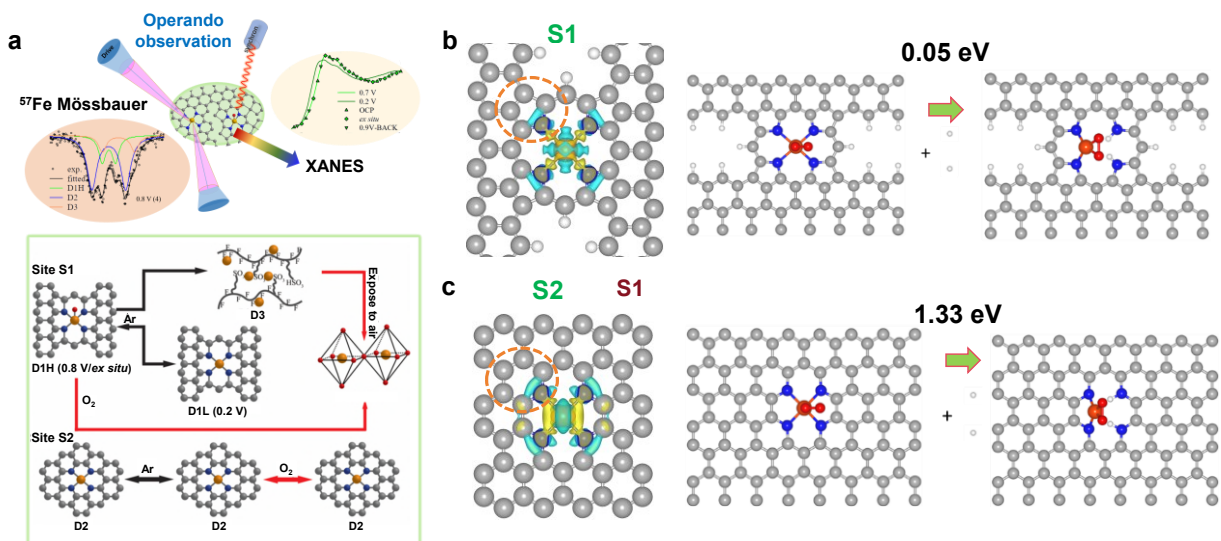


Figure 2. (a) Two types of FeN_4 moieties (S1 and S2 sites) with different nitrogen coordination (pyrrolic vs. pyridinic N) in Fe-N-C catalysts and their dynamic evolutions in the fuel cell cathode under Ar and O_2 atmospheres, determined using *operando* Mössbauer and X-ray absorption spectroscopies, reproduced with permission from REF.²⁵, Springer Nature Limited. DFT prediction of more optimal O_2 adsorption (higher activity) but lower stability of (b) pyrrolic FeN_4 S1 sites than (c) pyridinic FeN_4 S2 sites due to the low energy barriers (0.05 vs. 1.33 eV) of the demetallation process. Reproduced with permission from REF.²⁶, Springer Nature Limited.

Nitrogen coordination. The coordination environment of metal sites plays a crucial role in governing ORR activity and stability^{66,67}. Recent *operando* Mössbauer experiments identified two main FeN_4 site structures with different N coordination environments. One type of Fe sites is $\text{FeN}_4\text{C}_{12}$ (denoted as S1), with Fe at an oxidation state of close to 3+ in a pyrrolic-N ligation environment. During the ORR, they ultimately undergo irreversible transition to ferric oxides, e.g., Fe_2O_3 . By contrast, the electronic state of Fe in the pyridinic-N-coordinated site ($\text{FeN}_4\text{C}_{10}$, denoted as S2) is potential-independent, ferrous (Fe 2+) low- or medium-spin state (**Figure 2a**)^{25,27}. The DFT calculations suggested higher d-orbital occupation in the Fe atom in the S2 site, resulting in a stronger bond to O_2 and lower activity than that of the S1 site (**Figures 2b and 2c**)²⁶. Meanwhile, the calculated activation energy for demetallation caused by nitrogen protonation at the S2 site (2.08 eV) was found to be higher than at the S1 site (1.24 eV), thus suggesting better stability of the S2 sites²⁶. These theoretical predictions were verified by the measurements of catalytic performance and nitrogen coordination (by Mössbauer spectroscopy)²⁶. Thus, increasing the population of more stable S2 sites and/or stabilizing the S1 may be a right guiding principle for designing high-performance Fe-N-C catalysts in the future. While such a rational design of catalysts is highly desirable, the current theoretical models are still too simple to capture all factors influencing the highly complex ORR electrocatalysis, which include solvation, local pH variations, and dynamic changes of the active site driven by electrochemical potentials⁶⁸⁻⁷². More advanced theory methods are required for a comprehensive mechanistic understanding of the ORR and to predict the optimal nitrogen coordination and the local carbon structure²³.

Current limitations of elucidating single-metal sites and ORR mechanism. The single-metal sites such as MN_4 have been theoretically predicted and partially validated through spectroscopy. However, present-day models are still too basic as they only consider MN_4 sites imbedded in ideal graphene planes rather than extended to three-dimensional carbon structures in practical systems. The free-energy change for all elementary ORR steps at FeN_4 sites was calculated using the computational hydrogen electrode method⁷³, requiring several simplifications and approximations. For example, the approach did not account for the presence of electrolytes next to the active site and for applied potentials, nor did it account for their effects on the dynamic changes of chemistry and active site structure during the ORR. The solvent (water) molecules are expected to affect electrochemical reaction rates, selectivity, and stability *via* their interactions with the reactants, reaction intermediates (OOH^* , O^* , and OH^*), and products, as well as the active sites themselves⁷⁴⁻⁷⁶. The local pH changes can alter the speciation of reactants, products, and the reaction mechanism due to their effect on the local potential, the concentration of species, and the electric field in the electrical double layer^{77,78}.

The current understanding of ORR mechanisms continues to be superficial. For example, both single metal-atom-rich M-N-C catalysts and metal-free N-doped carbon catalysts are more active for the ORR in alkaline than acidic media^{79,80}. The exact reason for such a pH-dependent activity is not fully clear yet⁸¹. One possible reason for lower activity in acidic media may be the reduction of charge density *via* the protonation of nitrogen dopants next to the metal active sites⁸². In turn, the enhanced activity of Fe-N-C catalysts in alkaline media may be due to individual contributions from metal-free active sites⁸³ and residual Fe and/or Fe_3C nanocrystals⁸⁴, as well as due to a lower adsorption energy of O_2 and ORR intermediates at FeN_4 sites at high pH values^{85,86}. Ultimately, the effect of pH needs to be accounted for in the computational simulations before different possible ORR mechanisms can be critically assessed. In addition, the single-atom metal sites and their immediate environment may dynamically change during the ORR with changing potentials^{87,88}. Determining reaction pathways needs to account for the adsorption/desorption behaviour of the reaction intermediates as a function of the applied potentials and cell temperatures⁸⁹. The local microenvironments also play an important role in the activity and stability of FeN_4 sites. Recent DFT calculations predict that, thanks to the compressive-strain shortening of the Fe-N bond in FeN_4 sites in confined structures, such sites should have higher ORR activity than those imbedded in flat carbon planes⁵⁷. Furthermore, the FeN_4 sites located in interconnected open-ended, slit-shaped micropores greater than 0.7 nm in width are likely to undergo faster demetallation. This is due to relatively weak interactions with hydrophobic walls of the larger micropores, resulting in the richness of protons and oxygen, and thus more efficient removal of the metal from the FeN_4 site following Le Chatelier's principle⁹⁰.

To address the poor stability challenge, it is essential to elucidate the degradation mechanisms of M-N-C catalysts at different potentials and pH values^{91,92}. Presently, numerous fundamental questions remain unanswered, and some critical areas of PGM-free electrocatalysis research are unexplored. In addition to the Fe-, Co-, and Mn-based systems, catalysts derived using other transition metals may show high ORR activity and potentially attractive stability. In this context, worth mentioning are recent reports of good performance of single and dual-site catalysts based on Zr, Ce, and Cr^{93,94}. Compared to time-consuming “trial or error” experimental efforts, the progress in developing artificial-intelligence and machine-learning approaches⁹⁵⁻⁹⁷ with accurate data input from *in situ* and *operando* spectroscopy methods⁹⁸⁻¹⁰⁰ could significantly accelerate the exploration and development of viable catalysts, especially when combined with high-throughput synthesis and characterization techniques¹⁰¹. For example, an implementation of graph neural

networks trained on *ab initio* data can significantly speed up the catalyst discovery process by concurrently predicting site reactivity, surface stability, and catalyst synthesizability descriptors¹⁰².

Strategies for improving catalytic activity

While theory-guided rational catalyst design is desirable to improve the activity and stability of PGM-free ORR catalysts, current approaches mainly rely on experimental trial-and-error methods along with oversimplified first-principles DFT calculations, mostly to merely rationalize the experimental outcomes¹⁰. In addition, the development of effective multi-scale models to simulate mass and charge transport in three-dimensional electrodes needs to happen for overall performance improvement^{18,103}.

Adjusting local carbon structures to enhance ORR activity. Like Pt catalysts, the most active FeN₄ sites suffer from relatively strong adsorption of O₂ and ORR intermediates that reduce the activity^{48,104}. Thus, modifying the electronic structure of FeN₄ active sites to weaken interactions between the sites and reaction intermediates represents potentially effective strategies to enhance “intrinsic” ORR activity. DFT calculations have suggested that four-nitrogen-coordinated single-atom Fe sites (FeN₄) should be the most stable, have the lowest formation energy and the lowest energy barrier for the rate-limiting ORR step associated with the reduction of adsorbed OH* adsorption (**Figure 3a**)¹⁰⁵. Therefore, changing the N coordination number may not be a feasible path for improving “intrinsic” activity. Instead, altering the carbon environment next to the FeN₄ sites can reduce activation energy for the O-O bond break-up. DFT calculations have implied that the FeN₄-C₈ sites at the edge of micropores have lower activation energy for the O-O bond breaking, favouring a direct four-electron pathway. Besides, the theory studies have predicted that introducing defects into carbon planes can lower the adsorption energy of intermediates such as O₂*, OH*, and OOH* at adjacent FeN₄ sites, improving ORR activity²².

Catalysts containing highly ordered carbon often have low activity because graphitic carbons donate electrons to the metal centres, strengthening the adsorption of ORR intermediates¹⁰⁶. In contrast, the use of highly disordered carbon can result in electron withdrawal, lowering the electron density and downshifting in the *e_g*-orbital of metal sites, thus enhancing the ORR^{107,108}. Consequently, an intentional introduction of defects and micropore-rich carbon can yield catalysts with improved activity. Based on this presumption, using ammonia to etch high surface-area carbon black support (e.g., Black Pearls) produced highly active Fe-N-C catalysts^{109,110}. The activity enhancement was likely due to the increased density of active sites in the form of FeN₄-C₈ sites, confirmed by the ⁵⁷Fe Mössbauer spectroscopy. The post-pyrolysis heat treatment of Fe-N-C catalysts using ammonium-containing solid salts, such as NH₄Cl, is also effective in generating a high content of defects in the carbon lattice²⁶. The resulting Fe-N-C catalyst is highly active, delivering 44 mA cm⁻² at 0.9 V_{IR-free} in an H₂/O₂ fuel cell. Ammonium chloride decomposes into gaseous NH₃ and HCl at the high-temperature treatment, imparting similar defects in the carbon structure¹¹¹ to those achieved using a high-temperature NH₃-gas treatment^{110,112}. At the same time, the defect-rich carbons tend to be less resistant to corrosion and demetallation of FeN₄ active sites. They suffer from accelerated performance loss under fuel cell operating conditions, losing as much as 94% of their initial activity in an accelerated stress test (AST)¹¹³. Thus, new strategies for controlling local carbon defects without forgoing stability are desired.

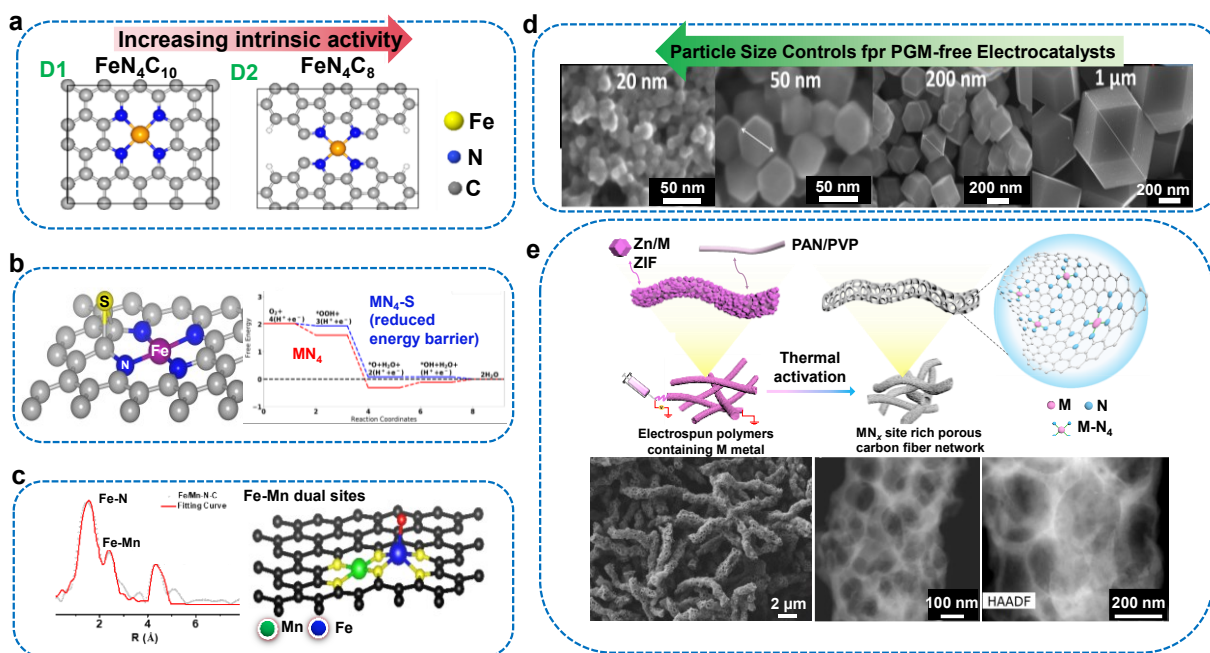


Figure 3. Strategies for improving “intrinsic” activity of M-N-C catalysts: (a) Controlling local carbon structures to populate FeN_4C_8 sites, reproduced with permission from REF.²² copyright 2017, American Chemical Society; (b) doping additional heteroatoms such as S to modify electronic structures of central Fe sites, reproduced with permission from REF.¹¹⁴, copyright 2021, American Chemical Society; and (c) designing dual metal site structures such as Fe-Mn sites to optimize intermediate adsorption/desorption during the ORR, reproduced with permission from REF.¹¹⁵ Elsevier; engineering catalyst morphologies and nanostructures to maximize mass activity by (d) tuning catalyst particle size to expose more active sites at the surface, reproduced with permission from REF.¹⁵, copyright 2017, American Chemical Society; and (e) imparting hierarchical porosity with optimal balance among micro-, meso-, and macro-pores to improve the active site accessibility and mass transport during the ORR, reproduced with permission from REF.¹¹⁶, Wiley.

Tuning surface basicity and hydrophilicity/hydrophobicity of the carbon *via* functionalization can affect electron delocalization and electron donating capability, further altering the interaction between the FeN_4 sites and ORR intermediates²⁸. Additional heteroatom doping with, *e.g.*, S, B, and P, have also been explored to create structural defects in the sp^2 carbon and optimize electronic properties of MN_x sites to weaken adsorption of ORR intermediates and improve ORR activity (**Figure 3b**)^{28,114,117-120}. However, the actual effect of additional dopants on the catalytic activity and stability is still under debate, with questions remaining about the accuracy of determining the structure and activity of studied catalysts due to the difficulties in discriminating between N and other lighter dopants, *e.g.*, S, B, Cl, or P, by conventional X-ray absorption spectroscopy.

Dual/multi-metal sites. If two atomically metal sites are sufficiently close for electronic interaction to occur, such an interaction can result in vastly different electrocatalytic properties. The two metal sites can be identical or involve different metals. Sites involving two different metals ($\text{M}_1/\text{M}_2\text{-N-C}$) are especially desirable, if successfully realized in a catalyst, as they can offer virtually unlimited opportunities for maximizing ORR activity and maintaining stability. Recently, such dual-metal catalysts containing nitrogen-coordinated and atomically dispersed metal sites have been experimentally and theoretically investigated to address the low activity and stability of single-metal sites^{121,122}. The catalytic performance of single-metal sites is constrained by either too weak

or too strong binding of some critical intermediates such as $^*\text{OOH}$ and OH^* . Tuning M-N coordination and bond geometry can improve the activity of M-N-C catalysts only to a certain degree but cannot fundamentally change the active site structure. Nitrogen coordination of two different metal sites is much different from that of the single-metal sites, offering an opportunity to modulate the site's electronic and steric properties. The configuration of two adjacent metal centres could provide favourable conditions for O_2 adsorption and subsequent O–O bond breaking. Possible charge transfer between the two metals can further modify the electronic properties and enhance reaction kinetics, as shown in **Figure 3c** for an Fe-Mn catalyst. Thus, incorporating a second transition metal could break the activity-stability trade-off and linear scaling relationships for M-N-C catalysts¹²¹.

Like single-metal catalysts, MOFs, e.g., ZIF-8, with their inherent compositional and structural versatility, are an ideal platform for achieving dual-atom and possibly even multi-atom chelation and controlling the active site density¹²³. However, maintaining atomic dispersion of the metals and controlling the formation of the $\text{M}_1\text{--M}_2$ bond in dual-metal sites remains challenging. The challenges involve in particular: (i) avoiding metal atom aggregation; (ii) mitigating metal clusters by establishing spatial confinement; and (iii) selecting right precursors to assure uniform growth of dual-metal sites within a given matrix. All these challenges call for the development of innovative precursors and new synthesis approaches. The correlation between the bimetallic centres and reaction mechanism needs new experimental and theoretical insights to answer whether both or only one metal is ORR-active in dual-metal catalysts.

In this context, worth mentioning are also the challenges in differentiating metal centres in bimetallic catalysts. Advanced atomic-level characterization is required to accurately define the geometry and electronic configuration of dual-metal sites, such as the type of adjacent atoms, coordination number, and interatomic distances. Combining X-ray absorption spectroscopy with DFT calculations is effective in modelling interactions between two metals (M_1 , M_2), local coordination environments, and their activity and selectivity, as well as in determining the dual-metal site structures¹²⁴. Given the very size of the search space for active metal-metal pairs, the development of machine learning algorithms for efficiently predicting materials with high performance will represent a powerful tool to accelerate the design of dual-metal site catalysts¹²⁵. In turn, *in situ* characterization techniques will be critical for building an in-depth understanding of the structure–performance relationships¹²⁶.

Increasing site density to improve mass activity. Enhancing the micropore content and increasing surface area in catalysts are promising strategies for accommodating high-density, single-atom metal sites within the limited catalyst volume in the cathode layer of membrane assembly electrodes (MEAs) in fuel cells. In one approach, the active-site density was maximized in an Fe-N-C catalyst by introducing a pore filler (phenanthroline) and ferrous acetate precursor into the micropore-rich Black Pearls 2000 carbon (BET surface area up to $1500 \text{ m}^2 \text{ g}^{-1}$)¹¹⁰. Recently, MOFs represent another micropore-rich, high surface-area class of materials successfully used as hosts of Fe and N precursors in the synthesis of M-N-C catalysts^{109,127}. For example, a highly active Fe-N-C catalyst, containing nearly identical Fe-sites was synthesized using ZIF-8, a popular MOF, as support, followed by two heat treatments in Ar and NH_3 , respectively.¹²⁷ In a different study¹², a chemical doping method was developed to incorporate Fe(III) ions into ZIF-8 *via* partial replacement of the original Zn ions in the ZnN_4 complex, enabling precise control over the Fe content. The subsequent one-step thermal activation was then used to convert the Fe in ion-doped ZIF-8 into atomically dispersed FeN_4 sites without producing any inactive metal species^{12,15}. While increasing the number of single-metal sites should lead directly to the mass-activity

enhancements, the maximum achievable content of atomically dispersed metal in current M-N-C catalysts is generally quite low (< 1.0 wt.%)^{10,17}. A major limitation in this case is the shortage of anchoring sites, such as nitrogen in M-N-C catalysts, which tend to get lost at high temperatures of the catalyst synthesis. This limitation makes increasing the number of active sites difficult. In addition, numerous single-metal active sites located in the micropores are still inaccessible to the reactants, leading to low active-site utilization.

Various strategies have been extensively explored to mitigate aggregation of single-metal sites, strengthen the interaction of metal sites and carbon, provide more stable nitrogen anchoring sites, and create optimal porosity for efficient mass/charge transport. One strategy involved the chemical doping of Fe ions into ZIF-8 nanocrystals, allowing to maximize the density of atomically dispersed FeN₄ sites^{12,15}. However, additional doping of Fe led to the formation of inactive Fe clusters, which, in turn, catalysed the formation of graphitized carbon with fewer defects to host single-metal sites¹². To address the challenge of increasing the FeN₄ content, it is thus important to identify stable nitrogen-containing ligands in 3D hydrocarbon compounds, as well as Fe precursors capable of gradually releasing Fe ions, instead of causing metallic Fe clusters, to form stable M-N bonds during the high-temperature treatment. Compared to traditional inorganic Fe salts, Fe₂O₃ nanoparticles have been found recently to be especially effective at yielding catalysts with a high density of FeN₄ sites in high-temperature synthesis²⁶. *In situ* high-temperature electron microscopy indicates that Fe₂O₃ nanoparticles are gradually converted to single-atom metal sites and then coordinated by nitrogen ligands without clustering when temperature exceeds 500 °C²⁶.

Thermal activation conditions such as gas atmosphere, temperature, and duration are crucial to assuring high content of nitrogen-coordinated single-atom metal sites. The use of the forming gas instead of argon during the activation process was reported to result in high surface-area hollow carbon structures as effective hosts of FeN₄ sites¹²⁸. Beyond currently explored chemical doping and adsorption methods, new approaches are still needed to enhance the active-site content in catalysts for mass activity improvements. They include the use of gaseous metal and nitrogen sources in chemical vapor deposition (CVD) methods^{55,129}.

Improvements to active-site utilization and mass and charge transfer via catalyst morphology optimization. Micropores (< 2 nm in size) in an M-N-C material are essential for achieving high content of FeN₄ sites at the edge of carbon planes (though it may limit the proton and O₂ transport in catalyst layers⁹). Macropores (> 50 nm in size) and mesopores (2-50 nm in size) play an important role at different stages of the ORR^{18,130,131}. Mesopores enable wetting of the catalyst surface, increasing the electrochemically active surface area¹³². Macropores promote uniform ionomer dispersion in catalysts and facilitate access of the reactants to active sites^{19,116}. Together, the micro-, meso-, and macropores, well connected into a “hierarchically porous structure”, are all required to assure high active site density and effective mass transport to/from active sites¹⁰³.

Linking porous structures of Fe-N-C catalysts and MEA performance has been the focus of extensive research to understand better the role porous structures play in the ORR^{19,133-135}. Compared to the early, largely heterogeneous precursors such as polyaniline, the highly uniform ZIF-8 can yield homogenous carbon morphology, allowing for accurate control over the catalyst porosity. Also, ZIF-8-derived M-N-C catalysts with a homogeneous particle-size distribution offer an opportunity to engineer particles in a wide range of sizes, from 30 to 1000 nm, as well as fine-tune the porosity for maximum catalyst utilization and optimal mass transport (**Figure 3d**)^{15,19}. Using either hard (metal oxides, sulfides, metal salts) or soft (polymers, surfactants) templates is also an effective method to create catalysts with ordered structures^{136,137}. Engineering the

hierarchical M-N-C catalysts *via* electrospinning has recently attracted more attention^{138,139} as a way of providing desirable porosity, including macropores in carbon fibers to mitigate particle agglomeration, mesopores for uniform ionomer distribution and efficient proton and mass transport, and micropores within individual nanofibers for high density of accessible MN₄ sites (**Figure 3e**)¹¹⁶. However, designing and realizing optimal hierarchical porosity continues to present a challenge due to difficulties in controlling the pore-size distribution and the lack of effective multiscale models to predict the optimal porosity^{4,140}.

Catalyst degradation mechanisms and strategies to improve stability

Degradation mechanisms. Following decades of development, the performance of M-N-C catalysts, Fe-N-C ones in particular, has approached that of Pt/C catalysts¹⁰ (though at high overall loadings, resulting in thick electrodes in MEAs). Current R&D efforts have largely shifted towards improving long-term stability while maintaining the activity^{113,141}. In 2011, the polyaniline (PANI)-derived FeCo-N-C catalyst showed promising durability stability for more than 700 hours in an H₂-air fuel cell³³, albeit at a low voltage of 0.4 V, limiting the voltage efficiency to 33%. As it turns out, Fe-N-C catalysts often suffer significant performance degradation at high voltages, > 0.6 V^{12,142}, especially at the initial stages of fuel cell operation^{12,26}. *Ex situ* and *operando* experiments suggest that the single-atom metal sites are converted to Fe nanoclusters or oxides following the scission of the Fe-N bonds in the FeN₄ moieties. The activity loss during the ASTs appears consistent with the loss of FeN₄ sites, determined in the electrochemical probe measurements²⁶. Partial recovery of the catalyst performance observed during the long-term stability tests, especially at the constant high potentials (> 0.7 V)¹², was likely due to the removal of oxygen-containing functional groups (hydroxyl, epoxy) from the carbon surface. Such electron-withdrawing groups are theoretically predicted to significantly decrease the O₂-binding energy, favouring the 2e pathway for H₂O₂ formation over the desirable 4e pathway to H₂O¹⁴³.

Demetallation of the FeN₄ sites during ASTs in N₂ versus O₂ showed similar activity losses²⁶. It was found to be primarily electrochemically driven rather than by chemical attacks by O₂ or H₂O₂. Unlike in aqueous electrolytes during rotating disk electrode (RDE) testing, H₂O₂ confined in the MEA cathode can generate significant quantities of free radicals to the detriment of the active sites and the carbon phase¹⁴⁴. Stability improvements could be achieved by adding scavengers (*e.g.*, CeO_x or Ta₂O₅) to eliminate free radicals in the cathode¹⁴⁴.

The degradation mechanisms fundamentally differ between the atomically dispersed Fe-N-C and the Pt nanoparticles. Demetallation of FeN₄ moieties due to the breaking of Fe-N bonds in harsh ORR environments can be accelerated by corrosion/oxidation of the local carbon structure^{12,145}. Therefore, strengthening the Fe-N bonds and developing carbon structures with improved resistance may be effective at enhancing the stability of Fe-N-C catalysts.

Activity-stability trade-offs. As mentioned above, when discussing two main types of FeN₄ sites with different nitrogen coordination (pyrrolic- vs. pyridinic-N)²⁵⁻²⁷, the activity-stability trade-off largely limits the development of high-performance Fe-N-C catalysts²⁷, as traditional synthesis methods cannot assure an effective control over the individual contents of S1 and S2 sites. Elucidating degradation mechanisms of the highly active S1 sites and enhancing their stability could prevent the trade-off limitation. With experimental studies of single-atom metal site degradation being difficult with currently available techniques, DFT calculations have been carried out to predict the stability of FeN₄ sites during the ORR²⁶. The demetallation has been found to be associated with the protonation of two N atoms in a FeN₄ moiety, causing the weakening of Fe-N bonds and further converting Fe sites to iron oxides during the ORR. In particular, the

demetallation of both FeN₄ sites (S1 and S2) was proposed to proceed through three sequential steps: (i) protonation of two N atoms in an FeN₄ moiety to form two N–H bonds; (ii) removal of the central Fe ion with adsorbed O₂ from the N₄ coordination into an inactive N₂ coordination; and (iii) desorption of the Fe–O₂ moiety from the catalyst. In this reaction sequence, the nitrogen protonation step was calculated to require the highest activation energy and proposed as the rate-determining step in the demetallation process. The activation energy values for that step were predicted to be 1.24 eV and 2.08 eV for the S1 and S2 sites, respectively, pointing to a better stability of the S2 site against demetallation. Therefore, regulating nitrogen coordination and local carbon structure to strengthen Fe–N bonds is crucial for enhancing ORR stability of FeN₄ sites²⁶.

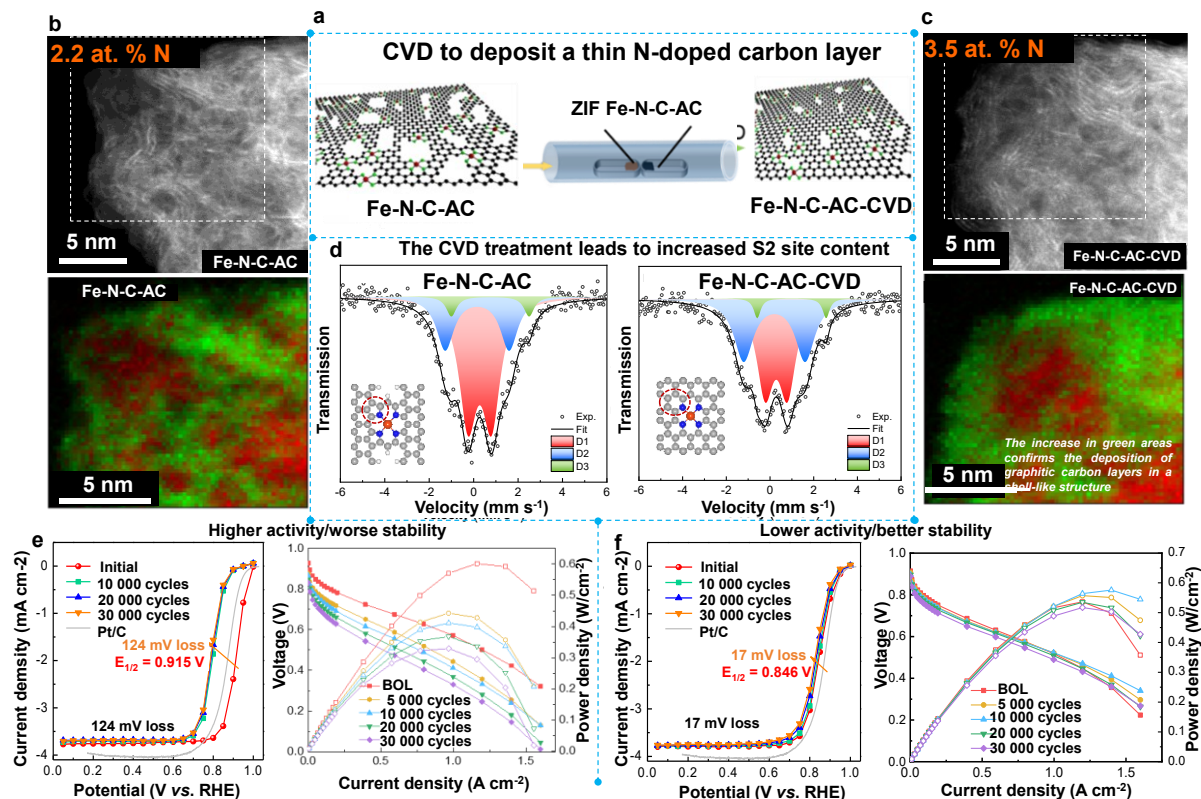


Figure 4. (a) An effective CVD approach to converting more active/less stable pyrrolic-N FeN₄ to more durable/less active pyridinic-N FeN₄ sites *via* depositing a thin layer of nitrogen-doped carbon layer derived from ZIF-8 onto an Fe-N-C catalyst at high temperatures (*i.e.*, 1100 °C). Electron microscopy and element mapping of Fe-N-C catalysts (b) before and (c) after the CVD showing more graphitized *sp*² structures at the surface (green areas indicating more graphitic structures relative to red). (d) Change in Mössbauer spectroscopy response after the CVD indicates considerable increase in highly stable/less active S2 sites relative to highly active/less stable S1 sites, leading to significant improvement of catalytic stability. (e-f) Accelerated stress tests at RDE in aqueous acidic electrolyte and in MEAs with a Nafion[®]-membrane to evaluate catalyst activity and stability/durability. (e) $E_{1/2}$ of 0.915 V (higher than for typical Pt/C catalyst at a 60 $\mu\text{g}_{\text{Pt}}\text{cm}^{-2}$ loading) initially measured with the highly active Fe-N-C catalyst but decreasing rapidly with time (by 124 mV) during the RDE tests *via* potential cycling (0.60 to 0.95 V in O₂-saturated 0.5 M H₂SO₄ solution at 25 °C) and MEA tests *via* voltage cycling (0.60 to 0.95 V under 150 kPa air at 80 °C). (f) Remarkable stability and durability improvements following CVD (only 17 mV loss in $E_{1/2}$) at an expense of mitigated initial activity ($E_{1/2}$ of 0.846 V). Data in all panels reproduced with permission from REF.²⁶, Springer Nature Limited.

Strategies to enhance stability. In view of the trade-offs discussed above, a significant increase in the content of S2 sites by modifying nitrogen coordination and local structure may be crucial for addressing the catalyst stability issue. One promising strategy to improve stability is *via* an increase in the sp^2 carbon content by the addition of nitrogen-carbon species in a high-temperature CVD approach (**Figure 4**), verified by Mössbauer spectroscopy and advanced electron microscopy²⁶. An Fe-N-C catalyst obtained using that approach showed promising long-term durability while maintaining respectable activity (60 mA cm^{-2} at 0.8 V after 30,000 AST cycles)^{26,66}.

Given the high ORR stability of S2 sites, the synthesis of an Fe-N-C catalyst with high content of S2 sites with enhanced activity would represent a significant step forward, breaking the activity-stability trade-off. Recently, it was reported that adding H_2 to the inert-gas atmosphere during the thermal activation of an Fe-N-C catalyst can significantly increase the density of FeN_4 sites¹²⁸, suppressing formation of unstable pyrrolic-N-coordinated S1 sites and favouring formation of the stable pyridinic-N-coordinated S2 sites with shortened Fe-N bonds. The more stable S2 sites were proposed to be incorporated in highly graphitized carbon layers, with the less stable S1 sites existing in less-graphitized carbon. The removal of S1 sites by H_2 treatment while retaining S2 sites during the pyrolysis is one example of breaking the otherwise very challenging activity-stability trade-off. When implemented into an H_2 -air fuel cell cathode, the thus-obtained Fe-N-C catalyst maintained a respectable current density of 67 mA cm^{-2} at 0.8 V after 30,000 voltage cycles¹²⁸. Innovative approaches are also needed to tune the local carbon structure and nitrogen coordination, targeting simultaneous improvements to the catalytic activity and stability of Fe-N-C catalysts.

Perspectives and outlook

The past decades have brought a very fast progress in the development of M-N-C catalysts for the oxygen reduction reaction. However, insufficient activity and long-term stability prevent this class of PGM-free catalysts from becoming fully viable. Gaining control over the local coordination environment and structure will be key to enhancing the “intrinsic” activity of single metal sites. In particular, the development of new precursors and synthesis approaches is needed for maximizing the content of single-atom metal sites, as is the design of carbon structures with optimal morphologies amenable to increasing the catalyst mass activity and mass transports¹⁴⁶.

Due to the prevalent activity-stability trade-off, the most electrocatalytically active materials developed to date are often unstable. Effective approaches are needed to mitigate this by stabilizing the active sites and/or maximizing their content in catalysts. Among the approaches explored to date, the design and synthesis of dual-metal site catalysts could help change the coordination and local structure of active metal sites, potentially overcoming the limitations associated with the activity-stability trade-off and the scaling relationship during the ORR electrocatalysis¹²¹.

As the active metal-nitrogen species are formed during the high-temperature process, determining the optimal thermal-activation conditions such as temperature, atmosphere, and duration will be critical for fine-tuning the M-N bond length and interaction of the active species with the carbon matrix. Among the explored metal sites, Fe-N-C catalysts have been the most promising PGM-free materials for catalysing ORR in the challenging acidic media due to their high activity and continuously improving stability. Co-N-C catalysts are likely more stable, but their activity is far below that of Fe-N-C catalysts and not competitive the incumbent Pt-based ORR catalysts. In addition, Mn-N-C catalysts are more active than Co-N-C ones, but they suffer from significant performance loss associated with the Mn-to- MnO_2 conversion during the ORR¹¹⁴.

One aspect worth bringing up here is possible detrimental role of Fe in Fe-N-C catalysts as a Fenton catalyst. While the primary source of Fe ions (and other “Fenton” metal ions) in the MEAs are likely the stainless-steel bipolar plates, any contribution of Fe originating from Fe-based catalysts should be determined and, if needed, mitigated. A relatively low Fe content in the present-day Fe-N-C catalysts (*ca.* 1 wt%) and improving site stability likely minimize the effect, which can be further controlled by peroxide scavenging, similar to the mitigation strategies implemented in PEM fuel cells (*e.g.*, by using ceria). Recently, it was reported that adding oxide scavengers, *e.g.*, Ta-TiO_x, to Fe-N-C catalysts could considerably mitigate risk associated with the use of Fe-containing catalysts in fuel cell cathodes¹⁴⁴.

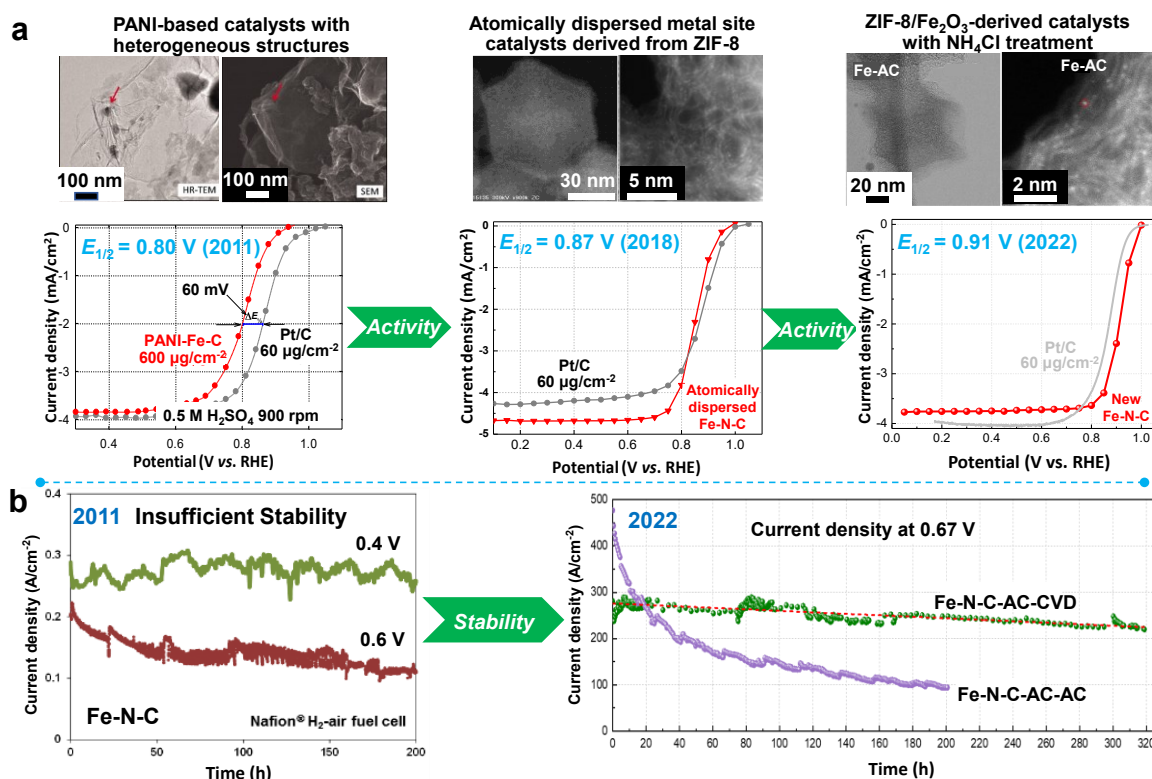


Figure 5. (a) Progress in ORR activity of Fe-N-C catalysts resulting in an overall *ca.* 100 mV increase in the $E_{1/2}$ value in RDE testing from highly heterogeneous PANI-derived catalyst ($E_{1/2}$ of 0.80 V), reproduced with permission from REF.³³, AAAS, ZIF-8-derived catalyst with atomically dispersed single metal sites ($E_{1/2}$ of 0.87 V), reproduced with permission from REF.¹², Royal Society of Chemistry, to ZIF-8/Fe₂O₃-derived material subjected to ammonia chloride (AC) treatment ($E_{1/2}$ of 0.91 V), reproduced with permission from REF.²⁶, Springer Nature Limited. (b) Progress in performance durability: from PANI-derived Fe-N-C catalyst suffering from fast degradation at a fuel cell voltage of 0.60 V, reproduced with permission from REF.³³, AAAS to CVD-treated ZIF-8/Fe₂O₃-derived Fe-N-C catalyst maintaining respectable performance at 0.67 V for up to 300 hours, reproduced with permission from REF.²⁶, Springer Nature Limited. Note: Higher fuel-cell voltage operation is desirable from the PEFC energy efficiency point of view, but more challenging from the point of view of maintaining performance durability.

The dual-atom sites offer a promising path to simultaneously improve both the ORR activity and performance durability. Advanced research tools, involving machine (adaptive) learning and high-throughput approaches developed in recent years have already yielded promising results in effectively optimizing synthetic chemistry parameters to improve catalyst performance. A combination of the advanced theory and *operando* spectroscopy tools will play a key role in acquiring a fundamental understanding of the dynamic evolution of active sites as a function of potential, pH, and temperature during the ORR and reveal possible degradation mechanisms associated with the M-N bond changing/breaking, carbon oxidation, as well as the active site demetallation and poisoning¹⁴⁷⁻¹⁴⁹.

The activity-stability trade-off can potentially be overcome by (i) designing and synthesizing dual-site catalysts, (ii) controlling local structures *via* the use of precursors with well-defined structures at the molecular level, and (iii) fine-tuning the thermal activation conditions. Since the first viable demonstration of Fe-N-C catalysts in PEFCs in 2011³³, their activity and stability (performance durability) have been greatly improved, resulting in *ca.* 100 mV positive half-wave potential shift, from approximately 0.80 V to 0.90 V in acidic electrolytes under identical RDE test conditions (**Figure 5a**). The initial performance of the best Fe-N-C catalysts in the H₂-air fuel cell cathode (at a high loading of *ca.* 4.0 mg cm⁻²) has approached that of the state-of-the-art Pt/C catalysts (at a 0.1 mg_{Pt}cm⁻² loading), a nearly 10-time improvement relative to 2011. A promising performance durability at a high fuel cell voltage of more than 0.6 V has been demonstrated recently, too (**Figure 5b**).

It is important to stress here that successfully reproducing high electrochemical-cell performance of M-N-C catalysts in an MEA has been challenging at times, just as it has been challenging with PGM-based ORR catalysts. The complex nature of the thick, porous fuel cell cathodes, typically containing large quantities of a solid-state ionomer, limits transport of O₂ and protons. In turn, restricted accessibility of active sites in electrode micropores limits catalyst utilization. As a result, it is the electrode structure that often plays a key role in generating current densities in both the kinetics- and mass transport-controlled regions of the fuel cell polarization curve. The electrode fabrication process and optimal ionomer content may differ for different catalysts, depending on the specific surface area and porosity of a catalyst. The degradation mechanisms of M-N-C catalysts in MEAs may be different from those occurring in aqueous electrolytes. In addition to the loss of ORR activity, the degradation of different interfaces in the fuel cell-type electrode due to changes in morphology and carbon corrosion are often responsible for at least partial performance loss in the MEAs, as is water flooding in thick M-N-C electrodes. Further experimental and modelling studies of MEAs with thick PGM-free cathodes are thus crucial for the development of high-performance MEAs and minimizing losses associated with the transfer from an electrochemical cell to an MEA.

Finally, the recent studies involving precious metal catalysts^{150,151} suggest that further progress in the PGM electrocatalysis can also be accelerated *via* employing PGM-free catalysts as innovative carbon supports and taking advantage of unique synergies between single-metal site-rich carbon and Pt nanoparticles^{152,153}.

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G. W. and P.Z. envisioned, developed, and wrote the Perspective.

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