

Atomically Dispersed Metal Catalysts for Oxygen Reduction

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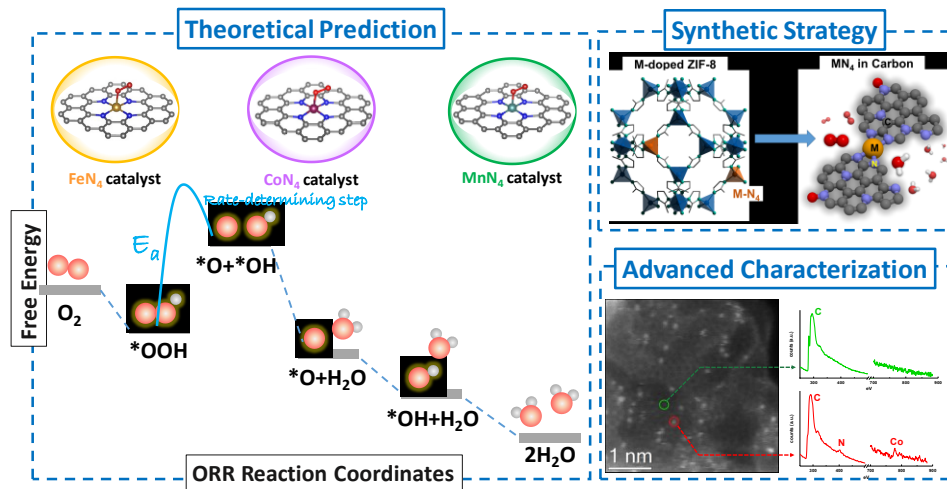
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Abstract: The unprecedented oxygen reduction reaction (ORR) activity of atomically dispersed and nitrogen coordinated metal site (*e.g.*, Fe, Co, or Mn) catalysts makes them promising low-cost candidates to replace platinum group metal (PGM) catalysts in proton exchange membrane fuel cells (PEMFCs). This perspective focuses on emerging developments in mechanistic understanding, innovative synthetic concept, and performance improvement of these high risk, high reward PGM-free catalysts. Starting from theoretical and computational analysis of active sites and ORR pathways, we provide a concise overview of recent progress in catalyst synthesis, characterization and catalytic performance with an aim to elucidate structure–property correlations. We also examine remaining challenges and future directions to realize atomically dispersed metal catalysts with sufficient activity and stability for viable PEMFC applications.

TOC GRAPHICS



With rising energy demands and increasing environmental concerns, development of sustainable and clean energy conversion technologies has become essentially important. Electrocatalytic reactions involving oxygen play a crucial role in energy conversion, especially the oxygen reduction reaction (ORR), which occurs at the cathode in proton exchange membrane fuel cells (PEMFCs). The ORR cathode is the bottleneck of this technology due to its poor kinetics and instability of catalysts under acidic and oxidative environments. Therefore, highly active and stable catalysts are required to promote the otherwise sluggish reaction. At present, platinum-based catalysts represent the state of the art in ORR electrocatalysis. However, the scarcity and cost of Pt have hindered widespread implementation in PEMFCs.¹⁻³ According to General Motors,⁴ to become competitive to the Pt usage in current internal combustion engine vehicles, the loading of Pt in PEMFCs needs to be reduced to 0.0625 mg/cm² and generates a power density of 1.0 W/cm². It is impossible to meet such a goal unless extremely active and durable ultra-low platinum group metal (PGM) catalysts are developed. Therefore, the grand challenge to meet the U.S.

Department of Energy (DOE)'s cost target (\$30/kW)¹ leads to intense and increasing interest in development of high-performance PGM-free catalysts.⁵⁻⁷ Among various PGM-free catalyst formulations, carbon catalysts doped with transition metals and nitrogen, denoted as M-N-C (M: Fe, Co, or/and Mn), show the encouraging ORR performance.⁸ These catalysts are particularly promising candidates to replace Pt catalysts because of the abundance and low cost of the component elements, as well as the high intrinsic ORR activity of M-N-C sites formed during pyrolysis.⁹⁻¹¹ The ORR performance of M-N-C catalysts depends on several materials characteristics, including types of transition metal, carbon structure and morphology, and nitrogen speciation, with the latter two characteristics being highly sensitive to synthetic methods and thermal conversion conditions.¹²⁻¹³

As early in 1964, scientists discovered that macrocyclic compounds with MN₄ configuration exhibited activity towards oxygen reduction, which opened the avenue for synthesizing PGM-free M-N-C catalysts through high temperature treatments of carbon and nitrogen precursors (*e.g.*, melamine, ethylene diamine, polyaniline, and polypyrrole), along with transition metals (*e.g.*, Fe, Co, or Mn).^{6, 14-20} However, the limited chemical control of these methods usually leads to formation of metal oxides/carbides or metal clusters, with highly heterogeneous catalyst morphology, making the investigation and verification of the chemical configuration of the active sites a difficult challenge. The emerging consensus in the field is that active sites for the ORR consist of transition metal centers coordinated by nitrogen, which is supported by the observed anion poisoning of catalysts and the low activity of metal-free catalysts especially in acid media.²¹⁻
²² In particular, MN₄ moieties have been identified as possible active sites for the ORR, as evidenced by advanced spectroscopy characterization and first principles calculations.²³⁻²⁶ The active site identification underscores the promising nature of catalysts based on earth-abundant

elements and paves the way to increase the activity of M-N-C catalysts by reducing the amount of metal present as inactive clusters, and increasing the amount of metal present as atomically dispersed metal sites coordinated by nitrogen. Compared with nanoparticles or nanoclusters, atomically dispersed metal sites exhibit well-defined ORR active centers, enabling improved fundamental mechanistic understanding by facilitating the construction of model structures and simplifying the required theoretical calculations. In return, the resulting improved mechanistic understanding can guide ORR performance optimization through modification of the coordination environments and geometric configurations at the atomic level. These distinct advantages have led to growing interest in atomically dispersed metal catalysts. Experimentally, the identification and examination of active sites can be conducted using powerful techniques such as synchrotron-based X-ray absorption spectroscopy (XAS), Mossbauer spectroscopy, and scanning transmission electron microscopy (STEM), which can provide unique insight into subtle details of local atomic-level structure and electronic properties, including coordination environment and chemical state of metal centers.²⁷⁻²⁹ The combination of these cutting-edge characterization techniques along with density functional theory (DFT) can elucidate the relationship between structure and performance, enabling precise rational design of improved PGM-free catalysts.^{25, 30-31}

Several reviews on PGM-free ORR catalysts have been published in past a few years in terms of their applications in energy conversion and storage.^{8, 29-30, 32-36} However, discussion on the fundamental scientific understanding on M-N-C catalyst technology with an emphasis on the atomically dispersed metal active sites is still needed, especially with regard to controlled catalyst synthesis and elucidation of synthesis-structure-property correlations. Atomically dispersed metal sites with high surface energy often have poor stability under the high temperature conditions required for active site generation. Thus, the formation of undesirable aggregated metal clusters

and/or particles remains as the main barrier preventing further improvement of high-performance ORR catalysts with sufficiently high density of atomically dispersed active sites. Improved control of local structure and chemistry by tailoring of synthetic conditions is essential for development of such catalysts. Herein, we provide a perspective on recent advances in atomically dispersed metal catalysts (also known as single-metal-atom catalysts) for ORR electrocatalysis. It should be noted that many outstanding studies on single-metal-site ORR catalysts had been published in the past five years.^{9-11, 24, 28, 30, 37-43} However, most examples chosen for discussion are based on our own work to provide deeper understanding. The atomic-scale mechanistic understanding is based on recent DFT calculations. The correlations of synthesis-structure-property are established in terms of several key factors of synthetic chemistry such as the selection of metal sources, precursor structure and morphology, thermal conversion conditions, and subsequent post-treatment. Based on advanced characterization, we highlight fundamental insights that can guide the development of advanced atomically dispersed metal catalysts. Lastly, current challenges and perspectives are presented, with the intention of stimulating further development and breakthroughs in this area.

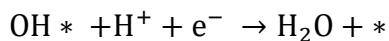
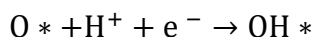
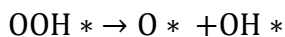
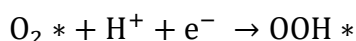
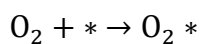
Theoretical understanding of active sites and reaction mechanisms provides a solid foundation for rational design and synthesis of atomically dispersed metal catalysts.

DFT calculations, which play a significant role in the field of electrocatalysis, have been coupled with thermochemical models in several studies in order to elucidate the feasibility of proposed ORR active sites and to evaluate possible catalytic pathways on M-N-C catalysts.⁴⁴⁻⁴⁶ First, it is helpful to calculate the formation energy of relevant atomic-scale structures by applying the DFT. It was reported that the formation of nitrogen-coordinated metal sites (denoted as MN_x) embedded in a carbon matrix was energetically feasible, supporting the hypothesis that these MN_x active sites

could be formed through appropriate synthetic methods.⁴⁵ Moreover, binding energies of O₂, ORR intermediates, and product H₂O, can be calculated via DFT, which are important thermodynamic parameters for ORR electrocatalysis. Their binding energies on active sites are known to vary with the types of transition metals, coordination environments, and local carbon structures.⁴⁷ Among proposed active sites, FeN₄,⁴⁷ CoN₄,⁴⁸ and MnN₄,⁴⁹ which show 4-fold coordination number, are found to be the most likely active sites based on binding energy calculations for possible ORR intermediates such as O₂, O, OH, OOH, HOOH, and H₂O.⁵⁰⁻⁵² In particular, Kattel *et al.* reported that CoN₄ shows lower formation energy and higher stability in the range U = 0-1.23 V than CoN₂, indicating that CoN₄ is a more likely candidate as a stable active site.⁵² They also predicted that O₂ would adsorb with different geometry on the different CoN_x sites, predicting O₂ binding on CoN₄ with an end-on configuration and on CoN₂ with a side-on configuration (**Figure 1a** and **1b**). Similar conclusions were obtained for FeN₄ and FeN₂ sites.⁵³ Zitolo *et al.* identified the structure of two candidate active sites in Fe-N-C catalysts, which has a FeN₄C_x moiety with O₂ bound in the end-on or side-on configuration in the porphyrinic planar architecture. Such porphyrinic moieties possibly formed either in the disordered graphene sheets or between zigzag graphene edges hosted in micropores.²⁴ Another study reported by Zelenay *et al.* also concluded that nitrogen-coordinated iron (FeN₄) sites embedded in carbon phases are active sites for the ORR, which was directly visualized with aberration-corrected scanning transmission electron microscopy (STEM) coupled with atomic level electron energy loss spectroscopy (EELS), and theoretically calculated at specific lattice-level in the carbon phase.

The improved understanding of the atomic structure of active sites developed in recent years has enabled improved predictions of the reaction mechanisms on these active sites. By calculating the activation energy of possible elementary chemical reactions during oxygen reduction, FeN₄

embedded in a carbon matrix was predicted to have comparable activity to platinum catalysts.⁴⁹⁻⁵⁰ The ORR can proceed on such metal centers via three possible pathways: O₂ dissociation pathway, HOOH dissociation pathway, and OOH dissociation pathway; of these, the OOH dissociation pathway is believed to predominate.⁴⁶ In this pathway, chemisorption of O₂ on an FeN₄ active site is followed by protonation to form OOH, followed by O-O bond scission to generate O and OH. In the end, H₂O will be the final product generated from the protonation of O and OH. The details can be described as below:



In short, after the adsorption step of dioxygen on active sites, each elementary reaction is associated with either O-O bond breaking or a protonation step. The OOH dissociation step, with a calculated activation energy of 0.56 eV, has been predicted to be rate-determining step (RDS). Apart from FeN₄, CoN₄ and MnN₄ can also facilitate oxygen reduction through a similar pathway (**Figure 1c**).^{49, 52} Following O₂ adsorption on active sites, oxygen reduction can proceed via either a two-electron pathway or a four-electron pathway, generating detrimental H₂O₂ or desirable H₂O, respectively. The selectivity of active sites on different pathways is determined by local atomic-scale structure. For instance, CoN₂₊₂ (a CoN₄ moiety bridging over two adjacent zigzag graphitic edges) has been predicted to catalyze the ORR via a four-electron pathway that is less favored on conventional CoN₄ sites within graphene sheets due to the higher activation energy (**Figure 1d**

and 1e).⁵⁴ **Figure 1e** shows that elementary reactions on CoN_{2+2} site are exergonic (negative free energy change), when the applied electrode potential is lower than 0.73 V, indicating that the four-electron pathway is energetically favorable. However, a significant free energy barrier (0.39 eV) was found for the OOH dissociation step on CoN_4 site, suggesting that $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ generation selectivity (four-electron selectivity) is relatively low. Moreover, calculations of the activation energy for OOH dissociation indicate an activation energy of 1.11 eV on CoN_4 sites, which is much higher than that on CoN_{2+2} site (0.69 eV). This result further indicates that, in addition to the metal center, the local active site structure plays a crucial role in determining the ORR pathway and selectivity. The active site location (bulk, edge, or between the layer),^{25, 39} local carbon configuration,⁵¹ porosity of catalyst,⁵⁵ and functional groups⁵⁶ should be considered for designing highly active and stable active sites for the ORR. These design decisions should ideally include stability prediction of MN_4 sites, including examination of the bonding strength between M, N, and C and the tolerance to poisoning under various ORR conditions. It should be noted that, due to the complexity of electrochemical reactions that involve solvent molecules and pH value changes, the capability of current DFT methods to fully elucidate active site structure and reaction pathways is still very limited.

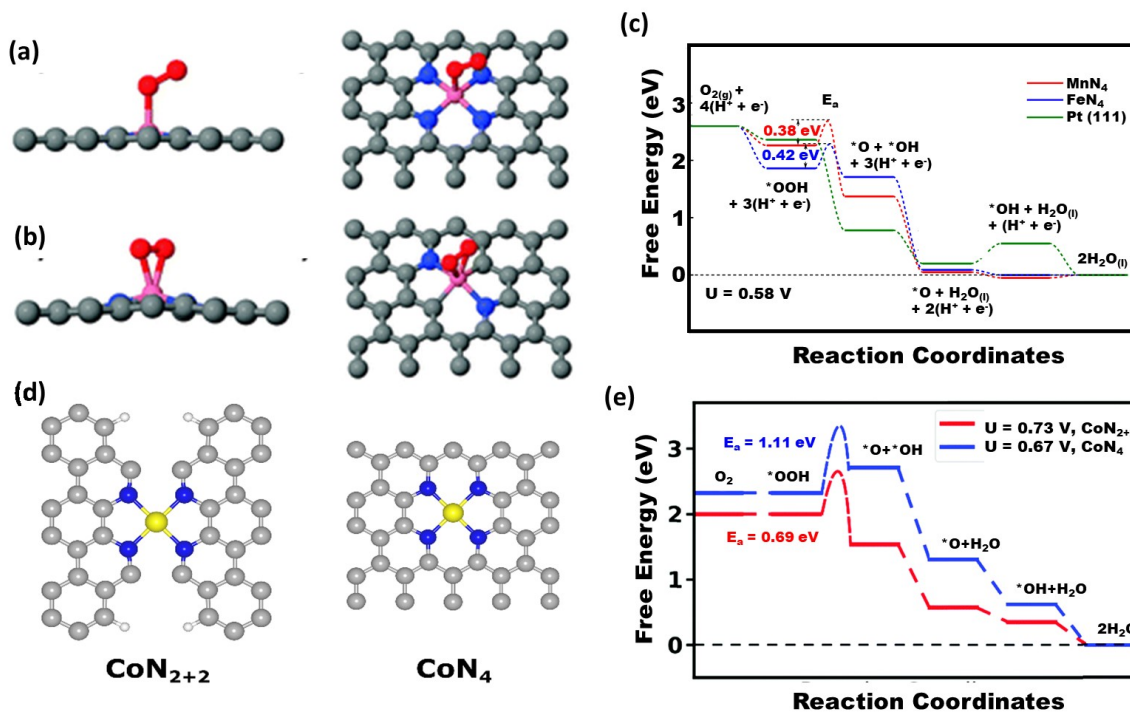


Figure 1. (a) Side view and top view of graphitic CoN₄ binding with O₂. (b) Side view and top view of graphitic CoN₂ binding with O₂. Reprinted with permission from Ref.⁵² Copyright 2013, The Royal Society of Chemistry. (c) Free energy diagrams for the four-electron oxygen reduction pathway on Pt(111), MnN₄, and FeN₄ sites under a limiting electrode potential of U=0.58 V. Reprinted with permission from Ref.⁴⁹ Copyright 2019, Elsevier. (d) Atomic structure comparison between CoN₂₊₂ and CoN₄ sites. (e) Predicted free energy diagrams for oxygen reduction via four-electron pathway on CoN₄ and CoN₂₊₂. Reprinted with permission from Ref.⁵⁴ Copyright 2019, The Royal Society of Chemistry.

The combination of advanced synthetic strategies, structural characterization, intrinsic catalytic activity measurements, and device performance evaluation is crucial for developing advanced single-metal-site catalysts.

Innovative synthesis methods for M-N-C catalysts with atomically dispersed MN_4 active sites have been a frequent topic of publication in recent years. Nevertheless, preparation of M-N-C catalysts that combine exclusively single-atom metal dispersion with high metal site density remains as a grand synthetic challenge, since individual metal atoms tend to aggregate into clusters or nanoparticles under typical synthetic conditions at high temperature. Therefore, a combination of appropriate precursor materials with improved synthetic approaches is needed to produce sufficient MN_x active site density in M-N-C catalysts.

Appropriate precursor materials should exhibit high surface area, porous structure, M-N-C integration at the molecular level, and tunable morphology and chemistry. Among potential precursors, metal-organic frameworks (MOFs) are particularly promising. Zeolitic imidazolate frameworks (ZIFs) are a subfamily of MOF, which are studied extensively for the synthesis of carbon-based catalysts with high-surface areas and porosity.^{15, 57-58} Also, zinc-based ZIF-8 is particularly favorable for preparation of single-atom ORR catalysts since this material can isolate and anchor single metal atoms effectively into a 3D hydrocarbon complex.⁵⁸ The abundant nitrogen provided by organic ligands, *i.e.* imidazolate, in ZIF-8 provides ample anchoring sites to complex with metal sites and therefore stabilizing them, enabling high density of active sites. Importantly, Zn ions in the ZnN_4 complexes can be partially substituted by other targeted metal ions (*e.g.*, Fe, Co, or Mn) to form MN_4 complexes connected within 3D organic framework nanocrystals. These Zn atoms and organic linkers can increase the spacing between metal sites to reduce the degree of metal aggregation. Therefore, targeted metal species will be captured by

nitrogen sites to form atomically dispersed MN_4 sites owing to the evaporation of zinc atoms under high-temperature thermal conversion. Importantly, the strong covalent bonds among M, N, and C in ZIF-8 precursors would be favorable for the formation of MN_4 sites embedded into the graphitized carbon planes during the direct thermal conversion.

Several innovative strategies for synthesis of single-atom ORR catalysts based on ZIF-derived precursors have been reported in recent literature, including approaches based on chemical doping,⁵⁹ cage-encapsulation,⁴⁰ adsorption,¹¹ and core-shell confinement.⁵⁴ Focused on preventing metal aggregation, those methods can be divided into three categories: i) the targeted metal ions are pre-doped into the MOF precursors to generate the possible MN_4 complexes before the high-temperature treatment; ii) the targeted metal species and/or extra nitrogen sources are spatially confined in the pores of MOF precursors, and iii) the targeted metal precursors are adsorbed into the MOF-derived carbon matrices with abundant doped nitrogen and other carbon defects. Besides MOF precursors, other synthetic methods were developed to prepare single-atom catalysts such as atomic layer deposition,⁶⁰ hydrothermal,⁴⁰ and hard template⁴¹ etc. However, those methods are usually subject to limited density of active sites. Some are time-consuming and require unique facilities, which are not desirable for scaled-up catalyst synthesis. Therefore, we mainly focus on the most promising and feasible MOF-derived approaches in this perspective.

Among all M-N-C catalysts, Fe-N-C catalysts have received the most attention since the intrinsic activity of FeN_4 sites is higher than other types of MN_4 sites, which has been confirmed by both experimental and theoretical results.^{6, 61} Our group has developed a facile approach to prepare atomically dispersed iron catalysts via chemically doping Fe ions into ZIF-8 precursors followed by one-step carbonization (**Figure 2a**).⁵⁹ The polyhedral morphology of Fe-doped ZIF is retained even after pyrolysis at 1100°C, and the particle size can be accurately controlled from 20

nm to 1000 nm by simply adjusting the solution concentration during the synthesis of Fe-doped ZIF-8 nanocrystal precursors (**Figure 2b**). This highly controllable synthesis, with precise tuning of Fe content and carbon morphology, has provided an excellent opportunity to establish the relationship between structure/composition and ORR activity. ORR activity of such atomically dispersed iron catalysts was found to be strongly dependent on carbon particle size, which may be due to different degrees of exposure of the FeN₄ active sites stemming from the different electrochemically accessible surface area (S_a) of the different nanocrystal sizes (**Figure 2c**). An optimal nanocrystal size was observed around 50 nm, which shows a half-wave potential ($E_{1/2}$) of 0.85 V vs. RHE in 0.5 M H₂SO₄. Further reduction of catalyst particle size leads to a fused morphology with fewer exposed active sites. The abundant atomically dispersed nitrogen-coordinated iron sites were visualized using STEM and chemically identified by EELS during STEM imaging (**Figure 2d**). During the chemical doping process, the Fe ions can coordinate with nitrogen by replacing Zn ions in the ZIF-8 nanocrystals. The subsequent heat treatment procedure is able to directly convert the Fe-N₄ complex to active FeN₄ sites embedded into carbon planes, which is confirmed by XAS analysis (**Figure 2e**). In addition to thermally drive the formation of active sites, the heating treatment is an important factor influencing the chemical structure and composition of catalysts, including metal and nitrogen content, porosity, and graphitization degree. Usually, temperatures higher than 800°C were found to be the critical for generating active sites with favorable Fe-N coordination hosted by partially graphitized carbon phases. As for this Fe-doped ZIF-8-derived catalyst, the higher heating temperature, the better activity, likely due to the effective removal of zinc species and sufficient degree of graphitization in carbon. Furthermore, in a collaboration with Litster at Carnegie Mellon University, the atomically dispersed Fe-N-C catalysts exhibited encouraging performance in PEMFCs, yielding a current density of 0.028

A/cm² at 0.90 V or 0.044 A/cm² at 0.89 V_{IR-free} in a membrane electrode assembly (MEA) using H₂-O₂ at 1.0 bar, approaching to the U.S. DOE target (0.044 A/cm² at 0.90 V_{IR-free}).⁶² In addition, under practical H₂-air at 1.0 bar conditions, the optimal catalyst generated respectful current densities of 120 and 380 mA/cm² at 0.8 and 0.7 V, respectively, as well as a power density of 0.41 W/cm² at 0.67 V.⁶³ Long-term durability at relatively high voltages (*i.e.*, 0.7 V) was also examined in MEAs, showing 50% loss after 120 hours, which is still not sufficient, but represents a significant improvement to previous works.^{17, 64-66}

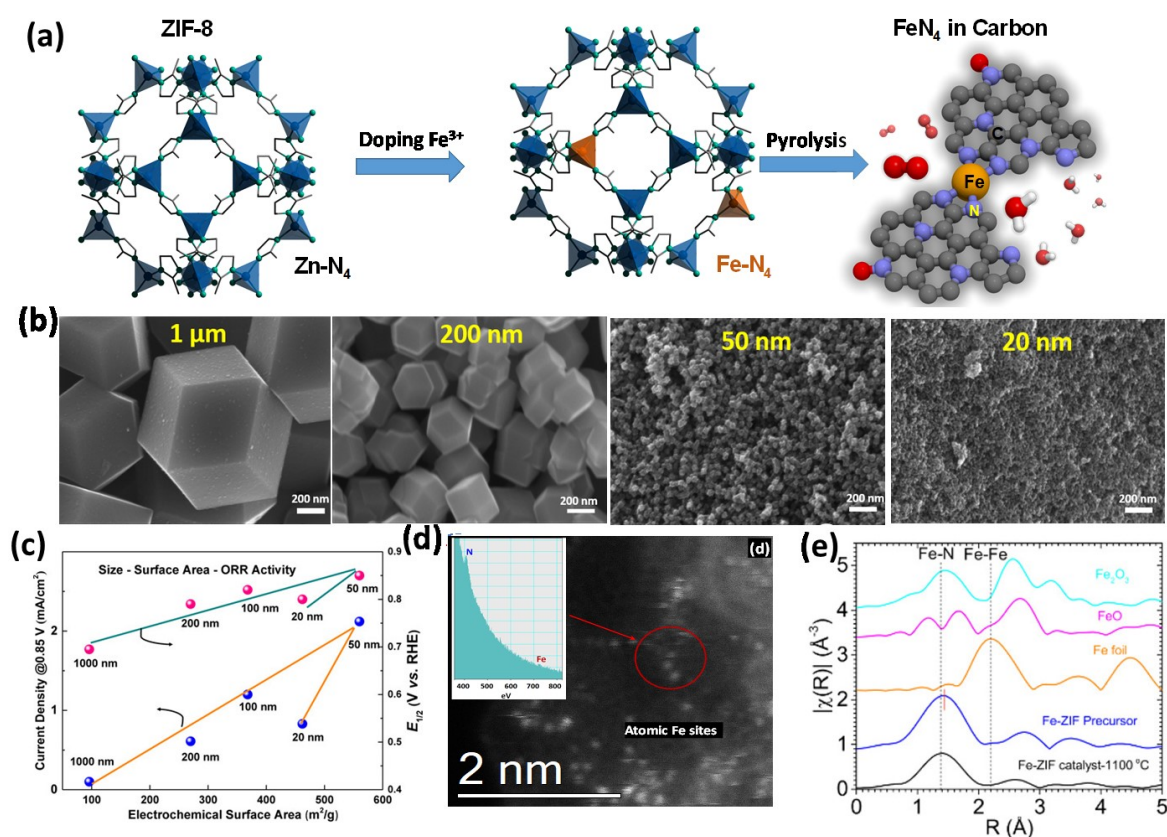


Figure 2. (a) Chemical doping strategy of ZIF-derived atomically dispersed iron catalysts. (b) Size control of ZIF-derived atomically dispersed iron catalysts from 20 to 1000 nm. (c) ORR performance and electrochemical surface area as a function of particle size. (d) HAADF-STEM images of ZIF-derived single-atom iron catalyst and EEL spectra. (e) Fe K-edge extended X-ray

absorption fine structure (EXAFS) spectra for ZIF-derived precursors and atomically dispersed iron catalysts. Reprinted with permission from Ref.⁵⁹, Copyright 2017, American Chemical Society.

In addition to chemical doping of active metal into ZIF-8 precursors, a spatial confinement strategy was also found effective for synthesis of single-metal-site catalysts. A typical study from Chen *et al.* reported an innovative cage-encapsulation strategy to synthesize isolated single-atom FeN_x carbon catalyst.⁴⁰ They claimed that only one Fe(acac)₃ molecule (diameter, ca. 9.7 Å) was trapped in each cage (diameter, ca. 11.6 Å) of ZIF-8. During the pyrolysis in inert atmosphere, isolated single iron atoms were stabilized on nitrogen-doped porous carbon carbonized from ZIF-8 precursors. According to elemental mapping images, Fe and N were uniformly distributed throughout the carbon matrix. Atomic-level characterization including HAADF-STEM and EXAFS was performed to confirm the atomically dispersed FeN₄ configuration. DFT calculations further suggested that the high intrinsic activity of this catalyst could be attributed to expedited electron transfer from single iron atoms to the adsorbed *OH species. Likewise, this useful spatial confinement strategy was also employed by Wang *et al.* to trap ferrocene molecules in ZIF-8 precursors for atomically dispersed Fe catalysts.⁶⁷

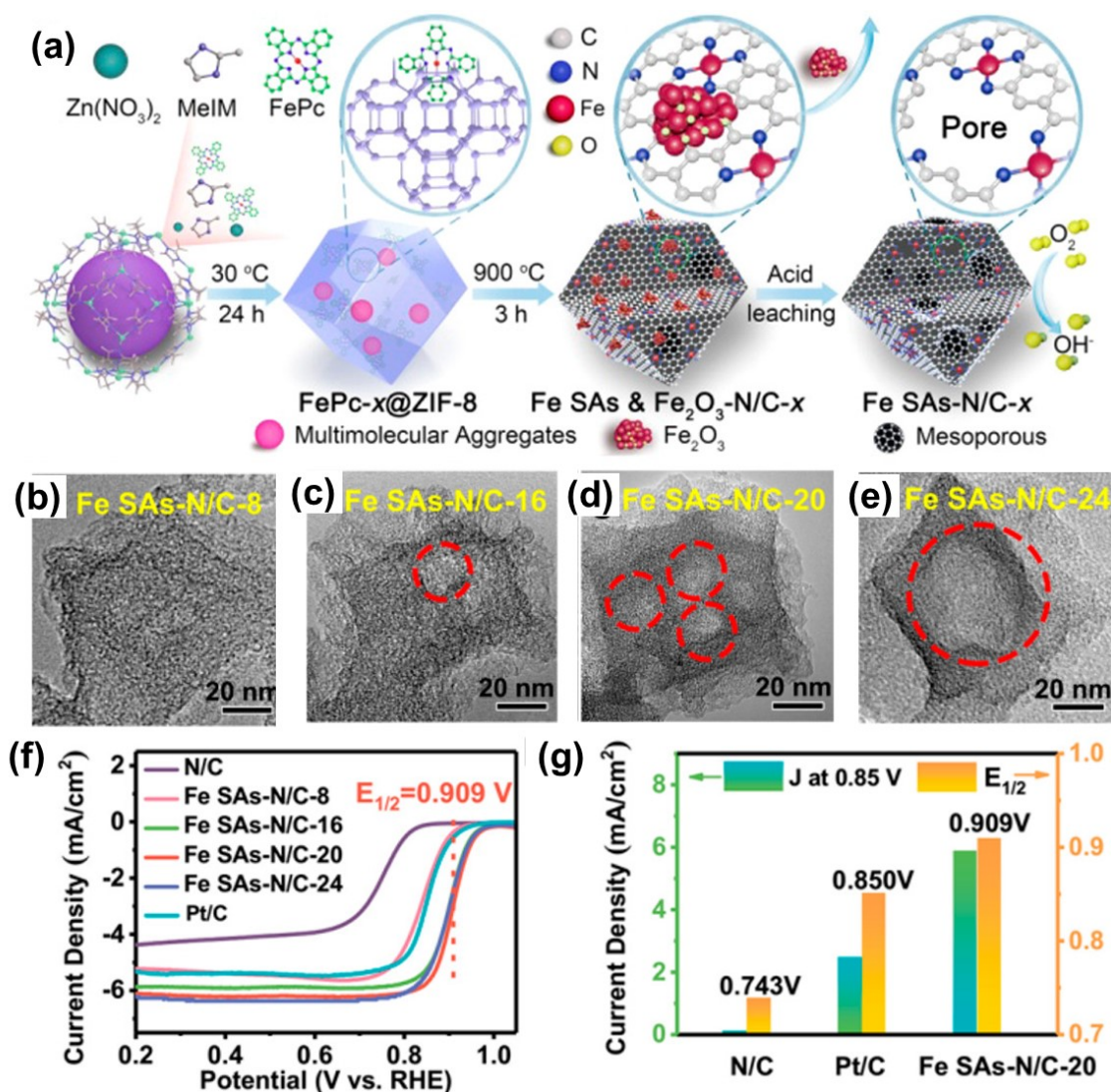


Figure 3. (a) Schematic illustration showing preparation of edge-site atomically dispersed iron catalysts. (b-e) TEM images of Fe single atoms (SAs)-N/C with increasing addition of FePc (red circles represent the mesopores formed by FePc). (f) ORR polarization curves of Fe SAs-N/C-x in 0.1 M KOH. (g) Comparison of current density and half-wave potential for different catalysts. Reprinted with permission from Ref.³⁹, Copyright 2019, American Chemical Society.

Based on the encapsulation strategy above, Jiang *et al.* burst the ZIF cage (diameter, ca. 9.7 Å) to break the confinement effect by trapping iron (II) phthalocyanine (FePc) molecule (diameter,

ca. 14.6 Å) into ZIF cage due to the relatively larger molecular diameter of FePc (**Figure 3a**).³⁹ After pyrolysis and acid leaching, the single FePc molecule trapped within broken cavities was reduced *in situ* to form edge-hosted, atomically dispersed FeN_x sites, which tailored the bonding environment of nitrogen atoms, significantly lowering the overall ORR barriers. The mesopores in the carbon matrix can be modulated by adjusting the amount of FePc (**Figure 3b-e**), as excessive FePc molecule would aggregate together to generate iron oxides/clusters and enlarged mesopores through the Kirkendall effect. The metal species and oxides can be removed by acid-leaching to obtain hierarchically porous structure. Thus, enhanced catalytic activity was achieved by such edge-site engineering and hierarchical micro-mesopore construction (**Figure 3f and g**).

Although atomically dispersed Fe-N-C catalysts have been considered as a promising alternative to precious metal catalysts, durability issues associated with iron present an obstacle to full deployment of these catalysts. In particular, iron ions (Fe²⁺/Fe³⁺) can catalyze the decomposition of H₂O₂ to generate highly reactive free radicals via the Fenton reaction, resulting in destruction of the active site, oxidation of carbon supports, and degradation of membranes in PEM fuel cells.⁶⁸ In contrast, cobalt and manganese ions are not active in the Fenton reaction and therefore are not subject to the same concerns associated with free radical generation. Therefore, atomically dispersed Co- or Mn-N-C catalysts are promising candidates as durable ORR catalysts in acidic media.

Many synthetic methods have been proposed to prepare Co-based single atom catalysts. In the early stages, similar to Fe-N-C catalysts, researchers typically focused on traditional methods via the pyrolysis of a mixture of nitrogen-rich molecules and transition metal salts along with carbon supports, such as carbon black, carbon nanotubes, carbon nanofibers, and graphene oxide.³⁸ However, the random distribution of Co and N components leads to uneven dispersion of active

sites over the carbon support. The poor composition distribution and non-uniform microstructure present a barrier to further improvement of performance. Furthermore, the use of inactive and amorphous carbon supports reduces the overall volumetric activity and generates potential durability issues. Thus, it is highly desirable to explore new synthetic methods for advanced catalysts with controllable carbon nanostructures and uniform morphologies. More recently, template-assisted methods based on templates including silica nanoparticles, ordered mesoporous silica SBA-15, and montmorillonite have been exploited to enhance catalytic activity and stability by precisely controlling the catalyst morphology with favorable active site utilization and mass transport. However, these methods require subsequent harsh chemical etching after pyrolysis to remove the hard templates, which often introduces excess oxygen functional groups onto the carbon and probably damages the CoN_x active sites. Such a complicated process is time-consuming and not ideal for large-scale preparation of catalysts. Therefore, template-free synthetic methods appear to be a more promising approach to prepare Co-N-C catalysts with increased active site density and favorable morphology.

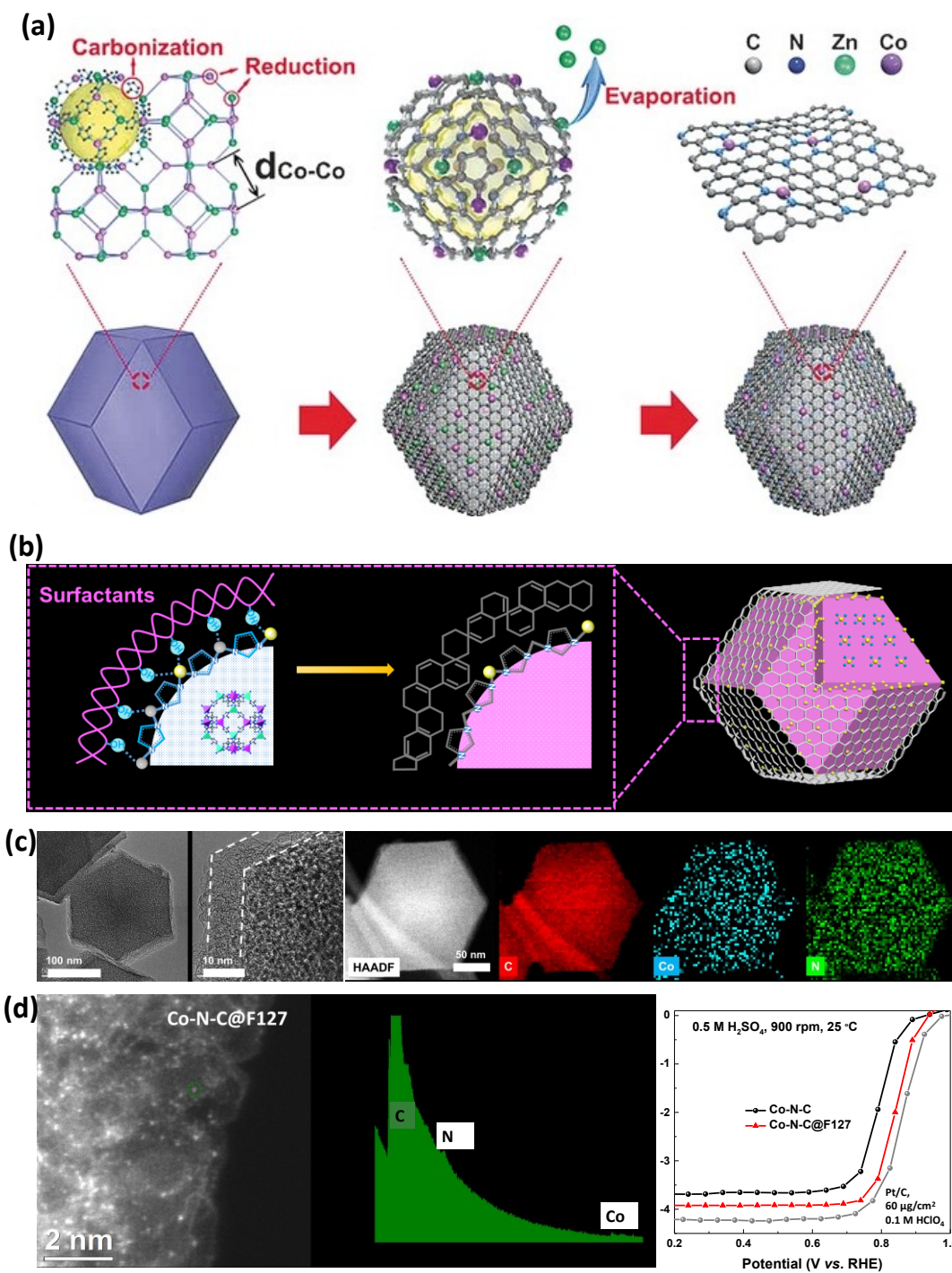


Figure 4. (a) The synthesis process of Co-based single atom catalysts. Reprinted with permission from Ref.⁹ Copyright 2016, John Wiley and Sons. (b) Confinement pyrolysis strategy to synthesize Co-N-C catalysts by using F127 surfactants. (c) Core-shell structured Co-N-C catalysts with

uniform dispersion of C, N, and Co. (d) Atomically dispersed and nitrogen coordinated C-N-C@F127 catalysts. (e) ORR polarization plots for Co-N-C catalysts derived from the F127 surfactants in 0.5 M H₂SO₄. Reprinted with permission from Ref.⁵⁴ Copyright 2019, The Royal Society of Chemistry.

As mentioned above, MOFs with controllable and interconnected pores have been employed as precursors to produce single atom M-N-C catalysts via spatial confinement and restriction of metallic species. It should be noted that, compared to Fe, chemical doping of Co ions into ZIF-8 is more favorable with a wide range of doping content. The Co-based ZIF-67 and Zn-based ZIF-8 share the same organic ligands, *i.e.*, 2-methylimidazole, resulting in similar structures. As shown in **Figure 4a**,⁹ the introduction of Zn could increase the distance between Co atoms, preventing Co aggregation during pyrolysis. Similar to Fe-N-C catalysts, Zn evaporation during heat treatments could provide high surface area and rich porosity in the resulting catalysts, thus generating atomically dispersed Co sites in the porous N-doped carbon matrix.⁹ The correlation between composition, structure, and corresponding ORR performance of bimetallic-ZIF catalysts by modifying the Zn/Co ratio in the precursors (0 to 30 at.%) and the thermal activation temperature (700 to 1100°C) were comprehensively explored by our group.⁴⁸ Although doping content of Co ranging from 0 to 100 at % in ZIF precursors can be easily realized, *i.e.*, gradually transferring from ZIF-8 to ZIF-67, the relationship between activity and Co content follows a volcano trend. The optimal doping content of Co is around 20 at% in terms of the maximum density of atomically dispersed Co sites. The resulting Co-N-C catalyst could be designed to prevent formation of metal aggregates, resulting in homogeneous morphology with well-dispersed atomic Co sites coordinated with N. Consequently, this atomically dispersed cobalt catalyst achieved

considerable ORR activity in acidic media. Encouraging ORR activity and stability at the MEA level were also confirmed by fuel cell tests.

Although great progress has been made in the synthesis of atomically dispersed Co catalysts, it remains a grand challenge to further increase the density of active sites. It is of no use to simply increase the Co content in the precursor, as this results in dramatic aggregation of Co during pyrolysis. Recently, we reported a new approach to increase Co single atom site density through the use of surfactants.⁵⁴ Direct carbonization of Co-doped ZIF-8@surfactant nanocomposites at 900°C resulted in Co-N-C@surfactant catalysts with a unique core-shell structure. The confinement effect produced by the graphitized carbon shell derived from surfactant polymers can suppress the agglomeration of cobalt atoms and alleviate the collapse of micropores in ZIF precursors during high-temperature thermal activation (**Figure 4b**).⁵⁴ The resulting catalysts exhibited uniform dispersion of atomic CoN₄ sites (**Figure 4c-4d**). Unprecedented ORR activity for Fe-free catalysts in acidic media was achieved approaching to state of the art Pt/C catalysts (**Figure 4e**), which can be attributed to the significantly increased ($\times 3$ times) density of Co active sites. The high ORR performance of this catalyst was also verified through H₂-O₂ fuel cell tests, exhibiting a high power density of 0.87 W cm⁻². According to the EXAFS analysis, this new atomically dispersed Co catalyst generated a large number of CoN₂₊₂ sites, thus promoting the desired four-electron selectivity and activity for the ORR in acids. Also, it can retain stable catalytic performance after an initial activity loss, which may be associated with surface carbon corrosion, an issue that still requires further study to fully address.

Generally, the stability of M-N-C catalysts depends on the type of MN₄ sites and on the graphitization degree of carbon, which determines the bond energy of MN₄ and the carbon oxidation resistance, respectively. Therefore, it is important to select stable MN₄ sites and

incorporate them in a robust carbon matrix with appropriate morphologies and structures. In previous research,⁶⁹⁻⁷⁰ we discovered that Mn doping promotes the stability of nanocarbon catalysts due to Mn-catalyzed graphitization during the carbonization process of catalyst precursors. In addition, Fenton reactions involving Mn ions are negligible because of the weak reactivity between Mn and H₂O₂. Motivated by the DFT prediction that MnN₄ site possess comparable ORR activity to FeN₄ sites,⁴⁹ we pursued synthesis of atomically dispersed Mn catalysts to achieve enhanced catalyst activity and stability. However, achieving high density of atomically dispersed sites is particularly difficult with Mn, since this metal tends to form ORR-inactive crystalline compounds during high-temperature treatments. Recently, we developed an effective two-step doping and adsorption approach to generate high density of MnN₄ sites, with promising catalytic activity and stability (**Figure 5a**).¹⁹ By coupling the chemical doping and spatial confinement strategy, this approach addresses the key problem in one-step thermal conversion, which is the inevitable formation of clusters or particles of Mn and Mn oxides. In a typical procedure, these catalysts were prepared by pre-doping of Mn into the ZIF-8 precursors, followed by a first thermal conversion to form some MnN₄ sites. After acid-leaching and a second heat treatment, the Mn oxides/clusters were removed completely. Subsequently, additional Mn and N-containing precursors were deposited in the micropores of this intermediate material, followed by a third heat-treatment to improve the density of MnN₄ sites. The XAS analysis and aberration-corrected STEM imaging coupled with atomic level EELS demonstrated that the atomically dispersed nitrogen-coordinated Mn sites were embedded in the partially graphitic carbon matrix with MnN₄ sites predominantly bridging over two adjacent zigzag graphitic edges (**Figure 5b** and **5c**)¹⁹. Relative to Fe-N-C catalyst prepared by the same procedure, the optimized atomically dispersed Mn-N-C catalyst (20Mn-NC-second) achieved comparable activity with an

$E_{1/2}$ of approximate 0.80 V vs. RHE in 0.5 M H₂SO₄ (**Figure 5d**), which was also confirmed in MEA testing showing encouraging performance (**Figure 5e**). More importantly, the Mn-N-C catalyst demonstrated a remarkable improvement in stability, likely originating from the robust MnN₄ structure and improved corrosion resistance of carbon due to Mn doping (**Figure 5f**).¹⁹ This research provides an atomic approach towards improved catalyst stability through structural modification of both the active sites and the carbon matrix.

Overall, desirable synthesis methods to prepare atomically dispersed metal site catalysts rely on the optimal coordination between N and M in precursors as well as the effective prevention of aggregation of metal species during heat treatment. Introducing targeted metal ions (Fe, Co, or Mn) through chemical doping, spatial confinement, and direct adsorption allows realization of atomic dispersion of MN₄ sites within the carbon matrix. While these MN₄ moieties are effective active sites for ORR, the low density of these atomically-dispersed sites, which is likely limited by low nitrogen dopant content, has thus far led to insufficient ORR activity for PEMFC applications. Therefore, increasing nitrogen content and controlling nitrogen distribution by using additional nitrogen precursors and surfactants during the synthesis is a promising route toward increasing the density of atomically dispersed MN₄ active sites.

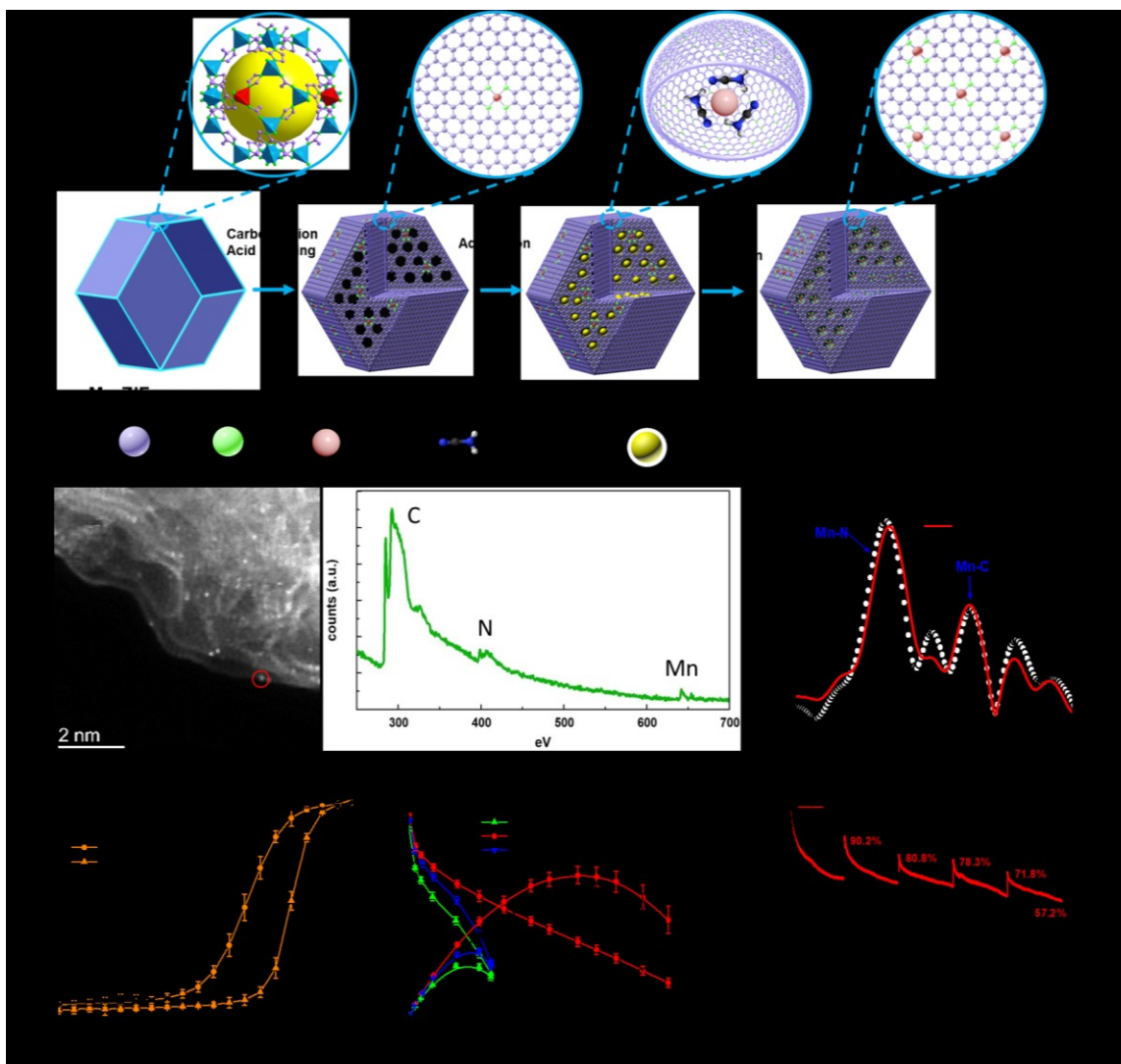


Figure 5. (a) Synthetic illustration of two-step doping-adsorption strategy. (b) The experimental K-edge XANES spectra of atomically dispersed manganese catalyst and reference samples. (c) Fourier transforms of Mn K-edge EXAFS spectra (open circles) and corresponding model-based fits (red line) of atomically dispersed manganese catalyst. (d) ORR polarization curves of Mn-N-C catalysts in 0.5 M H₂SO₄. (e) Polarization curves and power density of 20Mn-NC-second and 20Fe-NC-second catalysts in fuel cell. (f) i-t curves of 20Mn-NC-second and 20Fe-NC-second catalysts at constant potentials of 0.8 V in 0.5 M H₂SO₄. Reprinted with permission from Ref. ¹⁹

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Insufficient activity and stability of the atomically dispersed M-N-C catalyst along with non-optimal electrode structures need to be addressed for viable application in PEMFCs.

Given the low cost and intrinsic ORR activity of atomically dispersed metal catalysts, they are promising candidates to replace PGM catalysts for PEMFC applications (**Figure 6**)⁷¹. Fe, Co, or Mn-N-C catalysts have exhibited promising activity and stability in acidic media, but yet insufficient for viable applications. Especially, their much lower fuel cell performance relative to PGM cathodes remain as significant concerns. Among others, Fe-N-C catalysts currently perform the best, however Fe-related Fenton reactions may cause degradation of ionomers and membrane. Co-N-C catalysts could mitigate the Fenton effect to a certain degree, however, its relatively high cost may yield an additional issue. In addition, the relatively low intrinsic activity of CoN₄ vs. FeN₄ leads to significantly lower fuel cell performance at voltages higher than 0.7 V. Although Mn-based catalysts likely address the stability and cost issues simultaneously, the R&D efforts are still in the early stages, showing insufficient activity and fuel cell performance. Currently, some PGM-free catalysts demonstrating adequate performance may be applied for portable power or backup power, but they are still far below performance thresholds required to meet automotive requirements. Therefore, the development of advanced atomically dispersed metal catalysts still requires improved fundamental understanding and deeper insight into catalytic pathways and degradation mechanisms. Herein, we discuss future directions for research on atomically dispersed metal catalysts that could lead to resolution of current performance and durability challenges.

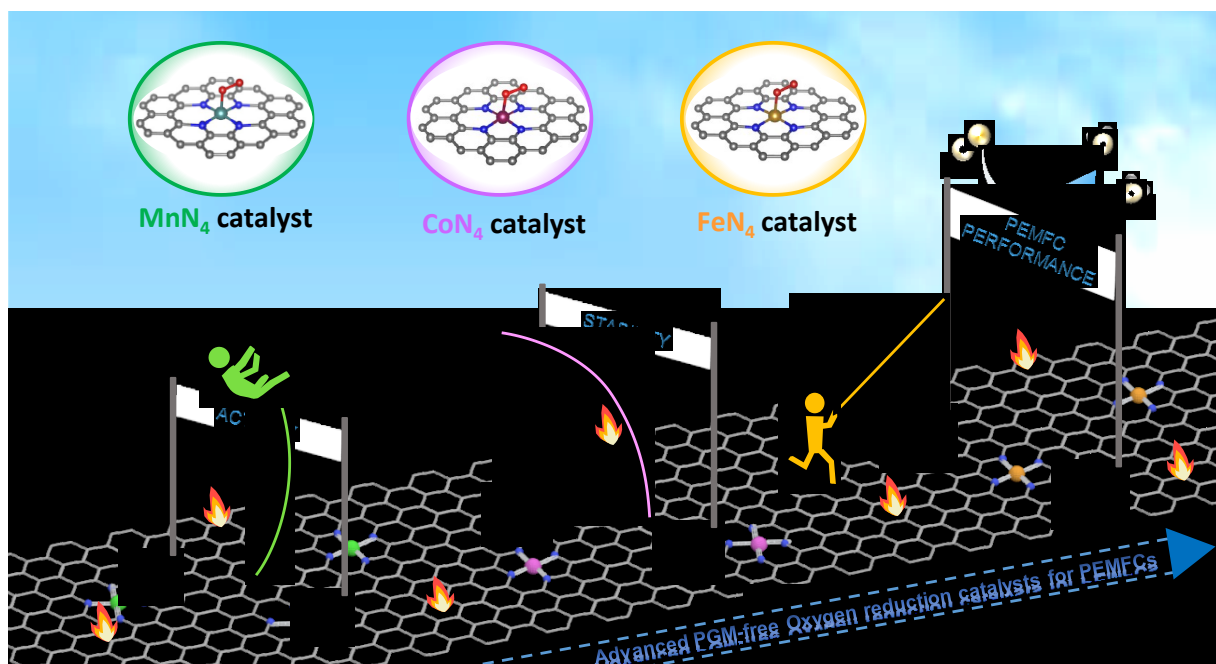


Figure 6. Current status of atomically dispersed metal site catalysts for PEMFCs. Reprinted from Ref ⁷¹ with permission, Copyright 2019, Springer Nature, Shanghai University and Periodicals Agency of Shanghai University.

Generally, strategies to further enhance the activity of atomically dispersed metal catalysts can be divided into two classes: i) increasing the number of atomically dispersed metal sites, and ii) improving the intrinsic activity of atomically dispersed metal sites. For the first strategy, the tendency of single atom to agglomerate due to their high surface energy makes increasing single atom site density while avoiding formation of multi-atom clusters or particles highly challenging. Rational design of 3D porous carbon structures, which can isolate and capture single metal atoms and maximize metal utilization by inhibiting aggregation, appears to be a promising approach to solve this problem. Single metal sites are often stabilized through nitrogen coordination, thus any effective methods to increase doped nitrogen content will be desirable. Moreover, single metal sites may be inaccessible due to charge and mass transport limitations. Therefore, rational design

of 3D mesoporous carbons can further improve performance by increasing the accessibility of active sites.

The intrinsic activity of atomically dispersed metal catalysts varies with different metal centers (Fe, Co, or Mn), which has been verified by experimental and computational results. Different reaction pathways may exist for different active sites. The application of bi-metal or even tri-metal active sites may also be an effective method to reduce the dissociation barrier of O₂ and OOH into O and OH.^{37, 40} Functional modification of carbon through introduction of defects or hetero-atom dopants also can change the mechanism of O-O bond cleavage on active sites. For instance, edge-hosted MN₄ (or MN₂₊₂) appears to generate higher ORR activity compared with bulk-hosted MN₄. In addition to the verified MN₄ sites, M-N-C catalysts may contain diverse potential active sites. Although metal-free CN_x sites have lower intrinsic activity in acidic media, they may affect the electron distribution of carbon surrounding MN₄ sites, generating possible synergistic effects. In addition to the extensively studied nitrogen, other types of heteroatom doping such as sulfur may provide additional benefits to enhance intrinsic activity of MN₄ sites. Due to the lack of accurate control of synthesis, the relevant understanding needs to be acquired from reliable DFT calculations.

Besides optimization of material synthesis, the electrode preparation also needs to be optimized to promote the utilization of MN₄ active sites in carbon catalysts. Even though it is useful to prescreen catalyst activity, selectivity, and stability in aqueous electrolytes by using RRDE methods, MEA design and fabrication for fuel cells requires significant effort to realize uniform ionomer distribution in catalysts with efficient mass and charge transfer. Compared to PGM catalyst MEAs that have been studying for decades, the research on PGM-free catalysts in MEA is relatively limited. Direct transfer of the high activity of atomically dispersed metal catalysts into

MEA performance has thus far proved challenging. Consequently, the optimization of electrode structure and innovative design of MEAs should be taken into consideration seriously, which includes ink preparation (solvent/ionomer), MEA fabrication and ink deposition methods, and *in-situ/ex-situ* electrode characterization.

Apart from activity, the limited stability of atomically dispersed metal catalysts needs special attention. Current stability of the atomically dispersed metal site catalysts is far below that of Pt catalysts in PEMFCs, especially at high voltage (> 0.6 V). Deep understanding of degradation mechanisms in acids, especially during fuel cell operation conditions, is therefore desperately needed. Recently, a mini review from Shao *et al.*, precisely highlighted possible degradation mechanisms of M-N-C catalysts.⁷² Several possible roots of catalyst degradation were identified in fuel cell cathodes including: i) demetalation of active sites, ii) carbon oxidation, iii) micropore flooding, and iv) active site poisoning.^{65, 72-77} These four causes likely affect performance loss to different degrees. Zelenay *et al.* further pointed out that performance degradation mechanisms can be further elucidated from analysis of changes in active site and macro/meso-scale interface structure within PEMFC electrodes.⁷⁸ Catalyst degradation mechanisms in aqueous acidic electrolytes (RDE tests) and solid-state Nafion-based cathode (MEA tests) are significantly different due to many variations associated with acidity, temperature, pressure, local concentrations of O₂ and H₂O₂, and proton/electron conductivity. It should be noted that, in addition to active site degradation, the MN_x sites mainly hosted in catalyst micropores⁷⁹⁻⁸⁰ could be easily flooded by water during the fuel cell operation, especially during the initial stage, leading to significant mass transport limitations and dramatic degradation of catalytic performance.^{66, 81} While RDE stability studies are useful to examine catalyst stability under various potentials, pH

values and temperature in acidic solution, full understanding requires MEA testing under more practical operation conditions.

As for intrinsic activity at the atomic level, the atomically dispersed and nitrogen coordinated MN_4 sites, such as FeN_4 , are significantly enhanced when compared to metal clusters or oxides in acids. The mitigated metal dissolution from catalysts to electrodes also benefits for reducing the possibility to generate radical groups and poison ionomer and membrane. However, the dissolution of single metal sites from M-N-C catalysts is still likely especially under high potentials of ORR or real fuel cell operation conditions. In 2018, Chenitz *et al.* proposed that FeN_4 active sites are thermodynamically stable in static acidic electrolyte, but they would be demetalated in the water flux running into the micropores, according to the *Le Chatelier* principle, which may be responsible for the fast degradation of the fuel cell performance in the initial stages. To effectively evaluate the stability of the atomically dispersed metal site catalysts in PEMFCs, establishment of appropriate accelerated stress test (AST) is necessary. Currently, there are two procedures used for stability studies based on U.S. DOE protocols. Dynamic potential/voltage cycling is used to mimic the dynamic operation condition in fuel cells, with testing typically consisting of triangle-wave cycling between 0.6 and 1.0 V or square-wave cycling between 0.6 and 0.95 V. In addition, cycling or holding at a high potential or voltage (*e.g.* 1.0-1.5 V) is also relevant to evaluate corrosion resistance of carbon phases in catalysts. Recently, we found atomically dispersed Fe-N-C catalysts are reasonably stable after 40,000 potential cycles (0.6-1.0 V) in O_2 saturated 0.5 M H_2SO_4 electrolyte, only losing 26 mV of $E_{1/2}$ value (**Figure 7a**).⁶² This attests to enhanced catalyst stability relative to conventional Fe-N-C catalysts containing multiple Fe species.⁸² The post-mortem microscopy analysis verified that the majority of FeN_4 sites are stable during the dynamic potential tests, as shown by the clear presence of Fe-N coordination and insignificant carbon corrosion

(**Figures 7a**). Significant activity loss (more than 70%) occurs when the test is carried out at a constant potential of 0.85 V for 100 hours, with an especially rapid decrease in the first 20 hours (**Figure 7b**)⁶³. During this stability test, the atomically dispersed Fe sites eventually agglomerated and formed small clusters. Although some isolated Fe sites survived, these atoms are apparently no longer coordinated with N, because Fe and N cannot be detected simultaneously by using EELS at the atomic level. The electron microscopy images also revealed significant carbon oxidation, with carbon particles agglomerated and their original edges no longer present.

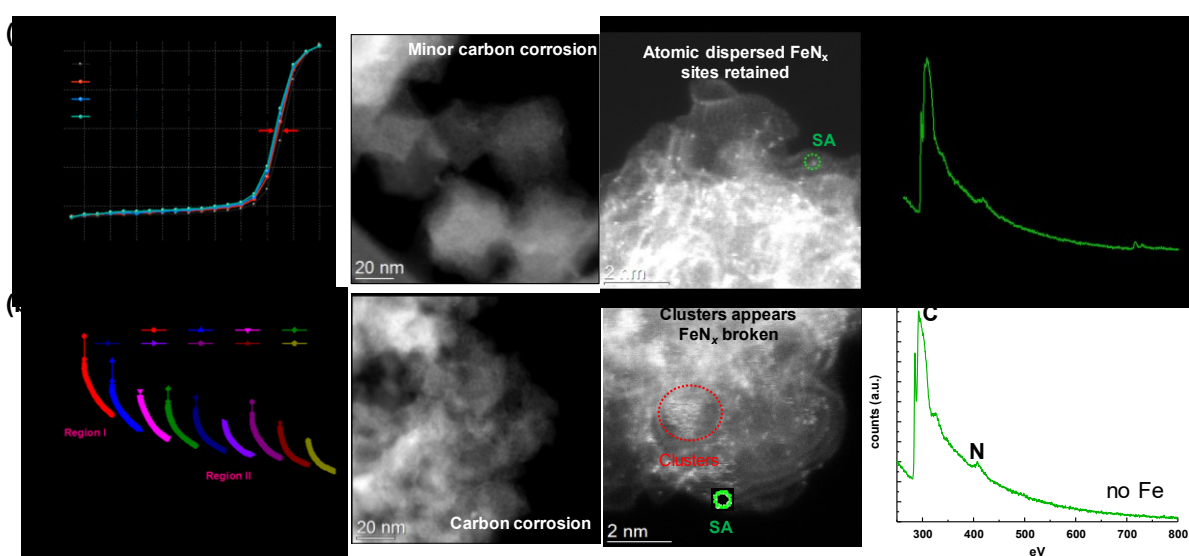


Figure 7. Stability tests in O₂-saturated 0.5 M H₂SO₄ electrolyte using different test protocols for a typical atomically dispersed Fe-N-C catalyst derived from Fe-doped ZIF-8 through one-step thermal activation at 1100 °C. (a) Potential cycling between 0.6 and 1.0 V for 30,000 cycles with insignificant activity loss, corresponding to minor carbon corrosion and nearly intact Fe-N coordinations. (b) Holding at a constant potential of 0.85 V for 100 hours results in significant degradation, especially at the initial stage, accompanied by the appearance of Fe clusters and Fe-N bond breaking. Reprint from Refs.⁶²⁻⁶³

Thus, holding at constant high potentials for the ORR is detrimental and causes cleavage of Fe-N coordination and significant carbon corrosion. Additionally, active site accessibility will be hindered by the collapse of pore structures and the stacking of the catalyst particles or catalyst layer, which results from carbon corrosion. Given that the carbon phase of the ZIF-8-derived atomically dispersed MN_4 site catalysts is generally disordered or only partially graphitized, carbon corrosion is a significant concern under high temperature, humidity, and potential during fuel cell operation. In addition to obvious carbon corrosion, the formation of oxygen-containing groups at the carbon surface also leads to structural disintegration and loss of active sites.^{77, 83} Besides electrochemical oxidation of carbon, chemical oxidation by H_2O_2 and associated free radicals also contributes to significant degradation of ORR performance as a result of destruction of active sites and damage to catalyst microstructure.⁸⁴⁻⁸⁵

During the stability studies, we noticed that activity loss could be classified into reversible and irreversible degradation. Such reversible loss is likely due to the active site poisoning, which are associated with the adsorption of ORR intermediates and the formation of oxygen-containing functional group on carbon. These adsorption occurring during the ORR impacts the binding environment for oxygen reduction intermediates either sterically or electronically. However, such a reversible activity recovery through potential cycling from 0 to 1.0 V does not alter the overall degradation rates eventually. Thus, the irreversible activity loss must be related to the chemical/electrochemical destruction of active sites. Therefore, the most prevalent and serious degradation mechanisms are demetalation and carbon oxidation, because the degradation of performance is usually unrecoverable during fuel cell operation.

Significant effort in development of catalysts and understanding of catalytic pathways and degradation mechanisms is required to improve catalyst stability and performance durability.

Meanwhile, degradation mechanisms may vary for the different kinds of catalysts including Fe-, Co-, and Mn-N-C catalysts. Also they are sensitive to structure and morphology of catalysts, which are in turn dependent on synthesis methods, metals and precursors used, and post-treatment strategies. For example, highly active catalysts often degrade faster especially at the initial stage, suggesting a possible tradeoff among the density of MN₄ sites and interaction with carbon morphology and structure. Although highly graphitized carbons offer enhanced carbon corrosion-resistance in catalysts, they often accommodate less nitrogen dopants and defects associated with active sites. Addressing the grand durability challenge of atomically dispersed M-N-C catalysts should be at both atomic and macroscopic levels, responsible for active sites stability related to demetalation, carbon corrosion, and site poisoning, and three-phase collapse, respectively. Also, standard protocols for stability measurements should be established at both RDE and MEA levels. Currently, PGM-free catalysts are tested under different protocols in different laboratories, preventing direct comparison of results between laboratories and complicating efforts to evaluate and compare degradation phenomena between different catalysts. Thus, more cooperation is needed to unify test standards. Elucidating degradation mechanisms and developing effective mitigation strategies requires *in situ* characterization techniques at the MEA level, which should be coupled with fuel cell performance testing.

In summary, development of atomically dispersed metal site catalysts is important for energy-related electrocatalysis, with a strong need for improved fundamental understanding of material synthesis, active site structures, and reaction pathways. Addressing stability challenges is critical for practical applications. Thus, developing such PGM-free catalysts for fuel cell applications is high-risk research, but the significant cost reduction that could result from effective PGM-free catalysts also makes this research high-reward. In contrast, combining the atomically dispersed

MN₄ sites with low-PGM to develop hybrid catalysts could be more meaningful and practically feasible for future PEMFCs.⁸⁶⁻⁹⁰

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Quotes from the Perspective

1. Theoretical understanding of active sites and reaction mechanisms provides a solid foundation for rational design and synthesis of atomically dispersed metal catalysts.
2. Highly controllable synthesis with precise tuning of composition and morphology would provide an excellent opportunity to acquire understanding on synthesis-structure-property correlations.
3. The combination of advanced synthetic strategies, structural characterization, intrinsic catalysis measurements, and device performance measurements is crucial for developing advanced single-metal-site catalysts.
4. Addressing the grand durability challenge of atomically dispersed M-N-C catalysts should be at both atomic and macroscopic levels, responsible for active sites stability and electrode robustness related to demetalation, carbon corrosion, site poisoning, and three-phase interfaces collapse.