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REVIEW ARTICLE

Gang WU

Current challenge and perspective of PGM-free cathode catalysts for PEM fuel cells

Abstract To significantly reduce the cost of proton exchange membrane fuel cells, platinum-group metal (PGM)-free cathode catalysts are highly desirable. Current M-N-C (M: Fe, Co or Mn) catalysts are considered the most promising due to their encouraging performance. The challenge thus has been their stability under acidic conditions, which has hindered their use for any practical applications. In this review, based on the author's research experience in the field for more than 10 years, current challenges and possible solutions to overcome these problems were discussed. The current Edisonian approach (i.e., trial and error) to developing PGM-free catalysts has been ineffective in achieving revolutionary breakthroughs. Novel synthesis techniques based on a more methodological approach will enable atomic control and allow us to achieve optimal electronic and geometric structures for active sites uniformly dispersed within the 3D architectures. Structural and chemical controlled precursors such as metal-organic frameworks are highly desirable for making catalysts with an increased density of active sites and strengthening local bonding structures among N, C and metals. Advanced electrochemical and physical characterization, such as electron microscopy and X-ray absorption spectroscopy should be combined with first principle density functional theory (DFT) calculations to fully elucidate the active site structures.

Keywords oxygen reduction, fuel cells, cathode, non-precious metal catalysts, carbon nanocomposites

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Gang WU (✉)
Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, New York 14260, USA
E-mail: gangwu@buffalo.edu

1 Introduction

Energy conversion and storage via the direct electrochemical oxygen reduction reaction (ORR) and evolution reaction (OER) are among the most important energy technologies of the modern day. Potential applications include proton exchange membrane fuel cells (PEMFCs), metal (Li or Zn)-air batteries, and water electrolyzers (Fig. 1). These technologies offer many advantages over traditional fossil fuel combustion such as improved overall efficiency, high energy density, and the significant reduction of CO_2 and other emissions [1–2]. In particular, PEMFCs are highly efficient chemical-to-electrical energy conversion devices that can be used as power sources in electric vehicles, portable and stationary applications. Most notably, fuel cell vehicles (FCVs) have the potential to significantly reduce our dependence on foreign oil [3]. They also run on hydrogen gas rather than gasoline and lower harmful emissions that result in environmental pollution and possible climate change [4]. The first commercial hydrogen fuel-cell vehicle "Mirai" made by Toyota has been sold in California in November 2014. Toyota plans to build 700 vehicles for global sales for each year. However, several grand challenges must be overcome including their high cost and insufficient performance durability, before FCVs can begin to compete with conventional gasoline vehicles.

The inherently slow reaction kinetics of the ORR process in challenging acidic media greatly limits the performance of the PEMFC [5–6]. It was found that the ORR over potential depends first and foremost on the intrinsic activity of catalysts [7–8]. As shown in Fig. 1, platinum-group metal (PGM) based catalysts (e.g., Pt) represent the state-of-the-art for the ORR in terms of their highest activity and durability. However, to significantly reduce the cost and realize a sustainable development, Pt must to be replaced. The development of highly active and stable platinum metal-group (PGM)-free catalysts has thereby become a very important topic in the field of electrocatalysis [9–13]. Exploring advanced catalyst

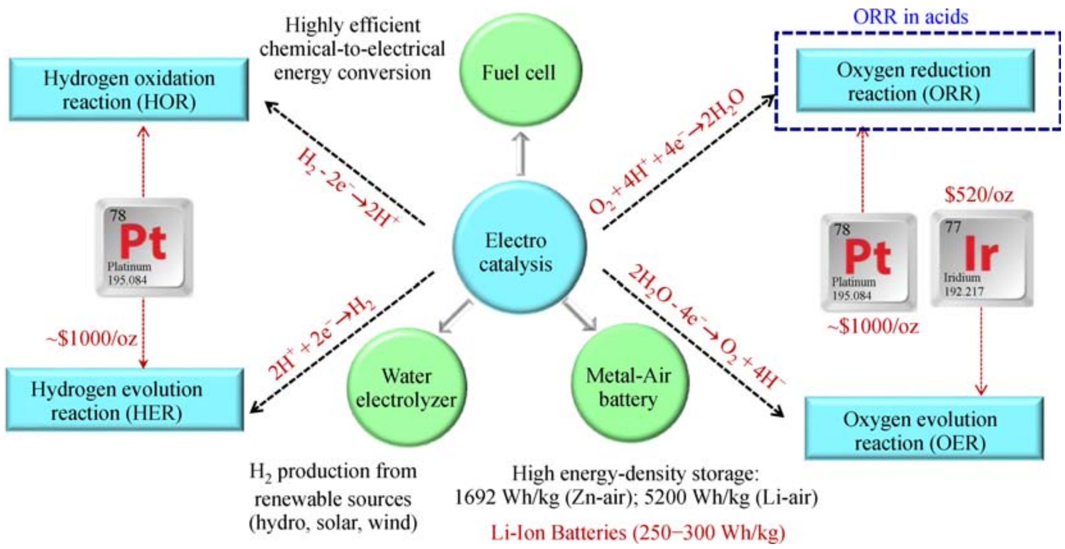
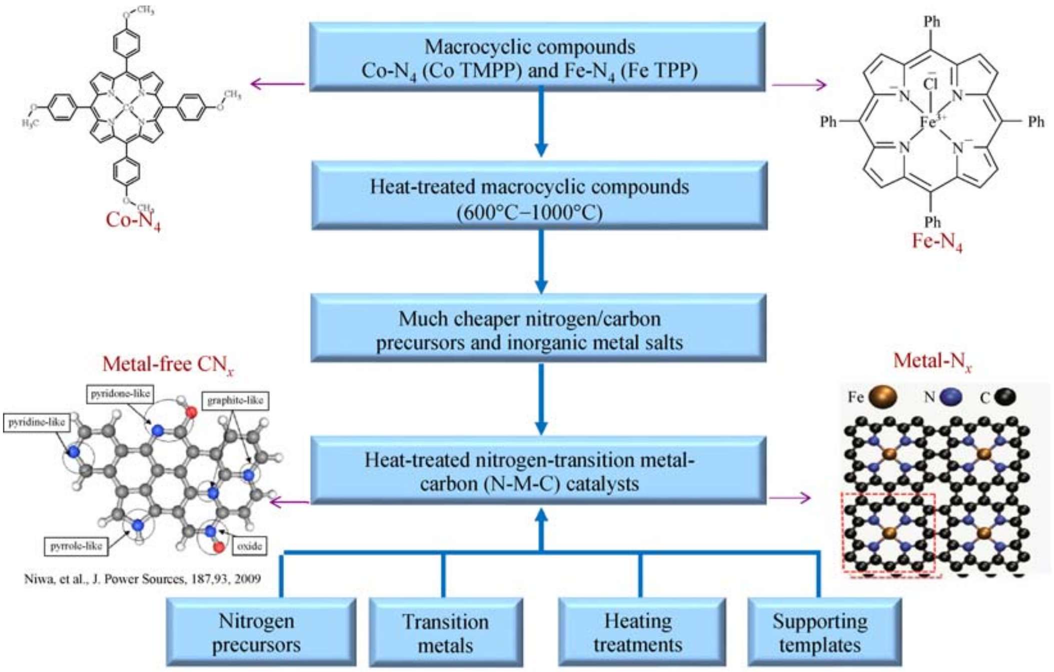


Fig. 1 Electrochemical energy conversion relying on oxygen and hydrogen electrocatalysis using precious metal catalysts

designs and synthesis strategies using earth-abundant elements to mimic the catalytic properties of precious metals is also of considerable scientific interest.

As shown in Fig. 2, during the several decades of searching for PGM-free catalysts for oxygen reduction, significant progress has been made in the synthesis, performance improvement, and mechanistic understanding of those catalysts [14]. A variety of PGM-free formulations have been explored including organometallic components, nonprecious-metal chalcogenides, metal oxides, and nitrogen-doped carbon catalysts [6, 15–20]. Initially, when compared to traditional macro cyclic compounds containing metal-nitrogen coordination structures, much improved ORR catalytic activity and stability had been observed after heating these macro cycles compounds to high temperatures (>700°C) [21]. It seems like the new active sites are generated during the pyrolysis step. In an effort to further explore such heat-treated non-precious metal catalysts, N-containing chemicals such as ammonium and amine as well as inorganic transition metal salts such as nitrate, sulfate and chloride have been explored as cheaper alternatives in the development of catalysts for the



Niwa, et al., J. Power Sources, 187,93, 2009

Fig. 2 Development of PGM-free catalysts for the ORR in last decade

ORR. So far, the nature of non-precious metal active sites in pyrolyzed catalyst is still under debate on the function of the transition metal during catalyst synthesis. Some believe that the metal simply serves to catalyze the nitrogen doping into graphitized carbon structure and is not a part of the functional active site. Oppositely, there is increasing evidence showing that the metal, especially Fe will directly participate in the active site by coordinating with nitrogen or carbon. Despite the controversy, recent progress in the development of high-performance PGM-free catalysts for the ORR by the author [9, 22–33] and other researchers [34–56] indicate that catalytic activity was found to be strongly dependent on the synthetic chemistry of catalysts including structure of the nitrogen precursor, transition metals, heating temperature, and supporting materials [30, 57, 58].

In 2011, researchers from Los Alamos National Laboratory (LANL) developed a new type of PGM-free catalyst derived from polyaniline and transition metals (Fe or Co) [9, 58]. As shown in Fig. 3, through properly selecting the precursors and designing the synthesis procedure, the novel catalyst has a significant increase in the increased density of active sites and a strong interaction between active site and supporting matrix. During the high temperature treatment, the polymer is predominately transformed into a graphitized carbon structure in the presence of transition metals [59]. The precise controls of the polymer morphology and the interaction between polymer, metal and supports during the thermal decomposition process are the keys to achieving high activity and durability. The resulting catalysts have demonstrated high performance, which have minimized the activity gap between Pt and nonprecious metal catalysts to 60 mV in terms of their half-wave potentials of polarization plots in an acid electrolyte. In addition to the high activity, the catalyst demonstrated for the first time a long-term durability at relatively low voltage 0.4 V in fuel cell life tests.

2 Challenges of PGM-free cathode catalysts

2.1 Insufficient activity

Despite significant progress over the last decade, state-of-the-art M-N-C (M: Fe or Co) catalysts are still far away from Pt-based catalysts in terms of activity and long-term durability, hindering their use in practical applications. The significant gaps between the most active Fe-N-C catalysts and state of the art Pt/C catalysts need to be bridged before they can be used in viable fuel cell applications such as transportation (Fig. 4) [9, 60–61].

A key step to further enhance the performance of the most promising Fe-N-C catalysts is to increase the density of the ORR active FeN_x sites embedded within a robust 3D carbon architecture. However, previous work has indicated that simply raising the Fe content in precursors during synthesis is not effective, as this only leads to inactive metallic iron, oxide, or carbide. Currently studied Fe-N-C catalysts are prepared by pyrolyzing a composite that was physically mixed with iron salts, nitrogen-carbon precursors, and high-surface area carbon black supports, followed by a tedious acidic leaching and second

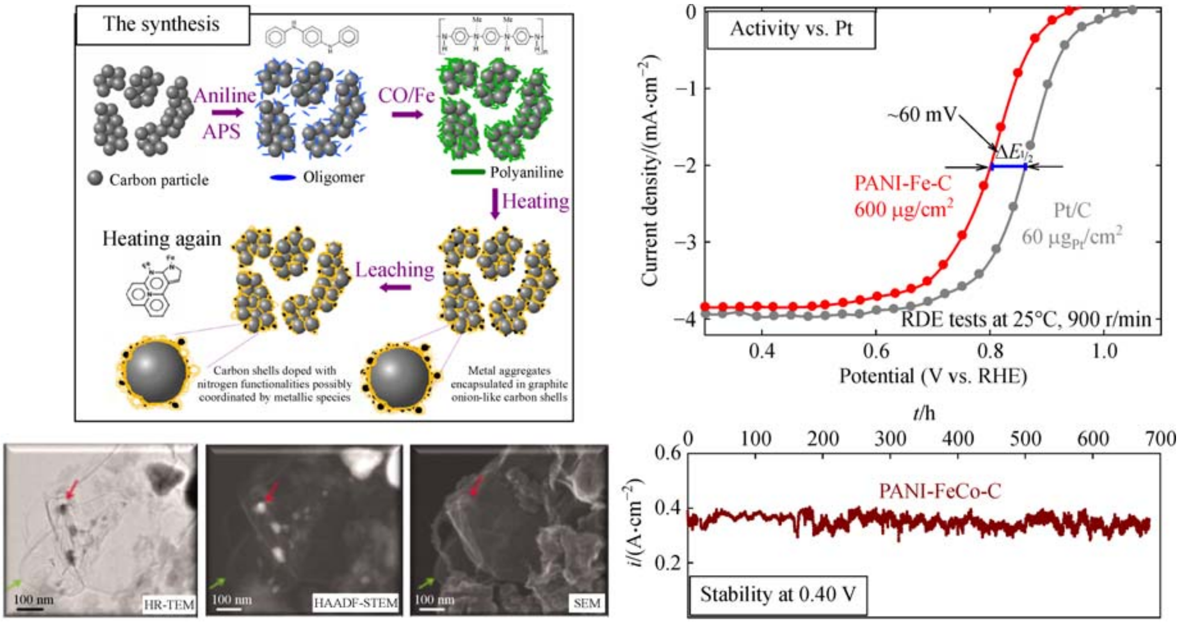


Fig. 3 Polyaniline-derived M-N-C catalysts demonstrating high activity and stability in an acidic electrolyte for oxygen reduction (Reprint with permission from Ref. [9], Copyright 2011 AAAS)

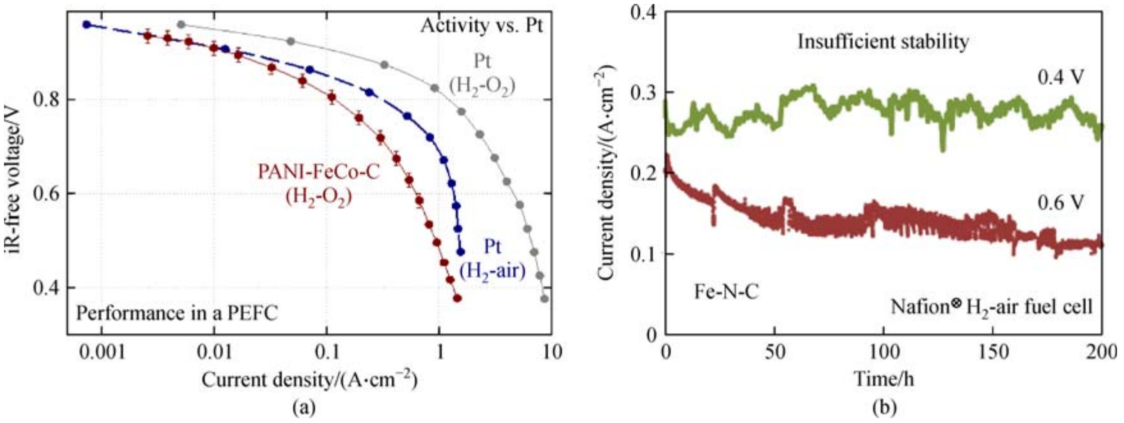


Fig. 4 Insufficient activity and stability of current PGM-free catalysts (Reprint with permission from Ref. [9], Copyright 2011 AAAS [9, 51, 61])

(a) Significant performance gap with Pt/C catalysts; (b) rapid performance degradation at high voltages (>0.6 V)

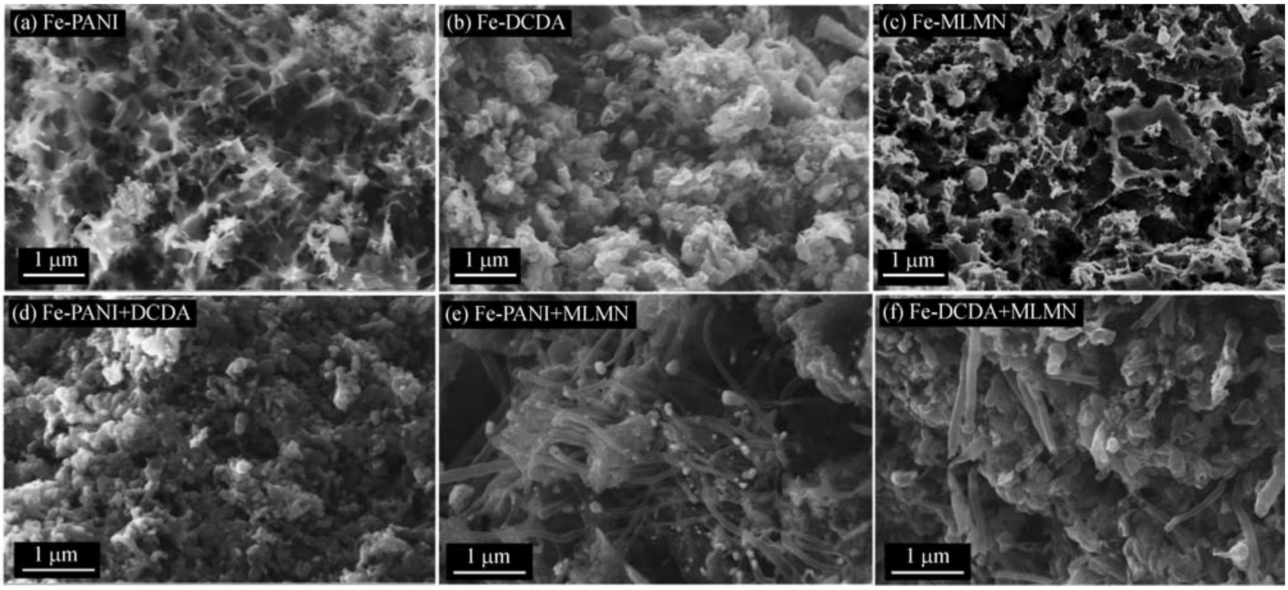


Fig. 5 Diversified carbon nanostructures observed in various M-N-C catalysts synthesized from different nitrogen/carbon precursors, showing highly heterogeneous morphology (Reprint with permission from Ref. [62], copyright 2017, Wiley)

treatments [9]. They often result in a largely heterogeneous morphology without accurate control of local environments for active sites. As shown in Fig. 5 [62], diversified carbon morphologies and structures appear in the catalysts including amorphous carbon and graphitized nanocarbon (onion-like carbon, carbon nanoshells, graphene-like carbon or carbon tubes). This presents a big challenge in the advancement of PGM-free catalysts for fuel cell applications. Moreover, the current Edisonian approach (i.e., trial and error) has been ineffective in overcoming currently remaining challenges and achieving revolutionary breakthroughs [61]. Thus, the challenge remains to find a method to uniformly disperse active atomic iron into the high-surface area carbon matrix with uniform morphology, capable of accommodating an increased number of active sites. To this end, new concepts and approaches are required to design advanced catalysts with well-controlled structures and chemistry.

2.2 Rapid degradation at high potentials

The stability problem must be addressed before PGM-free catalysts become viable for practical transportation applications. In principle, the catalyst degradation is due to two factors: 1) catalytic active sites (CN_x or FeN_x) are chemically and electrochemically oxidized; 2) carbon matrix corrosion leads to the loss of electrical contacts between activity sites and the carbon matrix. The degradation mechanism associated with these factors is not yet clear for the M-N-C catalysts during the ORR in an acidic environment. Our research has clearly indicated that catalysts containing dominant metallic iron exhibited inferior stability when compared to ones with only an atomic iron distribution. Therefore, avoiding the formation of meta aggregate is one of key factors in improving catalyst stability. Since carbon is the dominant component in the catalyst (e.g., large than 85% (at.)), corrosion of carbon is very likely an important factor causing catalyst degradation. In practice, most of the previous Fe-N-C catalysts were prepared by using large amounts of high-surface-area carbon black supports (e.g. Ketjenblack or Black Pearl 2000) to improve active site dispersion [21, 59, 63]. The addition of a carbon black support was often found indispensible to achieving high activity as determined by using rotating disk electrode tests in aqueous electrolyte and Nafion-based fuel cell tests [6, 64]. However, the amorphous carbon blacks in catalysts tend to be oxidized during the ORR and have caused significant carbon corrosion problems [57, 63, 65]. Also, the existence of extra inert carbon supports in catalysts results in a highly heterogeneous morphology and a significant reduction of volume metric activity [66]. Development of effective synthetic chemistry to eliminate the use of a carbon support is highly demanded for the advancement of PGM-free carbon catalysts. More importantly, an understanding of its degradation mechanism (active site oxidation and carbon corrosion) associated with key factors is essential to propose effective solutions and further address the grand stability challenge.

2.3 Knowledge lack of active site chemistry and structure

Unfortunately, the continuous improvement of activity and durability is significantly hindered due to the lack of understanding of the exact active site in M-N-C catalysts. Over the past decades, it has been an elusive, yet fundamentally key piece of information. The current understanding is based only on qualitative knowledge inferred from synthesis processes and on information from somewhat insensitive characterization techniques [67–68]. Most of the currently studied Fe-N-C catalysts are prepared by pyrolyzing a composite that was physically mixed with iron salts, nitrogen–carbon precursors, and high-surface area carbon black supports, followed by tedious acid leaching and secondary treatments [61]. Unlike Pt-based catalysts with well-defined Pt atoms as active sites, these Fe-N-C catalysts often lose their original precursor structure [69] and lead to a heterogeneous morphology without accurate control of the local environments of the active sites (Fig. 6) [9, 30, 70, 71].

For example, in M-N-C catalysts, carbon is the dominant component (up to 85% (at.)) and high levels of graphitic and pyridinic nitrogen (up to 8% (at.)) are successfully doped into the carbon structures to replace the carbon atoms at the inside and the edges of the planes, respectively [34]. These doped nitrogen atoms can be viewed as an n-type carbon dopant that assists in the formation of disordered carbon nanostructures and modifies the electron distribution on the carbon plane, thus enhancing catalytic activity for the ORR [72]. Furthermore, there is a possibility that a transition metal (e.g., Fe, up to 3% (at.) cation is able to coordinate with pyridinic nitrogen and embeds into the carbon plane to form a possible active site configuration [26], which would provide enhanced intrinsic ORR activity compared to the metal-free N-doped carbon. However, it is unclear whether the transition metal is the crucial center of the active site (s), or is only catalyze the process of nitrogen doping into carbon. Also, the bonding mechanism and optimal structures of nitrogen and carbon (e.g., in-plane, edge, subsurface) are yet to be conclusively identified. A more specific hypothesis to explain the role of carbon structures is that the carbon derived from the graphitization process of nitrogen-carbon precursors (e.g., polyaniline, ethylenediamine, melamine,

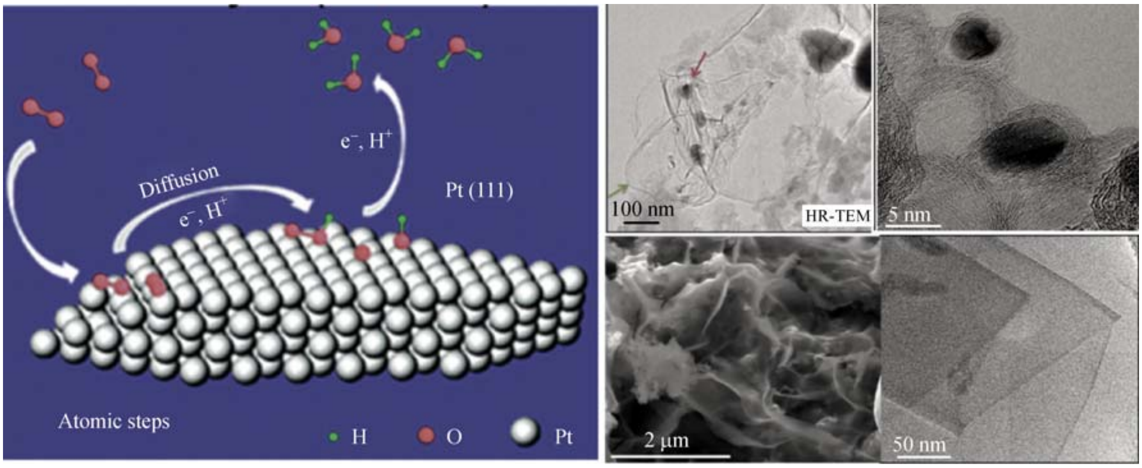


Fig. 6 Comparison between well-defined Pt catalyst (left) and highly heterogeneous Fe/Co-N-C catalysts (right) (Reprint with permission from Ref. [61], Copyright 2013, American Chemical Society)

or cyanamide) in the presence of transition metal species (Co or Fe) at high-temperatures (700°C – 1000°C) may serve as a matrix for hosting active nitrogen or metal moieties [9, 73]. Notably, the *in situ* highly graphitized carbon is greatly dependent on the type of employed transition metals and nitrogen-carbon precursors [9, 22, 25, 30, 58], which affect catalytic activity. Nevertheless, how the nitrogen and transition metal doping in carbon to enhance the catalytic activity remains a conundrum. It would be of fundamental interest to understand the underlying mechanism that affects the electro catalytic properties of M-N-C catalysts. Guidelines need to be developed for the future of catalyst design and synthesis to achieve the targets of higher intrinsic catalytic activity, enhanced stability, and an increased number of active sites.

3 Focuses in the future

Although great progress has been made over the last decade to develop M-N-C for ORR electro catalysis, the current synthetic methods have been insufficient in achieving revolutionary breakthroughs. The use of a systematically designed experimental and theoretical approach to truly control, understand and optimize the atomic arrangement in the catalyst is highly desired. Advanced electrochemical and physical characterization to elucidate fundamental rules that govern catalytic performance are dispensable to the advancement of PGM-free catalysts.

3.1 Structural controlled and ordered precursor design

The crux of the synthetic approach for the development of the PGM-free carbon catalysts is to properly and precisely incorporate dopants (e.g., heteroatoms and transition metal cations) into the carbon planes that are directly converted from well-designed 2D/3D frameworks. Using highly ordered 2D conjugated polymers and 3D frameworks including metal-organic frameworks (MOF), porous organic polymers (POP), and porous dendrite polymers with controlled nitrogen and metal incorporation can provide new pathways to the design of PGM-free catalysts with an increased density of active sites [74–75].

The author's group at the University at Buffalo (UB) recently developed a novel approach to the design and synthesis of highly active and stable PGM-free catalysts with atomic metal dispersion into high surface-area carbon phases by using Fe-doped MOF precursors. Unlike current catalyst synthesis, which relies on a physical mixture of iron, nitrogen and carbon precursors, the MOF precursors containing Fe-N_4 coordination bonded into a 3D hydrogen-carbon matrix was prepared via controlled chemical doping. This Fe-N_4 coordination-rich MOF precursor with well-defined chemical and structural properties is able to further convert to an atomic metal dispersed carbon catalyst via a facile thermal conversion. The excellent flexibility of building up MOFs by tuning ligands and metals provides a great opportunity to methodically optimize catalyst properties through precursor design. The significantly increased density of active sites and enhanced bonding between M and N/C have yielded high-performance PGM-free catalysts with greatly enhanced activity and stability. The newly developed synthesis approach and resulting carbon catalysts are illuminated in Fig. 7 [76]. The new method using the active metals (M)-doped MOF precursors to synthesize M-N-C PGM-free catalysts has many advantages over the conventional

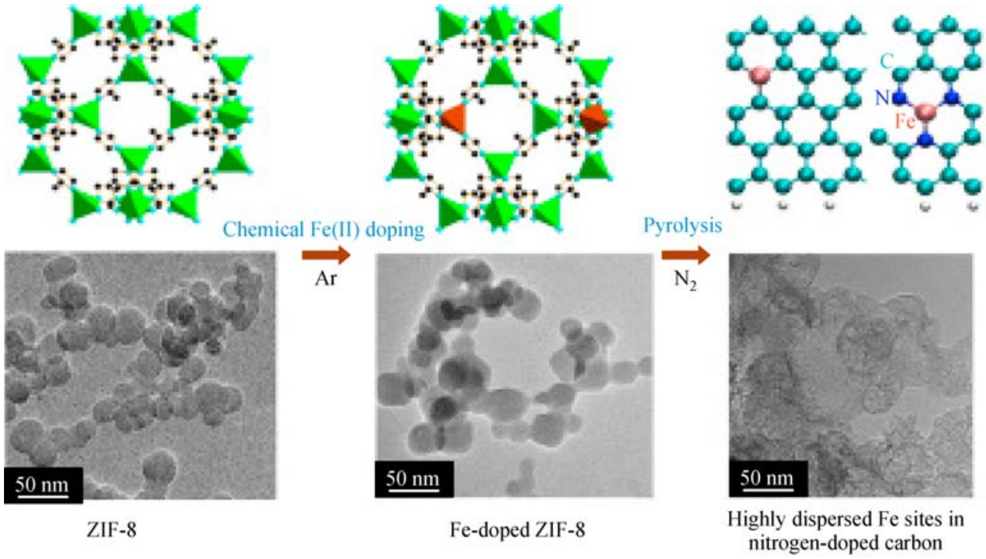


Fig. 7 MOF-derived catalysts with well controlled morphologies and structures (Reprint with permission from Ref. [74], copyright 2016, Elsevier)

methods [74]. (1) The chemical metal doping via solution reactions allows us to accurately control metal content and position. (2) It offers feasibility to adjust the ratios of N/C/M in MOF precursors by adding additional alkyl groups to imidazole in ZIF. (3) The uniform MOF crystal particle morphology can be directly converted to homogenous catalysts through a facile carbonization step. (4) The new synthesis approach eliminates the tedious post treatments including acidic leaching and the second heating treatment, which improves the feasibility for large-scale and low cost manufacturing. (5) The hydro-carbon network in MOFs is able to directly convert into carbon, and thus no additional carbon supports are required during the synthesis, improving volumetric activity of catalysts and reducing the cost.

It is worth mentioning that, in the newly developed M-N-C catalyst derived from MOFs, a dominant amorphous carbon morphology was found, but displayed an even higher ORR activity ($E_{1/2}$ up to 0.82 V vs. RHE) relative to state-of-the-art graphitized carbon-rich Fe-N-C catalysts (0.80 V). It seems that the graphitized carbon structures in the M-N-C catalysts are not necessary for generating high ORR activity, which is opposite to our previous understanding. Thus, the role of carbon within the catalyst still needs to be clearly elucidated. One of reasons for the high-performance of the MOF catalyst is the atomically-dispersed Fe atoms, which have been verified using advanced microscopy facilities. This is in widely in contrast with previous Fe-N-C catalysts, which contain significant inactive metallic iron aggregates. The identified correlation between structure and property further indicated that metal-doped MOF precursors are the foremost variable in controlling catalytic activity and stability along with various catalyst properties including particle size, porosity, graphitization, and nitrogen-doping.

3.2 Multiple nitrogen/carbon precursor to engineer catalyst structures

During catalyst synthesis, the nitrogen/carbon and Fe-rich compounds are carbonized together accompanied by direct doping N and Fe into the carbon matrix. The catalyst morphologies and structures were found to be very important to overall catalyst activity and stability, which are greatly dependent on the type of nitrogen/carbon precursors [62]. However, there is no conclusion yet about the most favorable morphology and structure for the Fe-N-C catalysts. Therefore, there is high demand to clearly elucidate the correlation of catalyst morphology and performance.

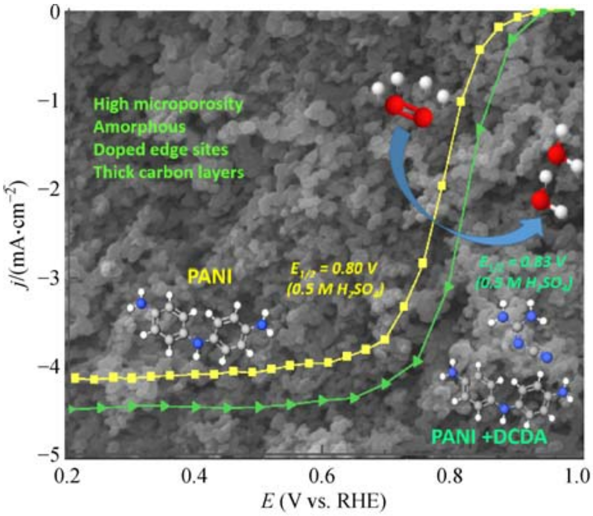


Fig. 8 Engineering favorable catalyst morphology and structure for the ORR [62] (Reprint with permission from Ref. [62], copyright 2017, Wiley)

In our ongoing effort (Fig. 8), we prepared the most favorable morphologies and structures of Fe-N-C catalysts for the ORR by using various nitrogen/carbon precursors including individual polyaniline (PANI), dicyandiamide (DCDA), melamine (MLMN) and their binary systems (PANI + DCDA, PANI + MLMN, and DCDA + MLMN) [62]. The nitrogen doping and the carbonized carbon structures associated with surface areas, porosity, and graphitization degree are found greatly dependent on the type of precursors. Compared to DCDA or MLMN, PANI is more favorable to result in thicker graphitic structures with a relatively lower degree of graphitization, larger microporosity, and higher nitrogen and Fe content. When binary precursors were used, the combination of PANI + DCDA provides optimal porosity and increased BET and electrochemical active surface areas. The addition of DCDA into PANI results in an increase of pyridinic nitrogen content doped into more amorphous carbon phases. Much thicker carbon layers in catalysts formed and were able to accommodate higher numbers of active sites associated with pyridinic N and atomic Fe despersion. Although a similar nature of active sites formed in all studied catalysts, tuning various precursors is effective in yielding favorable catalyst morphologies and structures including an increased density of active sites and a uniform active site (FeN_x) dispersion with minimized agglomerates of ORR inactive Fe/Fe_3C species. These features are responsible for enhanced catalyst activity and stability especially in acidic media. Also, the nitrogen precursors consisting of both conjugated aromatic (PANI) and C≡N bond (DCDA) systems are important to yield highly porous and amorphous carbon phases containing thick carbon layers with high content and uniform dispersion of active sites for maximum ORR activity.

3.3 Stability enhancement

The stability of metal-related active sites embedded into a carbon matrix can be improved by enhancing the M-N bonding in precursors with an optimal M-N_4 complex, local hydro-carbon groups, and crystalline size [74].

Optimal carbonization conditions (temperature, atmosphere, duration) are crucial for forming a stronger interaction between M, N, and C. Carbon corrosion is directly associated with catalytic activity degradation due to the loss of electrical contact, failure to provide a robust matrix for embedded active sites, reduction of reactive surface areas, and hindrance of local mass transport. Thus, stability enhancement can be achieved by the optimization of the local surrounding carbon bonding structures as well as carbon morphologies (defects, graphitization, and nanostructures) [17,57]. Several strategies can be employed to optimize the carbon structure for stability enhancement including: (1) controlling precursors to optimize the carbon microstructures; (2) adding additional nitrogen/carbon precursors (e.g., polyaniline, ethylenediamine, cyanimide) with precursors to optimize the carbon sources; (3) chemically co-doping Mn with Co to improve stability, as we recently discovered that Mn promotes the formation of carbon with much greater stability; (4) finding the optimal carbonization condition to achieve an ideal degree of graphitization and defect controls.

3.4 Active sites understanding

To shed more light on active site structure, experimental characterization and theoretical modeling need to be integrated. Advanced characterization help provide structural and chemical information about active sites. For instance, advanced microscopy monitors the changes of metal species in the catalyst during the AST tests. The measured activity is tied to the structural/chemical changes of metal-involved active sites and provides understanding of the degradation mechanism for M-N-C under different conditions [27]. Electrochemical *in situ* XAS gives an understanding of possible change in the metal bonding environment with nitrogen and carbon. By controlling the electrochemical potential during the ORR, the M-N bonds can be studied in terms of their content and structure [68]. Accelerated stress tests (ASTs) by using potential cycling can be combined with the unique *in situ* XAS to determine the stability of metal in catalysts associated with possible activity loss.

3.4.1 *Ex-situ* electron microscopy studies

Microstructural characterization helps identify the structures and phases of the nitrogen and metal doped M-N-C catalysts (e.g., carbon structures/phases, nitrogen incorporation, M-N interactions, etc.), as well as structural transformation from the highly ordered 2D/3D frameworks to model catalysts incurred via thermal treatment. These characterizations aid the elucidation of the structural and chemical properties of doped model catalysts. In particular, high-resolution imaging and analysis can elucidate the atomic-scale crystallinity of the carbon present in model catalysts. High-resolution TEM, Electron energy loss spectroscopy (EELS) and extended electron energy loss fine structure (EXELFS) can provide information about bonding characteristics of among N, C, and transition metals. The image of PANI-derived Fe-N-C catalysts, developed by the author shown in Fig. 9 [27], is capable of directly identifying the possible N and Fe doping into graphene planes at the atomic level. Thus, an understanding of carbon structure (amorphous vs. graphitized) along with the interactions between metal-nitrogen-carbon can be linked to the measured catalyst activity and stability.

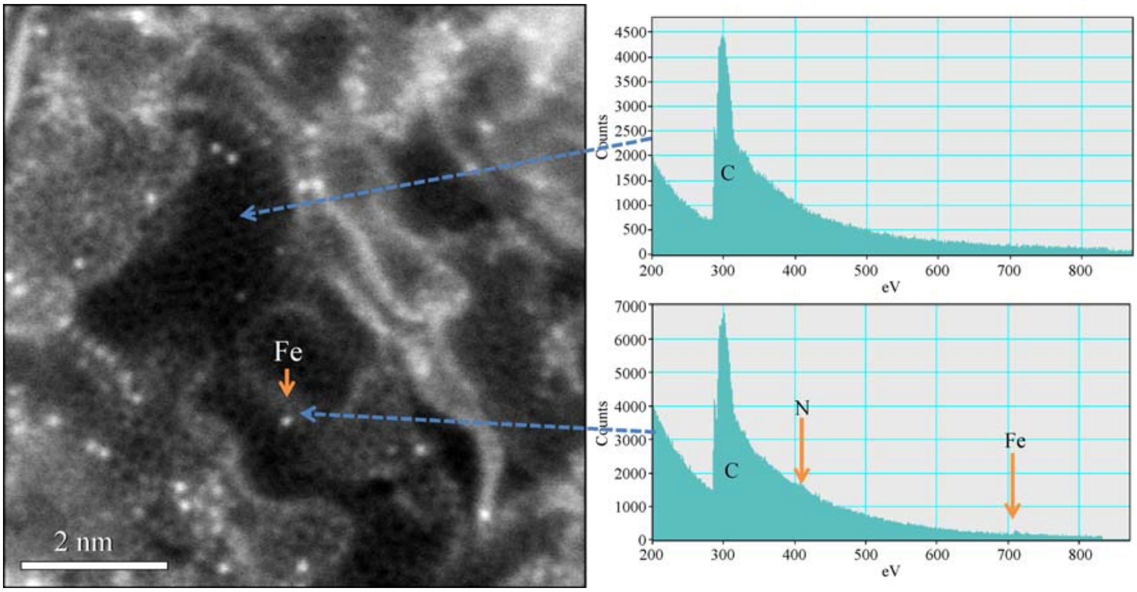


Fig. 9 One example of Microscopy analysis for PANI-derived Fe-M-C catalysts [27] (Reprint with permission from Ref. [27], copyright 2014, American Chemical Society)

Advanced microscopy can provide us with direct observation of catalyst structures at the atomic level to build up the corrections of synthesis-structure-properties, which is valuable to guide rational design of the next generation M-N-C catalysts.

3.4.2 *In situ* electrochemical X-ray absorption

In situ electrochemical XA, spectra can provide the correlations of oxidation state (X-ray absorption near-edge spectroscopy, XANES) and ligand environment of transition metals (X-ray absorption fine structure, XAFS) in the transition metals (Fe, Co, Ni, or Mn) as a function of applied potentials during the ORR [68, 77, 78]. Thus, new insights into the origin of the reversible redox couples related to metals and their effects on catalyst performance can be better understood. The changing of possible bonding structures associated with active sites can be monitored dynamically in real time to determine the catalytic mechanism involving metals. The coordination and bonding structural information of metals can be further linked to catalyst activity and reversibility data so as to establish the structure-property correlation for the doped M-N-C models.

3.4.3 Theoretical modeling and predictions

First-principles quantum chemistry has been shown to be a valuable and effective tool in the study of electrocatalytic problems in the context of energy conversion [79–85]. Much effort, especially focusing on metal-free heteroatom-doped carbon systems, has been devoted in recent years to developing concepts and methods, and protocols (e.g., *d*-band theory [86], e_g orbital occupation analysis [10]) to rationalize the nature of catalytic reactions occurring at doped carbon surfaces [87]. For instance, a frontier orbital analysis was introduced for boron-doped carbon, which suggests that the partially filled $2p_z$ orbital constitutes the main protruding lobe in the two highest occupied molecular orbitals of B-doped graphene, i.e., the HOMO is acting as the electron-donating site for the ORR [88]. In addition, it was found that the nitrogen atom in C-N-σ-bonds of N-doped systems exhibits sp^2-like hybridization. Such C-N-σ-bonds are considerably polarized due to the relative electronegativity differences between nitrogen and carbon. The positive polarization of the carbon atoms makes them more suitable for a nucleophilic attack by O_2 [88]. The N-doping and defects in the graphene lattice conversely increase the oxygen adsorption energy and can change the mode of adsorption [12, 88]. Consequently, the ideal N-doping (including amount, position, and type, in particular in the context of transition metal-involved M-N-C systems with possible M-N or M-C coordination) are unknown.

As shown in Fig. 10, using graphene as a model, the library generation can yield a distribution of candidates for each active site model system (i.e., Fe-N_4 vs. Fe-N_3, edge vs. vacancy) embedded in graphene structures with various nitrogen doping (pyridinic, pyrrolic, graphitic, and pyridinic N^+-O^-), and relevant defects resulting from N and metal doping (open "edge" vacancy, Fe/vacancy, cyclononane/cyclopentane relaxed vacancy, pyridinic vacancy structure, Fe/pyridinic vacancy, and pyridinic vacancy at near-edge). The qualitative analysis of weakening and scission of the O-O bond on each type of heteroatom-related moieties (e.g., C-N_x and M-N_x) will be conducted to simulate their catalytic activities during the electrochemical reduction of O_2. We will determine adsorption energies of the ORR intermediates (*O, *OH, *OOH) on various sites (M-N_x or CN_x). Thus, activity, selectivity, and stability can be predicted based on the entirety of the compiled data. Then synthesis targets can be derived from this molecular understanding in a new loop.

4 Conclusions

Active and durable platinum group metal (PGM)-free catalysts are in high demand as a replacement for Pt in current proton exchange membrane fuel cells (PEMFCs) due to its scarcity and cost. Great progress has been made over the last decade to develop transition metal-derived nitrogen-doped carbons (M-N-C, M: Fe or Co), the most promising class of NPMC for oxygen reduction reaction

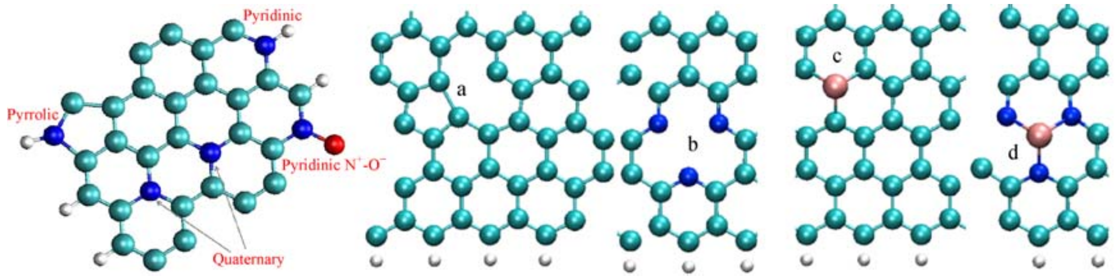


Fig. 10 DFT model for graphene with various nitrogen doping, resulted defects (a–cyclononane/cyclopentane relaxed vacancy; b–pyridinic vacancy structure), and the possible M-C (c) and M-N (d) coordination (Carbon atoms: cyan; Nitrogen: blue; Oxygen: red; Iron: light brown)

(ORR) electrocatalysis. However, current catalyst development conventionally relied on an Edisonian approach (i.e., trial and error), which has been insufficient in achieving revolutionary breakthroughs for producing technologically viable M-N-C catalysts. Rather, the field is in dire need of a systematically designed experimental and theoretical approach to truly control, understand, and optimize the atomic arrangement in this class of catalysts. As for new synthetic concepts, highly ordered 2D conjugated polymers and 3D precursors including metal-organic frameworks (MOF), porous organic polymers (POP), and porous dendrite polymers are effective in increasing active site density (i.e., volumetric activity) and in the enhancement of the intrinsic activity and stability in acidic electrolytes. Advanced electrochemical and physical characterizations are necessary to help elucidate active sites. Theoretical simulation and predictions can further provide an atomic level understanding of active sites and reaction mechanisms. Overall, to further advance PGM-free catalysts, new concepts and materials to significantly enhance activity and durability are needed. Novel synthesis strategies, which enable to maximize the atomic iron site dispersion into a robust carbon matrix, will lead to enhancement of activity and stability.

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