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Short Review

Synthesis of Non-Noble Nitrogen-Containing Catalysts for Cathodic Oxygen Reduction Reaction: A Critical Review

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This paper provides an overview of the literature on the preparation aspect of nitrogen-containing electrocatalysts for oxygen reduction reaction at the cathode side of fuel cells and metal-air batteries, in particular focusing on the selection of nitrogen precursors and the exploration of synthesis methods. At present, some remarkable progress has been made in catalyst preparation techniques, but the practicalities of these catalysts have not reached the level of Pt-based catalysts. Thus, it is proposed that both new nitrogen precursors from nature and innovative preparation methods are needed for the discovery of new catalysts and for the optimization of catalyst performance.

Keywords: Air electrode, Electrocatalyst, Oxygen reduction, Nitrogen precursor, Synthesis method

1. INTRODUCTION

Fuel cells (FC) and metal-air batteries (MAB) become new focuses of research in the field of electrochemical power sources owing to their distinctive characteristics of environmental compatibility, high power generation efficiency, and flexible assembly [1]. It is noteworthy that the oxygen reduction reaction (ORR) commonly occurs at the cathode side, and the oxygen is derived from the air. The cathode side of FC or MAB is called “air electrode (AE)”. However, the ORR in AE displays two adverse reaction characteristics: (i) the slow behavior of dynamics process; (ii) the diversity of the ORR pathways including two-electron and four-electron pathways. The former can influence the improvement of cell performance, and the ORR rate is far less than the anodic oxidation reaction of fuels which produces lower exchange current density and makes the minimum possible large current discharge. The ORR tends to be carried out under a higher over-potential, resulting in a large decrease of the effective output voltage of batteries [2]. A greater loading of cathode catalysts are required to enhance the overall current density of batteries, which further increases the production cost in practical applications. In addition, the latter can also arise two problems: (i) different electron-transfer pathways have caused the large difference of discharge efficiency, but the four-electron pathway is the most efficient reaction process; (ii) some thermodynamically unstable intermediates (H_2O_2, HO_2^-, *etc.*) produced in the reaction process of two-electron pathway will lead to negative effects on power systems, and the most representative effect is to damage the electrolyte membrane resulting in the decrease of the ORR activity [2].

A point worth emphasizing is that the electo-reduction process of oxygen molecular complies with a two-electron reaction pathway or a four-electron reaction pathway, mainly depending on the interaction between the oxygen and the electrode surface, because the ORR mechanism in the AE is extremely complicated. The optimization of electrocatalysts is one of key factors to achieve four-electron reaction pathways. Up to date, precious metal-based materials (*e.g.*, Pt and its alloys) are the most successful catalysts owing to their high activity for ORR in acidic and alkaline environments, but they have not tolerance to methanol and other special fuel molecules except their high cost and scarceness. Therefore, the development of new catalysts with inexpensive, high activity and stability, excellent selectivity to four-electron reaction pathway and outstanding methanol-tolerant performance to substitute Pt-based catalysts is of paramount importance to rapidly realize the commercialization of FC and MAB.

Since Jasinski et al. [3] reported that cobalt-phthalocyanine (CoPc) exhibited the catalytic activity towards ORR in alkaline solution, many efforts focused on the fabrication of a new type of catalysts (labeled as Me/N/C) from metal macrocyclic complexes containing Me-N_x (Me = Fe, Co, Mn, *etc*., x = 2, 4, 6, *etc*.) structures and their derivatives, in particular the Fe- and Co-based catalysts [4-7]. In 2008, Bezerraa et al. [8] has specifically reviewed the research progress of Fe/N/C and Co/N/C catalysts. Me/N/C catalysts is also considered to be one of the promising alternatives for Pt-based catalysts thanks to their excellent ORR performance and high electrochemical stability. Furthermore, the starting point of most of research reports on the catalyst preparation could be mainly attributed to two aspects: (i) the use of the precursor containing Me-N_x structures was an essential prerequisite for the synthesis of Me/N/C catalysts; (ii) Another important finding, proposed by Gupta et al. [9], was that pyrolyzing a mixture of Me precursors and nitrogen precursors impregnated on a carbon black in an inert atmosphere can produce Me/N/C catalysts for the ORR. Notably, the catalyst with ORR activity can be also obtained from the co-pyrolysis of a nitrogen source and a carbon support without addition of transition-metals. This breakthrough has caused the study of Me/N/C catalysts to be rapidly developed. Many kinds of ORR catalysts were successfully fabricated by using nitrogen-containing compounds instead of Me-N_x complexes as specific nitrogen precursors [10]. They exhibit reasonably ORR electrocatalytic activity and stability, but none can replace the Pt-based catalysts in a real sense until now. It can be concluded that the development of two characteristics of catalyst preparation will help to partially improve the catalytic performance, which are the selection of specific nitrogen sources to form the catalytic sites and the exploration of new synthesis methods, respectively. Hence we here put particular emphasis on reviewing the research progress of Me/N/C catalysts aimed at the aforementioned issues in order to provide new insights for synthesis of catalysts with a higher activity.

2. SELECTION OF NITROGEN PRECURSORS TO FORM Me/N/C CATALYSTS

2.1. Macrocyclic complexes containing Me-N_x structures

Since CoPc was found to have ORR electrocatalytic activity in 1964 [3], many researchers widely took advantage of metal porphyrins or metal phthalocyanines containing Me-N_4 structures for the preparation of Me/N/C catalysts. These coordination compounds were collectively called "N_4-macrocyclic metal complexes" [11]. Dodelet and his co-workers [12,13] prepared the Co/N/C catalysts by the pyrolysis of CoPc and its tetracarbonyl derivatives (CoPcTc) supported on the carbon black (Vlucan XC-72R) surface at high temperatures. Their results indicates that Co/N/C catalysts obtained at 500~700 °C have exhibited the best ORR electrocatalytic activity, and the corresponding ORR active sites can be contributed to a moiety of CoPc fragments such as Co-N_4 structure below 600 °C. Additionally, the Co/N/C catalyst from the heat treatment of CoPcTc at 900 °C may play a key role in enhancing the electrochemical stability in acidic medium and its catalytic sites for ORR can be related to inorganic cobalt present as metal and oxides, which is surrounded by a protecting graphite shell. Another Fe-based catalyst (Fe/N/C) was desigined by pyrolyzing tetracarbonyl iron phthalocyanine (FePcTc) loaded on the carbon black at 900 °C [14]. The Fe/N/C(900) demonstrated the best ORR electrocatalytic activity and the highest stability, but Fe-N_4 fragments from the decomposed product of FePcTc were not found and inorganic iron surrounded by a protecting graphite layer was also the active site for ORR. However, this perspective of active sites was not supported by Yeager and his co-workers [9,15], and they put forward two cogent reasons in favor of their opinions: (i) inorganic metal species inside Me/N/C catalysts can dissolve in acidic solution partly or absolutely; (ii) the Me species will be completely coordinated with the N sources to produce Fe-N_x structures adsorbing on the carbon surface during pyrolysis at high temperatures. Zhang and his co-workers also reported the preparation of Fe/N/C catalysts by using two derivatives of iron phthalocyanine (*e.g.*, 2, 11, 20, 29-tertbutyl-phthalocyanine and 2, 11, 20, 29-tertbutyl-naphthalocyanine) as nitrogen sources [16]. A Cu/N/C catalyst (CuPc/C) was further synthesized by using copper phthalocyanine (CuPc) as a nitrogen precursor *via* pyrolysis at 900 °C [17]. The ORR active sites of CuPc/C may be the Cu-N_x structures produced by the coordination of metallic Cu and pyridinic- or graphitic-N functional groups. He et al. [18] creatively formed a bi-core FeCu/N/C catalyst by the co-pyrolysis of CuPc and FePc complexes. This study showed that the electrocatalytic activity of single-core Fe/N/C catalyst was enhanced by addition of Cu atoms, but Me-N_x bonding structures have been maintained in the FeCu/N/C catalyst. X-ray absorption spectroscopy (XAS) analysis interestingly revealed that a fraction of an electron was transfered from Fe to Cu, which helps to lower the ORR kinetic barriers.

Dodelet and his co-workers [19] prepared a Fe/N/C catalyst (FeTPP/C) by thermally treating iron tetraphenylporphyrin (FeTPP) absorbing on the carbon support at 1000 °C. This study importantly pointed out a fact that only pyrolyzing a mixture containing Me source, N source, and carbon source at high temperatures can produce a Me/N/C catalyst. They further studied the catalytically active sites for ORR by using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) soon afterwards [20]. It was found that only $FeN_2C_4^+$ ion may be the ORR-active site and its formation is independent of preparation methods. Moreover, two factors of controlling the quantity of active sites have been also focused [21], which are the nitrogen content and micropore surface area, respectively. It was proposed that using non-porous carbons as the supports can benefit the development of Me/N/C catalysts with larger micropore surface area. A spherical, porous and uniform Co/N/C catalyst (CoTMPP/C) with high BET surface area (834 $m^2\ g^{-1}$) has been prepared by an ultrasonic spray pyrolysis (USP) technique [22], and its ORR activity was largely enhanced compared with a previous report [5]. Ma et al. [23] similarly reported the synthesis of CoTMPP/C at 900 °C and its ORR catalytic performance. A maximum power density of 150 mW cm^{-2} was generated from a single H_2-O_2 fuel cell with CoTMPP/C catalyzed cathode. The active sites for ORR of CoTMPP/C catalysts were systematically studied by Wang et al [24]. It was found that the active site structures in CoTMPP/C were changed by the pyrolysis process. The macrocyclic structure of CoTMPP was destroyed below 400 °C, and a stable Co-N_x structure adsorbing on the carbon surface was renewedly formed at 900 °C which may be responsible for the enhanced ORR performance.

2.2. Specific biomaterials containing Me−N_4 structures

In 2006, Maruyama et al. [25] innovatively prepared a new Fe/N/C catalyst (Hb825) with high BET surface area (1005 $m^2\ g^{-1}$) by the carbonization of hemoglobin (Hb) at 825 °C. It was proposed that the development of nanospace inside Hb825 can promote more active sites to be exposed to the surface improving the ORR activity, and the active sites for ORR can be the Fe-N_4 structure produced by the coordination of Fe (III) ions and four pyrrolic-like nitrogen atoms. Subsequently, enhanced catalytic properties was achieved by a change in the carbonization process from one step to two steps [26]. The modification of carbonization process reduced the Fe valence state from 3+ to 2+ in the carbonized materials, probably providing more O_2 bonding sites required in the first step of the multistep cathodic ORR process. Shortly afterwards, the formation and internal structure of intermediates obtained from partial carbonization of hemoglobin were intensively investigated [27]. It was found that the pyropolymer formation began at around 200 °C, and aromatic carbon developed with an increase in the pyrolysis temperature through transformation of the aliphatic carbon in hemoglobin. Notably, the Fe-N_4 structure was further confirmed as the active site for this carbonaceous material [28]. Our research group abandoned the routine perspectives about the selection of nitrogen sources, and interestingly studied the structural changes of blood pyropolymers from the carbonization of several animal bloods and their potential electrocatalytic activity towards ORR [29,30]. We have found that the change of particle phase depends on the pyropolymers formation, but has no effects on their internal carbon structures which are controlled by pyrolysis process only.

Besides, the blood pyropolymers are active to the ORR and can function as nitrogen precursors. It is the first time to propose a new idea of preparing ORR catalysts derived from inexpensive and abundant animal biomass [31].

Hemin as a biomaterial is the primary stabilizer to the molecular structure of hemoglobin, which was also reported to be an effective electrocatalyst for mediating the electroreduction of oxygen [32]. Liao and his co-workers [33] reported a strategy to design an ORR catalyst (Fe/N/C600) from hemin loaded on carbon black, followed by the heat-treatment at 600 °C, and measured its ORR catalytic activity and stability [34]. These results showed that the atomic ratio of Fe to N has decreased from 1:4.7 for hemin/C to 1:1.9 for Fe/N/C600 in the pyrolysis process, and the Fe-N_2 structure was considered as the active center in Fe/N/C600. Moreover, the pyrolysis can improve the stability of Fe/N/C by removing the organic groups in hemin, but leads to the loss of metal Fe particles which decreases its electrochemical stability in acid media. Jiang et al. [35] further modified the preparation process by combining an ultrasonic technique, which increased the BET specific surface area and the number of ORR-active sites of Fe/N/C catalysts derived from hemin. Graphene nanoplatelet has been also chosen as a new support to substitute the traditional carbon black for synthesis of Fe/N/C catalysts [36]. Remarkably, a single H_2-O_2 fuel cell fabricated with this synthesized catalyst yielded a power density of 300 mW cm^{-2}.

2.3. Other kinds of nitrogen-rich compounds

Maruyama et al. [37] reported that the pyrolysis of a mixture of Fe (II) lactate, glucose, and glycine produced a nitrogen-containing electrocatalyst with a Fe-N_4 moiety mimicking the center of heme by self-organization of Fe and N from glycine. Amazedly, the structural regularity has increased with the increasing of the glycine content in the starting mixture, leading to the improvement of ORR activity and durability of this catalyst. They also formed the noble-metal-free ORR catalysts by using six nitrogen-rich amino acids, such as tryptophan, asparagine, glutamine, lysine, histidine and arginine, as the nitrogen source for Fe-N_x structures, respectively [38]. It was found that the electrocatalytic activity of the catalyst increased with an increase in the number of nitrogen atom contained in the amino acid, and the activity increase was attributed to the improved efficiency of the Fe-N_4 active site generation. Besides, the Fe-N_4 active site embedded on the catalyst surface was exactly confirmed [39]. Wang et al. [40] prepared carbon-based ORR catalysts by pyrolyzing poly-*o*-phenylenediamine (PPDA)/C, and Fe- or Co-PPDA complexes deposited on carbon black at 900 °C under N_2 atmosphere. It was found that Fe-PPDA/C showed the best ORR performance compared to the Co-PPDA/C and PPDA/C catalysts. A new insight into the active site was also proposed that the role played by metal Co or Fe in the catalyst precursor is only to catalyze the formation of active sites for ORR, which was closely associated with the surface density of pyridinic-nitrogen species. Peng et al. [41] reported a Fe- and N-doped carbon catalyst (Fe-PANI/C-Mela) with graphene structure and the surface area up to 702 m^2 g^{-1}. In 0.1 mol l^{-1} $HClO_4$ electrolyte, the ORR onset potential for this catalyst is high up to 0.98 V (*vs.* RHE), and the half-wave potential is only 60 mV less than that of the 40 wt.% Pt/C catalyst. A graphene-based Me/N/C catalyst (FeCo-N-rGO) was successfully fabricated by Fu et al. [42], through pyrolysis of a mixture of Fe, Co salts, polyaniline, and reduced graphene oxide (rGO). This study suggested that the Me-N_x (Me = Fe or/and Co, $x = 2$ or 4) could act as catalytically active sites for ORR embedded into the graphene sheets, boosting the ORR electrocatalytic activity in acidic and alkaline environments. Importantly, it also demonstrated that the synergistic effect of binary metal may enormously improve the amount of active sites exerting large influence on their catalytic performances.

3. EXPLORATION OF SYNTHESIS METHODS FOR Me/N/C CATALYSTS

3.1. Liquid-phase impregnation

Me/N/C catalysts could be typically fabricated by a liquid-phase impregnation method which was proposed primarily based on that the formation of Me-N_x complexes was a prerequisite. Zhang et al. [43] has utilized triethylenetetramine (TETA) as nitrogen source to directly produce the Co-N_4 chelate with metal Co ions loading on the carbon (BP2000) surface, which was further pyrolyzed at 800 °C to yield a Co-TETA/C catalyst. An important finding is that face-centered cubic metal α-Co was embedded in the graphitic carbons in the Co-TETA/C catalyst. Bezerraa et al. [44] produced a series of carbon-suppported Fe/N/C catalysts *via* the pyrolysis of Fe-TPTZ complexes using 2, 4, 6-Tris (2-pyridyl)-1, 3, 5-triazine (TPTZ) as a ligand at 400~1100 °C. The results showed that the Fe/N/C catalyst obtained at 800 °C was the most active to the ORR in 0.5 mol l^{-1} H_2SO_4 solution with an ORR onset potential of 0.88 V (*vs.* RHE) higher than that of as-prepared Fe-TPTZ/C complex. Li et al. [45] similarly prepared a Co-TPTZ/C catalyst through the heat-treatment of Co-TPTZ complex at 700 °C. The stability tests at the current density of 3.5×10^{-2} mA cm^{-2} to record the electrode potential over time indicated that the degradation rates of 5 wt% Co-TPTZ/C, 5 wt% Fe-TPTZ/C, and TPTZ/C were found to be 1.64, 3.64, and 2.09 mV h^{-1}, respectively, implying that 5 wt% Co-TPTZ/C catalyst had the best stability in acidic solution.

3.2. Directly chemical reduction

A chemical reduction method for preparing the ORR catalysts was firstly proposed by Bashyam et al [46]. After that, this interesting method has attracted several research groups' attention, and some important research findings were obtained. Lee et al. [47] systematically improved the Co-PPY/C composite catalysts by combining chemical reduction method and high-temperature pyrolysis on the basis of reported results [46]. It was found that the pyrolysis of Co-PPY/C composite at 800 °C can effectively enhance its ORR activity, and a large difference of 115 mV on the ORR onset potential was observed by comparing cyclic voltammograms of Co-PPY/C composites before and after pyrolysis. More importantly, two new XPS peaks corresponding to pyrrolic (or pyridone) and graphitic (quaternary) nitrogen could be observed in the pyrolyzed composite, which were assigned as the active sites for ORR. Yuan et al. [48] reported a Co-PPy-TsOH/C catalyst, which was synthesized with *p*-toluenesulfonic acid (TsOH)-doped PPy/C as a N-rich and morphological support together with cobalt salt. The doping of TsOH can result in the increase of N content, which is a main reason for the enhanced electrocatalytic activity of Co-PPy-TsOH/C towards ORR. Recently, Wu et al. [49] developed a new approach to the synthesis of bi-metallic ORR catalysts (PANI-FeCo-C) by using polyaniline as nitrogen/carbon sources at 900 °C. The ORR activity and durability of PANI-FeCo-C were better than those of Co-PPY/C catalysts [46,48]. Lü et al. [50] also reported the preparation method of Co-PANI/C catalysts with a ORR current density of 128 mA cm^{-2} at -0.2 V (*vs.* Hg/HgO) referring to this report [46]. The results showed that Co-N active site could influence the adsorption and desorption processes of oxygen and the reaction intermediates.

3.3. Magnetron sputtering

The magnetron sputtering was recently developed a novel synthesis method for Me/N/C catalyts. Kim et al. [51] synthesized the Ta-C-N catalysts through the heat treatment of Ta-C-N film formed by reactive RF magnetron sputtering in the range of 70~800 °C. High ORR electrocatalytic activity could be observed at Ta-C-N catalysts in a H_2SO_4 solution, which increased with the increasing of the pyrolysis temprature. The electrocatalytic activity of Ta-C-N catalysts could be influenced by their intrinsic degree of crystallinity. Easton et al. [52] prepared a class of $Me_xC_{1-x-y}N_y$ (Me = Fe, Co; $0 < x < 0.09$; $0 < y < 0.5$) thin-films by combinatorial sputter deposition, followed by annealing at 700~1000 °C to induce structural and compositional changes. It was found that the ORR electrocatalytic activity coincided with the transformation from a homogenous amorphous Me-C-N thin-film to a heterogeneous mixture of (partially) graphitized nitrogen-containing carbon and either Fe_3C or β-Co at temperatures above 700 °C. Co-C-N thin-films retained their ORR activity up to 1000 °C because an appreciable nitrogen content can be still retained. $Co_xC_{1-x-y}N_y$ libraries heat-treated at 800 °C with $0.004 < x < 0.105$ and $0.026 < y < 0.097$ showed good catalytic activities towards ORR in 0.1 mol l^{-1} $HClO_4$ solution [53]. In addition, the influence of pyrolysis temperature on the ORR electrocatalytic activity of a sputtered Co-C-N sample were deeply studied [54]. The results demonstrated that the sample began to exhibit ORR activity in acidic electrolyte at 725 °C but showed ORR activity in alkaline electrolyte above 500 °C. The highest activity could be obtained at 850 °C. It was conluded that the electrocatalytically active sites for ORR of Co-C-N samples, obviously created below 725 °C, were easy to be blocked in acidic electrolyte.

3.4. Template-based method

The development of template methods for catalyst synthesis was commonly based on a principle that the particle size, morphology, specific surface area, structure and arrangement of resultant nanomaterials mainly depended on designer templates with space-confinement characteristics [28,55,56]. At present, several high-efficiency template-based methods, such as soft template [57,58], hard template [59-64], self-sacrifice template [65-67], and dual template [68], *etc*., have been also proposed. Ding et al. [55] presented a novel strategy for the selective synthesis of nitrogen-doped graphene (NG@MMT) by the use of the layered montmorillonite (MMT) with thick lower than 1 nm as a quasi-closed flat nanoreactor template, which constrained the formation of quaternary and oxidized-N because of its three-dimensional structure but facilitated the formation of pyridinic and pyrrolic-N (planar N) active species. Besides, a maximum power density of 320 mW cm^{-2} was generated from a single H_2-O_2 fuel cell with NG@MMT catalyzed cathode. The NG@MMT was also recognized as the best metal-free catalyst with such high activity reported in acidic environments. Shi, et al. [58] prepared a new nitrogen-doped graphene with an sandwich-like structure at a specific surface area of 370 m^2 g^{-1} by using a triblock copolymer (Pluronic F127) as a soft template. A new class of nitrogen-containing catalysts for ORR based on ordered mesoporous porphyrin carbons (Me-OMPC; Me=Fe, Co, or FeCo) with a tubular pore structure was formed by using a nanocasting mesoporous silica template and ultilizing metalloporphyrins as nitrogen/carbon precursors [62]. It was interestingly found that Me-OMPC catalyts exhibited a higher kinetic current density at 0.9 V compared to the commercial Pt/C catalysts. Pandiaraj et al. [65] synthesized high surface area carbons (MOFCN900) with a high nitrogen content of 7.0% using metal organic frameworks (MOF) as self-sacrificing template on account of their self-sacrificial nature, high carbon content and inherent porosity *via in situ* g-C_3N_4 formation.

3.5. Other methods

Other useful sysnthesis methods, *e.g.* solid-state reaction (SSR), chemical precipitation (CP) and chemical vaporous depositon (CVD), were also developed to produce the catalysts in addition to aforementioned methods. It is worth mentioning that the SSR method has abandoned a traditional viewpoint that the use of Me−N$_x$ complexes was a prerequisite of fabricating the Me/N/C catalysts, which has supported an important perspective proposed by Gupta et al. [9]. Recently, our research group intensively investigated the selection of nitrogen precurosrs changing from Me−N$_x$ complexes to simple nitrogen-rich compounds (*e.g.*, melamine and urea) [69-71] and natural biomaterials (e.g., soybean and blood protein) [72-73]. Sawai et al. [74] prepared different types of Me/N/C catalysts for ORR by adequately mixing a $K_3M''(CN)_6$ (M'' = Fe, Co) solution with a suspension of M′SO4 (M′ = Mn, Fe, Co, Ni, Cu) and acetylene black to yield $M'_3[M''(CN)_6]_2$ precipitation, followed by a pyrolysis process at high temperatures. Dai and his co-workers [75] have innovatively used a plasma etching technique combining with a CVD method to prepare an efficient metal-free nitrogen-doped carbon nanotubes (NCNTs). NCNTs exhibited higher ORR electrocatalytic activity and better stability in acidic medium comparing to the undoped CNTs. Li et al. [76] also synthesized N-CNTs *via* the CVD method at different temperatures of 800 °C, 850 °C, 900 °C, and 950 °C with the use of ethylenediamine and ferrocene as precursors. N-CNTs obtained at 800 °C exhibited the best ORR performance thanks to the formation of more pyridine-like nitrogen atoms. Additionally, the use of both ball-milling and two-step pyrolysis as a mixing method for the fabrication of microporous Fe/N/C catalysts has been proposed by Lefèvre et al. [77], and a possible Fe-N$_x$ active site was formed by metal Fe ions coordinating with pyridine-like nitrogen atoms.

4. CONCLUSIONS

This review has highlighted recent progress of nitrogen-containing electrocatalysts for ORR in air electrodes mainly in terms of the selection of nitrogen precursors, the exploration of synthesis methods. The selection of nitrogen precursors has gradually developed from original Me-N_x macrocyclic complexes to various nitrogen-containing compounds. Exploration of various synthesis methods would encourage the researcher to the directional design of Me/N/C catalytsts with diversiform nitrogen precursors. Thus, we here proposed future research directions in nitrogen-containing electrocatalysts would incude: (i) biomaterials and biological proteins from nature could help to explore novel electrocatalysts for the ORR processes, which benefited the development of newfashioned Me/N/C catalysts. *e.g.*, some enzymes can efficiently catalyze electrochemical reactions by providing both redox active sites and intramolecular/interfacial electron transfer pathways; (ii) mimicking natural oxygen catalytic processes would aid in searching for better catalysts; (iii) nanotechnologies open new avenues in catalyst development because nanostructured electrode materials are proven as a valuable option. In addition, a reasonable combination of *in situ* experimental study, theoretical analysis, nanoscale probing, and atomic scale modeling would provide in-depth insights into the catalytic mechanism and the correlation between materials properties and performance.

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