

Review

Recent Advances in Non-Precious Transition Metal/Nitrogen-doped Carbon for Oxygen Reduction Electrocatalysts in PEMFCs

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Abstract: The proton exchange membrane fuel cells (PEMFCs) have been considered as promising future energy conversion devices, and have attracted immense scientific attention due to their high efficiency and environmental friendliness. Nevertheless, the practical application of PEMFCs has been seriously restricted by high cost, low earth abundance and the poor poisoning tolerance of the precious Pt-based oxygen reduction reaction (ORR) catalysts. Noble-metal-free transition metal/nitrogen-doped carbon (M–N_xC) catalysts have been proven as one of the most promising substitutes for precious metal catalysts, due to their low costs and high catalytic performance. In this review, we summarize the development of M–N_xC catalysts, including the previous non-pyrolyzed and pyrolyzed transition metal macrocyclic compounds, and recent developed M–N_xC catalysts, among which the Fe–N_xC and Co–N_xC catalysts have gained our special attention. The possible catalytic active sites of M–N_xC catalysts towards the ORR are also analyzed here. This review aims to provide some guidelines towards the design and structural regulation of non-precious M–N_xC catalysts via identifying real active sites, and thus, enhancing their ORR electrocatalytic performance.

Keywords: proton exchange membrane fuel cells; oxygen reduction reaction; non-precious metal catalysts; transition metal/nitrogen-doped carbon

1. Introduction

The worldwide demand of energy is rising drastically with the rapid increasing global population and the progressing development of society [1–3]. However, there is an inevitable reality that the traditional fossil fuels have been in a danger of drying up with continuous exploitation and utilization, which has resulted in a universal concern about the energy crisis [4,5]. Besides, the urgent environmental issues caused by consuming fossil fuels, such as pollutants emission and global warming, have also severely threatened the future of human society. These problems have spurred intensive researches on the development of sustainable, eco-friendly and high-efficient new energy systems [6,7]. The fuel cell can convert chemical energy directly into electricity, and is regarded as one of the most promising energy technologies, due to its high efficiency and eco-friendliness [8–10]. Among various kinds of fuel cells, the proton exchange membrane fuel cells (PEMFCs) have attracted the most attention over the past decades, due to their high energy conversion rate, high reliability, quick startup, low operating temperature and low pollute emission etc. [11–13].

However, the widespread application of PEMFCs is greatly hampered by the high-cost and low-performance electrocatalysts towards the oxygen reduction reaction (ORR) at the cathode to

accelerate the sluggish reaction kinetics [14,15]. Typically, there are three main obstacles limiting the mass production of ORR catalysts: (i) the high cost. Currently, the most common-used and effective catalysts in PEMFCs are still Pt-based catalysts, of which the scarcity and high cost have resulted in an excessive pricing of PEMFCs [16]; (ii) the low performance. The complex mechanisms and sluggish reaction kinetics of ORRs necessarily lead to high potential demands and low current density outputs [17]. The main research aim is to fabricate suitable catalysts with abundant active sites and high reaction selectivity, and therefore greatly decreasing the ORR energy barrier and raising the conversion efficiency; (iii) the insufficient stability. The high stability of catalysts is the guarantee of the PEMFCs with excellent durability and lifetime. During the long-term operation of PEMFCs, the catalyst would go through Ostwald ripening that causes particle agglomeration and growth, surface oxidation state changes, component migration and loss, etc., which would gradually age and inactivate the catalyst, thus directly leading to the degradation of PEMFCs' performance [18–21].

From an economic point of view, some noble metal-based (Au, Ag, and platinum group metals: Pt, Pd, Ru, Rh, Ir and Os) electrocatalysts would definitely increase the manufacturing cost of fuel cells as the scarce and high cost of noble metals [22–24]. To solve these problems, numerous efforts have been devoted to exploring non-precious transition metal catalysts, owing to their abundant reserves, economic applicability and their potential catalytic activity comparable to noble metals, while most of the main group metals have shown little potential towards ORR catalysis [25,26]. Particularly, one of the exceptions is the hybrid of transition metal supported on nitrogen-doped carbon (M–N_xC, M = non-precious transition metals, generally $x = 2$ or 4 , which corresponds to the bonding of MN₂ or MN₄, respectively) due to two possible reasons below: (i) The introduction of carbon supports could greatly stabilize and disperse the transition metals, therefore enhancing the ORR catalytic performance; (ii) the synergetic effects between the nitrogen-doped carbon supports and transition metals could significantly increase the number of active sites and boost the catalytic behavior [17,27–30]. Nevertheless, the reaction kinetics, and in particular, the modulating mechanism of N atoms on the surface state and electronic structure of the catalysts still remains ambiguous.

In this review, we aim to provide an overview of the development of M–N_xC ORR catalysts and the summarization of recent advances in this area. Herein, we offer a brief introduction to the reaction of oxygen reduction and its thermodynamic mechanism. We specially pay attention to the research progress in M–N_xC ORR catalysts with emphasis on the choice of carbon sources and nitrogen sources, the state-of-the-art Fe–N_xC and Co–N_xC catalysts, and the analysis of their catalytic sites.

2. Brief Introduction of the ORR Mechanism

As shown in Figure 1, there are three sections in the PEMFC, including an anode where H₂ would be oxidized (hydrogen oxidation reaction, HOR), a cathode where O₂ would be reduced (ORR), and a proton exchange membrane through which H⁺ could be transferred from the anode to the cathode [31–33]. The reaction on the cathode, the ORR, is a complex process which involves various basic and irreversible intermediate reactions [34,35]. It can be seen from Figure 2 that the process could proceed through two pathways: A direct four-electron way or an indirect two-electron way, varying with the electrode material and pH of the electrolyte. When it comes to the two-electron pathway, the O₂ molecules would accept two electrons first to be reduced to H₂O₂ (in acid and neutral solution) or HO₂[−] (in alkaline solution), and then adsorb another two electrons to be transferred into H₂O or OH[−] eventually [36,37]. The generation of H₂O₂ in electrolyte surely cause damages to catalysts and the proton exchange membrane, thus reducing the lifetime of PEMFCs [38]. Hence, the most ideal mechanism of fuel cells is the four-electron pathway, where oxygen molecules could accept four electrons in succession to be reduced into H₂O (in acid solution) or OH[−] (in alkaline solution), with no detectable intermediates (H₂O₂) in the final electrolyte [39,40].

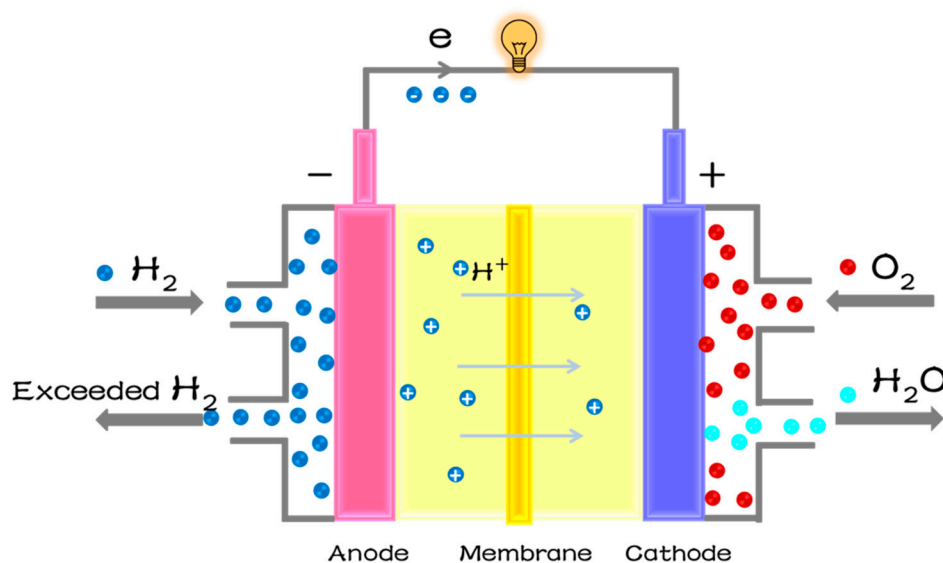


Figure 1. Schematic diagram of the proton exchange membrane fuel cells (PEMFC).

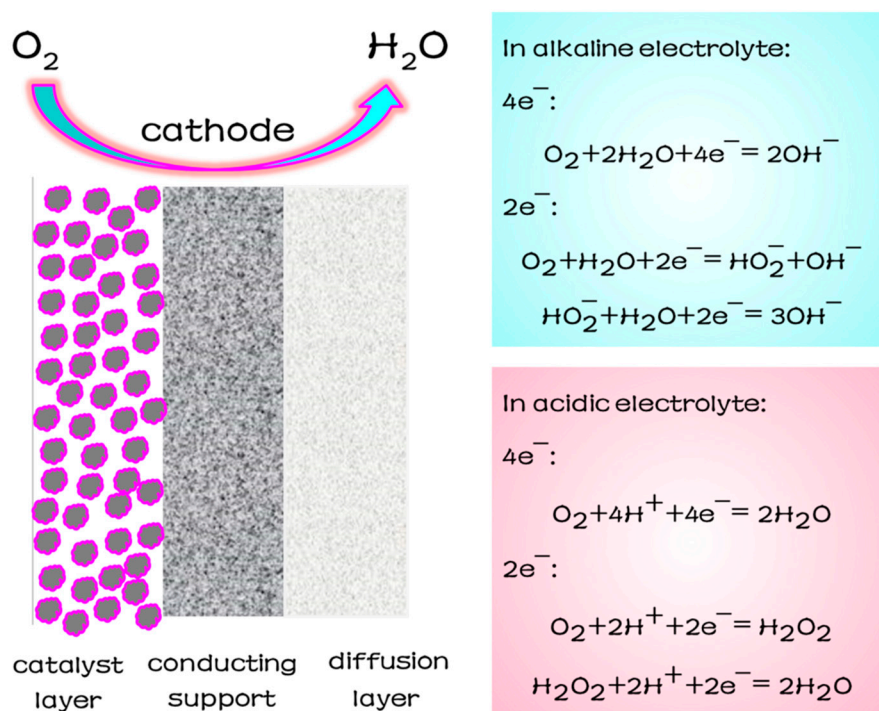


Figure 2. The structure of the cathode in PEMFCs and the oxygen reduction reaction (ORR) pathways on the cathode.

However, in most instances, the ORR proceeds via the two-electron pathway, or the parallelism of the two-electron and four-electron way on the electrode surface, as the dissociation energy of the O–O bond in O_2 is 498 kJ/mol, which is much higher than that in H_2O_2 (143 kJ/mol), suggesting a decreasing activation energy of the ORR. The best solution is to develop effective catalysts to selectively reduce the bond energy of O_2 , therefore boosting the four-electron process [41].

3. Previous M–N_xC Catalysts

To explore optimal approaches to produce highly stable and active catalysts with the M–N_xC structure, lots of efforts have been devoted to exploring the synthesis strategies and the nature of the catalytic active sites [42–49]. This section reviews the research progress in transition metal catalysts

supported on nitrogen-doped carbon with its emphasis on the choice of carbon sources and nitrogen sources, the control of experimental conditions, and the analysis of catalytic sites. Non-pyrolyzed and pyrolyzed transition metal macrocyclic compounds will be firstly discussed, as they are the pioneers of M-N_xC catalysts to provide the fundamental research conditions on which the design of the follow-up discussed recent developed M-N_xC catalysts are based.

3.1. Non-Pyrolyzed Transition Metal Macrocyclic Compounds

The earliest discovery of M-N_xC catalysts should date back to 1964 when cobalt phthalocyanine (CoPc), a kind of transition metal macrocyclic compound, was investigated as a fuel cell cathode catalyst in alkaline electrolyte by R. Jasinski [50]. Since then, macrocyclic compounds composed of various central transition metal atoms (e.g., Fe, Co, Ni, Mn, Cr, etc.) and ligands, such as tetraphenylporphyrin (TPP), tetraazaannulenes (TAA), tetramethoxyphenylporphyrin (TMPP), phthalocyanine (Pc), tetradithiacyclohexeno-tetraazaporphyrin (TDAP) etc., have entered the researcher's vision and study fields [51–53]. Also, their catalytic behaviors were sequentially demonstrated in acidic electrolytes [54–56].

Figure 3 shows the typical structure of these compounds where there is usually a chelating group of four nitrogen atoms coordinating with a central metal atom. It has been proven that the catalytic activity of these macrocyclic materials is directly related to the central metal ion and the surrounding ligand structure [57,58]. For a given metal center, the ORR catalytic activity is strongly affected by the nature and electron density of the ligand in macrocyclic compounds [51,59]. Alt et al. [60] experimented with the ORR catalytic behaviors of several Co-ligand compounds in acidic electrolyte, including Pc, TPP, TAA, TMPP, TDAP and TPAP (tetrapyrindino-tetraazaporphyrin), with an activity order of TAA > TDAP > MPP > Pc > TPAP > TPP. Similar conclusion was drawn by Song and his partners in 1998 [61]. Besides, K. Wiesener [62] and his colleagues proved that the catalytic performance depends greatly on central metal atoms (Fe, Co, Ni, Mn, Cu etc.) which mainly affect the ORR process, whether for a four-electron or a two-electron process for a given macrocyclic ligand. The ORR activities of various central transition metals coordinating with the Pc ligand followed the order of Fe > Co > Ni > Cu ≈ Mn. With many far previous explorations, transition metal macrocyclic compounds are regarded as a promising kind of cathode catalyst to substitute Pt for ORR. However, these macrocyclic materials are rarely used directly in PEMFCs, due to their poor performance in activity and durability. It was indicated that FePc could facilitate the ORR with a four-electron process, but with a poor stability, while CoPc with a good electrochemical stability were favorable to the two-electron pathway to produce H₂O₂ [63,64]. They were all limited by theses inherent drawbacks to be used as cathode catalysts in PEMFCs. Therefore, it is of great significance to design a method to raise the stability and activity of transition metal macrocyclic compounds synchronously.

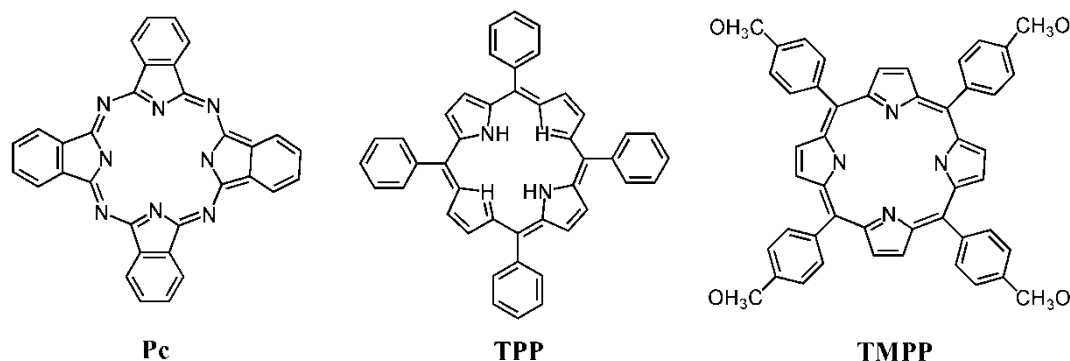


Figure 3. The structures of phthalocyanine (Pc), tetraphenylporphyrin (TPP) and tetramethoxyphenylporphyrin (TMPP).

3.2. Pyrolyzed Metal Macrocyclic Compounds

In 1973, Alt et al. [65] found that Co- and Fe-TMPP complexes were more stable in 3 N H₂SO₄ after a high-temperature treatment. In 1976, Jahnke et al. [66] pointed out in their article that the catalytic activity and stability of various N₄-chelates in acidic media could be considerably improved through thermal pretreatment in an inert gas atmosphere (e.g., argon gas). Since then, heat treatment has aroused great research interests, and also been viewed as an effective way to improve the catalytic performance of transition metal macrocyclic compounds [52,67–69]. Studies [70–72] have revealed that N₄-chelates could obtain the highest catalytic activity via a pyrolysis at 500–700 °C, while a temperature of 800 °C is required to achieve a stable catalytic performance in PEMFCs. Moreover, a higher temperature above 1000 °C would lead to an obvious decrease of stability and activity due to (i) the formation and growth of metal particles [73,74] and (ii) a decline in the nitrogen content of catalysts surface [75].

As for the accounts to why thermal treating could improve the macrocyclic compounds' behavior, there are three main statements [76–78]: (i) Heat treatment could improve the dispersity of coordination compounds, therefore boosting the catalytic activity; (ii) heat treatment could lead to the polymerization of macrocyclic compounds, which results in a highest activity at lower temperature; (iii) heat treatment could facilitate the formation of compounds containing M–N₄ groups, which are acknowledged to account for the rising activity and long-term stability in low temperature range (500–700 °C). Although these effects would improve the catalysts' electrocatalytic performance, and could provide reference guidelines to materials design, the material structure and active components of pyrolyzed metal macrocyclic compounds after thermal treating still remain controversial.

4. Recent Developed M–N_xC Catalysts

Although the aforementioned non-pyrolyzed and pyrolyzed transition metal macrocyclic compounds have presented impressive ORR electrocatalytic activities, some immanent problems restricting their further development should not be overlooked, including their high cost, complex fabrication process, low activity and stability in acidic electrolyte [79]. Hence, lots of efforts have been devoted to developing a kind of effective catalysts based on cheap and easily available precursors, while the metal macrocyclic compound itself serves as both a nitrogen source and metal donor on the carbon matrix. For the past few decades, researchers attempted to prepare M–N_xC catalysts through processing the total mixture of individual metal salt, nitrogen source and carbon support under the high temperature with a certain gas atmosphere [80]. For example, Bouwkamp-Wijnoltz et al. [81] prepared the catalysts from heat-processing the mixture of cobalt acetate, carbon black and various nitrogen donors, among which the best catalytic results comparable to that of heat-treated cobalt porphyrin were obtained with 2,5-dimethylpyrrole. The results of Extended X-ray Absorption Fine Structure (EXAFS) revealed similar active sites (CoN₄) in both types of catalyst. This approach provides more possibilities of fabricating a variety of catalysts via the flexible permutation and combination of different metals, N donors and carbon sources. Indeed, it has been acknowledged as one of the most cost-effective and preparation-effortless methods to prepare M–N_xC catalysts.

4.1. Choices of Nitrogen and Carbon Sources

As for the introduction of nitrogen and carbon sources, there are various options. First, just for transition metal macrocyclic compounds, such as FePc, the metal, N atoms and carbon support are provided by an individual precursor, which is usually expensive and hard-won in practical applications [82]. Second, the N atoms and carbon matrix in M–N_xC catalysts could be introduced by using a kind of precursor containing both nitrogen and carbon, such as polyacrylonitrile (PAN) [83], polyaniline (PANI) [84,85], polypyrrole (PPy) [86], polythiophene (PT) [87], ethylenediamine (EDA) [88], cyanamide (CA) [89] and other organic polymers. Most recently, Liu et al. [90] reported a kind of Co/N-doped cross-linked porous carbon (Co/N-CLPC) catalyst from PAN through a one-step, in-situ

synthesis method (Figure 4). Co/N-CLPC showed an excellent ORR catalytic activity with an onset potential of 0.805 V (vs RHE) and a limiting current density of $-5.102 \text{ mA cm}^{-2}$, which are comparable to those of commercial Pt/C catalysts.

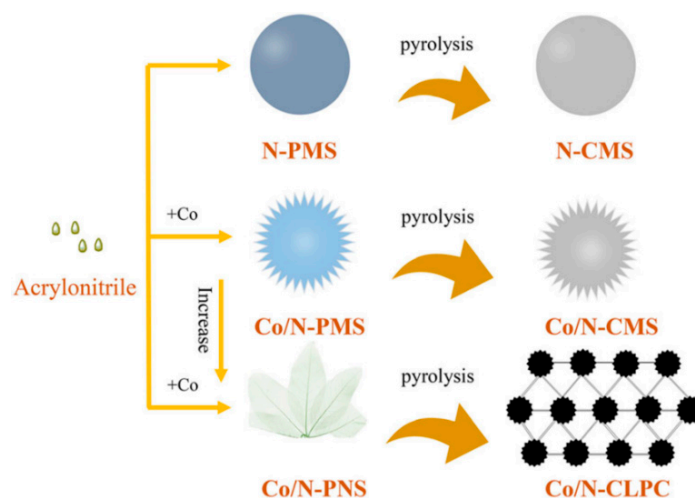


Figure 4. Schematic illustration for the fabrication of nanocarbons. Reproduced with permission from Xuefeng Yan, Xia Li, Xiaohui Jiang, et al., International Journal of Energy Research; published by John Wiley and Sons, 2019.

In most cases, to increase the electrical conductivity or form a certain structural morphology of the catalysts, researchers are pleased to introduce extra carbon supports. For example, Wu et al. [91] synthesized a kind of PANI-M-C catalysts with the short-chain aniline oligomers polymerizing together on the surface of carbon spheres, and then the metal aggregating encapsulated in carbon shells (Figure 5). Liu et al. [92] developed a kind of catalyst with single iron atoms immobilized on the wall of a carbon nanotube (SAICNT), where the pyrrole polymerizes on an organic template (methyl orange) to fabricate a nanotube structure which is favorable to electron transport, and increases the number of active sites (Figure 6). The SAICNT exhibited an ultrahigh ORR activity with a half-wave potential of 0.93 V and a current density of 59.8 mA cm^{-2} at 0.8 V, which are far better than that of commercial Pt/C. Besides, Huang et al. [93] prepared a trifunctional catalyst via electrodepositing Co ions and PPy onto carbon fibers to form a tube-shaped product with abundant active sites (Figure 7).

The third method to introduce nitrogen and carbon is to use two kinds of materials which contain N atoms and carbon basis, respectively. Generally speaking, the carbon precursors are the same as those used to prepare carbon nanomaterials, such as biomass materials, while the existential forms of carbon supports used for electrocatalysts preparation vary from two-dimension nanosheets (e.g., graphene and its derivatives [1,94–97]) to three-dimension carbon nanostructures (e.g., carbon nanotubes [98,99], carbon fibers [100–102], carbon spheres [103] and porous carbon [3,104]). As there are already some excellent reviews talking about the effects of carbon supports in electrocatalysts, we will not repeat them in this article. Nitrogen sources is an essential part of the M-N_xC catalysts so as to provide N atoms chelating with metal ions to form the MN₄ active sites. Apart from the aforementioned organic polymers, there are two types of common-used, individual nitrogen sources: (i) some organic monomers or small organic molecule compounds, such as pyrrole, phenanthroline, carbamide, melamine etc.; (ii) some inorganic compounds, such as NH₃.

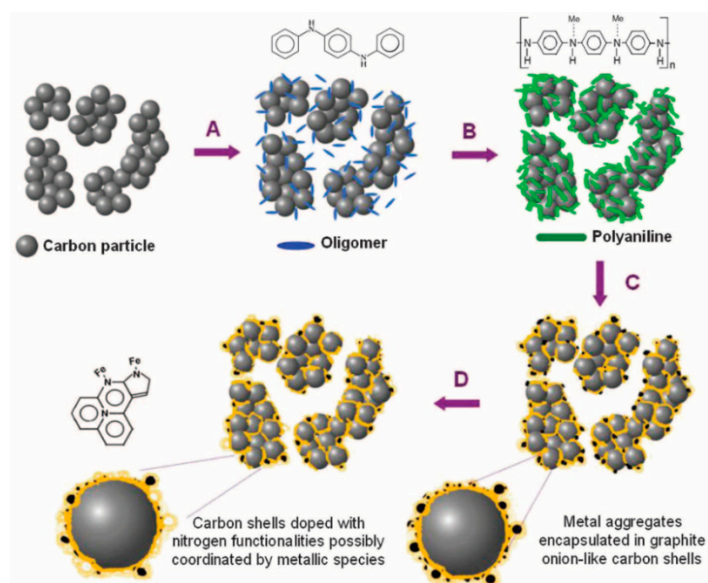


Figure 5. Schematic diagram of the synthesis of PANI-M-C catalysts. (A) Mixing of high-surface area carbon with aniline oligomers and transition-metal precursor (M: Fe and/or Co). (B) Oxidative polymerization of aniline by the addition of ammonium persulfate (APS). (C) First heat treatment in an N_2 atmosphere. (D) Acid leaching. Reproduced with permission from Gang Wu, Karren L. More, Christina M. Johnston, Piotr Zelenay, Science; published by the American Association for the Advancement of Science, 2011.

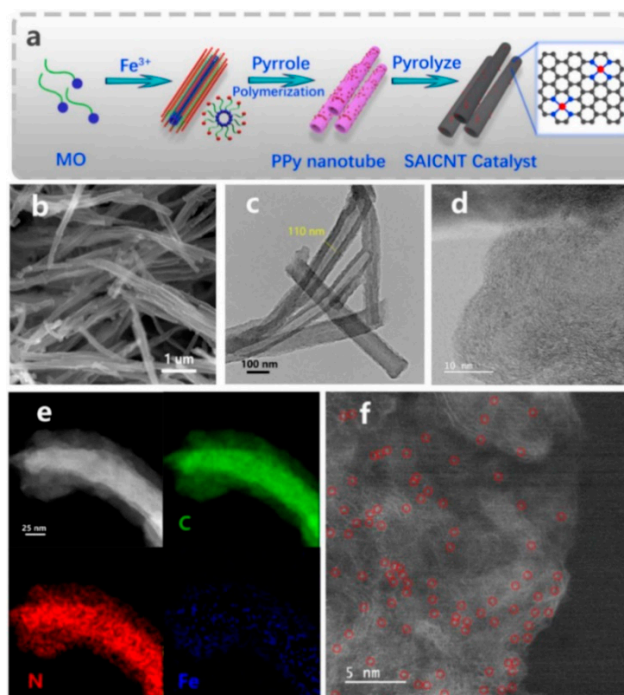


Figure 6. (a) Schematic illustration of synthesis process of the single iron atoms immobilized on the wall of a carbon nanotube (SAICNT) catalyst; (b) Scanning electron microscopy (SEM) image of Fe-modified polypyrrole (PPy); (c) Transmission electron microscopy (TEM) and (d) High-resolution TEM images of SAICNT-900; (e) Energy-dispersive X-ray spectroscopy (EDS) elemental mapping photos of SAICNT-900 (C, N and Fe); (f) High-angle annular dark-field imaging-scanning transmission electron microscope (HAADF-STEM) images of the SAICNT-900 catalyst. Reprinted with permission from Liu et al. (2019) [92]. Copyright 2019, American Chemical Society.

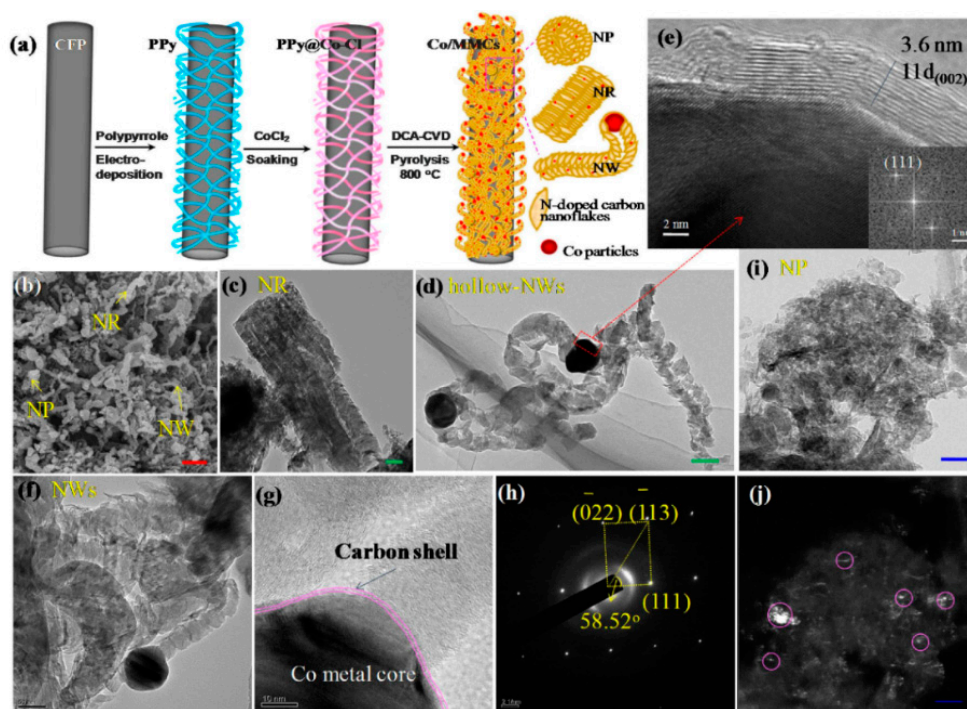


Figure 7. (a) The fabrication processes and schematic structure for Cobalt/Metal Matrix Composites (Co/MMCs). (b) SEM image of Co/MMCs. High-resolution transmission electron microscopy (HRTEM) images of the components of Co/MMCs with different morphologies: (c) nanorod, (d) hollow nanowire, (f) nanowire, and (i) nanoparticle. (e) The partially enlarged image of the surface area of a Co metal nanoparticle shown in (d), (g) partially enlarged image of (f). (h) Selected area electron diffraction (SAED) of the metal particle in (e). (j) dark-field high-resolution TEM images of the nanoparticle shown in (i). The red bar represents to 1 μm , green bar to 100 nm, and blue bar to 50 nm. Reproduced with permission from Niu Huang, Liu Yang, Mingyi Zhang, et al., ChemElectroChem; published by John Wiley and Sons, 2019.

For instance, Liang et al. [105] chose melamine and the ordered porous resin (OPR) as nitrogen and carbon sources, respectively, to prepare the catalysts of Fe–N–CNT–OPC, which displayed an ORR electrocatalytic activity similar to that of the 20% Pt/C catalyst. It was indicated that the Fe–N–CNT–OPC possessed abundant Fe–N active sites, high porosity favorable to the electron and transportation, as well as ample graphitic CNTs to ensure the conductivity (Figure 8). Kim et al. [106] reported a sort of Fe–N–C catalyst from pyrolyzing the mixture of phenanthroline and Ketjenblack carbon supports. According to X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) analyses, the active sites FeN_x would prefer to form with pyridinic N stemming from phenanthroline. Compared with organic nitrogen sources, the researches on inorganic compounds containing N atoms used for the electrocatalyst preparation are mainly focused on the utilization of NH_3 .

In 2016, Park et al. [107] reported a novel catalyst of $\text{Fe}_x\text{N}_y/\text{NC}$ nanocomposite with an excellent ORR activity, a long-term catalytic stability, and a direct four-electron pathway in alkaline electrolyte. As show in Figure 9, the mixture of carbon black and Fe salt was heat treated in NH_3 , thus obtaining the $\text{Fe}_x\text{N}_y/\text{NC}$ catalyst directly. Besides, some compounds which could release NH_3 under heating conditions, such as urea, have also drawn researchers' attention. For example, Liu et al. [108] fabricated a sort of Fe/NG/C catalysts with a comparable ORR activity to commercial Pt/C catalysts in 0.1 M KOH. The procedure was simply to thermally decompose the hybrid of graphene oxide, urea, carbon black and iron species, where the N-doping process was accomplished via the decomposition of urea to release NH_3 . Usually, some porous structure would be generated on carbon supports during the process of NH_3 blown off by heating the compounds adhering to the carbon precursor, that is to say the activation function of NH_3 [109,110].

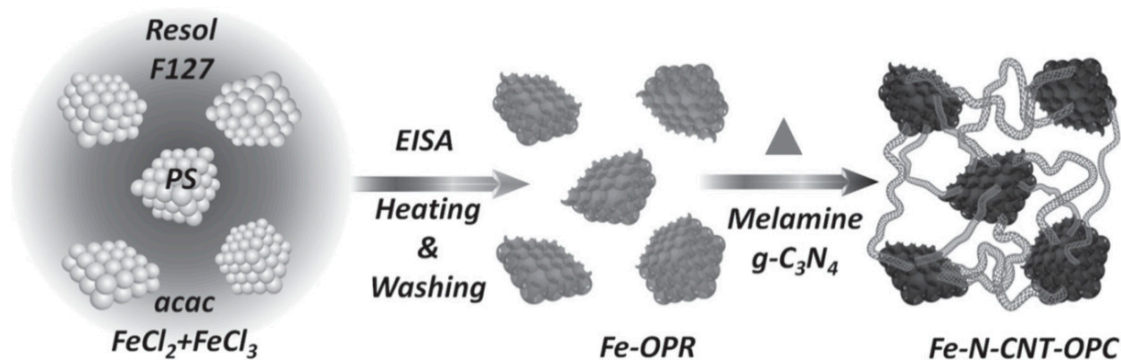


Figure 8. Synthetic procedure of the Fe-N-CNT-OPC material. Reproduced with permission from Ji Liang, Ruifeng Zhou, Xuemin Chen, et al., *Advanced Materials*; published by John Wiley and Sons, 2014.

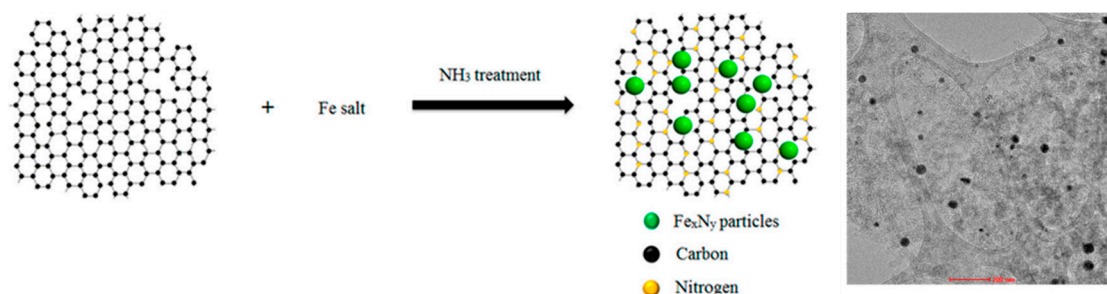


Figure 9. Illustration of Fe_xN_y/nanocomposite (NC) synthesis. Open Access.

4.2. Types of Metal

Apart from the aforementioned heat treatment, with choice of nitrogen and carbon precursors, the transition metal types also have extremely significant impacts on the nature and electrocatalytic performance of the M-N_xC catalysts. Generally, there are several non-precious transition metals which are researched in ORR electrocatalysis, including Fe, Co, Ni, Mn, Cu, Zn and so on, among which the most frequently-studied and effective are mainly Fe and Co. The major merit of Fe- and Co-based ORR M-N_xC catalysts is not only the low cost but also their excellent behavior in both acidic and alkaline media [111].

The Fe-N_xC and Co-N_xC catalysts have been widely studied for a long time, since the cobalt phthalocyanine was proven to exhibit a good oxygen reduction activity in alkaline solution in 1964 [50]. In the earliest studies, main attention was focused upon the exploration of the macrocycle compounds of these two metals used in ORR and the related study of performance improvements, active sites, as well as catalytic mechanism. Then, lots of efforts have been devoted into the exploration of inorganic and small organic metal donors, the design of new synthesis routes, and the structure and property optimization of Fe-N_xC and Co-N_xC.

Recently, researchers are challenging to raise the catalytic activity of Fe-N_xC and Co-N_xC catalysts in a wide pH range as high as possible via tuning and increasing the active sites [48]. Considerable progresses have been achieved in the synthesis and theoretical analysis of highly active M-N_xC catalysts toward ORR in both acidic and alkaline solutions during the past few years.

Very recently, one of the most attractive research issues about M-N_xC catalysts would be the design of single-atom M-N_xC, which is favorable to realize the utmost utilization of metal sites in catalysts, and the requirements of high catalytic activity. For example, Xia et al. [112] prepared the carbon nanotubes doped with Fe single atoms (Fe-N/CNT) through direct heat treatment of the mixture of the Fe precursor and carbon matrix in the NH_3 atmosphere (Figure 10). The Fe single atoms were incorporated with N atoms to form Fe-N_x active sites during the growth process of

CNT. As Figure 11 indicated, the single-atom Fe–N/CNT catalyst was more active and stable than the commercial Pt/C catalyst in 0.1 M KOH. In practice, the preparation of Fe or Co single atoms is relatively difficult, as these non-precious transition metal atoms would migrate together and aggregate into nanoparticles or compounds at high temperature. To solve this problem, Li et al. [113] developed a secondary-atom-assisted method to prepare monatomic Fe anchored on porous N-doped carbon nanowires (Fe–NCNWs). The Fe ions were surrounded by secondary atoms (Al, Mg, or Zn) which could ensure Fe ions be transformed into Fe single atoms rather than nanoparticles, and produce porous structure by their pyrolysis under high temperature (Figure 12). Similarly, Yin et al. [114] obtained the Co SAs/N–C catalysts through the pre-carbonation of bimetallic Zn/Co metal-organic frameworks, and then the evaporation of Zn above 800 °C. The prepared Co SAs/N–C showed an excellent catalytic performance towards ORR with a half-wave potential of 0.881 V, which is much higher than that of commercial Pt/C (0.811 V). Overall speaking, this approach makes the preparation of single-atom M–N_xC catalysts more facile and reliable. Apart from the fact that the monatomic catalysts have exhibited satisfactory activity towards ORR, recently Zeng’s group [115] found that Fe single atoms together with Fe nanoclusters anchored on nitrogen-doped carbon support (Fe_{AC}@Fe_{SA}–N–C) displayed superior ORR catalytic activity (Figure 13). Their work provides a novel insight and pathway to the catalysts design.

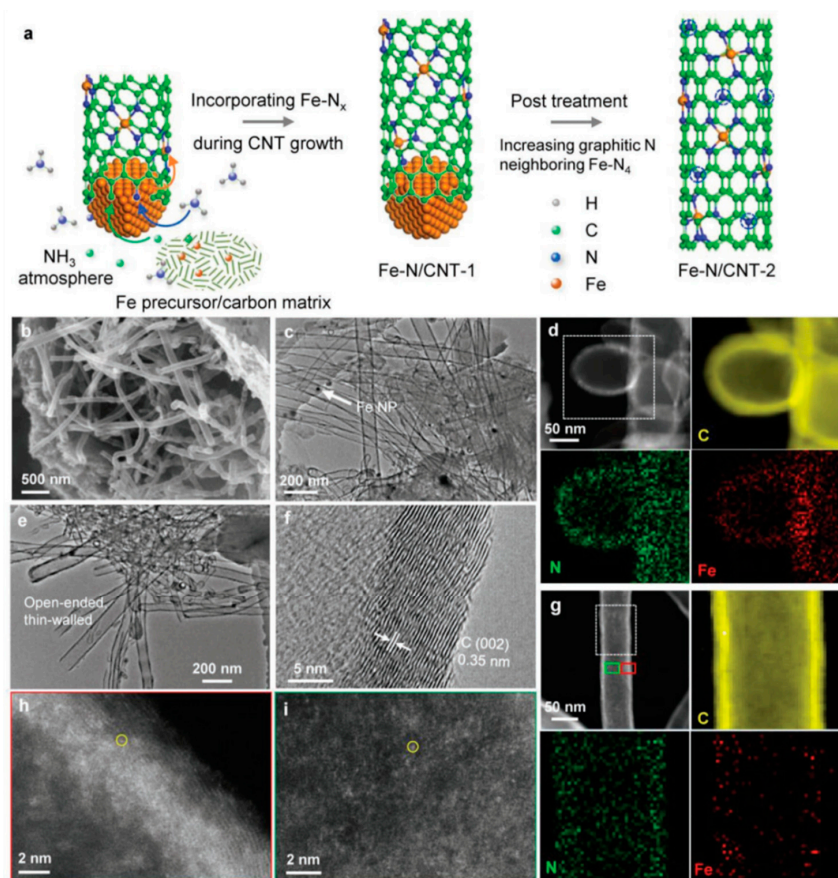


Figure 10. (a): Schematic illustration of NH₃-promoted catalytic growth of Fe–N/CNT-1. (b–d): SEM, TEM and scanning transmission electron microscope-electron energy loss spectroscopy (STEM-EELS) elemental mapping of the Fe–N/CNT-1 catalyst, respectively. (e–g): TEM, HRTEM, and STEM-EELS elemental mapping of the Fe–N/CNT-2 catalyst, respectively. (h–i): Aberration-corrected HAADF-STEM images of different regions of the Fe–N/CNT-2 catalyst marked in (g). Reproduced with permission from Feiyu Kang, Lin Gan, Jia Li, et al., *Advanced Functional Materials*; published by John Wiley and Sons, 2019.

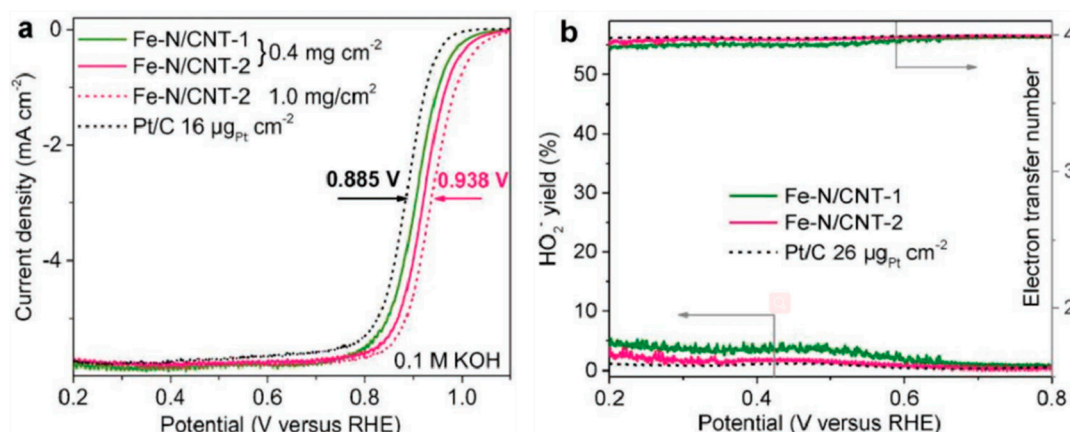


Figure 11. ORR activity measurement of the two Fe-N-CNT catalysts. (a) Linear sweep voltammetry (LSV) curves in O_2 -saturated 0.1 M KOH and (b) Calculated H_2O_2 yield and electron transfer number based on rotating ring-disc electrode (RRDE) tests. Reproduced with permission from Feiyu Kang, Lin Gan, Jia Li, et al., *Advanced Functional Materials*; published by John Wiley and Sons, 2019.

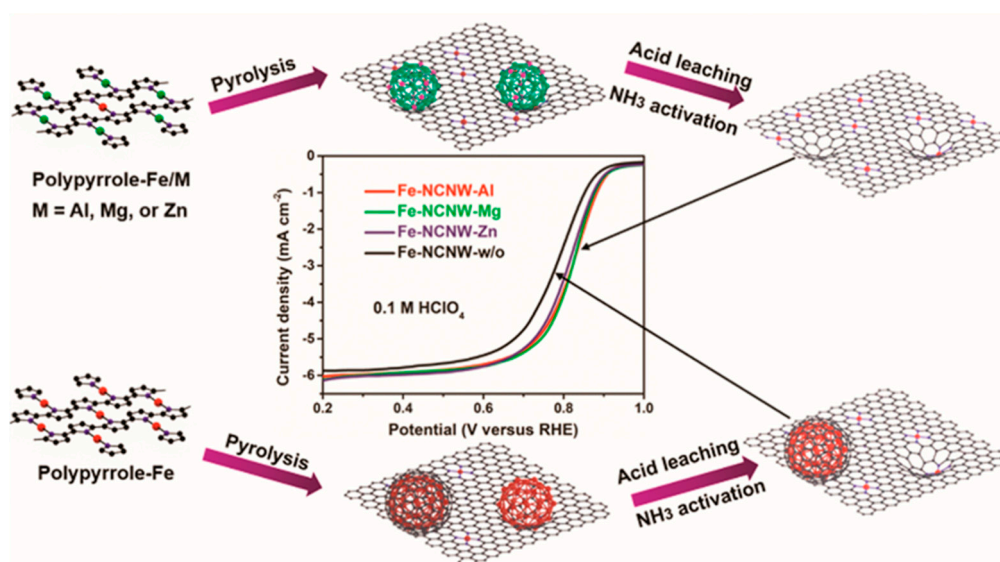


Figure 12. Schematic for achieving single-atom iron catalyst and traditional Fe-N-C catalyst. Reprinted with permission from Li et al. (2019) [113]. Copyright 2019 American Chemical Society.

To increase the active sites in catalysts, some porous organic materials with high surface areas, tunable compositions and various structural topologies, such as metal organic frameworks (MOFs) [116], zeolitic imidazolate frameworks (ZIFs) and covalent organic frameworks (COFs), are used to serve as carbon support after being heat treated. For example, Zhang et al. [117] used an MOF material named NH_2 -MIL-101@PDA to synthesize the Fe-N-C catalysts with higher ORR activity and stability than those of Pt/C catalyst (Figure 14). According to the XPS results, the Fe-N-C had a high content of N (8.07 at.%) and Fe-N_x (1.22 at.%), which is one of the reasons for high activity. Besides, the large surface area and porous structure are also favorable to the improvement of catalytic behavior. Mao et al. [118] studied the catalytic performance of several Co/N/C catalysts derived from Co-doped ZIF precursors by tuning the experimental conditions, such as the ratio of precursors, reaction temperature and reaction time. The sample of Co/N/C-1000, for which the heating temperature was 1000 °C, displayed a higher half-wave potential of 0.856 V than that of commercial Pt/C in alkaline condition and an outstanding stability in both alkaline and acidic solutions.

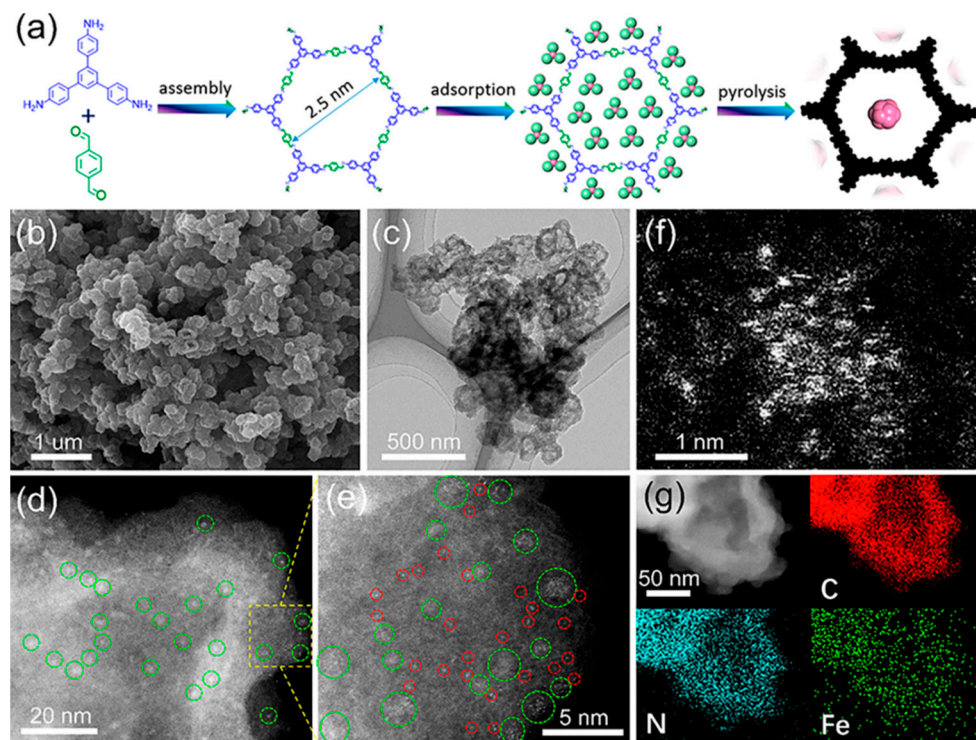


Figure 13. (a) Illustration of the synthesis process of Fe_{AC}@Fe_{SA}-N-C. (b) SEM image, (c) TEM image, and (d–f) HAADF-STEM image of Fe_{AC}@Fe_{SA}-N-C. (g) HAADF-STEM image and corresponding EDS element mapping images of Fe_{AC}@Fe_{SA}-N-C. Reprinted with permission from Ao et al. (2019) [115]. Copyright 2019, American Chemical Society.

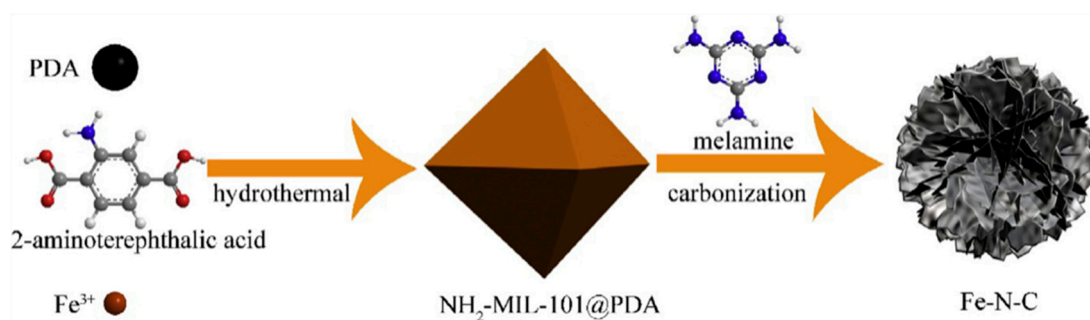


Figure 14. Schematic illustration of the synthesis of Fe-N-C. Reproduced with permission from Xiangkun Zhang, Xiaobo Huang, Wenhui Hu, Yongmin Huang, International Journal of Hydrogen Energy; published by Elsevier, 2019.

Apart from some traditional synthesis methods, some novel and effective approaches are emerging for facile synthesis of M-N_xC catalysts. For instance, Peng et al. [119] developed a non-pyrolysis method to prepare pfsAC-Fe catalysts via intermolecular interactions between the Fe-containing COF and the graphene matrix. The prepared catalysts exhibited the superior ORR activity with four times higher than that of commercial Pt/C. This method could also simplify the computational process, as no random structures are involved. Kiciński et al. [120] introduced a permanent magnet to the ORR test system to provide an external magnetic field (Figure 15). This method was proven effective to increase activity and boost the 4e[−] pathway, as the catalytic performance of Fe-N-C/S was obviously enhanced with an applied magnetic field in the test.

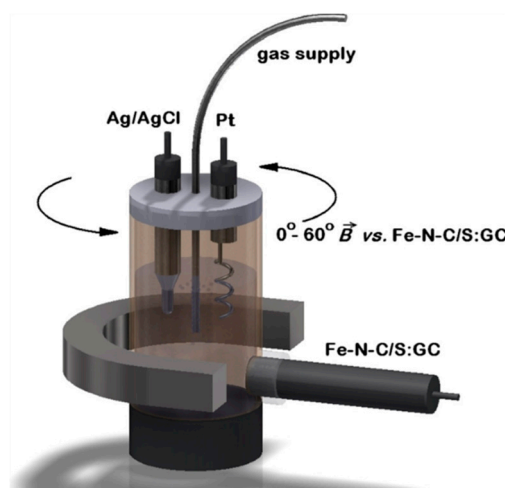


Figure 15. Schematic representation of the utilized electrochemical cell. Reproduced with permission from Wojciech Kiciński, Jakub P. Sęk, Edyta Matysiak-Brynda, et al., *Applied Catalysis B: Environmental*; published by Elsevier, 2019.

Since the earliest study of $M-N_xC$ catalysts, intensive focus and efforts have been attached to the exploration and discussion on the active structure favorable to the ORR. It should be noticed out that the ORR active site of $M-N_xC$ catalysts may be an integration of some active components varying with the potential changes, rather than a steadfast concrete structure. Although there are some people favoring of the statements that either some metal-free sites [121] or some carbon layer-coated metal sites [122,123] are the active sites in $M-N_xC$ catalysts for the ORR, the most widely accepted theory is still that $M-N_x$ sites are the true active components for ORR catalysis [124–126]. However, the debate, about whether $M-N_2$ or $M-N_4$ is the real active sites, never stop. For example, the majority of researchers believe the $Fe-N_4$ groups are the active sites towards ORR [127], while the rest of investigators think that $Fe-N_2$ would play a major part in ORR catalysis [128].

In practice, $M-N_xC$ catalysts are usually consisted of $M-N_x$ sites and graphene encapsulated metal nanoparticles simultaneously, which increases the difficulty to identify the true active sites in $M-N_xC$. Most recently, Feng's group [109] proposed a low-temperature NH_4Cl -treatment method to efficiently wipe off the graphene-encapsulated nanoparticles from $M-N_xC$ catalysts without destruction of $M-N_x$ groups (Figure 16). This strategy firmly demonstrates the dominant position of $M-N_x$ sites in catalyzing ORR. Wang et al. [129] used first-principles calculation to build a microkinetic model for ORR on single atom $Fe-N-C$ catalysts, and the modeling results indicated that the real active site of single atom $Fe-N-C$ is the $Fe(OH)N_4$ group, rather than inactive FeN_4 center, as the latter is covered with an intermediate OH^* which is a part of the active component, and the ΔG values along the associative path on the $Fe(OH)N_4$ center are more favorable to ORR catalysis than that of FeN_4 center (Figure 17).

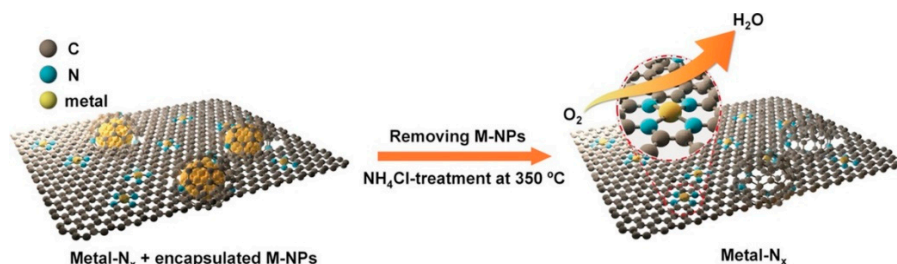


Figure 16. Schematic illustration of the removal of graphene-encapsulated M-NPs from $M-N-C$ ORR catalysts by a low-temperature NH_4Cl -treatment process. Reproduced with permission from Xinliang Feng, Haiwei Liang, Yuen Wu, et al., *Angewandte Chemie International Edition*; published by John Wiley and Sons, 2019.

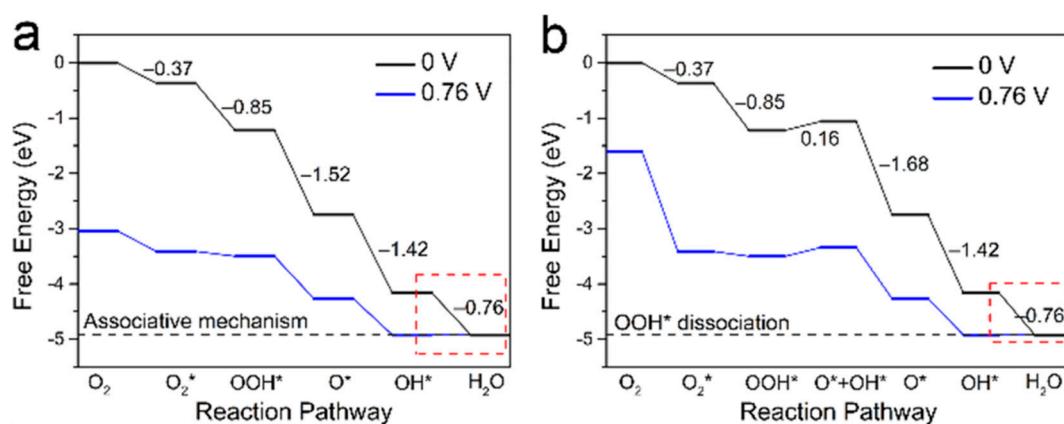


Figure 17. Free energy diagrams of ORR along (a) associative and (b) OOH* dissociative paths on Fe(OH)N₄ at 0 and 0.76 V. Reprinted with permission from Ref. [129]. Copyright 2019 American Chemical Society.

Then they applied the conclusion to analyze the mechanism of ORR catalyzed on single atom Fe–N–C (shown in Figure 18), and the result was in good accordance with the previous experimental results. For Co–N_xC, several studies have indicated that both the Co–N₂ and Co–N₄ sites have ideal catalytic performance towards ORR, while the Co–N₄ could be converted into Co–N₂, which has a stronger interaction with H₂O₂ under high temperature, therefore boosting the 4e[−] process of ORR [130–133]. Zhai et al. [134] prepared a catalyst of cobalt and nitrogen co-doped reduced graphene oxide (Co–N-rGO) with an increasing activity, a four-electron selectivity and a similar stability with commercial Pt/C. They gave some possible active sites in the Co–N-rGO towards ORR, including the edge plane CoN₂/C, CoN₄/C, and basal plane macrocyclic CoN₄/C, via DFT calculations shown in Figure 19. Most recently, Xiao et al. [135] firstly reported a novel binuclear active site structure of Co₂N₅ with a Co–Co distance of 2.1–2.2 Å. The strategy is to encapsulate the CoN₄ and Co particles in the carbon shell through the self-adjusting of the bimetal organic framework. The mechanism of Co₂N₅ for catalyzing ORR is shown in Figure 20. It was indicated that the ORR catalytic activity of Co₂N₅ is higher than that of CoN₄, which opens a new door to the fabrication of highly effective ORR electrocatalysts.

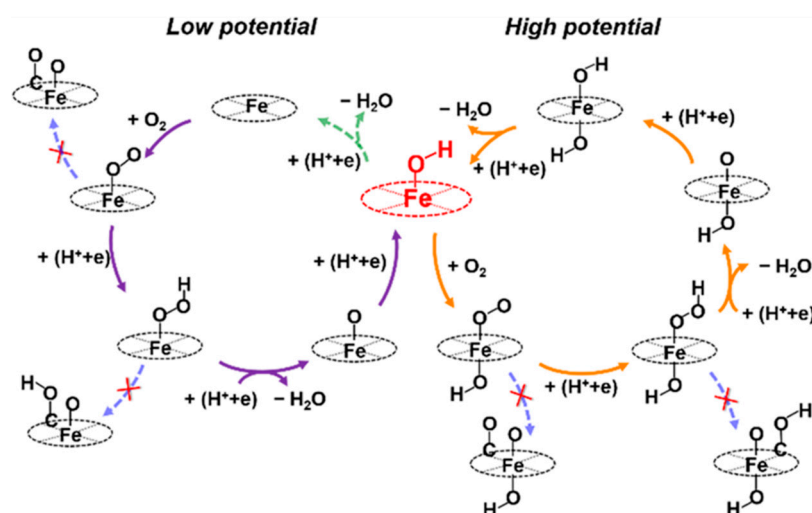


Figure 18. Mechanistic scheme for ORR on single atom Fe–N–C. Reprinted with permission from Wang et al. (2019) [129]. Copyright 2019, American Chemical Society.

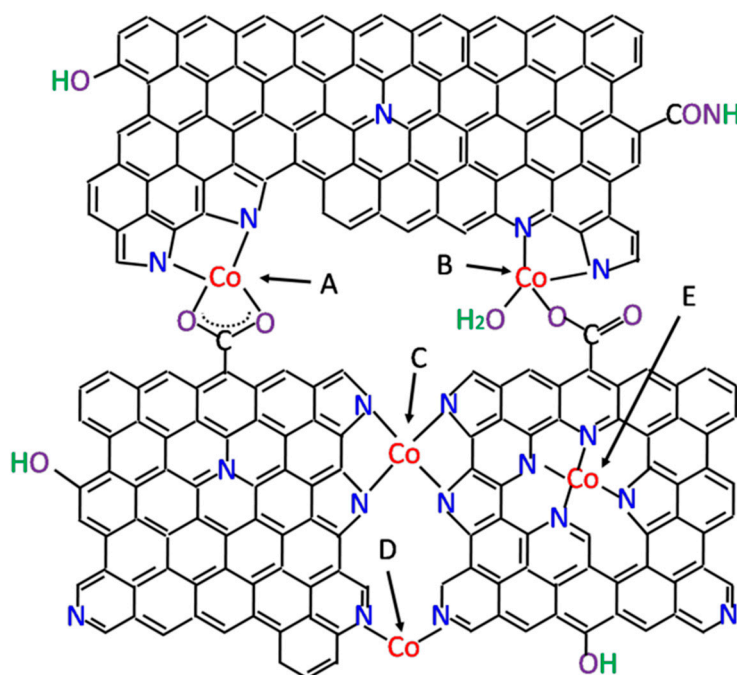


Figure 19. Possible catalytic active sites on Co-N-rGO. Reproduced with permission from Linfeng Zhai, Shiyu Kong, Huayang Zhang, et al., Chemical Engineering Science; published by Elsevier, 2019.

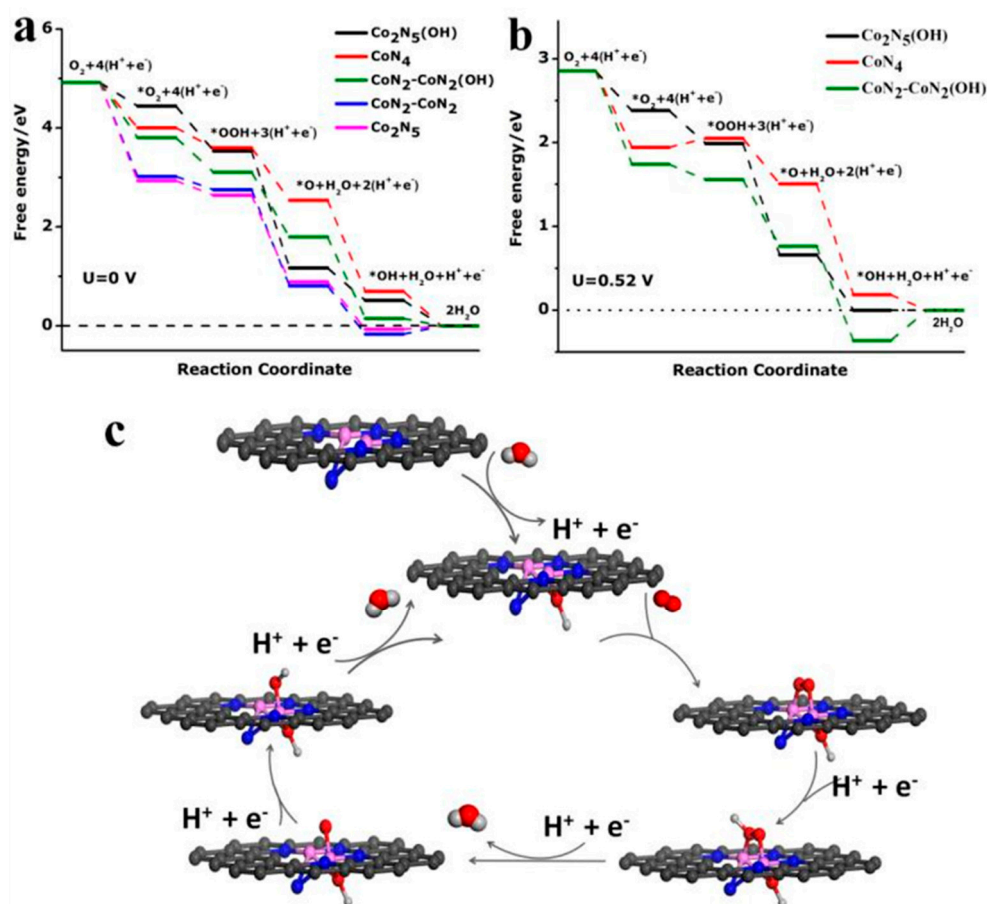


Figure 20. (a,b) Schematic energy profiles for the ORR pathway on different Co_xN_y active sites in acidic media. (c) Proposed mechanism for the ORR on the Co_2N_5 active site. Reproduced with permission from Meiling Xiao, Hao Zhang, Yongting Chen, et al., Nano Energy; published by Elsevier, 2018.

5. Conclusions

We have introduced the mechanism of ORR briefly and summarized the history of M–N_xC catalysts, including the earliest non-pyrolyzed transition metal macrocyclic compounds, then pyrolyzed transition metal macrocyclic compounds, and recent developed M–N_xC catalysts with simple and general structures. Besides, we give more detailed information about the currently developed M–N_xC catalysts from the perspectives of choice of carbon and nitrogen precursors, the recent emerging Fe–N_xC and Co–N_xC catalysts, the newly developed method to prepare Fe–N_xC and Co–N_xC catalysts, and their active sites analyses. The intrinsic structure and catalytic performance of M–N_xC catalysts are directly influenced by the choice of precursors. In most recent achievements, some porous organic materials with high surface areas, tunable compositions and various structural topologies, such as MOFs, ZIFs and COFs, have gained many priorities to be the precursors. The size of metals in the M–N_xC catalyst is reduced to single atoms, which contributes to an enhanced catalytic performance due to the utmost metal utilization and the low coordination to raise the activity, and the N-containing support's anchoring effect to improve the stability. The most acknowledged active sites of M–N_xC catalysts are M–N₂ and M–N₄ groups, while there are some trials to design new kinds of active sites, such as the binuclear active sites. Overall speaking, the thorough understandings about the M–N_xC catalysts stated in this review are favorable to provide a universal principle of highly effective M–N_xC catalysts' design.

In fact, although the M–N_xC catalysts with high ORR activities are demonstrated as one of the most promising substitutes for Pt-based catalysts, their performance is far from the practical requirements in PEMFCs due to the appeal to much higher activity and stability in acidic environments. According to this review, we think there are three main directions in the M–N_xC ORR catalysts field:

1. The study of the ORR catalytic mechanism. Understanding the character of M–N_xC and the catalytic kinetics in the catalytic process is helpful to us to regulate the catalyst structure and composition accurately, therefore improving the catalytic performance.
2. The study of active sites. Although there are already several researches on the identification of active structures, the true catalytic sites in M–N_xC catalyst are still confusing which drastically hinder the development of catalysts with adequate activity and stability. It is suggested that the atom-by-atom structural and chemical analysis in graphene can be achieved by the gentle ADF-STEM, which is a promising pathway to explore the local environment of active sites [136,137].
3. The exploration of new types of active sites. The aforementioned design of binuclear active sites, which are proven to be more positive than traditional M–N₂ and M–N₄ active sites, is a successful example to search for new kinds of active sites. It has inspired us greatly to enter a newly emerging but promising world to design satisfactory ORR catalysts.

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