

Atomically Dispersed M-N-C Catalysts in Proton Exchange Membrane Fuel Cells: Recent Progress and Perspectives

Haoran Kong^{1, a, *, †}, Jiarong Liu^{2, b, *, †}, Yu Yue^{3, c, *, †}

¹Chemistry and Materials Science, Shandong Agricultural University, Jinan, 271001, China

²Environmental Science and Engineering, BJTU, Chengde, Hebei province, 067000, China

³Faculty of Environment and Life, Beijing University of Technology, Beijing, 100049, China

[†]These authors contributed equally.

Abstract. The selection of oxygen reduction reaction (ORR) catalysts plays a key role in enhancing the performance of proton exchange membrane fuel cells (PEMFCs). To optimize the energy conversion technology in PEMFCs and improve the cost-effectiveness of ORR catalysts, atomically dispersed metal-nitrogen-carbon (M-N-C) catalyst is regarded as one of the most promising materials to replace Pt-based catalysts. In this review, we summarize the advantages of atomically dispersed M-N-C catalysts in both physical and chemical properties, including controllable dimensions, ease of accessibility, high surface area and excellent conductivity. Additionally, the unique merits of their cost-effectiveness are also described by a concise comparison with other ORR catalysts. Subsequently, some of its main synthesis methods are based on the most commonly used zeolitic imidazolate framework (ZIF) precursor. Several other precursors involve carbon, nitrogen, and one or more active transition metals (mainly iron or cobalt) are introduced briefly. Although there are a variety of synthesis methods, all these methods are in line with pyrolysis technology. Then, the recent advancements of atomically dispersed M-N-C catalysts related to their development and application of Fe-N-C, Mn-N-C, and Co-N-C catalysts are comprehensively described. Finally, based on some common M-N-C catalysts, many improvement ideas are also proposed. The focus is on how to control the negative reaction in Fe-N-C catalysts, improve the activity of Co-N-C catalysts and Mn-N-C catalysts, and find more suitable transition metal materials to prepare M-N-C catalysts.

1 Introduction

With the large-scale use of fossil fuels, while promoting social development, they also produce excessive NO_x, SO_x, CO₂ waste gas, resulting in an unprecedented environmental crisis. A direct fuel cell is a kind of energy device without the burning process. In the fuels (hydrogen, methanol, formic acid), chemical energy can be directly transferred into electricity through an electrochemical process with various advantages, including high energy conversion efficiency, large power generation, high specific energy, low noise range, a wide range of fuel, zero emissions and so on. Among them, proton exchange membrane fuel cell (PEMFC) is currently a new clean energy research hot spot.

For PEMFCs, the hydrogen oxidation (HOR) reaction occurred at the anode, while the oxygen reduction reaction (ORR) occurred at the cathode. Due to its sluggish kinetics, the ORR process leads to higher overpotentials (between 300 and 600 mV), which seriously reduces the actual overall efficiency of PEMFCs [1]. Therefore, it is necessary to develop efficient and stable catalysts to reduce the reaction energy barrier, accelerate the reaction rate and ultimately improve the energy conversion efficiency.

ORR is a complex reaction involving multiple electron transfer steps, whose reaction mechanism involves multiple elementary reactions and multiple intermediates. Therefore, there is an urgent need to develop low-cost, high-performance non-noble metal catalysts. The development of highly efficient and low-cost ORR catalysts is of great significance to the commercialization of PEMFCs. Atomically dispersed metal-nitrogen-carbon (M-N-C, M=Co, Fe, Mn, etc.) catalysts are considered the most promising ORR electrocatalysis candidates.

As a single-atom catalyst, the M-N-C one has many advantages: the stable existence of a single atom requires an appropriate electronic structure environment. Therefore, single atoms can only rely on the interaction with the surrounding carrier lattice to stabilize themselves, which will result in a series of changes in the electronic structure and form a more stable structure. The early M-N-C catalyst was directly synthesized by using carbon black as the precursor, which lacked precise control of morphology and structure. It was difficult to conduct a detailed analysis of its active site. Later, people used the metal organic framework (MOF) as the precursor to improving morphology and mass transfer. A higher performance M-N-C catalyst was obtained [2]. The M-N-C catalysts have been used at present in the majority of

*Corresponding author's e-mail: *2019211160@sdau.edu.cn,

^b17723019@bjtu.edu.cn, ^cbjuty@emails.bjut.edu.cn

chemical industrial processes as they have homogeneously dispersed active sites with maximal metal atom utilization and convenient adjustment. Therefore, this emerging field has been receiving enormous attention.

2 The Advantages of Atomically Dispersed M-N-C Catalysts

Oxygen reduction is at the core of fuel cells, and the development of high-performance catalysts is always a serious challenge faced by fuel cell technology. In recent years, the development of pyrolytic M-N-C catalysts and the application of metal-organic framework materials as precursors have greatly improved the performance of non-noble metal oxygen reduction catalysts.

In general, single-atom M-N-C catalysts, consisting of N-doped carbon skeleton and metal doping, provide many opportunities to prepare various functionalized catalytic materials to meet the requirements of catalytic and energy conversion devices. Carbon nanomaterials themselves, atoms formed by strong covalent bonds between carbons, have unique physical and chemical properties, including controllable dimensions, ease of accessibility, high surface area, excellent conductivity, controllable porosity, and abundant defects. The high surface area, hierarchical pore structure, and excellent conductivity of carbon materials are also the essential preconditions for mass/electron transfer and accessibility between reactants and active sites, which are the incomparable superiorities for pure metal oxides, and hydroxides or perovskites. Moreover, the potential strong metal-support interactions between well-dispersed single metal atoms and carbon substrates can limit the aggregation of metal atoms and the geometrical structure, and the electronic configuration of the active catalytic site is adjusted. Different coordination configurations of central atoms to a specific electrochemical reaction are of importance to the catalyst design. It might even change the number of electrons transferred by different pathways. M-N-C (M = Mn, Fe, Co, Ni, and Cu) are research results as catalytic centers that can change the ORR pathways spanning from 1e to 4e transfer processes. DFT calculations show that the electronic structures of atomic M can be finely tuned by bonding to diverse types of transition metals in the form of M-N₄ motifs, resulting in different target reaction pathways in the ORR.

The researchers found that the proper adsorption of the active center to the oxygen-containing intermediates is the key to achieve efficient catalytic oxygen reduction. Through DFT calculation, a volcanic curve was obtained by plotting the ORR activity to oxygen binding energy ΔE_{O_2} , and it was found that Pt was located at the top of it [4]. Pt catalyst is currently the catalyst with the highest catalytic activity and the best stability. Still, its high price and high load make it difficult to be used commercially on a large scale.

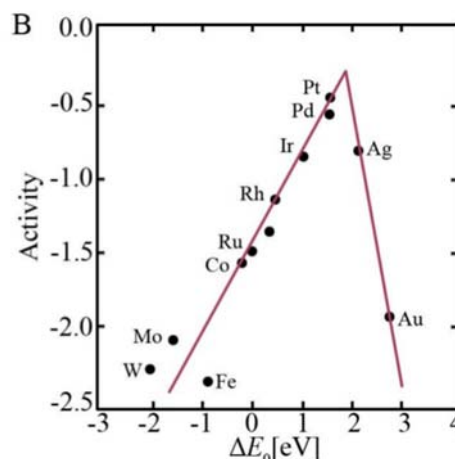


Figure 1: Oxygen reduction model proposed by Wroblowa[3] and (B) volcanic curve of oxygen reduction reaction[4]

Therefore, there is an urgent need to develop low-cost, high-activity non-noble metal-stabilized catalysts. Pyrolytic M-N-C catalyst is considered to be the most promising candidate catalyst. The early M-N-C catalyst uses carbon black as the precursor for direct synthesis. It lacks precise control of morphology and structure, making it difficult to conduct a detailed analysis of its active site. Later, one used the MOFs to improve the morphology and mass transfer problems and obtained the M-N-C catalyst with higher performance. The 2-methylimidazole ligands are rich in N and do not contain O, making N evenly distributed in the C skeleton. Many microporous structures can accommodate more active sites. The mesoporous structures are conducive to mass transfer and have excellent electrical conductivity and certain stability. Therefore, compared with conventional nanoparticles (NPs) or bulk catalysts, M-N-C is expected to become a more efficient alternative for boosting the practical applications of advanced conversion reactions and renewable energy devices.

3 The Synthesis Strategies of Atomically Dispersed M-N-C catalysts

Many methods for preparing M-N-C catalysts have been reported in the literature, such as pyrolysis, electrochemical deposition, and wet chemistry. The present study confirmed the pyrolysis is the most commonly used method to prepare M-N-C catalyst for ORR [5]. As shown in figure 2, there are the major research directions of advanced M-N-C catalysts [6]. Herein, based on the determination of the research direction, the main synthesis methods of M-N-C are summarized.



Figure 2: The main research directions of advanced M-N-C catalysts. Adapted with permission from Ref[6].

3.1 Approaches based on ZIF and ZIF derivatives for M-N-C synthesis

At present, the most common precursors are ZIFs (Zeolitic imidazolate framework), and based on this kind of precursors, the synthesis of M-N-C catalysts was

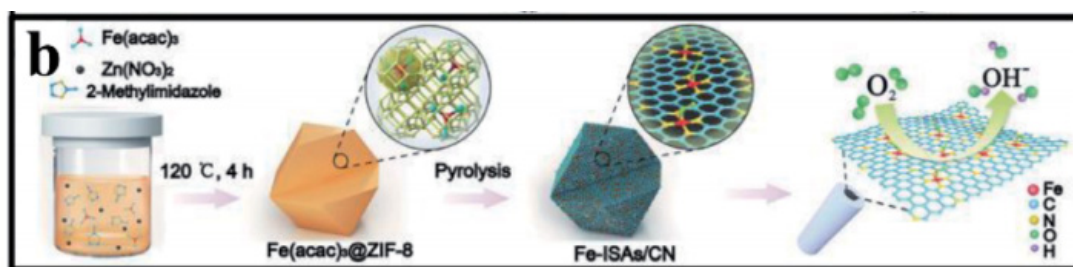


Figure 3: Spatial confinement method of a ZIF-8 derived atomically dispersed Fe-ISAs/ CN catalyst. Adapted with permission from Ref [11].

3.1.3 Impregnation adsorption method

The impregnation adsorption method can be divided into two steps. Firstly, ZIF-8 or ZIF-8 derivatives were carbonized to prepare porous carbon supports with the best nitrogen doping. Then, the target metal precursor was adsorbed into the porous carbon support by the wet impregnation method and the M-N_x catalyst with atomic dispersion obtained by thermal activation [12].

3.2 Approaches based on other precursors for M-N-C catalysts synthesis

In the synthesis of M-N-C catalysts, the three key elements C, N, and metal (M) come from different precursors and can be divided into the following three categories [13,14]:

- Approach 1: catalysts derived from carbon support and nitrogen-containing molecule;
- Approach 2: catalysts derived from silica sample and organic precursors (Hard Template Method);

summarized systematically [7].

3.1.1 Chemical doping method

The chemical doping method refers to using transition metal ions shown in figure 3, to partially replace zinc ions in ZIF-8 so that the target metal ions are doped into the precursor. The presence of zinc increases the distance between the target metal atoms and prevents them from agglomerating. On the other hand, the evaporation of zinc (boiling point: 900 °C) promotes the formation of nitrogen-containing anchor sites, thus stabilizing the target metal atoms [8]. Fe-N-C catalysts have the best ORR performance among all monoatomic M-N-C catalysts because of their excellent intrinsic activity [9].

3.1.2 Spatial confinement method

The space confinement method uses microporous ZIF-8 as a cage to capture and restrict small molecules containing target metals, such as Fe(ACAC)₃, Ir(ACAC)₃, and ferrocene. In this way, it can avoid migration and agglomeration during pyrolysis [10]. A typical study of Li and his colleagues [11] synthesized monoatomic Fe-N-C catalysts by space confinement, and it is schematically shown in Figure 4.

- Approach 3: catalysts derived from organic metal frameworks (MOFs) and other precursors.

3.2.1 Catalysts derived from carbon support and nitrogen-containing molecule

Figure 4(a) shows a typical synthesis route that can be used to obtain a catalyst. In the synthesis process, carbonaceous materials have dual purposes: provide excess C atoms and act as conductive carriers for ORR active sites. To effectively act as a support, C-based materials must have a high enough surface area (to ensure a high density of active centers) and good conductivity. Additionally, nitrogen-containing molecules are crucial to ensure the binding of N atoms to the carbon matrix of the support [15]. The most commonly used transition metal precursors are salts, mainly chlorides, nitrates, sulfates, and acetate [16]. In the whole synthesis process, pyrolysis is a key process. Due to that, it can form activated carbon sites. During this period, high-temperature pyrolysis

provides the energy needed to recombine chemical bonds, which is conducive to the combination of N and M atoms in the carbonaceous matrix of the support [17]. Another common procedure in M-N-C catalyst synthesis is acid leaching after pyrolysis. This is done to remove soluble acid metal-containing compounds (metal forms, oxides) that are not firmly bonded or embedded in the carbonaceous matrix. It means that the metal content of the catalyst will decrease after acid leaching [18].

3.2.2 Catalysts derived from silica template and organic precursors (Hard Template Method)

The core idea of this synthesis method is to use the shape of a template (usually porous silica) and copy its structure negatively by adding catalyst precursors. After the carbonization process (pyrolysis), to obtain the final catalyst, the silica template is removed by leaching out with appropriate chemicals that only react with silica and

do not damage the M-N-C material. The schematic diagram of this synthesis method is shown in Figure 4 (b) [19].

3.2.3 Catalysts derived from metal organic frameworks (MOFs) and other precursors

Metal organic frameworks (MOFs) are materials composed of metal ions and organic linkers, forming a highly ordered crystal structure with the particularity of porosity. The counterions (negatively charged) which balance the positive charge of metal ions are located in the pores and the residual solvent molecules in the synthesis process. The emphasis of the description is limited to the synthesis variables, which are used to adjust some related characteristics of MOF-derived catalysts. Finally, a typical synthesis process using MOFs is shown in Figure 4 (c) [20].

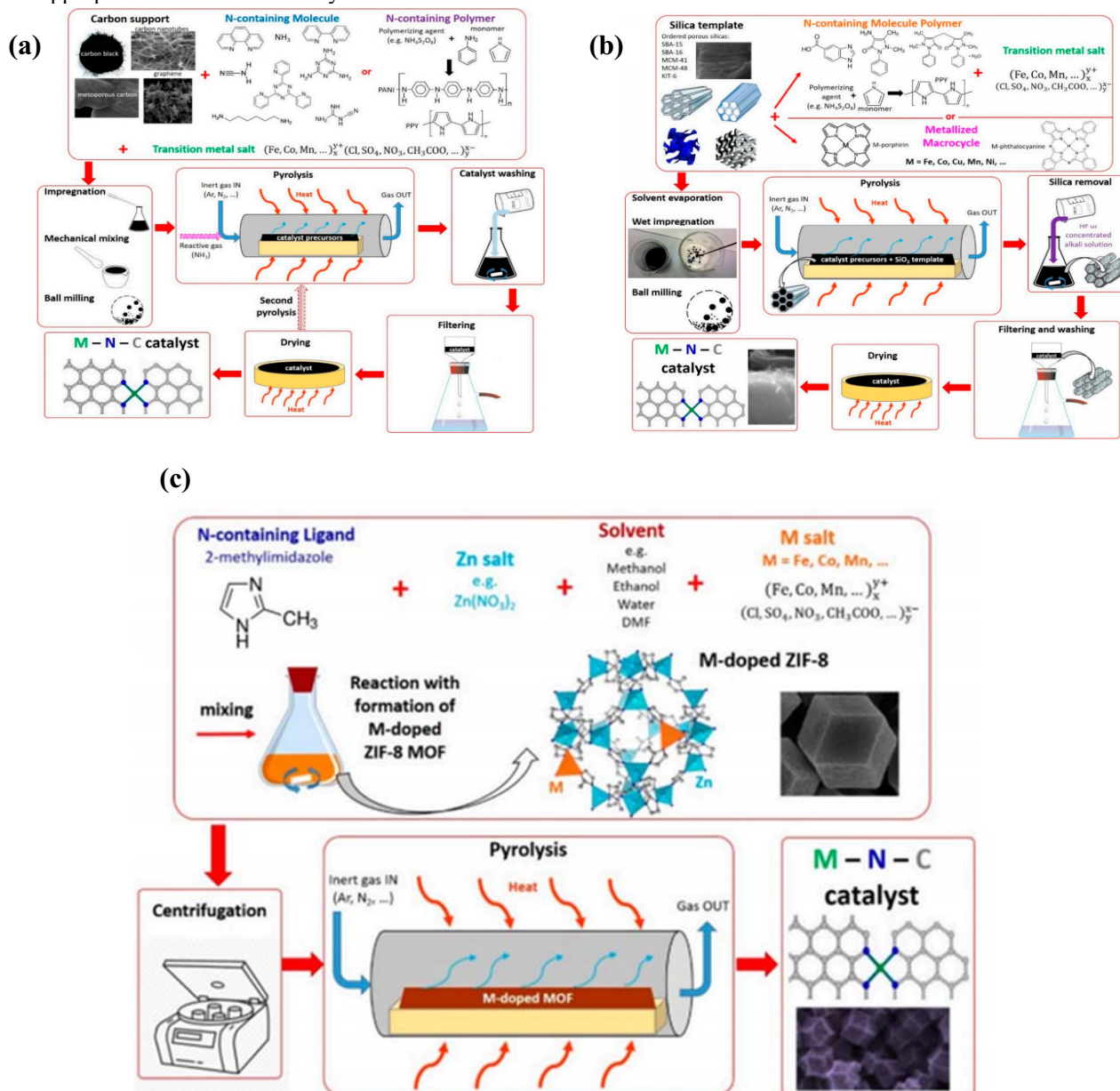


Figure 4: The steps for the synthesis of M-N-C catalysts.

(a) Scheme representing the typical steps for the synthesis of M-N-C catalysts with approach 1. (b) Scheme representing the typical steps for the synthesis of M-N-C catalysts with approach 2. (c) Scheme representing the typical steps for the synthesis of M-N-C catalysts with approach 3. Adapted with permission from Ref. [18].

4 Recent Progress of Atomically Dispersed M-N-C Catalysts

Transition metal oxides are rich in content, easy to synthesize, cheap, stable in alkaline and oxygen environments. They are a kind of material that is likely to replace precious metal Pt catalysts. Manganese, Iron, Cobalt oxide is widely studied transition metal oxide. Such as Fe_3O_4 , CO_3O_4 , MnO_2 , etc., have high oxygen reduction activity. However, the defect of metal oxide ORR catalyst is the poor conductivity of electrons because most oxides are semiconductor materials with large bandwidth, which is not conducive to oxygen reduction.

4.1 Fe-N-C catalysts

Fe-N-C materials have been reported to show very high electrocatalytic activity and stability to ORR in acidic and alkaline electrolytes. Some of which, such as starting potential, half-wave potential, can even be comparable to traditional catalysts and show better stability.

Preparation materials are Aniline, Ammonium persulphate, Iron (III) chloride hexahydrate, HG-1F, 5% Nafion solution [21]. The preparation process includes polymerization, carbonization, and acid treatment. Catalytic ORR changes like the volcanic shape with the prolongation of acid treatment time (Figure 5).

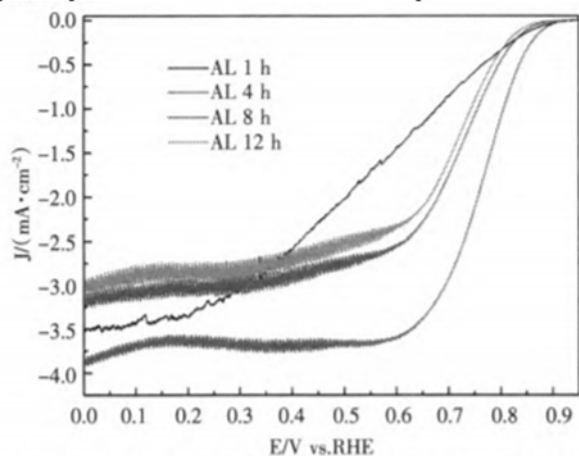


Figure 5: Catalyze the cathodic polarization curve of ORR.

This phenomenon may be because when the acid treatment time is too short, there are still many non-electrochemical active Fe on the surface. They hinder the contact between oxygen molecules and active Fe; when the acid treatment time is too long, some active Fe species will also be destroyed, resulting in the reduction of ORR activity.

Li and co-workers used Fe-N-C were synthesized from aniline as raw material, silicon dioxide as a template, and ferric chloride used as the iron source. Fe-N-C composites were synthesized as oxygen reduction catalysts by co-precipitation [22]. One important discovery is that it can be seen that after 7,000 s, Fe-N-C can still maintain 93.53%

of the relative current. In contrast, the current density of Pt/C is only 83.29 percent, indicating that the Fe-N-C composite catalyst is very stable (Figure 6).

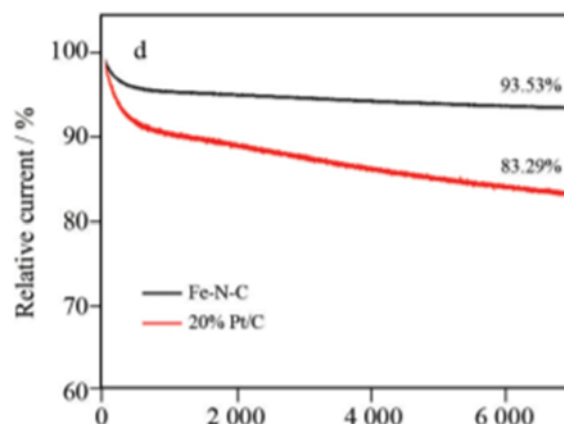


Figure 6: I-t curves of Fe-N-C and Pt/C in an O_2 -saturated 0.1 M KOH solution at 1,600 rpm.

Li also found that The Fe-N-C composite catalyst has a higher starting potential, half-wave potential, and limit current density than N-C, indicating that the introduction of Fe is conducive to improving the catalytic activity of ORR. The Fe-N-C composite catalyst's starting potential and half-wave potential are only lower than the commercial Pt-C, respectively (Figure 7).

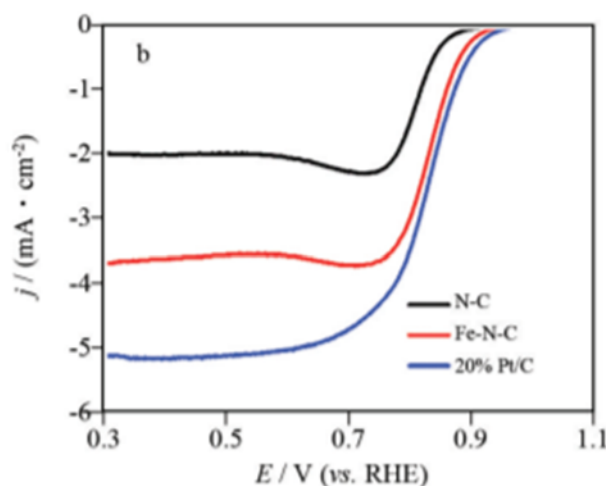


Figure 7: LSVs of N-C, Fe-N-C and 20% Pt/C in saturated- O_2 0.1 M KOH solution at 1 600 rpm

Zhang and co-workers synthesized the nitrogen source of nature polymeric compound base as a catalyst, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as a metal precursor, and graphite as a carbon carrier using natural polymer compounds: chitosan as raw material synthesizes Fe-N-C-t catalysts for heat treatment at different temperatures. The catalytic effect of Fe-N-C-1000 is best obtained by cyclic voltammetry. Combined with FT-IR and XRD characterization results, the effective catalytic activity potential in the Fe-N-C-t catalyst should be Fe_xN structure [23].

Although Fe-N-C has the best ORR catalytic activity under acidic conditions, due to the easy dissolution of iron to form iron ions under acidic conditions, the byproduct H_2O_2 reacting with ORR forms a highly oxidizing Fenton reagent. It has a very destructive effect on the proton exchange membrane and catalyst, resulting in rapid decay of catalyst performance and short-circuit failure.

4.2 Co-N-C catalysts

It is necessary to replace Fe with a metal that does not have a Fenton reaction. Compared to Fe-N-C catalysts, the Co-N-C catalyst has shown lower ORR activity and higher ($2e^-$) dual-electron reduction to form H_2O_2 selectivity. For example, cobalt acetate and acid pretreated carbon black powder are evaporated in distilled water. After entering ammonia, the reaction conditions are high.

According to the experiment of Lai, it can be seen that the reduction current of untreated carbon black electrodes is very small throughout the potential range [24].

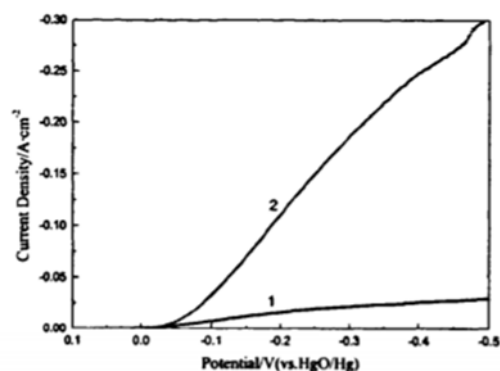


Figure 8: Cathodic polarization curve of ORR carbon powder without any treatment in Co-N-C complex catalytic material.

Compared with Co-N/C electrodes, the current density increases by 95 mA cm^{-2} to 110 mA cm^{-2} at the potential of 0.2 V in the figure, showing that cobalt nitride has excellent electrocatalysis performance for oxygen reduction.

According to the experiment results, Professor Xia concluded that the anionic group of cobalt salt has little effect on the morphology of the Co-N-C catalyst. However, on the surface chemical composition and content, carbon structure, graphitization degree, and cobalt valence state in the Co-N-C catalyst. Anion groups in cobalt salts affect the Co-N-C catalyst's electrochemical properties and ORR activity [25,26].

Reasonable Co-N-C catalysts should have high activity point density, reasonable micro-structure, aperture distribution, and good corrosion resistance. But Co-N-C catalysts need to further improve catalytic activity.

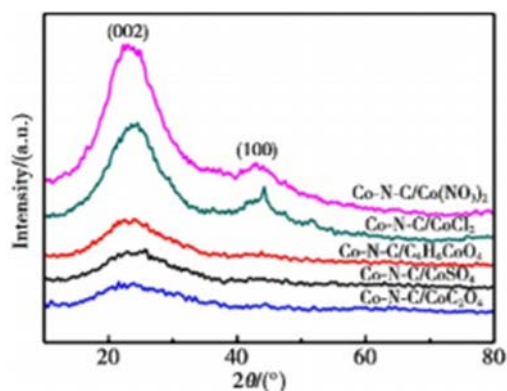


Figure 9: XRD patterns of different Co-N-C catalysts

4.3 Mn-N-C catalysts

Researchers are increasingly interested in pursuing iron-free and platinum-based electric catalysts to reduce oxygen to avoid harmful iron participating in the Fenton reaction. Manganese, as a transition metal element, is similar to iron, which provides a new idea for the study of M-N-C catalysts

The preparation of Mn-N-C catalysts was direct pyrolysis of an Mn(II)-based MOF followed by acid leaching and second heat-treatment, which was solvothermal synthesized from $Mn(ClO_4)_2$ N-rich organic linker of TTPBA-4.

Li found that single-crystal X-ray diffraction analysis reveals that Mn-TTPBA-4 shows a 3D cationic porous architecture assembled by 1-D ribbon chains extending in mutually vertical directions [27]. The best-performing Mn-N-C catalyst exhibits a half-wave potential ($E_{1/2}$) of 0.81 V in alkaline electrolyte comparable to the reference Pt/C and good long-term stability with only 10 mV negative shift in $E_{1/2}$ after 10,000 cycles.

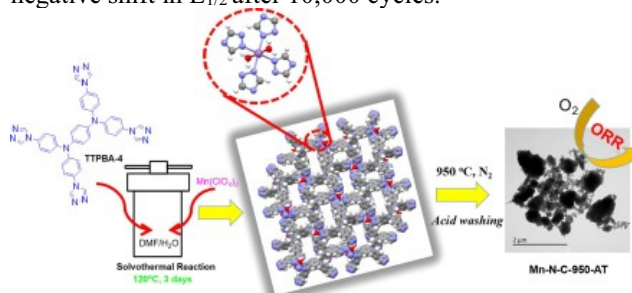


Figure 10: Preparation of Mn-N-C catalyst

The Mn-N-C catalysts are similar to the Co-N-C catalysts. It has excellent robustness but lacks chemical reaction activity. Future research is necessary to improve the reaction activity and find a more suitable synthesis method.

5 Conclusions and outlook

This review article summarizes the recent progress of atomically dispersed M-N-C catalysts in PEMFCs. As a new class of catalysts, atomically dispersed M-N-C catalysts have the many advantages of excellent ORR

activity and strong robustness. The synthesis strategies of atomically dispersed M-N-C catalysts are also highlighted. ZIF and ZIF derivatives for constructing M-N-C catalysts with different methods, such as chemical doping method, spatial confinement method, impregnation adsorption method, where diverse carbon supports and N-containing modules, silica template, organic precursors, metal-organic frameworks, and other precursors are involved. Then, this paper summarizes several atomically dispersed M-N-C catalysts with rapid development in recent years.

There are several atomically dispersed M-N-C catalysts under study. Fe-N-C catalysts have the best reaction activity, but because it produces H₂O₂ that is not conducive to the reaction, mainstream research now selects M-N-C catalysts that do not contain iron. Co-N-C catalysts as an M-N-C catalyst without iron and platinum it is very popular. But this kind of catalyst has high requirements for the reaction environment during preparation. Although the reaction activity is not as good as that of an iron catalyst, the robustness is outstanding, and most current studies are trying to improve its reaction activity. Mn-N-C catalysts have the same characteristics as Co-N-C catalysts, but there are less literatures at this stage.

In general, atomically dispersed M-N-C catalysts are a new research content that can improve the activity of ORR reactions in fuel cells, with great field and potential for progress. Future research can focus on how to control the negative reactions in the Fe-N-C catalyst or improve the reaction activity of the Co-N-C catalysts and Mn-N-C catalysts and find more suitable transition metal materials to make atomically dispersed M-N-C catalysts.

PEMFCs, which use PEM as electrolytes, have the advantages of low operating temperature, fast startup speed, modular installation, and easy operation compared with several other types of fuel cells. It is considered the best alternative power supply for electric vehicles, submarines, various removable power sources, power grids, and fixed power supplies. Based on the current research, the following aspects are carried out: 1) research on new materials to meet the needs of membrane materials such as proton exchange membranes, electrodes, and gas diffusion layers; 2) develop new catalysts to improve the performance of fuel cells; 3) design a reasonable battery structure so that components can fully play their respective roles; (4) study the process mechanism and establish a model of the performance constraints of PEMFC factors.

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