

Review Article

Recent Advances in M-N-C Electro-catalysts for O₂ Reduction Reaction in Fuel Cells

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Abstract

Transition metal–nitrogen–carbon (M-N-C) catalytic materials are widely considered the most promising non-Pt metal for oxygen reduction reaction (ORR), they are extensively studied as potential electrocatalysts in energy conversion and storage devices like fuel cells. The ORR is a critical reaction that significantly impacts the performance and efficiency of these devices. Recently, tremendous researches have been made to obtain high-performance M-N-C catalysts. This review article provides insights into the mechanism of the O₂ reduction reaction, offering insights that are crucial for designing effective catalysts. It also provides a detailed account of the recent progress in the synthetic methods, which are pivotal for tailoring the structure and properties of M-N-C materials. The article also examines different transition metal - nitrogen - carbon species, the choice of transition metal and its coordination environment significantly influence the electronic structure and catalytic activity. Furthermore, it highlights approaches to enhance the catalytic activity of M-N-C catalysts, these strategies aim to optimize the active sites and improve electron transfer, thereby boosting ORR performance. Finally, several key factors must be solved to create efficient and robust electrocatalysts are summarized briefly.

Keywords

O₂ Reduction Reaction, M–N–C Catalysts, Design Strategies, Catalytic Activity, Fuel Cells, Non-precious Metal Catalysts

1. Introduction

Owing to the constant increase in the demand for energy worldwide and severe environmental concerns, high-performance energy conversion and storage technologies with low cost have attracted immense attention [1-6]. Among the leading approaches under consideration, fuel cells have gained immense popularity as one of the leading clean energy technologies, owing to their ability to efficiently convert hydrocarbon fuels directly into electrical energy through cathodic O₂ reduction reaction (ORR) and anodic H₂ oxidation reaction (HOR), with H₂O as the only by-product [4, 7].

However, the slow ORR rate at the cathode, approximately five orders of magnitude lower in comparison to that of the HOR at the anode, severely limits the efficiency of the fuel cell [8-10]. Therefore, the development of electrocatalysts to boost the slow kinetics of ORR holds great significance in fuel cells [11]. Traditionally, Pt has been considered the most commonly used and effective ORR catalyst [12, 13]. However, the limited reserves and high cost of Pt have severely restricted the application of Pt-based catalysts for large-scale production of fuel cells [14-16]. According to the World Platinum Investment Council, the platinum market recorded a

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922,000 - ounce deficit in 2024 and is forecast to have a 966,000 - ounce deficit in 2025, representing about 12% of global demand. This persistent deficit threatens to deplete above - ground inventories within three years. In 2025, above - ground platinum stocks fell to 2.1 million ounces, down 25% from 2022 levels. Thus, numerous studies have investigated non-platinum metal materials as ORR cathode catalysts alternative to Pt-based catalysts [17-19].

Among the non-Pt metal catalysts for ORR, the transition metal (Mn, Co, Fe) and N-codoped carbon material (M-N-C) catalysts are considered the most promising candidates. Thus, they have been investigated extensively as potential electrocatalysts. Ever since M-N-C materials were first proven to catalyze ORR activity in the 1960s, later on, more and more researchers synthesized and studied the M-N-C catalysts. The advantages of M-N-C catalysts are comparable to noble metals, such as low cost, high activity, availability of a wide variety of precursor materials, and comparable catalytic activity [20-22]. However, to date, the activity of the commercial Pt/C ORR catalysts is still superior to the vast majority of M-N-C catalysts, due to their much lower intrinsic activity, needing a much higher loading of M-N-C catalysts to achieve a comparable level of activity to that of the Pt/C catalysts. Therefore, numerous recent studies have focused on developing high-efficiency M-N-C catalysts [23-26]. Precise control and carefully designed strategies are required to obtain excellent M-N-C catalysts and further bring their performance closer to that of the commercial Pt/C ORR catalysts. Also, an improved understanding and in-depth knowledge of the active sites is crucial for developing high-efficiency M-N-C catalysts.

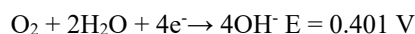
This review article offers an overview of the recent advances in M-N-C ORR catalysts. The ORR mechanism has been introduced first, followed by a summary of the synthetic methods, transition M-N-C species, and methods for enhancing the catalytic activity of catalysts based on these composites. Finally, several key factors must be solved to create efficient and robust electrocatalysts has also been presented.

2. Introduction of the ORR Mechanism

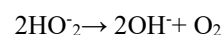
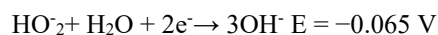
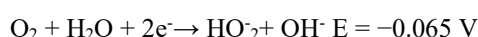
Generally, the ORR reaction on the cathode, can proceed via two pathways (As shown in Figure 1 [27]): a 4-electron pathway and a 2-electron pathway, distinguished with pH of the electrolyte and electrode material.

In alkaline or neutral electrolyte, the reaction mechanism is as follows [28]:

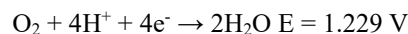
4-electron pathway:



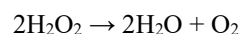
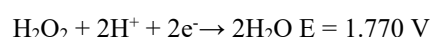
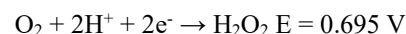
2-electron pathway:



In acidic electrolyte, the reaction mechanism is as follows: 4-electron pathway:



2-electron pathway:



Oxygen is directly converted to OH^- (in an alkaline solution) or H_2O (in an acidic solution) in the 4-electron pathway. However, O_2 is initially reduced to H_2O_2 in a 2-electron pathway, followed by the transformation from H_2O_2 into H_2O by the adsorption of another two electrons in an acid electrolyte. In alkaline or neutral electrolyte, O_2 is first reduced to HO_2^- , which is then converted into OH^- . The direct 4e transfer pathways generate two H_2O or OH^- , while 2e transfer pathways generate H_2O_2 which definitely cause damage to the proton exchange membrane and the catalysts, therefore, the direct 4e transfer pathway is preferred in fuel cells. [28, 29].

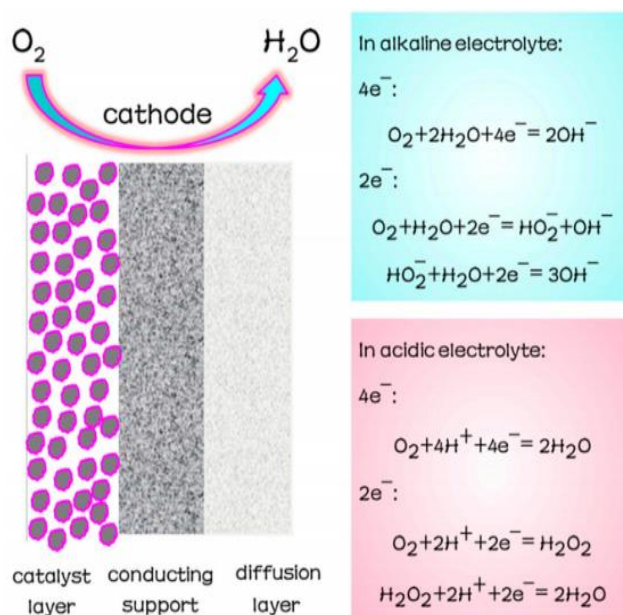


Figure 1. The structure cathode in proton exchange membrane fuel cells (PEMFCs) and ORR pathways on the cathode [27].

However, the ORR is inevitably carried out via the two-electron pathway or the parallelism of the 2-electron and 4-electron pathways on the electrode surface. This is linked to

many factors, including defects, the density of active sites, and the distance between particles. So, a better solution is to develop high-efficiency catalysts. The M-N-C catalysts have gained immense attention due to their high ORR activity compared to other class alternatives.

3. The Synthetic Methods

The physical properties (such as density of active sites, electronic conductivity, hydrophilicity, and porosity) and chemical properties (i.e., surface-specific catalytic activity) of the M-N-C catalysts play a vital role in fuel cell electrodes. The synthetic process strongly affects the chemical and physical characteristics of these catalysts. Hence, a lot of work has been done to develop an effective catalyst based on different synthetic methods. Common methods include Py-

rolysis, Deposition, Metal-Organic Frameworks Derivative, and so on.

Pyrolysis is a popular and easy-to-conduct approach for developing M-N-C catalysts. For instance, a highly efficient Fe-N-C catalyst was developed by Ren et al. by employing a novel precursor, adenosine [30]. As shown in Figure 2, adenosine (a) was used as the precursor. Fe-N-C nanotubes (c) were prepared firstly at 800°C, which were then ground into powder and stirred with 0.5 M H₂SO₄ at 80°C for 10 h, following the second pyrolysis under argon at 800°C for 3 h to synthesize the required Fe-N-C sample (d), which exhibited a high ORR electrocatalytic activity. As depicted in Figure 3, under moderate catalyst loading (2mg/cm²), the maximum power density value of Alkaline polymer electrolyte fuel cells (APEFCs) with the Fe-N-C as cathode exceeded 450 mW/cm².

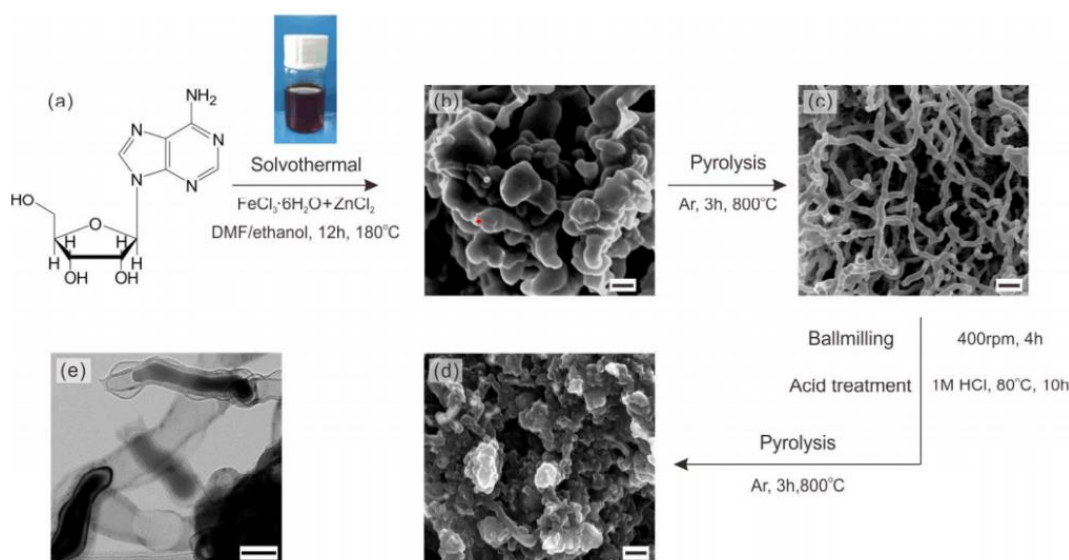


Figure 2. Schematic diagram illustrating the preparation method of Fe-N-C nanotubes derived from adenosine [30]. Scale bars: b, c, d = 200 nm; e = 50 nm.

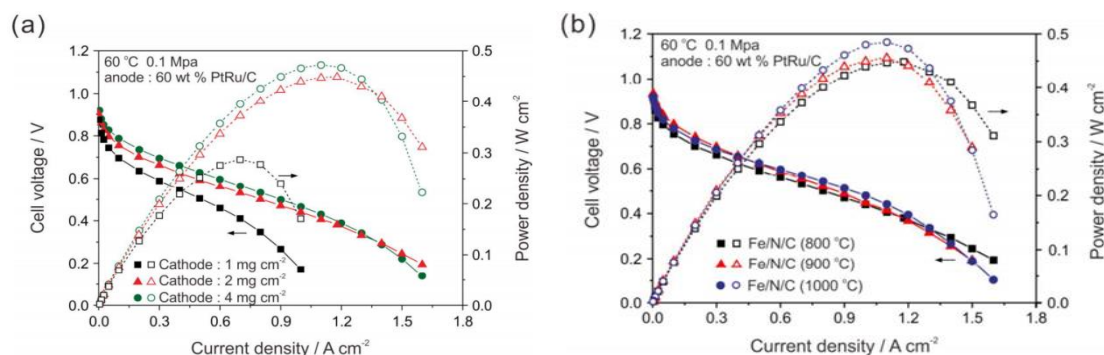


Figure 3. Single-cell performance of APEFCs (a: various Fe-N-C loadings; b: Fe-N-C catalysts synthesized at various temperature values) [30].

It is worth noting that studies using the pyrolysis method have found the aggregation of metals during pyrolysis. To

prevent the aggregation of metals, many methods are added to the pyrolysis process. One of the typical methods is to add the

template method which can be used to adjust the morphology and structural properties during the pyrolysis process or etching process after precursor pyrolysis. For instance, Liang, et al. [31] used SiO₂ as hard templates template to prepare mesoporous Co-N-C catalyst. The most active mesoporous catalyst (VB12/silica colloid) displayed significant ORR activity (with a half-wave potential ($E_{1/2}$) equal to 0.79 V),

outstanding electrochemical stability under acidic media (see Figure 4), and high selectivity (exhibiting an electron transfer number > 3.95). The remarkable ORR efficiency of the mesoporous catalysts was mainly attributed to introduce the hard template, forming a unique mesoporous structure, which increases the specific surface area of the material (as high as 572 m²/g) and fully exposes the active site inside the material.

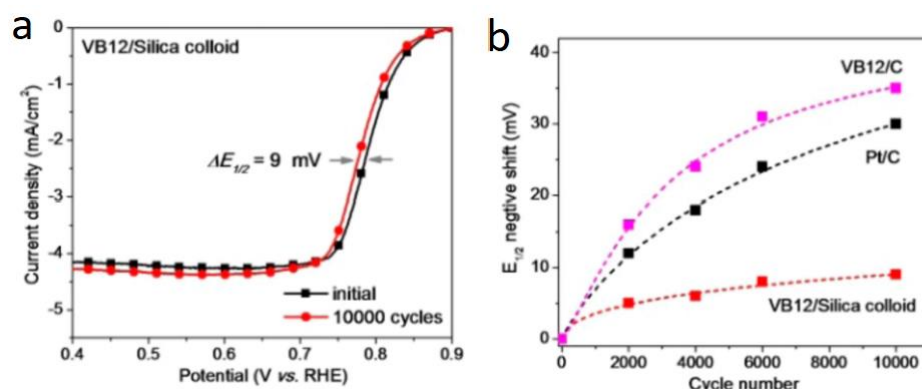


Figure 4. (a) The measured ORR polarization curves for VB12/Silica colloid in O₂-saturated electrolyte. (b) Under O₂ conditions, $E_{1/2}$ of VB12/Silica colloids, VB12/C, and Pt/C catalysts shift negatively with increasing number of repeated CV runs. [31].

Chu, H. and co-workers [32] fabricated a high-efficiency Fe-N-modified carbon nanofiber (CNF) catalyst using a template method with SiO₂-coated shells, as illustrated in Figure 5. The SiO₂-protected shells played a crucial role during the pyrolysis process by preventing the migration of Fe ions, thereby facilitating the development of highly active Fe-N_x sites via the growth of inorganic Fe-based nanoparticles. This method resulted in the creation of hierarchical, porous CNF

catalysts with a surface area (SA) equal to 941 m² g⁻¹. Such structural features led to excellent ORR efficiency of p-Fe-N-CNFs in 0.1 M HClO₄, achieving an $E_{1/2}$ value equal to 0.74 V (vs. RHE) and 4-electron transfer between 0.2 and 0.4 V. Moreover, the kinetic current density (J_K) of the catalyst at the $E_{1/2}$ was 6.29 mAcm⁻². Besides SiO₂, nano-ferric nitrate crystals [33] and Pluronic F127 [34] can also be utilized as templates to synthesize M-N-C electrocatalysts.

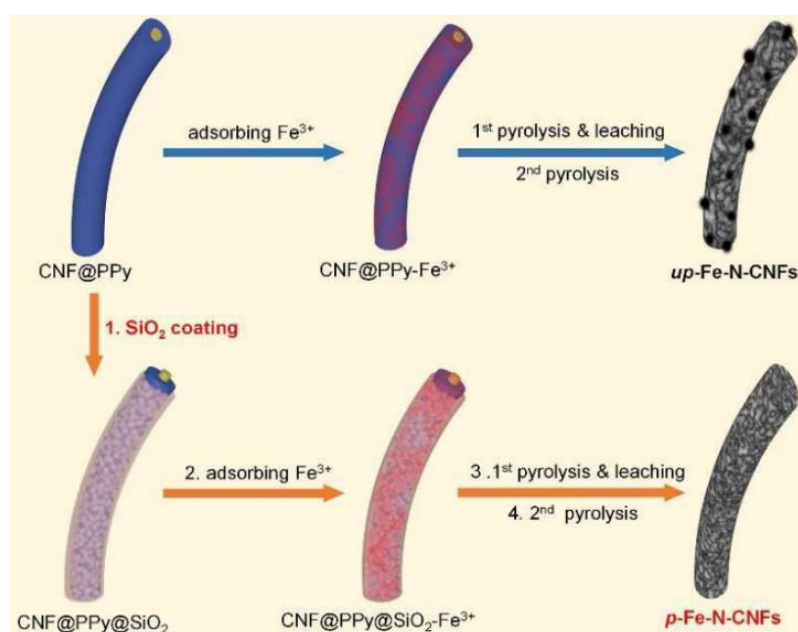


Figure 5. Schematic representation illustrating the preparation processes of CNFs of the unprotected Fe-N-CNFs (without SiO₂, labeled as up-Fe-N-CNFs) and protected (p-Fe-N-CNFs) catalysts. [32].

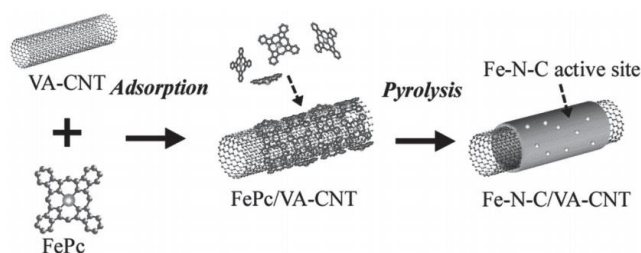


Figure 6. The synthesis approach used for the Fe-N-C/VA-CNT composite. [35].

Deposition is a conventional strategy for controlling the film thickness, active site distribution, consistency, and contact uniformity of nanomaterials. Satoshi Yasuda et al. [35] utilized chemical vapor deposition (CVD) to produce Fe-coordinated, N₂-rich nanographene (Fe-N-C) materials by adsorbing the pyrolysis products of Fe phthalocyanine (FePc) onto vertically-aligned carbon nanotubes (VA-CNTs). Through the direct combination of VA-CNTs and FePc, the authors obtained nanocatalysts with the active sites wrapped

within the carbon nanotube structure (Figure 6). The as-prepared samples displayed an outstanding ORR efficiency, providing onset potential (E_{onset}) and $E_{1/2}$ values equal to 0.97 V and 0.79 V (vs. RHE) in an O₂-saturated 0.5 M sulfuric acid, respectively.

Jiang et al. [36] developed a microporous M/N-MCN@CNT catalyst using CVD by pyrolyzing melamine. The resulting samples had a hierarchically porous structure with a large SA (519 m²/g), good electrical conductivity, low charge transfer resistance, and strong ORR activity. Similarly, Ximing Qu [37] deposited FeCl₂ into the pores of mesoporous Fe-N-C composite, creating numerous single-atom Fe-N_x active centers on the surface of the electrocatalyst (see Figure 7). This led to excellent ORR efficiency and stability at low pH, achieving $E_{1/2}$ and J_K values equal to 0.84 V and 31.02 mA/cm² at a potential of 0.8 V, respectively. This performance matched the highest-performing Fe-N-C and commercial Pt/C catalysts (refer to Figure 8).

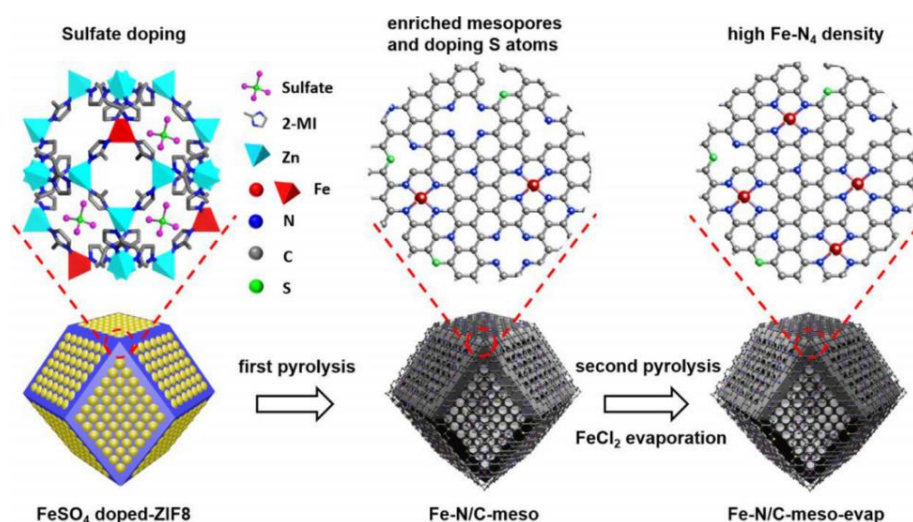


Figure 7. Synthesis scheme for preparing the Fe-N/C-meso-evap composite [37].

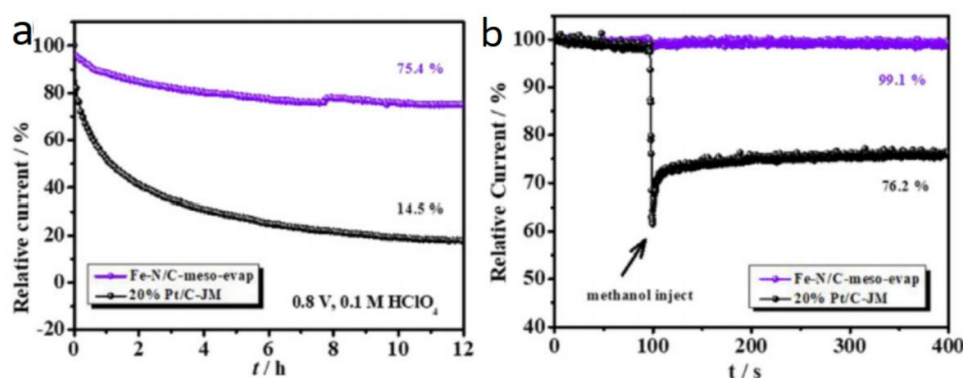


Figure 8. (a) Chronoamperometric tests of 20% Pt/C-JM and developed Fe-N-C catalyst (0.80 V vs. RHE, rotation speed: 200 rpm); (b) methanol resistance test of 20% Pt/C-JM and new Fe-N-C composite [37].

In addition to the CVD methods mentioned before, careful selection and regulation of reaction precursors is another effective approach to produce M-N-C materials with excellent ORR properties. Xinfu He et al. [38] developed high-performance F-N/FeCoNC₉₀₀ catalysts by co-doping N, F, and Fe atoms onto zeolitic imidazolate framework ZIF-67 without using any noble metals. The resulting materials achieved an optimal balance of specific SA, porosity, graphitization degree, and active site content. The catalysts demonstrated outstanding ORR performance, with a high E_{onset} equal to 0.97 V, an $E_{1/2}$ equal to 0.87 V, and a limiting current density (J_L) equal to 5.7 mA/cm², exceeding the performance of reference Pt/C catalysts (0.95 V, 0.85 V, and 5.3 mA/cm², respectively) (Figure 9). Additionally, the catalyst exhibited

favorable reversibility in electrocatalytic O₂ reactions ($\Delta E = 0.63$ V).

Qu Xi-Ming and colleagues [39] developed Co-N-C composites by carefully adjusting the relative amounts of reactants in MOF matrix. The resulting catalysts featured a combination of highly ordered graphitic CNTs and densely anchored Co-N₄ active centers. This unique structure gave the Co-N-C-1/4.4 catalyst (Figure 10) remarkable ORR activity ($E_{1/2} = 0.781$ V, $J_K @ 0.80$ V = 2.25 mA/cm²) and good stability, with only a 10 mV decay of $E_{1/2}$ after 30,000 repeated runs. Moreover, Co-N-C-1/4.4 delivered an ultra-high maximum power density (P_{max}) equal to 0.49 W cm⁻² in a hydrogen-air environment at 1 bar when employed as a cathode material in a fuel cell (Figure 11).

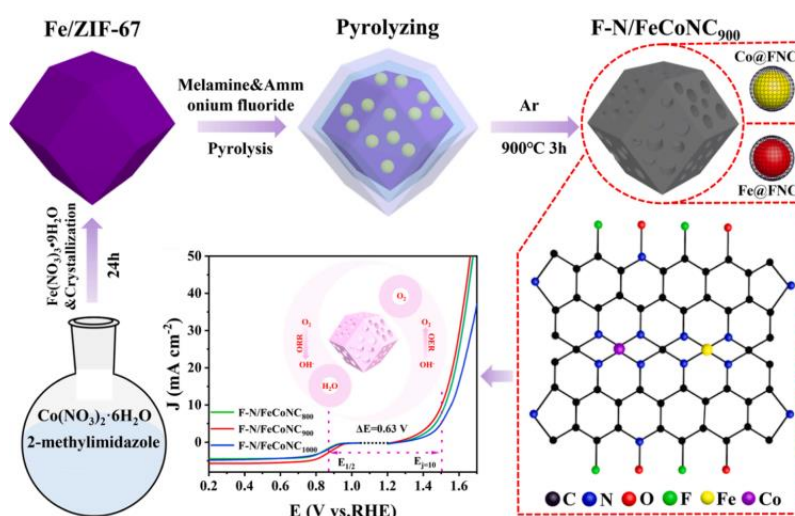


Figure 9. Schematic diagram of the F-N/FeCoNC900 preparation. [38].

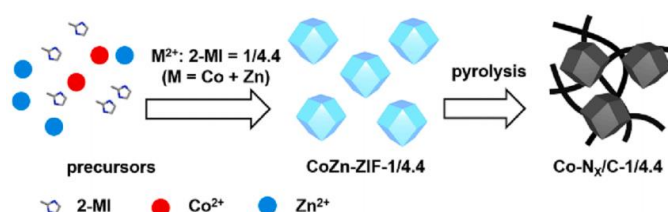


Figure 10. Synthesis scheme leading to Co-N-C-1/4.4 composite [39].

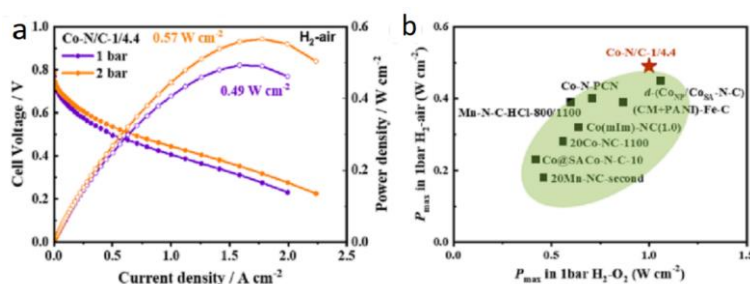


Figure 11. (a) The efficiency of Co-N-C-1/4.4 catalyst, and (b) The comparison of the P_{max} of this catalyst with other, structurally similar M-N-C composites applied in PEMFCs [39].

4. M-N-C ORR Catalysts

The earliest understanding of transition M-N-C composites dates back to 1964 when, in a study by Jasinski et al. [40], it was found that Co phthalocyanine exhibits some ORR activity. Since then, researchers have discovered that the heat treatment of various coordination compounds with different central metal ions, such as Mn, Ni, Co, and Fe in a complex with macrocyclic organic ligands, is an effective approach for enhancing the catalytic efficiency and robustness of these composites [41-43]. Among the wide variety of M-N-C electrocatalysts studied for ORR, Co-N-C and Fe-N-C are the most popular and have proven to be the most effective. Co-N-C and Fe-N-C reduce O_2 into H_2O through a four-electron mechanism and are considered a promising replacement for noble metal catalysts in PEMFCs.

4.1. Fe-N-C ORR Catalysts

In the past few years, numerous Fe-N-C composites have been developed, with some performing similarly to commercial 20 wt% Pt/C. Due to their excellent catalytic properties, Fe-N-C catalysts hold promise as potential replacements for noble metal catalysts in ORR applications. A highly active Fe-N-C composite was prepared in a study by Ren et al. [30] using adenosine as the source of nitrogen atoms. The solvothermal process induced the polymerization of this precursor, and the final catalyst was obtained by complete carbonization via pyrolysis. The synthesized Fe-N-C nanotubes displayed a high content of surface nitrogen atoms (8% of N relative to C), along with the excellent dispersion of active sites on the nanotube walls. Further experiments revealed that the Fe-N₄ clusters are the catalytic sites for ORR. The catalyst demonstrated ORR activity that matched reference Pt catalyst, along with superior stability in alkaline solutions (Figure 12).

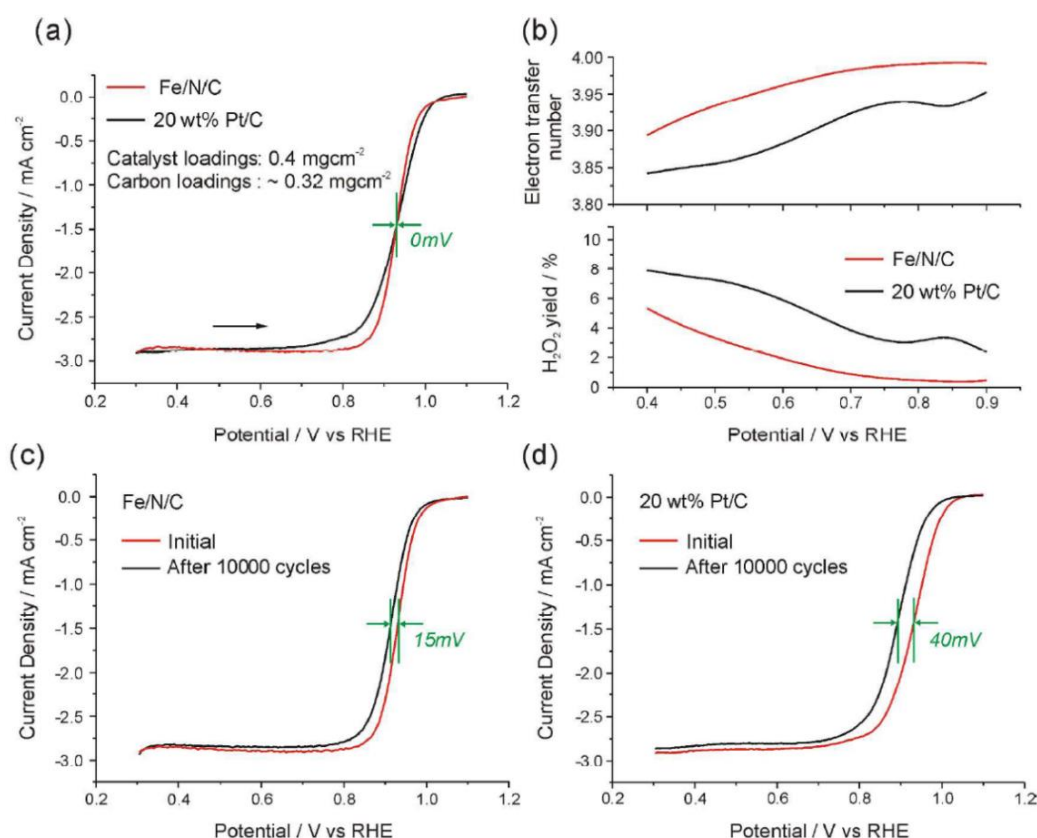


Figure 12. The electrocatalytic efficiency of the Fe-N-C composite in alkaline solutions and comparison with the reference Pt/C catalyst. [30].

An Fe-N-C catalyst was developed by Wang et al. [44], which comprised uniformly distributed Fe and N sites bonded to the ultrathin 2D graphene layer, as illustrated in Figure 13. During the pyrolysis process, adding a water-soluble surfactant, F127, restrained the agglomeration of iron nanoparticles while accelerating the generation of Fe-N_x active centers. The

ultrathin 2D structure allowed better exposure of the Fe-N_x active sites, maximizing their catalytic potential. Due to the well-dispersed Fe-N_x species and the ultrathin nanostructure, the F127-assisted Fe-N-C catalyst displayed enhanced ORR activity in alkaline media, with a 4-electron transfer pathway and an $E_{1/2}$ value equal to 0.85 V, which is 0.04 V above that

of 20 wt% Pt/C (Figure 14).

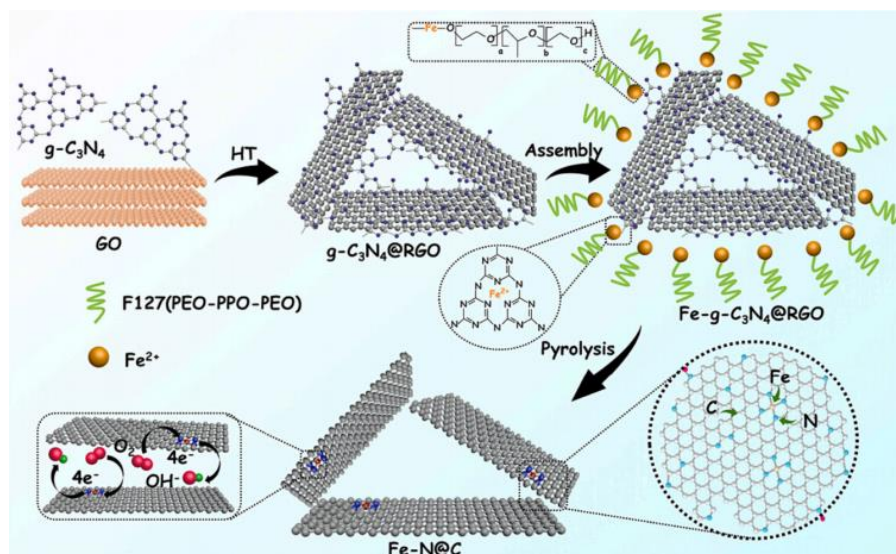


Figure 13. Illustration of the preparation and ORR catalytic mechanism of the Fe-N-C composite. [44].

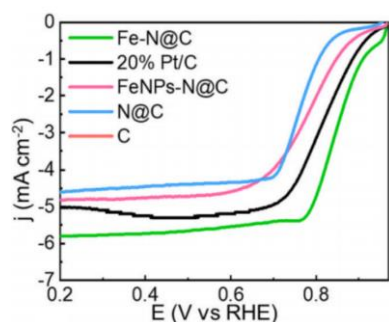


Figure 14. LSV profiles of the selected materials, and the comparison of their electrocatalytic activities in alkaline solution with the 20 wt% Pt/C. [44].

A high-porosity Fe-N-C catalyst material was synthesized by Patrick Teppor et al. [45] using hydroxyapatite (HA) as a solid template to introduce essential meso- and microporous structures (10-3000 nm). By conducting the pyrolysis at 1000°C and incorporating HA along with ZnCl₂ as a micropore-forming agent, the researchers were able to facilitate the generation of active centers. The prepared catalyst exhibited excellent ORR efficiency, achieving an $E_{1/2}$ value equal to 0.87 V. In AEMFC tests, the HA-templated catalyst performed comparably to the commercial Fe-N-C catalysts, achieving a $P_{\max}$ value equal to 1.06 W/cm² (Figure 15).

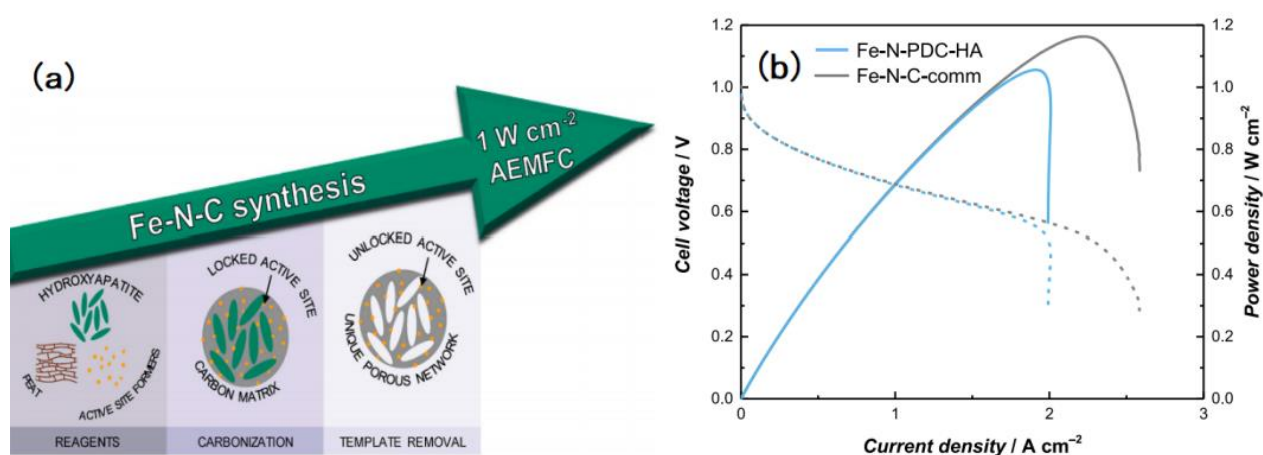


Figure 15. Illustration of the Fe-N-C electrocatalyst preparation (a) and single-cell performance in AEMFC test (b)[45].

4.2. Co-N-C ORR Catalysts

In addition to the Fe-N-C catalysts, Co-N-C composites have recently gained considerable popularity as another important type of M-N-C catalyst for ORR. Liu et al. [46] synthesized a 3D porous, nanostructure material using Co nanoparticles (NPs) embedded within nitrogen-modified macroporous carbon (Co/N-MC) through a two-step process involving precursor preparation followed by calcination. The resulting material demonstrated excellent ORR activity, thanks to its unique porosity, high amount of N atoms, and

uniform distribution of Co NPs.

Xiaochang Qiao [47] introduced an affordable and eco-friendly method to prepare Co and N co-modified graphene-CNT aerogel (Co-N-GCA) as an ORR electrocatalyst. The prepared catalyst featured a hierarchical meso- and macropores (Figure 16) with numerous active sites, promoting electron transfer and oxygen molecule diffusion. In terms of ORR activity, this catalyst outperformed 20 wt.% Pt/C catalyst in an alkaline media, showing a more positive E_{onset} and a higher J_L value. Moreover, the catalyst demonstrated outstanding stability.

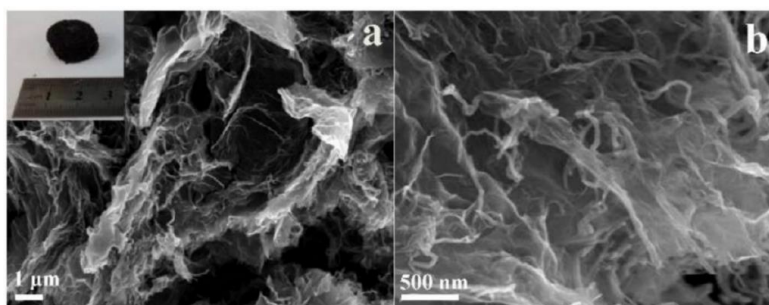


Figure 16. (a, b) The obtained SEM images for Co-N-GCA, with a macroscopic image of the synthesized aerogel given as inset in (a). [47].

Similar to the synthesis method described in [46], Yanghua He [48] reported a surfactant-aided MOF method to form a novel type of well distributed Co-N-C@F127 catalyst with a core shell morphology. This method allowed confined and more effective pyrolysis, leading to controllable synthesis of higher number of Co-N₄ sites uniformly dispersed on MOF support material. The developed Co-N-C@F127 catalyst

displayed improved ORR activity even at low pH, with an $E_{1/2}$ value equal to 0.84 V (vs. RHE). DFT calculations revealed that the CoN₂₊₂ sites favor the 4-electron mechanism of ORR. Using the developed catalyst as the cathode in PEMFCs, the authors found that the device exhibits an excellent early-stage performance yielding a P_{max} of 0.87 W/cm² combined with good durability (Figure 17).

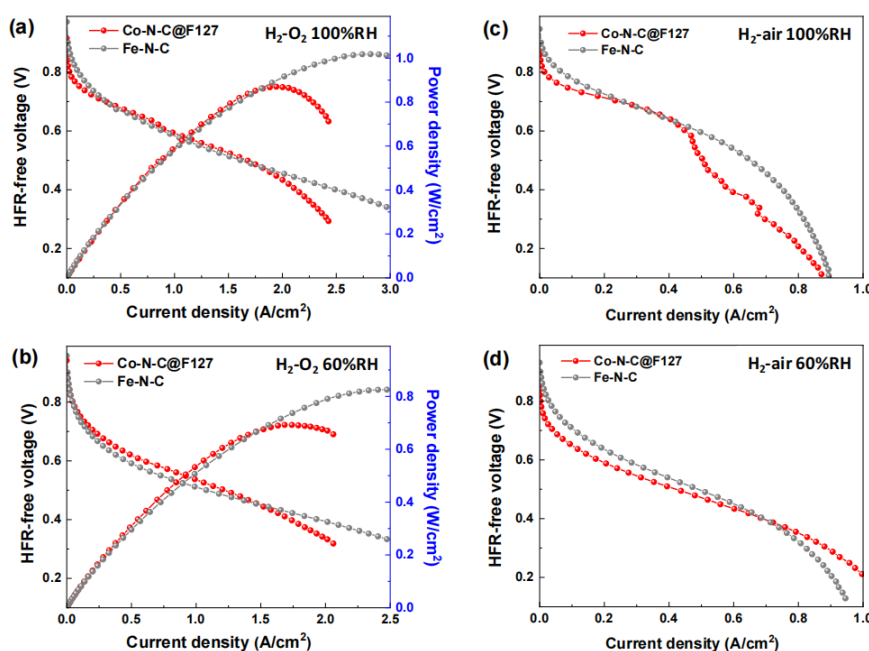


Figure 17. A comparison of the fuel cell parameters of the Co-N-C@F127 and Fe-N-C composites in the durability experiments. [48].

A high-efficiency Co-N-C composite was developed by Ruixiang Wang et al. [49] through pyrolysis of Co-modified ZIF-8 particles in a one-step process. These particles were in-situ synthesized on KJ600 carbon black with high surface area (SA). The porosity and large SA of KJ600 aided the spatial separation of ZIF-8 particles, which minimized their

agglomeration during pyrolysis. This contributed to the development of large number of active sites with Co-N coordinative bonds. In $\text{H}_2\text{-O}_2$ PEMFC tests that utilized CoNC@KJ600 as the cathode, a significant $P_{\max}$ 0.92 W/cm^2 was obtained, which matches that of reference Fe-N-C materials (Figure 18).

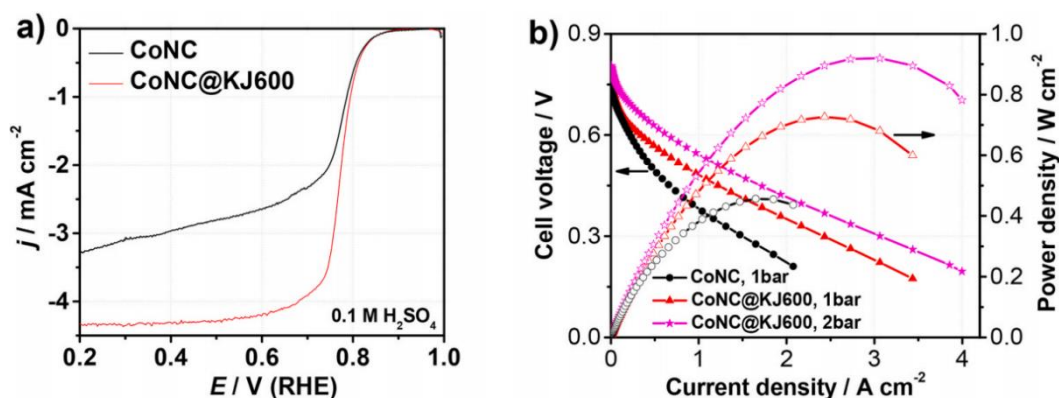


Figure 18. (a) ORR polarization plots for Co-NC and CoNC@KJ600 materials. (b) Cell performance of $\text{H}_2\text{-O}_2$ PEMFCs utilizing two cobalt-based catalysts. [49].

Lin Zhang [50] reported a novel method to prepare Co-NC catalysts starting from metal-containing cellulosic PILs, yielding materials with a low coordination number of metal ions in the active site and abundant pores with various sizes. Among several prepared materials, Co-N-C-850 displayed the highest E_{onset} value, equal to 0.827 V, and an $E_{1/2}$ value equal to 0.74 V for ORR in an alkaline solution, which was similar to 20 wt% Pt/C (0.833 V and 0.71 V, respectively). Four electrons participated in the ORR mechanism, resulting in low H_2O_2 yield along with long-term stability.

Using solvent effect modulation, Lingfeng Li et al. [51] obtained a Co-N-C composite with a high abundance of pyr-

ridinic N atoms (43.7% N_{py}) and a large number of active sites accessible for ORR. Thanks to the synergism between the N_{py} and well-defined Co-N_x sites, the best-performing Co-N-C catalyst showed superior ORR efficiency, with E_{onset} and $E_{1/2}$ values equaling 0.915 V and 0.785 V in acidic environments, respectively. These values are comparable to the highest-performing PGM-free catalysts reported so far. DFT calculations further confirmed that the interaction between the N_{py} and Co-N_x optimized the ORR activity (Figure 19). Although significant advancements have been achieved in M-N-C ORR catalysis, additional studies are necessary to obtain electrocatalysts with improved performance.

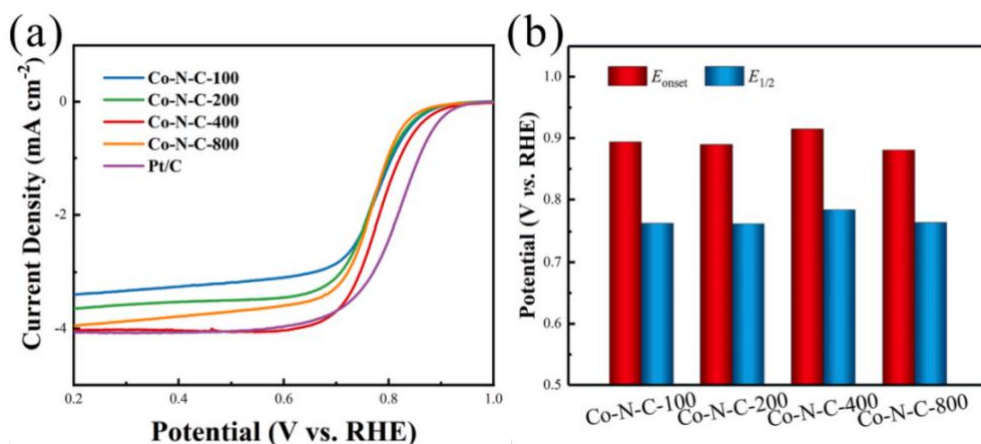


Figure 19. (a) ORR polarization plots at a rotation rate equal to 900 rpm. (b) The obtained E_{onset} and $E_{1/2}$ values for various Co-N-C catalysts [51].

4.3. FeCo-N-C ORR Catalysts

The development of porous, N-doped catalysts based on two metal ions is a feasible approach for improving the ORR efficiency of the M-N-C composites. For instance, Xiang et al. [52] synthesized a novel class of bimetal-, N-co-modified mesoporous carbon composites (FeCo-N-C-800) prepared via a facile hydrothermal procedure, as illustrated in Figure 20. The resulting electrocatalyst exhibited a remarkable ORR

activity comparable to Pt/C, with a positive E_{onset} (0.94 V), $E_{1/2}$ equal to 0.85 V (measured against RHE), and a high J_L value equal to 5.94 mA/cm² at high pH. Moreover, the developed catalysts exhibited remarkable resistance and stability to methanol. This excellent ORR activity was ascribed to the mesoporous structure, synergism of various active centers, appropriate nitrogen doping, and a high electrical conductivity of base material.

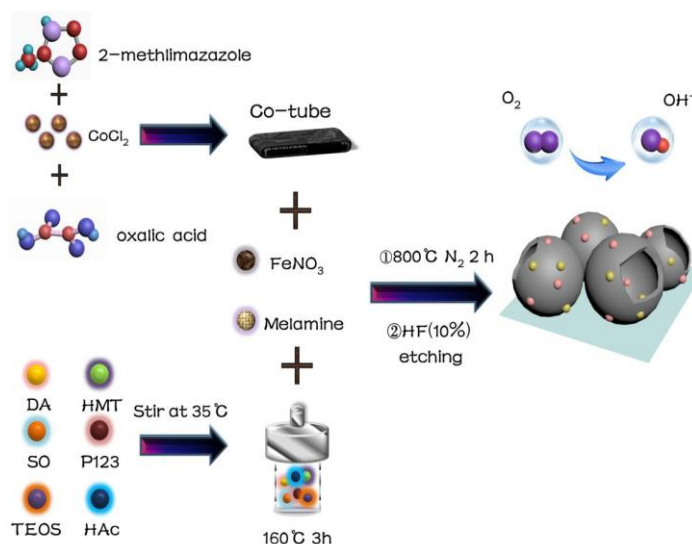


Figure 20. Illustration of the synthesis scheme for FeCo-N/C-800 catalyst. [52].

Silver Juvenen et al. [53] developed a novel FeCo-N-C composite through a straightforward single-step pyrolysis. In this study, rapeseed press cake was used as the organic precursor, Co and Fe salts served as the metal sources, and dicyandiamide provided nitrogen atoms. Following acid treatment, the resulting bimetallic Fe-Co catalyst (FeCoNCR-a) displayed a high E_{onset} value equal to 0.95 V and an $E_{1/2}$ value equal to 0.81 V in ORR tests conducted in 0.1 M potassium hydroxide. These values match those of reference Pt/C (E_{onset} = 0.97 V, $E_{1/2}$ = 0.83 V). Moreover, when used as the cathode in AEMFC, the bimetallic catalyst achieved a P_{max} of 131 mW/cm², demonstrating moderate performance.

5. Methods for Improving Catalytic Activity of M-N-C (M = Mn, Co, Fe)

In recent years, a wide variety of M-N-C materials have been reported, with much of the research focusing on understanding the active sites and optimizing nanostructures. In these materials, metal-nitrogen (M-N_x) sites within the carbon matrix are believed to be the most crucial for catalyzing the ORR [54-57]. The most recently developed M-N-C catalysts feature high SA and porosity, hierarchical pore structures, densely packed active sites, and high intrinsic activity.

For example, Fu and co-workers [58] introduced a technique for creating a Fe-N-C composite with a high density of active sites and well-developed micro/mesoporous structures by using NH₄Cl as a porogen. According to DFT calculations, the pore edges enhance the intrinsic activity of Fe-N₄ configuration. With its large number of active centers and extensive mesopores, this catalyst demonstrated remarkable ORR efficiency in PEMFC, providing a P_{max} value equal to 0.43 W/cm² under H₂-air conditions. The authors presented a new strategy to boost ORR activity by manipulating the edges of Fe-N₄ clusters.

More recently, a Fe-N-C catalyst was developed in a study by Sun et al. [59] using a carboxylate-assisted method and a ZIF-8 precursor. The resulting catalyst showed a large concentration of available active sites, entangled carbon nanotubes (CNTs), and improved mesoporosity. In PEMFC tests, the optimized Fe-N-C material achieved a P_{max} of 1.33 W/cm² under H₂-O₂ conditions (Figure 21). This high performance was attributed to three key factors: first, the large number of accessible active centers increased the kinetic activity; second, the entangled CNTs improved electron transport, reducing internal resistance; and third, the high mesoporosity enhanced mass transfer while reducing the catalyst loading. This strategy holds promise for developing

high-efficiency, cost-effective M-N-C catalysts, particularly those based on MOFs.

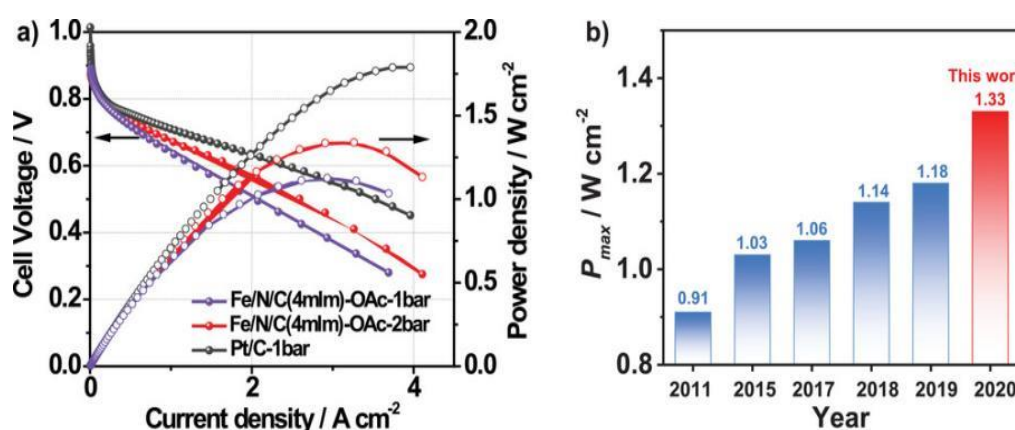


Figure 21. a) The results of the H₂-O₂ PEMFC assay for the newly developed Fe/N/C (4mlm)-OAc and a reference Pt/C catalyst. b) Recent advances in P_{max} of H₂ - O₂ PEMFCs comprising Fe-N-C composite as a cathode material. [59].

Im et al. [60] developed a Co single-atom catalyst (ma-Co-NC) starting from a melamine-coated Co-ZnO-C matrix and ZIF-8 template. The resulting catalyst featured both micro- and mesoporous elements, as well as a hollow structure (Figure 22). During high-temperature treatment, melamine had multiple roles: it acted as a porogen, the source of C and N atoms, and it also prevented agglomeration of Co atoms. Additionally, Density Functional Theory (DFT) calculations in-

dicated the preferred coordination of oxygen species in axial position Co-N₄ active sites, which favor the four-electron ORR mechanism in ma-Co-NC. As a result, PEMFCs with the ma-Co-NC catalyst displayed excellent durability, with only a 6.7% decrease in performance after 100 hours (Figure 23). The maximum power density achieved was 723 mW/cm² at a under back-pressure of 1 bar. This study is expected to contribute to the advancements of next-generation fuel cells.

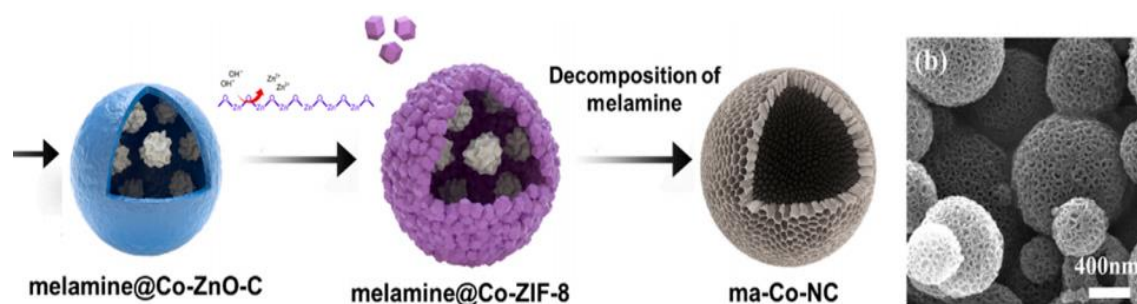


Figure 22. (a) The synthesis scheme of ma-Co-NC composites; (b) SEM images of the obtained catalyst [60].

Feng Sun and colleagues [61] developed Fe-N-C composites with a high specific SA (1444.4 m²g⁻¹) using NaCl as a pore-forming agent and combining mechanochemical synthesis with high-temperature pyrolysis. The optimized 2% Fe-ZIF@NaCl electrocatalyst exhibited a uniform dispersion of metal atoms, resulting in superior ORR activity in both RDE and PEMFC experiments. Specifically, the catalyst achieved an $E_{1/2}$ value equal to 0.831 V at a low pH and a P_{max} value equal to 0.504 W/cm² in H₂-O₂ PEMFCs. The ORR and BET analyses indicated that increasing the mesopores significantly enhanced electrocatalytic performance.

Inspired by the structure of jellyfish tentacles, Guolong Lu et al. [62] introduced a novel synthesis method to produce

high-efficiency Fe-N-C electrocatalysts with a layered, porous, and hairy morphology, providing abundant Fe-N_x active sites. Thanks to its hierarchical bio-inspired structure, along with a high specific SA of 737.6 m²g⁻¹ and numerous accessible Fe-N_x sites, the Fe-N_x/HC@NWs catalyst exhibited remarkable ORR efficiency with E_{onset} and $E_{1/2}$ values equal to 1.009 V and 0.868 V in O₂-saturated 0.1 M KOH, respectively. The catalyst also showed excellent long-term stability, with only an 8.74% loss in dynamic current intensity after 50,000 s of continuous operation compared to a 22.09% loss for commercial Pt/C. Overall, this catalyst shows similar performance to that of Pt-based catalysts supported on carbon.

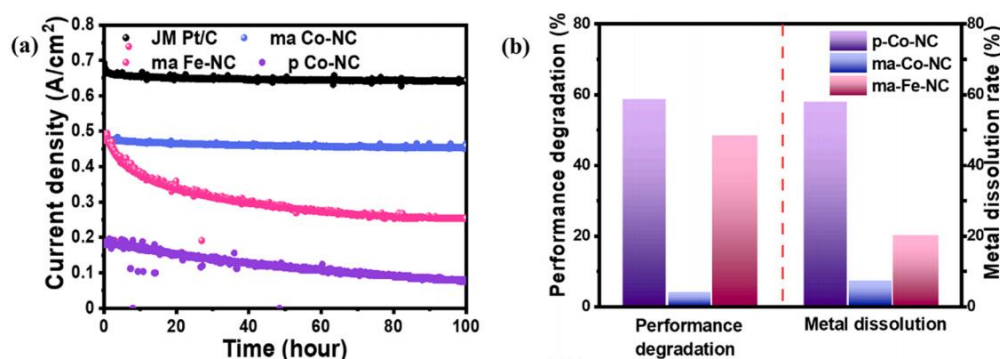


Figure 23. (a) The results of the durability test of a single cell operating at 0.7 V over 100 hours for the ma-Co-NC composite, and comparison with the reference Pt/C catalyst. (b) Performance drop and metal dissolution rates for p-Co-NC, ma-Co-NC, and ma-Fe-NC before and after the stability test. [60].

6. Conclusions

In summary, the synthesis and application of noble metal-free composites as alternatives to Pt-based catalysts for the ORR in PEMFCs offer significant potential. Despite the progress in M-N-C catalyst research, many challenges remain. Several key factors must be addressed to create efficient and robust electrocatalysts, including the morphology, atomic structure, reaction mechanisms, and active centers of the catalysts. Based on this review, we offer the following insights in the field of M-N-C catalysis. First, the active centers in M-N-C composites need to be more clearly identified and better understood. Second, advanced characterization techniques and standard models should be used to explore the correlation between catalyst structure and performance, as well as to study ORR mechanisms. Third, the design of M-N-C catalysts should follow well-established principles, focusing on optimizing catalyst structure and selecting appropriate reaction conditions to improve ORR performance. These approaches will help drive the development of effective and stable ORR electrocatalysts for fuel cells. Future research should center on optimizing synthesis processes and innovating catalyst structural design to enhance catalytic performance and stability.

Abbreviations

M-N-C	Metal–nitrogen–carbon
ORR	Oxygen Reduction Reaction
PEMFCs	Proton Exchange Membrane Fuel Cells
APEFCs	Alkaline Polymer Electrolyte Fuel Cells
CNF	Carbon Nanofiber
CVD	Chemical Vapor Deposition
ZIF	Zeolitic Imidazolate Framework
HA	Hydroxyapatite
NPs	Nanoparticles
DFT	Density Functional Theory

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Author Contributions

Bingxue Hou: Writing – original draft, Writing – review & editing

Rui Tang: manuscript correction

Conflicts of Interest

The authors declare no conflicts of interest.

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