Review Article

Fe-N-C Catalysts for Proton Exchange Membrane Fuel Cells: Advances from Synthesis to Practical Applications

.

ABSTRACT

|  |
| --- |
| Proton exchange membrane fuel cells (PEMFCs) represent a cornerstone technology for sustainable energy conversion, yet their widespread deployment remains constrained by reliance on platinum-group-metal (PGM) catalysts. This comprehensive review critically examines the development of iron-nitrogen-carbon (Fe–N–C) catalysts as a viable PGM-free alternative, addressing key challenges from atomic-scale active site engineering to full-cell integration. We present a systematic analysis of synthetic methodologies including pyrolysis, sacrificial templating, and MOF-derived approaches that enable precise control over Fe–N₄ moiety density and accessibility. Advanced characterization techniques, such as operando X-ray absorption spectroscopy and electron microscopy, reveal fundamental structure–activity–stability relationships governing oxygen reduction reaction (ORR) kinetics in acidic media. While the catalytic activity of the state-of-the-art Fe–N–C catalysts approaches promising half-wave potentials (E₁/₂ > 0.9 V vs. RHE) under specific conditions, these values can significantly vary with synthetic, testing procedures and electrode configuration. Their translation to practical membrane electrode assemblies (MEAs) necessitates innovative solutions to address durability limitations (<500 h operational stability) and mass transport constraints in thick catalyst layers (>50 μm). We further discuss emerging strategies in electrode architecture design, ionomer–catalyst interactions, and accelerated stress testing protocols. By bridging fundamental insights with engineering considerations, this review provides a roadmap for advancing Fe–N–C catalysts toward commercial viability in next-generation PEMFC systems. |

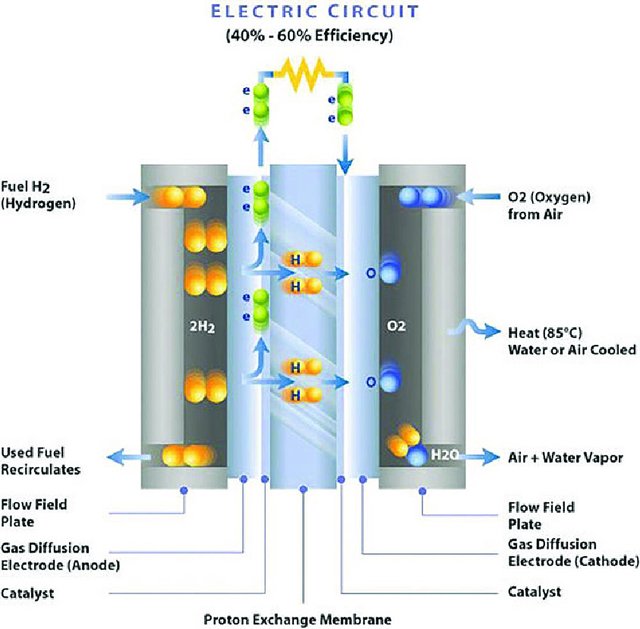
*Keywords: Proton exchange membrane fuel cells (PEMFCs), Fe-N-C catalysts, Oxygen reduction reaction (ORR), PGM-free electrocatalysts, Membrane electrode assembly (MEA), Durability and degradation*

1. INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) are among the most promising clean energy technologies due to their high-power density, rapid start-up, and low operating temperatures (Maximum 80 °C) [1]. These attributes make them especially suitable for transportation, portable, and residential energy applications [2,3]. Central to the operation of PEMFCs is the oxygen reduction reaction (ORR) at the cathode, a process known to be sluggish and kinetically limited, requiring the use of highly active catalysts to achieve practical performance levels [4,5]. Figure 1 clearly illustrate the basic structure of a PEM fuel cell [6].

Platinum-based catalysts have long been the benchmark for ORR due to their superior activity and stability. However, their high cost, scarcity, and susceptibility to poisoning and degradation under fuel cell operating conditions have significantly hampered the widespread commercialization of PEMFCs [7,8]. This economic and material bottleneck has motivated the scientific community to explore platinum-group-metal-free (PGM-free) catalysts as a cost-effective and sustainable alternative [9].

**Fig. 1. Schematic of a PEM Fuel Cell** [6]



**1.1 Emergence of Fe-N-C Catalysts**

Among the various classes of PGM-free catalysts investigated, iron–nitrogen–carbon (Fe-N-C) catalysts have emerged as the most promising candidates for the cathodic ORR in acidic environments [10]. The activity of Fe-N-C materials, particularly those containing atomically dispersed Fe sites coordinated by nitrogen (e.g., Fe–N₄ moieties), has reached performance levels that begin to rival those of commercial Pt/C catalysts [11,12].

The synthesis of Fe-N-C catalysts typically involves the pyrolysis of precursors containing iron, nitrogen, and carbon—often including metal-organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs), or polymeric templates. The result is a porous carbon matrix with active Fe–Nₓ moieties embedded within, which are now understood to be the primary sites responsible for ORR activity [13,14].

**1.2 Scientific and Technological Significance**

The use of Fe-N-C catalysts addresses multiple critical challenges in fuel cell technology:

• Cost Reduction: Iron and nitrogen are earth-abundant and inexpensive, offering an immediate solution to the high cost associated with platinum [15,16].

• Scalability: The synthetic routes for Fe-N-C catalysts are compatible with scalable manufacturing processes, such as spray pyrolysis, inkjet printing, and roll-to-roll methods [17,18].

• Environmental Sustainability: Eliminating Pt mining and refining reduces the environmental footprint of fuel cell production, aligning with global sustainability goals [19,20].

• Electrochemical Performance: Recent breakthroughs have shown Fe-N-C catalysts achieving half-wave potentials above 0.9 V vs. RHE and high kinetic current densities, particularly when optimized for porosity and Fe–Nₓ site density [21,22].

Despite these advantages, challenges remain. The durability of Fe-N-C materials under PEMFC operating conditions is still inferior to Pt-based catalysts, largely due to demetallation, carbon corrosion, and protonation of active sites. Furthermore, issues such as the formation of hydrogen peroxide intermediates and their role in catalyst degradation require deeper understanding [23,24].

**1.3 Current Research Motivation**

Given the growing demand for sustainable and affordable energy technologies, further research into Fe-N-C catalysts is not only warranted but essential. The specific motivations for advancing Fe-N-C catalysts in PEMFCs include:

• Active Site Elucidation: Although Fe–N₄ moieties are widely accepted as the dominant active sites, the exact structure–activity relationship remains elusive. Advanced characterization methods (e.g., Mössbauer spectroscopy, X-ray absorption spectroscopy, and DFT calculations) are needed to gain atomic-level insights [25].

• Durability Enhancement: Strategies such as heteroatom doping (e.g., S, P, or B), encapsulation of Fe sites within graphene layers, or alloying with other transition metals (e.g., Co, Mn) are being pursued to enhance long-term stability [22].

• Integration into Membrane Electrode Assemblies (MEAs): Translating lab-scale Fe-N-C performance into practical fuel cell devices requires optimization of ionomer interactions, catalyst layer structure, and electrode engineering [17,26,27].

• Understanding Degradation Mechanisms: A detailed understanding of the degradation pathways under realistic fuel cell conditions (humidity, cycling, contaminants) will enable the design of more robust catalyst systems [28].

The successful development and deployment of Fe-N-C catalysts could revolutionize the PEMFC landscape, making clean hydrogen-powered energy more accessible and economically viable. This would be a transformative step toward decarbonizing transportation and other sectors reliant on fossil fuels. Moreover, it aligns with the strategic energy policies of many countries that aim to reduce dependence on critical raw materials and promote circular economy principles [29–31].

2. Synthetic Approaches of Fe-N-C Catalysts

The catalytic activity of Fe–N–C materials is largely governed by the nature, density, and accessibility of the Fe–Nx moieties embedded within a conductive carbon matrix. Thus, the synthesis strategy plays a pivotal role in defining the structural, electronic, and catalytic characteristics of the Fe–N–C catalysts. A wide variety of synthetic approaches have been explored to optimize these parameters [32].

The synthesis of Fe–N–C catalysts typically involves three primary components:

• A metal precursor (e.g., FeCl₃, Fe acetate, Fe porphyrins)

• A nitrogen source (e.g., melamine, urea, polyaniline)

• A carbon source (e.g., ZIF-8, carbon black, graphene oxide)

These components are subjected to a thermal treatment (pyrolysis) under an inert atmosphere (N₂ or Ar), which facilitates the formation of Fe–Nx active sites within a conductive carbon matrix [33].

**2.1. One-Pot Pyrolysis Method**

It is a streamlined synthesis technique where all precursor components iron source, nitrogen-containing ligands or polymers, and carbon sources are mixed and subjected to a single pyrolysis step under an inert atmosphere (e.g., N₂ or Ar). This approach simplifies fabrication, improves uniformity of Fe–Nₓ active sites, and can enhance catalyst performance and scalability [34].

In a typical one-pot pyrolysis synthesis, an iron precursor, a nitrogen-rich organic compound, and a carbon source are thoroughly mixed in a solvent to form a homogeneous slurry. This mixture is then dried and pyrolyzed at 900 °C for 1 hour under an inert nitrogen atmosphere to simultaneously carbonize the precursor and generate atomically dispersed Fe–Nₓ active sites within the porous carbon matrix. Acid leaching is performed afterward to remove unstable iron particles and impurities, followed by a second heat treatment to stabilize the active sites. The resulting Fe–N–C catalyst exhibits a high Brunauer-Emmett-Teller (BET) surface area with a hierarchical porous structure favorable for mass transport. Electrochemical testing in acidic media shows a half-wave potential (E₁/₂) for oxygen reduction reaction (ORR) around 0.85–0.89 V vs. RHE, indicating excellent catalytic activity approaching that of commercial Pt/C catalysts [35].

**2.2. Two-Step Pyrolysis Method**

The Two-Step Pyrolysis method involves sequential thermal treatments to optimize the formation and stability of Fe–Nₓ active sites [36,37]:

• First pyrolysis: The precursor mixture containing Fe, N, and C sources is heated (typically 700–900 °C) under inert atmosphere. This step promotes carbonization and initial formation of Fe–Nₓ moieties.

• Acid leaching: The resulting material is treated with acid (e.g., HCl or H₂SO₄) to remove unstable iron species and metallic particles that could lower catalyst performance.

• Second pyrolysis: The acid-leached catalyst is reheated at similar or slightly higher temperatures (e.g., 900–1000 °C) to restore conductivity, increase graphitization, and stabilize Fe–Nₓ active sites.

This two-step process improves catalyst durability and enhances the density of active sites, resulting in superior ORR activity and fuel cell performance compared to single-step pyrolysis [38].

For example, Lingzheng Gu and his team A mixture of iron precursor (FeCl₃), nitrogen-rich organic compound (melamine), and carbon support (Ketjenblack) was first thoroughly mixed and subjected to pyrolysis at 900 °C for 1 hour under an argon atmosphere (first pyrolysis). The resulting material was then acid-leached in 0.5 M H₂SO₄ for 12 hours to remove unstable iron species and impurities. After washing and drying, the catalyst underwent a second pyrolysis at 950 °C for 1 hour under argon (second pyrolysis) to enhance graphitization and stabilize Fe–Nₓ active sites and the results as following [38]:

• Surface Area: BET surface area of ~850 m²/g with hierarchical micro- and mesopores beneficial for mass transport.

• ORR Activity: Half-wave potential (E₁/₂) in acidic electrolyte (0.1 M HClO₄) of approximately 0.88 V vs. RHE, close to commercial Pt/C catalysts (~0.90 V).

• Durability: Less than 10% loss in current density after 30,000 potential cycles, demonstrating improved stability over one-step pyrolysis catalysts.

• Fuel Cell Performance: When integrated into a membrane electrode assembly (MEA), the catalyst delivered a peak power density of ~650 mW/cm² at 80 °C and 100% RH.

**2.3. Sacrificial Support Method (SSM)**

SSM is a synthetic technique where a removable “sacrificial” template (usually silica nanoparticles) is mixed with Fe, N, and C precursors. After pyrolysis, the template is etched away (commonly with HF or NaOH), creating a porous carbon structure with well-dispersed Fe–Nₓ active sites ideal for oxygen reduction reaction (ORR) catalysis and this is the General Procedure [39,40]:

• Mixing: Fe precursor (e.g., FeCl₃), nitrogen-rich precursors (e.g., melamine or polyaniline), and a sacrificial support (typically silica nanoparticles or colloidal silica) are combined with a carbon source.

• Pyrolysis: The mixture is pyrolyzed under an inert atmosphere (N₂ or Ar) at high temperature (~900–1000 °C). This converts precursors into a carbon matrix with embedded Fe–Nₓ sites around the sacrificial template.

• Template Removal: The sacrificial support (silica) is removed by chemical etching, often using hydrofluoric acid (HF) or sodium hydroxide (NaOH), to create pores and expose active sites.

• Post-Treatment: Optional acid leaching to remove residual metal particles and improve catalyst purity.

the Sacrificial Support Method has gained prominence among Fe–N–C synthesis techniques, as it offers a number of compelling advantages [39–41]:

• Controlled Porosity and Surface Area: The use of a removable template (like silica nanoparticles) allows precise engineering of hierarchical pore structures (micro-, meso-, and macropores). This improves mass transport of reactants (O₂) and products (H₂O) within the catalyst layer, boosting overall fuel cell performance.

• Enhanced Active Site Exposure: By creating porous architectures, the SSM ensures better accessibility of Fe–Nₓ active sites to reactants, increasing the effective utilization of catalytic sites compared to dense or poorly porous catalysts.

• Improved Catalyst Stability: The porous carbon matrix formed through SSM helps stabilize Fe sites by preventing agglomeration and mitigating demetallation during operation, leading to longer catalyst lifetimes.

• Scalability and Versatility: SSM uses widely available sacrificial materials (silica, polymers) and straightforward removal processes (acid/base etching), making it compatible with large-scale manufacturing.

• Tailored Catalyst Morphology: Different templates can be used to tune pore size and distribution, enabling optimization of catalyst layers for specific applications (e.g., transport layers in PEM fuel cells).

3. Structural and Surface Characterization of Fe–N–C Catalysts

Understanding the structure and surface properties of Fe–N–C catalysts is essential to correlate synthesis conditions with catalytic performance in proton exchange membrane fuel cells (PEMFCs). Since the oxygen reduction reaction (ORR) occurs at atomically dispersed iron sites embedded in a nitrogen-doped carbon matrix, advanced characterization tools are critical for revealing the nature of these active sites, their distribution, and their stability.

**3.1. Textural and Porosity Analysis: N₂ Adsorption–Desorption Isotherms (BET)**

The Brunauer–Emmett–Teller (BET) technique is a widely used method for quantifying the specific surface area and porosity of catalysts, providing essential data for understanding the accessibility and density of active sites in Fe–N–C catalysts.

BET theory describes the physical adsorption of gas molecules (commonly nitrogen at 77 K) on a solid surface and is used to calculate the specific surface area (S\_BET) based on the adsorption isotherm. The method assumes multilayer adsorption and is particularly sensitive to surface features in the microporous and mesoporous range [42].

Fe–N–C catalysts typically exhibit high BET surface areas, ranging from 300 to over 1500 m²/g depending on synthesis conditions such as precursor choice, pyrolysis temperature, and templating methods [13]. While BET provides critical information about surface area and porosity, it does not directly identify chemical nature or electronic states of active sites. Therefore, BET is commonly combined with [42]:

• Electron microscopy (SEM/TEM).

• X-Ray Diffraction (XRD).

• X-ray photoelectron spectroscopy (XPS).

• X-ray absorption spectroscopy (XAS).

**3.2. Morphology and Porosity**

The morphology and porosity of Fe–N–C catalysts play a critical role in their electrocatalytic performance, particularly in the oxygen reduction reaction (ORR) under proton exchange membrane fuel cell (PEMFC) conditions. The surface area, pore structure, and distribution of active sites directly affect the mass transport, active site accessibility, and electrochemical utilization efficiency of Fe–Nx moieties [43].

**3.2.1. Scanning and Transmission Electron Microscopy (SEM)**

High-resolution imaging techniques such as Scanning Electron Microscopy (SEM) are pivotal tools for revealing the morphological characteristics and nano structural features of Fe–N–C catalysts. These techniques provide critical insights into the porosity, particle dispersion, graphitization, and Fe species location, which are directly correlated with electrocatalytic performance in proton exchange membrane fuel cells (PEMFCs).

SEM offers detailed surface topology information, highlighting the macro- and meso-structural organization of Fe–N–C catalysts. Most SEM micrographs of Fe–N–C materials reveal highly porous, sponge-like morphologies with irregular, interconnected carbon frameworks [43,44].

For instance, Fe–N–C materials synthesized using silica templates exhibit rod-like or spherical macroporous structures, mimicking the template morphology. After etching the silica (e.g., using HF or NaOH), the SEM images typically show well-developed open channels, indicating successful template removal and the presence of large meso/macropores beneficial for gas transport [44].

**3.2.2.** **X-Ray Diffraction (XRD)**

X-Ray Diffraction (XRD) is a fundamental analytical technique employed to elucidate the crystalline structure, phase composition, and crystallite size of Fe–N–C catalysts. XRD works by measuring the diffraction patterns of X-rays scattered by periodically arranged atoms within crystalline materials. The position, intensity, and shape of diffraction peaks provide insights into [45,46]:

• Phase identification: differentiating crystalline Fe phases (e.g., Fe, Fe₃C, Fe₂O₃) versus amorphous carbon.

• Crystallite size estimation: via peak broadening using the Scherrer equation.

• Degree of graphitization: assessment of carbon structural ordering.

**3.3. Surface Chemical Analysis**

**3.3.1. X-Ray Photoelectron Spectroscopy (XPS)**

X-ray Photoelectron Spectroscopy (XPS) is a surface-sensitive analytical technique (probing depth: 5–10 nm) that provides quantitative elemental composition and chemical state information by measuring the binding energies (BE) of core-level electrons [45]. For Fe–N–C catalysts, XPS is indispensable for:

• Identifying nitrogen doping configurations (pyridinic, graphitic, pyrrolic).

• Determining the oxidation state and coordination of Fe (Fe²⁺ vs. Fe³⁺, Fe–N₄ sites).

• Evaluating carbon matrix defects and functional groups that influence conductivity and stability.

**3.3.2. X-Ray Absorption Spectroscopy (XAS)**

XAS is a powerful, element-specific technique that provides detailed information on the oxidation state, coordination environment, and local atomic structure of Fe species in Fe–N–C catalysts. Unlike bulk techniques such as XRD, XAS is particularly suited to characterizing amorphous materials and atomically dispersed metal sites, making it indispensable for studying Fe–N₄ moieties that dominate activity in PGM-free electrocatalysts [47].

XAS includes two primary regions:

• X-ray Absorption Near Edge Structure (XANES): sensitive to the oxidation state and electronic structure of the absorbing atom. The position and shape of the absorption edge in the XANES region reflect the oxidation state of Fe species [48]:

- Atomically dispersed Fe in Fe–N₄ configurations generally exhibits edge energies between Fe(II) and Fe(III), indicating a mixed-valence state.

- The pre-edge feature (~7113 eV) arises from 1s → 3d transitions and is indicative of tetrahedral or square-planar coordination typical of FeN₄ sites.

• Extended X-ray Absorption Fine Structure (EXAFS): provides quantitative information about the local atomic environment—coordination number, bond lengths, and disorder. The EXAFS region yields structural information about Fe’s coordination [49]:

- Dominant Fe–N peak appears at ~1.5 Å (phase uncorrected), confirming Fe–N bonding.

- Lack of significant Fe–Fe or Fe–O peaks beyond 2.2 Å confirms atomic dispersion of Fe atoms and the absence of Fe nanoparticles or oxides.

- Quantitative EXAFS fitting yields; Fe–N bond distance: typically, ~1.95–2.05 Å and Coordination number (CN): close to 4, indicating FeN₄ configuration.

4. Electrocatalytic Performance Using Fe-N-C Catalyst in PEM Fuel Cells

The electrocatalytic activity of Fe-N-C catalysts for ORR is a complex interplay of active site density, site accessibility, intrinsic catalytic activity, and catalyst stability.

**4.1. ORR Mechanism on Fe–N–C Catalysts**

The ORR mechanism on Fe-N-C catalysts proceeds primarily through a four-electron (4e⁻) pathway, where Fe-N₄ sites facilitate O₂ adsorption and dissociation. Density functional theory (DFT) calculations suggest that the Fe²⁺/Fe³⁺ redox couple mediates electron transfer, reducing O₂ to H₂O with minimal peroxide (H₂O₂) formation [50].

Experimental studies using in situ X-ray absorption spectroscopy (XAS) confirm that Fe remains in a high-spin Fe²⁺ state during ORR, with axial ligand effects modulating reactivity [51]. Additionally, Mössbauer spectroscopy reveals that the most active Fe-N₄ sites exhibit a D4h symmetry, optimizing O₂ binding energy [48].

**4.2. Electrochemical Performance in Acidic Media**

Fe-N-C catalysts exhibit near-Pt ORR activity in acidic PEMFC environments, with half-wave potentials (E₁/₂) of 0.80–0.90 V vs. RHE in rotating disk electrode (RDE) tests. However, performance in membrane electrode assemblies (MEAs) is often lower due to mass transport limitations and ionomer poisoning [52].

Durability remains a challenge, with >30% activity loss after 30,000 potential cycles (0.6–1.0 V) due to Fe leaching and carbon corrosion. Advanced MOF-derived Fe-N-C catalysts (e.g., ZIF-8 precursors) improve stability by enhancing graphitization and active site retention [53].

**4.3. Kinetics and Reaction Pathways**

The ORR kinetics on Fe-N-C are governed by the rate-determining O-O bond cleavage, with DFT studies suggesting a bridging adsorption mode at Fe-N₄ sites. Microkinetic modeling indicates that the apparent activation energy (~0.4–0.5 eV) is comparable to Pt but suffers from stronger OH adsorption at high potentials [54].

pH-dependent studies reveal that Fe-N-C catalysts follow a 2×2e⁻ pathway in alkaline media but shift to a direct 4e⁻ mechanism in acidic PEMFC conditions. This transition is attributed to protonation effects on O₂ intermediates [55].

**4.4. Comparison to Platinum Catalysts**

Table 1. Summarizes the electrocatalytic performance parameters for platinum-based and Fe–N–C catalysts in proton exchange membrane fuel cells, including half-wave potential (E₁/₂), mass activity at 0.9 V vs RHE, peak power density under H₂/O₂ conditions, and durability metrics. Data are compiled from representative peer-reviewed studies to highlight the current state-of-the-art and ongoing improvements in PGM-free catalyst performance relative to commercial Pt/C benchmarks.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Table 1. Comparative Electrocatalytic Performance Metrics of Fe–N–C and Pt-Based Catalysts in PEM Fuel Cells** | | | | | |
| **Catalyst** | **ORR Activity (E₁/₂)** | **Mass Activity at 0.9 V (A/g)** | **Peak Power (mW/cm², H₂/O₂)** | **Durability  (50h @ 0.6 V)** | **Ref.** |
| Pt/C (20 wt%) | ~0.93 | >100 | >1000 | >95% retention | [56] |
| Fe–N–C (ZIF-8) | 0.90–0.92 | 35–45 | 750–850 | ~70–80% retention | [57] |
| Fe–N–C (graphitized) | ~0.89 | ~38 | ~700 | Enhanced by graphitization | [58] |

5. Integration of Fe-N-C Catalysts into PEM Fuel Cell Devices

While Fe-N-C catalysts exhibit promising intrinsic electrocatalytic activity for the oxygen reduction reaction (ORR) in acidic media, their successful integration into practical proton exchange membrane fuel cells (PEMFCs) involves addressing multiple engineering and materials challenges. This section discusses key considerations and recent advances in the fabrication and optimization of membrane electrode assemblies (MEAs) incorporating Fe-N-C catalysts.

**5.1. Catalyst Layer Fabrication and Electrode Architecture**

The catalyst layer serves as the functional interface where the oxygen reduction reaction (ORR) occurs, and where electron, proton, and mass transport must be simultaneously optimized. In Fe–N–C-based PEMFCs, the architecture of the CL must compensate for [49]:

• The relatively low intrinsic activity per site compared to Pt.

• Nonuniform distribution of Fe–N₄ active sites

• Low electrical conductivity and gas diffusion limitations, especially in thick layers

A well-designed CL enhances active site utilization, improves mass transport, and promotes water removal, which are essential for achieving high current densities.

**5.2. Electrode Ink Formulation**

The formulation of a stable and homogeneous catalyst ink represents a critical initial step in the fabrication of catalyst layers (CLs) for proton exchange membrane fuel cells (PEMFCs). A typical ink composition includes:

• Fe–N–C catalyst powder (as the electrocatalytically active component)

• Ionomer solution (commonly Nafion or alternative hydrocarbon-based ionomers, serving as the proton-conducting medium)

• Solvent system, typically a mixture of water and lower alcohols (e.g., isopropanol), to facilitate uniform dispersion and proper rheological behavior

• Optional additives, such as dispersing agents or binders, to enhance colloidal stability and film-forming properties

The proportion and distribution of the ionomer within the ink are especially critical to achieving high-performance CLs. Excessive ionomer content may lead to the blockage of active Fe–Nₓ sites and hinder gas-phase oxygen transport, while insufficient ionomer limits proton conductivity across the catalyst layer. Therefore, optimizing the ionomer-to-carbon (I/C) weight ratio is essential. Studies have demonstrated that I/C ratios in the range of 0.6 to 1.0 provide an effective compromise between proton conductivity and catalytic accessibility, enabling improved electrochemical performance [59].

Table 2. Summary of common catalyst layer deposition methods, highlighting their main advantages, associated challenges, and representative recent references. This overview assists in selecting appropriate fabrication techniques for optimizing catalyst layer performance in PEM fuel cells.

|  |  |  |  |
| --- | --- | --- | --- |
| **Table 2. Comparison of Catalyst Layer Deposition Techniques** | | | |
| Ultrasonic Spraying | Advantages | * Produces highly homogeneous catalyst layers with <5% thickness variation and enables graded electrode architectures by tuning spray parameters * Compatible with roll-to-roll manufacturing (up to 10 m/min) and Reduces material waste by >90% compared to blade coating * Low-impact droplet formation (20–50 µm size) minimizes Fe-N₄ site agglomeration and Works with water-based inks, avoiding toxic solvents | [60,61] |
| Challenges | * Fe-N-C particles >100 nm tend to clog nozzles, requiring rigorous ink dispersion, moreover Pulsed ultrasonic excitation reduces clogging by 70% * Achieving >100 µm layers often requires multiple passes, risking delamination * Ultrasonic waves can cause PFSA migration, creating proton-conduction bottlenecks | [62,63] |
| Slot-Die Coating | Advantages | * Achieves coating speeds of 5-15 m/min, making it ideal for roll-to-roll manufacturing * Can produce uniform layers from 20-200 μm by adjusting gap height and flow rate * Excellent Material Utilization 95% material transfer efficiency vs. ~60% for spray coating * Compatible with in-line drying/curing for integrated manufacturing | [61,64,65] |
| Challenges | * Requires precise control of viscosity (50-500 mPa·s) and surface tension * High solid content (>20 wt%) often needed for Fe-N-C, risking agglomeration * Fe-N-C particles >5 μm can block narrow slots | [62,66] |
| Electrospray Deposition | Advantages | * Achieves 20-50 μm thick catalyst layers with <3% thickness variation * Produces nanoscale droplets (1-10 μm) for atomic-level Fe-N₄ site dispersion * Minimal Material Waste 90% deposition efficiency vs. <50% for spray coating * Covers 3D porous substrates (e.g., carbon papers) with uniform loading * Operates at 25-60°C, preserving temperature-sensitive Fe-N₄ sites | [67] |
| Challenges | * Low Deposition Rates ypical throughput: 0.5-2 cm²/min vs. 100+ cm²/min for slot-die * Ink Conductivity Requirements: Needs 10⁻⁴-10⁻² S/cm electrical conductivity for stable Taylor cone formation * Fe-N-C particles >200 nm cause nozzle blockages * Ionomer Distribution Control: Electric fields can induce PFSA migration to coating surface | [64,68] |

**5.3. Membrane Electrode Assembly (MEA) Preparation**

The membrane electrode assembly (MEA) is the heart of a proton exchange membrane fuel cell (PEMFC), comprising the proton-conductive membrane, catalyst layers, and gas diffusion layers (GDLs). For platinum group metal-free (PGM-free) catalysts such as Fe–N–C, the MEA preparation process is critical in determining the real-world electrocatalytic performance, site utilization, water management, and long-term stability [1].

Due to the unique physical and chemical properties of Fe–N–C catalysts—such as lower site density, lower intrinsic conductivity, and thicker required layers—special considerations must be taken during MEA fabrication [69].

**5.3.1. The catalyst-coated membrane (CCM)**

The catalyst-coated membrane (CCM) technique has emerged as a preferred method for incorporating Fe–N–C catalysts into membrane electrode assemblies (MEAs) for proton exchange membrane fuel cells (PEMFCs). It offers significant electrochemical and structural benefits over conventional gas diffusion electrode (GDE)-based methods. However, the unique physicochemical properties of Fe–N–C materials also present integration-specific challenges that must be carefully addressed for reliable, high-performance operation [70].

Rationale for Using CCM with Fe–N–C Catalysts typically require thicker catalyst layers (3–6 mg cm⁻² loading), Efficient proton transport across the membrane interface, and minimized interfacial resistance. The CCM approach addresses these requirements by depositing the catalyst layer directly onto the membrane surface, ensuring uniform contact and reducing ohmic losses compared to GDE-based MEAs [71].

**5.3.2. The Catalyst-Coated Substrate (CCS)**

The Catalyst-Coated Substrate (CCS) method involves depositing the catalyst layer onto a gas diffusion layer (GDL) or microporous layer (MPL), which is then assembled with the proton exchange membrane to form the membrane electrode assembly (MEA). This approach contrasts with the catalyst-coated membrane (CCM) technique, where the catalyst is coated directly onto the membrane [72].

Early PEMFCs (1990s–2000s): Primarily used CCM due to better catalyst-membrane contact [73]. Mid-2000s: CCS gained traction for easier manufacturability, especially for high-temperature PEMFCs [74]. 2010s–Present: CCS became dominant in industrial-scale production due to compatibility with roll-to-roll coating [75].

For Fe–N–C catalysts, CCS offers practical advantages such as ease of fabrication, flexibility in catalyst layer thickness control, and the potential for better mechanical robustness. However, CCS-based MEAs can suffer from increased interfacial resistance between the catalyst layer and membrane, which can reduce proton transport efficiency and active site utilization. Additionally, challenges in achieving intimate contact and uniform ionomer distribution at the membrane–catalyst interface can affect water management and gas transport within the MEA [29].

Optimizing ink formulation, coating techniques, and hot-pressing conditions are critical to minimizing these limitations and improving the performance of Fe–N–C-based CCS cathodes in PEMFCs [76].

**5.3.3. Hot Pressing and MEA Assembly**

The assembly of a membrane electrode assembly (MEA) is a critical step in proton exchange membrane fuel cell (PEMFC) fabrication. For Fe–N–C catalysts, which are inherently different from platinum-based systems in terms of loading, porosity, and ionomer interaction, hot pressing is commonly used to fabricate robust MEAs with low interfacial resistance and good mechanical integrity [77].

Hot pressing is typically applied in both CCM (catalyst-coated membrane) and CCS (catalyst-coated substrate) configurations. It involves:

• Stacking the membrane and the gas diffusion electrodes (GDEs) or catalyst-coated layers.

• Applying heat (e.g., 120–140 °C) and pressure (e.g., 1–2 MPa) for a defined time (e.g., 2–5 minutes).

• Bonding the catalyst layer to the membrane, ensuring good mechanical contact and proton/electron transfer pathways.

This step determines the interfacial contact quality, which is essential for minimizing ohmic resistance and maximizing electrochemical performance [77].

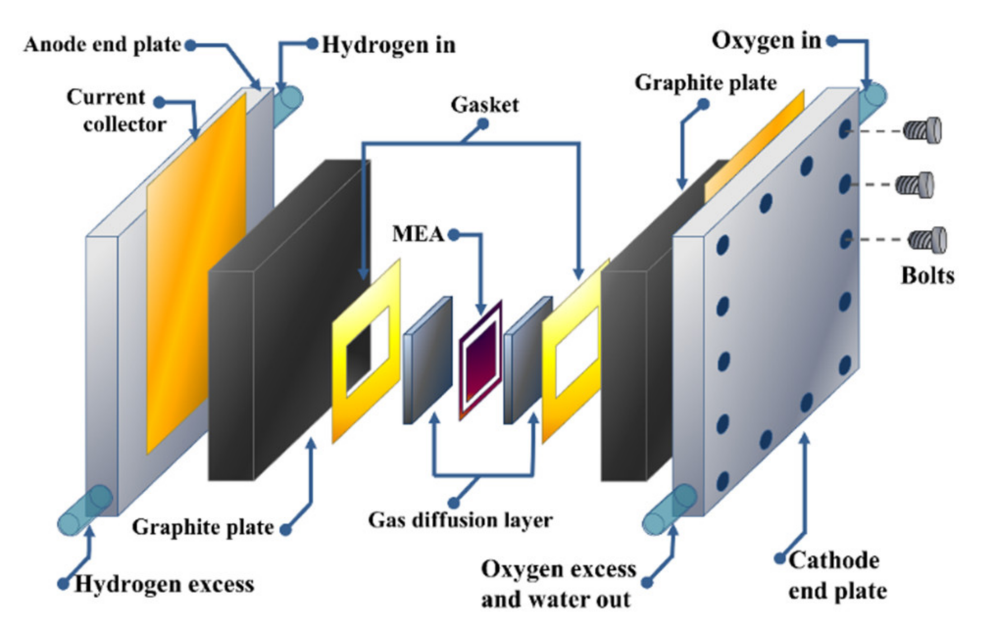
**5.4. Fuel Cell Testing Conditions**

Testing is usually performed using a single-cell fixture with active areas between 1 and 5 cm². The membrane electrode assembly (MEA) is fabricated by either the catalyst-coated membrane (CCM) or catalyst-coated substrate (CCS) method. The cell is assembled between graphite or stainless-steel bipolar plates with serpentine or interdigitated flow fields [78].

A polytetrafluoroethylene (PTFE) gasket is commonly employed in PEMFC single-cell assemblies to ensure uniform sealing and mechanical compression of the membrane electrode assembly, preventing gas leakage and maintaining consistent contact across cell components. Proper compression pressure is critical for optimizing the electrical contact between the catalyst layer and gas diffusion layer (GDL), while also preserving GDL porosity [79]. Figure 2. Illustrates the structural components in a single Proton Exchange Membrane Fuel Cell (PEMFC), including bipolar plates, gaskets, gas diffusion layers (GDLs), and the membrane electrode assembly (MEA); this unit configuration is the fundamental building block of a full fuel cell stack [80].

Table 3. provides Summary of typical fuel cell testing conditions employed for evaluating Fe–N–C catalyst performance in PEM fuel cells, including temperature, gas feed composition, pressure, humidity, and scan rates [81].

**Fig. 2. Layout of a Single PEM Fuel Cell Unit** [80]



|  |  |  |
| --- | --- | --- |
| **Table 3: Typical Operating Conditions for Single-Cell PEM Fuel Cell Testing of Fe–N–C Catalysts** | | |
| **Parameter** | **Typical Value** | **Notes** |
| **Cell temperature** | Maximum 80 °C | Matches DOE testing protocol for PEMFCs |
| **Anode gas** | Pure H₂ (99.999%) | Suggested H₂ humidified at 80 °C |
| **Cathode gas** | O₂ (or air) | O₂ for maximum performance; air for realistic operation |
| **Relative humidity** | 0-100% | Suggested fully humidified  Avoids dehydration of Nafion membranes |
| **Gas stoichiometry** | 1-3 | Gas stoichiometry is being calculated depend on active area |

6. Conclusion

The creation of high-performance Fe-N-C catalysts has reached a turning point, where their effectiveness in the lab is now comparable to traditional Pt-based systems. In our review, we found the path to commercial implementation demands concerted efforts across multiple fronts:

• Atomic-Scale Design: Precise engineering of Fe-N₄ coordination environments through advanced synthesis and doping strategies must be coupled with mechanistic understanding of degradation pathways (e.g., demetallation, carbon oxidation) under operational conditions.

• Electrode Engineering: Innovative approaches—such as hierarchically porous architectures, ionomer-gradient distributions, and hybrid catalyst systems—are required to overcome the intrinsic trade-offs between active site density, proton conductivity, and gas transport in thick catalyst layers.

• Durability Validation: The establishment of standardized testing protocols, including unified accelerated stress tests and in situ diagnostics, will enable meaningful comparison of stability metrics across research groups and facilitate technology transfer to industry.

• Manufacturing Innovation: Scalable deposition techniques (e.g., roll-to-roll slot-die coating) and quality control methods must be adapted to accommodate the unique physicochemical properties of Fe-N-C materials while maintaining cost targets (<$10 kW⁻¹).

The realization of Fe-N-C catalysts as a sustainable alternative to PGMs in PEMFCs hinges on interdisciplinary collaboration spanning materials science, electrochemistry, and process engineering. With continued progress in these areas, Fe-N-C-based PEMFC systems could play a transformative role in decarbonizing transportation and stationary power applications, ultimately contributing to global carbon neutrality goals. Future research should prioritize the development of predictive models that integrate multi-scale phenomena—from atomic-site kinetics to macro-scale transport to guide the rational design of next-generation PGM-free fuel cell systems.

Disclaimer (Artificial intelligence)

Author(s) hereby declare that generative AI technologies such as Large Language Models, etc. have been used during the writing or editing of manuscripts. This explanation will include the name, version, model, and source of the generative AI technology and as well as all input prompts provided to the generative AI technology

Details of the AI usage are given below:

The author(s) hereby disclose that generative AI technology, specifically OpenAI’s ChatGPT (model: GPT-4o-mini), was utilized during the editing phase of this manuscript to enhance language clarity and grammatical accuracy.

References

[1] Kiani M, Zhao Y, Zhang R. Proton exchange membrane fuel cells: recent developments and future perspectives. Chem Commun 2025;52:7890–7903. https://doi.org/10.1039/d5cc01478f.

[2] Yang G, Lee CH, Qiao X, Babu SK, Martinez U, Spendelow JS. Advanced Electrode Structures for Proton Exchange Membrane Fuel Cells: Current Status and Path Forward. Electrochem Energy Rev 2024;7:1–23. https://doi.org/10.1007/s41918-023-00208-3.

[3] Asghar MR, Zhang W, Su H, Zhang J, Liu H, Xing L, et al. A review of proton exchange membranes modified with inorganic nanomaterials for fuel cells. Energy Adv 2024;4:185–223. https://doi.org/10.1039/d4ya00446a.

[4] Wu G, Zelenay P. Nanostructured nonprecious metal catalysts for oxygen reduction reaction. Acc Chem Res 2013;46:1878–89. https://doi.org/10.1021/ar400011z.

[5] Janssen M, Weber P, Oezaslan M. Recent advances of various Pt-based catalysts for oxygen reduction reaction (ORR) in polymer electrolyte membrane fuel cells (PEMFCs). Curr Opin Electrochem 2023;40. https://doi.org/10.1016/j.coelec.2023.101337.

[6] Nsour W, Taa’mneh T, Ayadi O, Al Asfar J. Design of stand-alone proton exchange membrane fuel cell hybrid system under Amman climate. J Ecol Eng 2019;20:1–10. https://doi.org/10.12911/22998993/111800.

[7] Hu X, Yang B, Ke S, Liu Y, Fang M, Huang Z, et al. Review and Perspectives of Carbon-Supported Platinum-Based Catalysts for Proton Exchange Membrane Fuel Cells. Energy and Fuels 2023;37:11532–66. https://doi.org/10.1021/acs.energyfuels.3c01265.

[8] Liu M, Xiao X, Li Q, Luo L, Ding M, Zhang B, et al. Recent progress of electrocatalysts for oxygen reduction in fuel cells. J Colloid Interface Sci 2022;607:791–815. https://doi.org/10.1016/j.jcis.2021.09.008.

[9] Barrio J, Pedersen A, Sarma SC, Bagger A, Gong M, Favero S, et al. FeNC Oxygen Reduction Electrocatalyst with High Utilization Penta-Coordinated Sites. Adv Mater 2023;35. https://doi.org/10.1002/adma.202211022.

[10] Mo S, Du L, Huang Z, Chen J, Zhou Y, Wu P, et al. Recent Advances on PEM Fuel Cells: From Key Materials to Membrane Electrode Assembly. Electrochem Energy Rev 2023;6. https://doi.org/10.1007/s41918-023-00190-w.

[11] Li L, Wen Y, Han G, Liu Y, Song Y, Zhang W, et al. Tailoring the stability of Fe-N-C via pyridinic nitrogen for acid oxygen reduction reaction. Chem Eng J 2022;437. https://doi.org/10.1016/j.cej.2022.135320.

[12] Yu Y, Wang Y, Yang F, Feng D, Yang M, Xie PF, et al. Meso/Microporous Single-Atom Catalysts Featuring Curved Fe−N4 Sites Boost the Oxygen Reduction Reaction Activity. Angew Chemie - Int Ed 2025;64. https://doi.org/10.1002/anie.202415691.

[13] Chen G, Lu R, Li C, Yu J, Li X, Ni L, et al. Hierarchically Porous Carbons with Highly Curved Surfaces for Hosting Single Metal FeN4 Sites as Outstanding Oxygen Reduction Catalysts. Adv Mater 2023;35. https://doi.org/10.1002/adma.202300907.

[14] Dai X, Zhao Z. ZIF-L-derived FeN-hcC catalysts with curved carbon surfaces for effective oxygen reduction reaction over the entire pH range. New J Chem 2024;48:18719–27. https://doi.org/10.1039/d4nj04093g.

[15] Zhang M, Yang B, Yang T, Yang Y, Xiang Z. A ferric citrate derived Fe-N-C electrocatalyst with stepwise pyrolysis for highly efficient oxygen reduction reaction. Chinese Chem Lett 2022;33:362–7. https://doi.org/10.1016/j.cclet.2021.06.054.

[16] Santoro C, Serov A, Stariha L, Kodali M, Gordon J, Babanova S, et al. Iron based catalysts from novel low-cost organic precursors for enhanced oxygen reduction reaction in neutral media microbial fuel cells. Energy Environ Sci 2016;9:2346–53. https://doi.org/10.1039/c6ee01145d.

[17] Liu H, Ney L, Zamel N, Li X. Effect of Catalyst Ink and Formation Process on the Multiscale Structure of Catalyst Layers in PEM Fuel Cells. Appl Sci 2022;12. https://doi.org/10.3390/app12083776.

[18] Álvarez-Manuel L, Alegre C, Sebastián D, Napal PF, Lázaro MJ. Tailored Porous Carbon Xerogels for Fe-N-C Catalysts in Proton Exchange Membrane Fuel Cells. Nanomaterials 2024;14. https://doi.org/10.3390/nano14010014.

[19] Berretti E, Longhi M, Atanassov P, Sebastián D, Lo Vecchio C, Baglio V, et al. Platinum group metal-free Fe-based (Fe[sbnd]N[sbnd]C) oxygen reduction electrocatalysts for direct alcohol fuel cells. Curr Opin Electrochem 2021;29. https://doi.org/10.1016/j.coelec.2021.100756.

[20] Zha W, Gu H, Pan W, Sun X, Han Y, Li Z, et al. Controllable synthesis and n-doping of HMoOx nanoparticle inks through simple photoreduction for solution-processed organic photovoltaics. Chem Eng J 2021;425. https://doi.org/10.1016/j.cej.2021.130620.

[21] Adabi H, Shakouri A, Ul Hassan N, Varcoe JR, Zulevi B, Serov A, et al. High-performing commercial Fe–N–C cathode electrocatalyst for anion-exchange membrane fuel cells. Nat Energy 2021;6:834–43. https://doi.org/10.1038/s41560-021-00878-7.

[22] Zhou Y, Lu R, Tao X, Qiu Z, Chen G, Yang J, et al. Boosting Oxygen Electrocatalytic Activity of Fe-N-C Catalysts by Phosphorus Incorporation. J Am Chem Soc 2023;145:3647–55. https://doi.org/10.1021/jacs.2c12933.

[23] Pedersen A, Kumar K, Ku YP, Martin V, Dubau L, Santos KT, et al. Operando Fe dissolution in Fe-N-C electrocatalysts during acidic oxygen reduction: impact of local pH change. Energy Environ Sci 2024;17:6323–37. https://doi.org/10.1039/d4ee01995d.

[24] Zhan X, Bowden ME, Lu X, Bonnett JF, Lemmon T, Reed DM, et al. A Low-Cost Durable Na-FeCl2 Battery with Ultrahigh Rate Capability. Adv Energy Mater 2020;10. https://doi.org/10.1002/aenm.201903472.

[25] Damjanović AM, Freiberg ATS, Siebel A, Koyutürk B, Menga D, Krempl K, et al. Ex situ/Operando X-Ray Absorption Spectroscopy on Fe0.07Zr0.93O2-δ/C vs. Fe−N−C as Pt-Group-Metal-Free Oxygen Reduction Reaction Catalysts in Proton Exchange Membrane Fuel Cells. ChemElectroChem 2023;10. https://doi.org/10.1002/celc.202300185.

[26] Mohanta PK, Ripa MS, Regnet F, Jörissen L. Impact of Membrane Types and Catalyst Layers Composition on Performance of Polymer Electrolyte Membrane Fuel Cells. ChemistryOpen 2020;9:607–15. https://doi.org/10.1002/open.202000089.

[27] Mo S, Du L, Huang Z, Chen J, Zhou Y, Wu P, et al. Recent Advances on PEM Fuel Cells: From Key Materials to Membrane Electrode Assembly. Electrochem Energy Rev 2023;6. https://doi.org/10.1007/s41918-023-00190-w.

[28] Santori PG, Speck FD, Li J, Zitolo A, Jia Q, Mukerjee S, et al. Effect of Pyrolysis Atmosphere and Electrolyte pH on the Oxygen Reduction Activity, Stability and Spectroscopic Signature of FeN x Moieties in Fe-N-C Catalysts . J Electrochem Soc 2019;166:F3311–20. https://doi.org/10.1149/2.0371907jes.

[29] Zierdt T, Müller-Hülstede J, Schmies H, Schonvogel D, Wagner P, Friedrich KA. Effect of Polytetrafluorethylene Content in Fe-N-C-Based Catalyst Layers of Gas Diffusion Electrodes for HT-PEM Fuel Cell Applications. ChemElectroChem 2024;11. https://doi.org/10.1002/celc.202300583.

[30] Ratso S, Ranjbar Sahraie N, Sougrati MT, Käärik M, Kook M, Saar R, et al. Synthesis of highly-active Fe-N-C catalysts for PEMFC with carbide-derived carbons. J Mater Chem A 2018;6:14663–74. https://doi.org/10.1039/c8ta02325e.

[31] Yang X, Huang Z, Du L, Li Q, Ye S. Active Sites and Stability Study of Fe/N/C Catalyst in PEMFCs: A Decade of Stunning Progress and the Remaining Challenges. ACS Catal 2024;14:15471–88. https://doi.org/10.1021/acscatal.4c02871.

[32] Morankar A, Deshpande S, Zeng Z, Atanassov P, Greeley J. A first principles analysis of potential-dependent structural evolution of active sites in Fe-N-C catalysts. Proc Natl Acad Sci U S A 2023;120. https://doi.org/10.1073/pnas.2308458120.

[33] Maniatis I, Charalampopoulos G, Paloukis F, Daletou MK. Optimizing Fe-N-C Electrocatalysts for PEMFCs: Influence of Constituents and Pyrolysis on Properties and Performance. Catalysts 2024;14. https://doi.org/10.3390/catal14110780.

[34] Wang J, Shen Y, Liu S, Zhang Y. Single 2D MXene precursor-derived TiO2 nanosheets with a uniform decoration of amorphous carbon for enhancing photocatalytic water splitting. Appl Catal B Environ 2020;270. https://doi.org/10.1016/j.apcatb.2020.118885.

[35] Zhang X, Xu J, Yuan H, Zhang S, Ouyang Q, Zhu C, et al. Large-Scale Synthesis of Three-Dimensional Reduced Graphene Oxide/Nitrogen-Doped Carbon Nanotube Heteronanostructures as Highly Efficient Electromagnetic Wave Absorbing Materials. ACS Appl Mater Interfaces 2019;11:39100–8. https://doi.org/10.1021/acsami.9b13751.

[36] Zou R, Hasanzadeh A, Khataee A, Meng F, Angelidaki I, Zhang Y. Synergistic effect for efficient oxidization of refractory organics with high chroma by an innovative persulfate assisted microbial electrolysis ultraviolet cell. Chem Eng J 2021;419. https://doi.org/10.1016/j.cej.2021.129477.

[37] Li F, Ding XB, Cao QC, Qin YH, Wang C. A ZIF-derived hierarchically porous Fe-Zn-N-C catalyst synthesized: Via a two-stage pyrolysis for the highly efficient oxygen reduction reaction in both acidic and alkaline media. Chem Commun 2019;55:13979–82. https://doi.org/10.1039/c9cc07489a.

[38] Gu L, Jiang L, Li X, Jin J, Wang J, Sun G. A Fe-N-C catalyst with highly dispersed iron in carbon for oxygen reduction reaction and its application in direct methanol fuel cells. Cuihua Xuebao/Chinese J Catal 2016;37:539–48. https://doi.org/10.1016/S1872-2067(15)61049-X.

[39] Muhyuddin M, Mostoni S, Honig HC, Mirizzi L, Elbaz L, Scotti R, et al. Enhancing Electrocatalysis: Engineering the Fe-Nx-C Electrocatalyst for Oxygen Reduction Reaction Using Fe-Functionalized Silica Hard Templates. ACS Appl Energy Mater 2024;7:11691–702. https://doi.org/10.1021/acsaem.4c01215.

[40] Serov A, Artyushkova K, Atanassov P. Fe-N-C oxygen reduction fuel cell catalyst derived from carbendazim: Synthesis, structure, and reactivity. Adv Energy Mater 2014;4. https://doi.org/10.1002/aenm.201301735.

[41] Mostoni S, Mirizzi L, Frigerio A, Zuccante G, Ferrara C, Muhyuddin M, et al. In-Situ HF Forming Agents for Sustainable Manufacturing of Iron-Based Oxygen Reduction Reaction Electrocatalysis Synthesized Through Sacrificial Support Method. ChemSusChem 2025;18. https://doi.org/10.1002/cssc.202401185.

[42] Baldovino-Medrano VG, Niño-Celis V, Isaacs Giraldo R. Systematic Analysis of the Nitrogen Adsorption-Desorption Isotherms Recorded for a Series of Materials Based on Microporous-Mesoporous Amorphous Aluminosilicates Using Classical Methods. J Chem Eng Data 2023;68:2512–28. https://doi.org/10.1021/acs.jced.3c00257.

[43] Fan L, Zhang L, Li X, Mei H, Li M, Liu Z, et al. Controlled synthesis of a porous single-atomic Fe-N-C catalyst with Fe nanoclusters as synergistic catalytic sites for efficient oxygen reduction. Inorg Chem Front 2022;9:4101–10. https://doi.org/10.1039/d2qi00876a.

[44] Zheng X, Cao X, Sun Z, Zeng K, Yan J, Strasser P, et al. Indiscrete metal/metal-N-C synergic active sites for efficient and durable oxygen electrocatalysis toward advanced Zn-air batteries. Appl Catal B Environ 2020;272. https://doi.org/10.1016/j.apcatb.2020.118967.

[45] Zhao L, Zhang Y, Huang LB, Liu XZ, Zhang QH, He C, et al. Cascade anchoring strategy for general mass production of high-loading single-atomic metal-nitrogen catalysts. Nat Commun 2019;10. https://doi.org/10.1038/s41467-019-09290-y.

[46] Zitolo A, Ranjbar-Sahraie N, Mineva T, Li J, Jia Q, Stamatin S, et al. Identification of catalytic sites in cobalt-nitrogen-carbon materials for the oxygen reduction reaction. Nat Commun 2017;8. https://doi.org/10.1038/s41467-017-01100-7.

[47] Zhu FF, Chen WJ, Xu Y, Gao CL, Guan DD, Liu CH, et al. Epitaxial growth of two-dimensional stanene. Nat Mater 2015;14:1020–5. https://doi.org/10.1038/nmat4384.

[48] Zitolo A, Goellner V, Armel V, Sougrati MT, Mineva T, Stievano L, et al. Identification of catalytic sites for oxygen reduction in iron- and nitrogen-doped graphene materials. Nat Mater 2015;14:937–42. https://doi.org/10.1038/nmat4367.

[49] Chung HT, Cullen DA, Higgins D, Sneed BT, Holby EF, More KL, et al. Direct atomic-level insight into the active sites of a high-performance PGM-free ORR catalyst. Science (80- ) 2017;357:479–84. https://doi.org/10.1126/science.aan2255.

[50] Wenhua Zhuang, Thomas Asset, Karl J. J. Mayrhofer, Sebastian Cherevko SW. Highly Active Iron-Based ORR Electrocatalysts with Improved Stability through a Synergistic N-Coordination Environment. Ournal Am Chem Soc 2016;138:16177–16184. https://doi.org/https://doi.org/10.1021/jacs.5b11000.

[51] Li J, Chen M, Cullen DA, Hwang S, Wang M, Li B, et al. Atomically dispersed manganese catalysts for oxygen reduction in proton-exchange membrane fuel cells. Nat Catal 2018;1:935–45. https://doi.org/10.1038/s41929-018-0164-8.

[52] Seitz LC, Dickens CF, Nishio K, Hikita Y, Montoya J, Doyle A, et al. A highly active and stable IrOx/SrIrO3catalyst for the Oxygen evolution reaction. Science (80- ) 2016;353:1011–4. https://doi.org/10.1126/science.aaf5050.

[53] Serrano-Lotina A, Monte M, Iglesias-Juez A, Pavón-Cadierno P, Portela R, Ávila P. MnOx-support interactions in catalytic bodies for selective reduction of NO with NH3. Appl Catal B Environ 2019;256. https://doi.org/10.1016/j.apcatb.2019.117821.

[54] Vinogradov KY, Bulanova AV, Shafigulin RV, Tokranova EO, Mebel AM, Zhu H. Density Functional Theory Study of the Oxygen Reduction Reaction Mechanism on Graphene Doped with Nitrogen and a Transition Metal. ACS Omega 2022;7:7066–73. https://doi.org/10.1021/acsomega.1c06768.

[55] Tan W, Shi H, Qu J, Yu Y, Li H, Tao Z. Contributions of Boudouard reaction to NO electrocatalytic reduction by Fe-loaded carbon materials in the presence of O2. J Catal 2021;394:30–9. https://doi.org/10.1016/j.jcat.2020.11.034.

[56] Debe MK. Electrocatalyst approaches and challenges for automotive fuel cells. Nature 2012;486:43–51. https://doi.org/10.1038/nature11115.

[57] Xu J, Liang G, Chen D, Li Z, Zhang H, Chen J, et al. Iron and nitrogen doped carbon derived from ferrocene and ZIF-8 as proton exchange membrane fuel cell cathode catalyst. Appl Surf Sci 2022;573. https://doi.org/10.1016/j.apsusc.2021.151607.

[58] Wan X, Liu Q, Liu J, Liu S, Liu X, Zheng L, et al. Iron atom–cluster interactions increase activity and improve durability in Fe–N–C fuel cells. Nat Commun 2022;13. https://doi.org/10.1038/s41467-022-30702-z.

[59] Zhu J, Pedersen A, Kellner S, Hunter RD, Barrio J. Impact of ionomers on porous Fe-N-C catalysts for alkaline oxygen reduction in gas diffusion electrodes. Commun Chem 2025;8. https://doi.org/10.1038/s42004-025-01422-4.

[60] Wang J, Xu XL, Li X. Recent Progress of Multiferroicity and Magnetoelectric Effects in ABX3-Type Perovskite Metal–Organic Frameworks. Adv Mater Interfaces 2023;10. https://doi.org/10.1002/admi.202300123.

[61] Wen H, Qu W, Lin M, Zhou L, Guo X, Ma P, et al. Nitrogen-coordinated cobalt embedded in hollow carbon polyhedron for catalytic ozonation of odor CH3SH at ambient temperature. Chem Eng J 2023;471. https://doi.org/10.1016/j.cej.2023.144567.

[62] Lee CH, Ha H, Ahn Y, Liu H. Performance of single-layer paper-based co-laminar flow microbial fuel cells. J Power Sources 2023;580. https://doi.org/10.1016/j.jpowsour.2023.233456.

[63] Yu S, Cho YH, Lee WH, Yoon SG, Park J, Han J, et al. Interlayer mediated water motion-induced ionovoltaic electricity generation. Nano Energy 2024;123. https://doi.org/10.1016/j.nanoen.2024.109345.

[64] Acharya D, Muthurasu A, Ko TH, Bhattarai RM, Kim T, Chae SH, et al. Iron MOF-Derived Fe2O3/NPC Decorated on MIL-88A Converted Fe3C Implanted Electrospun Porous Carbon Nanofibers for Symmetric Supercapacitors. ACS Appl Energy Mater 2023;6:9196–206. https://doi.org/10.1021/acsaem.3c00567.

[65] Moshkovitz MY, Paz D, Magdassi S. 3D Printing Transparent γ-Alumina Porous Structures Based on Photopolymerizable Sol–Gel Inks. Adv Mater Technol 2023;8. https://doi.org/10.1002/admt.202300123.

[66] Cheng H, Ma Z, Kumar P, Liang H, Cao Z, Xie H, et al. Non-Flammable Electrolyte Mediated by Solvation Chemistry toward High-Voltage Lithium-Ion Batteries. ACS Energy Lett 2024;9:1604–16. https://doi.org/10.1021/acsenergylett.3c02789.

[67] Cyganik AKWK. Erratum: N-Heterocyclic Carbenes for the Self-Assembly of Thin and Highly Insulating Monolayers with High Quality and Stability (ACS Nano (2020) 14:5 (6043-6057) DOI: 10.1021/acsnano.0c01733). ACS Nano 2023;17:12933. https://doi.org/10.1021/acsnano.3c04567.

[68] Gao C, Zhang H, Qiao F, Huang H, Zhang D, Ding D, et al. In situ artificial wide-bandgap Cs-based recrystallized-arrays for optical optimization of perovskite solar cells. Nano Energy 2023;116. https://doi.org/10.1016/j.nanoen.2023.108765.

[69] Peng, X., Wang, J., Zhang, X., & Zheng L. Advances in Platinum Group Metal-Free Catalysts for the Oxygen Reduction Reaction in PEM Fuel Cells. Chem Eng J 2023;470.

[70] Gong Q, Li C, Liu Y, Ilavsky J, Guo F, Cheng X, et al. Effects of Ink Formulation on Construction of Catalyst Layers for High-Performance Polymer Electrolyte Membrane Fuel Cells. ACS Appl Mater Interfaces 2021;13:37004–13. https://doi.org/10.1021/acsami.1c06711.

[71] Li Y, Yin S, Chen L, Cheng X, Wang C, Jiang Y, et al. Boost the Utilization of Dense FeN4 Sites for High-Performance Proton Exchange Membrane Fuel Cells. Energy Environ Mater 2024;7. https://doi.org/10.1002/eem2.12611.

[72] Zhao P, Xiang Y, Xu Y, Wen Y, Zhang W, Zhu X, et al. Dense garnet-like Li5La3Nb2O12 solid electrolyte prepared by self-consolidation method. J Power Sources 2018;388:25–31. https://doi.org/10.1016/j.jpowsour.2018.03.072.

[73] Perry ML, Newman J, Cairns EJ. Mass Transport in Gas‐Diffusion Electrodes: A Diagnostic Tool for Fuel‐Cell Cathodes. J Electrochem Soc 1998;145:5–15. https://doi.org/10.1149/1.1838202.

[74] Batista MS, Santiago EI, Assaf EM, Ticianelli EA. Evaluation of the water-gas shift and CO methanation processes for purification of reformate gases and the coupling to a PEM fuel cell system. J Power Sources 2005;145:50–4. https://doi.org/10.1016/j.jpowsour.2004.12.032.

[75] Li Z, Lu YC. Polysulfide-based redox flow batteries with long life and low levelized cost enabled by charge-reinforced ion-selective membranes. Nat Energy 2021;6:517–28. https://doi.org/10.1038/s41560-021-00804-x.

[76] Reshetenko T, Serov A, Kulikovsky A, Atanassov P. Impedance Spectroscopy Characterization of PEM Fuel Cells with Fe-N-C-Based Cathodes. J Electrochem Soc 2019;166:F653–60. https://doi.org/10.1149/2.1431910jes.

[77] Lefèvre M, Proietti E, Jaouen F, Dodelet JP. Iron-Based catalysts with improved oxygen reduction activity in polymer electrolyte fuel cells. Science (80- ) 2009;324:71–4. https://doi.org/10.1126/science.1170051.

[78] Li Y, Fu Z, Li Y, Zhang G. A Comparative Study of CCM and CCS Membrane Electrode Assemblies for High-Temperature Proton Exchange Membrane Fuel Cells with a CsH5(PO4)2-Doped Polybenzimidazole Membrane. Materials (Basel) 2023;16. https://doi.org/10.3390/ma16113925.

[79] Yoo J, Lee YH, Park J, Oh HS, An JH, Joo WJ, et al. Study on low temperature and durability characteristics of gasket for polymer electrolyte membrane fuel cell (PEMFC) depending on cross-sectional geometry. Int J Hydrogen Energy 2024;50:1194–206. https://doi.org/10.1016/j.ijhydene.2023.10.145.

[80] Cruz-Martínez H, Tellez-Cruz MM, Guerrero-Gutiérrez OX, Ramírez-Herrera CA, Salinas-Juárez MG, Velázquez-Osorio A, et al. Mexican contributions for the improvement of electrocatalytic properties for the oxygen reduction reaction in PEM fuel cells. Int J Hydrogen Energy 2019:12477–91. https://doi.org/10.1016/j.ijhydene.2018.05.168.

[81] Peng HS, Zhong BJ. Experimental study on the relationships between composition distribution and laminar flame speed of pyrolysis products. Int J Hydrogen Energy 2022;47:17022–32. https://doi.org/10.1016/j.ijhydene.2022.03.166.