Achievements, Challenges, and Perspectives on Cathode Catalysts in Proton Exchange Membrane Fuel Cells for Transportation

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Proton exchange membrane fuel cells (PEMFCs) can use hydrogen and air to power clean electric vehicles. However, technical barriers including high cost, insufficient lifetime, and insufficient power density limit their broad applications. Advanced cathode catalysts for the kinetically-sluggish oxygen reduction reaction (ORR) in acidic media are essential for overcoming these barriers. Here, we highlight breakthroughs, challenges, and future directions for both platinum group metal (PGM) and PGM-free ORR catalysts. Among PGM catalysts, highly-ordered PtM intermetallic nanostructures exhibit enhanced activity and stability relative to PtM random alloys. Carbon supports, with optimal balance between graphitization degree and porosity, play an important role in enhancing overall performance. Among PGM-free catalysts, transition metal and nitrogen co-doped carbons (M-N-C) perform best. However, degradation at practical voltages (>0.6 V) prevents their practical application. For all catalysts, translating intrinsic activity and stability into device performance requires electrodes with robust three-phase interfaces for effective charge and mass transfer.

Keywords: oxygen reduction; PGM catalysts; PGM-free catalysts; fuel cells; transportation.

Proton exchange membrane fuel cells (PEMFC) have advanced tremendously in past decades, now providing hydrogen fuel cell vehicles (FCVs) with cruise ranges up to 650 kilometers. However, PEMFC commercialization has been limited by factors including high cost, insufficient durability, and limited power density. Due to sluggish oxygen reduction reaction (ORR) kinetics at the cathode, a high overpotential (*c.a.* 400 mV) is required to generate practical current density, leading to an open circuit voltage (OCV) significantly below the theoretical value of 1.23 V. Over 40% of the current cost of PEMFCs ($40/kW) arises from Pt catalysts used for the ORR. The United States Department of Energy (DOE) near-term cost target for PEMFCs for transportation applications is $30/kW[1]. Meeting PEMFC lifetime requirements of 8000 h for cars (150,000 miles equivalent) and 20000 h for buses, with <10% performance loss, remains a grand challenge due to catalyst deactivation[2]. High power density (> 1.0 W/cm^2) is desirable for transportation but is limited by inefficient mass transfer and charge transport in membrane electrode assemblies (MEAs), especially at ultra-low Pt loadings (<0.1 mg$_{Pt}$/cm^2). Low-platinum group metal (low-PGM) catalysts and PGM-free catalysts as outlined in **Figure 1** are both being studied to improve performance and reduce cost. PtM alloy nanostructures have been extensively investigated to enhance intrinsic activity and stability of Pt-based catalysts[3-9]. In the longer term, PGM-free catalysts could support large-scale commercialization of PEMFCs. Among PGM-free formulations, transition metal (*e.g.*, Fe, Co, or/and Mn) and nitrogen co-doped carbon (M-N-C) catalysts exhibit encouraging performance, but their activity and stability must improve substantially to make them viable. Recent years have witnessed great improvements in mechanistic understanding of the ORR, new catalyst synthesis concepts, and overall performance enhancement. Prior reviews have focused fundamental understanding, device performance, or industrial perspectives[8,10]. Herein, we highlight recent achievements in low-PGM and PGM-free cathode catalysts for PEMFCs, while outlining remaining challenges and potential solutions.

PGM catalysts for PEMFCs

ORR at the cathode governs overall PEMFC performance. Its sluggish kinetics, especially in acidic media, arise from the complex four electron transfer required for this multistep protonation process. Several reaction pathways are possible, and the rate determining steps (RDS) depend on the active sites and reaction conditions (*e.g.*, pH, temperature, and potential). Although mechanistic understanding remains incomplete, the most common viewpoint is that an efficient ORR catalyst should bind oxygen strongly enough to facilitate cleavage of O=O bonds, but weakly enough to release reaction intermediates and products. From this perspective, oxygen binding on pure Pt is too strong. Early research revealed that an oxygen binding energy about 0.2 eV lower than that of Pt should provide higher intrinsic activity[11]. Because most transition metals (M) are smaller than Pt, their incorporation into face-centered cubic (*fcc*) Pt produces contraction strain in the lattice[12,13]. Oxygen chemisorption on these compressed PtM surfaces is weaker than on pure Pt. Compressive lattice strain also directly influences the electronic structure of PtM, reducing the number of unoccupied projected electronic states and shifting the electronic *d*-band center downward[14]. Both geometric and electronic modifications contribute to enhanced activity of PtM alloy catalysts[11]. Unfortunately, leaching of M from PtM alloy catalysts limits their stability. In contrast, ordered PtM intermetallic nanoparticles exhibit both enhanced activity and stability for the ORR. Development of ordered PtM catalysts shows a great promise for addressing durability issues of PEMFCs.

Basic principles of PtM alloy catalyst design. A volcano-type relationship between catalytic activity and electronic structure (*d*-band center energy) of PtM catalysts has been established to rationalize the activity pattern of PtM and provide a basis for tuning electronic properties to maximize activity[15]. Initially, alloys with a 3:1 Pt:M ratio were most commonly used in theoretical and computational studies[11]. Adding a third metal might further improve performance[16,17], due to optimization of local oxygen binding energies and stabilization of M in Pt lattices[18]. The catalytic activity of PtM catalysts also depends upon particle size[19], nanostructure[20], and morphology[21]. Generally, catalyst particles are made as small as possible, to maximize surface area. However, early studies indicated that Pt particles with diameters of 3-4 nm are optimal for the ORR. This optimal size was attributed to variation in the fraction of surface atoms on (100) and (111) crystal faces with sizes, which changes the surface coordination number. ORR is structure-sensitive with activity increasing as (100) < (111) < (110) for Pt single-crystals according to Feliu[6,22] and Markovic's groups[23,24].

In addition to traditional spherical nanoparticles, one-dimensional (1D) anisotropic structures may also have enhanced electrocatalytic activity, due to rough surfaces that expose high-index facets and numerous edges, corners, and step-edge atoms, which are highly reactive[25]. Rationally introducing high-index facets provides a promising approach to maximize Pt utilization. Anisotropic structures fundamentally allow greater control over exposed surface facets compared to quasi-spherical structures[26-28]. Under-coordinated surface atoms on these structures are essential for enhancing ORR activity. Mechanical strain also decreased the binding energy of intermediates, further contributing to activity enhancement[28], as supported by DFT calculations[27].

Pt shells on various core substrates can show improved catalytic activity and Pt utilization[3,9]. Core composition, morphology, and number of shell layers each affect the core-shell interaction, potentially enhancing ORR activity[5,29,30], through changes in the electronic and geometric structures of the outer Pt shell[31,32]. A novel structural descriptor was recently proposed to capture the surface defectivity of PtNi catalysts with distinct compositions, sizes, and shape. It was used to rationalize changes in ORR activity and mechanism, showing that promoting surface defectivity in bimetallic catalysts can enhance ORR activity[4].

Nanoframes and nanocages, open nanostructures with three-dimensional (3D) edges, possess high intrinsic activity due to the richness of high-index facets and the optimal strains in surface Pt layers[33]. Their open construction of nano- and micro-lattice frameworks allows reactants to adsorb on both exterior and interior surfaces, making more Pt atoms available for the ORR[34,35]. Controlling surface composition and atomic configuration enables optimizing catalytic properties of the nanoframe/nanocage structures[36]. Chemical etching or dealloying processes selectively remove specific facets and undesirable elements from them[37-39]. Their high activity is often ascribed to reduced coverage of oxygenated intermediates on the Pt surface due to weaker oxygen binding, which also reduces Pt dissolution[39].

Structurally ordered PtM intermetallic catalysts. Atoms in PtM alloys are randomly distributed in the Pt *fcc* lattice[40]. In the corrosive PEMFC cathode environment, M is rapidly etched from these random alloys, reducing catalyst activity. In contrast, ordered intermetallic compounds combine metallic and ionic bonding. Pt and M occupy specific sites, forming an ordered atomic lattice with specific stoichiometry and crystal structure, as shown in **Figure 2**. The ordered geometric and electronic structures at the atomic-level can boost both intrinsic catalytic activity and stability[41]. Several PtM intermetallic catalysts have been studied, including PtCo[42-46], PtFe[47], PtCu[48], PtAl[49], PtCr[50], PtPb[51] and some corresponding ternary compounds[52,53].

Strategies to reduce the size of intermetallic nanoparticles. Intermetallic compounds are formed via high temperature (>700 °C) annealing of disordered PtM alloys. Heat treatment is crucial for producing ordered intermetallic structures. However, agglomeration and sintering during heating treatments significantly increases nanoparticle size, thus reducing mass activity. Coating PtM nanoparticles with oxide or carbon layers can help to maintain small particle sizes and narrow size distribution during the high-temperature treatment[54]. MgO-coated PtFe alloy nanoparticles showed no aggregation after phase transformation into the ordered face-centered tetragonal (*fct)* PtFe intermetallic compound[55]. However, this protection usually allows only partial transformation to ordered structures because of limited atom mobility within the MgO shell. A modified strategy of heating FePt-Fe_3O_4/MgO nanoparticles was proposed, in which the Fe_3O_4 was reduced to Fe to promote Fe and Pt diffusion, facilitating formation of fully ordered *fct*-FePt[56]. Nanoparticles can also be coated with polymers such as polydopamine to generate a thin carbon shell on their surface, which prevents nanoparticle coalescence and sintering/aggregation during annealing[57].

Structure-controlled synthesis of intermetallic catalysts. Controlling the morphology of PtM intermetallic catalysts is essential for maximizing activity[58]. Core-shell structures can form spontaneously during heat treatments, as excess Pt atoms preferentially occupy under-coordinated surface sites. Several layers of Pt atoms may coat the intermetallic core. Lattice contraction strain and electronic state modification due to lattice mismatch between core and shell layers can enhance ORR activity[39]. **Figure 3**a illustrates O_2 adsorption on $L1_0$-CoPt/Pt surface. Ordered $L1_0$-CoPt/Pt core/shell nanoparticles synthesized by co-reduction and heat treatment exhibited a record high half-wave potential ($E_{1/2}$) of 0.96 V (~20 $\mu g_{Pt}/cm^2$, 1600 rpm, 25 ºC) and mass activity (MA) of 2.26 A/mg_{Pt} in aqueous electrolytes by using a rotating disk electrode (RDE). After 30000 potential cycles (0.6-1.0 V) at 60 °C, $E_{1/2}$ shifted negatively by only 7 mV and mass activity was retained at 1.83 A/mg_{Pt} (**Figure 3b** and **3c**). Durability tests in MEAs at PEMFC operating temperature 80ºC suggested high stability of the ordered structure. In MEA tests at 80 °C, initial mass activity at 0.9 $V_{iR\text{-}free}$ achieved 0.56 A/mg_{Pt} and only declined to 0.45 A/mg_{Pt} (80%) after 30000 voltage cycles (0.6-1.0 V), exceeding U.S. DOE 2020 targets for PGM catalyst activity (0.44 A/mg_{Pt}) and stability (<40% loss) (**Figure 3d**). End of life (EOL) elemental analysis demonstrated well preservation of the $L1_0$ ordered core and thin Pt shell, with significant Co in the core (**Figure 3e** and **3f**). Large-area elemental mapping at EOL showed good uniformity of Pt and Co content (Figure **3g**). The $L1_0$ ordering in the core and thin Pt both prevented Co from leaching in the acidic environment and improved oxygenated species-binding energetics on the compressed Pt surface[59]. A simple synthesis strategy and excellent activity and stability in a real fuel cell environment make this highly-ordered $L1_0$-CoPt/Pt core/shell catalyst among the most promising for practical application in PEMFCs.

Although compressive strain in core/shell structures can improve ORR activity, DFT calculations indicated that tensile strain on the Pt (110) facet could also increase ORR activity, and low-coordinated surface atoms could be activated by large tensile strains[51]. Integrating strong lattice, an ordered intermetallic core, and an active shell enhances ORR performance[14,60]. Specific structures including skeleton frameworks[49,61], and 1D nanowires[45] with hierarchical and high-index facets can also improve catalytic activity, because ORR is highly structure-dependent. Porous structures increase reactant-accessible surface area, improving Pt utilization[48,62]. A unique mesostructured Pt-Al skeleton catalyst, with a single atomic layer of Pt on Pt_3Al or Pt_5Al intermetallic cores, was prepared by de-alloying. Its bimodal mesoporous architecture comprised quasi-periodic Pt_3Al/Pt ligaments and mesoporous channels, enhancing catalytic activity[49].

Figure 4a and **4b** summarize reported half-cell activity and stability of recent PtM catalysts, demonstrating the breakthrough provided by highly ordered PtM intermetallic catalysts. **Figure 4c** and **4d** further compare PEMFC performance of PGM cathodes, showing greatly-reduced Pt loading in MEAs using structurally ordered PtM intermetallic catalysts[7,63-68]. This exciting performance improvement suggests that practical applications in the PEMFC industry should emerge quickly.

Advanced carbon supports for low-PGM catalysts

Catalyst supports can be as important as PtM alloy nanoparticles themselves for determining overall MEA performance, which depends upon catalyst utilization, mass transfer, charge transport, and durability. The most common supports are spherical carbon blacks such as Vulcan XC-72 and Ketjenblack, which show reasonable performance. However, their corrosion at high voltages (up to 1.5 V) significantly reduces the electrochemically active surface area (ECSA) of Pt and degrades performance[69,70]. Their susceptibility to corrosion arises mainly from a low degree of graphitization, *i.e.* high amorphous carbon content and lack of long-range ordered graphitic structures[71]. Moreover, relatively weak PtM-support interactions allow migration and agglomeration of PtM nanoparticles under the dynamic operation conditions of PEMFCs. The weak interaction also increases electron-transfer resistance at the catalyst-support interface and thus increases the ORR overpotential. Ideal carbon supports should be highly graphitized to resist corrosion, have high surface area and optimal morphology for uniform nanoparticle dispersion, and exhibit strong metal-support interactions. The demanding U.S. DOE support stability target at the MEA level requires less than 30 mV voltage decrease after 5000 cycles from 1.0 to 1.5 V[7].

Many carbon and non-carbon materials have been studied in order to meet these demanding support stability targets. Although carbides and oxides have intrinsically high corrosion resistance, their poor electrical conductivity and low surface areas have prevented their practical use in PEMFCs.

The most promising supports are still carbon-based. Highly graphitized carbon tubes, particularly large-diameter (up to 500 nm) nitrogen-doped graphene tubes (NGT) have been developed recently. Tests of NGTs in acidic aqueous electrolytes demonstrated good stability under severe conditions, and showed that the graphitized carbon surface interacted strongly with metals[72]. However, their relatively low surface areas (~100 m^2/g) and hollow structures yield low ECSA of Pt and poor dispersion of ionomer within cathodes, leading to disappointing fuel cell performance. The negative outcome suggested that morphologies of carbon supports are crucial for catalyst dispersion with ionomers to increase Pt utilization, facilitate mass transfer, and boost MEA performance.

Engineering carbon supports with high surface area and porous structure is necessary for cathode catalysts. Recent approaches, using metal-organic frameworks (MOFs) to template carbon structures, particularly zeolitic imidazolate framework (ZIF)-derived carbon, show great promise[73,74]. Most of the ZIF's porosity is retained after carbonization. After Pt nanoparticles were deposited on porous carbon derived from Co-doped ZIF-8, Co atoms diffused into the Pt nanocrystals during the subsequent annealing, forming highly ordered Pt_3Co intermetallic particles with enhanced activity and stability. Metal-support bonding was also strengthened by this process[53]. However, the partially amorphous ZIF-derived carbon contains disordered carbon structures and cannot meet fuel cell stability requirements. Increasing corrosion resistance by controlling ligand structures and thermal activation conditions may enhance stability of ZIF-derived carbon supports. In fact, balancing graphitization degree and porosity remains a grand challenge for carbon materials. New synthetic concepts are crucial for overcoming this barrier. Recently, Mn-catalyzed carbonization of a polymer hydrogel showed promise to combine a high degree of graphitization with high surface area (~500 m^2/g) and porosity. The porous graphitic carbon (PGC) exhibited significantly enhanced activity and stability for Pt/C catalysts in MEA tests. Compared with the commercial Pt/C catalyst based on XC-72 carbon black, PGC-supported Pt exhibited five times lower carbon corrosion rates. After 5000 voltage cycles (1.0 to 1.5 V), the Pt/PGC catalyst only lost 30 mV at a current density of 1.0 A/cm^2, while the commercial Pt/C cathode lost more than 200 mV[7]. Exceptionally strong Pt-support interactions arise from optimal nitrogen doping, as demonstrated through X-ray absorption spectroscopy (XAS) and density functional theory (DFT) calculations. This PGC support met the challenging U.S. DOE stability milestone, and we expect this approach to eventually address the support stability issue in PEMFCs.

PGM-free catalysts for PEMFCs

Among PGM-free catalysts, transition metal and nitrogen co-doped carbons (M-N-C, M=Fe, Co, or/and Mn) show the most promising activity and stability in acidic media for the ORR. In particular, Fe-N-C catalysts containing atomically-dispersed FeN_4 moieties, have demonstrated activity approaching that of Pt in aqueous acids as well as encouraging performance in PEMFCs[75-78]. However, the low density of active sites, insufficient stability, and poor three-phase interfaces within the cathode remain grand challenges for these M-N-C catalysts.

Catalytic activity of atomically dispersed M-N-C catalysts. Traditional M-N-C catalyst synthesis methods involve high temperature treatments (>700 ºC) of nitrogen- and carbon-containing compounds, metal sources, and carbon supports[79-85]. However, this method often produces a highly heterogeneous catalyst morphology without precise control of the density and local environments of active sites. As shown in **Figure 5a**[79], polyaniline (PANI)-derived Fe catalysts supported on Ketjenblack exhibited encouraging activity and significantly reduced the gap between PGM-free catalysts and the standard Pt/C catalyst. Durability in a MEA was demonstrated for 700 hours at a relatively low voltage of 0.4 V. Unfortunately, applying a higher voltage of >0.6 V led to substantial performance loss. The catalyst contains multiple carbon phases and metal species, limiting our ability to understand its active components[79]. Designing optimal precursors consisting of N, M, and C sources uniformly mixed at the atomic level is crucial for increasing the density of active sites and strengthening bonds of M-N-C. Due to the unique structure and chemistry, MOFs have been newly emerged as promising precursors for M-N-C catalysts, capable of providing M, N, and C sources connected with covalent bonds. Dodelet *et al.* introduced ZIF-8, a type of MOF containing zinc ions and imidazolate ligands, as a microporous host for additional nitrogen and iron to design a catalyst precursor that was carbonized by multiple heating treatments[86,87]. The final catalyst exhibited enhanced performance in MEAs, especially the power density, suggesting an improvement of mass transfer. However, its nanostructure remained heterogeneous with poor control over chemistry and structure, resulting in insufficient activity. To overcome this issue, support-free synthesis methods use active metal (e.g., Fe or Co) doped ZIF-8 or polymer hydrogel precursors that provide nitrogen and metal dopant sources uniformly dispersed within 3D hydrocarbon frameworks. **Figure 5b** illustrates an example of this strategy, in which Fe ions partially replace Zn ions in tetrahedral Zn-N_4 complexes in ZIF-8 and are chemically bonded with imidazolate ligands[75]. These Fe-N_4 complexes were converted *in-situ* into FeN_4 active sites during thermal activation, providing atomic-level dispersion of Fe active sites[75]. Due to the relatively low boiling point of Zn (*i.e.*, 907 °C), the high-temperature treatment during the catalyst synthesis leads to the evaporation of Zn and creates highly porous carbon morphologies. Thus, most ZIF-8 micropores are retained in the final catalysts, providing exceptionally high active site density[88]. Eliminating inactive carbon supports further increases the active site density. The uniform polyhedral morphology of ZIF-8 was retained in the final Fe-N-C catalyst, providing a rare opportunity to tune particle size and shape of carbon catalysts. This atomically dispersed single Fe-site based Fe-N-C catalyst showed significantly enhanced ORR activity in acid ($E_{1/2}$ of 0.86 V *vs.* reversible hydrogen electrode-RHE), generating a current density of 0.044 A/cm^2 at 0.87 V in a MEA using H_2-O_2 at 1.0 bar, only 30 mV away from the U.S. DOE target at 0.9 V[89]. Under practical H_2-air at 1.0 bar conditions, it yielded current densities of 120 and 380 mA/cm^2 at 0.8 and 0.7 V, respectively[90]. Engineering catalyst morphologies with optimal particle size, shape, and porosity could further increase active-site density and improve mass transfer. Recently, ZIF-8-dervied concave-shaped Fe-N-C catalysts provide large external surface areas and mesopores, therefore exposing more FeN_4 sites inside the carbon particles with enhanced mass transfer. The catalyst exhibited a current density of

0.022 A/cm^2 at 0.9 V$_{IR\text{-}free}$ at 1.0 bar H_2-O_2, and achieved a current density of 129 mA/cm^2 at 0.8 V$_{IR\text{-}free}$ under practical 1.0 bar H_2-air conditions[91].

Atomically dispersed Fe active sites are likely associated with N coordination. Recent DFT calculations, XAS, and Mößbauer spectroscopy analyses suggest that FeN_4 or FeN_{2+2} moieties are the most likely active sites[92,93]. Their electronic structures provide appropriate adsorption energies for O_2 and reaction intermediates. Monotonically decreasing free energy for each successive intermediate step up to OH* should result in excellent electrocatalytic activity and 4e$^-$ selectivity[87]. Novel synthesis procedures to form FeN_4 or FeN_{2+2} coordination with homogeneous distribution in a favorable porous carbon structure is one of future directions to advance Fe-N-C catalysts.

Despite their promise, a major concern for Fe-N-C catalysts is dissolution of Fe in acid to form Fe^{2+}, which reacts with H_2O_2 to generate free radicals through the Fenton reaction, leading to performance degradation and cell failure. Thus, catalysts that are both PGM-free and Fe-free have attracted great attention recently. Co-based catalysts are of interest because of the relatively lower activity of Co for the Fenton reactions. However, previous Co-based catalysts exhibited disappointing activity and Co in these catalysts was mainly present as nanoparticles, limiting the density of CoN_x active sites, and thus the ORR activity[94]. Recently, chemically Co-doped ZIF-8 precursors were prepared, with some Zn atoms replaced by Co to achieve atomic-level homogeneous distribution of Co. The existence of optimal Zn content in precursor helped to maintain the distance between Co^{2+} ions, preventing formation of Co-Co bonds during pyrolysis[95,96]. As a result, atomically dispersed Co coordinated with N atoms was retained after Zn evaporation. A volcano plot relationship between Co content and ORR activity was obtained, in which low Co content results in few CoN_4 active sites, while excess Co content leads to formation of inactive crystalline Co aggregates[97]. Increasing dispersion of CoN_4 sites without clustering is the key to further enhancing catalytic activity. Due to weaker adsorption of O_2 on CoN_4 compared with FeN_4, Co-N-C catalysts are intrinsically less active than Fe-N-C. DFT calculations predict that modifying local defects and carbon structures adjacent to

CoN_4 sites may strengthen O_2 adsorption and reduce the activation barrier for O=O bond breaking. A core-shell structured atomically dispersed Co-N-C catalyst prepared using a surfactant template (F127) exhibited record ORR activity in acidic media, with an $E_{1/2}$ of 0.84 V *vs*. RHE. Cohesive interactions between the surfactant and ZIFs suppressed Co agglomeration and prevented collapse of the ZIF microstructure. More micropores were retained during thermal activation producing an increased density of active sites, likely as CoN_{2+2}. DFT calculations suggest that these sites exhibit enhanced ORR activity through a $4e^-$ pathway compared with traditional CoN_4 sites[98,99]. Like Fe-N-C catalysts, Co-based catalysts also suffer from significant initial activity loss at high voltages (>0.6 V). In addition, compare to Fe, the high cost of Co (~$30,000 per ton) is still a concern. Thus, new chemistry and concepts are still needed for development of more stable and low-cost PGM-free catalysts.

Manganese promotes formation of highly graphitized carbon with enhanced corrosion resistance in electrochemical oxidative environments[100,101]. Fenton reactions involving Mn ions are nearly negligible[102]. DFT calculations predict promising intrinsic activity and stability for the ORR on MnN_4C_y sites. Thus, Mn-based catalysts may provide a new opportunity to achieve enhanced catalyst stability. Unlike Fe and Co, it is very challenging to realize atomically dispersed and nitrogen coordinated Mn single metal sites, due to the strong tendency of forming Mn aggregates and clusters. A two-step doping-adsorption method based on Mn-doped ZIF-8 precursors increased the density of MnN_4 active sites without forming Mn clusters[103]. The atomically dispersed Mn-N-C catalysts exhibited encouraging activity and significantly enhanced stability in acidic media relative to Fe-N-C. The unique porous structure and nitrogen doping of carbon hosts derived from ZIF-8 are crucial for accommodating sufficient MnN_4 sites.

Among Fe-, Co-, and Mn-based catalysts explored as PGM-free catalysts for PEMFCs, Fe-N-C catalysts perform the best so far. As illustrated in **Figure 6a**,[79,90,104] significant activity enhancement of Fe-N-C catalysts, including a positive shift of 100 mV, was achieved over the past ten years using well-defined Fe-coped ZIF-8 precursors rather than the ethylenediamine and PANI used in early studies. However, Fenton reactions must be mitigated. Co-N-C and Mn-N-C catalysts exhibit encouraging activity, but both intrinsic activity and the density of atomically dispersed active sites must be improved to reach practically useful performance levels. **Figure 6b** and **6c** summarize the continued performance improvement of M-N-C catalysts in $E_{1/2}$ and MEA fuel cell power density, respectively. Although the difference in $E_{1/2}$ between M-N-C and benchmark Pt/C catalysts in aqueous acidic electrolytes was only dozens of millivolt, the performance of M-N-C catalysts in real MEAs still falls far short of that of commercial Pt/C. Despite encouraging activity and stability improvements, no PGM-free catalyst has reached the DOE activity target of >0.044 A/cm^2 @ 0.9 $V_{\text{IR-free}}$ in MEAs.

Controlling atomic metal (*e.g.*, Fe, Co or/and Mn) dispersion in partially graphitized and disordered carbon, rather than highly graphitized carbon covering metal aggregates, is crucial for enhancing ORR activity in acidic media **(Figure 7a)**[75]. Two straightforward methods to improve catalytic mass activity and intrinsic activity are outlined in **Figure 7b**[92,97]. Mass activity is improved by maximizing the density of nitrogen-coordinated single metal sites, and intrinsic activity of MN_4 sites can be further enhanced by controlling local geometric and electronic structures.

Stability enhancement of M-N-C catalysts. Limited durability of M-N-C catalysts remains a grand challenge[105]. Mechanistic understanding of degradation is the foundation for addressing stability issues. Stability of M-N-C catalysts is related to both the MN_4 active centers and the carbon phases hosting these active sites. Early fuel cell stability tests using voltage cycling in N_2-saturated aqueous acids/MEAs or tests at a constant low potential of 0.4 V suggested promising durability[79]. However, in the presence of O_2 at more practical potentials (>0.6 V), significant performance loss (~50%) occurred over a few hundred hours[106]. Most catalyst degradation is divided into two phases. Fast degradation in the first phase (up to 20 hours) occurs in both aqueous acidic electrolyte and solid-state electrolyte-based MEAs. Demetallation is a straightforward mechanism for performance loss of M-N-C catalysts containing MN_4 active sites[107-109]. However, deeper understanding of the dependence of demetallation on metal type and operating conditions including voltages, temperature, humidity, pressure, and local chemical environment (*e.g.*, O_2 or H_2O_2 concentration) is still needed. The resulting solvated metal ions within electrodes can further catalyze deterioration of membranes and ionomers, reducing proton conductivity.

Because carbon is the dominant component of M-N-C catalysts (>85 at.%), thermodynamically favorable electrochemical corrosion (0.207 V *vs.* standard hydrogen electrode-SHE) of carbon was identified as a major cause of long-term performance loss. While CO_2 evolution was only detected during fuel cell tests at voltages above 0.9 V, the oxidation of carbon in water to yield oxygen-containing functional groups (*e.g.*, COOH, -C=O, -C-O) takes place at lower voltages. Chemical attack by H_2O_2 and radicals within cathodes also causes carbon corrosion. Carbon corrosion or formation of functional groups can, in turn, drive demetallation of MN_4 sites next to oxidized carbon atoms. Collapse of carbon structures generates additional barriers for mass transfer and charge transport.

ZIF-8-derived atomically-dispersed M-N-C catalysts show encouraging stability, especially at the fully viable and challenging voltage of 0.7 V in MEAs. However, initial fast degradation still limits their practical application[98,103]. MnN_4 sites seems more stable than FeN_4 sites against demetallation during ORR based on recent experimental and theoretical results[103]. Increasing graphitization degree in catalysts may benefit catalyst stability by mitigating carbon corrosion. Use of highly graphitized carbon structures such as graphene and carbon nanotube matrices provides improved corrosion resistance[77,81]. However, increased graphitization leaves fewer defects to accommodate M and N dopants, implying a trade-off between activity and stability for M-N-C catalysts. Performance loss at the MEA level is more complex. Collapse of three-phase interfaces within electrodes, due to degradation of catalyst-ionomer interfaces, hinders charge transport (*i.e.*, of electrons and protons), and mass transfer (*i.e.*, of O_2 and H_2O).

Outlook

Realizing large-scale commercialization of PEMFCs for transportation applications requires addressing key issues of cost, durability, and power density. Low-PGM and PGM-free catalysts are being developed for near- and long-term PEMFC applications, respectively. Several PtM intermetallic catalysts with highly ordered structures have exceeded DOE 2020 activity targets (0.44 A/mg$_{Pt}$) in MEAs with encouraging durability (<40 mV change in voltage loss after 30000 cycle, 0.6-0.95 V). Carbon support durability targets (1.0-1.5 V for 5000 cycles, <30 mV loss) have also been met using highly graphitized porous carbon supports. Achieving power density targets (>1 W/cm^2) at ultra-low Pt loading (<0.15 mg$_{Pt}$/cm^2 in MEAs) requires further advances in both catalysts and electrodes. MEA performance of atomically dispersed Fe-N-C cathodes is approaching the DOE activity target (0.044 A/cm^2 at 0.9 V $_{IR\ \mathrm{free}}$). However, significant improvement in both activity and stability remain essential. In addition to new synthetic chemistry and advanced in-situ characterization tools, theoretical research on ORR pathways and active sites is crucial for further enhancing activity and eventually addressing stability issues of current M-N-C catalysts.

Perspectives on low-PGM catalysts. Fully ordered PtM intermetallic nanoparticles exhibit significantly enhanced activity and stability in both aqueous acids and MEAs. Among studied first-row transition metals (M), Pt-Ni polyhedral nanocrystals have shown the highest activity. However, compositional segregation was often observed in shaped PtNi nanoparticles, with a Pt-rich frame along the edges and corners and Ni atoms segregated in (111) facets. Moreover, due to concerns about the negative impact of Fe-catalyzed Fenton reactions on membranes and ionomers, Fe is virtually excluded from practical fuel cell catalysts. Thus, Co is currently the most promising first row transition metal. Highly-ordered core-shell PtCo structures (*i.e.*, $L1_0$-CoPt/Pt system) showed significantly enhanced activity and durability in MEAs through improved Pt utilization and tuning of the strain of Pt layers for maximum activity[59]. The tetragonal $L1_0$-PtM has M:Pt in a 1:1 ratio, and M (3d) and Pt (5d) atomic orbitals are strongly coupled along the crystallographic c direction. Detailed mechanisms clearly linking the ordered structures and enhanced catalytic performance remain to be fully elucidated. In principle, a maximum of activity can be realized when both the adsorption and reduction of oxygen occur rapidly. Deviations from this optimum lead to either less adsorption of oxygen on the surface or slower reaction of adsorbed species and desorption of products. Deep understanding of ORR mechanisms of these PtM catalysts can guide optimization of Pt layer thickness and Pt:M ratio in the core, which tune the biaxial strain and optimize the ligand effect of M, further weakening the binding of all oxygenated intermediates on the Pt surface and enhancing ORR activity.

During dynamic fuel cell operation, dissolution and reprecipitation of Pt can drive particle agglomeration, reducing ECSA and degrading intrinsic activity. Dissolved Pt and M can diffuse and precipitate in the proton-exchange membrane and ionomer, reducing proton conductivity. Development of robust carbon supports with favorable morphology and metal-support interactions is crucial for enhancing durability by improving dispersion of PtM nanoparticles, mitigating carbon corrosion, and inhibiting migration of PtM nanoparticles. Highly ordered intermetallic particles well dispersed onto advanced carbon supports with strengthened metal-support interactions may provide the ultimate solution to performance and stability of low-PGM catalysts.

Perspective on PGM-free Catalysts. Unlike early stage M-N-C catalysts containing inactive and unstable metallic aggregates, 3D MOF- and polymer hydrogel-derived catalysts contain atomically dispersed MN_4 sites within robust carbon structures at significantly increased density. Fe-N-C catalysts exhibit the best activity, but Fe-free catalysts are needed to avoid concerns about Fenton chemistry. Therefore, Co- and Mn-N-C catalysts also hold great promise. Current PGM-free catalysts are not commercially viable due to insufficient activity and stability. To address these grand challenges, researchers in the field should be focussing on the four interrelated objectives outlined in **Figure 8.**

Design structurally-defined 3D precursors with M-N_4 coordination. Tuning the structure of precursors such as MOFs can control active metal site distribution, M-N bonding, and surrounding carbon morphology and structure. The modular nature of MOFs[86] enables precursor production with a range of ligands, local hydrocarbon networks, and M-N_4 content. Correlating catalyst structure to precursor structure will help to explain performance trends. Other available controls include physical properties of MOFs such as crystal size, shape, and porosity. The overall catalyst morphology can be engineered by directly transferring those precursor features into final catalysts through a one-step thermal activation.

Elucidate the roles of metal in promoting activity (*e.g.*, Fe, Co, Ni, or Mn). Precursors with well-defined M-N_4 content are an ideal model system to elucidate active site formation during catalyst synthesis. Key factors associated with mechanistic understanding the role of metals include atomic MN_4 site formation, N doping, and the associated carbon structure and morphology. The behavior of Fe, Co, and Mn in active site formation may each be different and remain to be fully understood.

Identify the optimal carbon in catalysts. Carbon is the dominant component in M-N-C catalysts (>85 at.%), but its role remains controversial. We initially speculated that *in situ* formation of highly graphitized nanocarbons was critical for active site generation[110]. However, recent ZIF-derived atomically dispersed Fe-N-C catalysts with disordered, partially-graphitized carbon show even higher ORR activity ($E_{1/2}$ up to 0.86 V *vs* RHE), relative to graphitized carbon-rich Fe-N-C catalysts (~0.80 V) under identical testing conditions. The role of carbon structure and morphology in determining activity and stability must be understood.

Illuminate catalyst degradation mechanisms. The stability problem must be addressed to make PGM-free catalysts practically viable. Strengthening M-N and C-N bonding in a robust and corrosion-resistant carbon is crucial, subject to precursor structure requirements (*e.g.*, M-N_4 complex formation, local hydrocarbon groups, and crystal sizes) and active site formation during thermal conversion (*e.g.*, temperature, duration, pressure, and atmosphere). Experimental and theoretical studies should focus on metal site dissolution, doped N oxidation, and carbon corrosion.

Translating catalyst activity and stability into MEA performance. For both PGM and PGM-free catalysts, translating the activity and stability observed in aqueous electrolytes into high-performance MEAs remains a grand challenge due to the lack of accurate nanoscale control of three-phase interfaces within electrodes. Trends and observations of RDE activity and MEA performance are often inconsistent. In MEAs, solid-electrolyte ionomers and thicker catalyst layers inhibit transport of both

O_2 and protons, compared to experiments in liquid electrolytes. MEA fabrication methods strongly affect MEA performance in voltage ranges where performance is controlled by kinetics and mass transfer. Different catalysts with unique surface and structural properties may require different fabrication parameters. The durability of catalysts in fuel cells should be studied intensively during long-term operation. Degradation mechanisms of catalysts in MEAs might not be identical to those in acidic liquid electrolyte. Along with degradation of catalysts, collapse of interfaces due to morphology changes of ionomers and carbon corrosion also cause significant performance loss in MEAs.

Compared to PGM catalysts, translating PGM-free catalysts into high MEA performance is even more difficult, due to thicker PGM-free cathodes[104]. We identified the dependence of MEA performance on the particle size of atomically-dispersed Fe catalysts, suggesting that catalyst morphology and nanostructure play important roles in overall MEA performance[90]. Water flooding is more critical in thick PGM-free cathodes. Thus, a balance between hydrophilicity and hydrophobicity, associated with surface chemistry and porosity, is more critical for M-N-C catalysts. Recently, nano-CT was used to study PGM-free cathodes to determine porosity and ionomer dispersion in electrodes and further link these features to fabrication methods and MEA performance[111]. Advanced *in situ* and *ex situ* techniques will be valuable to explore the properties of MEAs, providing new insight into MEA performance and degradation under varied operating conditions.

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Competing interests

The authors declare no competing interests.

Author Information

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Fig. 1 | Development of cathode catalysts for PEMFCs. Low-platinum group metal (PGM) and PGM-free catalyst approaches are currently explored for near- and long-term applications for transportation, respectively.

Fig. 2 | Highly ordered PtM intermetallic catalysts. **a**, Schematic illustration of transformation from a disordered PtM structure to an ordered one. **b**, Multislice simulated ADF-STEM image of an idealized nanoparticle of Pt_3Co and the idealized atomic structure of the Pt_3Co core–shell nanoparticle, in which white and blue spheres represent Pt and Co atoms, respectively[46]. **c**, STEM image of a typical $L1_0$-CoPt intermetallic, where $L1_0$ designates the particular crystal unit cell structure. Pt is colored in red and Co is colored in blue[59]. Panels reproduced from: **b**, ref.[46], Springer Nature; **c**, ref.[59], Elsevier.

Fig. 3 | $L1_0$-CoPt/Pt NPs and their ORR catalytic performance in both rotating disk electrode (RDE) and MEA experiments. **a**, Modeling of O_2 adsorption on CoPt/Pt NPs, **b**, ORR polarization curves obtained before and after accelerated stress testing (AST), **c**, Specific activity and mass activity at 0.9 V at different numbers of cycles tested in aqueous acidic electrolytes via RDE. **d**, Beginning-of-life (BOL) mass activities of $L1_0$-CoPt/Pt tested via current DOE protocols in MEAs for transportation applications. **e**, STEM image of $L1_0$-CoPt/Pt after 30,000 AST cycles in the MEA at 80°C. **f**, Elemental mapping of a representative CoPt NP after cycling in the MEA. **g**, Wide-area elemental mapping of the MEA at end-of-life (EOL)[59]. Panels reproduced from: **a-g,** ref. [59], Elsevier.

Fig. 4 | Current development of PGM catalysts. **a**, Specific activity and mass activity @0.9 V for different PtM intermetallic catalysts in aqueous electrolytes via RDE tests. **b**, Mass activity @0.9 V before and after 10k potential cycling AST (Refs. for Panels **a**, **b**: ● 18 ◈ 28 ▲ 57 ▼ 50 ◆ 17 ▶ 43 ★ 58 ● 44 ⬟ 44 ◨ 45 ◒ 51 △ ▽ 53 ★ 59). **c**, Mass activity @0.9 V for low-Pt catalysts, calculated from PEMFC performance by using H_2-O_2, 1.0 bar, 80°C, and 100 RH%. **d**, Mass activity @0.9 V in beginning of life (BOL) tests and end of life (EOL) tests after 30k potential cycles in PEMFCs (Refs. for Panels **c**, **d**: ■ 63 ○ 64 ▲ 7 ▼ 61 ◇ 42 ◀ 73 ▷ 59 ★ 74 ⬟ 65 ● 66 ☆ 67 ⬠ 68).

Fig. 5 | Typical M-N-C catalyst synthesis using carbon supports (*e.g.,* Ketjenblack) and self-templating material (*e.g.,* ZIF-8). **a**, Carbon supported PANI-FeCo-N catalysts prepared by in situ polymerization onto Ketjenblack with a combination of FeCo species, showing heterogeneous morphologies and containing multiple phases of metals and nanocarbon[79]. **b**, Atomically dispersed Fe-N-C catalyst derived from chemically doped Fe-ZIF-8 without any additional carbon support, showing homogeneous carbon particle morphology and atomic dispersion of Fe-based active sites uniformly dispersed within porous carbon[75]. Panels reproduced from: **a**, ref.[79], AAAS; **b**, ref.[75] , ACS.

Fig. 6 | Current development of PGM-free catalysts. **a**, Significant activity enhancement of Fe-N-C catalysts was achieved gaining a positive shift of 100 mV in past ten years through using well-defined Fe-coped ZIF-8 precursors relative to ethylenediamine and PANI studied in early stages. [79,104] **b**, Half-wave potential of various M-N-C catalysts tested in acidic electrolytes. **c**, Maximum power density for PEMFCs using M-N-C as cathode catalysts under H_2-O_2 conditions at 80ºC and 100RH%. Pressures are 1.0 bar and specified otherwise. Refs for b, c: ▼[94](no MEA test), ▶[106], ⬢[85], ★[81](1.4 bar), ⬟[83], ●[96], ⊞[75](no MEA test), ⊠[97] (2.0 bar), ◧[99](no MEA test), ●[98], ⬡[77](no MEA test), ⨻[76], ⬟[88], ◒[84], ●[91](2.5 bar), and ☆[103]. Panels reproduced from: **a**, ref.[96], Elsvier; ref.[74], AAAS.

Fig. 7 | Directions to improve catalytic activity of M-N-C catalysts. **a**, Controlling atomic metal (*e.g.*, Fe) dispersion into partially graphitized and disordered carbon phase, instead of highly graphitized carbon covering metal aggregates[75]. **b**, Strategies to improve the density of active sites in the form of MN_4 and enhance intrinsic activity by modifying local carbon structure adjacent to MN_4 sites.[92,97] Panels reproduced from: **a**, ref.[75], ACS; **b**, ref. [92], ACS and ref.[97], Wiley.

Fig. 8 | Four interrelated scientific objectives for advancing M-N-C based PGM-free catalysts. They are the designing structurally-defined 3D precursors with M-N_4 coordination, the elucidating the roles of metal in promoting activity, the identifying the optimal carbon in catalysts, and the illuminating catalyst degradation mechanisms.