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Application and Development of Non-noble Metal Catalysts in Hydrogen Fuel Cells

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Abstract. Hydrogen fuel cells are a cornerstone technology for future sustainable energy systems, prized for their high energy density and zero-emission operation, particularly for electric vehicle applications. While platinum-based catalysts currently dominate the market due to their excellent oxygen reduction reaction (ORR) activity, their prohibitive cost and scarcity represent significant obstacles hindering the large-scale commercialization of fuel cells. Consequently, significant research has focused on developing cost-effective alternatives, including nitrogen-coordinated transition metal/carbon composites, functional transition metal oxides, and heteroatom-doped carbons. This review highlights recent advancements in these non-noble metal catalysts, summarizing their catalytic mechanisms, discussing prevailing challenges, and outlining key strategies for enhancing their performance toward practical implementation.

Keywords: catalyst, hydrogen fuel cell, oxygen reduction reaction, non-noble metal, electrocatalysis

1. Introduction

The growing urgency of energy shortages and environmental degradation has driven the pursuit of sustainable and environmentally friendly energy alternatives. Recognized for their superior efficiency and low environmental impact, hydrogen fuel cells are considered a compelling energy alternative. These devices electrochemically convert hydrogen and oxygen into electricity, with water as the sole byproduct, positioning them as a critical solution for mitigating climate change [1]. For instance, a breakthrough by the University of Science and Technology of China resulted in a hydrogen battery with an energy density of 2825 Wh/kg, a near tenfold increase over typical lithium-ion batteries (250–300 Wh/kg), promising to significantly extend electric vehicle range. Moreover, Fuel cells exhibit 50–60% efficiency, rising beyond 90% in CHP setups, markedly outperforming conventional thermal engine efficiency [2]. The fundamental electrochemical reactions in a fuel cell include hydrogen oxidation at the anode and oxygen reduction at the cathode. The working principle is depicted in Figure 1. The representative electrode reactions under alkaline conditions are:

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$$\begin{aligned} \text{Cathode}: &\quad O_2 + H_2O + 2e\mu \rightarrow 2OH\mu \\ \text{Anode}: &\quad H_2 + 2OH\mu \rightarrow 2H_2O + 2e\mu \\ \text{Overall}: &\quad H_2 + O_2 \rightarrow H_2O \end{aligned}$$

While the HOR is kinetically facile, due to its multi-electron transfer pathway, the ORR is notoriously sluggish and kinetically limited. The ORR proceeds nearly 100,000 times slower than the HOR, establishing it as the dominant rate-limiting step in hydrogen fuel cells [3]. The choice of catalyst critically determines the overall efficiency and output of hydrogen fuel cells. Most commercial fuel cells depend heavily on platinum-based catalysts due to their superior catalytic efficiency. Nonetheless, their exorbitant cost, scarcity, and susceptibility to CO poisoning greatly hinder widespread commercial deployment. This challenge has spurred intensive research into durable and cost-effective non-noble metal catalysts. Transition metal-based systems, particularly those involving iron, cobalt, and manganese, have garnered significant attention for their natural abundance and promising catalytic properties [4]. Advancing these materials plays a pivotal role in promoting the broad adoption of fuel cell technologies. This review systematically summarizes the recent progress, key challenges, and future outlook for non-noble metal ORR catalysts, aiming to provide guidance for their future design and commercial deployment [5].

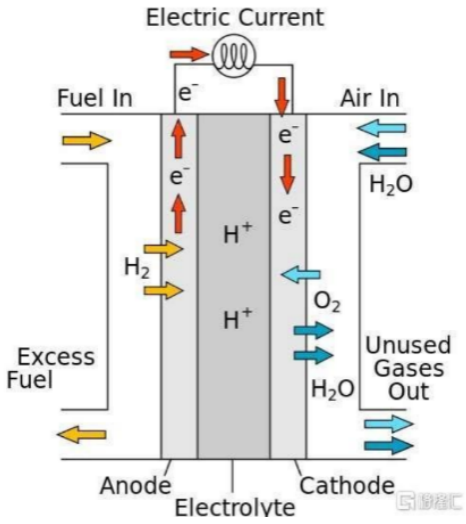


Figure 1. Schematic illustration of hydrogen fuel cell operation

2. Iron based catalyst

2.1. Fe-N-C catalyst

The widespread use of hydrogen fuel cells has been severely restricted by the high cost of noble metal catalysts like platinum and their vulnerability to CO poisoning, even at trace levels. As a result, researchers have devoted increasing efforts to developing non-noble metal catalysts that are both cost-effective and stable, with the goal of facilitating the widespread adoption of hydrogen energy systems. Among them, M–N–C catalysts exhibit significant potential for improving catalytic performance. In these materials, M typically refers to transition metals such as Fe, Co, or Mn. Their unique electronic properties and structural features endow them with remarkable oxygen reduction reaction (ORR) activity, making them one of the most promising alternatives to traditional platinum-based catalysts. Typically, M–N–C catalysts are produced via pyrolysis of nitrogen-containing

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organic compounds, carbon materials, and metal salts under inert conditions. A typical synthesis route is illustrated in Figure 2. For example, Zelenay and co-workers [6] developed a synthesis strategy by mixing short-chain aniline oligomers, carbon materials, and metal precursors, followed by polymerization induced by ammonium persulfate. The mixture then underwent pyrolysis, acid leaching, and a secondary thermal treatment. Among the resulting materials, obtained materials, Fe–N–C catalysts exhibited superior catalytic activity, achieving a peak power density of 0.55 W/cm² in H_2–O_2 PEMFCs. Structural insights from spherical aberration–corrected TEM confirmed the presence of atomically dispersed Fe active sites [7]. Although FeN_4 moieties embedded in the carbon matrix act as essential active sites for ORR, Fe–N–C catalysts still face challenges in maintaining long-term durability. Zhao et al [8]. investigated the degradation mechanism using cyclic voltammetry and relaxation time distribution analyses. Their results showed that monodispersed iron atoms gradually leach from the active sites as Fe^{2+}/Fe^{3+} ions during operation. This leads to a rapid decline in the concentration of metallic iron active centers. After just a few hours of operation, nearly 75% of the active sites became inactive due to iron demetallation. The released iron ions can either cluster into inert iron oxide nanoparticles or diffuse into the electrolyte, leading to a reduction in electrochemical surface area and hindering proton and electron transport within the catalyst matrix. These structural and compositional changes significantly degrade the catalytic performance. Moreover, carbon corrosion can compromise the structural integrity of the electrode, leading to the collapse of the three-phase interface and weakening the interaction between catalyst nanoparticles and ionomers. This ultimately reduces conductivity and hinders proton transfer, further increasing the diffusion distance for reactants and decreasing the overall ORR rate at the cathode. At present, the oxygen reduction capabilities of most M–N–C catalysts remain inferior to those of commercial Pt/C counterparts. Notably, the mechanisms underlying Fe–N–C catalyst degradation under fuel cell operating conditions remain inadequately elucidated [9]. Future investigations should aim to enhance catalyst longevity by refining both the metal active sites and the supporting carbon matrix [10]. Furthermore, rational design of a robust and stable catalyst layer and the incorporation of porous structural materials are essential to enhance the overall performance of cathodic ORR [11].

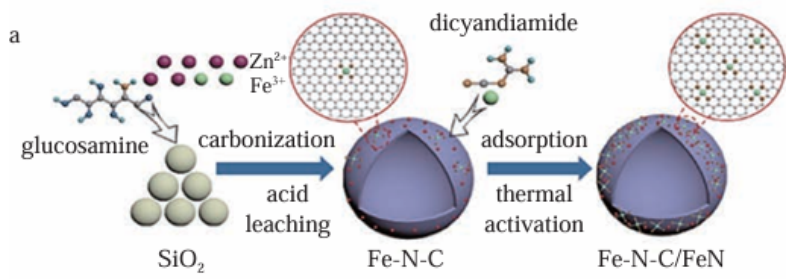


Figure 2. Schematic diagram of Fe-N-C catalyst synthesis process

2.2. Iron cobalt binary catalyst(FeCoTETA/C catalyst)

In iron-based single-atom catalysts such as Fe-N-C, iron atoms are dispersed individually on the catalyst support, theoretically enabling full utilization of metal sites. However, it has been proposed that the performance and reaction specificity of monometallic catalysts can be further enhanced by introducing an additional metal element to construct dual-metal catalytic systems. Notable examples include PtPd and Pt_3Ni catalysts, where alloying platinum with palladium or nickel significantly improves oxygen reduction reaction (ORR) activity. Similarly, heat-treated tetraphenyl porphyrin bimetallic complexes (TMTPP, where TM = V/Fe, Co/Fe, Ni/Fe, or Cu/Fe) also demonstrate high

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catalytic activity. Nevertheless, these systems often rely on expensive metal carbonyl precursors or macrocyclic complexes, limiting their practical scalability. To address these limitations, Zhang et al. synthesized a cost-effective FeCo bimetallic catalyst using triethylenetetramine (TETA) as a simple chelating ligand. The FeCoTETA/C catalyst was prepared by high-temperature pyrolysis of the Fe-Co-TETA complex supported on carbon under an argon atmosphere, with cobalt partially substituted by iron. Structural and morphological features of the obtained catalyst were validated by XRD, TEM, EDX, and XPS analyses. These characterizations are presented in Figure 3. As shown in the XRD pattern (Figure 3a), a broad diffraction peak centered at 24.5° was observed, along with two distinct peaks at approximately 45° and 65°, indicating the formation of face-centered cubic (fcc) FeCo alloy particles incorporated within the carbon framework. TEM imaging and EDX analysis (Figure 3b) clearly reveal the presence of FeCo particles, although they appear to be unevenly distributed across the carbon support. The XPS spectrum (Figure 3c) displays a pronounced C 1s signal at 285 eV, whereas the O 1s (532 eV) and N 1s (400 eV) peaks are relatively less intense. Such weak peaks are presumably attributed to surface-bound oxygen- and nitrogen-containing functional groups on the carbon matrix. Overall, FeCoTETA/C represents a potential ORR electrocatalyst based on earth-abundant metals. When applied in hydrogen fuel cells as a cathodic catalyst, the FeCoTETA/C material achieved a peak power density of 256 $mW \cdot cm^{-2}$ and a current of 514 $mA \cdot cm^{-2}$ at 500 mV, demonstrating its potential for practical applications.

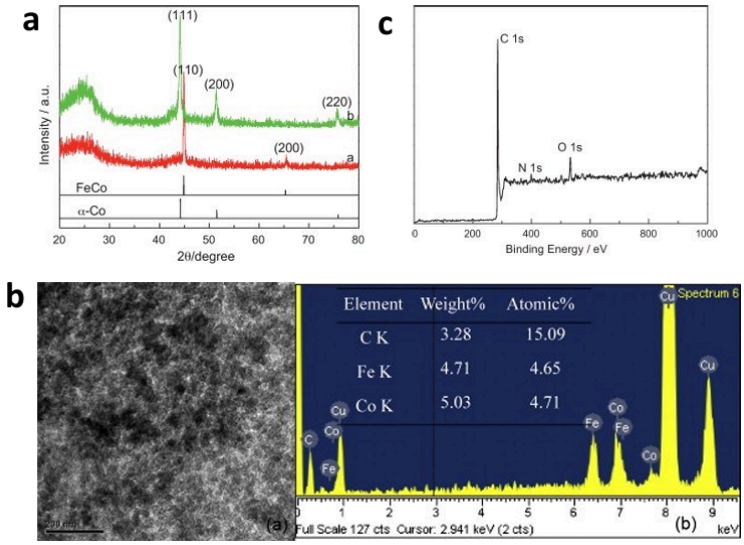


Figure 3. Structural and morphological characterization of the FeCoTETA/C catalyst: (a) XRD patterns of FeCoTETA/C and CoTETA/C. (b) TEM image and EDX spectrum of FeCoTETA/C. (c) XPS spectrum of FeCoTETA/C

3. Manganese-based catalysts

3.1. Manganese oxide catalysts

Among transition metal oxides, group IV and V elements often exhibit high chemical stability in acidic electrolytes. Various Mn-based oxides (e.g., MnO, MnO_2, Mn_3O_4, MnOOH, Mn_2O_3, and Mn_5O_8) have emerged as potential ORR electrocatalysts [12]. In recent studies, MnO has drawn significant interest owing to its low cost, non-toxic nature, and versatile valence states, which provide tunable redox properties. However, most manganese oxides suffer from a large band gap

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and inherently low conductivity, which hinders efficient electron transfer during electrocatalysis. Furthermore, the scarcity of active oxygen adsorption sites on MnO_x surfaces often leads to poor ORR kinetics [13]. To overcome these limitations, approaches such as surface engineering, heteroatom incorporation, and constructing finely dispersed nanostructures have been explored. Among these strategies, creating surface defects—particularly oxygen vacancies—has proven highly effective. For instance, Tian et al. [14] synthesized MnO catalysts with abundant oxygen vacancies via a hydrothermal method. These vacancies, combined with high-valence Mn species, provided a strong synergistic effect that facilitated oxygen molecule adsorption and reduction, achieving a half-wave potential as high as 0.895 V under alkaline conditions. Liu et al. [15] fabricated a series of transition metal oxide thin films using radio-frequency magnetron sputtering. Their findings indicated that oxygen-deficient metal oxides exhibited enhanced electrical conductivity and ORR activity, along with improved resistance to fuel crossover. Moreover, tuning the atomic coordination environment induced surface strain effects, which effectively lowered the adsorption energy of ORR intermediates and accelerated the reaction kinetics. Surface structure also plays a key role in determining ORR performance. Hyeon and colleagues [16] synthesized uniform polymetallic spinel oxide nanoparticles composed of Mn, Co, and Fe. The coexistence of tetrahedral and octahedral coordination sites within the spinel lattice enabled strong synergistic interactions among the metal centers, leading to improved catalytic activity.

3.2. Manganese nitride catalyst

Transition metal nitrides, characterized by metallic conductivity and exceptional resilience, are increasingly regarded as a novel class of ORR-active materials. The nitridation process modifies the d-band configuration of the metal site, leading to a compressed band structure and an elevated electron density near the Fermi energy. This shift enhances electron transport during the catalytic process and improves overall reaction kinetics. A representative manganese-based nitride catalyst, The Mn–N_4 catalyst was fabricated through a sequential two-step synthesis process. The resulting material featured highly dispersed Mn atoms anchored at nitrogen-coordinated sites with abundant accessible active centers. Electrochemical testing revealed that the Mn-N_4 catalyst achieved a half-wave potential of 0.80 V versus RHE in 0.5 M H_2SO_4, with 88% retention of the initial current density after 100 hours of continuous operation. In H_2–O_2 fuel cell testing, a peak power output of 0.46 $W \cdot cm^{-2}$ was recorded [17]. Despite underperforming relative to commercial Pt/C in terms of metrics, Mn-nitride catalysts present advantages in durability and economic feasibility, making them attractive candidates for large-scale implementation. However, their intrinsic conductivity still lags behind that of Pt-based systems and even M-N-C materials [18]. To compensate for this limitation, future investigations should emphasize the development of conductive porous carbon scaffolds with large surface areas to form stable composite structures. Optimizing pore size distribution and catalyst-support interaction will be critical for improving the overall catalytic performance of manganese nitrides in fuel cell systems.

4. Cobalt based catalyst

4.1. Cobalt oxide catalyst

Cobalt, as a Group VIII transition metal, has emerged as a viable non-precious catalyst option for hydrogen fuel cells, owing to its affordability, low toxicity, environmental friendliness, and chemical stability. Compared with iron-nitrogen–carbon catalysts, cobalt oxides such as CoO, Co_2O_3, and

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Co_3O_4 have demonstrated distinct advantages in electrocatalysis. The catalytic efficiency in ORR for cobalt oxides is strongly influenced by both morphology and particle dimensions. For instance, smaller CoO nanoparticles typically exhibit higher catalytic activity than their larger counterparts, and nanorod-shaped Co_3O_4 shows superior ORR performance compared to its nanoparticle form [19]. Recent studies have reported significant advances in the design and optimization of cobalt oxide catalysts. Bhubanendran et al. [20] synthesized three types of Co_3O_4 spinel oxides with different morphologies using a hydrothermal method. Among them, this plate-shaped morphology showed an increased Co^{3+}/Co^{2+} ratio along with rich oxygen vacancies, leading to a half-wave ORR potential of 0.78 V (vs. RHE, 0.1 M KOH). Moreover, both the diffusion-limited and kinetic current densities surpassed those recorded for standard Pt/C catalysts. Sun et al. investigated CoO/carbon (CoO/C) composites and found the improved ORR performance of smaller CoO particles was attributed to reinforced interfacial coupling with the carbon matrix. Liang et al. directly grew Co-based nanocrystals on oxidized multi-walled carbon nanotubes, obtaining a Co/carbon nanotube composite catalyst. This material exhibited enhanced oxygen reduction performance compared to commercial Pt/C under alkaline conditions, underscoring its promising applicability.

4.2. Cobalt nitride and composite catalysts

Transition metal nitrides (MN_x, M = Fe, Co, Mn) have attracted attention as cathodic ORR catalysts for hydrogen fuel cells due to their robust M–N bonds and resistance to corrosion under extreme pH and pressure conditions. Yang et al. [21] investigated a series of cobalt nitride-based materials (Co_xN/C, x = 2, 3, 4), among which Co_4N/C delivered the most favorable ORR performance. In 1 M KOH, it exhibited a half-wave potential of 0.875 V vs. RHE, comparable to that of commercial Pt/C. This performance was ascribed to a well-defined core–shell structure, where a conductive cobalt nitride core was encapsulated within a thin (~2 nm) cobalt oxide layer. Such architecture facilitated efficient charge transport and provided additional active sites, synergistically enhancing ORR kinetics [22]. Building on this, Tang et al. [23] developed $Nb_{0.95}Co_{0.05}N$ with a nanogrid morphology, in which cobalt incorporation modulated the electronic structure of niobium, improving both catalytic activity and material robustness. These studies highlight the promise of multi-metallic nitride systems for tuning electronic states and boosting ORR efficiency. In another study, Wu et al [24]. fabricated a Co_9S_8–N–C composite by integrating cobalt sulfide with nitrogen-doped carbon, as schematically shown in Figure 4. Benefiting from the high electronic conductivity of Co–S compounds and the intrinsic catalytic features of nitrogen-doped carbon, the hybrid structure delivered enhanced ORR performance under alkaline conditions [25].

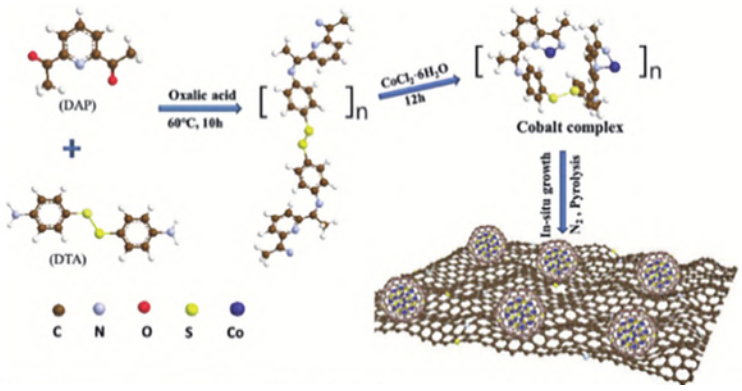


Figure 4. Schematic illustration of the synthesis of the Co_9S_8-N-C composite catalyst

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4.3. Cobalt–conductive polymer composite catalysts

Conductive polymers such as polyaniline (PANI) and polypyrrole (PPy) have garnered interest for their chemical versatility, redox tunability, and controllable conductivity. The integration of cobalt with these polymers offers a promising route to develop efficient electrocatalysts for the oxygen reduction reaction (ORR). In such composites, cobalt often coordinates with nitrogen or sulfur atoms within the polymer framework, resembling the active configuration of cobalt–porphyrin complexes while preserving the polymer's backbone structure. Martínéz et al. synthesized several Co–polymer hybrids via chemical routes, including C–PANI, C–PPy, and C–P3MT systems. Among these, C–PPy–Co exhibited the most favorable performance under both O_2 and N_2 atmospheres, with C–PANI–Co and C–P3MT–Co following. Figure 5 displays the CV profiles for C–PPy and its Co-doped variant. In parallel, a nickel-modified series—PANI–Ni, PPy–Ni, and P3MT–Ni—was also explored alongside their precursors. FTIR analysis verified the successful incorporation of Ni–N and Ni–S coordination in the respective nitrogen and sulfur-rich polymer matrices. The polymeric frameworks maintained morphological integrity, as evidenced by SEM. TGA revealed that Ni doping enhanced high-temperature thermal stability, despite a moderate decline at mid-temperature. This is consistent with the improved carbon framework interaction. Electrochemical tests confirmed ORR activity for all samples. Notably, C–PPy–Ni demonstrated the highest current density (~4×10^{-5} mA·cm^{-2}), reflecting efficient catalytic kinetics. These composites also exhibited excellent operational stability in acidic media (0.5 M H_2SO_4). Furthermore, Ni–polymer hybrids shifted the ORR onset potential positively, whereas nickel-free systems showed a slight negative deviation, indicating different metal–active site interactions.

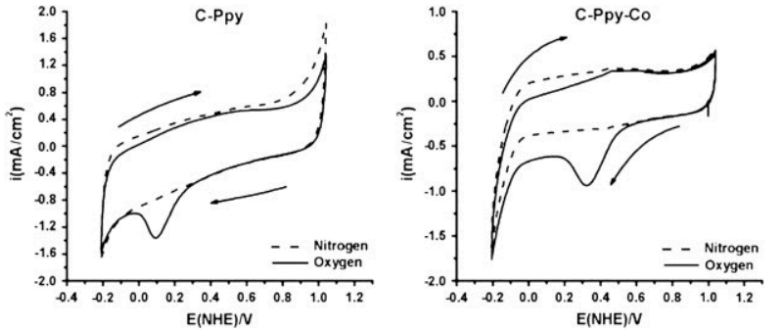


Figure 5. CV profiles of C-PPy and C-PPy-Co recorded in 0.5 M H_2SO_4 at ambient temperature under a 20 mV/s scan rate

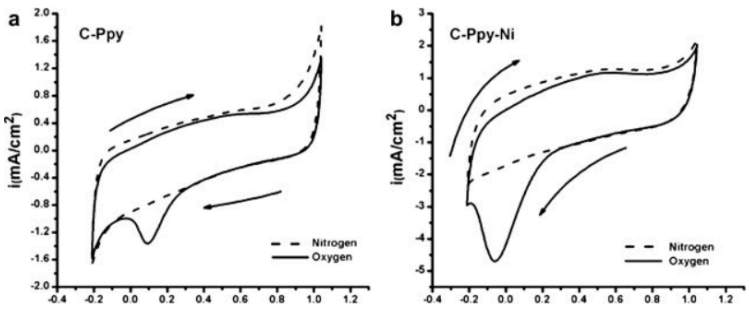


Figure 6. Cyclic voltammograms of (a)C-PPy and (b)C-PPy-Ni acquired in 0.5 M H_2SO_4 at room temperature with 20 mV/s sweep rate

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5. Conclusion

In summary, this review highlights the recent advancements in designing cost-effective alternatives to platinum-based catalysts for the oxygen reduction reaction (ORR) in hydrogen fuel cells. Transition metal catalysts based on iron, manganese, and cobalt have been extensively studied as substitutes. Among them, Fe–N–C catalysts show considerable promise, although their long-term operational stability demands further optimization of active sites and support structures. Manganese oxides and nitrides are attractive due to their affordability, albeit often constrained by insufficient conductivity, thus benefiting from conductive supports or defect engineering strategies. Cobalt-based materials—including oxides, nitrides, and polymer hybrids—have exhibited catalytic activity comparable to or exceeding that of commercial Pt/C under alkaline conditions, underscoring the potential of synergistic interfacial mechanisms [26]. Although non-precious metal catalysts pave a feasible route toward affordable fuel cell technologies, performance degradation in acidic environments remains a key challenge. Looking forward, breakthroughs in heteroatom doping, controlled nanostructuring, and multifunctional composite integration will be essential. With sustained innovation, earth-abundant metal-based catalysts are well-positioned to become central components of the next generation of viable hydrogen fuel cell systems.

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