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Advances and Challenges in Catalysts for Proton Exchange Membrane Water Electrolysis

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Abstract. The development of low-cost, high-stability catalysts is central to accelerating the industrialization of proton exchange membrane (PEM) water electrolysis for hydrogen production and to supporting the global carbon neutrality goal. This review provides a comprehensive overview of the latest advances in PEM water electrolysis catalysts, with particular emphasis on structural optimization of noble metal catalysts and performance breakthroughs of non-noble metal catalysts. Recent studies demonstrate that the loading of precious metals (e.g., Ir <0.3 mg·cm^{-2}) can be significantly reduced while intrinsic activity is enhanced through approaches such as nanoengineering and alloying. Meanwhile, non-precious metal systems—including transition metal phosphates, sulfides, and single-atom catalysts—have shown activity approaching that of precious metals. However, their rapid dissolution and deactivation in strongly acidic anodic environments (e.g., Fe dissolution >50% within 100 h) lead to operational lifetimes far below the industrial requirement (>1000 h). This paper further summarizes the mechanisms and effects of heterojunction construction, heteroatom doping, and strain regulation on catalytic performance, and discusses the role of catalytic layer architecture and membrane–electrode integration in determining macroscopic efficiency. Finally, existing gaps in industrial-level current density validation and mechanistic understanding of degradation are highlighted, pointing to research directions for future catalyst design and system integration toward next-generation high-performance PEM electrolyzers.

Keywords: PEM water electrolysis, hydrogen production, electrocatalysts, noble metal catalysts, non-precious metal catalysts

1. Introduction

Hydrogen, as an important clean and renewable energy source, is one of the key carriers for achieving global carbon neutrality. Major economies around the world are accelerating their hydrogen industry deployment: China plans to demand 37.15 million tons of hydrogen annually by 2030 and increase to about 130 million tons by 2060 [1–2], while the United States aims for 41 million tons of domestic demand by 2050 [3]. In the face of such huge demand, electrolytic water hydrogen production has emerged as the core direction of the green energy transition due to its readily available raw material (water) and pollution-free products. Among the various technologies, proton exchange membrane (PEM) water electrolysis shows significant potential because of its

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compact structure, high efficiency, high hydrogen purity, and fast dynamic response [4–5]. The efficiency of PEM electrolysis is closely tied to the catalytic activity of hydrogen evolution (HER) and oxygen evolution (OER) reactions, making catalyst performance the key to breaking through energy efficiency bottlenecks under harsh acidic and high-potential conditions.

Despite its promise, large-scale application of PEM electrolysis faces several bottlenecks. First, current systems rely heavily on scarce and expensive precious metals such as platinum (Pt) and iridium (Ir), with Ir being indispensable for OER at the anode, thus driving high costs [4]. Second, both noble metal catalysts and carbon-based carriers suffer from serious dissolution, oxidation, agglomeration, and corrosion in the strongly acidic and oxidative environment of PEM systems (particularly OER >1.5 V vs. RHE), severely limiting long-term durability. Third, while non-precious metal or ultra-low precious metal loading catalysts have shown promise in reducing costs, they still face the unresolved challenge of balancing high intrinsic activity with long-term stability under industrial operating conditions. Finally, compatibility issues in integrating high-performance catalysts with membrane–electrode assemblies remain significant, as advanced structures such as nanostructures, core–shell designs, and non-carbon carriers often encounter interfacial instability and additional resistance when scaled to practical devices.

This review aims to systematically analyze recent progress in catalysts for PEM water electrolysis, focusing on both noble metal and non-noble metal systems. By comparing industrially relevant metrics—such as overpotentials below 280 mV at Ir loadings of 0.3–0.5 $mg \cdot cm^{-2}$ versus non-noble catalysts achieving ≈340 mV in transition metal systems —this paper highlights both advances and limitations in current research. Special attention is given to degradation mechanisms, such as Ir dissolution rates above 10^{-5} $mol \cdot m^{-2} \cdot h^{-1}$ in strongly acidic conditions (pH <1) and carbon corrosion currents exceeding 1 $\mu A \cdot cm^{-2}$ [6], and to strategies for extending catalyst lifetimes beyond 5000 hours at industrial current densities [7]. The significance of this study lies not only in proposing material-level design strategies to reduce precious metal loadings to <0.2 $mg \cdot cm^{-2}$ but also in establishing a comparative framework for evaluating catalysts under industrial-grade operating conditions. At the industrial level, adopting low-Ir pathways could reduce electrolyzer costs by over 30% and cut global CO_2 emissions by millions of tons annually; at the policy level, the insights offered here provide technical roadmaps to support initiatives such as China's medium- and long-term hydrogen strategy and the EU's REPowerEU plan.

2. Literature review

2.1. Fundamentals of proton exchange membrane electrolysis water for hydrogen production technology

Proton exchange membrane (PEM) electrolysis has become a mainstream hydrogen production technology due to its high efficiency, compact structure, and ability to produce high-purity hydrogen. The core processes rely on catalysts to drive the hydrogen evolution reaction (HER, Eq. (1)) at the cathode and the oxygen evolution reaction (OER, Eq. (2)) at the anode.

$$\text{cathode } 2H^+ + 2e^- \rightarrow H_{2(g)} \quad \left(E^\circ = 0V_{vs.SHE}\right) \tag{1}$$

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$$\text{anode } 2H_2O_{(g)} \rightarrow O_{2(g)} + 4H^+ + 4e^- \quad \left(E^\circ = 1.23V_{VS.SHE}\right) \tag{2}$$

In the PEM system, the strongly acidic environment (pH 0–2) and high operating potential (>1.5 V vs. RHE) impose stringent requirements on catalysts, demanding excellent corrosion resistance, activity, and stability. Noble metal catalysts (Pt for HER and IrO_2/RuO_2 for OER) currently represent the performance benchmark. However, the high cost of these materials, which accounts for 35–50% of the total electrolyzer cost, is a major barrier to large-scale deployment. Therefore, developing low-cost non-precious metal or low-loading noble metal catalysts has become an important research priority..

2.2. HER catalysts

2.2.1. Structural optimization of noble metal catalysts

Platinum-based catalysts have long dominated due to their superior acidic HER activity (overpotential of only 20 mV@10 mA·cm^{-2} in 0.5 M H_2SO_4). Recent studies have enhanced atomic utilization through nanostructure design:

Porous PtNi nanowires reduce platinum loading to 0.1 mg·cm^{-2} and maintain overpotential at 29 mV. The PtCo core-shell structure has an overpotential of only 50 mV at A current density of 1 A·cm^{-2}. However, the scarcity of platinum resources and price fluctuations still limit its large-scale application.

2.2.2. Non-precious metal HER catalysts

Transition metal compounds and carbon-based materials have become the core direction for alternatives to platinum-based catalysts. Studies have shown that transition metal phosphates (TMPs) such as CoNiP/C exhibit near-precious metal activity in acidic media, reaching a 10 mA·cm^{-2} current density at 0.5 M H_2SO_4 with an overpotential of only 43 mV, and the overpotential increase at 500 mA·cm^{-2} is controlled within 17 mV, The decay trend is significantly better than that of traditional Pt/C catalysts. Two-dimensional transition metal sulfides (TMDs) further optimize electron transport through heterostructure design. The MoS_2/Ni_3S_2 heterojunction reduces overpotential to 48 mV at 10 mA·cm^{-2} and achieves stable operation for more than 100 hours at a current density of 100 mA·cm^{-2}. Single-atom catalysts (SACs) such as the Fe-N-C system have mass activity up to 12 times that of commercial Pt/C (0.9 V vs. RHE) by maximizing atomic utilization, and maintain activity decay of less than 5% for 200 hours at 0.5 A·cm^{-2}. However, the dissolution of metal-active sites in acidic environments (such as Co^{2+} leaching rate >5×10^{-6} mol·h^{-1}) remains a key bottleneck restricting long-term stability, and degradation needs to be suppressed through carrier passivation or surface encapsulation strategies [8].

2.3. OER catalyst

2.3.1. Performance boundaries and innovations of iridium-based catalysts

Commercial IrO_2 requires A current density of 1 A·cm^{-2} driven by 1.67 V, and the iridium loading is typically >2 mg·cm^{-2}. Nanostructure engineering significantly improves atomic efficiency [9]:

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Mesoporous Ir nanosheets (loading 0.5 mg·cm^{-2}) achieved an overpotential of 240 mV@10 mA·cm^{-2} [10]. rO$_2$@RuO$_2$ core-shell material outputs 3 A·cm^{-2} at 1.79 V with 60% reduction in iridium usage. The extreme scarcity and price of iridium resources remain a bottleneck for industrialization.

2.3.2. Optimization of non-precious metal catalysts

Research and development of non-precious metal OER catalysts focused on ruthenium-based materials, transition metal oxides, and perovskite systems. Ruthenium-based catalysts have attracted much attention due to their high intrinsic activity, but they are prone to dissolution at strong acidic high potentials (dissolution rate up to 4.2 μg·h^{-1}@1.5 V). Recent studies have reduced the overpotential to 210 mV@10 mA·cm^{-2} by single-atom Pt modification of RuO$_2$ (Pt$_1$/RuO$_2$) and maintained A low cell voltage of 1.791 V at an industrial-grade current density of 3 A·cm^{-2}, enhancing stability for more than 500 hours. Layered double hydroxides (LDHs) such as MnCo$_2$O$_4$/NiFe LDH optimize OER dynamics through interface-electron coupling, with an overpotential of 270 mV at 10 mA·cm^{-2}, A stable cell voltage of 1.85 V at 1 A·cm^{-2}, and a lifetime exceeding 1000 hours. Perovskite oxides such as SrIrO$_3$ have high mass activity (3.2 times that of IrO$_2$), but their stability at >0.5 A·cm^{-2} is still limited to 300 hours [11]. It is notable that manganese-based oxides have made a breakthrough in acid stability, running at 1000 mA·cm^{-2} in 1 M H$_2$SO$_4$ for more than 700 hours without significant decay, making it possible to industrialize completely non-precious metal systems [12]. The current core challenge lies in balancing high activity with durability by using atomic-level doping (such as Ce, La) or protective layer design to suppress the dissolution of active components.

2.4. Technical anchor points and innovative pathways of this study

For the problem of metal dissolution of non-noble metal catalysts at industrial-grade current densities (such as the activity decay of CoNiP/C at >500 mA·cm^{-2}) and the high potential dissolution challenge of ruthenium-based materials (Ru dissolution rate >4 μg·h^{-1}@1.5 V), this study proposes a systemic solution: By constructing A titanium nitride nanorod array carrier (TiN NRA) to load CoNiP nanoparticles and taking advantage of TiN's superior acid resistance (corrosion current <0.1 μA·cm^{-2}) to suppress the dissolution of active components, the goal is to control the overpotential increase within 20 mV at 1 A·cm^{-2}; A cerium doping strategy was employed to develop the CE-Ruo $_2$ solid solution, with the lattice oxygen stabilization effect of the Ce^{3+}/Ce^{4+} REDOX pair, aiming to reduce the ruthenium dissolution rate to below 1 μg·h^{-1}; Further design Ir@Ru core-shell nanoparticles (core size <2 nm), with the strain effect regulating the surface d-band center (Δd-band = -0.3 eV) to achieve an iridium loading <0.1 mg·cm^{-2} and A cell voltage ≤1.75 V at a current density of 2 A·cm^{-2} [13]. The synergistic breakthrough of the above technical paths is expected to drive a reduction of more than 80% in the use of precious metals in PEM electrolyzers, providing a material basis for lowering the cost of green hydrogen to $2/kg.

3. Method

To build an objective, reliable, and accurate literature analysis basis that reflects the development trends in the field, this study employed a systematic search and critical screening process. The time span was set from 2010 to May 2024, as international hydrogen energy research entered a new stage of activity after 2010, covering key transitions from material innovation to engineering applications.

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The search covered both English and Chinese literature from major research regions (North America, Europe, Asia-Pacific) to ensure comprehensiveness. Core sources included the Web of Science (WOS) core collection and the Scopus database, supplemented by Google Scholar to capture important conference papers and preprints. The search strategy adopted a phased, multi-round iterative approach: the first round used the core formula ("proton exchange membrane" OR PEM) AND ("water electrolysis" OR "hydrogen production") AND (catalyst OR electrocatalyst), followed by refinements based on specific topics. For example, when focusing on anode catalysts, we added AND (OER OR "oxygen evolution reaction") AND ("iridium" OR "IrO_2" OR "non-precious metal" OR "low-iridium"), while performance analysis introduced keywords such as "overpotential", "stability", and "durability". Literature screening followed strict inclusion–exclusion criteria, prioritizing peer-reviewed research and reviews providing repeatable electrochemical performance data (e.g., overpotential at defined current densities, continuous operation duration, turnover frequency) under clearly simulated PEM acidic conditions (such as 0.5 M H_2SO_4 or 0.1 M $HClO_4$). Excluded works included those on alkaline (AWE), anion exchange membrane (AEM), or solid oxide (SOEC) electrolysis, purely theoretical studies lacking experimental data, papers with unclear methodologies, and conference abstracts only. Duplicates were removed with EndNote, after which titles, abstracts, and then full texts were screened. A major challenge was the variability in testing conditions (electrolyte temperature, sweep speed, reference electrode, electrode preparation), so rather than directly comparing reported values, we emphasized relative performance trends and extracted the “best performance” data most representative of each study. All key metrics were standardized (e.g., overpotential as mV@10 $mA \cdot cm^{-2}$, stability as h@10/500 $mA \cdot cm^{-2}$) and compiled into tables for analysis. The analysis went beyond simple listing, focusing on critical comparisons and trend mining across three main dimensions: (i) performance–cost, correlating overpotential at similar current densities with precious metal loading or material cost; (ii) activity–stability trade-offs, evaluating whether “high performance” catalysts passed long-cycle tests or sacrificed durability; and (iii) effectiveness of technical strategies such as nanostructure engineering, alloying, doping, and single-atom catalysis in addressing challenges like Ir dissolution and Pt agglomeration. To minimize bias, literature screening and data extraction were conducted independently by two researchers, with disagreements resolved by third-party arbitration or group discussion. Industry reports and patents were treated cautiously, used only as supplementary validation rather than primary evidence.

4. Result

4.1. HER catalyst

Precious metal platinum (Pt) -based catalysts maintain performance leadership with their ultra-low overpotential, such as a 40% reduction in overpotential at 0.5 M H_2SO_4 compared to commercial Pt/C for lattice strain optimized Pt nanofilms, but resource scarcity (Pt crustal abundance ≈0.005 ppm) and high cost constrain large-scale application; Non-precious metal systems such as sea urchin-like CoP nanocrystals achieve an overpotential of 180 mV@100 mA cm^{-2} in an acidic medium, and P/N co-doped Ru clusters achieve industrial-grade performance of 132 mV@1000 mA cm^{-2} under alkaline conditions [14]. In particular, the self-supporting MoC-Mo_2C heterojunction electrode stably operated for 2400 hours at a current density of 500 mA cm^{-2}, but its long-term durability in acidic environments lagged behind that of Pt-based materials (degradation rate >3 μV h^{-1} vs. <1 μV h^{-1} for Pt).

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4.2. OER catalyst

Iridium-based catalysts (such as IrW nanochannel carriers with A decay rate as low as 4 μV h^{-2} in a 2 A cm^{-2} strong acid environment) remain irreplaceable anode materials for PEM electrolyzers [7], mainly due to their stability advantage under pH≈0 conditions; Ruthenium-based and transition metal oxides (such as NiFe hydroxides with an overpotential of 236 mV@10 mA cm^{-2} in alkaline media) perform well in anion exchange membrane (AEM) electrolyzers, but face serious metal dissolution problems in strongly acidic environments (Fe dissolution rate >50%/100 hours) There are no non-precious metal alternatives to meet the industrial demand (>1000 hours @500 mA cm^{-2}).

4.3. Optimize strategy effectiveness

Nanostructure engineering significantly enhances the utilization rate of precious metals (such as a 6-fold increase in the mass activity of ultra-thin Pt films) and the stability of non-precious metals (the MoC-Mo_2C heterojunction can withstand industrial-grade current density) [15]. Heteroatom doping (P-doped Ru catalyst decay <5% after 100,000 cycles) and single-atom catalysis (Ru single-atom hydrolysis energy barrier reduced to 0.12 eV) optimized the reaction kinetics; Strain control (grain boundary torsion reduces IrO_2 overpotential by 15%) effectively delays the dissolution of precious metals. However, the strategy has yet to break through the core bottleneck: insufficient stability of non-noble metal catalysts in acidic OER environments (<100 hours), poor compatibility of nanostructures with membrane electrode processes (thermal pressure collapse results in activity loss >30%), and the absence of industrial condition validation (<10% study tests >500 mA cm^{-2} current).

5. Conclusion

This research systematically summarizes the research progress of catalysts for proton exchange membrane (PEM) water electrolysis hydrogen production. Precious metal catalysts exhibit outstanding performance, but their high cost and resource scarcity severely constrain large-scale industrial deployment. In contrast, non-precious metal catalysts have attracted extensive attention due to their lower cost and significant potential, yet their long-term stability and catalytic activity remain insufficient to fully meet industrial requirements.

Key research advances have been achieved through structural engineering optimization of noble metal catalysts and the composite design of non-noble metal catalysts, including strategies such as heteroatom doping, alloying, and heterostructure construction. These approaches have effectively enhanced activity and stability, showing promising directions for addressing the limitations of individual catalyst systems. Nevertheless, the fundamental mechanisms underlying improved durability under strongly acidic conditions are not yet fully understood, and the lack of standardized evaluation protocols hinders cross-comparison among studies.

Future research should prioritize the clarification of unified standards for industrial performance testing, particularly under high current density and long-term operating conditions. Moreover, accelerating the exploration of scalable synthesis routes and cost-effective catalyst production will be crucial to bridge the gap between laboratory findings and practical applications. These efforts are essential to support the industrialization of PEM water electrolysis technology and to advance the realization of the global hydrogen energy strategy

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