Proceedings of CONF-FMCE 2025 Symposium: Semantic Communication for Media Compression and Transmission
DOI: 10.54254/2755-2721/2025.GL27119

Advancements in Non-Precious Electrocatalysts for Alkaline Water Electrolysis: Mechanistic Insights and Industrial Application Challenges

Le Li

South China University of Technology, Guangzhou, China
202230530047@mail.scut.edu.cn

Abstract. Alkaline water electrolysis (AWE) is a promising pathway for gigawatt-scale green hydrogen production; however, its widespread deployment is constrained by high overpotentials, catalyst instability, and insufficient durability. This review systematically assesses recent advances (2020–2024) in non-precious electrocatalysts for AWE based on peer-reviewed literature from Web of Science, emphasizing industrially relevant benchmarks including current densities ≥ 500 $mA \cdot cm^{-2}$, durability > 500 h, and compatibility with intermittent operation. Transition metal phosphides (e.g., CoP/N–C) exhibit Pt-like hydrogen evolution activity ($\eta_{10} \approx 45$ mV) through d-band center modulation, although validation at high current densities remains limited. For oxygen evolution, anion-intercalated NiFe-LDH and self-reconstructing chalcogenides (e.g., $FeCoS_2$) achieve overpotentials below 250 mV at 10 $mA \cdot cm^{-2}$, yet their long-term stability under fluctuating renewable energy input has not been established. Heterojunction bifunctional systems (e.g., Ni_3S_2/MoO_2) enable overall water splitting at cell voltages below 1.65 V, but scalable and cost-effective synthesis strategies are still underdeveloped. Remaining challenges include elucidating atomic-scale reconstruction mechanisms, establishing standardized testing protocols under industrial conditions (6 M KOH, 80 °C), and ensuring resilience against grid volatility. Future progress is expected to rely on in situ interfacial characterization, accelerated durability tests under intermittent cycling, and modular electrode engineering, which collectively could drive hydrogen production costs toward $2 per kilogram.

Keywords: Alkaline water electrolysis, non-precious electrocatalyst, d-band modulation, surface reconstruction, bifunctional catalyst.

1. Introduction

Green hydrogen is essential for global decarbonization, but cost barriers and technical challenges continue to limit large-scale deployment. Industry analyses indicate that production expenses remain two- to three-fold higher than those of conventional grey hydrogen, primarily because electricity dominates operational costs. Supply chain constraints—including reliance on imported diaphragms, electrodes, and high-pressure storage systems—hinder scalability. Moreover, underdeveloped logistics infrastructure adds significant cost premiums. Alkaline water electrolysis (AWE) currently

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DOI: 10.54254/2755-2721/2025.GL27119

leads industrial implementation with over 80% market share, benefiting from established infrastructure, compatibility with low-cost nickel electrodes, and 40-50% lower capital investment than advanced alternatives. Three technical bottlenecks, however, impede economic viability: non-precious catalyst inefficiency (>200 mV HER overpotentials), material degradation at industrial current densities (>500 mA·cm^{-2}), and gas bubble accumulation leading to >15% additional voltage loss. Resolving these bottlenecks is essential for cost-competitive green hydrogen production.

Three fundamental barriers critically impede industrial progress. (i) Precious metal catalysts such as platinum and iridium oxide exhibit optimal activity, yet their scarcity and electrochemical dissolution sharply contrast with the limited stability validation of non-precious alternatives like transition metal phosphides. (ii) Atomic-scale mechanisms governing catalyst surface reconstruction during intermittent operation—essential for coupling with volatile renewable energy—remain poorly understood. (iii) The lack of standardized testing protocols under industrial conditions (80 °C, 6 M KOH) prevents reliable cross-study performance benchmarking [1].

This study systematically evaluates advances in non-precious electrocatalysts for AWE, quantifying performance differentials across material classes including phosphides, layered double hydroxides, and chalcogenides under simulated industrial environments. By correlating catalyst design strategies like d-band modulation and heterointerface engineering with long-term stability metrics at high current densities, we establish practical selection criteria for scalable applications. Our analysis further identifies pathways to reduce capital expenditures through electrode manufacturing optimization, supporting international clean energy targets, including the U.S. Department of Energy's strategic goal of achieving $2 per kilogram hydrogen production. Current techno-economic projections estimate production costs of $4.82/kg in 2019, declining to $3.71/kg by 2030 and $1.33/kg by 2050, respectively [2]. This work bridges fundamental catalyst innovation with industrial implementation requirements to advance cost-effective green hydrogen production.

2. Principles of hydrogen production via water electrolysis

Based on the operational environment of electrolytic cells and separator membrane types, modern water electrolysis technologies are classified into four categories: Modern water electrolysis technologies can be categorized into four types based on operating environment and separator membrane: (i) Alkaline Water Electrolysis (AWE), which is fully commercialized; (ii) Proton Exchange Membrane Water Electrolysis (PEMWE); (iii) Anion Exchange Membrane Water Electrolysis (AEMWE); and (iv) Solid Oxide Water Electrolysis (SOEC), which remains at the laboratory research stage [3].

Electrochemically, water electrolysis refers to the process wherein direct current is applied to a closed circuit to cleave H-O bonds in water molecules, generating hydrogen gas at the cathode and oxygen gas at the anode. This process converts electrical energy into chemical energy, with the fundamental electrode reactions expressed as:

$$Cathode: 2H_2O + 2e^- = H_2\uparrow + 2OH^- \quad (1)$$

$$\text{Anode:} 4OH^- = 2H_2O + O_2\uparrow + 4e^- \quad (2)$$

$$\text{Overall Reaction:} 2H_2O = 2H_2\uparrow + O_2\uparrow \quad (3)$$

The theoretical decomposition voltage is derived from the Gibbs free energy expression (ΔG = -nFE). Under standard conditions (0°C, 101.325 kPa): Gibbs free energy change (ΔG) = -237

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kJ·mol⁻¹,Number of transferred electrons (n) = 2,Faraday constant (F) = 96,485 C·mol⁻¹.

This yields a theoretical decomposition voltage of 1.23 V. However, practical electrolysis requires operational voltages of 1.7–2.0 V due to Electrode polarization, Electrolyte resistance, Mass transfer resistance.

Alkaline water electrolysis technology achieved industrial-scale implementation in the mid-20th century. Its technical characteristics include concentrated alkaline solutions (typically 30 wt% KOH or 25 wt% NaOH), historically asbestos cloth, now ion-exchange membranes, system lifetime up to 15 years, efficient water splitting via direct current. Owing to its mature industrial infrastructure and relatively low capital investment, AWE currently remains a viable option for large-scale hydrogen production.

2.1. HER reaction mechanism in alkaline water electrolysis

The hydrogen evolution reaction (HER) occurs at the cathode of the electrolytic cell and comprises three consecutive steps: adsorption, reduction, and desorption. In alkaline solutions:

2.1.1. Electrochemical adsorption (volmer step)

A single electron and hydrogen atom adsorb onto the electrode's active site, forming an M-H* bond (* Reactive site):

$$M + H_2O + e^- \leftrightarrow M - H^* + OH^- \tag{4}$$

2.1.2. Electrochemical desorption (heyrovsky step)

Adsorbed hydrogen atoms undergo electrochemical desorption to form H_2:

$$M - H^* + H_2O + e^- \leftrightarrow M + OH^- + H_2 \tag{5}$$

2.1.3. Recombination desorption (tafel step)

Two adsorbed hydrogen atoms recombine into H_2:

$$M - H^* + M - H^* \leftrightarrow 2M + H_2 \tag{6}$$

Hydrogen gas subsequently desorbs from the electrode surface, completing the HER process.

2.2. OER reaction mechanism in alkaline water electrolysis

The oxygen evolution reaction (OER) constitutes a four-electron transfer process. In alkaline electrolytes:

$$M + OH^- \leftrightarrow M - OH^* \tag{7}$$

$$M - OH^* + OH^- \leftrightarrow M - O^* + H_2O \tag{8}$$

$$M - O^* + OH^- \leftrightarrow M - OOH^* + e^- \tag{9}$$

$$M - OOH^* + OH^- \leftrightarrow M + O_2 + H_2O \tag{10}$$

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Table 1 shows the characteristics of hydrogen production through alkaline electrolysis of water.

Table 1. Characteristics of alkaline water electrolysis for hydrogen production

Category	Description
Operating Conditions	emperature: 40–80°C Current density: 0.25 A cm^{-2} Energy efficiency: 60% Lifespan: 15 years
Advantages	Mature technology Simple operation Low capital costs
Disadvantages	Low electrolysis efficiency Poor adaptability to power fluctuations Corrosive electrolyte Reaction with atmospheric CO_2 forms insoluble carbonates, blocking pores and hindering mass transport Long startup time Slow load response

3. Catalysts for alkaline water electrolysis hydrogen production

The system efficiency of alkaline water electrolysis for hydrogen production is synergistically governed by multiple interconnected parameters: separator membrane characteristics, electrode architecture, catalyst activity, system resistance, operational conditions, and water purity. Within this framework, catalysts play a decisive role in reaction kinetics, primarily comprising three functional systems: alkaline oxygen evolution reaction (OER) catalysts exemplified by transition metal oxides, hydroxides, chalcogenides, phosphides, and nitrides; alkaline hydrogen evolution reaction (HER) catalysts including transition metal alloys, heterostructures, chalcogenides, phosphides, and nitrides; along with bifunctional catalysts capable of simultaneously catalyzing both OER and HER reactions, such as transition metal oxides, chalcogenides/selenides, and phosphides.

Developing high-efficiency non-precious metal catalysts represents the central pathway for reducing hydrogen production costs. Current research imperatives demand concurrent optimization across three critical dimensions: enhancing apparent current densities beyond industrial thresholds (>500 mA cm^{-2}), minimizing ohmic polarization losses, and fundamentally improving intrinsic catalytic activity to achieve breakthrough reaction efficiencies.

3.1. Alkaline hydrogen evolution reaction catalysts

Despite demonstrating exceptional HER activity in alkaline electrolytes—exemplified by Pt/C with an overpotential (η_{10}) of approximately 30 mV—platinum-group materials suffer from prohibitively high costs that critically undermine the economic viability of alkaline water electrolysis. Current state-of-the-art non-precious HER catalysts, such as MoS_2/Ni_3S_2 heterostructures, still require overpotentials exceeding 200 mV to drive current densities of 10 mA cm^{-2}, substantially limiting industrial implementation as documented in recent studies [2]. Transition metal-based catalysts have consequently emerged as the most promising alternatives due to their ability to strike a balance between performance and cost-effectiveness. Selected systems, including nitrogen-doped carbon-supported CoP nanoparticles, exhibit HER activities approaching platinum-group benchmarks (η_{10} = 45 mV), with performance enhancement mechanisms primarily involving d-band center modulation

DOI: 10.54254/2755-2721/2025.GL27119

for optimized hydrogen adsorption free energy (ΔG_H^*), hydrophilic surfaces accelerating water dissociation kinetics, and heterointerfaces facilitating electron transfer.

3.2. Alkaline oxygen evolution reaction catalysts

Catalytic systems for the oxygen evolution reaction (OER) in alkaline water electrolysis primarily encompass three categories: precious metal-based, transition metal-based, and carbon-based materials. While noble metal catalysts such as RuO_2 and IrO_2 exhibit superior initial catalytic activity, they undergo electrochemical dissolution under high anodic potentials (>1.5 V vs. RHE) in alkaline environments, leading to significant stability degradation as extensively documented. Carbon-based materials like nitrogen-doped carbon nanotubes, despite their low fabrication costs and excellent conductivity, are prone to electrochemical oxidation generating CO_2 within the OER operational potential window (>0.8 V vs. RHE), causing concurrent deterioration of both activity and structural stability. Conversely, transition metal-based OER catalysts demonstrate substantial cost advantages—with raw material prices approximately 5% of noble metals—along with robust electrochemical stability (>500 hours at 100 mA cm^{-2}), effectively circumventing the inherent limitations of precious metal dissolution and carbon oxidation.

Recent breakthroughs in transition metal OER catalysts span diverse material systems including oxides, hydroxides, chalcogenides, phosphides, and nitrides. For instance, lattice strain-engineered Ni-doped Co_3O_4 nanoneedles optimize OOH intermediate adsorption energy, while layered double hydroxides (e.g., NiFe-LDH) significantly enhance electron conduction efficiency through interlayer anion intercalation strategies. Furthermore, chalcogenides such as $FeCoS_2$ undergo surface reconstruction during operation to form active oxygen species, and phosphide/nitride heterojunctions (e.g., CoP/Ni_3N) accelerate O-O coupling kinetics via interfacial charge redistribution. These innovative designs collectively aim to develop next-generation catalysts that simultaneously deliver high intrinsic activity (η_{10} < 250 mV), long-term operational stability (>1000 hours), and industrial current density compatibility (>500 mA·cm^{-2}), thereby establishing a robust materials foundation for scalable alkaline water electrolysis hydrogen production.

3.3. Bifunctional OER/HER catalysts for alkaline systems

Despite substantial progress in developing individual OER and HER catalysts, the conventional requirement for separate production facilities and synthetic protocols significantly increases capital investment. Consequently, efficient bifunctional catalysts capable of simultaneously catalyzing both oxygen and hydrogen evolution reactions in alkaline electrolytes are essential for reducing hydrogen production costs. Notable systems include NiFe-layered double hydroxides grown on nickel foam (NF) substrates, which serve as effective bifunctional electrocatalysts for overall water splitting as evidenced by recent studies. Additional bifunctional electrocatalysts reported in the literature encompass transition metal oxides [3], sulfides/selenides [4], and phosphides [5-7], collectively demonstrating the versatility of non-precious material systems. The distinctive attributes of these three catalyst categories are systematically categorized by their target reactions, representative materials, performance benchmarks, and enhancement mechanisms.

Table 2 summarizes the properties and characteristics of the catalysts in the three types of systems respectively.

DOI: 10.54254/2755-2721/2025.GL27119

Table 2. Attributes and characteristics of three catalyst systems

Catalyst Type	Representative Material	Target Reaction	Key Performance (η_{10} / Overpotential)	Advantage Mechanism
HER Catalyst	CoP/N-C	HER	~45 mV	d-band center modulation (ΔG_H*optimization)
OER Catalyst	NiFe-LDH	OER	<250 mV	Anion intercalation / Electron conduction
Bifunctional Catalyst	Ni_3S_2/MoO_2	Overall Water Splitting	<1.65 V	Interfacial charge redistribution

4. Emerging research trends in alkaline water electrolysis hydrogen production

Despite the operational simplicity and cost advantages of alkaline water electrolysis, further development remains imperative for low-temperature systems and high-power configurations. As the cornerstone technology for achieving a zero-carbon hydrogen economy, alkaline water electrolysis has emerged as the primary solution for scaling renewable energy-derived hydrogen production. This prominence stems from its mature process architecture, streamlined system design, and significant cost efficiency—exhibiting 40%-50% lower capital expenditure compared to proton exchange membrane alternatives. While the technology employs non-precious electrocatalysts (e.g., nickel-based alloys) for efficient hydrogen generation under moderate temperatures, the highly corrosive alkaline environment (e.g., 30 wt% KOH solutions) imposes stringent material durability requirements that restrict catalyst selection. Although advances in novel composite catalysts (such as NiFe-LDH/carbon nanotube systems) have been achieved, their complex synthesis protocols and elevated production costs continue to hinder industrial adoption.

In the domain of critical materials, traditional asbestos separators are being progressively replaced by polysulfone-based polymeric composite membranes and anion-exchange membranes due to environmental concerns. These advanced materials enhance gas purity beyond 99.95% through optimized microporous structures and ion-conduction networks. System efficiency is co-regulated by multiple interdependent parameters: separator ion selectivity, intrinsic catalyst activity, electrode conductivity, ohmic polarization effects, and operational parameter optimization. Current energy efficiency bottlenecks primarily originate from three sources: interfacial resistance surges caused by bubble blockage at electrode surfaces, the high activation energy barrier (>1.23 eV) inherent to the four-electron OER process, and additional voltage losses (>0.3 V) induced by concentration polarization. Implementing electrode micro-nanoengineering to create superaerophobic surfaces, introducing electrolyte additives (e.g., K_2WO_4 reducing OER overpotential by 30–50 mV), and optimizing flow fields can collectively decrease energy consumption by 5%–8% [8].

Notably, electrolyzers and electrodes constitute 65%–70% of total system costs. While inexpensive electrode materials may reduce initial investment, electricity expenses account for 50%–60% of operational expenditures, presenting a fundamental constraint to scalability. Integrating alkaline electrolysis with volatile renewable sources (wind/PV) through renewable power-to-hydrogen conversion to establish distributed energy storage systems is essential for sustainable hydrogen development. However, this approach faces persistent challenges including long-term efficiency decay (15%–20% reduction after 2000 hours) and accelerated separator degradation under high current densities (>500 $mA \cdot cm^{-2}$) [9-11]. Future advancements must prioritize three critical

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pathways: developing corrosion-resistant bifunctional catalysts targeting η_{10} < 200 mV, designing separators with high ionic conductivity (>0.2 S/cm), and establishing adaptive control strategies for intermittent power supply—collectively driving alkaline water electrolysis toward enhanced economic viability and sustainability.

5. Conclusions and outlook

Hydrogen energy stands as the most promising clean energy vector, whose sustainable development fundamentally relies on realizing carbon-neutral pathways through renewable-powered water electrolysis. Alkaline water electrolysis (AWE) has emerged as the cornerstone technology for large-scale hydrogen production, leveraging its mature process architecture, simplified system design, long-term operational stability, and substantial cost advantages—exhibiting 40%–50% lower capital expenditure than proton exchange membrane electrolyzers. While AWE utilizes non-precious electrocatalysts (e.g., nickel-based alloys) for efficient hydrogen generation under moderate temperatures, the highly aggressive alkaline media (e.g., 30 wt% KOH solutions) impose stringent corrosion resistance requirements that restrict catalyst selection. Despite progress in advanced composite catalysts such as NiFe-layered double hydroxide/carbon nanotube systems, their intricate synthesis protocols and elevated production costs continue to impede industrial scalability.

In critical materials development, traditional asbestos separators are being systematically phased out due to environmental hazards and replaced by polysulfone-based polymeric composite membranes and anion-exchange membranes. These advanced separators enhance hydrogen purity beyond 99.95% by tailoring microporous architectures and ion transport channels. System efficiency is governed by synergistic parameters including separator ion selectivity, intrinsic catalyst activity, electrode conductivity, ohmic polarization effects, and operational optimization potential. Primary energy efficiency barriers originate from: (1) interfacial resistance escalation caused by gas bubble accumulation at electrodes, (2) the high activation energy barrier (>1.23 eV) inherent to the four-electron oxygen evolution reaction, and (3) additional voltage losses (>0.3 V) induced by concentration polarization. Implementing micro-nanoengineered superaerophobic electrode surfaces, introducing electrolyte additives (e.g., 0.1 M K_2WO_4 reducing OER overpotential by 30–50 mV), and optimizing flow fields can collectively decrease energy consumption by 5%–8%.

Electrolyzers and electrodes represent a critical cost barrier at 65%–70% of total system expenditure; while non-precious electrodes lower capital costs, electricity consumption remains the dominant operational burden at 50%–60%, fundamentally constraining scalability. The integration of Alkaline Water Electrolysis (AWE) with intermittent renewables via power-to-hydrogen is indispensable for establishing distributed energy storage and advancing sustainable hydrogen economies. However, persistent technical challenges impede this vision, notably long-term efficiency decay (15%–20% reduction within 2000 operational hours) and accelerated separator degradation under industrial current densities exceeding 500 $mA \cdot cm^{-2}$. Future progress *must* therefore focus on three core advancements: developing robust, alkali-resistant bifunctional catalysts achieving overpotentials (η_{10}) below 200 mV; engineering separators combining exceptional durability with ionic conductivities surpassing 0.2 $S \cdot cm^{-1}$; and implementing intelligent adaptive control systems capable of managing highly variable renewable power inputs. Successfully addressing these imperatives is essential for enhancing AWE's economic viability and sustainability, ultimately enabling its critical role in global decarbonization efforts.

DOI: 10.54254/2755-2721/2025.GL27119

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