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Nickel-Based Electrocatalysts for Hydrogen Evolution: A Comprehensive Review of Recent Progress

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ABSTRACT

The escalating severity of global climate challenges, coupled with the progressive depletion of fossil fuel reserves, has rendered energy transition an urgent global imperative. Electrochemical water splitting powered by renewable energy sources represents a promising and sustainable strategy for hydrogen production. In this context, the development of efficient electrocatalysts for the HER (Hydrogen Evolution Reaction) is crucial. Among various candidates, nickel-based electrocatalysts have attracted significant attention due to their natural abundance, excellent corrosion resistance, high electrical conductivity, and outstanding electrocatalytic activity across a wide range of electrolytes. Platinum-based materials are considered standard electrocatalysts for the HER. These materials exhibit nearly zero overpotential and high stability as hydrogen producers. However, the high cost and the scarcity of noble metal-based materials hinder their practical use in large-scale applications. This review article focuses on the recent advances in Ni-based electrocatalysts for HER.

Keywords: *Electrocatalyst, Ni-based electrocatalysts, Hydrogen Evolution Reaction (HER), Water splitting*

1. Introduction

Alkaline water electrolysis is a key technology in sustainable hydrogen production, playing a crucial role in the shift toward renewable energy systems. This process relies on the electrochemical decomposition of water to produce hydrogen and oxygen, with its efficiency mainly depending on the catalysts used at the cathode and anode for the HER[1] and OER[2], respectively (1). Hydrogen has been widely recognized as a promising and sustainable next-generation energy carrier to address the above issues due to its high combustion value ($1.42\times10^{8} JKg^{-1}$) and zero emissions with only one product, i.e., water. The electrochemical water splitting ($H_2O_{(L)} \rightarrow H_{2_{(g)}} + \frac{1}{2}O_{2_{(g)}}$, $\Delta G^0 = +237.1\ kJ\ mol^{-1}, E^0 = 1.23V$ versus reversible hydrogen electrode (RHE), 298 K, 1 atm) encompasses HER and OER. However, in practical applications, the overpotentials of the HER and OER, that is, potentials needed to overcome some resistances (such as solution resistance and contact resistance), determine the external applied voltage required to drive the electrochemical water-splitting process, which leads to the potential much larger than 1.23 V. Therefore, one of the main bottlenecks of water splitting is to reduce the overpotentials of the HER and OER through the development of efficient electrocatalysts (2). Nickel-based catalysts have emerged as a central focus in electrocatalysis research, owing to their advantageous electrochemical properties, economic viability, and greater availability compared to noble metal catalysts such as platinum. Nickel inherently possesses catalytic activity toward both the HER and OER, which can be further enhanced through metal alloying or integration into composite

[1] *hydrogen evolution reaction*
[2] *Oxygen evolution reaction*

structures. Recent progress has led to the development of diverse nickel-based materials (including hydroxides, oxides, and phosphides) that demonstrate improved activity and stability, particularly in alkaline media. However, despite these advancements, the practical implementation of nickel-based catalysts in industrial-scale systems remains challenging, primarily due to sluggish reaction kinetics in alkaline environments and concerns regarding long-term durability under operational conditions (3). Continued research efforts are essential to elucidate the underlying degradation mechanisms and to engineer more durable electrocatalysts, maintaining high efficiency under prolonged operational conditions and harsh environments (4). This review presents a comprehensive overview of recent progress in nickel-based electrocatalysts for the HER. The first section outlines the fundamental HER mechanisms across different electrolyte environments, providing essential context for catalyst design. The subsequent sections delve into the latest advancements in Ni-based electrocatalysts, encompassing synthesis strategies, performance evaluation metrics, and comparative analyses of catalytic activity. To facilitate clarity and systematic understanding, the discussed materials are categorized based on their chemical composition, including nickel phosphides, nitrides, carbides, alloys, and oxides/hydroxides.

2. Mechanism of the Electrocatalytic HER

Electrochemical water splitting consists of two fundamental half-reactions: the hydrogen evolution reaction (HER) occurring at the cathode, and the oxygen evolution reaction (OER) taking place at the anode, as illustrated in Fig. 1a (5). The hydrogen evolution half-reaction exhibits different forms depending on the pH of the electrolyte. Under acidic conditions, the HER proceeds on the Electrocatalyst surface according to the following reaction:

$$2H^+ + 2e^- \rightarrow H_2 \qquad (1$$

The OER is with the following reaction(6):

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \qquad (2$$

In alkaline environments, water splitting is typically divided into two fundamental half-reactions: hydrogen evolution at the cathode and oxygen evolution at the anode.

The OER is with the following reaction:

$$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^- \qquad (3$$

The HER mechanism under these conditions is widely understood to proceed through three elementary steps Fig. 1b.

$$H_2O + e^- \leftrightarrow H_{ads} + OH^- \quad \text{(Volmer Step)} \qquad (4)$$
$$H_{ads} + H_2O + e^- \leftrightarrow H_2 + OH^- \quad \text{(Heyrovsky step)} \qquad (5)$$
$$2H_{ads} \leftrightarrow H_2 \quad (Tafel\ step) \qquad (6)$$

The initial Volmer step involves the cleavage of a water molecule, leading to the adsorption of hydrogen atoms onto available active sites on the catalyst or electrode surface. Subsequent hydrogen evolution can proceed via two distinct pathways: an electrochemical route known as the Heyrovsky step, or a chemical route referred to as the Tafel step. Research findings suggest that at low overpotentials, the HER mechanism is primarily governed by the Volmer step, with concurrent contributions from both Heyrovsky and Tafel processes. In contrast, under high overpotential conditions, the Tafel pathway becomes insignificant, and the reaction predominantly follows the Volmer–Heyrovsky route (7).

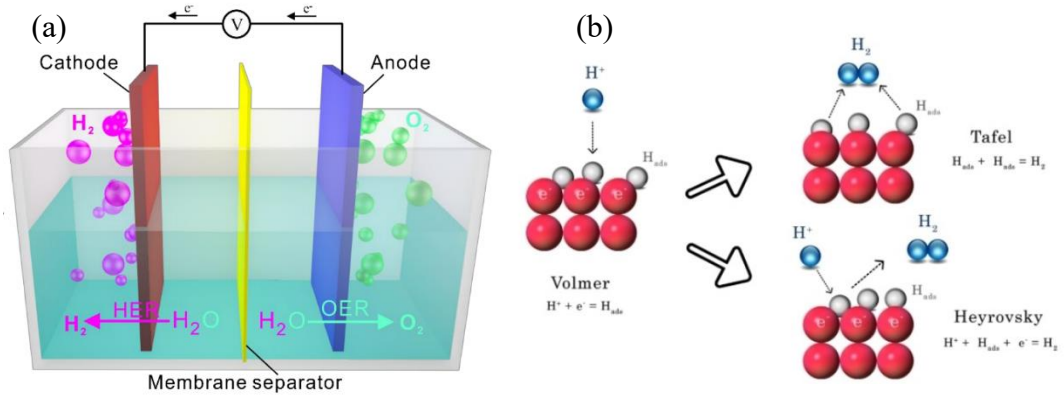

Fig. 1. *(a) Schematic representation of the hydrogen and oxygen evolution reactions (HER and OER) occurring within an electrolyzer (5), (b) Mechanism of the HER in alkaline media (7).*

The HER activity of an electrocatalyst is closely linked to the strength of the metal–hydrogen (Me–H) interaction. This correlation is commonly illustrated using a "volcano" plot, which maps HER current density against Me–H bond strength. As shown in Fig. 2, this trend reveals that an optimal bond strength exists, neither too strong nor too weak, that yields the highest catalytic performance among pure metals (8).

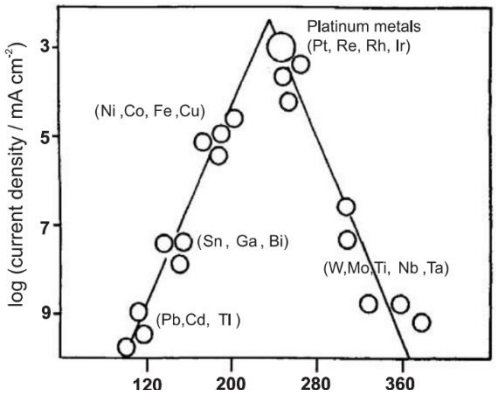

Fig. 2. *The volcano-type relationship between the catalytic activity of various metals and their corresponding metal–hydrogen (Me–H) binding energies (8).*

Nickel-based electrocatalysts enhance the HER by modulating their electronic structure to achieve optimal hydrogen adsorption energies. This tuning can be accomplished through alloying with transition metals such as molybdenum (Mo) or cobalt (Co), or by introducing non-metal dopants like nitrogen (N), which collectively reshape the local binding environment of hydrogen intermediates. These modifications reduce the energy barriers associated with water molecule dissociation and accelerate the recombination of adsorbed hydrogen atoms (H), thereby improving reaction kinetics. In alkaline media, the scarcity of free protons and elevated pH levels hinder HER kinetics, making efficient water activation a critical factor for catalytic performance. This pH-dependent limitation emphasizes the need for surface engineering strategies that tailor the catalyst's microenvironment. Recent studies have demonstrated*

that manipulating local surface conditions, such as inducing pH gradients or designing hydrophilic/hydrophobic interfaces, can significantly lower kinetic barriers and facilitate water activation.

Additionally, incorporating support materials or functional surface groups that promote proton transfer has been shown to enhance HER activity and improve long-term stability in alkaline electrolytes. Given the need for economically viable large-scale hydrogen production, the development of high-performance Ni-based HER electrocatalysts is essential. Extensive research has focused on synthesizing and optimizing the morphology of various nickel-based compounds, as well as investigating their structure–activity relationships and HER mechanisms in different electrolytic environments. This section provides a comprehensive review of recent progress in Ni-based electrocatalysts, covering synthesis methods, electrocatalytic performance, and enhancement strategies (9).

3. Recent Progress in the Development of Nickel-Based Electrocatalysts

Nickel-based compounds have gained recognition as promising alternatives to platinum for HER applications, thanks to their environmental compatibility, wide natural availability, low cost, strong resistance to corrosion, excellent electrocatalytic efficiency, and high electrical conductivity (3). To make large-scale hydrogen production economically viable, it is crucial to develop advanced Ni-based electrocatalysts with high HER activity. A substantial body of research has been dedicated to the synthesis and morphological optimization of various nickel-based materials to improve their catalytic performance. This review provides a comprehensive summary of synthesis methods, evaluations of electrocatalytic activity, comparative performance analyses, and strategies for improvement. The discussion is systematically categorized based on the types of nickel-based compounds, including phosphides, nitrides, carbides, alloys, and (hydro) oxides.

3.1. Nickel Phosphides

Nickel phosphide (Ni_2P) has proven to be an effective industrial catalyst for hydrodesulfurization (HDS) and the water–gas shift (WGS) reaction. Since both HDS and HER involve catalytic processes centered on hydrogen adsorption and dissociation, materials that perform well in HDS applications, such as Ni_2P, are also considered promising candidates for efficient HER electrocatalysis (10). Density functional theory (DFT) calculations conducted in 2005 revealed that the (001) surface of Ni_2P exposes both nickel and phosphorus active sites. The intense interaction between hydrogen atoms and surface Ni sites significantly boosts the HER rate, rendering it comparable to that of [NiFe] hydrogenase enzymes. Ni_2P uniquely combines the high catalytic efficiency characteristic of [NiFe] hydrogenase with the thermal stability of its own surface, positioning it as a compelling non-precious alternative to platinum for HER applications (11). Fig. 3 presents several representative crystalline phases of nickel phosphides, such as Ni_3P, $Ni_{12}P_5$, Ni_2P, Ni_5P_4, NiP, NiP_2, and NiP_3 (12).

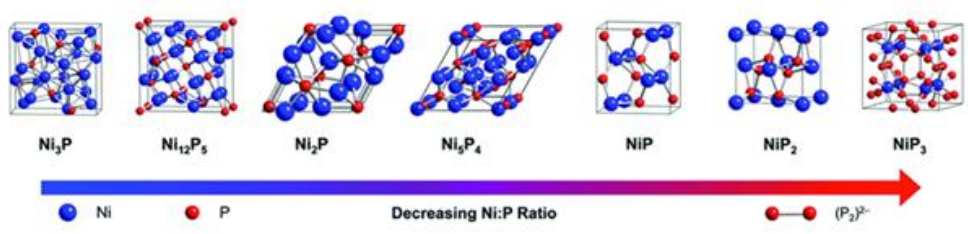

Fig. 3. T*he crystal structures of several nickel phosphide phase (12).*

Studies have revealed that among nickel phosphides, Ni_5P_4 exhibits the highest electrocatalytic activity for the HER, followed by Ni_2P and $Ni_{12}P_5$. This trend shows the critical influence of the Ni:P atomic ratio on HER performance, with phosphorus-rich phases generally demonstrating superior catalytic efficiency (13). Researchers employed density functional theory (DFT) to evaluate the hydrogen adsorption free energy (ΔG) on the (001) surface of four nickel phosphide phases: $Ni_{12}P_5$, Ni_2P, Ni_5P_4, and NiP_2. Fig. 4a and b show the most energetically favorable hydrogen adsorption configurations for each compound and the corresponding ΔG values, respectively. Among these, NiP_2 exhibited the highest ΔG value of approximately 0.16 eV, suggesting superior HER activity compared to the other phases. Interestingly, although Ni_5P_4 showed the lowest theoretical HER activity based on ΔG, experimental results revealed that notable catalytic HER efficiency in nickel phosphides is influenced by factors beyond crystal phase (14).

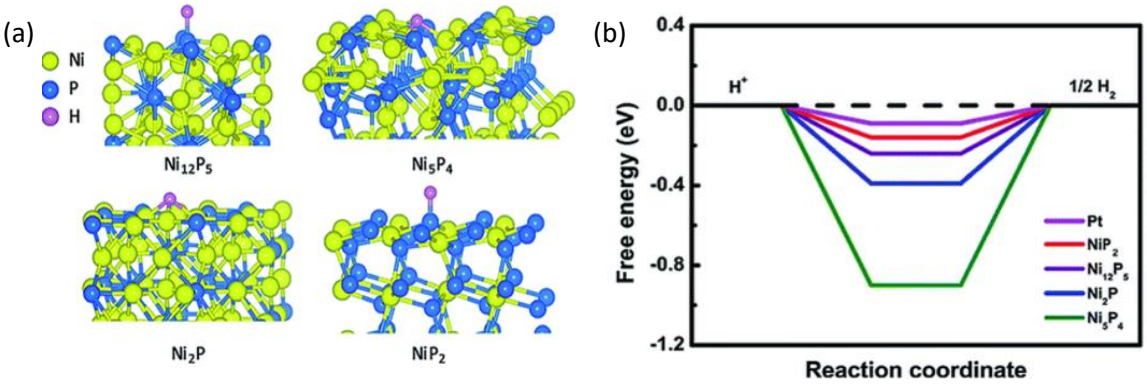

Fig. 4. (a) The most energetically favorable hydrogen adsorption configurations on the (001) surface of different nickel phosphide phases, b) the associated free-energy profiles (14).

To date, several synthesis techniques have been established for preparing nickel phosphide electrocatalysts for the HER, including solution-phase synthesis, solid-state phosphidation, hydrogen-assisted reduction, and electrochemical deposition. Among these, methods such as oil-phase reactions, hydrothermal processes, and solvothermal treatments are typically classified under the broader category of solution-phase approaches (15). Wang et al (16). Investigated iron incorporation into Ni_2P nanosheet arrays and found that Fe doping improved both HER and OER activities. Wang et al (17) explored manganese doping in NiP_2 nanosheets. Linear sweep voltammetry (LSV) results showed that Mn incorporation enhanced HER performance across a broad pH range, from acidic to alkaline conditions. Consistent with previous findings on transition metal-doped nickel phosphides, Mn doping facilitated faster HER kinetics, reduced charge transfer resistance, and increased the electrochemical surface area (ECSA), contributing to improved catalytic efficiency.

Woldu et al (18) developed a series of nickel phosphide electrocatalysts with single-, dual-, and triple-phase compositions, each coated with a thin layer of nitrogen-doped carbon. These materials, namely Ni_5P_4@CN, Ni_2P@CN, Ni_5P_4–NiP_2@CN, and Ni_5P_4–Ni_2P–NiP_2@CN, were synthesized via controlled calcination of a nickel dimethylglyoxime (Ni (dmg) $_2$) precursor followed by phosphating at tailored temperatures. Among them, the triple-phase (Ni_5P_4–Ni_2P–NiP_2@CN) exhibited the highest HER activity, attributed to the emergence of the Ni_5P_4 phase and the formation of multiple heterointerfaces. Electrochemical measurements revealed that this heterostructured catalyst required low overpotentials of 106 mV (acidic) and 150 mV (alkaline) to achieve a current density of 10 $mA{\cdot}cm^{-2}$, along with favorable Tafel slopes and excellent stability. Density functional theory (DFT) calculations supported the experimental findings, showing that the Ni_5P_4 phase and its interfaces with Ni_2P and NiP_2 provided optimal Gibbs free

energies for hydrogen adsorption. This study introduces a rational and scalable strategy for designing multi-phase nickel phosphide catalysts with enhanced HER performance across diverse pH environments.

3.2. Nickel Nitrides

Transition metal nitrides (TMNs) possess distinctive electronic structures that facilitate effective proton adsorption on their surfaces during catalytic reactions. Among TMNs, nickel nitrides have attracted considerable attention as promising HER electrocatalysts, supported by both theoretical modeling and experimental validation. For instance, Cross and co-workers (19)employed dispersion-corrected DFT calculations to investigate the HER activity of Ni_3N across various crystallographic planes, including (111), (110), (001), and (100). Their results revealed that the (111) surface exhibits the most favorable water adsorption energy. The (001) surface demonstrates the lowest activation energy for the Volmer step, indicating its superior capability for water dissociation. These insights offer a deeper understanding of the HER mechanism, particularly the Volmer step. To synthesize nickel nitrides, several methods have been developed, such as solid-state nitridation, plasma-assisted techniques, and solution-phase approaches. Among these, solid-phase nitridation remains the most widely adopted strategy, primarily due to the challenges associated with conventional solution-phase nitridation processes. Sun et al (20) investigated the electrocatalytic performance of transition metal nitrides, specifically Co_2Mo_3N and Ni_2Mo_3N, as potential HER catalysts for proton exchange membrane (PEM) electrolyzers operating in acidic media. Both nitrides demonstrated promising activity, achieving low overpotentials of $149 \pm 8\ mV$ (Co_2Mo_3N) and $158 \pm 10\ mV$ (Ni_2Mo_3N) at a benchmark current density of $10\ mA \cdot cm^{-2}$ in 0.5 M H_2SO_4. When immobilized on nickel foam, both materials maintained stable current densities exceeding $500\ mA \cdot cm^{-2}$ at relatively low voltages, confirming their operational robustness. A key finding of the study was the superior practicality of Ni_2Mo_3N over Co_2Mo_3N, attributed to nickel's lower cost and greater abundance. To identify the catalytically active sites, the authors synthesized a series of Fe-substituted nitrides ($Fe_xNi_{2-x}Mo_3N$, $0.5 \leq x \leq 1.25$). The observed decline in HER activity with increasing Fe content indicated that Ni sites, rather than Mo or N, are primarily responsible for catalytic performance. Complementary XPS analysis further confirmed the inactivity of nitrogen sites and emphasized the importance of maintaining low oxidation states in transition metals for optimal HER activity. Additionally, the comparison between Co_2Mo_3N and Co_3Mo_3N revealed that reducing the number of Co atoms per formula unit leads to higher overpotentials, suggesting that d^8/d^9 metal centers play a critical role in HER catalysis. Overall, this work highlights Ni_2Mo_3N as a promising non-precious metal catalyst for acidic water electrolysis and provides valuable insights into structure–activity relationships in nitride-based HER systems.

3.3. Nickel Carbides

Transition metal carbides (TMCs) have attracted growing attention as efficient electrocatalysts for the hydrogen evolution reaction (HER), owing to their low cost, high electrical conductivity, and exceptional chemical and thermal stability. Their ability to facilitate hydrogen adsorption with minimal energy barriers, along with a favorable density of states (DOS) near the Fermi level, contributes to catalytic behavior comparable to that of platinum. Within this class, nickel carbides have emerged as excellent candidates for HER applications. To date, several synthesis methods have been employed to fabricate nickel carbides, including chemical vapor deposition (CVD), high-temperature thermal treatment, atomic layer deposition (ALD), and solvothermal approaches (21). Yang et al (22) proposed a universal strategy to enhance the hydrogen evolution reaction (HER) activity of transition metal carbides (TMCs) by introducing surface-adsorbed nickel atoms (Ni/TMC). While TMCs such as VC, Fe_3C, Cr_3C_2, and Mo_2C possess high intrinsic catalytic activity and stability, their intense hydrogen binding limits HER efficiency. The Ni activation approach significantly reduces overpotentials and Tafel slopes in both acidic and alkaline media. For example, Ni/VC and Ni/Fe_3C achieved overpotentials as low as 128 and 93 mV in 1 M KOH, and 111 and 112 mV in 0.5 M H_2SO_4 at $10\ mA \cdot cm^{-2}$, outperforming even Pt/C under alkaline conditions. The authors synthesized Ni-activated VC on nickel

foam coated with graphene (Ni-GF/VC) using hydrothermal and magnesium thermal methods. The 3D graphene foam provided a conductive network and high surface area, facilitating rapid electron transfer and efficient hydrogen bubble release. DFT calculations and X-ray absorption analyses confirmed that Ni atoms modulate the d-band center, weaken hydrogen binding, and increase the number of active sites. Additionally, metal activation lowered the synthesis temperature and improved electrochemical stability. Overall, this study presents a versatile and scalable method for activating TMCs through the incorporation of surface metal atoms, providing a promising foundation for high-performance HER electrocatalysts in both acidic and alkaline environments.

3.4. Ni-Based Alloys

In electrocatalytic HER systems, designing nanostructured materials with high surface area is a key strategy for enhancing performance. Such architectures provide a greater number of accessible active sites, thereby enabling higher current densities under the same overpotential. To improve HER efficiency, considerable efforts have been directed toward the synthesis of nickel-based nanostructures, including pure Ni and Ni alloys with tailored morphologies and enlarged surface areas. Among the commonly employed fabrication methods are direct chemical reduction of nickel salts and electrodeposition, both of which offer scalable and controllable routes for producing high-surface-area catalysts (23). Lotfi et al (24) present a comprehensive review on the design and synthesis of nickel-based alloy nanostructured electrocatalysts for HER, with a particular focus on electrodeposition techniques. Recognizing the lack of dedicated reviews in this area, the authors first outline the fundamental HER mechanisms in alkaline media and highlight the challenges associated with catalyst design. They then introduce electrodeposition as a versatile and scalable method for fabricating binder-free, high-surface-area alloy electrodes with tunable morphologies and compositions. The review categorizes Ni-based alloys into single, binary (e.g., Ni–Cu, Ni–Co, Ni–Fe, Ni–W, Ni–Mo), and ternary systems. They discuss how variations in deposition parameters such as voltage, current density, and bath composition can yield diverse nanostructures, including nanowires, nanosheets, nanotubes, nanocones, dendrites, and flower-like architectures. Both template-based and template-free approaches are examined, with emphasis on how structural control and synergistic alloying effects enhance electrocatalytic activity and stability. Ultimately, the authors conclude that electrodeposited Ni-based alloy nanostructures offer a promising route toward efficient and economically viable hydrogen production. Their review serves as a practical guide for selecting appropriate alloy systems and optimizing synthesis conditions to achieve high-performance HER electrodes suitable for industrial applications.

3.5. Ni-Based (Hydro) Oxides

Nickel oxides and hydroxides have been extensively investigated as effective electrocatalysts for the oxygen evolution reaction (OER) in alkaline media. Although their relatively high reduction overpotentials suggest potential applicability for the hydrogen evolution reaction (HER), pristine Ni (hydro) oxides are generally unsuitable for HER catalysis. This limitation arises from excessively strong hydrogen adsorption on oxygen sites and insufficient interaction with nickel sites. Nevertheless, their electronic structure can be strategically modified through the incorporation of metallic species such as Ni or Pt to enhance their catalytic suitability for HER (25). Despite this potential, further efforts are needed to develop cost-effective and highly active Ni (hydro) oxide materials to enhance the overall efficiency and durability of electrolyzers (26). Sayyar et al(27) explored the impact of morphological engineering on the electrocatalytic performance of nickel oxide/nickel foam (NiO/NF) electrodes for the hydrogen HER in alkaline media. Using a hydrothermal synthesis method, they fabricated binder-free NiO/NF electrodes with three distinct morphologies: nanoporous, nanoparticle, and nanograin. Comprehensive characterization via SEM, XRD, and ATR spectroscopy, along with electrochemical measurements, revealed that the nanoporous NiO/NF structure exhibited superior HER activity. The nanoporous NiO/NF electrode achieved an overpotential of 185 mV at 10 $mA \cdot cm^{-2}$, a Tafel slope of 82.7 $mV \cdot dec^{-1}$, and a high electrochemical surface area (ECSA) of 299 cm^2. Its 3D interconnected porous network provided abundant active sites and facilitated efficient charge transfer. Additionally,

electrochemical activation removed surface passivation layers, further enhancing catalytic performance. Stability tests confirmed the robustness of the nanoporous architecture, showing only a 12 mV increase in overpotential after 500 CV cycles, outperforming the other morphologies. This study underscores the importance of morphology control in designing efficient, durable, and cost-effective HER electrocatalysts. The findings offer valuable insights into scalable water-splitting technologies using non-precious metal-based systems.

4. Conclusion

Nickel-based electrocatalysts have demonstrated significant potential as cost-effective and efficient alternatives to noble metal catalysts for the hydrogen evolution reaction (HER), particularly in alkaline media. Through systematic advancements in material design, including phosphides, nitrides, carbides, alloys, and (hydro) oxides, researchers have achieved notable improvements in catalytic activity, stability, and scalability. The ability to tailor electronic structures, optimize surface morphologies, and integrate synergistic components has opened new avenues for enhancing HER performance. Despite these achievements, challenges such as sluggish reaction kinetics under alkaline conditions and long-term durability remain critical barriers to industrial deployment. Continued efforts in mechanistic understanding, advanced synthesis strategies, and rational catalyst engineering are essential to unlock the full potential of nickel-based systems for sustainable hydrogen production and overall water splitting technologies.

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