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Research Article

Mini Review on Innovative Metal-Based Electrocatalysts for Sustainable Hydrogen Production through Water Splitting

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Hydrogen Evolution reaction (HER)[57]

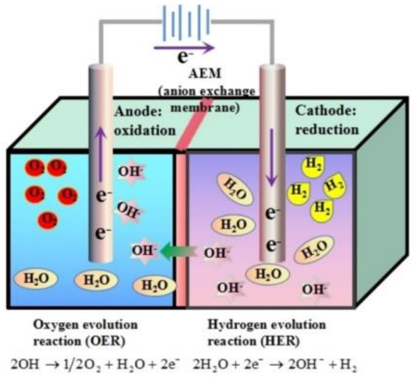

Figure 1: Evolution of Hydrogen from Water

ABSTRACT: The rising global demand for fossil fuels, together with the consequent pollution, has generated substantial environmental issues over energy generation. Hydrogen, as a clean and sustainable energy source, is positioned to be essential in tackling these difficulties both presently and in the future. Water splitting is an effective and promising technique for hydrogen synthesis, with catalysts playing a vital role in the hydrogen evolution reaction (HER) as shown in figure 1. Platinum (Pt) has exceptional efficacy in hydrogen evolution reaction (HER) electrocatalysis, marked by a minimal overpotential approaching zero and a Tafel slope of roughly 30 mV dec^{-1}. The principal barrier to the extensive use of hydrogen production is the advancement of economical and efficient catalysts. Transition metal complexes, recognized for their electrocatalytic efficacy and electrochemical robustness, have surfaced as prime candidates for hydrogen evolution reaction electrocatalysis. This work seeks to examine the present state and recent progress in the design and development of nanostructured electrocatalysts for noble and non-noble metals in hydrogen evolution reactions (HER). Principal methods to improve hydrogen evolution reaction (HER) performance encompass doping, crystallization regulation, structural modification, integration of carbon nanomaterials, and morphological alteration to increase active sites. This study will examine the challenges and potential opportunities in the development of functional and stable electrocatalysts for efficient hydrogen production via water-splitting electrolysis.

Keywords: Hydrogen Production; Electrocatalyst; Green energy, Water Splitting, Hydrogen Evolution

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1. Introduction

The depletion of fossil fuel supplies, rising pollution, climate change, and the ensuing effects on ecosystems and human beings are just a few of the urgent energy and environmental issues facing the world today[1,2]. The pursuit of cleaner, greener, and more sustainable energy sources has become essential as conventional energy systems, mostly reliant on fossil fuels, are increasingly untenable due to their environmental impacts[3]. Hydrogen has emerged as a leading alternative energy source due to its high energy density, environmental friendliness, and promise for clean burning that generates no emissions[4].

Hydrogen possesses several advantages over conventional fuels like gasoline and diesel. For instance, the energy yield from hydrogen is approximately three times compared to traditional fuels like gasoline and diesel, hydrogen has a number of advantages. The energy output from hydrogen is around thrice more, rendering it exceptionally efficient. Hydrogen produces roughly 120 MJ/kg, while gasoline and diesel provide around 45 MJ/kg, demonstrating a substantial energy advantage.[5] Furthermore, hydrogen can energize fuel cells, which exhibit greater efficiency over internal combustion engines. Internal combustion engines dissipate a significant amount of energy as heat, while hydrogen-powered electric motors in fuel cells conserve the majority of energy, experiencing less than 10% energy loss as heat.[6]

Besides its efficiency, hydrogen is economically appealing. At now, hydrogen can be created by various methods, with water electrolysis (WE) being the most promising for the generation of green hydrogen.[7] Electrolysis entails the dissociation of water molecules into hydrogen and oxygen, and when integrated with renewable energy sources, this method can produce hydrogen devoid of environmental implications.[8,9] One of the primary obstacles to the broad adoption of water electrolysis is the necessity for optimal electrocatalysts that can effectively promote the hydrogen evolution reaction (HER) with minimal energy requirements.[10]

Recent developments in the design and development of nanostructured metal-based electrocatalysts, with an emphasis on both noble and non-noble metals, are the subject of this study.[11] Researchers are enhancing the activity, stability, and overall performance of HER electrocatalysts through strategic improvements including doping, crystallization control, and nanostructure engineering.[12] Furthermore, we will examine the obstacles in electrocatalyst design and future outlooks intended to enhance large-scale hydrogen production by water splitting.[13,14]

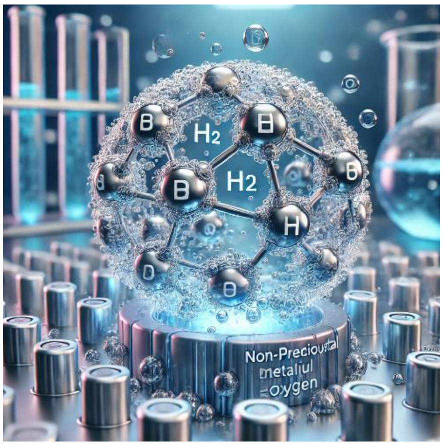

Figure 2. Illustration of non PGM electrocatalysts for Hydrogen Production

2. Hydrogen Evolution Reaction (HER) Overview

Despite its extensive application in the chemical industry, hydrogen's utilization as an energy source has been constrained by infrastructural impediments and production expenses. Conventional hydrogen generation techniques, like steam methane reforming (SMR) and coal gasification (CG), remain widespread but are ecologically detrimental due to their reliance on fossil fuels. Conversely, water electrolysis (WE) is a more environmentally sustainable technique that generates hydrogen with a purity above 99.99%.[15] Notwithstanding these advantages, the substantial expenses linked to WE constitute a considerable obstacle to its extensive adoption. However, research forecasts a reduction in these prices as innovations in renewable energy and electrocatalyst technology evolve.[16]

The process of water electrolysis involves the separation of water into its elemental constituents, hydrogen and oxygen, through the use of electrical energy. This approach requires efficient catalysts to lower the activation energy necessary for the process, particularly for the hydrogen evolution reaction (HER). While platinum (Pt)-based catalysts are currently the most efficient, their prohibitive cost makes them unfeasible for extensive application.[17] Consequently, there is a growing interest in developing alternative electrocatalysts that are both cost-effective and efficient (Figure 2).[18]

2.1. HER Fundamentals

The hydrogen evolution reaction (HER) encompasses three critical stages: adsorption, reduction, and desorption, occurring on the surface of an electrocatalyst. The hydrogen evolution reaction (HER) mechanism has three primary chemical pathways: the Volmer, Heyrovsky, and Tafel stages.

1. Volmer Step: This initial step involves the adsorption of hydrogen ions (protons) onto the catalyst surface through the reduction of water.

2. **Heyrovsky Step**: In this step, the adsorbed hydrogen reacts with an additional proton and an electron, releasing hydrogen gas.
3. **Tafel Step**: This step occurs when two adsorbed hydrogen atoms recombine to form molecular hydrogen (H_2).

$H_2O + e^- \rightleftharpoons H_{ads} + OH^-$ (Volmer step) (1)

$H_{ads} + H_2O + e^- \rightleftharpoons H_2 + OH^-$ (Heyrovsky step) (2)

$2H_{ads} \rightleftharpoons H_2$ (Tafel step) (3)

Among these steps, the Volmer step is often considered the rate-limiting step as it involves the initial bond-breaking process that requires substantial energy. The effectiveness of an electrocatalyst for HER largely depends on its ability to lower the activation energy needed for the adsorption and desorption of hydrogen atoms.[19] Platinum (Pt) is considered one of the best electrocatalysts because the free energy of hydrogen adsorption (ΔGH^*) on Pt is very close to the thermoneutral value, meaning that Pt facilitates the adsorption and release of hydrogen without requiring excess energy.[20]

However, Pt's scarcity and high cost limit its broad application, pushing researchers to seek alternative materials that can approach Pt's performance without the associated cost. The study of transition metals and their compounds as electrocatalysts has revealed promising results in terms of both activity and stability in facilitating HER.

2.2. Acidic and Alkaline Media

The efficiency of the HER process is highly dependent on the medium in which it occurs both in acid or alkaline environments can facilitate the reaction, but the mechanisms and the required catalysts vary.

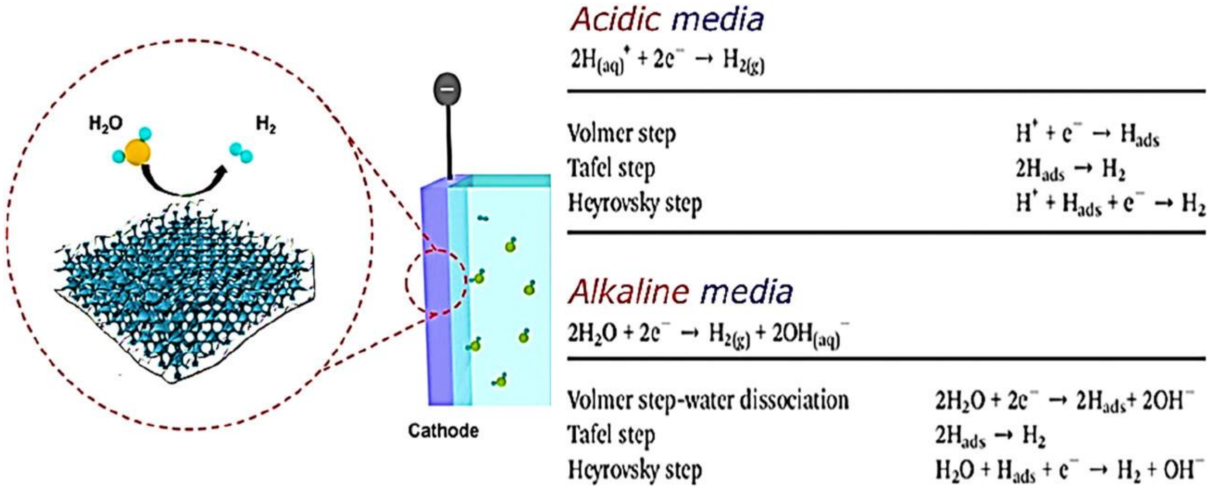

Figure 3. Different mechanisms on the surface of the catalyst in acidic and alkaline environments[60]

In an acidic medium, the key step involves the combination of a proton from the electrolyte with an electron from the electrode to produce hydrogen as depicted in figure 3.[21] In an alkaline medium, the absence of protons necessitates the dissociation of water molecules to provide the necessary hydrogen ions for the reaction. This dissociation makes the reaction kinetics slower in alkaline environments, presenting an additional challenge for catalyst development.[22]

Despite these challenges, alkaline water electrolysis is often favored for large-scale hydrogen production due to the lower cost of materials and the possibility of using non-noble metal-based catalysts. Alkaline media also offer the advantage of greater flexibility in terms of the types of electrocatalysts that can be used, making it a key focus for research into affordable hydrogen production solutions.

2.3 Reaction Rates and Catalytic Efficiency

An essential element in optimizing the hydrogen evolution reaction (HER) is minimizing the kinetic barriers that impede the process. The electrochemical water-splitting reaction necessitates a voltage of 1.23 V at 25 °C and 1 atm pressure. Nevertheless, owing to the significant kinetic barriers present, supplementary potential—referred to as overpotential—is necessary to facilitate the reaction. The catalyst's function is to reduce overpotential by decreasing activation energy, therefore improving the process's overall efficiency.

Figure 4 (a,b,c) illustrates that the catalytic performance of materials in the hydrogen evolution reaction (HER) is often assessed using critical parameters such as overpotential, Tafel slope, and exchange current density.[23] The Tafel slope quantifies the rate of rise in current density relative to overpotential, providing insights into reaction kinetics. A diminished Tafel slope indicates accelerated reaction kinetics, implying that reduced energy is required to generate hydrogen at a specified current density.

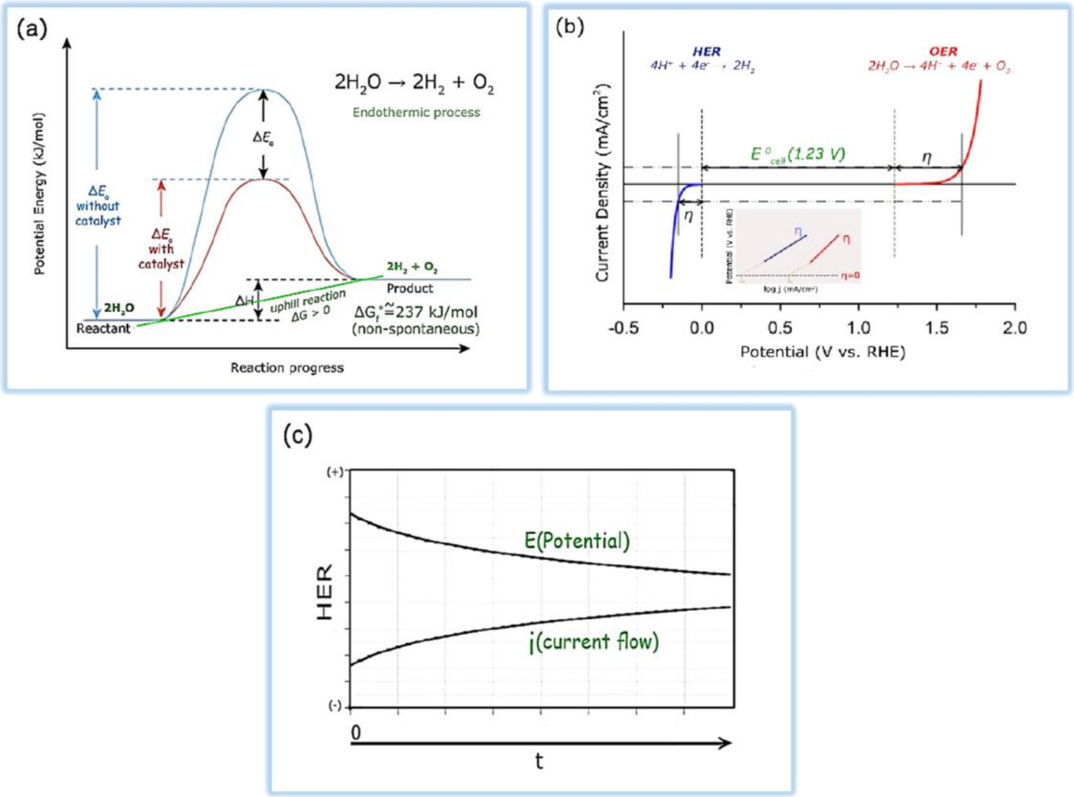

Figure 4. Schematic representation of (a) the catalyst's function in diminishing the activation energy barrier in the reaction; (b) performance assessment criteria for the electrocatalyst, encompassing activity metrics such as overpotential, Tafel slope, and exchange current density; (c) performance assessment criteria for the electrocatalyst, focusing on stability as indicated by current and potential/time curves. Data taken from ref 60

An exceptionally active catalyst demonstrates a synergy of low overpotential, low Tafel slope, and high exchange current density, all of which enhance hydrogen production efficiency. Beyond these metrics, stability is another critical measure. A catalyst that demonstrates long- term stability under operating conditions term stability under operating conditions. Without significant loss in performance is ideal for large-scale hydrogen production.[24,25]

2.4 The Importance of Hydrogen-Bonding Energy and Pseudo capacitance

The adsorption and desorption of hydrogen on the electrocatalyst surface are crucial in influencing the effectiveness of the hydrogen evolution reaction (HER). The free energy of hydrogen adsorption (ΔG_H*) is a crucial metric for quantification. An effective electrocatalyst should provide a ΔG_H* value near zero, indicating that hydrogen adsorption is neither too strong (which would impede desorption) nor excessively weak (which would obstruct adsorption). This ideal equilibrium guarantees that hydrogen may efficiently adsorb and desorb from the catalyst surface, facilitating continuous hydrogen evolution.[26,27]

A further factor influencing HER performance is the pseudocapacitive behaviour of the electrocatalyst. Pseudocapacitance refers to the capacity of the electrocatalyst to store and discharge charge via a rapid, reversible redox reaction, which directly affects the hydrogen adsorption mechanism. An optimal electrocatalyst must exhibit significant pseudo capacitive behaviour, facilitating the effective adsorption of hydrogen species throughout the reaction cycle.[27]

2.5 Volcano Plots: Understanding Electrocatalyst Efficiency

Volcano plots (Figure 5) have traditionally served as a visual instrument to evaluate the efficacy of different electrocatalysts about their hydrogen-bonding energy. These figures often illustrate the correlation between exchange current density (an indicator of catalytic activity) and hydrogen adsorption energy (ΔG_H*). Metals located around the summit of the volcano curve, such as platinum, are regarded as superior electrocatalysts due to their equilibrium between robust and feeble hydrogen adsorption.[28]

In alkaline environments, the hydrogen evolution reaction (HER) activity often diminishes relative to acidic ones, principally due to reduced kinetics of water dissociation. Nonetheless, alkaline water electrolysis continues to be a feasible choice for industrial applications, as it permits the utilization of non-precious metal catalysts, hence enhancing cost-effectiveness. The aim is to build electrocatalysts that function effectively in alkaline conditions by optimizing hydrogen bonding energy and enhancing water dissociation efficiency.[29]

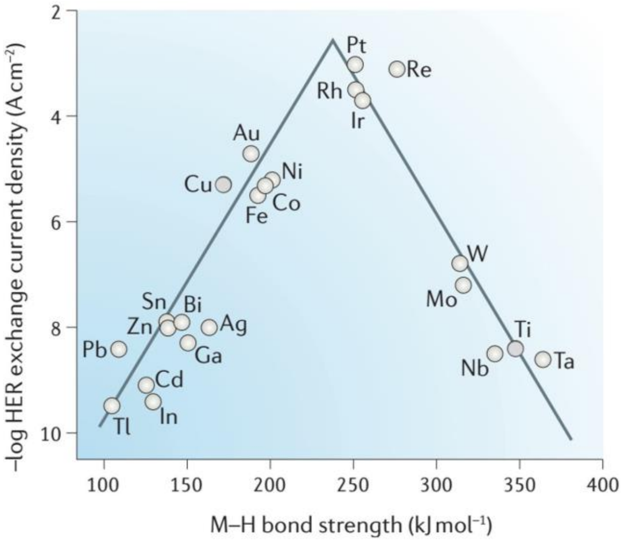

Figure 5. Trasatti's volcano plot for hydrogen evolution reaction (HER). The plot shows the exchange current densities for HER versus the metal–hydrogen bond strength when H adsorbed on the electrode surface. Reprint from[58]. Copyright(2021), with permission from Elsevier.

2.6 Kinetic Isotope Effect (KIE) in HER Studies

The kinetic isotope effect (KIE) is an essential instrument for elucidating the mechanisms of chemical processes, especially those that entail proton transfer. The KIE is founded on the premise that the reaction rate may vary according to the mass of the reacting atoms. KIE experiments in the context of HER generally compare reaction rates between H_2O (light water) and D_2O (heavy water). The denser deuterium ion (D^+) traverses the electrolyte at a reduced velocity relative to the lighter hydrogen ion (H^+), leading to a diminished reaction rate when D_2O is employed.

The detection of a kinetic isotope effect in hydrogen evolution reaction helps elucidate the rate-determining phase of the process. A notable isotope effect indicates that proton transfer is the rate-limiting step in the process. These findings allow researchers to enhance catalysts for accelerated reaction speeds and increased efficiency.[30]

3. Criteria for HER Electrocatalysts

Efficient hydrogen production by electrolysis necessitates the selection of electrocatalysts that fulfil particular performance standards. The criteria encompass parameters including overpotential, Tafel slope, exchange current density, electrochemically active surface area (ECSA), and stability. Each metric is essential in assessing the overall efficiency and feasibility of an electrocatalyst for industrial-scale hydrogen production.

$$2H^+(aq, 1\ M) + 2e^-\ \ H_2(g, 1\ atm)\ E^\circ = 0\ V \qquad (4)$$

3.1 Overpotential, Tafel Slope, and Exchange Current Density

Overpotential (η) is a primary criterion for assessing electrocatalysts. Overpotential is defined as the disparity between the theoretical voltage necessary to initiate the reaction and the actual voltage required. A reduced overpotential indicates a more efficient catalyst. An effective electrocatalyst must exhibit a minimal overpotential at a standard current density of 10 mA/cm².[31]

The Tafel slope, an essential parameter, conveys insights into the reaction kinetics of the hydrogen evolution reaction (HER) process. It is obtained from the Tafel equation (5), which correlates the overpotential with the logarithm of the current density. A diminished Tafel slope signifies accelerated reaction kinetics, resulting in enhanced catalytic activity.

$h = a + b \cdot \log|j|$, where (5
)

a= [2.303.RT/aF] log j_0 (6)

b= -2.303.RT/aF (7)

In this equation, η is the overpotential, and j is the current density.

Exchange current density (j_0) is a measure of the intrinsic catalytic activity of an electrocatalyst. It represents the rate of electron transfer at equilibrium, with a higher exchange current density indicating a more active catalyst. Together, these three parameters—overpotential, Tafel slope, and exchange current density—offer a comprehensive picture of a catalyst's efficiency in facilitating the HER.

3.2 Electrochemically Active Surface Area (ECSA)

The electrochemically active surface area (ECSA) of an electrocatalyst is a crucial determinant of the catalyst's surface availability for participation in the hydrogen evolution reaction (HER). An increased ECSA correlates with a greater number of active sites for hydrogen adsorption, resulting in enhanced catalytic performance. ECSA can be improved by diverse ways, including the implementation of nanostructures or surface changes. Researchers can enhance the overall efficiency of the electrocatalyst by augmenting surface roughness or introducing material flaws, which increases the number of potential active sites.[32]

3.3 Faradaic Efficiency

Faradaic efficiency (FE) is a metric that measures the efficacy of an electrocatalyst in promoting the intended electrochemical reaction (HER) while minimizing side reactions. In the realm of hydrogen evolution, faradaic efficiency denotes the ratio of the total electric charge utilized for hydrogen production relative to other byproducts. A catalyst exhibiting high Faradaic efficiency is advantageous as it guarantees the optimal conversion of energy into hydrogen generation.[33]

Faradaic efficiency = $nH_2/(Q/2F)$ (8)

F is the Faraday constant, ≅96 500 C/mol.

3.4 Turnover Frequency (TOF)

Turnover frequency (TOF) quantifies the catalytic efficacy of a singular active site. It denotes the quantity of hydrogen molecules produced per active site per unit of time. Elevated TOF values signify that each active site substantially contributes to the overall catalytic process, enhancing the efficiency of the electrocatalyst. TOF is very advantageous for evaluating the performance of several electrocatalysts under comparable conditions.[34]

The TOF for HER and OER is computed using the following formulae :

TOFHE = $JA/2nF\ /2$ (9)

TOFOER $JA/4nF/4$ (10)

where A represents the area of the working electrode and J is thecurrent density; the number 2 represents the electrons forH_2/ mol, and the number 4 represents the electrons for O_2/mol; also, n embodies the mole number of active sites, and F is the Faraday constant.

3.5 Hydrogen Bonding Energy (HBE)

The hydrogen-bonding energy (HBE) between hydrogen atoms and the electrocatalyst surface is a crucial factor influencing the efficiency of the hydrogen evolution reaction (HER). If hydrogen bonds excessively to the surface, desorption becomes challenging, hence impeding the reaction rate. If the hydrogen bonds are too weak, the adsorption process is impeded. Consequently, an appropriate hydrogen binding energy is essential to provide efficient hydrogen adsorption and desorption throughout the hydrogen evolution reaction process.

The hydrogen-bonding energy (HBE) between hydrogen atoms and the electrocatalyst surface is a vital determinant affecting the efficiency of the hydrogen evolution process (HER). Excessive hydrogen bonding to the surface complicates desorption, hence hindering the reaction rate. Weak hydrogen bonds hinder the adsorption process. Thus, an optimal hydrogen binding energy is crucial for facilitating effective hydrogen adsorption and desorption throughout the hydrogen evolution reaction process.

3.6 Stability of Electrocatalysts

Stability is a critical factor in the selection of electrocatalysts for the hydrogen evolution reaction, especially for large-scale applications. An electrocatalyst must preserve its activity and structural integrity over prolonged operation. Stability studies frequently entail prolonged electrolysis experiments, during which the overpotential is observed across thousands of cycles to evaluate the catalyst's longevity.[35,36]

Besides short-term stability assessments, industrial applications necessitate that electrocatalysts operate reliably for thousands of hours. Consequently, the creation of materials that withstand degradation in extreme operating circumstances, including elevated temperatures and acidic or alkaline environments, is a primary priority for researchers.[37,38]

3.7 Electrochemical Methods for HER Measurement: The Three-Electrode System

To assess the performance of electrocatalysts in the hydrogen evolution reaction (HER), accurate experimental configurations are essential. A commonly utilized technique is the three-electrode electrochemical cell, comprising a working electrode (WE), a counter electrode (CE), and a reference electrode (RE). This configuration facilitates precise regulation and quantification of the electrochemical reactions taking place at the working electrode.

The working electrode, typically made from materials like glassy carbon or noble metals, serves as the surface on which the hydrogen evolution reaction takes place. The counter electrode provides a surface for the oxidation reaction, ensuring charge balance within the system. Finally, the reference electrode, such as a saturated calomel electrode (SCE) or a reversible hydrogen electrode (RHE), provides a stable voltage reference point, allowing for precise measurement of the overpotential and reaction kinetics at the working electrode.[39,40]

The rotating disk electrode (RDE) is particularly preferred for hydrogen evolution reaction (HER) investigations among the several forms of working electrodes. The RDE operates at regulated velocities, facilitating a consistent electrolyte flow across the electrode surface. This configuration mitigates mass transfer constraints, yielding a more precise assessment of the electrocatalyst's catalytic performance. Controlling the rotation rate allows researchers to elucidate the mass transport characteristics and inherent kinetics of the hydrogen evolution reaction on the catalyst surface.[39,40]

3.8 Pitfalls in HER Data Interpretation and Measurement

Precise assessment of electrocatalytic performance is crucial for the advancement of efficient HER catalysts; yet, specific errors in the methodology may result in inaccurate outcomes. A prevalent problem is electrode fouling. Over time, chemical byproducts or adsorbed species may collect on the working electrode's surface, diminishing its activity and distorting the measurement of overpotential and current density. Consistent maintenance of the electrode surface and meticulous experimental design can alleviate these effects.

The selection of electrolyte significantly impacts the hydrogen evolution reaction (HER) process, since various electrolytes can affect reaction kinetics and catalyst stability. It is essential to choose a suitable electrolyte that corresponds to the reaction conditions, including pH and ionic strength. Furthermore, researchers must consider the impact of the electrolyte on the catalyst's performance to guarantee that the acquired data accurately represents the catalyst's genuine capabilities.

A further drawback stems from the data analytic methodologies employed to interpret the findings. Inadequate analytical techniques, such as erroneous baseline subtraction or neglecting double-layer charging effects, may result in erroneous results on the catalyst's efficacy. Researchers must utilize rigorous methodologies, like Tafel analysis and electrochemical impedance spectroscopy (EIS), to guarantee precise interpretation of electrocatalytic performance data.

4. Classes of HER Electrocatalysts

The search for efficient hydrogen evolution reaction (HER) catalysts has led to the exploration of a variety of materials. Broadly, these materials fall into three main categories[37,40]:

Noble Metal-Based Electrocatalysts
Non-Noble Metal-Based Electrocatalysts
Metal–Organic Framework (MOF)-Derived Electrocatalysts

Each category brings unique advantages and challenges to the table. Noble metals, such as platinum (Pt) and palladium (Pd), are well-known for their excellent catalytic performance but are expensive and limited in supply. On the other hand, non-noble metal-based electrocatalysts, such as transition metal carbides and phosphides, offer a more cost-effective solution but often suffer from reduced activity or stability. MOF-derived materials represent an emerging class of catalysts that combine tunable structures with promising catalytic properties.

4.1 Noble Metal-Based Electrocatalysts

Noble metals like platinum group metals (PGMs), including Pt, Pd, Rh, Ru, and Ir, have long been considered the most effective catalysts for the HER due to their optimal hydrogen adsorption properties. These metals occupy the peak of the so-called "volcano plot," which correlates catalytic activity with hydrogen bonding strength. Their unique electronic configurations enable them to facilitate both hydrogen adsorption and desorption efficiently, making them highly effective for HER applications.[41]

Despite their unparalleled catalytic performance, the high cost and scarcity of noble metals limit their large-scale application. Consequently, researchers are focusing on strategies to reduce the use of noble metals by alloying them with cheaper metals or optimizing their loading onto high-surface-area supports. For instance, Pt can be alloyed with transition metals like Co or Ni to enhance catalytic performance while reducing the amount of Pt required. Additionally, Pt nanoparticles can be dispersed on conductive carbon supports to maximize their utilization and reduce overall costs.[42]

Another noble metal frequently used in HER electrocatalysis is ruthenium (Ru). Although Ru is more abundant than Pt, it still offers excellent catalytic performance. For instance, Ru-based catalysts deposited on multi-walled carbon nanotubes (MWCNTs) as illustrated in Figure 4 have been shown to exhibit low overpotentials and remarkable stability in both acidic and alkaline environments. Such strategies help reduce reliance on platinum and demonstrate the potential of alternative noble metals in electrocatalysis.[43]

However, even with such innovations, the high costs associated with noble metals remain a significant barrier to their widespread use, driving the search for more affordable, non-noble metal alternatives.

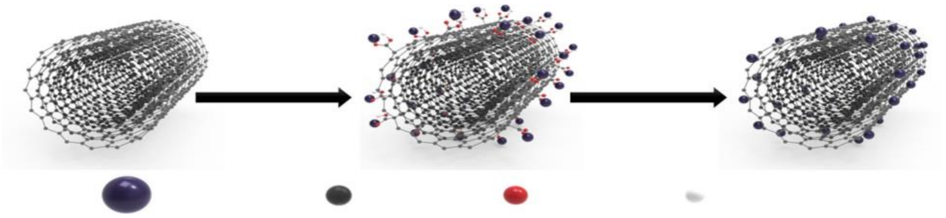

Figure 6. Schematic illustration of the process steps for forming Ru@MWCNT catalyst.

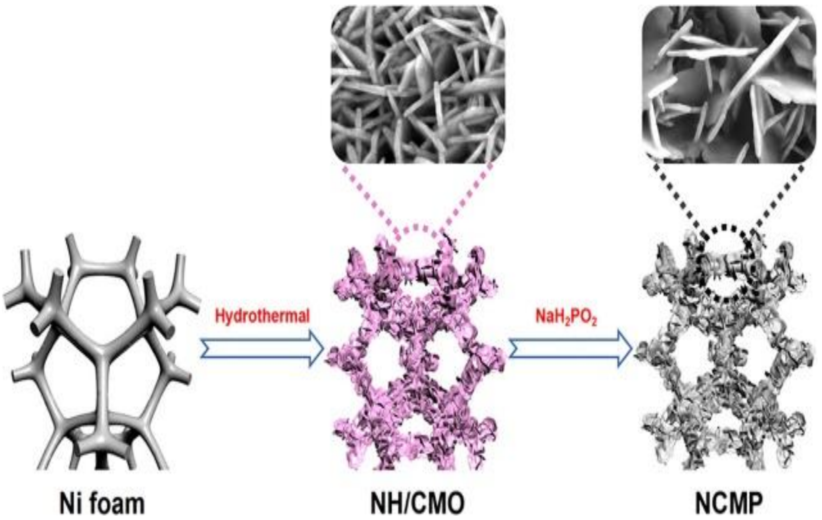

Figure 7. Schematic Illustration of the formation process of NCMP. [Data taken from ref 59]

4.2 Non-Noble Metal-Based Electrocatalysts

Transition metals such as iron (Fe), cobalt (Co), and nickel (Ni) have garnered significant attention for their potential as cost-effective alternatives to noble metals in HER electrocatalysis. These metals, often combined with nonmetal elements like sulfur (S), nitrogen (N), and phosphorus (P), can form a range of compounds—such as metal sulfides, phosphides, nitrides, and carbides—that exhibit promising catalytic properties as summarized in Table 2 by Tehrani and all[44]

4.2.1 Transition Metal Carbides

Transition metal carbides (TMCs), especially those derived from tungsten (W) and molybdenum (Mo), are some of the most promising non-noble metal catalysts for the hydrogen evolution reaction (HER). These materials demonstrate electrical characteristics akin to platinum, rendering them appealing candidates for water-splitting applications. Tungsten carbide (WC) has catalytic activity comparable to platinum (Pt) owing to its advantageous electrical structure.[45]

Innovative methods have been devised by researchers to improve TMCs' catalytic performance. A technique entails the integration of carbon nanomaterials, such as graphene or reduced graphene oxide (rGO), to enhance charge transfer and augment the quantity of active sites. For example, WC supported on rGO has exhibited markedly enhanced HER performance in both acidic and alkaline conditions, with overpotentials akin to those of Pt-based catalysts.

Molybdenum carbides (Mo_2C) demonstrate significant catalytic activity for the hydrogen evolution reaction (HER). Research indicates that Mo_2C surpasses other transition metal nitrides and borides owing to its advantageous hydrogen adsorption characteristics. Furthermore, the amalgamation of molybdenum carbide with additional materials, like carbon-based supports or transition metal alloys, significantly improves its catalytic efficacy and durability.[46]

4.2.2 Transition Metal Phosphides and Sulfides

Transition metal phosphides (TMPs) and sulfides (TMSs) represent a promising category of non-noble metal catalysts for hydrogen evolution reactions (HER). These materials frequently have superior catalytic activity owing to their distinctive electronic structures, which facilitate hydrogen adsorption and desorption. Nickel phosphide (Ni_2P) and cobalt phosphide (CoP) have been extensively researched for their hydrogen evolution reaction (HER) efficacy in both acidic and alkaline conditions.[47,48]

It has also drawn attention to the catalytic activity of transition metal sulfides (TMSs), like molybdenum disulfide (MoS_2). MoS_2 is regarded as a highly effective electrocatalyst owing to its layered architecture, which reveals active areas for hydrogen adsorption. Moreover, surface changes and the incorporation of defects can augment the catalytic efficacy of MoS_2 by elevating the quantity of accessible active sites.[49,50]

4.3 MOF-Derived Electrocatalysts

Metal–organic frameworks (MOFs) have recently emerged as a novel category of materials for electrocatalysis owing to their highly adjustable topologies. Metal-organic frameworks (MOFs) comprise metal ions coupled with organic ligands, resulting in porous, crystalline structures. These materials can be engineered with particular characteristics, such as elevated surface area and regulated pore size, rendering them optimal candidates for hydrogen evolution reaction applications.[51]

Electrocatalysts formed from metal-organic frameworks (MOFs) are often produced by transforming MOFs into metal-containing nanostructures by heat decomposition or chemical treatment. The resultant materials preserve the structural benefits of the original MOF, like elevated porosity and extensive surface area, while also integrating catalytically active metal cores. Transition metals incorporated in carbon matrices formed from metal-organic frameworks (MOFs) have superior hydrogen evolution reaction (HER) performance owing to their elevated density of active sites and improved electron transport characteristics.

4.4. Non-Noble Metal Nitride and Selenide Electrocatalysts

Transition metal nitrides (TMNs) and selenides (TMSes) have emerged as attractive candidates for the hydrogen evolution reaction (HER) among non-noble metal-based electrocatalysts. These materials have exceptional stability and activity, akin to noble metal-based catalysts, albeit at a significantly reduced cost. TMNs demonstrate advantageous electronic characteristics that can augment hydrogen adsorption and boost conductivity.[52]

Nickel and cobalt nitrides have been thoroughly investigated for their significant catalytic activity in both acidic and alkaline conditions. Nickel nitride (Ni_3N) and cobalt nitride (Co_3N) exhibit superior performance owing to their excellent hydrogen adsorption energy, facilitating effective hydrogen bonding and release.[53,54]

Transition metal selenides (TMSes) have garnered interest, especially for their improved stability in alkaline conditions. Selenium-derived compounds such as nickel selenide ($NiSe_2$) and cobalt selenide ($CoSe_2$) demonstrate significant catalytic efficacy and longevity, rendering them suitable for sustained hydrogen generation. These materials can be enhanced through doping and structural changes, hence augmenting their HER performance.[55,56][

5. Challenges and Future Directions in Electrocatalyst Development

Notwithstanding considerable progress in the design and optimization of electrocatalysts for hydrogen evolution, numerous hurdles persist in realizing large-scale, efficient hydrogen synthesis. A critical difficulty is enhancing the long-term stability of non-noble metal electrocatalysts, especially under severe conditions like elevated temperatures or abnormal pH levels. Noble metal-based catalysts have enhanced stability; however, their prohibitive cost restricts broad use, necessitating an emphasis on augmenting the durability of non-noble alternatives.

A significant problem is improving the catalytic activity of these materials to equal or exceed that of platinum-based catalysts. Although some transition metal-based electrocatalysts exhibit encouraging activity, few have attained performance levels comparable to platinum. The advancement of novel materials, including multi-component alloys and heterostructures, presents a promising avenue for progress. These materials amalgamate the characteristics of many components to provide synergies that improve catalytic efficacy and durability.

Moreover, additional investigation into the fundamental mechanisms of HER is crucial for directing the advancement of more efficient electrocatalysts. This encompasses an in-depth analysis of reaction routes, adsorption energies, and charge transfer mechanisms, employing methodologies like as density functional theory (DFT) and experimental approaches like electrochemical impedance spectroscopy (EIS). This research will uncover critical parameters that affect catalytic activity and facilitate the systematic design of advanced catalysts.

6. Conclusion

The hydrogen evolution reaction (HER) constitutes a vital phase in the water-splitting process for hydrogen generation. Although platinum (Pt) is the standard catalyst for the hydrogen evolution reaction (HER), its exorbitant cost and limited availability have prompted the exploration of alternate materials. Electrocatalysts based on non-noble metals, such as transition metal carbides, phosphides, nitrides, and selenides, present advantageous alternatives owing to their reduced cost and widespread availability. Recent developments in catalyst design, including doping, structural alterations, and the creation of nanostructures, have markedly enhanced the performance of these materials.

Nonetheless, obstacles persist in attaining the requisite high activity, enduring stability, and scalability essential for industrial applications. Subsequent research must concentrate on addressing these problems through the development of novel materials, enhancing our comprehension of the HER mechanism, and optimizing the structural and electrical characteristics of catalysts.

As hydrogen increasingly emerges as a clean and sustainable energy source, the advancement of effective, low-cost electrocatalysts will be essential for facilitating the broad implementation of water-splitting technology. By overcoming the existing obstacles to large-scale hydrogen generation, the scientific community can facilitate a future fuel by green hydrogen.

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Figure 2. Illustration of non PGM electrocatalysts for Hydrogen Production was created by AI tool.

Conflict of Interest

The authors declare no conflict of interest.

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