Review

A Mini Review on Doped Nickel-Based Electrocatalysts for Hydrogen Evolution Reaction

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Abstract: The energy crisis and environmental pollution have attracted much attention and have promoted researches on clean and sustainable hydrogen energy resources. With the help of highly active and stable transition metal nickel-based catalysts, the production of hydrogen from water electrolysis from electrolyzed water has become an inexpensive and efficient strategy for generating hydrogen energy. In recent years, heteroatom doping has been found to be an effective strategy to improve the electrocatalytic hydrogen evolution reaction (HER) performances of nickel-based catalysts in acidic, neutral, and alkaline media. This review will highlight many recent works of inexpensive and readily available heteroatom-doped nickel-based HER catalysts. The evaluation methods for the performances of HER catalyst will be briefly described, and the role of heteroatom doping and its application in nickel-based catalyst will be summarized. This article will also point out some heteroatom doping strategies, which may provide references and inspire the design of other catalysts with dopants.

Keywords: nickel-based catalysts; heteroatom doping; electrochemical hydrogen evolution reaction

1. Introduction

As the pace of industrialization accelerates, non-renewable energy resources like fossil fuels are continuously consumed and their reserves are gradually reduced. Excessive consumption of fossil fuels is also causing the problem of continuous deterioration of the natural environment. The search for new sustainable energy sources has become a major concern in many countries [1]. In the past few decades, energy resources such as wind, solar, hydroelectric power, and hydrogen, have been regarded as sustainable and environmentally friendly alternatives to fossil fuels [2]. Hydrogen is among the most attractive energy sources for sustainable development owing to its high energy density. In addition, the combustion product of hydrogen, which is water only, is pollution-free.

Nowadays, H₂ mainly comes from the steam methane reforming of natural gas, which converts methane and water steam into carbon monoxide and hydrogen. However, this process has low energy efficiency, high cost, and produces carbon-containing residues that affect the purity of hydrogen and pollute the environment [3]. Another hydrogen production technology is the use of electricity to electrolyze water so as to produce hydrogen. Hydrogen production through water splitting using solar-generated electricity has been considered as an efficient and clean way and has attracted much attention [4]. Water electrolysis consists two half reactions: the hydrogen evolution reaction (HER) at the cathode, and the oxygen evolution reaction (OER) at the anode [5]. The cathodic hydrogen evolution process involves two electronic transfers, and the pathways have been proposed as follows: [6].

(1) Volmer step:

(2) Heyrovsky step:

or Tafel step:

(H*: adsorbed hydrogen at the active site of the catalyst)

At present, the most effective electrocatalysts for HER are platinum-based materials. However, the low abundance and high cost of platinum has limited its application in industry [7]. Therefore, the development of catalysts with low cost, large reserves, good stability, and high catalytic activity has become a key step in the industrial production of H_2 from water electrolysis. As a result, those inexpensive and readily available transition metal (Mo, Fe, Co, and Ni)-based electrocatalysts have been massively developed [8–11].

Nickel-based catalysts with high stability and activity have been widely concerned for H_2 -evolving reaction [12]. Various types of nickel-based catalysts have been continuously developed, such as nickel oxides, hydroxides, phosphides, sulfides, nitrides, alloys, and so on [13–18]. The catalytic performances of these nickel-based catalysts can be further improved through fine surface design, elemental doping, and addition of carbon materials [19]. Studies have shown that doping or alloying of those catalysts that have been developed is an effective strategy to improve their performances [20]. Doping with other elements, can induce the formation of more active sites and new active centers [21,22]. In addition, appropriate elemental doping can also improve the intrinsic activity of the catalyst by increasing its conductivity and changing its electronic structure [23,24].

Although elemental doping has been widely explored and considered as an effective strategy to enhance the HER performance of the nickel-based catalysts, there still exist difficulties in controlling the type, amount, and dispersion of the dopants [25]. Therefore, this article summarizes and discusses recent progresses made in the design and manufacture of doped Ni-catalysts, hoping to deepen the understanding of the doping mechanism and provide reference for the design and manufacture of other doped transition metal-based catalysts.

In this review, a brief summarization of the evaluation methods for electrocatalysts is provided first. Next, we summarize the recent progresses made in the design and manufacture of doped nickel-based catalysts. The role of dopants and their applications in nickel-based HER catalysts are discussed in detail. We hope this work can deepen the understanding of the doping mechanism, so as to provide some insights into resolving the difficulty of controlling the type, quantity, and dispersion of the dopants. Finally, by understanding the correlation between the dopants and the HER activity of the Ni-based catalysts, we expect to provide some perspective on the future research of high-performance doped catalysts.

2. Evaluation Approaches of HER Electrocatalysts

2.1. Overpotential

Under standard conditions, the H_2 -evolving potential is zero. However, in the practical HER processes, there exist kinetic barriers due to the activation energy required for the reaction [26]. The difference between the actual reaction potential and the equilibrium potential is defined as the overpotential (η) of HER. Overpotential is considered as one of the most important values for evaluating water-splitting catalysts, because a large reaction overpotential will result in low energy conversion efficiency. In general, the overpotential at a current density of 10 mA/cm^2 is the benchmark for evaluating catalyst performance [27]. For those electrodes with high catalyst loadings, the reaction

potentials at 50 and 100 mA/cm² current densities can also be considered as important criteria for evaluating catalysts in practical applications.

2.2. Tafel Slope and Exchange Current Density

The Tafel slope is a significant parameter to evaluate the inherent HER activity of a catalyst [28]. A smaller Tafel slope suggests that a lower overpotential is required to increase the current density by the same amount, which means a more rapid charge-transfer kinetic [19]. The most common method for obtaining Tafel slope value is by taking the logarithm of the absolute value of the current density to replot the polarization curve (potential versus log |current density|) and fitting the linear region to the Tafel equation $\eta = b \log(j/j_0)$, where η is the overpotential, j is the current density, j_0 is the exchange current density and b is the Tafel slope [19]. Alternatively, Hu and his colleagues calculated the slope of the linear fitting plots of log charge-transfer resistance (R_{ct}) vs. overpotential based on the impedance data obtained through electrochemical impedance spectroscopy to acquire the Tafel slope [29]. The Tafel slope calculated by this method, in contrast to that obtained from voltammetry data, is not influenced by catalyst resistances, and therefore can purely reflect the charge-transfer kinetics.

The exchange current density (j_0) of the reaction is the current density at the equilibrium potential, where the cathode current is equal to the anode current. It can be obtained by extrapolating the linear part of the Tafel plot to intersect with the X axis [19]. The exchange current density can also reveal the inherent activity of a catalyst. A large exchange current density indicates that only a small driving force is required for the evolution of the reaction.

2.3. Stability

Stability is an important evaluation criterion for HER electrocatalysts. There exist two major approaches for stability tests: repeated cyclic voltammetry (CV) or linear scanning voltammetry (LSV) and constant current or constant potential electrolysis. Stability of a catalyst can be evaluated by comparing its polarization curves before and after continuous CV measurements (typically 500–10,000 times) [19,26,30]. If the polarization curve after the cycles coincides with the original polarization curve or shows only small offset (e.g., less than 10% deviation), the catalyst is of good stability. Similarly, when evaluating the stability by constant current or constant potential electrolysis, if the working potential or working current of the catalyst only shows a small ($\leq 10\%$) change at an applied constant current density or constant potential after a duration of at least 10 h, it indicates that the catalyst is of good stability.

2.4. Electrochemical Impedance Spectroscopy

The HER kinetics and the reactions at the interface of the electrode/electrolyte could be probed through electrochemical impedance spectroscopy (EIS). The charge-transfer resistance (R_{ct}) value, obtained from the diameter of the semicircle in the high frequency zone of the EIS Nyquist plot, reflects the interface charge-transfer rate of the electrode. R_{ct} is mainly dependent on the intrinsic properties of the catalyst material; hence, a small R_{ct} value indicates a fast reaction rate [26,31]. In addition, the semicircle in the low frequency region represents the adsorption resistance (R_{ad}) that originates from the adsorption of oxidized species on the electrode surface. R_{ad} reflects the onset potential of HER, therefore a small R_{ad} indicates an early HER onset [31].

2.5. Free Energy of Hydrogen Adsorption

Free energy of hydrogen adsorption (ΔG_{H^*}), which can be obtained via density functional theory (DFT) calculations, is also one of the key parameters to estimate the HER activity of a catalyst. In general, a good HER electrocatalyst should have a hydrogen bonding energy that is neither too weak nor too strong [32]. Weak adsorption leads to difficulty in combining protons with the electrocatalyst, while strong adsorption of H^* leads to its difficulty in the desorption from the catalyst surface. The free energy of hydrogen bonding should be close to 0 for a good HER electrocatalyst [33].

3. Heteroatom-Doped Nickel-Based HER Electrocatalysts

3.1. Noble Metal Doping

Nickel-based oxides, hydroxides, phosphides, sulfides, etc., have been concerned for HER catalysis [34–38]. Among them, $\text{Ni}(\text{OH})_2$ has been extensively studied for its excellent durability and superior water adsorption capacity. However, $\text{Ni}(\text{OH})_2$ material was not considered as an efficient HER catalyst because of its low intrinsic activity and excessively high free energy of hydrogen adsorption [39]. Wang et al., through Ru doping by a hydrothermal method, promoted the HER activity of $\text{Ni}(\text{OH})_2$ in alkaline electrolyte [40]. The incorporation of Ru^{3+} (Ru/Ni atomic ratio: ~ 0.22) greatly changed the surface morphology of the $\text{Ni}(\text{OH})_2$ deposited on Ti mesh (Ru doped $\text{Ni}(\text{OH})_2/\text{TM}-0.2$), though some small sheets still existed on the Ru-doped $\text{Ni}(\text{OH})_2$ surface (Figure 1A,B). The overpotential of this Ru-doped $\text{Ni}(\text{OH})_2$ was decreased to 135 mV at a current density of 10 mA/cm^2 while the overpotential of $\text{Ni}(\text{OH})_2$ material was $>210 \text{ mV}$ (Figure 1C). The enhanced HER activity could be attributed to the accelerated charge transfer rate, increased electrochemically reactive surface area, and appropriate Ru-H bonding strength on Ru sites. The Ni atoms were more positively charged due to Ru doping, which reduced the water dissociation barrier, and thus promoted the Volmer step (Figure 1D). In addition, the introduction of Ru dopants into $\text{Ni}(\text{OH})_2$ increased the electrochemical active surface area (ECSA) of the catalyst, leading to an increased number of reactive sites exposed. Finally, due to the appropriate bonding strength between Ru and H, Ru sites were suitable active centers for H intermediate bonding and the following H_2 formation and dissociation processes.

Figure 1. (A) SEM image of $\text{Ni}(\text{OH})_2/\text{TM}$. (B) SEM image of Ru-doped $\text{Ni}(\text{OH})_2/\text{TM}-0.2$. (C) Polarization curves of TM, $\text{Ni}(\text{OH})_2/\text{TM}$, Ru doped $\text{Ni}(\text{OH})_2/\text{TM}-0.1$, Ru doped $\text{Ni}(\text{OH})_2/\text{TM}-0.2$, and Ru doped $\text{Ni}(\text{OH})_2/\text{TM}-0.3$. (D) The proposed synergistic effect in Ru doped $\text{Ni}(\text{OH})_2/\text{TM}$ for HER (reprinted with permission from ref [40]. Copyright © 2019, Elsevier).

He et al., employed a nickel-vacancy-mediated synthesis strategy to accomplish the synthesis of Ni_5P_4 nanoparticles containing 3.83 wt% single-atom Ru ($\text{Ni}_5\text{P}_4\text{-Ru}$) [41]. The Ru sites were first incorporated into a nickel-vacancy-rich nickel hydroxide, with the nickel vacancies stabilizing the Ru^{3+} . A subsequent phosphorization treatment further transformed the material to $\text{Ni}_5\text{P}_4\text{-Ru}$, which incorporated single-atom Ru^0 dopants. The $\text{Ni}_5\text{P}_4\text{-Ru}$ exhibited a low initial potential of 17 mV vs. RHE and a small overpotential of 54 mV at a current density of 10 mA/cm^2 (Figure 2). Spin-polarized

DFT method was employed to perform calculations. The Perdew–Burke–Ernzerhof (PBE) functional of generalized gradient approximation (GGA) was used as the electron exchange–correlation potential. Spectral analysis combined with DFT calculations revealed that Ru doping polarized the local structure of Ni_5P_4 , lowered the hydrolysis barrier, and optimized the free energy for H adsorption. Hence, appropriate integrated structural adjustment and active site incorporation could be the strategy to achieve efficient electrocatalysts.

Figure 2. (A) Schematic illustration of the fabrication of $\text{Ni}_5\text{P}_4\text{-Ru}$. (B) Hydrogen evolution reaction (HER) linear scanning voltammetry (LSV) curves for the $\text{Ni}_5\text{P}_4\text{-Ru}$ and Pt/C loaded on carbon cloth (CC). The inserted figure showed the Tafel plot of $\text{Ni}_5\text{P}_4\text{-Ru/CC}$. (C) Free energy of hydrogen adsorption on Ni_5P_4 and $\text{Ni}_5\text{P}_4\text{-Ru}$ (reprinted with permission from ref [41]. Copyright © 2020, John Wiley and Sons).

Chen et al., employed Co leaf-like zeolitic imidazolate framework (Co ZIF-L/NF) as precursor to synthesize the Ru-doped 3D flower-like bimetallic phosphide on nickel foam (Ru-NiCoP/NF), through Ru^{3+} etching and low-temperature phosphorization strategy [42]. This Ru-NiCoP/NF (quantitative percentage of Ru: 0.42 at%) exhibited an overpotential of only 44 mV at a H_2 -evolving current density of 10 mA/cm^2 and a small Tafel slope of 45.4 mV/dec in 1.0 M KOH . It was proposed that Ru dopants in the Ni sites of NiCoP , which served as the active sites for H_2 evolution, could optimize the Gibbs free energy of hydrogen adsorption (-0.034 eV) and increase the charge transfer rate; therefore, promoting the HER performance of the catalyst.

Recently, Li et al., reported an Ir-doped NiV layered double hydroxide (IrNiV-LDH) catalyst, which was synthesized via a one-step hydrothermal method, for electrochemical water splitting [22]. It was found that in pristine NiV-LDH without Ir dopants, V ions were in +3, +4, and +5 valence states. The bridging oxygen atom between Ni and V was the active center of HER. The ΔG_{H^*} of bridge oxygen was appropriately modified by the vanadium dopants, making the bridge oxygen atoms HER-active centers. In further research work, iridium doping was conducted to the NiV-LDH to further enhance the performance of the catalyst. DFT+U (Hubbard-U correction) method was also employed in this study to illustrate the effect of Ir doping. After a nickel atom was replaced by an Ir^{3+} , the ratio of V^{3+} increased significantly, indicating the Ir dopants introduced a decrease in the valence state of the V ions. The charge density at the bridge oxygen atom between the vanadium and the Ir decreased significantly, which reduced the excessively strong adsorption of the H intermediates; therefore, enhancing the HER performance of the catalyst. Moreover, the Ir dopants exhibited lower energy barrier for water dissociation compared to the V sites; hence, serving as the new reactive centers for the Volmer step in alkaline solutions. Therefore, Ir doping in NiV LDH achieved the synergistic HER catalysis at the double active centers of the Ir atom and the bridge oxygen atom. As a result, with Ir dopants in NiV LDH ($\text{Ni}_{0.57}\text{V}_{0.29}\text{Ir}_{0.14}\text{-LDH}$), a small overpotential of only 41 mV was achieved at a H_2 -evolving current density of 10 mA/cm^2 on the catalyst (Figure 3).

Figure 3. (A) Polarization curves and (B) Tafel slopes of Ni(OH)₂, NiV-LDH, NiVr-LDH, and Pt/C. Water dissociation barriers on (C) V and (D) Ir sites in NiVr (reprinted with permission from ref [22]. Copyright © 2019, American Chemical Society).

Fan et al., used a simple low-temperature solvothermal and spontaneous galvanic displacement reaction (Ir ions replacing NiCo in the NiCo layered double hydroxide) in atmosphere to fabricate Ir-doped NiCo LDH catalyst (Ir content: 3.4 wt%) [43]. The Ir-doped NiCo LDH exhibited an overpotential of 21 mV at a H₂-evolving current density of 10 mA/cm² and a low Tafel slope of 33.2 mV/dec in 1.0 M KOH. The X-ray photoelectron spectroscopy (XPS) results showed an increased valence state of the iridium dopants compared to the initial Ir³⁺ reactant. In addition, the binding energies of Ni 2p and Co 2p shifted to higher and lower values, respectively. These results indicated that Ir doping altered the electronic structure of the NiCo LDH. Moreover, Ir-doped NiCo LDH showed a significantly larger electrochemical active surface area and higher conductivity compared to the NiCo LDH, contributing to the excellent HER performance of the catalyst. A summary of the HER performances of the representative doped Ni-based catalysts under different conditions is presented in Table 1.

Table 1. HER performances of various doped nickel-based electrocatalysts.

Catalyst	Electrolyte	Overpotential (mV) η_{10}	Tafel Slope (mV/dec)	Ref.
Ru doped Ni(OH) ₂ /TM-0.2 ¹	1.0 M KOH	135	63.7	[40]
Ni ₅ P ₄ -Ru	1.0 M KOH	54	52.0	[41]
Ru-NiCoP/NF ²	1.0 M KOH	44	45.4	[42]
Ni _{0.57} V _{0.29} Ir _{0.14} -LDH	1.0 M KOH	41	35.9	[22]
Ir-doped NiCo LDH	1.0 M KOH	21	35.0	[43]
Mo-Ni ₂ P	1.0 M KOH	81	53.4	[44]
(Fe _{0.048} Ni _{0.952}) ₂ P/NF	1.0 M KOH	103	76.6	[45]
	1.0 M PBS	90	82.7	
	0.5 M H ₂ SO ₄	81	41.6	[46]
NiCoP/rGO ³	0.5 M H ₂ SO ₄	58	50.0	
V-Ni ₂ P NSAs/CC ^{4,5}	1.0 M KOH	85	95.0	[47]
Ni _{0.82} Co _{0.18} O@C/NF ⁶	1.0 M KOH	102	139.0	[48]
Fe ₁₁ %-NiO/NF	1.0 M KOH	88	49.7	[49]
Ni(Cu)VO _x	1.0 M KOH	21	28	[50]
NiP _{1.93} Se _{0.07}	0.5 M H ₂ SO ₄	84	41.0	[20]
Ni(S _{0.61} Se _{0.39}) ₂	1.0 M KOH	62.7	62.0	[51]
b-S-Ni ₃ Se ₄ &b-Se-Ni ₃ S ₂ /NF ⁷	1.0 M KOH	87	61.0	[52]
C-Ni _{1-x} O	1.0 M KOH	27	36.0	[53]
C, N-NiPS ₃	1.0 M KOH	53.2	38.2	[54]

¹ TM, Ti mesh; ² NF, Ni foam; ³ rGO, reduced graphene oxide; ⁴ NSAs, nanosheet arrays; ⁵ CC, carbon cloth;

⁶ C, conductive carbon; ⁷ b, bulk.

3.2. Non-Precious Metal Doping

Nanostructured Ni_2P is an active HER electrocatalyst composed of the cheap and abundant earth elements Ni and P. In order to further improve its catalytic activity, various metal dopants have been developed [55]. Zhang et al., synthesized a Mn-doped Ni_2P nanosheet array ($\text{Mn}_{0.05}\text{Ni}_{0.95}\text{P}_{0.52}$) on nickel foam (NF) by a hydrothermal and a subsequent low-temperature phosphorization method for efficient HER electrocatalysis [56]. XPS results revealed the Mn ions were in +2 valence state. The Mn- Ni_2P /NF only required a low overpotential of 103 mV to drive a H_2 -evolving current density of 20 mA/cm^2 in 1.0 M KOH, which was 82 mV lower than the Ni_2P /NF. The doping of Mn not only improved the electron transfer rate of Ni_2P but also increased its surface area and therefore resulted in more active sites exposed, thus greatly enhancing the HER activity of the catalyst.

Wang et al., reported a Mo-doped hollow nanostructure Ni_2P (Mo- Ni_2P) that prepared by solvothermal and in-situ phosphorization method. The Mo-doped Ni_2P (with a Mo mass ratio of 8.3%) showed an overpotential of only 81 mV at a H_2 -evolving current density of 10 mA/cm^2 in 1.0 M KOH electrolyte (Figure 4A) [44]. First-principles DFT was employed to investigate into the Gibbs free energy of hydrogen adsorption. The Perdew–Burke–Ernzerhof (PBE) functional of generalized gradient approximation (GGA) was used as the electron exchange-correlation potential. Four types of relatively stable sites were also taken into consideration. The researchers found that in pristine Ni_2P , P atoms served as the active sites for HER because the ΔG_{H^*} of the P site in Ni_2P was ~ 0.33 eV, smaller than that of the Ni-Ni site. After Mo was doped, the ΔG_{H^*} of the P site was reduced to 0.25 eV. Moreover, Mo-Ni sites with a lower ΔG_{H^*} of ~ 0.21 eV appeared, which functioned as the new active centers for HER. This result indicates that proper atom doping can introduce new active centers, enlarge electrochemical active surface areas, and optimize the ΔG_{H^*} at the active sites; thereby, improving the overall HER performance of the catalyst (Figure 4B).

Figure 4. (A) Schematic illustration of the synthesis of Mo-doped Ni_2P hollow nanostructures. (B) Free energy diagram for HER on Ni-Ni site in Ni_2P , P site in Ni_2P , Mo-Ni site in Mo- Ni_2P and P site in Mo- Ni_2P (reprinted with permission from ref [44]. Copyright © 2019, Royal Society of Chemistry).

Zhang et al., reported the fabrication of single crystalline $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ nanosheets on Ni foam by hydrothermal method and a subsequent low-temperature phosphorization strategy [45]. Notably, the $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ catalyst showed excellent performance for HER at universal pH values. Through first-principle-based DFT calculations, it was found that Fe dopants can trigger the charge

accumulation around the P active site, which decreased the Gibbs free energy of H^* and H_2O adsorption and therefore reduced the energy barrier for H_2 evolution (Figure 5). In addition, due to the Fe dopants, the accumulated charge at the P sites tended to transfer to the hydrogen atom, which also benefited H_2 formation. Fe dopants also enlarged the electrochemical active surface area of the catalyst, contributing to the enhanced HER performance.

Figure 5. (A) Hydrogen adsorption free energy of $Fe_8Ni_{76}P_{42}$, $Fe_6Ni_{78}P_{42}$, $Fe_4Ni_{80}P_{42}$, $Fe_3Ni_{81}P_{42}$, $Fe_2Ni_{82}P_{42}$, and $Ni_{84}P_{42}$ in acidic HER with their P sites. (B) Water dissociation energy and hydrogen adsorption free energy of $Fe_8Ni_{76}P_{42}$, $Fe_6Ni_{78}P_{42}$, $Fe_4Ni_{80}P_{42}$, $Fe_3Ni_{81}P_{42}$, $Fe_2Ni_{82}P_{42}$, and $Ni_{84}P_{42}$ in alkaline HER with their P sites (reprinted with permission from ref [45]. Copyright © 2019, Elsevier).

Li et al., developed a series of Co-doped nickel phosphide catalysts ($Ni_{2-x}Co_xP$) and their hybrids with reduced graphene oxide (rGO) by co-precipitation and a subsequent phosphorization method, which exhibited excellent HER performances at universal pH values between 0 and 14 [46]. The HER activity of the $Ni_{2-x}Co_xP$ catalyst was found relying on the ratio of Ni and Co, and a Ni: Co atomic ratio of 1:1 delivered the best HER activity. Moreover, the hybridization of rGO onto $Ni_{2-x}Co_xP$ could further improve the HER activity of the catalyst. As a result, the NiCoP/rGO showed a small overpotential of only 55 mV to drive a H_2 -evolving current density of 20 mA/cm² in acid media, as well as a low Tafel slope of 45.2 mV/dec. DFT calculations showed that the presence of Co dopants in NiCoP not only optimized the adsorption of H intermediates but also accelerated the desorption of H_2 at a high surface coverage of H, contributing to the superior HER activity of the catalyst. In addition, the introduction of rGO increased the amount of the exposed active sites and accelerated the charge transfer rate, which also conducted to the enhanced HER performance of NiCoP/rGO.

Wen et al., fabricated an 8 at% V-doped Ni_2P nanosheet arrays on carbon cloth (CC) substrate (V- Ni_2P NSAs/CC) via hydrothermal and low-temperature phosphorization method for alkaline HER [47]. XPS results revealed that after doping with V, the binding energies of Ni shifted to lower values, indicating a higher electron density on the Ni. It was proposed that the interaction between the vanadium and nickel atoms would cause lattice defects and distortions to Ni_2P ; thereby, adjusting its electronic structure and increasing its specific reactive surface area (Figure 6). In addition, the in situ growth of the catalyst on carbon cloth endowed a rich contact interface between V- Ni_2P and CC; therefore, facilitating their charge carrier migration rate. In addition, the porous structure and rough surface of V- Ni_2P /CC could promote the release of H_2 bubbles; hence, accelerating the HER process. Therefore, the V- Ni_2P NSAs/CC catalyst exhibited superior HER performance, with a low overpotential of 85 mV at a current density of 10 mA/cm² in 1.0 M KOH and also an impressive long-term electrochemical stability.

Figure 6. (A) Schematic illustration of synthesis of the V-Ni₂P NSAs loaded on carbon cloth. (B) SEM images of V-Ni₂P NSAs/CC. (C) Polarization curves of bare CC, Ni₂P NSAs/CC, V-Ni₂P NSAs/CC and Pt/C (reprinted with permission from ref [47]. Copyright © 2019, Royal Society of Chemistry).

Apart from Ni₂P, researchers have also been employing non-precious metal doping to improve the HER performance of NiO catalyst [48]. Like most transition metal oxide-based catalysts, NiO shows good activity for oxygen evolution reaction (OER), however, its catalytic activity for HER is not satisfactory [57]. Yang et al., fabricated a Co-doped NiO coupling with conductive carbon on nickel foam (Ni_{0.82}Co_{0.18}O@C/NF) for overall water splitting catalysis via an immersion-adsorption-pyrolysis method [48]. Owing to the increased conductivity, accelerated charge transfer rate, additional defect active sites, increased exposed reactive surface area and enhanced mass transfer capability, this catalyst exhibited an only 62 mV overpotential at a H₂-evolving current density of 10 mA/cm² in 1.0 M KOH. It is also worth noting that the catalyst only required an ultra-low battery voltage of 1.42 V for overall water splitting at 10 mA/cm². Wu et al. incorporated a different transition metal, Fe, to fabricate Fe-doped NiO mesoporous nanosheet arrays on nickel foam (Fe_{11%}-NiO/NF, 11%: atomic content of Fe dopants) by a solvothermal and subsequent annealing strategy [49]. Their results revealed that Fe³⁺ ions could induce a partial-charge-transfer process that activated the Ni²⁺ centers of NiO, which effectively promoted the HER catalytic performance. Hence, the optimized Fe_{11%}-NiO/NF catalyst showed an overpotential of 88 mV at a H₂-evolving current density of 10 mA/cm² and a small Tafel slope of 49.7 mV/dec in 1.0 M KOH (Figure 7).

Figure 7. (A) Schematic illustration of the formation of Fe-doped mesoporous NiO on Ni foam. (i) Solvothermal synthesis of Fe-doped β-Ni(OH)₂ and (ii) the calcination of Fe-doped β-Ni(OH)₂ in air to produce Fe-doped mesoporous NiO array. (B) Polarization curves of NF (nickel foam), NiO/NF, Fe_{11%}-NiO/NF and Pt/C/NF. (C) Tafel slopes of NF, NiO/NF, Fe_{11%}-NiO/NF and Pt/C/NF (reprinted with permission from ref [49]. Copyright © 2018, Elsevier).

Ni, as a non-noble metal catalyst, shows poor HER performance due to its inherent electronic structure. Li et al., fabricated a Ni(Cu)VO_x catalyst with highly active Ni-O-VO_x sites by doping VO_x into Cu-doped Ni via a one-step electrodeposition method [50]. XPS revealed that Cu dopants were in metallic state while the V existed as VO_x with low vanadium oxide valence states of +4 and +5. The molar ratios of Cu/Ni and V/Ni were measured to be ~0.120 and ~0.034, respectively. This Ni(Cu)VO_x displayed excellent HER performance, with an overpotential as low as 21 mV at 10 mA/cm² and a small Tafel slope of 28 mV/dec in 1 M KOH (Figure 8A,B). The spin-polarized DFT calculations indicated the excellent performance was attributed to the synergistic effects generated by the VO_x and Cu dopants. The incorporation of VO_x into Ni(Cu)VO_x would induce partial electron transfer from the Ni to VO_x to form super-active Ni-O-VO_x sites while the Cu dopants could further weaken the H* binding; hence, promoting the HER performance (Figure 8C). In addition, Cu and VO_x doping enlarged the electrochemically reactive area of the catalyst, which also contributed to the enhanced HER performance of the Ni(Cu)VO_x (Figure 8D).

Figure 8. (A) Polarization curves of Ni, Ni(Cu), NiVO_x, Ni(Cu)VO_x, *iR*-Ni(Cu)VO_x and Pt/C. (B) Tafel plots of Ni, Ni(Cu), NiVO_x, Ni(Cu)VO_x, and Pt/C. (C) The calculated ΔG_{H^*} of Ni(111), V-Ni(111), Pt(111), and V/Cu-Ni(111). (D) Double-layer capacitances of Ni, Ni(Cu), NiVO_x, and Ni(Cu)VO_x calculated from their CVs at different scan rates (reprinted with permission from ref [50]. Copyright © 2020, Springer).

3.3. Non-Metal Doping

Studies have shown that doping anions from a different group into an existing catalyst is an effective strategy to improve the HER performance [58–60]. Zhuo et al., systematically investigated a series of pyrite-phase nickel selenide and phosphide materials that prepared via a hydrothermal and subsequent thermal conversion method. Among samples with various P/Se ratios, Se-doped NiP₂ (NiP_{1.93}Se_{0.07}) showed the best HER performance, with an overpotential as low as 84 mV at 10 mA/cm² and a small Tafel slope of 41 mV/dec in 0.5 M H₂SO₄ aqueous electrolyte [20]. The performance improvement of NiP₂ was proposed to be attributed to the introduction of Se elements, which modified the electronic structure of NiP₂. The changes in the electronic structure further optimized the free energy of hydrogen adsorption on the catalyst and therefore improved the HER activity of NiP₂ catalyst.

A different work by Zhou et al. also revealed the importance of anion doping in enhancing the activity of water splitting catalyst [51]. The researchers investigated into the anion doping effect in pyrite-structured nickel disulfide (NiS₂) or nickel diselenide (NiSe₂) that prepared via a solvothermal and subsequent calcination and chemical vapor deposition strategy. The authors found

that $\text{Ni}(\text{S}_{0.61}\text{Se}_{0.39})_2$ had a remarkable HER activity with an overpotential of only 62.7 mV at a current density of 10 mA/cm^2 in 1 M KOH. The XPS results revealed that Se doping in NiS_2 , due to the smaller electronegativity of Se compared to S, led to a decrease in the valence of Ni. Further DFT calculations, which employed the Perdew–Burke–Erzenhof exchange and correlation functional with Hubbard U correction (PBE+U), revealed that appropriate anion doping regulated the d-band center of the catalyst, which led to a neither too strong nor too weak binding strength of H^* -catalyst, therefore enhancing its intrinsic HER activity.

Liu et al., utilized a hydrothermal strategy to synthesize the bulk S-doped Ni_3Se_4 and the bulk Se-doped Ni_3S_2 hybrid catalyst (b-S- Ni_3Se_4 & b-Se- Ni_3S_2 , atomic contents of Se, S, and Ni: 30.7%, 18.5% and 50.8%, respectively) for HER [52]. Through DFT calculations, it was found that dopants in and beneath the nickel chalcogenide catalyst surface would both contribute to the HER performance. Compared to surface-only doping, bulk doping can optimize the ΔG_{H^*} of the S-doped Ni_3Se_4 and the Se-doped Ni_3S_2 ; hence, promoting the intrinsic activity of the catalyst. In addition, b-S- Ni_3Se_4 & b-Se- Ni_3S_2 showed a porous structure and had a large electrochemical active surface area, which also contributed to the enhanced HER performance of the catalyst. As a result, the b-S- Ni_3Se_4 & b-Se- Ni_3S_2 exhibited a low overpotential of 87 mV at a H_2 -evolving current density of 10 mA/cm^2 in 1.0 M KOH electrolyte.

Kou et al., through an anodization and subsequent annealing treatment, successfully doped carbon into NiO to activate the catalyst for alkali HER catalysis [53]. Carbon doping caused distortions to the NiO local structure because the coordination number and radius of carbon did not match with the Ni. As a result, the coordination number of top-layer Ni decreased from 6 to 3 with C doping (Figure 9A). This change led to an increase in the charge density of the Ni sites, making Ni more favorable for H^* adsorption. In addition, DFT calculations (PBE+U) revealed that carbon dopants facilitated the dissociation of H_2O molecules based on its low energy barrier of 0.81 eV, while without carbon dopants, the energy barrier was as high as 1.17 eV. Therefore, the 1.83 at% carbon-doped Ni_{1-x}O exhibited excellent HER performance, with only 27 mV overpotential at a H_2 -evolving current density of 10 mA/cm^2 and a small Tafel slope of only 36 mV/dec in 1.0 M KOH aqueous electrolyte (Figure 9B,C).

Figure 9. (A) Density functional theory (DFT) calculations for the structure changes of NiO with carbon doping. (B) Polarization curves of NF, C-Ni_{1-x}O-Air (annealed in air), C-Ni_{1-x}O, and Pt/C in N_2 -saturated 1.0 M KOH. (C) Tafel slopes of NF, C-Ni_{1-x}O-Air, C-Ni_{1-x}O, and Pt/C (reprinted with permission from ref [53]. Copyright © 2020, Springer).

Semiconductor-like substances, for example NiPS_3 , due to its semiconducting nature and inert basal plane, does not exhibit satisfactory HER performances. Wang et al. theoretically designed and successfully introduced a series of nonmetals into exfoliated NiPS_3 catalyst via chemical vapor deposition method to enhance the HER activity [54]. Through DFT calculations, which employed

GGA+U method (with $U = 4.5$ and $J = 0.5$ eV) to address the strong correlation effect among the partially filled Ni-3d orbitals, the authors predicted that B and C heteroatom doping into NiPS₃ could decrease its bandgap via bringing about the appearance of electronic states around the Fermi level; therefore, the catalyst could transform to a metal-like material. The free energy of hydrogen adsorption on NiPS₃ was also dominated by the degree that the valence band of NiPS₃ was filled. Only appropriate doping with moderate filled state of valence band could contribute to the optimized ΔG_{H^*} approaching 0 eV. Thereafter, the authors experimentally synthesized a series of nonmetal-doped NiPS₃ and found that the HER performances of the catalysts corroborated the theoretical predictions. The 4.271 wt% C-doped NiPS₃, due to the moderate filled state of valence band, optimized the ΔG_{H^*} and therefore promoted the HER performance, while C (3.989 wt%), N (2.10 wt%) co-doped NiPS₃ could even deliver a Pt-like HER performance (Figure 10).

Figure 10. (A) Polarization curves of (C, N)-, C-, B-, N-, O-NiPS₃, pristine NiPS₃, and Pt/C. (B) Calculated free energies of hydrogen adsorption on different catalysts under steady-state H coverage by the Volmer–Heyrovsky mechanism (reprinted with permission from ref [54]. Copyright © 2020, John Wiley and Sons).

Yang et al., successfully incorporated B, in the form of borate (BO_3^{3-}), into NiCo LDH supported on Ni foam by dipping the solvothermally prepared NiCo LDH in 1 M NaBH₄ solution for 24 h at room temperature [61]. It was found that the borate ions partially replaced the lattice OH⁻ in crystalline NiCo LDH, resulting in the transformation from crystalline to amorphous structure of the catalyst. The amorphization of NiCo LDH introduced rich oxygen vacancies and unsaturated atoms, which were proposed to work as the new reactive sites for HER. In addition, the introduced oxygen vacancies also increased the conductivity of the catalyst, enabling enhanced charge transfer ability. As a result, this B-doping induced amorphous NiCo LDH on Ni foam (A-NiCo LDH/NF) demonstrated excellent HER performance that small overpotentials of only 286 and 381 mV were required to drive the H₂ evolution at 500 and 1000 mA/cm², respectively.

4. Summary and Outlook

During the past years, continuous efforts have been made in improving the HER performances of nickel-based electrocatalysts so as to achieve promising substitutes for Pt-based materials. Among various developed methods, elemental doping can be used to improve HER performance of Ni-based materials because appropriate doping can increase the charge transfer rate, adjust the free energy of hydrogen adsorption, and introduce new active centers to the catalysts. For example, incorporation of Ru dopants into Ni(OH)₂ accelerated the charge transfer rate, and Ru dopants also functioned as the new active centers for H adsorption and the following H₂ formation [40]. As for NiP₂, Se dopants could optimize the adsorption energy of hydrogen intermediates, and therefore improved the HER performance [20].

Considering the recent remarkable progress made by researchers in doped Ni-based HER catalysts, we would like to highlight the following points, which we suppose not only suitable for Ni-based materials, but also applicable to other transition metal-based catalysts.

1. Single- vs. double-doping mode. As mentioned before, heteroatom doping can affect its free energies of H^* adsorption and H_2 release on Ni metal [50]. However, most heteroatom doping is in single-doping mode, and its ability to adjust the electronic structure might still be limited. Instead, the double-doping mode can trigger synergistic effect and can fine-tune the electronic structure of the catalyst rather than too strongly or too weakly; thereby, improving the HER performance. Hence it is desirable that more efforts could be made in the judicious selection of different doping modes so as to achieve an optimization of the HER catalysts.
2. Single atom doping. As mentioned above, the introduction of single-atom Ru into Ni_5P_4 would cause localized structure polarization and then create electron-rich Ru sites, reducing the energy barriers of hydrolytic ionization [41]. In addition, the localized interstitial structures would optimize the hydrogen adsorption energy; thereby, enhancing the HER performance of the Ni_5P_4 -Ru catalyst. Hence, we highlight single-atom doping as a strategy worthy of reference for promoting catalyst performances. Notably, single-atom doping is still of great difficulty because with smaller particle size, the free energy of metals increases significantly and therefore aggregation will occur. However, the judicious selection of an appropriate substrate that provides strong interactions with the metal species can stabilize the metal centers and significantly prevent this aggregation (e.g., Ni vacancies in nickel hydroxides can stabilize the Ru sites); hence, single-atom doping can be achieved [41,62].
3. Making full use of DFT calculations. DFT calculations play an increasingly important role in catalysis research. Apart from using DFT as a standard tool for answering such questions like why doping heteroatoms can increase the activity of a certain catalyst, we highlight that researchers could also employ DFT calculations as a powerful technique to predict the performances of nonexistent catalysts and therefore select out those catalysts with appropriate electronic structures for further experimental investigation. For example, Wang et al. theoretically designed and introduced a series of nonmetals (B, C, N, and O) into $NiPS_3$ catalyst, and predicted that B and C dopants could transform the semiconducting basal plane to a metal-like property [53]. Their further experimental results corroborated the DFT predictions, showing that introduction of B or C dopants did successfully activate the inert basal plane and promote the conductivity of the $NiPS_3$ catalyst, hence enhancing the HER performance.

Finally, we would like to suggest the employment of operando techniques, such as operando Raman, IR, and XAS, for the investigation into the reactive sites and HER reaction pathways of the catalysts. These operando techniques could provide insightful information about reaction mechanisms, and along with DFT calculations, a more comprehensive understanding of the catalytic process could be obtained. This understanding would further play a guiding role in the design and synthesis of more efficient catalysts.

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