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Review

NiFe-based nanostructures on nickel foam as highly efficiently electrocatalysts for oxygen and hydrogen evolution reactions

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ABSTRACT

Water splitting, as an advanced energy conversion technology, consists of two half reactions, including oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). However, the ideal electrocatalysts are noble metal based catalysts. Their high cost and scarcity in earth seriously restrict the large deployments. NiFe-based materials have attracted great attention in recent years due to their excellent catalytic properties for OER and HER. Nevertheless, their conductivity and electrochemical stability at high current density are unsatisfactory, resulting in ineffective water splitting due to high impedance and low stability. Recently, a series of catalysts coating NiFe-based materials on 3D nickel foam were found to be extremely stable under the circumstance of high current density. In this review, we summarized the recent advances of NiFe-based materials on nickel foam for OER and HER, respectively, and further provided the perspectives for their future development.

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1. Introduction

The accelerating depletion of fossil fuels and the ever-growing issue of environment have attracted widespread concerns. The development of new energy resource has become an urgent challenge [1–3]. In this regard, as a highly efficient and clean technology, electrochemical water splitting (WS) is easily coupled to other renewable energy resource, such as wind power, wave power and solar energy, and stands out in various hydrogen production technologies. It is well known that WS is composed of oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) processes [4–6]. However, the practical applications of WS are restrained due to the high overpotentials of anodic OER and cathodic HER [7,8]. Thus, it is necessary to develop an efficient catalyst to reduce the overpotentials of WS. Currently, Ru/Ir- and Pt-based materials are the most efficient catalysts for OER and HER, respectively [9,10]. However, these high cost and scarce catalysts impede the widespread application of WS. Moreover, due to the inharmonious of optimum electrolyte pH, most of catalysts become difficult to trigger WS efficiently when they are in an integrated electrolyte [11]. Besides, the stability of catalysts is another important factor for application. Therefore, it is an urgent demand to design a catalyst with high activity, low cost and long-term stability to replace noble metal-based catalysts.

Recently, transition metals (such as Mn [12–14], Ni [15–17], Co [18–20] and Fe [21,22]) based catalysts have been widely investigated for WS. Moreover, the combination of the two metals will tend to bring higher electrochemical performance towards OER and HER [23–28]. Significantly, compared with other electrocatalysts (NiCo-based, NiMn-based, CoFe-based, etc.), NiFe-based catalysts show superior performance in both OER and HER. More interestingly, Ni and Fe are always found together in the earth and trace Fe in Ni(OH)₂ electrodes can significantly improve OER performance of Ni(OH)₂. According to the previous reports, NiFeO_xH_y is regarded as the best OER catalyst. Besides, the excellent HER performance of NiFe-based catalysts has also been proved in many researches [29,30]. The reserves of Ni and Fe in earth are abundant, which can reduce the cost of commercialization. At present, there are two main methods for preparing WS catalyst electrodes [31]. The commonly used one is to drop a slurry composed of catalyst and conductive binder onto the electrodes [32–34]. However, such method has two drawbacks: (i) the electrical insulating binder used to make up slurry will decrease the contact area of catalyst and electrolytes, which will reduce the electrocatalytic performance [35]; (ii) the attached catalysts are liable to shed out from the electrode under high current density due to the large producing rate of H₂/O₂ bubbles, which causes a poor stability. In order to overcome the above bottlenecks, people combined the WS catalysts and conductive substrates as the another WS catalysts preparation method, such as carbon paper [36–41], copper foils [42–45], FTO [46–49], nickel foils [50–53], iron substrates [54], stainless-steel [51,55] and nickel foam [56–58]. As a 3D porous substrate, nickel foam has the advantages of good electrical conductivity (accelerate the diffusion of electrons), high specific surface area (conductive to the dispersion of the catalysts) and the porous structure

(diffuse the generated gas in timely) [59,60]. Therefore, the application of nickel foam in WS has attached great attention, especially at high current density. At present, more and more catalysts on nickel foam have been reported, which can withstand a long period of time at high current density. Thus, they attract much more attention for practical applications. Generally, the assembling of catalysts and nickel foam mainly includes hydrothermal reaction and electrodeposition. The hydrothermal reaction can obtain the catalysts with high purity, good crystallinity and regular morphology, but it is time consuming. The electrodeposition has the advantage of timesaving, but this approach has a complex operation with high cost in practical applications. We summarized the methods of NiFe-based electrocatalysts on nickel foam in Table 1.

There are several meaningful reviews about the NiFe-based electrocatalysts and the electrocatalysts on nickel foam [61]. However, no systematic review about the combination of them for OER and HER has been reported yet. Therefore, in this review, we summarize the reports of NiFe-based catalysts on nickel foam in OER and HER, respectively. This review will provide a more comprehensive understanding of NiFe-based electrocatalysts on nickel foam and provide some references for the design of such electrocatalysts in the future.

2. Electrochemical parameters for oxygen and hydrogen evolution reactions

Since the first report on WS with a cathode and an anode in an electrolyte in 1789, enormous efforts have been made to develop high-performance WS catalysts. Earlier comparisons of catalytic performance focused on the current density at a certain overpotential. With the deepening of research, there are several main parameters to evaluate the catalytic performance such as, overpotential (Fig. 1(a) and (b)), Tafel slope (Fig. 1(c)), electrochemical impedance spectrum (EIS) (Fig. 1(d)), electrochemical active surface area (ECSA) (Fig. 1(e) and (f)), turnover frequency (TOF) (Fig. 1(g)), faraday efficiency and stability (Fig. 1(h)) [5,10,62].

2.1. Onset overpotential and overpotential

The onset overpotential generally refers to the applied potential when the obvious current begins to appear. However, it is difficult to determine the precise potential values due to external factors such as materials and environment. To compare the activity of catalysts quantitatively, scientists make the overpotential at 10 mA cm⁻² as an important Ref. [63]. In addition, for the performance of catalysts based on nickel foam, the overpotential at a higher current density is another evaluation parameter. In brief, an ideal catalytic material requires a higher current density at lower overpotential. In order to unify the standard of evaluation, the Ag/AgCl electrode and the saturated calomel electrode (SCE) are used as a Ref. [64]. The final data should be converted to the potential vs. RHE according to the calculation below:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E_{\text{Ag/AgCl}}^0 + 0.059 * \text{pH} \quad (E_{\text{Ag/AgCl}}^0 = 0.197 \text{ V})$$

$$E_{\text{RHE}} = E_{\text{SCE}} + E_{\text{SCE}}^0 + 0.059 * \text{pH} \quad (E_{\text{Ag/AgCl}}^0 = 0.242 \text{ V})$$

2.2. Tafel plot

The Tafel slope, which can be obtained from three methods, acts as an important character in determining the reaction kinetics of OER and HER [65]. The first method is calculated from the LSV linear, according to the Tafel equation ($\eta = b \times \log j + a$, where η is overpotential, j is the current density, and b is the Tafel slope). This is the most commonly used method because it is calculated under low overpotential and without bubbles interference. The second method is to directly obtain it by use of electrochemical workstation, in which the test voltage should be consistent with the

Table 1. The comparison of the different methods to construct NiFe-based electrocatalysts on nickel foam.

Catalyst/nickel foam	Method	Materials	Reaction condition	Ref.
NiFe-LDH	Hydrothermal reaction	Nickel foam, Ni(NO ₃) ₂ , Fe(NO ₃) ₃ , urea	120 °C, 12 h	[88]
FeNi _{10-x} Co _x -LDH	Hydrothermal reaction	Nickel foam, Fe(NO ₃) ₃ , NiCl ₂ , CoCl ₂ , urea, trisodium citrate;	150 °C, 2 day	[94]
Fe-Ni(OH) ₂	Hydrothermal reaction	Nickel foam, FeCl ₃ ; HCl	180 °C, 6 h	[64]
NiFeRu-LDH	Hydrothermal reaction	Nickel foam, Ni(NO ₃) ₂ , Fe(NO ₃) ₃ , RuCl ₃ , urea	120 °C, 12 h	[97]
NiFeV-LDH	Hydrothermal reaction	Nickel foam, Ni(NO ₃) ₂ , Fe(NO ₃) ₃ , VCl ₃	120 °C, 12 h	[98]
NiFe-LDH	Electrodeposition	Nickel foam, FeSO ₄ , Ni(NO ₃) ₂	Room temperature, < 300 s	[93]
NiFeAl _x -LDH	Hydrothermal reaction	Nickel foam, Ni(NO ₃) ₂ , Fe(NO ₃) ₃ , Al(NO ₃) ₃ , triethanolamine, hexamethylenetetramine	95 °C, 10 h; 6 M HCl, 15 min	[95]
NiFeMo	Hydrothermal reaction	Nickel foam, NiAc ₂ , Fe(NO ₃) ₃ , (NH ₄) ₆ Mo ₇ O ₂₄ , urea	160 °C, 2–10 h	[102]
FeNi ₃ N	Oil bath and NH ₃ atmosphere	Nickel foam, FeCl ₂ , trisodium citrate; NH ₃	Oil bath: 90 °C, 6 h; NH ₃ : 500°C, 2 h	[109]
N-(Ni,Fe) ₃ S ₂	Solid reaction	Nickel foam, thiourea	500 °C, 2 h	[113]
Fe ₂ Ni ₂ N	Hydrothermal reaction and NH ₃ atmosphere	Nickel foam, Ni(NO ₃) ₂ , Fe(NO ₃) ₃ , urea; NH ₃	Hydrothermal reaction: 120 °C, 12 h; NH ₃ : 380 °C, 2 h	[114]
(Ni _{0.33} Fe _{0.67}) ₂ P	Hydrothermal reaction and solid reaction	Nickel foam, Ni(NO ₃) ₂ , Fe(NO ₃) ₃ , urea; NaH ₂ PO ₂	Hydrothermal reaction: 120 °C, 12 h; solid reaction: 300 °C, 2 h	[120]
Ni _{1.85} Fe _{0.15} P	Hydrothermal reaction and solid reaction	Nickel foam, Ni(NO ₃) ₂ , Fe(NO ₃) ₃ , hexamethylene tetramine; NaH ₂ PO ₂	Hydrothermal reaction: 100 °C, 10 h; solid reaction: 300 °C, 2 h	[121]
NiFe-OH/NiFeP	PH ₃ gas plasma-assisted approach and Electrodeposition	Nickel foam, PH ₃ , Ni(NO ₃) ₂ , Fe(NO ₃) ₃	PH ₃ gas plasma-assisted approach: 200 °C, 15 min; electrodeposition: 15 min, -1 V vs. Ag/AgCl	[122]
(Ni _{0.5} Fe _{0.5}) ₂ P	Hydrothermal reaction and solid reaction	Nickel foam, Ni(NO ₃) ₂ , FeSO ₄ , urea, NH ₄ F; NaH ₂ PO ₂	Hydrothermal reaction: 100 °C, 8 h; solid reaction: 400 °C, 2 h	[123]
Fe _{11.8%} -Ni ₃ S ₂	Hydrothermal reaction	Nickel foam, FeSO ₄ , L-cysteine	150 °C, 10 h	[125]
Ni _{0.7} Fe _{0.3} S ₂	Hydrothermal reaction and solid reaction	Nickel foam, Ni(NO ₃) ₂ , FeSO ₄ , urea, NH ₄ F; S	Hydrothermal reaction: 100 °C, 8 h; solid reaction: 300°C, 1 h	[126]
Ni ₂ FeS ₄	Electrodeposition	Nickel foam, NiCl ₂ , thiourea	-1.2 V and +0.2 V (vs. Ag/AgCl) at a scan rate of 5 mV s ⁻¹ , 15 sweep cycles	[127]
NiFeP	Solid reaction	Nickel-iron foam, Red P.	450°C, 3 h	[139]
NiFe-P	Electrodeposition	Nickel foam, NiSO ₄ , FeSO ₄ , NaH ₂ PO ₂ , NaOAc	-1 V and -0.3 V (vs. Ag/AgCl) at a scan rate of 5 mV s ⁻¹ for 15 sweep cycles	[142]
FeNiP _x	Water bath and solid reaction	Nickel foam, FeCl ₂ , trisodium citrate, NaH ₂ PO ₂	Water bath: 90°C, 6 h; solid reaction: 300°C, 2 h	[143]
Fe-Ni ₃ S ₂	Hydrothermal reaction and ion exchange reaction	Nickel foam, Ni(NO ₃) ₂ , Fe(NO ₃) ₃ , urea, NH ₄ F; Na ₂ S	Hydrothermal reaction: 120 °C, 6 h; ion exchange reaction: 100 °C, 8 h	[150]
FeNi-S film	Electrodeposition	Nickel foam, Ni(NO ₃) ₂ , Fe(NO ₃) ₃ , thiourea	50 °C, -1.2 V and 0.2 V (vs. Ag/AgCl) at a scan rate of 20 mV s ⁻¹ for 20 sweep cycles	[152]
(Fe _{0.048} Ni _{0.952}) ₂ P	Hydrothermal reaction and solid reaction	Nickel foam, Ni(NO ₃) ₂ , Fe(NO ₃) ₃ , urea, NH ₄ F; NaH ₂ PO ₂	Hydrothermal reaction: 140°C, 12 h; solid reaction: 450°C, 3 h	[69]

voltage range of the LSV test. The third one is to calculate the Tafel slopes from the plot of $\log R_{ct}$ vs. overpotential, in which R_{ct} represents the charge transfer resistance in the equivalent circuit fitted in impedance spectroscopy. Tafel slopes obtained from this method reflect purely the charge transfer kinetics, compared with Tafel slopes obtained from the above two methods which may include contributions from catalyst resistance. The obtained Tafel slopes can provide significant kinetic information on the reaction mechanism. For example, the lower Tafel value represents the faster reaction kinetics. The exchange current density (j_0) is another important parameter that can reflect the intrinsic electrocatalytic activity. It can be obtained from the Tafel equation ($\eta = b \times \log(j + a)$) when η is assumed to be zero. The calculated j_0 is considered to be proportional to the catalytic active surface area. The large j_0 indicates the large surface area and fast electron transfer rate. Therefore, the high-performance electrocatalysts in OER and HER should have low Tafel slope and high exchange current density [66].

2.3. Electrochemical impedance spectrum (EIS)

EIS is a small amplitude alternating current (AC) signal with different frequencies, which is to measure the ratio of AC signal voltage to current (that ratio is the impedance of the system) with the variation of sinusoidal frequency (ω) or the phase angle (Φ) of impedance varies with ω . It can probe the kinetics of WS and the electrode/electrolyte interface reactions. The

semicircle in the Nyquist plot attributes to the charge-transfer resistance (R_{ct}), which is related to the interface charge-transfer process of the electrode. The smaller diameter of the semicircles means the lower R_{ct} and the lower R_{ct} value indicates a faster reaction rate [67].

2.4. Electrochemical active surface area (ECSA)

To understand the reaction mechanism of catalysts, the ECSA of the catalysts are investigated based on the electrochemical double-layer capacitance (C_{dl}). The C_{dl} can be calculated from CV curves, which is tested in a certain potential window without the faradaic processes. In general, 5–10 consecutive CV curves at different sweep speeds (5–200 mV s⁻¹) are taken. The obtained CV curves are preferably close to the rectangle. After selecting the intermediate value of the applied potential range, the difference of current density under the current potential is calculated ($\Delta j = j_1 - j_2$), and the slope is obtained by linear fitting with different sweep speeds as X-axis and Δj as Y-axis. The slope is twice the value of C_{dl} . The larger value represents higher current density and more exposed surface reactive sites [68].

2.5. Turnover frequency (TOF)

At present, in the process of electrochemical measurement, especially for the electrocatalysts grown on the substrate, it is not easy to exactly determine the loading amount of a catalyst. In order to solve this problem, TOF has been proposed to characterize

Fig. 1. The parameters of evaluating the catalytic performance. (a) and (b) LSV of HER and OER; (c) Tafel slope; (d) EIS; (e) C_{dl} ; (f) ECSA; (g) TOF; (h) Stability [62].

the performance of catalysts widely. The value of TOF is defined as the amount of reactants that per unit of catalytic active site in unit time can be converted into a desired product. The TOF (s^{-1}) can be calculated according to the following equation:

$$TOF = \frac{J \times A}{(\alpha \times F \times n)}$$

Where J ($mA\ cm^{-2}$) is the current density at a given overpotential during the LSV measurement; A is the area of the working electrode; α is the electron number of the target product; F is the Faraday constant (a value of $96485.3\ C\ mol^{-1}$); n (mol) is the number of moles of the active materials. The TOF value is useful for comparing the property of similar catalysts and the high TOF value represents higher catalytic activity [62].

2.6. Faraday efficiency (FE)

FE is a term commonly used in electrochemical fields such as fuel cells and water electrolysis reaction, which can be understood as the percentage of actual products and theoretical products. For the WS, the FE is equal to the ratio of the amount of gas produced by experiment to the amount of gas produced theoretically, and plays an important role in analyzing the reaction process of the catalysts [11].

2.7. Stability

In addition to excellent electrochemical performance, long-term stability of an electrocatalyst is important, as it directly determines whether the materials can be developed for practical applications. Generally, two main methods are often used: cyclic CV method and chronoamperometry ($E-t$ curve) or chronopotentiometry test ($I-t$ curve). $E-t$ curve or chronopotentiometry is measured for a long period with a given applied potential or current density. The given applied potential and current density should generally ensure that the current density is larger than $10\ mA\ cm^{-2}$. Normally, more than 20 h of testing can be used as a benchmark for an ideal catalyst [69].

3. NiFe-based electrocatalysts on nickel foam for OER

Since the OER undergoes four electrons pathway, the OER requires more energy input than HER (two electrons pathway) [70]. Thus, most of the OER catalysts tend to exhibit higher overpotentials, and the OER plays an essential role in WS [44,71]. The sluggish OER can significantly hinder the efficiency of the overall reactions and thus impede the practical application. Therefore, developing stable and efficient OER catalysts with low overpotential is still profoundly desired.

Table 2. The performance of the NiFe-based electrocatalysts in OER.

Catalyst/nickel foam	Electrolyte	η at x mA cm ⁻² (mV)	Tafel slope (mV dec ⁻¹)	Stability	Ref.
NiFe-LDH	0.1 KOH	$\eta_{30} = 280$	50	More than 10 h at 200 mA cm ⁻² (1.0 KOH)	[88]
FeNi _{10-x} Co _x -LDH	1.0 KOH	$\eta_{10} = 220$	42	More than 11 h at 10 mA cm ⁻² (1.0 KOH)	[94]
Fe-Ni(OH) ₂	1.0 KOH	$\eta_{10} = 260$	51.5	More than 100 h	[64]
NiFeRu-LDH	1.0 KOH	$\eta_{10} = 225$	31	More than 10 h at 10 mA cm ⁻² (1.0 KOH)	[97]
NiFeV-LDH	1.0 KOH	$\eta_{20} = 260$	42	More than 18 h at ~190 mA cm ⁻² (1.0 KOH)	[98]
NiFe-LDH	1.0 KOH	$\eta_{10} = 224$	52.8	More than 50 h	[93]
NiFeAl _x -LDH	1.0 KOH	$\eta_{20} = 304$	50	More than 18 h at 20 mA cm ⁻² (1.0 KOH)	[95]
NiFeMo	1.0 KOH	$\eta_{10} = 280$	40	More than 24 h	[102]
FeNi ₃ N	1.0 KOH	$\eta_{10} = 202$	98	More than 60 h at 100 mA cm ⁻² (1.0 KOH)	[109]
N-(Ni,Fe) ₃ S ₂	1.0 KOH	$\eta_{170} = 350$	70	More than 10000s at ~50 mA cm ⁻² (1.0 KOH)	[113]
Fe ₂ Ni ₂ N	1.0 KOH	$\eta_{100} = 250$	34	More than 10 h at ~150 mA cm ⁻² (1.0 KOH)	[114]
(Ni _{0.33} Fe _{0.67}) ₂ P	1.0 KOH	$\eta_{50} = 230$ mV	55.9	More than 24 h at ~170 mA cm ⁻² (1.0 KOH)	[120]
Ni _{1.85} Fe _{0.15} P	1.0 KOH	$\eta_{20} = 270$ mV	96	More than 10 h at 100 mA cm ⁻² (1.0 KOH)	[121]
NiFe-OH/NiFeP	1.0 KOH	$\eta_{10} = 199$ mV	39	More than 24 h at 10 mA cm ⁻² (1.0 KOH)	[122]
(Ni _{0.5} Fe _{0.5}) ₂ P	1.0 KOH	$\eta_{20} = 219$ mV	57	More than 24 h at 20 mA cm ⁻² (1.0 KOH)	[123]
Fe _{11.88} -Ni ₃ S ₂	1.0 KOH	$\eta_{100} = 253$ mV	65.5	More than 14 h	[125]
Ni _{0.7} Fe _{0.3} S ₂	1.0 KOH	$\eta_{10} = 198$ mV	56	More than 5000 s at 10 mA cm ⁻² (1.0 KOH)	[126]
Ni ₂ FeS ₄	1.0 KOH	$\eta_{100} = 231$ mV	55	More than 200 h at 80 mA cm ⁻² (1.0 KOH)	[127]

At the early stage, most of the studies focused on precious metal catalysts. Among them, Ru-based and Ir-based materials were considered to be the highly efficient OER catalysts [72–75]. Nevertheless, their scarcity and high cost hinder the large-scale deployment. Recently, transition metal compounds came into view with the advantage of low cost and high activity for OER including MnO [76,77], FeO [78,79], CoO [80,81] and NiO [82,83]. Some of them were coated on nickel foam to enhance the OER performance and high stability [60,84,85]. Particularly, the NiFe-based materials on nickel foam exhibit superior performance (Table 2).

3.1. NiFe-LDH-based electrocatalysts on nickel foam for OER

Due to the typical layered structure, the properties of NiFe-LDHs can be adjusted in a wide range by tuning the ratio of Ni and Fe, and the type of anions at the interlayers and the porosity [66,86–88]. This makes that NiFe-LDHs become a class of materials with great potential for energy conversion and storage. However, the original NiFe-LDH has poor electrical conductivity [88–90], which could result in the unsatisfactory performance. To solve this problem, some researchers assembled NiFe-LDH with the conductive nickel foam substrate [7]. In 2014, Lu et al. directly grow NiFe-LDH on nickel foam by using hydrothermal method [88]. The obtained NiFe-LDH film presents mesoporous structures with the thickness of ~200–300 nm and the excellent OER performance in 1.0 M KOH (Fig. 2(a)–(c)). For instance, the onset overpotential of NiFe-LDH film (~230 mV) is smaller than those of β -Ni(OH)₂ film (~450 mV) and nickel foam (~520 mV). After the OER test, the authors found that the NiFe-LDH is converted to NiOOH according to the Raman spectra results, which means that the real OER catalyst might be the NiOOH. The structure reconstruction of NiFe-LDH from hydroxide to oxyhydroxide during the OER process is also found by other groups [91,92], and the resultant oxyhydroxide phase might be the crucial factor of the outstanding OER activity towards NiFe-LDH. Also in 2014, Luo and co-workers combined the perovskite tandem cell with NiFe-LDH on nickel foam electrodes for water splitting [1]. Benefiting from the outstanding OER performance of NiFe-LDH on nickel foam, the efficiency of solar to hydrogen reaches as high as 12.3%. Such combination provided a new form of energy conversion from solar energy to hydrogen production. In 2015, Duan's group reported a universal electrochemical approach to fabricate various LDH [93]. The approach has the advantage of saving time and cost, which provides a viable commercial route. The obtained NiFe-LDH on nickel foam from this method shows excellent OER performance ($\eta_{10} = 224$ mV) and sta-

bility of large current (50–250 mA cm⁻²) for long time (more than 50 h). After the stability test, the current density has no attenuation, which proved that the catalysts would have great potential in practical application of WS.

Recently, many efforts have been made to improve the activity of NiFe-LDH on nickel foam by heteroatom doping or defect making. Both of the onset overpotential and current density can be significantly improved by using the two methods [94,95]. Firstly, heteroatom doping could modify the electronic structure and improve the conductivity of the electrocatalyst, thus enhancing the OER performance [96]. Long et al. successfully introduced Co into NiFe-LDH and improved the catalytic performance of NiFe-LDH efficiently [94]. The authors synthesized ultra-thin FeNiCo-LDH by replacing Fe salt with Co salt. The atomic force microscopy (AFM) shows the thickness of LDHs decreased with the increase of Co doping amount. The thicknesses of FeNi₉Co-LDH and FeNi₈Co₂-LDH are around 1.5–1.8 nm and 1.2–1.5 nm, respectively. The LSV results show that the thinner NiFe₈Co₂-LDH with higher cobalt content shows the lower onset potential of ~0.21 V. They thought that the OER performance enhancement stems from Co substitution. With the development of the DFT calculation in WS, some works about heteroatom doping have been reemphasized. Chen and co-workers used the similar synthesized method to replace part of Fe(NO₃)₃ with RuCl₃ in reactant to grow NiFeRu-LDH on nickel foam [97]. The NiFeRu-LDH shows a zero onset HER overpotential, and the current densities under the same overpotentials are larger than that of Pt/C. Through the DFT calculation, the water dissociation energy of NiFeRu-LDH is only 0.5 eV, much lower than that of NiFe-LDH (1.02 eV). Li and co-workers reported the formation of the NiFeV-LDH on nickel foam through the common hydrothermal reaction with better OER performance than NiFe-LDH [98]. To achieve the current density of 20 mA cm⁻², NiFeV-LDH only needs a low overpotential of 195 mV compared that of NiFe-LDH (249 mV). Because the doped V can change the chemical environment of Fe, the authors selected the Fe as the active sites, and calculated the Gibbs free energy. The calculated energy of rate determining step on NiFeV-LDH (1.64 eV) is smaller than that on NiFe-LDH (1.89 eV), which indicates that the doped V could decrease the OER energy barrier and thus enhances the OER performance of NiFe-LDH. Benefiting from the 3D porous structure, NiFeV-LDH supported on nickel foam shows the outstanding stability of more than 18 h at a high current density of 187 mA cm⁻². Although this is still far from the current density required for commercial industrial electrolytic water (1 A cm⁻²), it has an enormous advantage over most reports (10 mA cm⁻²) [99]. The

Fig. 2. (a) Low-magnification SEM images of NiFe-LDH NP film (inset: cross-view SEM image; scale bar: 100 nm); (b) polarization curves of various catalysts; (c) stability testing of NiFe-LDH NP film at constant potentials in 0.1 M and 1.0 M KOH solution and the 20 wt% Ir/C catalyst; (d) in situ Raman spectroscopy of NiFe-LDH films with (1.6 V vs. RHE) and without OER operation [88].

changes in the chemical environment of metal sites after heteroatom doping are also discovered on NiFeCr on carbon paper reported by Yang and co-workers [100]. Such phenomenon is very important to study the mechanism of heteroatom doping in NiFe-LDH. In addition, the catalytic performance of NiFe-LDH could be further enhanced by etching the substituted atoms and inducing defects. For example, as the Al³⁺ can partially dissolve in strong alkaline solution, the defective NiFeAl_x-LDH was synthesized by Liu and co-workers [95]. The obtained Ni₃FeAl_{0.91}-LDH shows the best catalytic performance among the Ni₃FeAl_{1.27}-LDH, Ni₃FeAl_{2.73}-LDH and nickel foam. The current density of Ni₃FeAl_{0.91}-LDH at the potential of 1.60 V vs. RHE is as high as 235 mA cm⁻², which is much higher than those of Ni₃Fe-LDH (53 mA cm⁻²), Ni₃FeAl_{1.27}-LDH (120 mA cm⁻²), Ni₃FeAl_{2.73}-LDH (105 mA cm⁻²) and pristine Ni foam (20 mA cm⁻²).

In addition to doping cations to improve the catalytic performance of OER, adjusting the anions between NiFe-LDH layers could significantly improve the performance of OER [101]. In 2105, Li's group directly fabricated NiFeMo-LDH onto nickel foam by hydrothermal method in the presence of urea as precipitant in [102]. The doped Mo atoms could form molybdate salt between the LDH layers with the assistance of urea (Fig. 3(a) and (b)). The formed MoO₄²⁻ reduces the average thickness of LDHs to 0.5 nm, which is much thinner than those of NiFe-LDHs prepared by other co-precipitation methods [90,103,104]. Such results indicate that the interlayer anions are critical to the formation of these ultra-thin LDHs. Although NiFeMo-LDH and NiFe-LDH have the same Tafel slope (40 mV dec⁻¹), the current density of NiFeMo-LDH is obviously greater than that of NiFe-LDH at the same overpotential.

Unfortunately, the real OER active site of NiFe-LDH is still undefined. Presently, there are two hypotheses about the real active

sites of NiFe-LDH: the Ni active sites and Fe active sites. In early research, people mainly thought that the OER activity of Ni is higher than that of Fe in NiFe-LDH [105]. However, Friebe and co-workers confirmed the high OER activity of Fe in Ni_xFe_yOOH through density-functional theory (DFT) calculation. The authors also debated that the Fe might act as the OER-active site when it incorporated into NiOOH [106]. At present, the debate about active sites continues.

3.2. NiFe-based nitrides and phosphides and sulphides on nickel foam for OER

Since the industrial-scale manufacturing of precious metal electrocatalysts is limited by their low natural reserves and high costs, transition metal nitrides, phosphides and sulphides have attracted much attention because of their excellent catalytic ability. Recently, much attention has been paid to develop efficient NiFe-based nitrides, phosphides and sulphides electrocatalysts.

3.2.1. NiFe-based nitrides on nickel foam for OER

Metal nitrides such as Ni₃FeN nanoparticles and Ni₃N nanosheets have been proved to possess faster charge-carrier transportation and better conductivity than metal oxide [107,108]. Thus, they are believed to be promising candidate electrocatalysts for OER. In 2016, Zhang et al. reported an in-situ growth of iron-nickel nitride nanostructures on nickel foam (FeNi₃N/NF) by surface redox etching for the first time [109]. In the synthesis process, the nickel foam not only acted as the substrate but also served as a slow-releasing Ni precursor that was induced by redox etching of Fe precursor (Fe³⁺) (Fig. 4(a)). The catalysts obtained by this method have stronger adhesion with the nickel foam substrate and can withstand larger electric currents (Fig. 4(b)).

Fig. 3. (a) Schematic crystal structure of NiFeMo. (b) XRD patterns of NiFeMo along with NiFe and $\beta\text{-Ni(OH)}_2$ for comparison, the suppressed (001) peaks of NiFeMo are indicative of ultrathin nanosheet thickness. (c) Raman spectra of NiFeMo and NiFe showing the fingerprint vibrations of Ni-OH and MoO_4^{2-} [102].

Fig. 4. (a) Schematic illustration of the formation of FeNi₃N/NF; (b) iR-corrected LSV curves for OER measured at a scan rate of 5 mV s⁻¹; (c) corresponding Tafel plots of different materials [109].

For instance, the FeNi₃N/NF has almost no attenuation stability over 30 h at a large current density of 100 mA cm⁻². As shown in Fig. 4(c), the Tafel slope of FeNi₃N/NF (40 mV dec⁻¹) is much smaller than that of RuO₂ (58 mV dec⁻¹). In addition, massive studies have shown that N doping can improve the catalytic performance of OER by improving the conductivity of the catalytic materials, such as Co₄N [110] and N-CoFe LDHs [111]. Recently, Chen and co-workers reported that the surface N atoms of Ni₃S₂ could regulate the electronic structure and then optimize the adsorption energy of active sites. Thus, the OER performance of Ni₃S₂ has been greatly improved [112]. In such circumstances, Jin and co-workers developed a facile one-step method to fabricate the N-(Ni,Fe)₃S₂/NIF (NIF is Ni-Fe alloy foam) as efficient OER

catalyst [113]. The obtained N-(Ni,Fe)₃S₂/NIF catalyst has a low overpotential of 167 mV at 10 mA cm⁻², which exhibits the best OER performance so far. The authors attributed such superior OER performance to the surface N-anion decoration, because the decorated N atoms could increase the density of states near the Fermi level, and then enhance the electrical conductivity of (Ni,Fe)₃S₂/NIF. The stability at high current density of NiFe-based nitrides on nickel foam was reported by Duan's group in 2016 [114]. The Fe₂Ni₂N on nickel foam was synthesized through two steps: the NiFe-LDH by simple hydrothermal method and then the Fe₂Ni₂N from NiFe-LDH under the reaction with NH_3 . The Fe₂Ni₂N catalyst are both active in OER and HER. For instance, the OER activity is much better than Ir/C and the HER activity is closed

Fig. 5. (a) Scheme for the synthesis of α -NiFe-OH/NiFeP/NF hierarchical electrocatalyst for water oxidation; (b) *iR*-corrected LSV curves for the NiFeP/NiFe-OH recorded at a scan rate of 0.5 mV s^{-1} , along with NiFeP, NiFe-DH, and Ni foam for Comparison; (c) corresponding Tafel plots of different materials; (d) plots showing the extraction of the double-layer capacitances allow the estimation of the electrochemically active surface area (ECSA) [122].

to Pt on nickel foam. Combining with the super stability, such catalyst would be a potential candidate for It/C and Pt in WS.

3.2.2. NiFe-based phosphides on nickel foam for OER

Like metal nitrides, the metal phosphides are also developed as potential OER catalysts. The introduction of phosphorus not only enhances the conductivity of some metal catalysts, but also tunes the adsorption energy of active sites [115]. However, the enhanced OER performance of metal phosphides is still far from the best performance of the noble metal, such as FeP [116–118] and NiP [16,119]. To solve this issue, Li and co-workers reported the synthesis of Fe-doped Ni_2P nanosheets on nickel foam [120]. The $(\text{Ni}_{0.33}\text{Fe}_{0.67})_2\text{P}$ electrode shows the best OER performance with overpotential of $\sim 230 \text{ mV}$ at 50 mA cm^{-2} . In addition, the thickness of $(\text{Ni}_{0.33}\text{Fe}_{0.67})_2\text{P}$ nanosheets decreases from $\sim 40 \text{ nm}$ to $\sim 20 \text{ nm}$ with the introduction of Fe, which suggests that the doped Fe atoms can not only regulate the electronic structure, but also affect the morphology of the catalyst. In 2017, Wang and co-workers also reported the preparation of Fe-doped Ni_2P on nickel foam [121], where the amount of Fe was precisely controlled. Through the inductively coupled plasma atom emission spectrometry (ICP-AES) analysis, the authors confirmed that the Fe-doped Ni_2P with the best OER performance is $\text{Ni}_{1.85}\text{Fe}_{0.15}\text{P}$. The results show that the OER performance of Ni_2P can be improved significantly with only about 8% Fe doping. However, the role of such trace Fe has not been discussed further in this paper. Therefore, there is still a lot of work need to be carried out to clarify the role of doped trace Fe. In addition to regulating the amount of doped Fe, surface modification of NiFeP is a very effective way

to improve the properties of OER. An NiFe-OH/NiFeP electrocatalyst on nickel foam for OER was reported by Liang et al. [122]. In order to further improve the OER performance of NiFeP, the authors deposited another layer of α -NiFe-OH on NiFeP (Fig. 5(a)). The obtained NiFe-OH/NiFeP achieves a large current density of 300 mA cm^{-2} at a low overpotential (258 mV) (Fig. 5(b)), a low Tafel slope of 39 mV dec^{-1} and a large ECSA of 6.3 mF cm^{-2} (Fig. 5(c) and (d)) in 1.0 M KOH . The authors ascribed the enhanced OER performance to the strong electronic interactions between the deposited NiFe-OH and NiFeP. Such intense electron interaction can significantly reduce the adsorption energy of H_2O and lead to the enhanced OER performance. In 2017, Yu and co-workers reported an OER catalyst $((\text{Ni}_{0.5}\text{Fe}_{0.5})_2\text{P})$ with the good stability more than 24 h and studied the structure changes after the OER process [123]. The authors found that the metal phosphides disappeared and Ni-Fe oxo/hydroxide species were generated after the OER test. They thought that the outstanding OER activity might be originated from Ni-Fe oxo/hydroxide. This phenomenon is also found on the NiFe-based nitrides and sulphides.

3.2.3. NiFe-based sulphides on nickel foam for OER

NiFe-based sulphides have many similarities in physical-chemical properties with NiFe-based phosphides, such as the strong metal-metalloid bonds (NiFe-P or NiFe-S) and the strong covalent metalloid-metalloid bonds (P-P or S-S) [124]. However, the application of NiFe-based sulphides on nickel foam in OER has not been explored before 2015. Cheng and co-workers reported the synthesis of Fe-doped Ni_3S_2 particle film with 11.8% Fe on nickel foam ($\text{Fe}_{11.8\%}\text{-Ni}_3\text{S}_2/\text{NF}$) for high-efficiency OER [125].

Fig. 6. XPS spectra (a) in the S (2p) region; (b) in the O (1s) region; (c) in the Ni (2p) region and (d) in the Fe (2p) region of $\text{Ni}_{0.7}\text{Fe}_{0.3}\text{S}_2$ after OER test [126].

The SEM image and TEM image reveal that the nickel foam is fully covered with $\text{Fe}_{11.8\%}\text{-Ni}_3\text{S}_2$ particles and the diameters of $\text{Fe}_{11.8\%}\text{-Ni}_3\text{S}_2$ particles are 400–800 nm. The obtained $\text{Fe}_{11.8\%}\text{-Ni}_3\text{S}_2/\text{NF}$ shows a lower overpotential of 253 mV compared with the overpotential of $\text{Ni}_3\text{S}_2/\text{NF}$ (431 mV) when the current density reaches 100 mA cm^{-2} in 1.0 M KOH. The XPS spectra and the Raman spectra of $\text{Fe}_{11.8\%}\text{-Ni}_3\text{S}_2/\text{NF}$ after OER confirm the formation of NiOOH and FeOOH . These observations conclude that the NiOOH and FeOOH on $\text{Fe}_{11.8\%}\text{-Ni}_3\text{S}_2$ surface are the true active phases for OER. Such change of chemical constitution was reported in by Yu and co-workers. They synthesized the ternary nickel-iron sulfide as a robust electrocatalyst, $\text{Ni}_{0.7}\text{Fe}_{0.3}\text{S}_2$ [126]. The further characterization after the OER measurement shows that the Ni-Fe oxo/hydroxide species appear, indicating that the OER catalytic activity of $\text{Ni}_{0.7}\text{Fe}_{0.3}\text{S}_2$ might originate from the formation of Ni-Fe oxo/hydroxide species (Fig. 6). The more details of such phenomenon were discussed in 2016, in which Shanmugam's group reported an ultra-durable electrocatalyst through an inexpensive electrochemical synthesis [127]. The stability over 200 h of $\text{Ni}_2\text{FeS}_4/\text{NF}$ (NF represents nickel foam) in 1.0 M KOH makes it possible to apply in the alkaline electrolyte membrane water electrolysis. The $\text{Ni}_2\text{FeS}_4/\text{NF}$ was synthesized via chronoamperometry (Fig. 7(a)), and the reaction followed the following equations:

The Ni_2FeS_4 was obtained by the reduce of $\text{Ni}(\text{Thiourea})_2$ intermediate, and the thickness of coated Ni_2FeS_4 can be controlled by

controlling deposition time. The OER activity of $\text{Ni}_2\text{FeS}_4/\text{NF}$ with deposited thickness of $2.71 \mu\text{m}$ ($\eta_{100} = 231 \text{ mV}$) is greater than that of $\text{Ni}_3\text{S}_2/\text{NF}$ ($\eta_{100} = 400 \text{ mV}$) and RuO_2 ($\eta_{100} = 460 \text{ mV}$) in 1.0 M KOH (Fig. 7(b)). The low Tafel slope of 74 mV cm^{-2} in 1.0 M KOH confirm the facile electrode kinetics (Fig. 7(c) and (d)). The authors considered that this is owing to the emergence of a new active phase during the reversible oxidation of NiFe sulphides to NiFe oxy-sulphides. This phenomenon often occurred on metal chalcogenides through the following reaction steps.

The generated larger S atoms in the $\text{Ni}_2\text{FeS}_4/\text{NF}$ could adsorb more hydroxide ions, thus increasing the kinetics of the OER reaction.

4. NiFe-based electrocatalysts on nickel foam for HER

HER has received a lot of attention recently as another important half reaction in WS. It plays an important role in contemporary clean-energy revolution, such as proton exchange membrane (PEM) [128–130], chlor-alkali electrolyzers [131], water-alkali electrolyzers [132] and solar water-splitting devices [2,133]. However, the large overpotential and the high requirement of non-noble metal catalyst in the electrolyte restricted its practical applications. It is difficult to develop a HER catalyst that is both efficient and

Fig. 7. (a) Schematic illustration of electrochemical deposition of nickel iron sulphides on nickel foam; (b) the OER polarisation curves and (c) the corresponding Tafel slopes of NiFeS-1/NF, NiFe-1/NF, Ni_3S_2 /NF and RuO_2 ; (d) OER chronopotentiometric durability of NiFeS-1/NF [127].

Table 3. The performance of the NiFe-based electrocatalysts in HER.

Catalyst/nickel foam	Electrolyte	η at $x \text{ mA cm}^{-2}$ (mV)	Tafel slope (mV dec ⁻¹)	Stability	Ref.
NiFeP	0.5 H_2SO_4	$\eta_{100} = 185$	64.6	More than 12 h at 10 mA cm^{-2}	[139]
	1.0 KOH	$\eta_{100} = 247$	84.24	More than 12 h at 10 mA cm^{-2}	
NiFe-P	1.0 KOH	$\eta_{200} = 355$	48	More than 12 h	[142]
FeNiP _x	1.0 KOH	$\eta_{100} = 161$	80	More than 90 h at 50 mA cm^{-2}	[143]
Fe-Ni ₃ S ₂	1.0 KOH	$\eta_{100} = 232$	95	More than 20 h at 173 mA cm^{-2}	[150]
FeNi-S film	1.0 KOH	$\eta_{100} = 186$	77	More than 10,000 s	[152]
(Fe _{0.048} Ni _{0.952}) ₂ P	0.5 H_2SO_4	$\eta_{50} = 126$	41.6	More than 10 h at 50 mA cm^{-2}	[69]
	1.0 KOH	$\eta_{50} = 162$	76.6	More than 20 h at 100 mA cm^{-2}	
	1.0 PBS	$\eta_{50} = 169$	82.7	More than 20 h at 100 mA cm^{-2}	

stable. On the other side, as the best reactive condition for OER is in alkaline medium, for ideal WS, HER should also have excellent HER performance in alkaline medium. However, due to that the electric conductance ($G=1/R$) of H_2SO_4 is greater than that of KOH and phosphate buffer solution (PBS) [134], the developed HER electrocatalysts are more active in acidic medium than in alkaline and neutral medium. Herein, we summarize the NiFe-based electrocatalysts from different electrolytes (Table 3).

4.1. NiFe-based electrocatalysts on nickel foam for HER in acidic electrolytes

Towards the electrocatalysts based on nickel foam, acidic electrolyte is unfavorable to them because long-term soaking will corrode the nickel foam, leading to bad stability. Nevertheless, some catalysts on nickel foam were found to be durable in the acidic media within a certain voltage range. Chen's group reported that the nickel foam could stay stable more than 5 days for HER in 0.5 M H_2SO_4 . This is because the metallic Ni will be passivated to the unsolvable Ni_2SO_4 under 0.5 M H_2SO_4 at a suitable overpotential following the equation [135]:

The calculated results above showed that the nickel foam could be stabilized under 0.5 M H_2SO_4 when the overpotential is greater than -0.246 V . The subsequent experiments also proved this finding [136,137]. In addition, the Ni_2P nanosheets were successfully grown on nickel foam ($\text{Ni}_2\text{P}/\text{Ni}$) by Shi et al. The sample displays excellent HER performance at all pH values, and its stability under acidic condition is remarkable [138]. For instance, the stability of $\text{Ni}_2\text{P}/\text{Ni}$ was tested at the overpotential of -0.175 V for nearly 70 h, and almost no decay was observed. In 2016, Wang's group reported the preparation of self-supported porous NiFeP nanocomposite as an efficient electrocatalyst via the direct reaction of Ni-Fe foam and P vapor [139]. The obtained NiFeP shows the outstanding performance in both acidic (0.5 M H_2SO_4) and alkaline (1.0 M KOH) solution. For example, the NiFeP exhibits a low onset potential (40 mV), and its overpotentials with current densities of 10 and 100 mA cm^{-2} are merely located at 89 mV and 185 mV in 0.5 M H_2SO_4 (Fig. 8(a)). The results are superior to those of the reported Ni-P foam ($\eta_{10} = 120 \text{ mV}$ and $\eta_{100} = 200 \text{ mV}$). Besides, the Tafel slope (64.6 mV cm^{-2}) of NiFeP is only barely inferior to that of Pt/C (30.8 mV cm^{-2}) in 0.5 M H_2SO_4 . In addition, the NiFeP shows the excellent HER performance in 1.0 M KOH (Fig. 8(b)). The onset potential is located at 75 mV, which is much close to that of Pt/C. The η_{10} , η_{50} and η_{100} of NiFeP are 142 mV, 212 mV and 247 mV, respectively, which are better than that of Ni-Fe foam and Ni foam (Fig. 8(c)). As shown in Fig. 8(d), the NiFeP

Fig. 8. (a) Polarization curve for pristine Ni foam, Ni-Fe foam, Ni-Fe-P foam and Pt/C in 0.5 M H_2SO_4 solution at a scan rate of 5 mV s^{-1} ; (b) Tafel plots for Ni foam, Ni-Fe foam, Ni-Fe-P foam and Pt/C; (c) polarization curve for pristine Ni foam, Ni-Fe foam, Ni-Fe-P foam and Pt/C in 1.0 M H_2SO_4 solution at a scan rate of 5 mV s^{-1} ; (d) Tafel plots for Ni foam, Ni-Fe foam, Ni-Fe-P foam and Pt/C [139].

also shows small Tafel slope (84.24 mV cm^{-2}) in 1.0 M KOH, suggesting that the Volmer–Heyrovsky mechanism occurs during HER process.

4.2. NiFe-based electrocatalysts on nickel foam for HER in alkaline electrolytes

Although the NiFe-LDH and the other NiFe oxides show the unsatisfied catalytic performance towards HER in alkaline electrolytes, the NiFe compounds, such as NiFeP [140], NiFeS [141] and NiFeN [5], present the unexpected excellent HER performances. Xing et al. reported the synthesis of porous Ni-Fe phosphate film on nickel foam (NiFe-P/NF) [142], and the NiFe-P/NF presents remarkable HER performance ($\eta_{10} = 87 \text{ mV}$ and $\eta_{200} = 355 \text{ mV}$) in 1.0 M KOH. As shown in Fig. 11(a), the SEM image shows that a film of active materials could be observed on nickel foam, and many nanoparticles could be seen on top of the film. The similar surface feature occurs on Ni-P film on nickel foam (Ni-P/NF) (Fig. 9), but the η_{200} of Ni-P/NF is 384 mV, which is larger than that of NiFe-P/NF. The Tafel slope of NiFe-P/NF is 48 mV dec^{-1} , which is much lower than that of Ni-P/NF (90 mV dec^{-1}). These results indicated that the introduction of Fe into Ni-P/NF could facilitate electron transportation and thereby enhance the HER activity. In 2017, Xiao and co-workers used nickel foam as substrate and Ni source to fabricate FeNi_x/NF (NF represents nickel foam) catalysts for HER [143]. Benefiting from advantages of bimetallic composite and nickel foam, the FeNi_x/NF catalyst exhibits low overpotentials of 106 mV at 10 mA cm^{-2} and 161 mV at 100 mA cm^{-2} , respectively. Significantly, the FeNi_x/NF shows larger current density compared with the most catalysts on conductive substrate, such as FeCo₂S₄ on nickel foam, Fe-doped CoP on Ti foil and NiO on Ni film [144–146]. The authors declared that this is due to that the newly etched Ni ions from nickel foam can be in-situ deposited, which makes the combination of FeNi_x and nickel foam more stable and enhances the stability of FeNi_x/NF during the process of

HER. Nearly 400 h of stability testing at 50 mA cm^{-2} was carried out to confirm the advantage of this in-situ deposited method.

Ni sulfides have drawn much attention to HER due to their low cost and facile fabrication [130], and several works about Ni sulfides on nickel foam have been reported, such as Ni sulfide nanosheets on nickel foam (NiS/NF) and porous Ni sulfide on nickel foam (NiS_x/NF) [147,148]. The overpotentials at 10 mA cm^{-2} of NiS/NF and NiS_x/NF are 112 mV and 60 mV, respectively. Fe doping has been well established as an effective strategy by optimizing electronic structure to further improve the HER activity of Ni sulfides [149]. For instance, Zhang et al. found that the electrocatalytic performance could be enhanced by Fe doping in Ni₃S₂ nanosheets on nickel foam in 2018 [150]. The Fe–Ni₃S₂ catalyst was obtained by a facile two-step strategy and the Fe–Ni₃S₂ nanosheets grown vertically on nickel foam (Fig. 10(a)). It should be pointed out that there was the extra electron transfer to S atoms after Fe doping according to XPS of Fe_{17.5%}–Ni₃S₂ (Fig. 10(b)). This could change the electronic structure of Fe_{17.5%}–Ni₃S₂ and enhance the HER performance. Then the authors calculated the value of adsorption free energy of H^* (ΔG_{H^*}) of Fe_{17.5%}–Ni₃S₂ on S-ended surface and Ni-ended surface, respectively. All the values of ΔG_{H^*} are closed to thermoneutral energy compared with that of Ni₃S₂, indicating that the Fe doping can optimize the adsorption of H^* on active sites and reduce the reaction energy barrier. The electrochemical performances of Fe_{17.5%}–Ni₃S₂/NF were consistent with the above calculated results, and the overpotentials of Fe_{17.5%}–Ni₃S₂/NF at 10, 20 and 100 mA cm^{-2} were 47, 142 and 232 mV, respectively (Fig. 10(c)). The authors also calculated the Tafel slope of the Fe_{17.5%}–Ni₃S₂/NF, and the low value (95 mV dec^{-1}) represented the fast reaction kinetics (Fig. 10(d)). In order to confirm whether the real active sites changed during the HER process. The authors used XPS measurement coupled with Ar⁺ sputtering technique to analyze the changes of Fe_{17.5%}–Ni₃S₂/NF after the long-term HER process. No obvious change has been observed, which was a good proof that the Fe_{17.5%}–Ni₃S₂/NF has always maintained the same composition during HER. This work confirmed that the

Fig. 9. (a) Low magnification SEM images of the as-deposited NiFe-P on Ni foam scaffolds (inset: corresponding high magnification SEM images); (b) polarization curves obtained in 1.0 M KOH and (c) corresponding Tafel slopes; (d) chronopotentiometric curves of NiFe-P at 0.1 V for 12 h (inset: [142]).

Fig. 10. (a) SEM images of Fe_{17.5%}-Ni₃S₂/NF; (b) high-resolution S 2p XPS spectra of Fe_{17.5%}-Ni₃S₂/NF and Ni₃S₂/NF; (c) *iR*-corrected linear sweep voltammetry curves of Fe-Ni₃S₂/NF with various Fe doping levels, Ni₃S₂/NF, and Pt/C/NF for HER in 1.0 M KOH at 5 mV s⁻¹; (d) Tafel plots for Fe_{17.5%}-Ni₃S₂/NF, Ni₃S₂/NF, and Pt/C/NF [150].

Fe doping can enhance the HER performance of Ni_3S_2 from experiment and theory calculation, and the active sites of $\text{Fe}_{17.5\%}\text{-Ni}_3\text{S}_2/\text{NF}$ are stable in HER.

The surface morphology of the electrocatalysts is another key parameter for efficient HER, and such advantageous surface morphology will expose more active sites and obtain the excellent catalytic performance. However, it is a challenge to tune the morphology in a facile way [151]. Shang and co-workers successfully tuned the morphology of FeNi-S film on nickel foam by liquid crystal template (LCT) [152]. The existence of LCT could lead to the porous FeNi-S film with high surface area, which could expose more active sites and lead to an excellent catalytic performance. Compared with the overpotential of nonporous Fe-Ni-S film without LCT (178 mV) at the current density of 10 mA cm^{-2} , the overpotential at the current density of 10 mA cm^{-2} of Fe-Ni-S film (LCT) is only 47 mV. This method might provide a facile strategy by tuning catalytic morphology to obtain highly active catalysts for HER.

4.3. NiFe-based electrocatalysts on nickel foam for HER under all pH electrolytes

As the slow HER kinetics in neutral media, the studies of highly efficient neutral HER catalysts were relatively rare. We summarize some works on nickel foam applied for HER under all pH value here. Duan's group synthesized FeCoP on nickel foam through simple in situ phosphidation from FeCo-LDH [153]. The FeCoP shows excellent HER performance and long-time stability in different pH electrolytes ($\text{pH} = 0, 6.5, 13$ and 14). For further understanding the HER mechanism of FeCoP , the authors built FeCoP model and calculated the adsorption behavior of H_2O (-0.05 eV). The results indicate a more thermodynamically favorable H_2O adsorption on FeCoP , which results in the low reaction barrier of FeCoP in basic electrolyte. In another work, similar results have been discussed. The NiCoSe_2 nanosheets on nickel foam were obtained from NiCo-LDH nanosheets through selenization [154]. The authors calculated the adsorption energies of H_2O and H^+ to explain the outstanding HER performance under all pH electrolytes. The calculated results show that the NiCoSe_2 had the larger adsorption value compared with NiSe_2 , which indicates that the doped Co would decrease the energy barriers for adsorbing H_2O and H^+ of NiSe_2 . Our group reported an efficient HER electrocatalysts of $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ at all pH values [69]. After adjusting the appropriate amount of Fe doping into Ni_2P , we obtained the $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ with excellent HER performance and outstanding stability at high current density (100 mA cm^{-2}) at all pH values. According to the amount of doped Fe, we designed different models of $\text{Fe}_x\text{Ni}_{84-x}\text{P}_{42}$ to represent $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ catalysts and calculated the hydrogen adsorption free energy (ΔG_{H^+}) and water dissociation energy ($\Delta G_{\text{H}_2\text{O}}$). The calculated results show that the doped Fe could significantly decrease the absolute value of ΔG_{H^+} and $\Delta G_{\text{H}_2\text{O}}$, which indicates that the doped Fe could reduce the reaction barrier of HER under all pH electrolytes. Besides, according to the charge density difference calculations, we found that the doped Fe could make the active sites more active. The above reports are of great significance for the development and application towards neutral HER catalysts at high current density.

5. Perspectives and future directions

This review highlights the recent research in the development of NiFe-based materials on nickel foam for OER and HER. Nickel foam not only can serve as an ideal catalyst substrate due to its good conductivity and porosity, but also can participate in the reaction as the reactant. Meanwhile, nickel foam can keep the stability under $0.5 \text{ M H}_2\text{SO}_4$ for a long time during the appropriate voltage range, which relatively expands its application range.

As outlined in our review, numerous works reported that the combination of NiFe-based materials and nickel foam has considerable advances on OER and HER performance and stability. However, there are still several challenges in NiFe-based catalysts on nickel foam: (i) the role of Fe is sketchy in most researches, especially the specific doped amount; (ii) the reaction mechanism is still in its infancy and the theoretical research is deficient; (iii) the real active site is controversial in both OER and HER. To solve these issues, some advanced methods should be applied to future studies of NiFe-based catalysts on nickel foam, such as in situ spectroscopy and theoretical calculations. The understanding of basic mechanism is beneficial to discover the advanced NiFe-based catalysts with higher activity and stability.

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