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### Review

# Demystifying the active roles of NiFe-based oxides/(oxy)hydroxides for electrochemical water splitting under alkaline conditions



COORDINAT

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#### ABSTRACT

NiFe-based compounds have received increasing attention due to their low cost, availability, as well as excellent  $H_2$  evolution reaction (HER) and the  $O_2$  evolution reaction (OER) catalytic properties. Although it is agreed that the implementation of high activity, the co-existence of Ni and Fe is essential, the identification of active sites and the mechanism of water splitting in NiFe-based compounds have long been controversial. This review focuses on the catalytic centers of NiFe-based oxides/(oxy)hydroxides and related mechanism in alkaline water oxidation process from the perspective of thermodynamics and kinetics. Furthermore, NiFe layered double hydroxides (NiFe LDHs) are introduced separately, emphasizing the necessity of LDH phase formation during water splitting. The review highlights the roles of Fe<sup>3+</sup> and the third transition metal Co in NiFe-based catalysts. Finally, a brief perspective on NiFe-based catalysts is proposed. This review will be a good complement to the existing literatures and will contribute to a better study of NiFe-based catalysts.

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#### 1. Introduction

Over the past half century, population growth, urbanization and improving living standards stimulate rapidly increased societal energy depletion as well as environmental burdens. Energy depletion is expected to keep on increasing dramatically in the future with associated environmental issues [1–3]. Global energy supply

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and the ensuing environmental issues are prompting scientists to seek renewable, clean and alternative energy sources to replace depleted fossil fuels [4]. The electrochemical water splitting reaction,  $H_2O \rightarrow H_2 + O_2$  ( $E^0 = -1.23$  V), produces  $H_2$  in the cathode and  $O_2$  in the anode highlights an immense ascendancy in response to the energy crisis [5,6]. Electrochemical water splitting can convert renewable energy such as solar and wind energy into  $H_2$  fuel, which can be used as a fuel itself or as a raw material for liquid fuel, thus, electrochemical water splitting has been widely studied as a promising technology to solve the energy crisis caused by fossil fuel consumption [7–9]. Regrettably, due to the sluggish kinetic properties of the  $H_2$  evolution reaction (HER) and the  $O_2$  evolution reaction (OER), especially the huge dynamic barrier caused by the four-step proton-coupled electron transfer of the OER, an efficacious catalyst is needed to narrow the gap between theoretical calculations and actual required potentials [8,10,11]. As a result, catalysts play a key role in designing efficient processes and systems that maximize the value of raw materials while minimizing waste generation and energy demands although there is currently no universal solution that addresses all energy and environmental related issues [1].

Although some noble metal-based materials have been shown to act as highly efficient electrocatalysts to enhance water splitting processes, such as Pt-based materials for HER and Ir/Ru oxides for OER, the high cost and scarcity of these noble metals severely hinder their widespread applications [4,8,12,13]. According to the Sabatier principle, the best catalyst should possess a medium strength that binds atoms or molecules. A weak interaction is not conducive to the activation of the reactants, while an excessive interaction is not beneficial to the desorption of the product [14,15]. To this end, metal-based catalysts, especially transition metals (such as Fe, Co and Ni) based catalysts, are of great importance in efficient, extensive catalytic applications [16,17]. The adjustable structure flexibility and excellent performance of these catalysts are ideal for meeting the stringent requirements of energy and environmental applications [1]. Nevertheless, with the development of emerging applications related to environment and energy, single component transition metal catalysts can't meet the requirements for activity, selectivity and stability [1].

Bimetallic catalysts tend to exhibit superior performance mainly originating from their inherent electronic and chemical properties being different from their parent metals, including: i) the existence of considerable exposed surface metal atoms can offer an ultra-high specific surface area for better contact with the electrolyte; ii) the 2D plane characteristic of bimetals empowers for the modification of existing catalytic sites by phase, surface and defects engineering as well as the construction of new catalytically active sites: iii) the bimetallic framework structure can anchor other active materials to form a synergistic composite: and iv) ideally, the atomic model in the bimetallic structure provides a possible basis for investigating the relationship between the active centers and the catalytic mechanism from the atomic level [18]. More importantly, bimetallic bonds usually involving redistribution of charge around the metal centers show great stability in catalytic reactions [19]. Since the founding of Exxon Research and Engineering in the early 1960s, research on bimetallic compounds have been significantly enriched, especially in the past five years [1]. Among of them, NiFe-based compounds have received increasing attention mainly due to their low cost and rich earth content, and indeed, the NiFe-based catalysts do exhibit excellent catalytic properties in both OER and HER [16,20-22]. Even many of the catalytic activities exhibited by NiFe-based catalysts reported in recent years are expected to replace expensive noble metal catalysts [1]. After a detailed survey of recent publications on NiFe-based catalysts, we found that most of them focused on energy-related catalytic reactions, especially electrochemical water splitting reaction, while very few were environmentally visible, which could conclude that the application of NiFe-based catalvsts in energy should not be underestimated.

In fact, there are many review articles have reported the preparation and application about NiFe-based compounds as well as rational coordination of Ni and Fe atoms to promote the catalytic process in detail. They provide us with useful information to further understand NiFe-based compounds. Although it is agreed that the implementation of high activity, the co-existence of Ni and Fe is necessary, but for a long time, the identification of the active sites and the mechanism of the water splitting reaction in the NiFe-based compounds are still at a controversial stage. Whether the water splitting reaction is carried out through Ni or Fe sites, or both, is controversial. It is undeniable that the synergistic mechanism between Ni and Fe is the key to catalysis and has been emphasized, but the identification of the atomic structure of the catalyst itself and the precise control of the atomic level of the reaction centers, especially the exploration of active sites of polyatomic composition based on Ni-Fe is still a huge challenge.

Different from other related reviews, this mini review only emphasizes the catalytic active centers and mechanism of NiFebased oxides, (oxy)hydroxides (including layered double hydroxides, LDHs) catalysts in alkaline water oxidation. In this review, the water splitting technology and its need for current energy demand are introduced. The basic principles of electrochemical water splitting are elaborated in detail from the perspective of thermodynamics and kinetics. The mechanism of water splitting on NiFe-based catalysts are discussed in depth according to more experimental and theoretical reports, emphasizing the necessity of LDH phase formation under OER conditions. Furthermore, the roles of Fe<sup>3+</sup> in improving the water splitting performance of NiFe-based catalysts and the advantages over other trivalent cations are clarified.

To the best of our knowledge, there is no review involved in detail the active sites of NiFe-based oxides/(oxy)hydroxides catalysts. This review provides a systematic description and analysis for the active sites of NiFe-based oxides/(oxy)hydroxides, which will be a great complement to existing literatures and will provide useful information for future research about NiFe-based compounds. Additionally, this review also offers readers an insight into the latest advances in water splitting technology for such NiFe-based catalysts, contributing them to work more efficiently in related fields to meet the energy needs of the future.

#### 2. NiFe-based compounds

The most promising water splitting catalysts based on the earth-rich elements are mixed NiFe-based compounds, mainly including NiFe-based oxides, NiFe-based (oxy)hydroxides (including LDHs), which perform the best catalytic activity especially in alkaline electrolytes [20,23]. Numerous studies have illustrated that the synergistic effect of Ni and Fe can change the electronic structure of the catalyst, increase the number of redox reaction centers, improve the conductivity, thereby enhancing the OER electrocatalytic activity [24]. Various studies on the NiFe system indicated that the catalyst consisting of 60–90 wt% Ni held the best OER activity, and the best range of Ni content reported was mainly due to the difference in the synthesis method and heat treatment method of the sample [25,26].

#### 2.1. Mixed NiFe-based oxides

Indeed, various NiFe-based oxides (Ni<sub>1-x</sub>Fe<sub>x</sub>Oy) represent some of the most active OER catalysts in alkaline solutions due to higher activity and stability than other oxides, which usually require only an overpotential of about 300–400 mV to achieve a current density of 10 mA cm<sup>-2</sup> on the two-dimensional (2D) or three-dimensional (3D) substrate [27–29].

We start with the simplest spinel NiFe oxides with the general formula NiFe<sub>2</sub>O<sub>4</sub>, in which the divalent cation Ni<sup>2+</sup> occupy the octahedral position, and the trivalent cation Fe<sup>3+</sup> occupy an octahedral and a tetrahedral position [30]. NiFe<sub>2</sub>O<sub>4</sub> is a superior candidate for electrocatalysis owing to the existence of multivalent Ni<sup>2+</sup>/Ni<sup>3+</sup> and Fe<sup>2+</sup>/Fe<sup>3+</sup> redox couples [31]. When a trivalent cation M<sup>3+</sup> (such as Al<sup>3+</sup>) was introduced into the above oxide crystal lattice (NiFeAlO<sub>4</sub>), Fe<sup>3+</sup> and Al<sup>3+</sup> ions may occupy the sites of tetrahedron

or octahedron (Fig. 1a) [30]. This redox-inert  $Al^{3+}$  ion produced a short-range inductive effect on the closest Ni<sup>2+</sup>, thereby interfering with the extended electronic structure of the solid oxide (Fig. 1b). The similar properties of NiAl<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub> indicated that OER activity was independent of Fe-based redox activity, while NiFeAlO<sub>4</sub> exhibited improved OER performance relative to NiFe<sub>2</sub>O<sub>4</sub> and NiAl<sub>2</sub>O<sub>4</sub>, suggesting that Fe and Al played a synergistic role in water oxidation (Fig. 1c). The mechanism of Al<sup>3+</sup> in NiFeAlO<sub>4</sub>, including but is not limited to the modulation of Ni redox properties [30]. The effect of this redox is not unique for Al, thus it can be extended to other trivalent cations (such as Mn<sup>3+</sup>, Cr<sup>3+</sup>, V<sup>3+</sup>, etc.) that can be introduced into the oxide lattice, however, the further research is needed to clarify the synergistic effect of Al and Fe mentioned in these systems.

Actually, most of the NiFe-based oxides are initially Fe-doped NiO<sub>v</sub> systems. Generally, the transition metal doping leads the electron density to rearrange near the center of the catalytically active metal, thereby changing the potential required for the catalyst to initiate the OER [32,33]. In addition, doping also affects the rate of electron transfer inside the catalyst, as well as has an effect on both current density and reaction kinetics. Another aspect of doping is the ability to design multiple components to provide multiple catalytically active sites for catalytic reactions, promoting the electrons transfer in the multi-metal network, as well as providing stability to the catalytic system [34,35]. Therefore, the OER activity of NiFe oxides is strongly dependent on the local environment of Ni and Fe, which has been extensively investigated by in-situ X-ray absorption spectroscopy (XAS) and voltammetric techniques [36]. Considering Fe-doped NiO<sub>x</sub> nanotubes as an example, Fe doping introduced Ni vacancies and lattice distortion in nanotubes (Fig. 2a), thereby achieving dramatical modification of the local atomic and electronic structures of nanotubes. Moreover, due to the formation of the Ni<sup>3+</sup> active centers and Ni vacancies, the strength of the first shell Ni-O looked the same in the Fourier transformed extended X-ray absorption fine-structure (FT-EXAFS) curve of the Ni K-edge, however, it clearly showed a lower peak intensity on the higher coordination shell (Fig. 2c, d),



**Fig. 1.** (a) Simplified structural representation of NiFeAlO<sub>4</sub> showing only site occupancy of the metals.  $M^{2+}$  ion (grey) occupies an octahedral site while  $M^{3+}$  ions (brown) occupy both octahedral and tetrahedral sites. (b) Structural representations of NiO and inverse spinel oxides. (c) Steady-state Tafel plot of the oxides in the low current density linear regime. Data shown are the average of three trials with error bars indicating one standard deviation. The error bars for NiFe<sub>2</sub>O<sub>4</sub> is very small and hidden within the data point symbols. Reproduced with permission from Ref. [30]. Copyright © The Royal Society of Chemistry 2014.



**Fig. 2.** (a) Schematic view of atomic structure of the hierarchical Fe-doped NiO<sub>x</sub> nanotubes. (b) Nyquist plots of NiO<sub>x</sub> nanotubes, Fe-doped NiO<sub>x</sub> nanosheets and the hierarchical Fe-doped NiO<sub>x</sub> nanotubes at an overpotential of 330 mV. Z' is realimpedance and Z'' is imaginary impedance. FT k<sup>3</sup>-weighted  $\chi(k)$ -function of the EXAFS spectra for (c) Ni K-edge and (d) Fe K-edge. Reproduced with permission from Ref. [36]. Copyright © 2017 Elsevier Ltd.

which indicated that the Fe-doped  $\text{NiO}_x$  nanotubes exhibited a different local atomic structure from NiO. As a result, the charge transport resistance in Fe-doped  $\text{NiO}_x$  nanotubes was significantly reduced due to changes in geometric and electronic structures (Fig. 2b) [36].

Furthermore, in another Fe-doped NiO<sub>x</sub> system, the Fe K-edge spectrum in EXAFS exhibited some changes under OER, which indicated that the Fe atoms were further coordinated under OER conditions and were affected by the reaction conditions [37]. And the average coordination number of Fe was also significantly increased under the OER conditions. This directly mean that Fe actively involved in the OER process when doped at the NiOx interface. Increased Fe atoms coordination can be presumed to be two points: i) Fe atoms moved from a tetrahedral position to an octahedral position within the spinel structure, which can be found in nanophase NiFe<sub>2</sub>O<sub>4</sub>; and ii) the Fe<sub>2</sub>O<sub>3</sub> phase was formed under oxidizing conditions. However, the latter seems impossible, as Fe<sub>2</sub>O<sub>3</sub> is considered as a poor electrocatalyst for OER, mechanism involving Fe<sub>2</sub>O<sub>3</sub> are expected to deactivate the catalyst surface, which is in contrast to the constant steady-state current on the electrocatalyst observed during the experiment. Thus, NiFe<sub>2</sub>O<sub>4</sub> may be the phase responsible for the enhanced OER activity when NiO<sub>x</sub> is doped with Fe [37,38]. However, the report proposed by Louie et al. later denied this formation of NiFe<sub>2</sub>O<sub>4</sub> when investigating the surface properties of the NiFe oxide film by in-situ Raman scattering [39]. It was clearly shown that after aging for 6 days in the Fe-containing electrolyte, no signal of possible formation of NiFe2-O4 was observed even at a sufficiently high overpotential. This supported the fact that structural restructuring, which occurred at least on the surface of the NiFe oxide film [39]. This work opens up a whole new direction for people to explore the local electronic structure of NiFe-based oxide surface.

Since the performance of  $Ni_{1-x}Fe_xO_y$  was initially confirmed by Corrigan that Fe in NiO introduced by co-deposition or impurities in the electrolyte had a profound effect on the OER activity [40–42]. Nowadays, it is generally accepted that the Fe incorporated in the NiO structure or the trace amount of Fe in the electrolyte solution is a key component for obtaining higher OER activity [28]. In light of this finding, many existing and ongoing research efforts aim to clarify the special roles of Fe in the electrocatalysis of NiFe-based oxides [20,43–46]. To date, the nature of the active centers in NiFe-based oxides as well as the sources of high catalytic activity remain diverse. Regrettably, there are few reports on how the addition of Fe directly influences the electrochemical activity and structural integrity of NiFe-based oxides under water splitting conditions. From this point of view, the basic understanding of the effect of Fe on the water splitting behavior in NiFe-based oxides is particularly important.

Combined with electrochemical methods and XAS, local electronic structures and structural changes in a series of Ni<sub>1-x</sub>Fe<sub>x</sub>O<sub>y</sub> nanomaterials have been elucidated [28]. At first, the oxidation states and local structures of the series of Ni<sub>1-x</sub>Fe<sub>x</sub>O<sub>v</sub> samples were investigated by in-situ XAS, and Fig. 3a showed the X-ray absorption near-edge structure (XANES) spectrum of the Ni K-edge in different samples. It was clear that all samples contained the pre-edge features of NiO at about 8333 eV, which corresponded to the 1 s-3 d transition that occurred when Ni was present in an octahedral environment. The edge positions of Ni<sub>90</sub>Fe<sub>10</sub>O<sub>v</sub> and Ni<sub>70</sub>Fe<sub>30</sub>O<sub>v</sub> (8343.2 eV) were only slightly higher than the edge position of NiO (8343.0 eV), which could be inferred that the presence of Fe did not significantly affect the oxidation state of Ni. Moreover, the amount of Fe added seemed to have no effect on these bond distances considering that Ni<sub>90</sub>Fe<sub>10</sub>O<sub>v</sub> and Ni<sub>70</sub>Fe<sub>30</sub>O<sub>v</sub> had approximately the same Ni-O and Ni-Ni bonding distance (Fig. 3b), while the decrease in peak amplitude observed in  $Ni_{70}Fe_{30}O_v$  indicated that the ligand environment around the metal center was more distorted than NiO or  $Ni_{90}Fe_{10}O_{v}$ , which may be due to the relatively high amount of Fe<sup>3+</sup> substituted Ni<sup>2+</sup> in the NiO rock salt structure. Similarly, in the XANES spectra of the Fe K-edge (Fig. 3c), it can be seen that both  $Ni_{90}Fe_{10}O_v$  and  $Ni_{70}Fe_{30}O_v$  contained 3+ oxidation state of Fe, which was expected to the presence of Fe<sup>3+</sup> in NiFe-based oxides. The FT-EXAFS fitting of Fe showed that the Fe-O bonding distance in  $Ni_{90}Fe_{10}O_v$  and  $Ni_{70}Fe_{30}O_v$  were 1.99 and 1.96 Å, respectively (Fig. 3d), which was much smaller than the distance of Ni-O bond (2.089 Å fitted from Fig. 3b), the shorter distance was consistent with the higher oxidation state of Fe in the rock salt structure than Ni. The absence of any change in the Ni K-edge positions of  $Ni_{90}Fe_{10}O_y$  and  $Ni_{70}Fe_{30}O_y$  strongly indicated that the electronic state and local geometry of the Ni center were stable in the presence of Fe during polarization. Meanwhile, the presence of Fe severely inhibited the redox transition of  $Ni^{2+}/3^+$ . On the other hand, how do the oxidation states and local electronic structures of Fe in these NiFe-based oxides change? However, due to the relatively low concentration of Fe in the sample and the limited sensitivity of measuring XAS in the transport mode, this work does not continue to clarify whether Fe plays a more important role in the OER of  $Ni_{1-x}Fe_xO_y$ .

When the NiFe-based oxides is doped with a non-metallic heteroatom (such as P, B or S), the catalytic role is still the center of the NiFe, but the presence of the heteroatom further tunes the electronic structure around Ni and Fe. which is beneficial to accelerate the charge transport process and may also result in the increase of the average oxidation state of Ni in the composites, thereby promoting the water oxidation reaction [24]. Typically, when reacted with the P source, the binding energy of Ni  $2p_{3/2}$  and Fe  $2p_{3/2}$  in the high-resolution X-ray photoelectron spectroscopy (XPS) of Ni-Fe-O-P showed a slight positive shift compared to the Ni-Fe-O system, and a similar phenomenon appeared in Ni-Fe-O-S. While for Ni-Fe-O-B, a negative shift was observed in the binding energy of Ni and Fe, which may be due to the lower electronegativity of the B atom (Fig. 4a, b) [24]. The displacement of the binding energy indicated that the electrons around Ni and Fe environment were further modulated to facilitate electron transport during electrocatalysis when doped with non-metallic elements. Furthermore, the doping of non-metallic elements has also been confirmed to modulate the redox properties of Ni species in NiFe oxides, which can be obtained by cyclic voltammetry (CV) curve. Fig. 4c clearly showed the inconspicuous anode peak and significant cathode peak of Ni-Fe-O-H (H = P, B, S), which mean that the oxidation and reduction of Ni<sup>2+</sup>, in stark contrast to the negligible redox peak on Ni-Fe-O [24]. The appearance of the anode peak can be attributed to the formation of NiOOH, which is generally considered to be the active center of OER and will undergo deprotonation to form oxygen [47]. While doped with metal heteroatom (such as Mn),



**Fig. 3.** Normalized XANES spectra and FT-EXAFS spectra of the Ni<sub>1-x</sub>Fe<sub>x</sub>O<sub>y</sub> samples and measured sample standards at the Ni (a and b) and Fe (c and d) K-edges. All Ni  $\chi(k)$  functions were Fourier transformed over a k-range of 2.6–14.0 Å while the Fe  $\chi(k)$  functions were transformed over a range of 3–11.5 Å. Reproduced with permission from Ref. [28]. Copyright © The Royal Society of Chemistry 2018.



**Fig. 4.** High-resolution XPS spectra of Ni 2p (a) and Fe 2p (b) for Ni-Fe-O-P, Ni-Fe-O-B, Ni-Fe-O-S, and Ni-Fe-O. (c) CV curves of Ni-Fe-O-P, Ni-Fe-O-B, Ni-Fe-O-S, and Ni-Fe-O at a scan rate of 50 mV s<sup>-1</sup>. Reproduced with permission from Ref. [24]. Copyright © The Royal Society of Chemistry 2018. (d) Complementary operando EXAFS measurement confirming the potential-induced bond contraction at both Fe and Ni sites. Reproduced with permission from Ref. [20]. Copyright © 2015 American Chemical Society.

considering that the order of oxophilicity of Ni, Fe, and Mn is: Ni < Fe < Mn, and the oxophilicity of their corresponding (oxy)hydroxides compounds follows the same trend, the passivation of the residual Mn and Mn oxides in the composite are expected to prevent further corrosion of the NiFeMn-based oxide composite during water oxidation in alkaline solutions, thereby improving catalyst stability although the roles of Mn are not clear [48]. In another work, the introduction of Mo did not change the phase composition of the NiFe-based oxide catalyst, but due to the higher oxidation state of Mo<sup>4+</sup>, it was assumed that the insertion of Mo lead to the shrinkage of the Ni-O and Ni-Fe bond distances, which could promote charge transport between atoms of two different elements and increase the conductivity of the oxide [25,49].

It is worth noting that in the general electrodeposition process, a fractal structure occurs due to the difference in the degree of adsorption of the material on the surface of the carrier, and deposition occurs preferentially at the protrusions, resulting in surface roughness, which can be used to explain that a layer of highly active NiFe oxide film is produced when electrodepositing Ni on steel without further Fe doping [50,51].

#### 2.2. NiFe-based (oxy)hydroxides

As early as 1987, Corrigan observed that Fe impurities incorporated into  $\alpha$ -Ni(OH)<sub>2</sub> significantly promoted OER [40]. Since then, considerable effects have been done to explain the mechanism and the unusual dynamic effect in this kind system. It has been determined that the doping of Fe into Ni (oxy)hydroxides (i.e. NiFe (oxy)hydroxides) can significantly increase OER activity by taking advantages of synergistic metal-metal interactions [27,52]. The most direct evidence indicated that OER activity increased directly with increasing Fe<sup>3+</sup> content in the  $\beta$ -Ni(OH)<sub>2</sub> lattice [53]. In NiFe (oxy)hydroxide, the NiOOH lattice is an indispensable ingredient for such type catalysts. Studies have concluded that amorphous NiOOH structures could act as real active phases to contribute to high performance in OER process [8]. Generally, in the OER system, the  $\alpha$  phase and the  $\beta$  phase of the Ni(OH)<sub>2</sub> catalyst undergo phase

transitions to  $\gamma$ -NiOOH and  $\beta$ -NiOOH, respectively [38]. In addition, the formation of  $\gamma$ -NiOOH is also observed when the  $\beta$ -NiOOH is over charged. Between these two transitions, the transformation involved in the conversion of  $\alpha$ -Ni(OH)<sub>2</sub> to  $\beta$ -NiOOH is a transition that undergoes more structural changes and corresponding electron transfer steps [38,54]. The suggested activity tendency is as follows: Fe doped  $\beta$ -NiOOH >  $\beta$ -NiOOH > Fe doped  $\gamma$ -NiOOH >  $\gamma$ -NiOOH [55]. For more than a decade, the formation of β-NiOOH has been considered to be the active structure of OER in alkaline electrolytes [54]. For instance, it has been reported that  $\beta$ -NiOOH obtained by electrochemical oxidation of  $\beta$ -Ni(OH)<sub>2</sub> without phase structural transformation was a suitable hydroxide type for catalyzing OER [53]. Thus, more research on the active sites in NiFe-based (oxy)hydroxide seems to be centered on NiOOH. Typically, Trotochaud et al. demonstrated that the incorporation of Fe in the Ni(OH)<sub>2</sub>/NiOOH film enhanced its electrical conductivity and produced a partial charge transfer activation effect on NiOOH, resulting in a dramatic increase in OER catalytic activity [43].

Besides, hexagonal Ni(OH)<sub>2</sub> is also a very interesting system because it provides a layered structure that acts as a matrix for cations with unusual valence states [56]. In the electrochemical oxidation process, in the case where Fe<sup>3+</sup> occupies the Ni lattice site in Ni(OH)<sub>2</sub>, unusual oxidation state metal ions (Ni<sup>4+</sup> and  $Fe^{4+}$ ) tend to form due to the stable and suitable matrix [57]. This can be confirmed by operando Mossbauer spectroscopy, in the steady state water oxidation process, Fe<sup>4+</sup> species were detected in the Ni hydroxide catalyst, while Fe<sup>4+</sup> was not detected in the Fe oxide catalyst, thus the NiOOH lattice held a stabilizing effect on Fe<sup>4+</sup> [58]. More specifically, the Mossbauer spectroscopy of NiFe (oxy)hydroxide indicated that 21% of Fe ions were oxidized from Fe<sup>3+</sup> to Fe<sup>4+</sup> during electrocatalysis, and even after the applied voltage was removed, the Fe<sup>4+</sup> site still existed, thus it was expected that Fe<sup>4+</sup> has an effect on the structure and catalytic behavior of the material although it does not have catalytic ability [58].

Although it is agreed that the co-existence of Ni and Fe is necessary to achieve the high activity, the evaluation of the structure of the active phase and the active center in the NiFe-based (oxy)hydroxides has been controversial all the time, and unfortunately, only a few research reported the energy that Ni-Fe involved in OER intermediates [20]. Therefore, it is necessary to have a basic understanding of the interaction of Ni and Fe and their contribution to the high OER activity in NiFe-based (oxy)hydroxides before proceeding with the later discussion. And a central theme of modern research in NiFe-based (oxy)hydroxides is to determine the roles of Fe ions in the water splitting process. Since unary Fe oxides are poor catalysts, some researchers have suggested that Ni centers act as active sites for OER in NiFe-based (oxy)hydroxides, where Fe ions play an indirect role [59]. The most straightforward proof is that XAFS and in operando XAS analysis of hydrothermally synthesized NiFe (oxy)hydroxides indicated that Fe ions were still in the Fe<sup>3+</sup> state, while the average oxidation state of Ni was decreased under the catalysis, which was usually interpreted as Fe<sup>3+</sup> stabilizing the Ni center in a low oxidation state [45]. In addition, Görlin et al. revealed that Fe doping may lead to the migration of partial electrons from the center of the mixed NiFe (oxy)hydroxides to Ni to stabilize the Ni<sup>2+</sup> atoms and promote the formation of Fe<sup>4+</sup> [45]. However, the analysis of the electrodeposited NiFe (oxy)hydroxides via electrochemical technique and XANES demonstrated the reversed results, in which the average oxidation state of Ni ions increased from 3.2 to 3.6 as the Fe content increased from 0 to 10 mol% [60]. Therefore, it was considered that the high Lewis acidity of Fe<sup>3+</sup> promoted the oxidation of Ni<sup>2+</sup> to Ni<sup>4+</sup>, thereby contributing catalysis. Furthermore, the negatively charged active sites called adsorbed "active oxygen" have been observed by spectroscopy, and Ni<sup>4+</sup> formed by the incorporation of Fe has been found to promote catalytic redox activity, indicating that Ni was the active center of OER [60,61]. It should be noted that Ni<sup>4+</sup> in pure NiFe (oxy)hydroxides is difficult to form without introducing any other elements [62].

Of course, there is also controversy that Fe is a catalytically active center. This view was initially based on XAFS for the study of NiFe (oxy)hydroxides via cathodically electrodeposition [20]. It was found that there was a strong correlation between the Fe-O, Ni-O bond lengths and the nearest metal-metal distance, indicating that Fe could replace Ni in both  $\alpha$ -Ni(OH)<sub>2</sub> and  $\gamma$ -NiOOH. Additionally, at nearly twice the distance between the nearest Ni-Ni and Fe-Ni, the peaks in the EXAFS of Fe and Ni K-edge were the same (Fig. 4d), predominantly from multiple-scattering in collinear Fe-Ni-Ni, Ni-Fe-Ni and Ni-Ni-Ni arrangements, which clearly showed that Fe was not embedded between the hexagonal [NiO<sub>2</sub>] sheets, but instead replaced Ni in the crystal lattice [20]. This modification had no effect on the oxidation state of the Ni cation, but significantly increased the OER activity. The reason for this activity enhancement was presumed to be two points: first, in the  $\gamma$ -NiOOH lattice, the substituted Fe<sup>3+</sup> site became more active due to changes in the electronic environment; second, the Fe<sup>3+</sup> replaced the  $\gamma$ -NiOOH lattice and changed the electronic properties of the Ni<sup>3+</sup> site, resulting in the increased activity of the Ni<sup>3+</sup> site [20]. This clearly confirmed that in  $\gamma$ -Ni<sub>1-x</sub>Fe<sub>x</sub>OOH, the active centers of OER were  $Ni^{3+}/^{4+}$  and  $Fe^{3+}$ , rather than a single Ni site. Analogous conclusions have also been reported by Diaz-Morales et al [63], in which a small ligand effect at the Ni site (Fig. 5a)



Fig. 5. (a) Effect of doping on Ni sites. It is observed that doping with Mn, Fe, Co, Cu, and Zn causes slight increases in the OER overpotential of Ni sites, while doping with Cr causes a slight decrease. (b) Activity of dopants in a NiOOH lattice. The overpotentials are rather different depending on the transition metal, and Fe and Mn are near the top of the volcano. Reproduced with permission from Ref. [63]. Copyright © 2015 American Chemical Society. (c) NiO<sub>x</sub>H<sub>v</sub> cycled (10 mV s<sup>-1</sup>) initially in Fe-free aq. 1 M KOH (red, cycle 1-4) then moved to a 1 M KOH solution with 1 mM  $Fe(NO_3)_3$  (cycle 5–104). The inset depicts a possible schematic of Fe incorporation into a NiO<sub>x</sub>H<sub>v</sub> platelet as a function of cycling in Fe saturated solution. From the cyclic voltammetry, (d) the percent change in e<sup>-</sup> per Ni (triangles) and (e) the change in overpotential (mV) at 1 mA cm<sup>-2</sup> (open circles) and position of  $E_{pa}$ (mV) (squares) as a function of cycling relative to the last cycle in Fe-free conditions. Fe content listed is from inductively coupled plasma optical emission spectrometer (ICP-OES) analysis on samples cycled in identical conditions for 2 (orange), 10 (green), 30 (blue), and 100 cycles (violet) after Fe-spiking. The error bars are based on samples in triplicate with ~3-5  $\mu g\,cm^{-2}$  loading. Reproduced with permission from Ref. [44]. Copyright © 2017 American Chemical Society. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

was observed, while it was significant on the doped transition metal sites, especially Fe (Fig. 5b), which indicated that the effect in electrocatalytic doping not only depended on the interaction between the metal and the lattice oxygen, but also on the interaction between the host and the guest metal in the stretched lattice. This interaction could be visually observed by the bond length, when Fe was embedded in the NiOOH lattice, the Fe-O distance was different from its pure oxide distance. Therefore, compared with NiOOH, the metal center where the catalytic activity of NiFeOOH was significantly improved was Fe, rather than Ni. It could be inferred from the volcano plots (Fig. 5a, b): i) NiOOH was located on the weak side of the volcano, thus, its potential limiting step was to convert \*OH to \*O, and the Ni centers should be covered by \*OH under OER conditions; and ii) the potential limiting step for Fe oxides was to convert \*O to \*OOH. so these Fe sites on the NiFeOOH surface were typically covered by \*O under OER conditions. Coverage effects are sometimes important because lateral adsorption-adsorbate interactions may weaken or enhance adsorption energy [64].

The roles of Fe in (Ni,Fe)OOH system are further elaborated. When Fe into the solution was introduced to NiO<sub>x</sub>H<sub>v</sub>, the electronic properties, reduction potential, redox peak size, peak shape, etc. of the Fe-NiO<sub>x</sub>H<sub>y</sub> film were independent of its activity (Fig. 5c) [44]. Unlike co-deposition of Ni and Fe, Fe may initially be introduced at the edges/defects and further incorporated into the "blocky" of  $NiO_xH_v$  nanosheets. The e<sup>-</sup> per Ni in the redox wave slightly increased with the addition of Fe, but with the large incorporation of Fe, the material remained active even if e<sup>-</sup> decreased (Fig. 5d). And the conductivity of Fe-NiO<sub>x</sub>H<sub>v</sub> in the Fe-containing solution decayed with increasing cycle time, even if the sample became more active (Fig. 5e). These results demonstrated that the "bulk" (oxy)hydroxide electronic structure was not a major factor affecting OER activity. The deposition method and electrochemical regulation were directly related to the position of Fe and the local environment of the film, but did not change the activity of the catalyst. Recently, a study of NiFe (oxy)hydroxides prepared by pulsed laser ablation reported that penta-coordinated Fe<sup>5+</sup> species were formed at the terminal sites, which may be responsible for OER [65].

Most of the points mentioned are concentrated on a single active site and emphasize the modification of the main active sites by other components. Recently, a new perspective further explained the significant improvement in the catalytic performance of the (Ni,Fe)OOH systems, namely, Ni and Fe had two different key functions required for OER [66]. In fact, synergistic effect derived from two or more different active sites in the same multicomponent catalyst that participate in the reaction process are widely considered as a key strategy for multi-step catalytic reactions [67]. The reactants and intermediates are adsorbed and catalyzed by adjacent but different active centers, since elementary reactions occur at different active centers, and the overall reaction will eliminate the scale relationship, thereby maximizing the efficiency of each elementary reaction [59,68]. The two active centers with different adsorption energies for the intermediates can cooperate with each other to make the elementary reactions proceed smoothly [59]. In order to decipher the characteristics of the catalytically active sites on the (Ni,Fe)OOH systems, it is necessary to use a catalyst owing a good, uniform atomic structure and a tunable complex environment. From a fundamental point of view, the (Ni,Fe)OOH composite containing the isolated metal atom structure dispersed on the carrier is expected to clarify the interaction between Ni and Fe in the catalytic OER process [59]. Polymeric carbon nitride (PCN) may act as an ideal matrix for anchoring Ni or/ and Fe metals (NiOH@PCN, FeOH@PCN, and NiFeOH@PCN) [59]. On the basis of assuming that the metal atoms were the active centers, the free energy was first calculated to study the synergistic

effect between the Ni and Fe centers. For NiFeOH@PCN, the adsorption energy results showed the Fe was the active site due to the similar trend of free energy with FeOH@PCN, and at high potentials, the third and fourth steps remained rising (Fig. 6a, b). Compared with the FeOH@PCN, the introduction of Ni transferred the rate-limiting step of OER from the fourth step to the third step  $(O^* \rightarrow OOH^*)$  although their active centers were the same Fe atoms. This difference in OER mechanism was mainly due to the weak adsorption strength of OOH\* on the NiFeOH@PCN substrate [59]. Furthermore, it was found that the most stable adsorption site for O\* and OH\* was Fe, while OOH\* tended to bind to the Ni site (Fig. 6c), which mean that there were two types of active sites that activated the intermediates. Therefore, the first and second steps of the OER occurred at the Fe sites, while the third step occurred at the Ni sites, which constituted the reaction path I:  $(H_2O(1) \rightarrow O(1))$  $H^* \rightarrow 0^* \rightarrow 00H^{\#} \rightarrow 0_2(g)$  (Fig. 6c). Another reaction pathway  $(H_2O(1) \rightarrow OH^* \rightarrow O^* + OH^{\#} \rightarrow O_2(g))$  (Fig. 6d) was also proposed based on the path I, in which another intermediate (OH<sup>#</sup>) of OH was adsorbed on the Ni site and reacted with O\* generated at the Fe site in the second step to directly generate O<sub>2</sub>. Therefore, Ni and Fe sites with different adsorption energies participated in the entire OER process.

Even in  $Ni_{1-x}Fe_xOOH$ , it was found that both  $Fe^{4+}$  and  $Ni^{4+}$ played an important role in OER [69]. High-spin  $d^4$  Fe promotes the active site with free radical properties on the metal-oxo (MO) bond, while low-spin  $d^6$  Ni provides a site for O-O bond coupling, which is why Ni<sub>1-x</sub>Fe<sub>x</sub>OOH leads to a lower overpotential and better catalytic activity of OER than NiOOH. The above theory can be well explained through the free energy approach [69]. The OER mechanism of Ni<sub>1-x</sub>Fe<sub>x</sub>OOH and NiOOH was investigated starting from State 1 (Fig. 7), it was found that the incorporation of Fe greatly changed the path and energy of NiOOH in OER. The energy required for the first oxidation-deprotonation step in Ni<sub>1-x</sub>Fe<sub>x</sub>OOH was close to NiOOH, while the apparent energy difference occurred in State 3 and State 4, where the energy required in the potential determining step (PDS) step was reduced to 1.68 eV when the key O. intermediate was formed at the Fe<sup>4+</sup> site because the unpaired electrons of O· were stabilized by high spin  $d^4$  Fe<sup>4+</sup> site (Fig. 7c, d). The O–O coupling was achieved via the interaction of O. with another H<sub>2</sub>O from the third oxidation step, hydrogenating the bridged O between the Ni<sup>4+</sup> sites. It is worth noting here that O., as a key intermediate of OER, determined the initial potential of OER, and the O. formed at the Ni<sup>4+</sup> site was not as stable as the Fe<sup>4+</sup> site ( $\Delta G_{4-4'} = -0.46$  eV in Ni<sup>4+</sup> in Fig. 7c,  $\Delta G_{4-4'-Fe} = +0.41$  eV in Fe<sup>4+</sup> in Fig. 7d). Therefore, the beneficial effect of Fe doping with NiOOH was to stabilize the key intermediate O, thereby reducing overpotential ( $\eta$ ) and enhancing the electrocatalytic activity of OER.

Based on these, for Ni or Fe is the active center, people seem to be able to sit in the right place. However, when related to the more different and complicated systems, further investigation is necessary. In any case, the amount of Fe is a key factor that cannot be ignored. It has been confirmed that when the Fe doping amount in Ni(OH)<sub>2</sub> was increased from 5% to 25%, the electrical conductivity of the catalyst was remarkably increased, moreover, the CV curves of Ni(OH)<sub>2</sub> with 5%, 15% and 25% Fe doped before and after OER had different peaks [55]. In the existing research, the following criteria may be used as a quantitative criterion to identify the roles of Ni and Fe in NiFe (oxy)hydroxides. Under catalytic conditions, when Fe content in FeNi (oxy)hydroxides is less than 4%, Ni atoms exist in the form of Ni<sup>4+</sup>, and when Fe content exceeds 4%, Ni atoms are stabilized in a low-valent oxidation state, thus OER activity state can be described as Ni<sup>2+</sup>Fe<sup>3+</sup>OOH (Fig. 8a) [45].

#### 2.3. NiFe LDHs

When the divalent Ni ion is replaced by  $Fe^{3+}$ , the brucite-type layered structure of  $\beta$ -Ni(OH)<sub>2</sub> is converted into a NiFe bilayer structure similar to  $\alpha$ -Ni(OH)<sub>2</sub> [70], i.e. the common NiFe LDH, which is a class of layered materials comprising positively charged metal hydroxide layers and charge-balancing anions between the layers [71]. NiFe LDH is considered to be  $Fe^{3+}$ -doped Ni(OH)<sub>2</sub> [72]. Due to typical layered structural characteristics, the properties of NiFe LDH can be improved over a wide range by adjusting the ratio of Ni and Fe, as well as the anion type and porosity between the layers [73]. This makes NiFe LDH a very promising



**Fig. 6.** Free energy diagrams at different potentials for the OER on FeOH@PCN (a) and NiFeOH@PCN (b) surfaces. (c and d) Atomic configurations of OH, O, and OOH adsorbed on the NiFe(OH)<sub>2</sub>@PCN surface with an OOH<sup>#</sup> pathway (c) and  $O^* + OH^#$  pathway (d). The green, yellow, red, blue, gray and white balls are Ni, Fe, O, N, C and H atoms, respectively. Notably, the active site of the OER changes from the Fe site to Ni site for the O<sup>\*</sup> to HOO<sup>#</sup> step on NiFe(OH)<sub>2</sub>@PCN with double OH. Reproduced with permission from Ref. [59]. Copyright © The Royal Society of Chemistry 2019. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 7.** Models for NiOOH and Ni<sub>1-x</sub>Fe<sub>x</sub>OOH OER electrocatalysts. (1 0 0) slab models with one explicit water layer for (a)  $\gamma$ -NiOOH and (b)  $\gamma$ -Ni<sub>1-x</sub>Fe<sub>x</sub>OOH. Blue, purple, red, white, green, and gray atoms indicate Ni<sup>4+</sup>, Ni<sup>3+</sup>, O, H, K<sup>+</sup>, and Fe<sup>4+</sup>, respectively. Chemical structures for each model surface are shown as insets. (Note that the intercalating K<sup>+</sup> and H<sub>2</sub>O are not shown in the insets for clarity.) (c) Mechanism for OER on NiOOH catalyst leading to  $\eta = 0.83$  V. (d) Mechanism for OER on Ni<sub>1-x</sub>Fe<sub>x</sub>OOH catalyst leading to  $\eta = 0.45$  V. Reproduced with permission from Ref. [69]. Copyright © 2018 American Chemical Society. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

material for energy conversion and storage. Generally, the Fe site may exist in three styles in NiFe LDH: the center, the edge along the long axis and the corner of the minor axis edge (Fig. 8b), and the Fe site at the edge position is considered to be the most active value [73]. The addition of Fe facilitates the formation of the LDH phase, thereby increasing the effective electrochemical surface area (ECSA), and it has been confirmed that such an LDH crystal structure is more active than the calcined spinel phase Ni-Fe catalyst [25]. Notably, most reports focus on coupling NiFe LDH with conductive carbonaceous materials (such as graphene, carbon nanotubes) to accelerate charge transfer kinetics and some so-called



**Fig. 8.** (a) XAS-derived structural motifs prevalent during OER catalysis at high and intermediate Ni-content. At high Ni-content the dominating host is the layered  $\gamma$ -NiOOH (a "NiO<sub>2</sub>" phase) with octahedrally coordinated edge-sharing Ni<sup>4+</sup>. In the presence of Fe there is a mixture of edge- and corner sharing octahedra. Above 4% Fe, the dominant host is the Ni(OH)<sub>2</sub> with Ni<sup>2+</sup>. Reproduced with permission from Ref. [45]. Copyright © 2016 American Chemical Society. (b) Fe sites in the basic NiFe LDH ([Ni<sub>9</sub>Fe<sub>1</sub>(OH)<sub>18</sub>]<sup>3+</sup>) cluster fragment. Colors: Ni green, Fe maroon, O red, H white. Reproduced with permission from Ref. [73]. Copyright © The Royal Society of Chemistry 2016. (c) Schematic illustration of preparation of Fe-doped Ni(OH)<sub>2</sub> nanosheets. H atoms are omitted. Contact angle measurements of (d) pure Ni(OH)<sub>2</sub> (25°), (e) Ni<sub>0.83</sub>Fe<sub>0.17</sub>(OH)<sub>2</sub> (13°), and (f) NiFe LDH (32°). Reproduced with permission from Ref. [72]. Copyright © 2018 American Chemical Society. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

synergistic effect in order to increase catalytic activity [71,74]. Regrettably, little attention has been paid to enhancing the intrinsic activity of NiFe LDH and/or increasing its active sites. For most transition metal based 2D materials, the active centers are predominantly located at the edge, and the oxidation reaction that forms the catalytic phase of the high valence state is somewhat hindered by the closely packed basal plane [75,76]. Therefore, activation of these basal planes is critical to further increase the catalytic activity of the nano-NiFe LDH. At present, NiFe LDH is mainly synthesized by one-pot method, mainly including homogeneous co-precipitation, hydrothermal and electrodeposition [72]. However, NiFe LDH synthesized by these methods imparts a close-packed basal plane, which greatly limits the exposure of active sites [72]. An NiFe LDH composed of Fe-doped Ni(OH)<sub>2</sub> nanosheet (Ni<sub>0.83</sub>Fe<sub>0.17</sub>(OH)<sub>2</sub>) prepared by cation exchange process was proven to overcome the above obstacles to maximize electrocatalytic properties due to defect-rich holey basal planes (Fig. 8c) [72]. The morphology of the holey nanosheets as well as the rich Ni and O vacancies caused by the chemical etching of Fe<sup>3+</sup> were beneficial to expose more ion-accessible sites, thereby providing more active sites. Secondly, the better wettability of Ni<sub>0.83</sub>Fe<sub>0.17</sub>(OH)<sub>2</sub> was a key factor (Fig. 8d-f). This improved catalyst surface wetting property ensured rapid penetration of electrolytes, accelerated hydroxyl migration and release of oxygen during water splitting [77].

In fact, the most attractive application of NiFe LDHs is as a superior bifunctional electrocatalyst for water splitting, and this bifunctional electrocatalytic pathway (i.e. HER and OER) can be explained by Raman spectroscopy [78]. In a dynamically selfoptimized NiFe LDH, based on Raman spectroscopy, it was observed that the activity pattern between 400 and 600 cm<sup>-1</sup> exhibited a potential-dependent trend (Fig. 9a, d) [78]. In Fig. 9b, the bands at 455 and 526 cm<sup>-1</sup> were attributable to the vibration of metal-oxygen in Ni(OH)<sub>2</sub> and FeOOH (Fe<sup>3+</sup>), and it could be seen that the presence of Fe seemed to inhibit the electrochemical selfreduction activity of Ni complex, which in turn promoted the water dissociation (H<sub>2</sub>O +  $e^- \leftrightarrow H + OH^-$ ). During HER, the hydrolyzed intermediates H and OH were adsorbed on the Ni<sup>2+</sup> center (H<sub>ad</sub>-NiO) and  $Fe^{3+}$  center (OH<sub>ad</sub>-FeO), respectively, and then the H in the second H<sub>2</sub>O combined with the H in the H<sub>ad</sub>-NiO group to form H<sub>2</sub> (Fig. 9c). In general, the species formed in NiFe LDH (i.e. H<sub>ad</sub>-NiO and OH<sub>ad</sub>-FeO) are compatible with the Volmer reaction in the water splitting step. Actually, the kinetics of HER depends not only on the rate of adsorption of H<sub>ad</sub>, but also on the rate of electron transfer and the ability of the released species to activate the active sites [78]. In NiFe LDH, the synergistic effect of Ni-Fe is mainly through the formation of FeOOH to enhance the bond association with H<sub>ad</sub>-NiO and the second hydrogen to meet the transition energy release requirements, thereby optimizing the HER reaction route [78]. While the reaction path of OER is more complicated than that of HER due to more reaction intermediates are involved before O<sub>2</sub> evolution. Fig. 9d showed the transition of Ni(OH)<sub>2</sub> to NiOOH on the NiFe LDH surface with an increase in overpotential, the observed bands at 477 and 557 cm<sup>-1</sup> matched well with spectral features of  $\gamma$ -NiOOH with the average Ni oxidation state of +3.3 to +3.7 at the larger overpotential (Fig. 9e), which conduced to achieve a high OER activity. Therefore, at a low potential, it was suggested that OH<sub>ad</sub> was adsorbed to the Fe site in the FeOOH formed on the NiFe LDH electrode, while at a higher potential, with the appearance of Raman characteristics of NiOOH, H<sub>ad</sub> tended to adsorb or migrate to the Ni site, then the adsorbed OH group reacted with other OH groups to form the reaction intermediate, which was further oxidized to  $O_2$  and  $H_2O$  (Fig. 9f). As a matter of fact, this behavior is easy to explain, as a strong Lewis acid, the interaction between OH and Fe<sup>3+</sup> is stronger than that of Ni<sup>2+</sup>, when the applied potential is increased, the electronic effect of Fe<sup>3+</sup> leads to a higher Ni value, resulting the Ni center is more easily combined with OH [60,78]. When NiFe LDH nanosheets (NiFe LDH-NS) were integrated onto defective graphene (DG), direct interfacial contact of such transition metal atoms with defects on carbon was maximized (Fig. 10a), which could be explained by electronic distribution [79]. It could clearly be seen that in the geometries of the fully relaxed NiFe LDH-NS@DG (Fig. 10b), the electrons were redistributed, especially around defects marked with blue dash frames (Fig. 10c). The accumulation of such local electronics in the defect centers was considered to be the key to enhancing HER. On the other hand, electron transfer lead to the accumulation of holes on NiFe LDH-NS, which was beneficial to OER (Fig. 10d). Therefore, the hybridization of NiFe LDH-NS and DG lead to holes separation on NiFe LDH-NS as well as electrons redistribution on DG, respectively, allowing HER and OER to proceed smoothly at favorable active sites.

In pursuit of high-performance OER electrocatalysts, the modulation of the local electronic structure of Ni<sup>2+</sup> provides the necessary motif. To this end, direct modification of local chemical components is the most intuitive and effective strategy [80]. Typically, the co-existence of Fe<sup>3+</sup> and Ni<sup>2+</sup> in a bimetallic catalyst can redistribute electron density and even rearrange their coordination structures through partial charge transfer, which is beneficial to the oxidation of Ni<sup>2+</sup> and enhance its OER catalytic activity [80]. It has been reported that only surface Fe species adsorbed at the edge/defect centers (i.e. not in the bulk) of the Ni-based phase could effectively promote the improvement of Ni<sup>2+</sup> catalytic performance [44]. It was speculated that surface transition metal ions may have incomplete oxygen coordination [81]. In this case, if the active site of OER was Fe, one possibility for the increase in OER activity was the structural flexibility of Fe<sup>3+</sup>, which could be coordinated by octahedron, tetrahedron and square pyramid [81]. This flexibility came from the high spin  $Fe^{3+}$ :  $t_2^{3}e^2$  with no net crys-



**Fig. 9.** (a) In-situ Raman spectra collected in a large wavenumber region from NiFe LDH during HER process in 1 M KOH at various overpotentials vs. RHE. (b) Magnification of the corresponding orange wavelength region of (a). Schematic illustration (c) showing the reaction mechanism for HER on NiFe LDH. (d) In-situ Raman spectra collected in a large wavenumber region from NiFe LDH during OER process in 1 M KOH at various overpotentials vs. RHE. (e) Magnification of the corresponding green wavelength region of (d). (f) Schematic picture showing the OER mechanism of NiFe LDH. Reproduced with permission from Ref. [78]. Copyright © The Royal Society of Chemistry 2019. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 10. (a) Schematic illustration of the preparation of NiFe LDH-NS@DG nanocomposite. (b) Density functional theory (DFT) calculation studies of Ni-Fe LDH-NS@DG (DG-5, DG-585, or DG-5775) based composite. The top views (b) of optimized Ni-Fe LDH-NS@DG (DG-5, DG-585, or DG-5775) based composite interfaces. (c) The side views of 3D charge density difference plot for the interfaces between a defective graphene sheet (DG-5, DG-585, or DG-5775) and a NiFe LDH-NS layer are demonstrated. Yellow and cyan isosurfaces represent charge accumulation and depletion in the 3D space with an isosurface value of 0.002 e  $Å^{-3}$ . Green, brown, silver, and red balls represent C, Fe, Ni, and O atoms, respectively. The different defect types and associated enhanced charge density areas are marked with a blue solid line and a blue dash line, respectively. (d) The schematic of the probable electrocatalytic mechanism of NiFe LDH-NS@DG for HER and OER is presented based on the DFT calculation results. The pink and purple spheres represent electrons and holes, respectively, Reproduced with permission from Ref. [79]. Copyright © 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

tal field stabilization energy or preference for octahedral vs. tetrahedral coordination, moreover, the flexibility of this structural coordination may also contribute to the adsorption and desorption of intermediates in the OER process [81]. For NiFe LDHs, the local electronic structure of Ni<sup>2+</sup> can be well regulated by replacing part of the Ni<sup>2+</sup> sites with bivalent Fe<sup>2+</sup> [82]. For example, a recent study suggested that FeOOH nanoparticles (NPs) could greatly enhance the OER catalytic performance of NiFe LDH through strong interfacial interactions [80]. In this FeOOH/LDH nanocomposite, a large number of FeOOH-NPs with an average size of 2.0 to 18.0 nm were stably anchored to the thin nano-petals of the hierarchically structured NiFe LDH flowers (Fig. 11a, b). The high oxidation state  $Fe^{(3+\delta)+}$  species presented in FeOOH-NP interacted with NiFe LDH and regulated the local electronic structure of its Ni<sup>2+</sup> site by forming an oxygen bridge with a shorter bond length such as  $Fe^{(3+\delta)+}-O-$ Ni<sup>2+</sup> (Fig. 11c). This interfacial interaction facilitated the oxidation of Ni<sup>2+</sup> in NiFe LDH to enhance the electrochemical catalytic behavior. The FeOOH/LDH complex had a strong catalytic synergistic effect on OER, and the effect was more and more obvious when the average particle size of FeOOH-NP was reduced from 18.0 nm to 2.0 nm due to the increased surface atomic ratio and unsaturation as well as enhanced interaction between FeOOH and NiFe LDH [80]. This study focusing on solid–solid interface chemistry can improve the OER catalytic performance even controlling the change of catalytic activity by adjusting the size of FeOOH-NP. and it is theoretically possible to achieve a level far beyond its catalytic limit, which opens up a new avenue for the designing in NiFe LDHs electrocatalytic systems. The increase in the valence state of this surface Ni was further confirmed when NiFe LDH was modified by MoO<sub>x</sub>, in which the most of the metal Ni on the surface were converted to  $Ni^{2+}/^{3+}$ , while the valence state of Fe hardly changed (Fig. 11d, e) [83].



**Fig. 11.** (a) One-pot synthesis where (1) the intermediate LDH flower is formed in the early stage, on which later FeOOH NPs are deposited to form (2) the FeOOH<sub>2 nm</sub>/ LDH composite. (b) The stepwise synthesis where (3) the preformed LDH is used as a support for preferential deposition of FeOOH NPs with various average sizes to give (4) the FeOOH/LDH. (c) Schematic depiction of the interfacial interaction via the formation of oxygen bridges (e.g.,  $Fe^{(3+\delta)+}-O-Ni^{2+})$  with relative short bond length between the FeOOH NPs with NiFe LDH. Reproduced with permission from Ref [80]. Copyright © 2018 American Chemical Society. XPS spectra of (d) Ni 2p and (e) Fe 2p in the NiFe alloy and NiFe-MOO<sub>x</sub> nanosheet. Reproduced with permission from Ref. [83]. Copyright © The Royal Society of Chemistry 2017.

Different from the synergistic roles of Fe and Al in NiFeAlO<sub>4</sub> mentioned above for water oxidation reaction, when Al<sup>3+</sup> was substituted for partial Fe<sup>3+</sup> in NiFe LDH, the conductivity of NiFe LDH was increased, meanwhile, the dissolution of Al<sup>3+</sup> under alkaline conditions lead to the formation of a Ni-rich active center on the surface of NiFe LDH with the formation of low-coordinate Ni and Fe atoms with defective structures, resulting in an observed increase in OER [84]. It should be noted that although Al<sup>3+</sup> has been reported to enhance the OER activity of NiFe LDH, they eventually formed the LDH phase [55]. So, was this enhancement of OER due to the enhancement of Al<sup>3+</sup> similar to Fe<sup>3+</sup> or the formation of LDH phase? If it was the former, the reinforcing effect of the interface between Fe and Ni(OH)<sub>2</sub> film was obvious even if Fe was in a trace amount, however, it was not found this enhancement at the current trace levels of Al<sup>3+</sup> [55]. Therefore, it can be concluded that in the improvement of OER performance in the NiFe LDH in which Al<sup>3+</sup> participated, the LDH phase formed by the hydroxide as the core system was indispensable, namely, the enhancement of Al<sup>3+</sup> ions did not follow the active structure and reaction pathway as in the case of Fe<sup>3+</sup>. This also means that Fe<sup>3+</sup> is still a better dopant in the LDH phase compared to Al<sup>3+</sup> or other trivalent ions (such as Mn<sup>3+</sup>, Cr<sup>3+</sup>, V<sup>3+</sup>, etc.) [55].

In most of the above reports, the purpose of adding Fe to the core catalyst system is to improve the overall water splitting performance of the catalyst, and the observed valence of Fe is mostly 3+. Although the Fe precursors used in the synthesis of some NiFe LDH initially contain  $Fe^{2+}$  ions, they are eventually oxidized to  $Fe^{3+}$  by high-temperature hydrothermal reaction or by addition of, for example, a dilute peroxide solution. Although there are some reports claimed that the formed NiFe LDH contained  $Fe^{2+}$  ions and exhibited equally impressive OER properties, the oxidation state of Fe in the form of impurities or dopants was mainly 3+ in NiFe oxides or (oxy)hydroxides with few exceptional cases. Furthermore, under OER conditions, the oxidation of  $Fe^{3+}$  is most likely to occur at an applied potential. Therefore, in order to obtain better OER performance, the oxidation state of Fe is usually strictly 3+ or higher, and it is almost impossible to prohibit  $Fe^{2+}$  from oxidizing to  $Fe^{3+}$  under OER.

#### 3. Co-involved NiFe-based compounds

To the best of our knowledge, there is still a common and inexpensive Co element between Fe and Ni in the periodic table. The use of Fe-Co-Ni ternary transition metal as a state-of-the-art electrocatalyst for the HER or OER will represent a major advancement in the field of catalysis [21]. In the design of robust electrocatalysts containing Fe, Co and Ni, people often start from two aspects: i) increasing the covalent bond around the transition metal centers to increase the catalytic activity; and ii) using the transition metal doping therein to increase the catalytic activity via reducing the overpotential [34]. At the atomic level, multimetal ions doping is effective in the regulation of electrocatalytic activity. In general, in OER catalysis, mixed metal (Fe, Co, Ni) oxides/hydroxides may exceed the corresponding single metal oxides/hydroxides, mainly due to the changes in the charge distribution between different metal cations and optimized oxophilicity (e.g. metal-OH bond strength), which are contributed to the triggering the OER process [85]. A large number of studies have shown that Co and Fe codoped Ni-based trimetallic catalysts have better OER and HER activity than Fe-doped Ni-based bimetallic catalysts. It is considered to be an effective way to improve OER and HER by changing the  $Co^{3+}/Co^{2+}$  ratio and the oxygen vacancies, or by changing the Co/Fe ratio in the trimetallic catalyst to regulate the unsaturated coordination of hydroxyl groups on the oxide/hydroxide surface, thereby optimizing the surface state [86]. In generally, in Codoped Ni-based catalysts. Co tends to push some electrons toward the Ni sites, increasing  $O^{2-}$  as the number of proton adsorption centers, thus forceing the HER charge transfer faster. In contrast, in Fe and Co co-doped Ni-based trimetallic systems, Fe can extract some electrons from the Ni/Co active centers, thereby increasing the electron affinity of Ni/Co sites to OER [85]. For optimized Ni<sub>0.8</sub>- $Co_{0.1}Fe_{0.1}O_xH_v$ , Ni and Co were both active centers for adsorbing OH in both OER and HER processes, and with the co-doping of Co and Fe, the  $Co^{3+}/Co^{2+}$  ratio increased (Fig. 12a-c), indicating that Co tended to push some of its electrons to the Fe site instead of the Ni center in Ni<sub>0.8</sub>Co<sub>0.1</sub>Fe<sub>0.1</sub>O<sub>x</sub>H<sub>v</sub> [85]. The generated Co<sup>3+</sup> may form an electron pull (non-push) effect on the Ni site, promoting the adsorption of OH and increasing the binding energy of OH (Fig. 12d). Therefore, this Co and Fe co-doped Ni<sub>0.8</sub>Co<sub>0.1</sub>Fe<sub>0.1</sub>O<sub>x</sub>H<sub>v</sub> catalyst exhibited the best OER performance due to the double increase of OH<sup>-</sup> adsorption and active sites (Fig. 12e).

In another optimized relaxed structure of  $Co_{0.5}Ni_{0.5}Fe_2O_4(0\ 0\ 1)$  with B-layer termination (B-layer with octahedrally coordinated Co/Ni) (Fig. 13a) [87], the site identification of Co was more clear, the relaxed structure of the intermediate indicated that all of the groups were attached separately to the Co reaction center (Fig. 13b). Therefore Co acted as a reaction site, and the most effective step was the \*OH formed by the dissociative adsorption of the second H<sub>2</sub>O molecule on the \*O intermediate. The OER was carried out at the oxygen vacancies at the top of the Co, which had the lowest formation energy compared to the position of the Fe or Ni surface.

The construction of a separate 3D porous nanostructure catalyst on a conductive substrate and its direct use as an electrode pro-



**Fig. 12.** XPS spectra of Co 2p for Ni-based hydroxides at different conditions: (a) Co 2p spectrums for the as-prepared specimens, (b) specimens after OER tests and (c) HER tests. (d) Schematic illustration of electronic push/ pull effect of Co/Fe doping on tuning the HER and OER activities of Ni-based catalysts electrodeposited on Ni foam. (e) Electronic pull mechanistic schematics of OER process for the Ni<sub>0.8</sub>Co<sub>0.1</sub>-Fe<sub>0.1</sub>O<sub>2</sub>H<sub>y</sub>. Reproduced with permission from Ref. [85]. Copyright © 2018 American Chemical Society.

vides rich exposure active sites and buffer volume change [21]. In this regard, the electrocatalytic OER performance of a ternary Ni-Fe-Co mixed-metal oxide (MMO) film supported on Ranev Ni was investigated [25]. First, the Fe/Raney Ni sample showed a weak Ni<sup>2+</sup>/<sup>3+</sup> redox peak, indicating the presence of an Fe-rich surface (Fig. 14a) [25]. The previous study has reported that the Ferich surface of the mixed Ni-Fe system did not show OER enhancement [37]. It should be noted that the redox peak observed on the Co/Raney Ni sample occurred at a much lower potential than the redox peak characteristic of the  $Ni^{2+}/^{3+}$  transition (Fig. 14a). The same analysis was carried out by loading these samples on the C carrier, and it was found that the redox peak observed on the Ni-Co/C sample was the lowest among all the samples (Fig. 14b) [25]. This indicated that Co promoted the oxidation of  $Ni^{2+}$  to Ni<sup>3+</sup> at a lower potential. On the contrary, Fe seemed to stabilize the oxidation state of Ni<sup>2+</sup>, which was consistent with the abovementioned conclusion of Görlin et al. [45]. The effect of Co on the redox peak of Ni was also noted by Corrigan et al. [88], in which a significant cathodic shift in the Ni redox peak in the coprecipitated Ni-Co oxide film was found. Interestingly, the addition of Co to the Ni oxide film did not increase the activity of the OER, instead, both Fe-containing samples exhibited significantly enhanced OER activity. Although Fe did improve the conductivity of the Ni oxide film, this effect did not fully explain the increase in the redox activity of the Ni-Fe surface [43]. Moreover, FeOOH itself was not sufficient to act as a catalyst at low overpotentials, experiments and calculations showed that the Fe sites in Ni or Co oxides had an ideal binding energy to the -OH and -OOH intermediates [20]. Therefore, the further enhancement of the OER in the Ni-Fe-Co catalyst may be due to the charge transfer effect of the Co component activating the more conductive Ni<sup>3+</sup>OOH phase (comparison to the non-conductive  $Ni^{2+}(OH)_2$  phase) at a lower



**Fig. 13.** (a) Side and top views of the B-layer. (b) Cumulative free energies  $\sum \Delta G_i$  of the intermediates for the B-layer terminations. Side view of the corresponding intermediate structures for the mixed oxide are also shown. The intermediate steps 1–4 are denoted by their products \*OH, \*O, \*OOH, and \*(). Reproduced with permission from Ref. [87]. Copyright © 2018 American Chemical Society.



**Fig. 14.** (a) CV data (20 mV/s) showing Ni<sup>2+/3+</sup> redox peaks and OER activity from Raney Ni supported samples. Conditions: 250 µg/cm<sup>2</sup> catalyst loading on GC RDE substrate; tested in O<sub>2</sub>-purged 0.1 M KOH at room temperature (-23) and 2500 rpm. (b) CV data (20 mV/s) showing Ni<sup>2+/3+</sup> redox peaks and OER activity from C-supported samples used for XAS analysis. All samples are 30 wt% MMO/C. Atomic ratios of MMO films are 1:1 Ni:Co, 9:1 Ni:Fe, and 8:1:1 Ni:Fe:Co. Summary of XAS analysis: shifts in Ni K-edge energy due to the presence of Fe and/or Co. (c) Ni K-edge energy shift is most apparent). (d) Graphical representation of shifts in Ni K-edge energy (relative to 8333 eV) for various MMO samples as a function of applied potential. The arrow shows the correlation with the observed shift in Ni<sup>2+</sup>/<sup>3+</sup> redox potential. (e) Ni-O and (f) Ni-M bond-lengths from EXAFS fitting. Reproduced with permission from Ref. [25]. Copyright © 2015 American Chemical Society.

overpotential [25]. This conjecture was further confirmed by Ni Kedge XANES data (Fig. 14c), in which the difference in oxidation state of the different samples was the most obvious. Fig. 14d depicted the relative displacement of the Ni K-edge energy as a function of applied potential for each sample, the data supported well the CV results of Fig. 14b, which further confirmed that Fe stabilized Ni<sup>2+</sup>, while Co promoted the oxidation of Ni<sup>3+</sup> at a lower applied potential. It is worth noting that the insertion of Co lead to the shrinkage of the Ni-center bond distance, including Ni-O and Ni-M (M stands for Ni, Fe and/or Co) (Fig. 14e, f). This effect was caused by the substitution of the  $Ni^{2+}$  with  $Co^{3+}$  with shorter bond distances due to the higher oxidation state [25]. This strain effect on bond length has been shown to promote charge transfer between two different atoms (here Ni and Co) [89], and another beneficial effect of this Co-induced strain was to increase the MMO's conductivity. Specifically, if Fe was the active center, the shortening of the bond distance would lead to a further increase in OER activity, because Fe had a super-binding effect on the OER intermediate adsorbate, moreover, the strain effect mentioned could reduce the binding energy between the Fe and OER intermediates. On the other hand, if Ni was the active center, it would not increase the activity of OER because the bounding of Ni and OER intermediates were too weakly [24]. Thus, in this Ni-Fe-Co MMO film, Co component promoted oxidation of Ni to a more conductive NiOOH phase at a lower overpotential, thereby effectively activating the dormant Fe sites in the non-conductive Ni(OH)<sub>2</sub> phase and promoting OER performance.

Analogous analysis can be obtained when Co-doped NiO/ NiFe2O4 mixed oxide mesoporous nanosheet arrays were constructed on nickel foam, and the roles of Co and Fe atoms in such Co-doped NiFe mixed oxides and their effect on OER activity were further revealed [21]. The OER catalytic activity of Co-doped NiO was somewhat improved compared with pure NiO when only Co source was added, while the catalytic activity of the NiFe composite oxide was significantly improved as compared with pure NiO when only the Fe source was added, which indicated that Co and Fe atoms played a synergistic role in improving the OER catalytic activity of NiO. This synergistic effect was further refined into the introduction of the NiFe<sub>2</sub>O<sub>4</sub> active phase and the doping of Co<sup>2+</sup>. In other words, the enhanced conductivity in Co-doped NiO/Ni<sub>2</sub>-FeO<sub>4</sub> improved the charge transfer kinetics of the overall catalyst and thus facilitated the electrochemical performance of OER and HER (Fig. 15a) [21]. The Co doping in the NiFe composite oxide made it possible to transfer electrons of Ni atoms to Fe atoms and Co atoms. The electron-deficient Ni atom could easily adsorb (oxy)hydroxyl groups and contributed to the OER reaction, while the charge transfer effect of Co promoted correspondingly the oxidation of Ni to a more conductive NiOOH phase at a lower overpotential [25]. At the same time, electron-rich Co atoms readily acquired electrons and reacted with adsorbed H<sub>2</sub>O molecules to form hydrogen atoms, thereby producing highly efficient HER activity. Since the kinetics of OER and HER were most favorable in the moderate intermediates coverage, proper electron transfer in Co<sub>6.25</sub>Fe<sub>18.75</sub>Ni<sub>75</sub>O<sub>x</sub> endowed it the best OER and HER activity (Fig. 15b, c) [21].



**Fig. 15.** (a) Nyquist plots of the Co-doped NiFe mixed oxide electrodes. As a comparison, the plot of NiO is also presented. (b) Polarization curves for the Co-doped NiFe mixed oxides, NiO, commercial RuO<sub>2</sub> on Ni foam and bare Ni foam for OER. (c) Polarization curves for the Co-doped NiFe mixed oxides, NiO, commercial Pt/C on Ni foam and bare Ni foam for HER. Reproduced with permission from Ref. [21]. Copyright © The Royal Society of Chemistry 2018.

Recent studies have shown that combining transition metal components with carbon materials is an effective way to reduce metal demand while improving the apparent electrocatalytic properties of the composite [90]. The presence of the carbon support will significantly improve the dispersion of the metal nanoparticles, preventing their aggregation, and promoting the transport of electrons during the reaction [91–93]. Today, more research are devoted to reducing the metal species required on carbon to the atomic scale, so that, not only the metal content on the carbon can be further reduced (usually <1 at%), but also the metal atoms can coordinate with the heteroatoms (usually nitrogen) in the carbon matrix to form a metal-nitrogen-carbon (M-N-C) bond that acts on reactions such as HER [94–96]. However, one of the great challenges faced by this strategy is the instability of the M-N-C bond formed, namely, the metal components on the carbon surface fall off in the long-term catalytic process [90]. Another attractive way to integrate transition metal species and carbon is to encapsulate metal nanoparticles in graphene or graphitized carbon shells, forming like-lantern composite (abbreviated as M@C) [97]. The lantern core (i.e. transition metal composite) can be protected in a corrosive reaction environment to extend stability, on the other hand, the synergy between the lantern shell and the core further enhances the catalytic activity for specific reactions [98,99]. Typically, the higher OER catalytic activity of NiCoFe@C was believed to be primarily the coordination of the alloy core with its surrounding carbon shell, thereby regulating the binding strength of the reaction intermediates during different reaction periods [90].

To be additional, when a foreign atom (such as Ce) was further doped in the Ni-Fe-Co MMO film ((Ni-Fe-Co-Ce)O<sub>x</sub>), the active material was still the same transition metal (oxy)hydroxides, just the type of hydroxides may be limited to Ni and Co atoms close to CeO<sub>2</sub> [100]. The CeO<sub>2</sub> formed in the composite itself did not own redox activity under catalytic conditions, and the oxygen spillover of CeO<sub>2</sub> into the transition metal oxides indirectly changed the type of transition metal in the catalytic process. Furthermore, by means of DFT and in-situ XAS, Zheng et al. found that Ni in NiCoFeP was easily oxidized to Ni<sup>4+</sup>, emphasizing that highvalent Ni had a higher reactivity against water oxidation as we discussed earlier [101].

#### 4. Conclusions and perspectives

The urgent demand for environmentally sound and sustainable energy is unstoppable. With the continuous consumption of traditional energy, it is time to concentrate more on the conversion and consumption of non-traditional energy. Although fuel cell technology and electrochemical water splitting to produce H<sub>2</sub> have been developed and applied decades ago, the revolution caused by nanoscience and nanotechnology in recent years has opened up a new road to further improve the efficiency of fuel cells and reduce energy loss in electrolytes.

Different from other related reviews, this review only emphasizes the mechanism of NiFe-based oxides, (oxy)hydroxides as well as LDH phase catalysts in alkaline water oxidation and catalytic active centers. In this review, the water splitting technology and its need for current energy demand are introduced. The basic principles of electrochemical water splitting are elaborated in detail from the perspective of thermodynamics and kinetics. According to more experimental and theoretical reports, the mechanism of water splitting on NiFe-based catalysts are discussed in depth, emphasizing the necessity of LDH phase formation under OER conditions. Furthermore, the roles of Fe<sup>3+</sup> in improving the OER performance of NiFe-based catalysts and the advantages over other trivalent cations are clarified.

Of course, with the deepening of research and the development of analysis technology, there are still many problems that need to be emphasized.

- i) In most cases, the roles of the multi-metal surface and the roles of each metal counterpart in the reaction have been discussed rigorously. Even in some systems, the above roles have not been elucidated, but at least the synergic mechanism in the system are analyzed. It can be concluded that some reactions are advantageous on specific surfaces, therefore, continuing to focus on the rational design of surfacespecific bimetallic or trimetallic catalysts, as well as an understanding of the structure-activity relationship for better catalytic performance is vital.
- ii) In addition to the proper catalyst design based on a basic understanding, another major problem is the stability of the multi-metal catalysts under the reaction conditions. One possible way to reduce the cost and improve the stability of the catalysts without affecting the activity of the catalysts is to introduce non-metallic elements such as P, B and S, etc. The compounds such as Ni-P or Ni-B have high activity and corrosive resistance.
- iii) Many of the research methods involved in this review, such as in-situ Raman and XAS spectroscopy, provide effective approaches to analyze the structure of NiFe-based catalysts. Therefore, conducting high-level in-situ research is still a top priority to dissect the mechanism and reaction pathway of the water splitting as well as the precise formation of the structure–activity correlation.
- iv) The difference in water splitting reaction mechanism of different catalysts should be more specific, such as the influence of intercalation anion on the conductivity and performance of LDH phase materials as well as the relationship between interlayer distance and activity of catalysts.
- v) DFT has not yet developed an important frontier in the calculation of these highly active electrocatalytic materials. For most of NiFe-based catalysts with reasonable electrochemical activity, a deeper understanding of the catalyst atoms involved and the deprotonation reaction is required.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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