Effects of Metal Combinations on the Electrocatalytic Properties of Transition-Metal-Based Layered Double Hydroxides for Water Oxidation: A Perspective with Insights

Zheng Wang, Xia Long, and Shihe Yang

1. INTRODUCTION

The hydrogen and oxygen generation from water splitting is of great importance since it can simultaneously tackle the issues of energy crisis and environmental pollution problems. Indeed, it has aroused extensive research interest ever since the concept of water splitting was demonstrated, which has intensified in the recent few decades.1 Electrochemical (EC) water splitting separates the whole process into two half-reactions, hydrogen evolution reactions (HERs) and oxygen evolution reactions (OERs). As is well known, compared to HER, OER is much more kinetically sluggish and requires a very high overpotential, thus limiting the water splitting efficiency and hindering the development of the hydrogen production industry based on water splitting.

The state-of-the-art catalysts of RuO2 and IrO2 show effective water oxidation activity.2 However, the high cost of Ir ($16 181 kg−1) and Ru ($2000 kg−1) significantly limits their large-scale utilization. Fortunately, the first-row transition-metal-based compounds with controlled chemical composition and microstructures have been found to have comparable water splitting performance, with much more bountiful resources and lower prices. Among these materials, transition-metal-based layered double hydroxides (TM LDHs) have emerged as highly efficient water oxidation catalysts. They are promising and have the potential to replace the rare and expensive precious metal-based ones such as RuO2 and IrO2, which have been well established. In this perspective, we will summarize the current development of TM LDHs as oxygen evolution reaction (OER) catalysts toward electrochemical water splitting. Particular emphasis will be placed on the roles of the transition-metal cations and the effects of their combination on their catalytic performance for the OER. It is hoped that this perspective will provide fundamental guidelines for future researches in this booming area.

ABSTRACT: Transition-metal-based layered double hydroxides (TM LDHs) have emerged as highly efficient water oxidation catalysts. They are promising and have the potential to replace the rare and expensive precious metal-based ones such as RuO2 and IrO2, which have been well established. In this perspective, we will summarize the current development of TM LDHs as oxygen evolution reaction (OER) catalysts toward electrochemical water splitting. Particular emphasis will be placed on the roles of the transition-metal cations and the effects of their combination on their catalytic performance for the OER. It is hoped that this perspective will provide fundamental guidelines for future researches in this booming area.

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2. BASIC CRITERIA FOR OER CATALYSTS AND MECHANISMS OF OER

The basic criteria to evaluate OER catalysis will be introduced in this section. Overpotential \( (\eta) \), calculated by the difference between the applied potential \( (E) \) to reach a certain current density and the equilibrium potential \( (E_{eq}) \) (as shown in eq 1), is the critical and most frequently used descriptor to evaluate the performance of an OER catalyst. \( E_{eq} \) is the half reaction's thermodynamically determined reduction potential, and \( E \) is the potential at which the redox event is experimentally observed. Generally, \( \eta \) is usually given at the onset of OER and at the current density of 10 mA cm\(^{-2} \), which corresponds to a 10% solar to hydrogen efficiency under 1 sun illumination. The existence of overpotential implies that the cell requires more energy than thermodynamically expected to drive a reaction. Therefore, a lower overpotential suggested a better OER activity.\(^2\)

\[
\eta = E - E_{eq} \tag{1}
\]

Tafel slope \( (b) \), which describes the influence of potential/overpotential on steady-state current density, is another key descriptor to evaluate OER kinetics. The value of \( b \) could be calculated by eq 2, where \( R \), \( T \), and \( F \) are ideal gas constant, temperature, and Faradaic constant, respectively. \( \alpha \) is the transfer coefficient that is highly related to Tafel slope. It has been reported that if \( b = 120 \text{ mV} \text{ dec}^{-1} \), the rate-determining step is dominated by the single-electron transfer step. If \( b = 60 \text{ mV} \text{ dec}^{-1} \), it hints that the chemical reaction after one-electron transfer reactions is the rate-determining step. If \( b = 30 \text{ mV} \text{ dec}^{-1} \), the rate-determining step is the third electron transfer step. Therefore, from the value of Tafel slope, we can roughly determine the rate-determining step of OER. Generally, small Tafel slope indicates fast reaction kinetics, and the rate-determining step is supposed to be at the ending part of the reaction.\(^7\) Therefore, catalysts with small Tafel slopes often show good catalytic activity for OER. However, it should be noted that the Tafel slope is often overestimated if geometric current density is used because of the fact that the geometric current density is usually smaller than the specific current density. Moreover, Tafel slope is not accurate to describe the performance of OER catalysts because of its oversimplified assumptions.\(^6\)

\[
b = \frac{2.303RT}{\alpha F} \tag{2}
\]

Turnover frequencies (TOFs) refer to the turnover per unit time, representing the total number of moles transformed into the desired product by one mole of active site per time. Therefore, the number of TOFs determines the level of activity of the catalysts, which is given by eq 3, where \( j \) is the current density at a specified overpotential, \( A \) is the area of the electrode, and \( m \) is the number of moles of active materials deposited onto the electrodes.\(^7\) Moreover, it has been suggested that TOFs at different overpotentials could be different; therefore, the applied overpotential should be provided when presenting TOF.\(^5\)

\[
\text{TOF} = \frac{jA}{4Fm} \tag{3}
\]

Exchange current density \( (i_0) \) is defined as the current density at \( \eta = 0 \) \( (i_0) \) divides surface area \( (A) \); the magnitude of \( i_0 \) reflects the intrinsic charge transfer between reactant and catalyst (eq 4). A higher \( i_0 \) hints at better catalytic performance. \( i_0 \) can be described by eq 5, in which \( k^\omega \) is the rate constant, and \( \rho \) and \( \omega \) are the reaction orders of Red and O\(_2\), respectively.\(^7\)

\[
i_0 = \frac{i_0}{A} \tag{4}
\]

\[
i_0 = k^\omega [\text{Red}]^\rho [\text{O}_2]^{\omega} \tag{5}
\]

Different from exchange current density, geometric current density \( (j_g) \) is given by the current density normalized by geometric surface area at a certain overpotential. \( j_g \) has practical meaning in developing water splitting devices; however, it usually overestimates the electrochemical performance of a catalyst due to the larger actual surface area than the geometric surface area. Figure 1 shows the Tafel slopes of Co\(_3\)O\(_4\) and IrO\(_2\) by using the current density calculated by Brunauer–Emmett–Teller (BET), electrochemical (EC), and disk surface area, respectively. From Figure 1, we can also see that the Tafel slope of Co\(_3\)O\(_4\) is smaller than that of IrO\(_2\) with respect to the geometric surface area. One may rush to conclude that the OER performance of Co\(_3\)O\(_4\) is better than IrO\(_2\). However, if the BET or EC surface area is used, the performance of Co\(_3\)O\(_4\) is poorer than that of IrO\(_2\),\(^10\) suggesting that the applied active surface area is quite important to determine the performance of a catalyst.\(^10\) Generally, the more accurate the surface area used, the more accurate the current density that is obtained, leading to a more precise evaluation of the catalyst.

Understanding the mechanism of OER has a fundamental importance in designing new OER catalysts; therefore, let us first discuss the general mechanisms of OERs before presenting the detailed reactivity about LDH. The catalytic cycle is shown in Figure 2; association mechanism and oxy–oxy coupling mechanism are generally proposed. There are four elementary steps for the association mechanism (eqs 6–9): association of hydroxide anions to form absorbed OH\(^*\) accompanied by losing one electron, generation of reactive oxy intermediate O\(^*\) from OH\(^*\) with loss of one electron and generation one molecule of water, nuclophilic attack of absorbed oxy O\(^*\) by the hydroxide anion with release of one electron to form O=O bond giving OOH\(^*\), and formation of one molecule of oxygen with release of an electron and one molecule of water to regenerate the catalyst and complete the catalytic cycle. For the oxy–oxy coupling mechanism (eqs 6, 7, and 10), one molecule of oxygen will be generated accompanied by the regeneration of catalyst after
generating the oxy intermediate O*-O*. For the association mechanism, the formation of OOH* is generally regarded as the rate-determining step due to the large energy barrier according to density functional theory (DFT) calculations. For the oxy-oxy coupling mechanism (given by eqs 6, 7, and 10), the coupling between two oxy is supposed to withstand a very high kinetic barrier and thus is the rate-determining step.

In the above-mentioned processes, formation of OOH* involves oxidation of oxygen from O* to OOH*, which is usually regarded as the rate-determining step. Therefore, LDH with high oxidation ability would facilitate the formation of OOH*. In addition, OER involves formation and cleavage of metal-oxygen bonds; in principle, catalysts with superior OER activity should possess a suitable oxygen bonding strength, neither too strong nor too weak. As oxidation ability and oxygen binding energy of LDH vary with the change of transition metals, they have a critical influence on the OER activity of LDH. Therefore, in this perspective, we will focus on the effects of chemical composition on the oxygen binding energy and oxidation ability of LDH. Unary, binary, and ternary transition-metal-based LDHs toward OER will be discussed.

\[
\begin{align*}
M + OH^- & \rightarrow M - OH + e^- \\
M - OH + OH^- & \rightarrow M - OH + H_2O + e^- \\
M - O + OH^- & \rightarrow M - OOH + e^- \\
M - OOH + OH^- & \rightarrow M + H_2O + O_2 + e^- \\
M - O + M - O & \rightarrow M + O_2
\end{align*}
\]

(6) (7) (8) (9) (10)

3. UNARY METAL-BASED LDH

Unary metal-based LDHs exhibited limited OER activity, but they provide an ideal platform for us to understand the intrinsic OER activity of LDHs due to their structural simplicity. In this part, we will first introduce Ni-based LDH, followed by Fe-based LDH, Co-based LDH, and the recently reported V-based LDH. As transition-metal hydroxide and transition-metal-oxy/hydroxide can interconvert via Bode’s Diagram, we also treated transition-metal oxyhydroxide as LDH for simplicity. The performance evaluation factors such as overpotential at 10 mA cm\(^{-2}\), Tafel slope, and TOF of unary metal LDHs are given in Table 1.

### 3.1. VIII Group Single Transition-Metal Hydroxides/Oxyhydroxides

Ni-based compounds are the most widely used OER catalysts; actually, NiO was employed for OER early in the 1980s. However, it did not arouse research interests until 2012 when Boettcher in situ generated nickel layered hydroxide/oxyhydroxide from NiO, through an electrochemical conditioning process (Figure 3). The as-in situ-generated Ni hydroxide/oxyhydroxide exhibited an outstanding OER performance, with a low overpotential of 297 mV at 1 mA cm\(^{-2}\), an extremely small Tafel slope of 29 mV dec\(^{-1}\), and a considerably large TOF of 0.17 s\(^{-1}\) at \(\eta = 300\) mV in 1 mol L\(^{-1}\) (M) KOH, better than that of the state-of-the-art catalyst of IrO\(_x\) (\(\eta = 378\) mV at 1 mA cm\(^{-2}\), \(b = 49\) mV dec\(^{-1}\), TOF = 0.0089 s\(^{-1}\) at \(\eta = 300\) mV in 1 M KOH).

NiFe LDH is the most effective for OER (will be discussed in Section 4.1), but NiOOH and Ni(OH)\(_2\) are not so effective toward OER. Therefore, studying the OER activity of Fe-based LDH is important to understand the superior activity of NiFe LDH and has aroused much attention. Friebel and Bell studied the intrinsic OER activity of \(\gamma\)-FeOOH and found that the overpotential at 10 mA cm\(^{-2}\) of \(\gamma\)-FeOOH is 550 mV in 0.1 M KOH, which is smaller than that of Fe-free \(\gamma\)-NiOOH (\(\eta = 660\) mV at 10 mA cm\(^{-2}\) in 0.1 M KOH). However, it is much higher than that of (Ni,Fe)OOH (\(\eta = 360\) mV at 10 mA cm\(^{-2}\) in 0.1 M KOH). Moreover, the calculations also indicated that the overpotential of \(\gamma\)-FeOOH is 520 mV, in good agreement with experiments. Boettcher also studied the OER activity of FeOOH and suggested that FeOOH had high OER activity, but was limited by its poor conductivity, which has a measurable conductivity of 2.2 \times 10^{-2} mS cm\(^{-1}\) only when the overpotential is larger than 400 mV.

Similar to Ni and Fe, the remaining first-row group VIII transition metal, cobalt, can also form a layered double hydroxide structure and, of course, has received much interest. Wang compared the OER activities of \(\alpha\)-Co(OH)\(_2\), \(\beta\)-Co(OH)\(_2\), and \(\gamma\)-CoOOH and found that \(\alpha\)-Co(OH)\(_2\) will transform to \(\gamma\)-CoOOH before the OER, and the resulting \(\gamma\)-CoOOH inherits a large basal distance of \(\alpha\)-Co(OH)\(_2\). It has an overpotential of 400 mV at 10 mA cm\(^{-2}\) in 0.1 M KOH.

**Table 1. Overpotential at 10 mA cm\(^{-2}\), Tafel Slope, and TOF in 1 M KOH of Unary-Transition-Metal-Based LDHs**

| Catalysts       | Overpotential at 10 mA cm\(^{-2}\) (mV) | Tafel slope (mV dec\(^{-1}\)) | TOF (s\(^{-1}\)) | References |
|-----------------|----------------------------------------|-------------------------------|------------------|------------|
| Ni(OH)\(_2\)/NiOOH | 297\(^a\)                              | 29                            | 0.17             | Boettcher\(^6\) |
| \(\gamma\)-NiOOH     | 660\(^b\)                              |                               |                  | Friebel and Bell\(^7\) |
| \(\gamma\)-FeOOH      | 550\(^b\)                              |                               |                  | Friebel and Bell\(^7\) |
| \(\alpha\)-Co(OH)\(_2\) | 400\(^b\)                              | 44                            | 0.070            | Wang\(^19\) |
| \(\beta\)-Co(OH)\(_2\) | 463\(^b\)                              | 39                            | 0.021            | Wang\(^19\) |
| \(\beta\)-CoOOH       | 426\(^b\)                              | 36                            | 0.042            | Wang\(^19\) |
| Co LDH             | 393                                    |                               | 0.001            | Hu\(^25\)  |
| Co LDH             | 340                                    | 56                            | 0.801            | Kang and Yao\(^21\) |
| monolayer Co LDH   | 350                                    | 45                            | 0.003            | Hu\(^25\)  |
| VOOH              | 270                                    |                               | 0.68             | Liang and Wang\(^24\) |

\(^a\)Overpotential at 1 mA cm\(^{-2}\). \(^b\)In 0.1 M KOH solution.
interestingly, a Tafel slope of 44 mV dec$^{-1}$ when $\eta$ is smaller than 350 mV, and 130 mV dec$^{-1}$ when $\eta$ is larger than 350 mV. Moreover, $\alpha$-$\text{CO(OH)}_{2}$ is more active than $\beta$-$\text{CO(OH)}_{2}$, which might be due to the large interlayer space in the $\alpha$-$\text{CO(OH)}_{2}$.

Materials with ultrathin structures usually have high specific and exposed surface area and are abundant in vacancies, leading to a higher number of active sites and thus higher activities. Pan and Wei synthesized an atomically thin $\gamma$-$\text{COO(OH)}$, with a thickness of only 1.4 nm. Expectedly, the as-prepared $\gamma$-$\text{COO(OH)}$ has very high mass activities and abundant-active sites, thus leading to a sharp increase of OER activity with $\eta = 300$ mV at 10 mA cm$^{-2}$ and a Tafel slope of 38 mV dec$^{-1}$ in 1 M KOH. Interestingly, the as-prepared $\gamma$-$\text{COO(OH)}$ is half-metallic in contrast to its bulk, which was proposed to be related to the presence of dangling bonds in the CoO$_{6}$ octahedron as supported by DFT calculations.\textsuperscript{20} Kang and Yao also prepared Co-based LDH with atomic thickness for OER. Owing to its ultrathin structure, the OER activity of the Co-based LDH can have an overpotential of 340 mV at 10 mA cm$^{-2}$, and a Tafel slope of 56 mV dec$^{-1}$, and a TOF of 0.801 s$^{-1}$ at $\eta = 350$ mV in 1 M KOH.\textsuperscript{17} Besides ultrathin structures, a larger interlayer spacing of LDH can also lead to a higher number of active sites. Sun and Chen reported benzoate anion interacted with CoOOH with an interlayer spacing as large as 14.72 Å, which allows the easy permeation of water and hydroxide, resulting in a higher number of active sites.\textsuperscript{23} And the overpotential at 50 mA cm$^{-2}$ is only 291 mV in 1 M KOH.

3.2. V-Hydroxides/Oxyhydroxides. In addition to the intensively studied VIII transition-metal-based LDH, V and Mn compounds have also been investigated. In 2012, Markovic studied the trends for OER on 3d transition-metal hydr(oxo)-oxide catalysts (M$^{n+}$O$_{n}$(OH)$_{2-n}$/Pt(111)) and discovered that the reactivity toward OER is in the order Mn $<$ Fe $<$ Co $<$ Ni, which is governed by the OH bond, which is proposed to be unfavorable for OER, VOOH hollow nanospheres, structurally resembling lepidocrocite FeOOH as evidenced by their similar X-ray diffraction (XRD) pattern (Figure 4a), have been employed as an efficient OER catalyst by Liang and Wang,\textsuperscript{24} exhibiting an overpotential of 270 mV for OER at 10 mA cm$^{-2}$ and a Tafel slope of 68 mV dec$^{-1}$ in 1 M KOH. It has been well established that V is an early transition metal, favoring its high oxidation states, +5 and +4, whereas V has an oxidation state of +3 in VOOH. It may be of concern that VOOH is unstable during OER; however, the stability test given in Figure 4b shows that VOOH is quite stable during OER. And the reactivity of VOOH does not decrease even after 5000 cycles, as shown in the inset of Figure 4b. Moreover, the prepared VOOH can be used as HER catalyst, with an overpotential of 164 mV at 10 mA cm$^{-2}$ and a Tafel slope of 104 mV dec$^{-1}$. The advanced water splitting performance of VOOH in this work was contributed to the large surface area from the hollow sphere morphology.
TOF is 0.56 s\(^{-1}\) at an \(\eta\) = 300 mV in 1 M KOH. Moreover, the NiFe-CNT LDH exhibited a better stability than Ir/C at a constant current density of 5 mA cm\(^{-2}\). In 2014, Yang reported graphene oxide (GO) intercalated NiFe LDH by substitution of anions (CO\(_3\)\(^{2-}\) or Cl\(^-\)) with GO (Figure 5b).7 The as-prepared NiFe-GO LDH has an overpotential as low as 210 mV at 10 mA cm\(^{-2}\) and a Tafel slope of only 38 mV dec\(^{-1}\) in 1 M KOH. Moreover, the TOF can reach 0.38 s\(^{-1}\) at \(\eta\) = 300 mV.

Since the conductivity of GO can be enhanced by reduction, we further reduce NiFe-GO LDH by hydrazine to obtain reduced GO intercalated NiFe-reduced graphene oxide (rGO) LDH; the overpotential and Tafel slope can be further lowered to 195 mV at 10 mA cm\(^{-2}\) and 39 mV dec\(^{-1}\), respectively. Moreover, the TOF can reach 0.98 s\(^{-1}\) at \(\eta\) = 300 mV. The higher conductivity of FeNi-rGO LDH is evidenced by alternating current impedance spectra. It should be noted that the basal spacing of FeNi-rGO LDH is 1.1 nm, which is much larger than the basal spacing of FeNi-CO\(_3\) LDH (0.75 nm), suggesting that GO has successfully intercalated into the NiFe LDH. And the enlarged basal distance of NiFe LDH allows efficient association of reactants and dissociation of products, and that is why a sharp increase of TOF is observed. Later, NiFe LDH-GO and NiFe LDH-rGO have also been reported through solvothermal and chemical reduction methods by Zhan and Hou.26j

Besides combination with conductive carbon materials, other conducting materials were also applied to reduce the charge transfer resistance of the LDHs. Wang and Qiu prepared hierarchical NiFe LDH/Ti\(_3\)C\(_2\)-MXene for OER.28 Owing to the stabilization by Ti\(_3\)C\(_2\)-MXene, better conductivity, and electronic interaction between Ti\(_3\)C\(_2\)-MXene and NiFe LDH, the as-prepared hierarchical NiFe LDH/Ti\(_3\)C\(_2\)-MXene exhibited a Tafel slope of 43 mV dec\(^{-1}\) and overpotential of \(\sim\)300 mV at 10 mA cm\(^{-2}\) in 1 M KOH. The TOF at \(\eta\) = 300 mV is 0.26 s\(^{-1}\).

Zhang and Huang grew NiFe LDH on conducting Ni\(_3\)S\(_2\) nanorods, as shown in Figure 5c.27 As Ni\(_3\)S\(_2\) nanorods are much more electron rich than NiFe LDH, electrons will flow to NiFe LDH, leading to the partial reduction of NiFe LDH. To maintain the charge neutrality, oxygen vacancies are generated in NiFe LDH as evidenced by X-ray photoelectron spectroscopy (XPS). As a result, the intrinsic activity of NiFe LDH was enhanced. Moreover, the number of active sites also increased after being loaded on the Ni\(_3\)S\(_2\) nanorods.

| catalysts                  | overpotential at 10 mA cm\(^{-2}\) (mV) | Tafel slope (mV dec\(^{-1}\)) | TOF (s\(^{-1}\)) | references  |
|---------------------------|----------------------------------------|-------------------------------|------------------|--------------|
| (Ni,Fe)OOH                | 336                                    | 30                            | 0.028            | Boettcher\(^16\) |
| NiFe LDH                  | 208                                    | 48                            | 0.0028           | Yang\(^7\)    |
| NiFe LDH                  | 245                                    | 40.4                          | 0.05             | Kuang and Sun\(^{34}\) |
| monolayer NiFe LDH        | 300                                    | 40                            | 0.05             | Hu\(^{25}\)   |
| NiFeCNTs LDH              | 290\(^a\)                              | 31                            | 0.56             | Dai\(^{16a}\) |
| NiFe-rGO LDH              | 195                                    | 39                            | 0.987            | Yang\(^7\)    |
| NiFe-GO LDH               | 210                                    | 40                            | 0.38             | Yang\(^7\)    |
| NiFe LDH/Ti\(_3\)C\(_2\)-MXene | 300                                  | 43                            | 0.26             | Wang and Qiu\(^{28}\) |
| NiFe LDH/Ni\(_3\)S\(_2\) nanorods | 190                                | 38                            | 0.138            | Zhang and Huang\(^{27}\) |
| NiCo LDH                  | 271                                    | 72                            | 0.0025           | Qian and Li\(^{40}\) |
| NiCo LDH                  | 290                                    | 113                           | 0.01             | Jiang and Al\(^{27}\) |
| NiCo LDH                  | 282                                    | 42.6                          | 0.38             | Huang\(^{25}\) |
| NiCo LDH                  | 385                                    | 65                            | 0.0025           | Hu\(^{25}\)   |
| monolayer NiCo LDH        | 338                                    | 41                            | 0.01             | Hu\(^{25}\)   |
| NiMn LDH                  | 640\(^a\)                              |                               |                  | Sun\(^{30}\)  |
| NiMn LDH                  | 312                                    |                               |                  | Huang\(^{38}\) |
| NiV LDH                   | 250                                    | 50                            | 0.054            | Sun\(^{31}\)  |
| NiTi LDH                  | 420                                    | 290                           | 0.009            | Zhang\(^{40}\) |
| CoFe LDH                  | 321                                    | 57.05                         | 1.12             | Wang\(^{26}\) |
| ultrathin CoFe LDH        | 266                                    | 37.85                         | 4.78             | Wang\(^{26}\) |
| CoFe LDH                  | 290                                    | 83.0                          |                  | Li and Ge\(^{45}\) |
| CoMn LDH                  | 325                                    | 43                            | 0.075            | Hu\(^{48}\)   |
| CoMn LDH                  | 255                                    | 38                            |                  | Cheng and Liu\(^{49}\) |
| CoCr LDH                  | 240                                    | 81                            | 0.195            | Huang\(^{39}\) |
| ZnCo LDH                  | 340                                    |                               | 0.061            | Asefa\(^{24}\) |

\(^{a}\)Overpotential at 5 mA cm\(^{-2}\).

Figure 5. Schematic layout of the structure of NiFe-CNT LDH (a),26a NiFe-GO LDH (b),7 and NiFe LDH on conducting Ni\(_3\)S\(_2\) nanorods (c).27 Reproduced with permission. Copyright 2013 American Chemical Society, Copyright 2014 John Wiley and Sons, reproduced by permission of The Royal Society of Chemistry.
10 mA cm$^{-2}$ is as low as 190 mV, and the Tafel slope is also only 38 mV dec$^{-1}$ in 1 M KOH. Wang reported NiFe LDH@Au hybridized nanoarrays on nickel foam. The as-prepared NiFe LDH@Au/Ni foams exhibited overpotentials of only 221, 235, and 270 mV at 50, 100, and 500 mA cm$^{-2}$, respectively, in 1 M KOH. Moreover, the Tafel slope decreased to 48.4 mV dec$^{-1}$, in comparison to NiFe LHD/Ni foam with a Tafel slope of 71.1 mV dec$^{-1}$. Huang reported single-crystalline NiFe LDH array on a Ni foam, and the as-prepared NiFe LDH array showed an excellent OER activity. The overpotentials at 10, 50, and 100 mA cm$^{-2}$ are only 210, 240, and 260 mV in 1 M KOH, which is smaller than the coated NiFe LDH film. Moreover, the Tafel slope is 31 mV dec$^{-1}$ in the overpotential region of 240–260 mV, suggesting a faster OER kinetics and large current density. Xie, Zheng, and Sun grew an amorphous NiFe-borate layer on a NiFe LDH surface and found that the OER performance was greatly boosted owing to the higher surface roughness and increased number of active sites. NiFe LDH is effective toward OER but suffers from lower conductivity. It has been reported that substitution of the very electronegative oxygen to other less electronegative elements, such as sulfur, selenium, phosphorus, and nitrogen, can push up the valence bond of NiFe LDH, thus leading to a higher conductivity and a better OER activity.

### 4.2. Other Ni-Based Binary Metal LDHs.

Besides NiFe LDHs, other Ni-based bimetal LDHs, including NiCo, NiMn, NiCr, NiTi, NiV, NiGa, and NiAl LDHs, also have been well studied, which will be discussed in this section. Qian and Li reported NiCo LDH nanosheet arrays on Ni foam for overall water splitting. The as-prepared NiCo LDH has an overpotential of 271 mV at 10 mA cm$^{-2}$ and a Tafel slope of 72 mV dec$^{-1}$ in 1 M KOH. And it should be noted that it was used as a bifunctional catalyst for overall water splitting for the first time, which showed an overpotential of 162 mV for HER at a current density of 10 mA cm$^{-2}$. Similarly, Jiang and Ai reported NiCo LDH nanosheets for OER that has an overpotential of 290 mV, Tafel slope of 0.054 ± 0.003 s$^{-1}$ in 1 M KOH, whereas the related monolayer NiFe LDH (Ni$_{0.75}$Fe$_{0.25}$-LDH) has a overpotential of 300 mV, Tafel slope of 0.064 mV dec$^{-1}$, and a TOF of 0.021 ± 0.003 s$^{-1}$. Electrochemical impedance spectroscopies (EISs) indicated that Ni$_{0.75}$V$_{0.25}$-LDH has a lower charge transfer resistance, thus bearing with a high conductivity. Moreover, the as-prepared NiCo LDH exhibited considerable stability, as shown in Figure 6b. DFT calculations have been performed on the OER mechanism catalyzed by Ni$_{0.67}$V$_{0.33}$-LDH. Here, V is supposed to be the active site, where H$_2$O* and OH* interact and the rate-determining step is formation of OOH* from O*, which has an overpotential of 620 mV.

In addition, some main-group element-Ni LDHs are also reported; as expected, their OER activity is very low. To synthesize porous $\beta$-Ni(OH)$_2$, Wang and Jin first prepared NiGa LDH in which the Ga$^{3+}$ will be removed through base etching. And it was found that the prepared NiGa LDH exhibited a better OER activity than the $\beta$-Ni(OH)$_2$ nanosheet, but it was much poorer than the porous $\beta$-Ni(OH)$_2$ prepared by etching NiGa LDH. Similarly, the NiAl LDHs are also prepared as a precursor to synthesize the porous LDH. For example, Zhang and Xie employed NiAl LDH as a precursor to prepare $\beta$-Ni(OH)$_2$ ultrathin nanomesh. The prepared $\beta$-Ni(OH)$_2$ ultrathin nanomesh has an excellent OER activity, whereas the NiAl LDH only shares a similar OER activity with the $\beta$-Ni(OH)$_2$ nanosheet.

### 4.3. Co-Based Binary Metal LDH.

Cobalt, with one less d electron than nickel, also received much attention. Li and Ge reported CoFe LDH fabricated by coprecipitation, in which the
The Co/O to Fe can be tuned from 0.5 to 7.4. The Co$_2$Fe LDH gave the best OER activity with an overpotential of 290 mV at 10 mA cm$^{-2}$ and a Tafel slope of 83 mV dec$^{-1}$ in 1 M KOH. Again, ultrathin LDHs with abundant defects are supposed to have higher OER activities. Wang prepared ultrathin CoFe LDHs through Ar plasma etching. The Ar plasma etched has a thickness of 0.6 nm, compared to the bulk with a thickness of 20.6 nm. The ultrathin CoFe LDHs are abundant in Co, Fe, and O vacancies, as evidenced by the decreased coordination numbers of Co, Fe, and O. The ultrathin CoFe LDH-Ar has a TOF of 4.78 s$^{-1}$, whereas the bulk CoFe LDH has a TOF of 1.12 s$^{-1}$. Moreover, the Tafel slope and overpotential at 10 mA cm$^{-2}$ of CoFe LDH-Ar is 37.85 mV dec$^{-1}$ and 266 mV, respectively, which are much lower than those in bulk CoFe LDH (57.05 mV dec$^{-1}$ and 321 mV at 10 mA cm$^{-2}$). It should be noted that ultrathin CoFe LDH-Ar has a much smaller charge transfer resistance. Xiong and Sun reported an ultrathin CoFe-borate-layer-coated CoFe LDH nanosheet array supported on Ti mesh. The as-prepared catalysts showed good OER activity at near-neutral condition (0.1 M K$_2$B$_4$O$_7$ solution, pH = 9.2), with an overpotential of 418 mV at 10 mA cm$^{-2}$.

Table 3. Overpotential at 10 mA cm$^{-2}$, Tafel Slope, and TOF in 1 M KOH of Ternary Metal-Based LDHs

| Catalysts          | Overpotential (mV) | Tafel Slope (mV dec$^{-1}$) | TOF (s$^{-1}$) | References          |
|--------------------|--------------------|-----------------------------|---------------|---------------------|
| NiCoFe             | 265                | 47                          | 0.106         | Yan and Strongin$^{19}$ |
| NiCoFe             | 210                | 42                          | 0.7           | Yang$^{19}$         |
| NiFeMn LDH         | 289$^a$            |                             |               | Sun$^{19}$          |
| NiFeV LDH          | 195$^a$            | 42                          |               | Liu and Sun$^{51}$  |
| NiFeAl LDH (Al%: 6.1%) | 310$^a$         | 69.6                        |               | Kuang and Sun$^{54}$ |
| D-NiFeAl LDH (Al%: 3.9%) | 270$^a$          | 46.1                        |               | Kuang and Sun$^{54}$ |
| NiFeZn LDH (Zn%: 25.2%) | 298$^a$          | 63.8                        |               | Kuang and Sun$^{54}$ |
| D-NiFeZn LDH (Zn%: 3%) | 200$^a$          | 34.9                        |               | Kuang and Sun$^{54}$ |

$^a$Overpotential at 20 mA cm$^{-2}$.
and the Tafel slope is 83 mV dec$^{-1}$. The TOF at $\eta = 700$ mV is 3.56 s$^{-1}$, much higher than that of ZnCo LDH prepared by the coprecipitation method. CoAl LDH has been reported as a precursor to prepare Al-doped CoP nanoarrays for overall water splitting.

5. TERNARY METAL-BASED LDH

Although binary metal-based LDHs exhibited an improved OER activity than unary metal-based LDH, they often suffer from poor conductivity. One may think incorporation of a third metal could involve new states in the forbidden band of binary metal-based LDH, thus leading to a higher conductivity. Moreover, introduction of another metal might increase the number of active sites. The overpotential at 10 mA cm$^{-2}$, Tafel slope, and TOF of ternary metal LDHs are given in Table 3. By the way, there are some examples of Ru$^{58}$ and Ir$^{59}$-doped NiFe LDHs but with the focus on the HER in alkaline condition, which will not be discussed here.

In 2014, Yang reported ultrathin NiCoFe LDH for OER.$^{57}$ The prepared Ni$_x$Co$_{1-x}$Fe$_{1-2x}$LDH has a low overpotential of 210 mV at 10 mA cm$^{-2}$, a Tafel slope of 42 mV dec$^{-1}$, and TOF of 0.7 s$^{-1}$ in 1 M KOH at an overpotential of 300 mV, outperforming the Ni$_{10}$Fe LDH with $\eta = 210$ mV at 10 mA cm$^{-2}$, Tafel slope of 55 mV dec$^{-1}$, and TOF of 0.53 at $\eta = 300$ mV. The specific surface area of Ni$_x$Co$_{1-x}$Fe$_{1-2x}$LDH is 80.44 m$^2$ g$^{-1}$, much larger than that of Ni$_{10}$Fe LDH (46.05 m$^2$ g$^{-1}$), suggesting that Co incorporation might lead to more exposed active sites. In addition, charge transfer resistance also decreased a lot upon incorporation of Co. Inspired by the fact that Ni$_{2+}$/Co$_{2+}$ configuration was thought to act as a shield of iron effective than NiFe LDH, which has an overpotential of 401 mV at 20 mA cm$^{-2}$, and TOF of 0.7 s$^{-1}$ in 1 M KOH, and the resulting Ni$_{10}$FeZn LDHs are abundant at the Ni–O–Fe unit, which is regarded as the active site. DFT calculations suggested that formation of O* from OH* is the rate-determining step, and the D-NiFeZn LDH has a lower overpotential than D-NiFeAl LDH. Interestingly, Rezvani and Habibi reported that ternary NiFeZn has a superior OER activity than binary NiFe LDH.$^{62}$ Moreover, the OER can take place at neutral condition, and the Tafel slope can be reduced to as low as 16 mV dec$^{-1}$, whereas the NiFe LDH has a Tafel slope of 29 mV dec$^{-1}$. However, the current density is only 5.41 mA cm$^{-2}$ at an overpotential of 300 mV. The better OER performance of ternary NiFeZn was attributed to its higher conductivity modified by Zn$^{63}$.

6. MECHANISTIC STUDIES

Although transition-metal-based OER catalysts have been studied experimentally, the theoretical investigation of their structure–composition–performance relationship is far from satisfactory because of the inaccurate models. Actually, only the structure of $\beta$-Ni(OH)$_2$ has been accurately determined,$^{53}$ which belongs to the $P\bar{3}m1$ (brucite) space group, and the lattice parameters are $a = b = 3.12$ Å and $c = 4.66$ Å. Carter performed DFT + U calculations and found that the pure $\beta$-NiOOH has a proton-staggered structure and is antiferromagnetic (Figure 8).

![Figure 8. Experimental structure of $\beta$-Ni(OH)$_2$ and calculated structure of $\beta$-NiOOH. Reproduced with permission from ref 64. Copyright 2015 American Chemical Society.](image-url)
and adsorption at the \{01\overline{1}\}N and \{01\overline{2}\}N surfaces, which decreased the numbers of dangling bonds. Here, only low-index surfaces are studied on the consideration that low-index surfaces are much more stable than high-index surfaces and that there is no experimental evidence of generation of high-index surfaces during reactions (Figure 9).

Owing to its simplicity and great importance, the OER mechanism catalyzed by NiOOH has been well studied.\textsuperscript{14b,66} Considering that the \{00\overline{0}1\} surface is the most stable, OER takes place on the \{00\overline{0}1\} surface most likely. Carter calculated the single-site association mechanism, binuclear \(\text{H}_2\text{O}^-\text{O}\) mechanism, binuclear \(\text{OH}^-\text{OH}\) mechanism, and binuclear \(\text{H}_2\text{O}_2\) mechanism on the \{00\overline{0}1\} surface of \(\beta\)-NiOOH and found that the binuclear \(\text{H}_2\text{O}_2\) mechanism is energetically highly unfavorable, whereas the binuclear \(\text{H}_2\text{O}^-\text{O}\) mechanism and the binuclear \(\text{OH}^-\text{OH}\) mechanism have the lowest overpotentials (∼0.5 V), lower than the single-site association mechanism (∼0.6 V).\textsuperscript{66} However, as mentioned in Section 2, the binuclear mechanism is kinetically unfeasible.\textsuperscript{13}

Nørskov and Bell performed DFT calculations to study the OER mechanism catalyzed by \(\beta\)-CoOOH, and it was found that the \{01\overline{1}4\} surface (\(\eta = 480\) mV) gives a lower overpotential than the \{01\overline{1}2\} surface (\(\eta = 800\) mV). The \{01\overline{1}4\} surface is abundant in Co\(^{3+}\) ions, whereas the \{01\overline{1}4\} surface has more Co\(^{3+}\) ions. Association of \(\text{OH}^-\) to generate \(\text{OH}^*\) would oxidize Co\(^{3+}\) to Co\(^{3+}\) on the \{01\overline{1}4\} surface, whereas it oxidizes the Co\(^{3+}\) to Co\(^{4+}\) on the \{01\overline{1}2\} surface. Transformation of Co\(^{3+}\) to Co\(^{4+}\) leads to a too-weak \(\text{OH}^*\) binding, and formation of \(\text{OH}^*\) becomes the rate-determining step. However, for the \{10\overline{1}4\} surface, the formation energy of \(\text{OH}^*\) has an optimal value of 1.23 eV.\textsuperscript{67}

There is a debate on whether Ni or Fe is the active site in NiFe LDH, and most work supports that Fe is the active site.\textsuperscript{26m,48} The debate has been well reviewed by Kundu;\textsuperscript{5d} therefore, we will not review the debate on the active sites of NiFe LDH.

However, recently, Goddard performed extensive calculations using grand canonical quantum mechanics to have a better understanding of the synergy between Fe and Ni in (Ni,Fe)-OOH, which sheds light on the debate. They suggested that both Fe and Ni are active sites; high-spin d\(^4\) Fe(IV) can stabilize the active O radical intermediate, whereas the low-spin Ni(IV) catalyzes the subsequent O–O coupling. Therefore, it is the synergy between Fe and Ni that leads to the optimal OER activity of (Ni,Fe)OOH. Furthermore, overpotential and Tafel slope were calculated to be 420 mV (Figure 10) and 23 mV dec\(^{-1}\), in good agreement with experiments, 300–400 mV and 30 mV dec\(^{-1}\), respectively.\textsuperscript{12b}

Having established the idea that Fe could stabilize the O radical thus facilitating OER, Goddard further performed DFT calculations to substitute Fe with other transition metals (groups 3–9). And it was found that Co-, Rh-, and Ir-doped NiOOH could better stabilize O radical and exhibited even lower overpotentials, 270, 150, and 20 mV, respectively.\textsuperscript{68} Although NiCo LDH was proposed to have a better OER activity than NiFe LDH by Goddard, it actually showed a poorer performance than NiFe LDH, which probably is due to the smaller
stabilization ability of Co with the formed oxy (O*) group because of the larger number of electrons in the antibonding orbitals of metal and oxygen π bonds, as shown in Figure 11. It can be expected that lower number of electrons in the d orbitals could lead to stronger metal−oxy bond; however, if the metal−oxy bond is too strong, it is also unfavorable for OER, and that could be the reason why NiMn LDH and NiTi LDH exhibited poor OER activities.

As Ni⁴⁺ is responsible for catalyzing O−O coupling due to its strong oxidizing ability, one can expect that if the oxidation ability of metal is decreased, the ability of metal to catalyze the O−O coupling should also decrease. In the first-row transition metal, oxidation ability of metal ions with the same positive charge would decrease because of its lower electronegativity. Indeed, changing Ni to Co, we can see a decrease of OER activity, and that is why CoFe LDH exhibited a lower OER activity than NiFe LDH.

7. SUMMARY AND OUTLOOK

In this perspective, we summarized the recent developments on OER catalyzed by LDH. The basic criteria to evaluate the performance of OER catalyst have been presented. Unary metal-based LDH has been discussed to have a deep understanding of the intrinsic activity of LDH. Basically, unary metal-based LDH is not effective for OER due to its poor conductivity and absence of synergistic effect. On the other hand, binary metal-based LDH is much more OER active. In particular, NiFe LDH is the most effective binary metal-based LDH toward OER. It outperformed other Ni-based binary metal LDHs owing to its suitable M−OH bond strength, which is neither too strong nor too weak. And it exhibited better OER activity than non-Ni-based LDH because Ni⁴⁺ has a strong oxidation ability, which can facilitate the formation of O−O bond. Finally, ternary metal-based LDH shows better OER activity due to its increased conductivity. Moreover, introducing divalent defects leads to exposure of the Ni−O−Fe unit, which would greatly increase the OER activity of LDH.

Although LDH as a promising OER catalyst has been well studied over the past few years, some critical issues should be tackled to realize the practical application of these catalysts on hydrogen production via electrochemical water splitting.

1. It is known that LDH with a high OER activity almost always has a very high conductivity, but the underlying mechanisms are still not understood. Moreover, it has been noted that the conductivity of LDH depends on the applied potential. Therefore, the influence of conductivity on the OER activity of LDH catalysts should be addressed systematically, especially the intrinsic conductivity of LDH, the contact resistivity between LDH and substrate, and the applied potential-dependent conductivity.

2. The synergistic effect between transition metals should be studied further to obtain the fundamental details, instead of simply going by the observation that the LDHs with more different transition metals are more OER active. Nowadays, the synergistic effect between Ni and Fe in NiFe LDH seems to be clearer, but the synergistic effect between other binary transition-metal-based LDHs and ternary transition-metal-based LDHs remains to be elucidated.

3. Close interplay between theoretical and experimental studies should be encouraged to tackle not only the thermodynamics but also the kinetics and dynamics of the intermediate steps of OER catalysis. For example, the key transition states leading to the formation of OOH* and O* should be located to have a better understanding of the kinetics of OER catalysis. For most LDHs, transition metals will be peroxided before OER takes place. Thus, preoxidations should be taken into considerations in future studies to have a better understanding of the active phase of LDH, which is usually ignored in the current practice.

4. Most OER experiments are performed in highly basic condition (pH > 13), but the OER performed in acidic and neutral conditions with more practical utilization is less reported and thus should be studied further in the future.
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