Review Article

Layered Double Hydroxides for Oxygen Evolution Reaction towards Efficient Hydrogen Generation

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Received 30 June 2022; Accepted 9 August 2022; Published 7 September 2022

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Electrochemical water splitting is one of the effective ways to obtain highly pure hydrogen. However, as one of the two half reactions, oxygen evolution reaction (OER) has a high overpotential, resulting in the low-energy utilization efficiency. Therefore, numerous electrocatalysts have been developed to reduce the energy barrier of OER. Among them, layered double hydroxides (LDHs) are excellent OER electrocatalysts with flexible composition and structure, which have been widely investigated in the past decade. Recent studies have been focusing on the identification of active sites for LDHs during OER process, trying to reveal clear reaction mechanism for designing more efficient LDHs electrocatalysts. Hence, this review tries to discuss the advances in identifying active site of LDHs based OER electrocatalysts for efficient hydrogen generation. We first introduce the effect of structure, composition, and defects to the OER performance of LDHs. Furthermore, main attention is paid on the active sites and mechanisms during OER, especially the coordination structures and catalytic mechanisms of active sites. At the end of this review, we put forward the existing problems and shortcomings in this fields, and propose the corresponding solutions, aiming to further promote the development of outstanding OER electrocatalysts towards efficient hydrogen production.

1. Introduction

With the rising demand and consumption of fossil fuels, energy shortage and environmental pollution are becoming severe and unignorable. This makes it necessary to explore sustainable and renewable energy, among which hydrogen is a new energy with splendid application prospects [1–3].

Up to now, hydrogen is obtained mainly by steam reforming of natural gas or other fossil fuels (e.g., propane, methanol, ethanol, and diesel), which suffers from high cost and low purity of hydrogen [4]. Production of highly pure hydrogen can be achieved by electrochemical water splitting using the electricity transformed from renewable energy such as wind and solar energy [5, 6]. Electrochemical water splitting is carried out in a cell with cathode, anode, and diaphragm. The whole reaction is made up of two half reactions which can be expressed in different ways depending on reaction conditions (Figure 1). The thermodynamic potential of electrochemical water splitting is 1.23 V, corresponding the Gibbs free energy of 237.1 kJ mol^{-1} [7]. However, no matter for HER (hydrogen evolution reaction) and OER, a high overpotential is always needed to achieve a considerable current density, resulting a huge overall overpotential in practical use. Also, as one of the half reactions, OER is a four-electron process, which causes a low efficiency of energy utilization [8–10]. Therefore, it is necessary to develop cost-effective and high-performance electrocatalysts for more efficient electrochemical water splitting [11, 12].

In acidic media, noble metal-based catalysts (e.g., RuO$_2$ and IrO$_2$) have been widely applied, while transition metal-based catalysts, especially first-row transition metal-based compounds (e.g., transition metal oxides/hydroxides/oxyhydroxides, nitrides, and phosphides), are always used in alkaline medias [13–16]. Although noble metal catalysts are the main commercial electrocatalysts, their scales are restricted due to the high cost and shortage. Owing to the advantages of earth-abundant and excellent activity, these transition metal-based catalysts have attracted great attentions. Among them, layered double hydroxides (LDHs), because of their wide tunability of the types and molar ratios of metal element and the nature of interlayer anions, are outstanding catalysts for OER in alkaline medias [17–21].
During the past decade, a great number of works have been focused on the development of LDHs electrocatalysts [22–24], aiming at better performance for OER towards hydrogen production.

In addition to the fabrication of advanced LDHs electrocatalysts, the identification and monitoring of real active sites in LDHs under OER conditions are also of great importance, which can further promote the understanding of the catalytic mechanism and the development of optimal electrocatalysts. Recently, advanced characterization methods include ex-situ (e.g., XPS, TEM, and EELS) and in-situ (e.g., Raman electrospectroscopy and EXFAS) characterizations combined with DFT calculation, which are generally used to reveal the change of local coordination environment and electronic states of the electrocatalysts during electrocatalytic process. The research of active sites not only guides researchers to create plentiful sites for OER through controlling synthesis conditions and modified strategies but also helps to optimize the electron structures to improve the electron transfer capability. To date, plenty of reviews have summarized the synthesis strategies, structural characters, and electrochemical performance for the LDHs and their derivatives [25–29], but only few reviews mention about the recognition and the assignment of active sites in LDHs during water splitting. Therefore, the latest research progress with respect to the LDHs electrocatalysts for water splitting has been concluded in this review. Moreover, recent exploration in the identification of active sites in LDHs under OER condition has also been summarized. Possible problems and development directions in this domain are also mentioned in this review. We wish this review can give inspiration to the design advanced LDHs electrocatalysts in order to promote the development of OER towards hydrogen production.

2. LDHs Electrocatalysts for OER

LDHs are a large kind of two-dimensional materials that can be represented as $[\text{M}^{\text{II}}\text{M}^{\text{III}}\text{O}_2\text{OH}]^{\text{2+}}\cdot\text{mH}_2\text{O}$. As shown in Figure 2, divalent (e.g., Ni$^{2+}$, Co$^{2+}$, Cu$^{2+}$, or Zn$^{2+}$) and trivalent (e.g., Fe$^{3+}$, Mn$^{3+}$, or Al$^{3+}$) metal cations are assembled into electropositive nanoscale laminates through covalent interaction and electronegative anions between two layers, which are connected to the metallic-element-containing layers by weak interaction such as electrostatic interaction and hydrogen-bond interaction [30–34]. These two-dimensional laminates and anions are formed longitudinal, orderly, and spatially into threedimensional crystal structures. The highly dispersed metal cations in the lamella provide abundant active sites for electrochemical reactions with excellent activity and stability in alkaline environment [35–38].

2.1. Structural Design of LDHs towards Efficient OER

Although LDHs with various composition have shown great potential for OER towards efficient hydrogen production, the poor electron transport ability and inadequate exposure of active sites are still limiting their activity and stability [39–42]. Therefore, compared to low-dimensional materials, hierarchically structural materials with nanoscale are widely reported to apply to highly efficient OER [43–46]. Our group successfully designed a one-step method to synthesize NiFe-LDH hollow microsphere (HMS) [47]. Such a structure provides a high surface area, great hydrophilicity, and mesoporous structure (Figure 3(a)). Further electrochemical measurement has shown a low OER onset overpotential with 239 mV at 10 mA cm$^{-2}$ and a large current density with 71.69 mA cm$^{-2}$ at $\eta = 300$ mV of NiFe-LDH-HMS, which was better than commercial Ir/C catalyst. NiFe-LDH HMSs could catalyze OER at $\eta = 300$ mV in 1 M KOH solution over 40,000 s, which represent splendid long-term stability. This method could also apply to synthesize other LDH-HMSs (e.g., CoFe-LDH, CoNi-LDH, and NiAl-LDH) with a great improvement of OER performance compared to LDHs in nanoparticles (NPs).

Recently, a great innovation of LDHs is the structural transition from powder to integrated nanosheet arrays, which are directly grown on conductive substrates [48–50]. Compared to powder samples, nanosheet array has larger specific surface area and more stable electronic transfer as well as the conductive base film, which can provide a channel for transferring electrons and reduce the resistance [51–54]. Plenty of efficient synthetic strategies have reported to obtain ultrathin LDHs nanosheets with outstanding morphologies and crystallinity. Among them, template method is a mild and low-cost way to obtain ultrathin LDHs with abundant active sites and defects. Sun et al. developed a topotactic conversion tactic under hydrothermal conditions to transform metal-organic frameworks (MOFs) into LDHs with more edge sites and lattice defects, which led to better OER performance (Figure 3(b)) [55]. Analogously, Tian et al. reported utilizing electric-field assisted hydrolysis to...
Figure 2: The idealized structure of carbonate-intercalated LDHs and typical distribution of the metal sites in LDHs for OER.

Figure 3: (a) Schematic diagram of the synthetic path to NiFe-LDH HMS [47]. (b) Schematic illustration of MOFs topologically transformed to LDHs [55]. (c) Schematic diagram of the synthetic path to the MFe-LDH (M = Ni, Li, and Co) nanosheets arrays. (d) SEM image of NiFe-LDH. (e) Linear sweep voltammetric curves of the MFe-LDH (M = Ni, Li, and Co) nanoplatelet arrays and Ir/C. (f) Photographs of NiFe-LDH nanosheet arrays synthesized on nickel form substrates at different scales (inset: SEM image of NiFe-LDH on the 100 cm² nickel form substrate) [18].
transform MOFs into ultrathin LDHs fleetly (20 s) [56]. Moreover, our group first proposed a fast, precisely controllable, and economic electrochemical synthesis method for the fabrication of NiFe-LDH nanosheet arrays, which possessed effective electrocatalytic performance for OER [18, 57]. As shown in Figure 3(c), ultrathin NiFe-LDH nanosheets with 200-300 nm in lateral length and 8-12 nm in thickness (Figure 3(d)) are synthesized on the substrate surface vertically within only hundreds of seconds (<300 s, while other methods typically needed several hours) under cathodic potential. It was worth noting that NiFe-LDH exhibited outstanding OER activity with lowest Tafel slope of OER (Figure 3(e)) as well as the largest current density under the same potential, much superior than the OER catalysts reported in the same period. Furthermore, the growth scale of NiFe-LDH nanosheet arrays could be expanded from 2 cm² to 100 cm² on nickel form substrate with an equally distributed subface appearance (Figure 3(f)). This electrochemical synthesis method also could be applied to grow other LDH nanosheet arrays (e.g., Co-containing LDHs and Mn-containing LDHs) on the surface of several conducting substrates (e.g., conducting cloths and FTO). It was a prominent innovation of synthesis methods of LDHs and made possible to manufacture larger and intricately composed LDHs for future works. With the profounder comprehend of material structures, monolayer LDHs are developed with freer regulation of electronic structures and better OER performance. Monolayer NiCo-LDH was proved to possess a more convenient release of hydrogen and oxygen, leading to more dynamic catalytic sites for OER at a lower potential [58].

2.2. Component Regulation of LDHs towards Efficient OER. It is convenient to regulate the OER performance of LDHs through adjusting the composition of them due to the adjustable metal elements on laminate and anions in the interlayer [59–61]. On the one hand, the built-up ways of metal elements on laminate are multitudinous. Researchers have developed a new synthesis method with the regulation of atomic structure to obtain a series of α-M₄(II)M₉(III) LDH and β-M₄(OH)₆ (M₄ = Ni and Co and M₉ = Co, Fe, and Mn) electrocatalysts and found different groups of metal elements on host layers as dual-metal site feature had disparate synergistic effects. Among them, Fe-containing LDHs revealed highest OER activities, then followed by Co-based Fe-free LDHs, finally by Co-free Fe-free LDHs (Figure 4(a)). Further DFT calculation displayed OH-O content determined by elementary composition could influence OER performance of LDHs [62]. Our group successfully synthesized a series metal-doped NiFeM-LDHs (M = Ti, V, Cr, Mn, Co, Cu, Zn, Mg, and Al), and NiFeV-LDH had the lowest Tafel slope and best OER performance in high potential (Figure 4(b)) [63]. DFT calculation elucidated that NiFeV-LDH (1.491 eV) had a less Gibbs energy change of rate-
Fe-O-M droped and the electron structure of Fe active site vacancies [69, 70]. Sun et al. reported a memory effect in CoFe-LDH nanosheets as well as the formation of plentiful defects in Figure 5(a)), leading to the exfoliation of ultrathin CoFe-LDH laminate which caused an active nature of OER, and such an effective transfer promoted the electron transfer during OER and provided sites to adsorb oxygen species. Our works show that different OER active metal sites in LDHs cause distinct OER performance, so it comes necessary to identify OER active sites which play a significant role in the design and synthesis of optimal OER catalysts based on LDHs. In addition to inserting another element, we also attempted to use transition elements with a larger atomic mass. NiLa-LDH nanosheet arrays were successfully compounded via electrochemical synthesis with a low onset overpotential of 209 mV at 10 mA cm\(^{-2}\), which transcended most of LDH electrocatalysts reported before [64].

On the other hand, numerous anions are appropriate to insert into the interlayer of LDHs, which can further influence the chemical environment of LDHs. Intermittent anions can not only improve the electrical conductivity, but also promote \(\text{OH}^-/\text{O}_2^-\) transport through increasing the intersheet space. Hunter et al. reported different OER performances of NiFe-LDH caused by diverse interlayer inorganic anions (e.g., \(\text{NO}_3^-, \text{BF}_4^-, \text{Cl}^-, \text{CO}_3^{2-}\), and \(\text{PO}_4^{3-}\)) [65]. The results have shown that the pKa of the conjugate acid of interlayer inorganic anions was closely related to OER catalytic ability of LDHs. Further, DFT calculation found \(\text{N}1\) s species in the precatalyst could combine with edge-site Fe, which led to an excellent OER performance. Our group successfully assembled well-organized LDH nanosheets (NSs)/iron porphyrin (Fe-PP) with ultrathin films through electrochemical layer-by-layer technique, which has shown a distinct enhancement compared to pristine LDH NSs [34].

2.3. Vacancies Construction of LDHs towards Efficient OER. The formation of vacancies is an efficient way to improve local electronic environment and increase active sites. The vacancies construction on LDHs can also enhance the nature activity of LDHs [66–68]. Many typical works have been reported to form valid vacancies on the surface of LDHs towards high-efficiency OER. Wang et al. successfully developed plasma-etching methods both in gaseous and liquid conditions to break the interlayer electrostatic interactions of LDHs (water-plasma exfoliation is shown in Figure 5(a)), leading to the exfoliation of ultrathin CoFe-LDH nanosheets as well as the formation of plentiful vacancies [69, 70]. Sun et al. reported a memory effect method which could create multiple vacancies on the surface of NiFe-LDH (Figure 5(b)) [71]. These vacancies increased the number of structural distortion and dangling bonds around the metal sites, resulting in the decrease of surface energy and the enhancement of structural stability. Such unordered conditions around metal sites could observably improve the nature activity of OER.

Further explorations are made based on these advanced achievements. Our group developed an in-situ electrochemical method to synthesize ultrathin CoAl-LDH nanosheet arrays (E-CoAl-LDH-NSA), which were transformed from CoAl-LDH nanosheet arrays via hydrothermal methods (B-CoAl-LDH-NSA), towards high-efficient electrocatalytic performance (Figures 5(c) and 5(d)) [72]. Co 2p XPS (Figure 5(e)) spectra have shown the valence decrease of Co species and the reduction of Al content on the surface. And O 1s XPS spectra (Figure 5(f)) exhibited the disappearance of lattice oxygen (529.7 eV) which meant the introduction of oxygen vacancies. As shown in Figure 5(g), the coordination number of Co-O (1.547 Å) decreases from 4.2 to 3.7 after the exfoliation process, which proved the existence of oxygen vacancies in E-CoAl-LDH-NSA. Multiple atom defects also were observed via HADDF-STEM. The creation of oxygen vacancies changed the electronic structure of LDHs and increase reactive sites on the surface lead to the improvement of OER performance. Besides, long-term test was conducted to appraise the stability of E-CoAl-LDH-NSA, and no decrease in performance was observed during 110 h at 10 mA cm\(^{-2}\) in 1 M KOH solution. Recently, a polyoxometallic acid wet-etching method was reported to rebuild active species on NiFe-LDH. The reconfiguration of active sites could create multiple Ni, Fe, and O vacancies and accelerated the surface dynamic process, giving rise to improvements of OER performance [73].

2.4. Topochemical Conversion of LDHs towards Efficient OER. Moreover, LDHs can transform into other OER electrocatalysts (e.g., metal alloy, oxide, sulfide, nitride, and phosphide) with outstanding OER activity through topological conversion. Our group successfully used LDHs as precursors to obtain FeCoP ultrathin nanosheet arrays (UNSA) [74]. CoFe-LDH nanosheet arrays were firstly grown on Ni foam via electrolysitosynthesis and then transformed into FeCoP UNSA through an in-situ phosphatized process (Figure 6(a)). The modified electronic structure of highly exposed active sites on the surface of FeCoP could lead to the improvement of \(\text{H}_2\) adsorption and convenience of hydrogen dissociation. It exhibited excellent OER electrocatalytic activity with a low Tafel slope of 63 mV dec\(^{-1}\) and long-term cycling stability (Figure 6(b)). Furthermore, FeCoP UNSAs have shown outstanding stability with operating time over 20 h at 10 mA cm\(^{-2}\) in 1 M KOH solution.

OER performance of LDHs can be further enhanced through combining LDHs with highly reactive components (e.g., quantum dots and noble metal single atoms) [75–79]. A hydrothermal method was reported to substituting Au atoms for Fe atoms in NiFe-LDH (Figure 6(c)), which caused the improvement of conductivity and optimization of electron transfer. NiFeAu-LDH has shown low overpotential for both OER (181 mV at 10 mA cm\(^{-2}\)) and HER
Moreover, the Tafel slope of NiFeAu-LDH was smaller than that of NiFe-LDH and IrO₂ (Figure 6(d)) [80]. Our group developed an interface engineering strategy that constructs (Ni, Fe)S₂@MoS₂ heterostructures as bifunctional electrocatalysts towards efficient water splitting [81]. NiFe-LDH arrays were grown on carbon fiber paper via a hydrothermal way at first, and (Ni, Fe)S₂@MoS₂ was further obtained by combining sulfuretted NiFe-LDH, thioacetamide, and Mo⁴⁺ together in a stainless-steel autoclave (Figure 6(e)). The construction of interfacial active sites could cause outstanding activity to both OER and HER. Also, the Tafel slope of (Ni, Fe)S₂@MoS₂ for OER was only 43.21 mV dec⁻¹ (Figure 6(f)). In addition, the long-term stability was tested at 10 mA cm⁻² in 1 M KOH solution over 40 h, signifying excellent potential for application.

2.5. LDHs Electro catalysts for OER under Other Conditions. Actually, compared to OER conditions in the laboratory, overall water splitting catalyzed by LDHs is always conducted in more severe environments in practical application.
with enhanced alkalinity and higher operating potential. A few works have been reported to synthesize stable LDH-based electrocatalysts used in severe conditions. Because of the metal hydroxide on host layers, most LDHs and their deuterogenic catalysts possess strong alkali resistance. In addition, reasonable design of spatial structure can reinforce mass transfer process and keep the LDHs stable under large current densities. 2D LDH-Birnessite hybrid was proved to catalyze water oxidation under industrial hydrogen production conditions (6 M KOH, a current density of 100 mA cm\(^{-2}\)) for over 20 hours. And it had a low overpotential (407 mV) at a large current density (400 mA cm\(^{-2}\)) and small Tafel slope (43 mV dec\(^{-1}\)) of OER [82]. NiFe-LDH/MoS\(_2\) constructed on iron-nickel foams was also reported to electrocatalyze OER for over 100 hours at large current densities, with overpotentials of 156 and 201 mV at current densities of 100 and 400 mA cm\(^{-2}\), respectively [83]. Also, in the actual application process, the design of LDHs towards efficient hydrogen production is always focused on both HER and OER performances. Therefore, advanced modification strategies aim to synthesize bifunctional LDHs are widely reported. Combining

![Diagram](image_url)

**Figure 6:** (a) Schematic diagram of the synthetic path to FeCoP UNSAs. (b) Tafel slope of CoP, FeCoP, NiCoP, and MgCoP UNSAs [74]. (c) Schematic illustration of the substituting of Au. (d) Tafel slope of NiFeAu-LDH, NiFe-LDH, and IrO\(_2\) [80]. (e) Schematic diagram of the synthetic path to (Ni, Fe)\(_2\)S\(_2@MoS\(_2\)\) heterostructures. (f) Tafel slope of (Ni, Fe)\(_2\)S\(_2@MoS\(_2\)/CFP, (Ni, Fe)\(_2\)S\(_2\), MoS\(_2\), and Ir\(_2\)O [81].
LDHs with components which have highly active HER performance is a universal method. CoFe-LDH@NiFe-LDH nanosheets were reported as outstanding bifunctional electrocatalysts with an overall potential of 1.59 V at 10 mA cm\(^{-2}\) [84]. Besides, PtFeNi alloys/NiFe-LDH heterostructure were successfully constructed, and the optimized electronic transfer led to low overpotentials of 265 and 406 mV at 10 and 300 mA cm\(^{-2}\), respectively [85].

Carrying overall water splitting in neutral/near neutral conditions is another feasible means, while LDHs always have higher overpotentials and slower reaction rates compared to that in alkaline conditions. Due to the lack of OH\(^-\), the design of electrocatalysts is mostly focused on the regulation of efficiently catalytic sites and improvement of conductivity. For instance, NiFe-LDH with multivacancies was proved to have low overpotential (270 mV at 10 mA cm\(^{-2}\)) for OER in 1 M phosphate buffered saline electrolyte (pH=7) [71], while the reported overpotential of defective NiFe-LDH in 1 M KOH (pH=14) was 195 mV at 10 mA cm\(^{-2}\) [86]. Moreover, Foruzin successfully optimized electron transportation via regulating the amount of Zn\(^{2+}\) in NiZnFe-LDH, which shown onset potential of 0.96 V (vs SCE) and Tafel slope of 16 mV dec\(^{-1}\) [87], while the onset potential of NiZnFe-LDH in 1 M KOH (pH=14) was much higher [63].

3. Identification of Active Site in LDHs for OER

3.1. OER Pathways in Alkaline Solution. Except for developing strategies to exploit highly efficient electrocatalysts, researches on OER pathways and mechanisms are also important, which can give guidance to the recognition of active sites. Because LDHs are composed of metal hydroxide, electrochemical water splitting is always carried out in alkaline solution. The universally accepted pathway of OER in alkaline media (adsorbate evolution mechanism, AEM) is shown in Figure 7(a), in which “M” is on behalf of the active metal site. The whole process includes the following steps. In the first step, the active site absorbs a hydroxide radical via one-electron oxidation and turns into M-OH. Then, a couple of electron and proton is removed from M-OH and causes the creation of M-O. Next, there are two conversion routes for M-O. On the one hand, two M-O species integrate into M and O\(_2\). On the other hand, M-O transforms into M-OOH by coupling with a hydroxide radical through one-electron oxidation, and a proton-coupled electron transfer is further started which leads to the generation of O\(_2\) and the renewing of the active site [88–90]. Different with AEM, another reaction pathway of OER (lattice oxygen oxidation mechanism, LOM) is shown in Figure 7(b), which only happens under the circumstance of two adjacent oxidized oxygen can substitute a part of sacrificing metal-oxygen and hybridize oxygen holes by themselves. In the process of LOM, O-O bonds can form directly and further separate from metal ions as O\(_2\). At present, LOM is only reported to be possible for Co-containing LDHs, while AME is appropriate for most LDHs [61]. Nevertheless, whatever the mechanism is, the comprehension of OER intermediates and their behavior on the surface of electrocatalysts is important to further reveal the truly active sites and improve OER performance. Further efforts need to make to match the OER mechanisms to specific electrocatalysts, which means the recognition of active sites on the surface of LDHs and interaction between the active sites and intermediates.

3.2. Distribution Location of Active Sites for OER in LDHs. The exposed facet of the LDHs, which influences the chemical coordination environment, has an immense impact on their electrocatalytic activity. However, few researches report the theoretical and experimental evidence of the truly active facet of NiFe-LDH for OER. Our group employed finely control of edge facet ratio combined with molecular probe strategy and DFT calculation to reveal the active edge facet of NiFe-LDH. NiFe-LDH with the same crystallinity and different edge area ratio were synthesized by reverse microemulsion strategy [91]. The result of linear sweep voltammetric curves expounded that with the increase of edge area radio, both overpotential and Tafel slope of OER decreased. As shown in Figure 8(a), OER edge active sites could be blocked by cyanate anion, which was the intermediate during synthetic process, and were released after cyclic voltammetry cycling; this results further proved the edge site was the active site. Besides, DFT calculation of Gibbs free energy on different sites and facets has shown that although (001) facet had the lowest surface energy, (001)-O site emerged a high Gibbs free energy change, which caused...
a high overpotential, while both edge (110)-Ni site and edge (100)-Ni-Fe site have shown a low overpotential (Figure 8(b)). The discovery of active facets can give an important guidance to reveal the active sites of LDHs and design optimal electrocatalysts.

3.3. Single Site as Main Active Site for OER in LDHs. The change of electronic structures and metal valence can make a large influence on the performance of LDHs for OER. Metal elements are always binary transition metal cations in LDH (e.g., Ni²⁺/Ni³⁺, Co²⁺/Co³⁺, and Fe²⁺/Fe³⁺). Also, among transition metal-based catalysts, NiFe-LDH has the almost best catalytic performance in OER with a low Tafel slope and onset potential [92]. Therefore, the identification and calculation of active sites are always based on NiFe-LDH.

There is a view that consider single site (Ni or Fe) as the main OER active site in NiFe-LDH. As early as 1988, Weaver et al. found that Ni(OH)₂ deposited on gold electrodes tended to transform into NiOOH during scanning cyclic voltammograms in 1 M KOH by in-situ surface Raman spectroscopy and NiOOH had widely been identified as the main active site for OER in Ni-based LDH [93]. In 2016, Koper et al. used in-situ surface enhanced Raman spectroscopy to prove that NiOOH could deprotonate in highly alkaline pH and produce negatively charged surface species.

Figure 8: (a) Schematic illustration of the OER active site blocked by cyanate and (b) OER activity volcano diagram of Gibbs free energies of OER intermediates [91].
which are virtual active species for OER [94]. Further researches discovered that the existence of Fe could improve the OER catalytic performance of Ni(OH)₂ to a great extent and considered Fe sites were truly active sites for OER [95]. Normally the active species in NiFe-LDH can be transformed from NiₓFe₋ₓ(OH)₂ to γ-Ni₋ₓFeₓOOH during OER, and such a transformation can lead to electron transfer between Ni sites and Fe sites, which may cause the changes of active site. An earlier representative work revealed the role of Fe sites in NiFe-LDH is published in 2015, and Bell et al. resoundingly used HERFD-XAS to reveal the local structure at Fe and Ni sites in (Ni, Fe)OOH [96]. The result of Fe K-edge and Ni K-edge XAS (Figure 9(a)) has shown that the Fe-O and Ni-O bond lengths change from 2.01 Å and 2.06 Å at a potential of 1.12 V to 1.90 Å and 1.89 Å at 1.92 V, respectively, and almost all of Ni²⁺ sites were oxidized.

Figure 9: (a) Complementary operando EXAFS measurement confirming the potential-induced bond contraction at both Fe and Ni sites. (b) Structure model of (Ni, Fe)OOH. (c) Fe K-edge XAS and (d) Ni K-edge XAS. (e) Theoretical calculation of OER overpotentials at Ni sites and Fe sites in pure and doped γ-NiOOH and γ-FeOOH structure models [96].

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Figure 10: (a) Cyclic voltammetric curves used for the operando experiments with Mössbauer spectra collected at open circuit (gray), at 1.49 V (purple), 1.62 V (yellow), and 1.76 V (red). (b)–(j) Mössbauer spectra at different potentials [97].
was successfully observed experimentally through Mössbauer spectroscopy. Fe$^{4+}$ species were found with an energy of 1.12 V to 1.92 V, while Fe$^{3+}$ sites remained no change (Figures 9(c) and 9(d)). These XAS data are further used to establish the electronic structures of Ni and Fe sites in (Ni, Fe)OOH and calculate Gibbs free energies of reaction intermediates, as Figure 9(e) shown, compared to Ni sites in (Ni, Fe)OOH, and Fe sites could achieve a lower overpotential, which meant Fe sites are truly active sites for OER. Although the change of energy caused by the import of Fe has been calculated, the oxidation state of Fe species at high OER potentials remains fuzzy. It is worth noting that Fe$^{3+}$ may have a higher valence during OER which the curves of 1.12 V and 1.92 V are mildly different in Figure 9(d). Therefore, the change of valence state of Fe species on the surface of 3:1 Ni:Fe-LDH during OER was successfully observed experimentally through Mössbauer spectroscopy. Fe$^{4+}$ species were found with an account for 21% of the total Fe at the potential of 1.76 V (vs RHE) during cyclic voltammetric scanning [97]. As shown in Figures 10(d)–10(f), a shoulder appears at $\eta = 0.27$ mm s$^{-1}$, which meant the reflected intensity of Fe$^{4+}$ species only existed at the potential of significant catalytic OER on the surface of NiFe-LDH, while such a shoulder was not be observed at the OER active potential on the surface of hydrous Fe oxide (Figures 10(h)–10(j)). Combined with the mentioned work of Bell et al., they speculated that Ni$^{3+}$ ions in the NiFe-LDH and Fe oxyhydroxide lattice had more electrons in $\pi$-symmetry ($t_{2g}$) d-orbitals compared to Fe$^{3+}$, thus the electron-donating ability of the $\pi$-symmetry long pairs of the bridging oxygen atoms would be increased and the existence of high valent such as Fe$^{4+}$ would be stabilized. Moreover, Fe
species located in the edge, corner, or defect sites would have higher catalytic activity, which made it easier to make protonic transfer possible and transform Fe$^{3+}$-OH into Fe$^{4+}$ = O. The Fe$^{4+}$ = O was highly reactive and unstable, and then, OER would occur at these reactive Fe$^{4+}$ species.

Other methods are also reported to prove Fe site as main catalytically active sites in NiFe-LDH. Combined applications of in-situ Raman spectra and $^{18}$O isotope labeling experiment were reported to observe the conditions of lattice oxygen during OER and further provide direct evidence for the different active sites in Fe-free and Fe-containing Ni oxides [98]. In pure Ni-LDH, the $\delta$(Ni$^{3+}$-O), $\nu$(Ni$^{3+}$-O) and the $\nu$(O-O) band of NiOO$^-$ peaks were shifted to lower frequencies (Figure 11(a)), represented that $^{18}$O in pure Ni-LDH were substituted by $^{16}$O in the electrolyte after subjecting to the OER at 1.65 V for 20 minutes, which meant that Ni sites were active sites and catalyzed OER via a NiOO$^-$ precursor, and lattice oxygen atoms constituted NiOO$^-$ as redox-active oxygen intermediates during OER. While there seemed no change of $\delta$(Ni$^{3+}$-O), $\nu$(Ni$^{5+}$-O), and $\nu$(O-O) peaks (Figure 11(b)) which was the evidence for $^{18}$O exchange in NiFe-LDH, it signified that lattice oxygen atoms no longer formed NiOO$^-$ and participated in OER and illustrated that Ni sites were no longer the active sites, as a highly reactive surface active site based on Fe was created.

3.4. Synergic Interaction between Different Active Sites for OER in LDHs. Recent researches are more likely to attribute the excellent OER performance of NiFe-LDH to the synergy between Ni sites and Fe sites. The first representative job was reported by Goddard III et al. in 2018 [99], and they successfully predicted the synergy between Fe and Ni which lead to the optimal performance for OER via grand canonical quantum mechanics and DFT calculation, and they predicted the
OER mechanisms on NiOOH and (Ni, Fe)OOH as well. Compared with Figures 12(d) and 12(e) and 12(f), it is obvious that the Gibbs free energy needed for O radical formation was reduced from 2.44 eV (pure γ-NiOOH) to 1.99 eV (one-third surface Fe doping γ-(Ni, Fe)OOH) and 1.20 eV (one-third surface Fe doping plus one-third subsurface Fe doping γ-(Ni, Fe)OOH), which caused the OER overpotential reduced from 1.22 V to 0.83 V and 0.42 V. But both in Figures 12(c) and 12(f), catalyzing the O-O coupling on the surface of Fe$^{4+}$ site needs a larger barrier than that on the surface of Ni$^{4+}$ sites and made Fe$^{4+}$-OOH unviable at the 2e step on thermodynamics. In a summary, the high spin $d^6$ Fe$^{4+}$ utilizes exchange interaction to generate and stabilize the O radical, while the nearby $d^0$ Ni$^{3+}$ catalyzes the O-O coupling.

The synergy between Ni and Fe is further proved experimentally. Edvinsson et al. reported that NiFe-LDH could dynamically self-optimized active sites during OER and lead to an improved performance of OER [100]. The change of active sites was manifested via XPS and in-situ Raman spectra. Ni 2p spectra have shown that there was an increase in Ni$^{3+}$ relative to Ni$^{2+}$ for NiFe-LDH after OER. For the O 1s spectra, the decrease of the peak at lower energy (529.5 eV), which was assigned to lattice oxygen, and the increase of the peak at higher energy (530.6 eV) could be attributed to the bond between lattice oxygen and Ni$^{3+}$. As Figures 13(d) and 13(e) shown, the frequencies of 477 and 557 cm$^{-1}$ match well with spectral features of γ-NiOOH which meant the transformation from Ni(OH)$_2$ to NiOOH at high potentials and further oxidized to O$_2$ and H$_2$O. The existence of Fe could inhibit the self-oxidation of Ni and lead to the creation of γ-NiOOH and higher valance Ni, which was the substance of synergistic electronic interplay between Fe and Ni sites in NiFe-LDH.

4. Summary and Prospects

LDHs are considered as outstanding OER catalysts which have widely studied and reported. In this review, we summarized four common strategies applied to improve the OER performance of LDHs. Through these strategies, the overpotential of OER can be decreased obviously, leading to a high efficiency of energy utilization. Furthermore, some works about the identification of active sites for LDHs are introduced. Revelation of reaction mechanism and active sites provide us the theoretical guidance to design efficient electrocatalysts. It is viable to analysis the impact caused by different elements and manufacture exterior active sites via adjusting the types and content of metal elements. Besides, the conclusion of the researches of Ni and Fe sites can be extended to analogous oxides, hydroxides and oxyhydroxides.

Although many works have reported a lot of outstanding catalysts with a low overpotential of OER in alkaline media, several challenges still exist. First of all, the development and exploration of OER catalysts are mostly in the experimental stage at present, which cannot meet up the standards for large-scale practical use. For instance, problems are still remained to enlarge the size of catalysts and maintain the stability during OER with a severe condition (e.g., high alkalinity and high temperature). Besides, most reported preparation methods of LDHs based catalysts are complicated and time-consuming, which brings high cost and restricts their application as well as popularization. Beyond that, more visualized and systematic experimental data is needed to provide to prove whether the highly active OER performance of NiFe-LDH is caused by single active site (Ni or Fe site) or the synergistic interaction between Ni and Fe sites. Moreover, the recognition of reactive oxygen species such as oxygen species adsorbed by active sites on the surface of electrocatalysts and oxygen radical dispersed in the solution during OER still remains ambiguous due to the instable and unapparent existence of reactive oxygen species. After recognizing these reactive oxygen species, how to take advantage of them for more efficient OER is still vital.

Facing these problems and challenges, much effort is still needed to further promote the application of electrochemical water splitting towards efficient hydrogen production. Above all, it is necessary to develop innovative, simple, and low-cost synthetic methods, which can achieve facile and large-scale production of LDHs electrodes satisfying the severe requirements for industrialized OER towards efficient hydrogen production. Besides, more in-situ characterization analyses should be developed and used to identify the concrete form of reactive oxygen species and their effect on facilitating the reaction process. Furthermore, advanced computational chemical technology such as density function theory and molecular dynamics combined with big data should be used to analyze the reaction mechanism and predict electrocatalytic performance of catalysts. In addition, it is a feasible way to use the reactive oxygen species produced during the OER process in organic oxidation reactions for the harvesting of value-added products. Reactive organics are usually difficult to convert by conventional catalysts and always have lower oxidation potential than OER. More importantly, the final products should be obtained readily through physical (e.g., extraction, distill) and chemical (e.g., precipitation) methods. Therefore, many organics are reported (e.g., 5-hydroxymethylfurfural, methanol, and glycine) to add in anolyte; thus, the hydrogen production can be conducted at lower overpotential, and value-added products can be obtained simultaneously. Therefore, it is of great importance to not only develop electrocatalysts with excellent performance but also enhance the recognition of OER active sites. We hope this review can offer ideas to further identify the active sites for LDHs with the purpose of providing guidance to design more advanced electrocatalysts towards electrochemical water splitting.

Data Availability

The data and materials used to support the findings of this study are available from the corresponding author upon reasonable request.
Conflicts of Interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service, and company that could be construed as influencing the position presented in the manuscript.

Authors’ Contributions

M. S. led the project. The manuscript was primarily written by X. W., and further Y. S., M. S., and H. Z. revised. All authors contributed to the manuscript.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (22090031, 21922501, and 21871021) and the project funded by the China Postdoctoral Science Foundation (2021M690319).

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