Transition metal-based catalysts for electrochemical water splitting at high current density: current status and perspectives

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As a clean energy carrier, hydrogen has priority in decarbonization to build sustainable and carbon-neutral economies due to its high energy density and no pollutant emission upon combustion. Electrochemical water splitting driven by renewable electricity to produce green hydrogen with high-purity has been considered to be a promising technology. Unfortunately, the reaction of water electrolysis always requires a large excess potential, let alone the large-scale application (e.g., >500 mA cm⁻² needs a cell voltage range of 1.8–2.4 V). Thus, developing cost-effective and robust transition metal electrocatalysts working at high current density is imperative and urgent for industrial electrocatalytic water splitting. In this review, the strategies and requirements for the design of self-supported electrocatalysts are summarized and discussed. Subsequently, the fundamental mechanisms of water electrolysis (OER or HER) are analyzed, and the required important evaluation parameters, relevant testing conditions and potential conversion in exploring electrocatalysts working at high current density are also introduced. Specifically, recent progress in the engineering of self-supported transition metal-based electrocatalysts for either HER or OER, as well as overall water splitting (OWS), including oxides, hydroxides, phosphides, sulfides, nitrides and alloys applied in the alkaline electrolyte at large current density condition is highlighted in detail, focusing on current advances in the nanostructure design, controllable fabrication and mechanistic understanding for enhancing the electrocatalytic performance. Finally, remaining challenges and outlooks for constructing self-supported transition metal electrocatalysts working at large current density are proposed. It is expected to give guidance and inspiration to rationally design and prepare these electrocatalysts for practical applications, and thus further promote the practical production of hydrogen via electrochemical water splitting.

1. Introduction
1.1 Water electrolysis background
The large-scale development of sustainable and renewable energy is crucial to replace the heavy dependence on fossil fuels by the carbon-neutral economy nowadays.1 Hydrogen, as one of the zero-carbon and clean energy carriers, has widely attracted a lot of attention with its high gravimetric energy density, zero CO₂ and other pollutant emission advantages.2–4 Traditional hydrogen production processes mainly occurring by steam reformation of natural gases and gasification of coal always lead to the emission of immeasurable CO₂, and are regarded as unsustainable.5 Recently, electrochemical water splitting (2H₂O + energy → 2H₂ + O₂) with renewable energy has been considered as one promising way for producing hydrogen to relieve the aggravating fossil energy crises and environmental issues, due to its various advantages, including the high purity hydrogen product, zero carbon emission, abundant resources and easy fabrication with low equipment input.6–9 Water electrolysis involves two half-reactions, i.e., the cathode reaction of the hydrogen evolution reaction (HER) and the anode reaction of the oxygen evolution reaction (OER), as shown in Fig. 1. To drive water electrolysis, the thermodynamic equilibrium potential is 1.23 V vs. reversible hydrogen elec-
to overcome the overpotentials of the OER/HER and the ohmic drop caused by ion conduction in the aqueous electrolyte.20–22 Therefore, considerable works have been devoted to exploring efficiently active electrocatalysts with high durability to overcome the kinetic barrier for promoting reaction kinetics, particularly for the four electron-involved complex reaction of OER.

1.2 Design strategies and requirements for electrocatalysts working at high current density

In terms of electrolytic activities, to date, the state-of-the-art HER and OER electrocatalysts are the Pt/C and the Ru/Ir-based oxides, respectively.16–18 Generally, they exhibit small onset potentials, but their overpotentials become very high under the large-scale water electrolysis process.3,17,19 Additionally, the scarcity, high price, poor adhesion ability with those substrates (e.g. carbon cloth and nickel foam) and low stability (especially during the water oxidation) of the noble metal-based electrocatalysts hinder their wide application.20–22 Thus, it is imperative to design non-precious transition metal-based electrocatalysts, such as chalcogenides,23,24 carbides,25,26 and phosphides27,28 for HER, and oxides,29,30 (oxy)hydroxides,31,32 borides33 and perovskites34 for HER, and oxides,29,30 (oxy)hydroxides,31,32 borides33 and perovskites34 for OER. Normally, the noble metal-free HER electrocatalysts work well in acid environments, and are even two or three orders of magnitude better than those in basic media. Conversely, the performance of the noble metal-free OER electrocatalysts is superior in alkaline electrolyte. Meanwhile, these electrocatalysts always exhibit slow intrinsic kinetics for both HER and OER in neutral electrolytes.6,13,29,35,36 Recently, significant advances have been made to explore bifunctional electrocatalysts with excellent electrocatalytic activities for both HER and OER. Unfortunately, it is challenging to obtain OER or HER electrocatalysts that satisfy the needs of industrial electrolyzers operating at a high current density (≥1 A cm⁻²), especially for the bifunctional electrocatalysts. Under high current densities, large amounts of H₂O₂ bubbles are always formed vigorously on the electrodes. In this case, the accumulation of gas bubbles on the interface of electrocatalysts and electrolyte can seriously hinder the mass transfer of liquid, slow the transfer of electrons and decrease the exposure of active sites, leading to worse electrocatalytic activity and durability.14,37,38 Therefore, it is still necessary to explore earth-rich and cost-efficient OER/HER electrocatalysts for water electrolysis under the high current density condition.

In-depth investigations of the gas–solid–liquid triple phase interface properties have been considered to design and develop novel electrocatalysts with higher activity and longer-term stability at higher current density. In this regard, the critical steps are smartly joined to achieve high electrocatalytic activity, in which the main three steps are mass transfer in the electrolyte to and from the electrochemical surface, charge transport from the conducting support to the active sites and redox intermediates, and charge transfer and surface conversion (e.g., reactants adsorption, interfacial charge transfer, and intermediates/products desorption from the active centres).38,39 As for the surface conversion, many efforts have been devoted to increasing the density of active sites and regulating the binding energies to optimize the adsorption and desorption energy for evolution intermediates on the electrocatalyst surface.40–42 For the improvement of the exposed active sites, various nanostructures such as nanowires,43 nanosheets,11 nanoarrays,44 microspheres45 and nanocubes46 have been constructed for the electrocatalysts. Meanwhile, composition engineering is a feasible way to improve the quality of the active sites. In particular, the creation of multi-component systems could induce the synergistic effects and enhance the intrinsic activities.3,6,13,47 Furthermore, the intrinsic electrocatalytic activity is always related to the adsorption/desorption of those key intermediates with a volcano-shape plot corresponding to the electrocatalytic activity and surface adsorption ability.6,13,22,48 It is well known that the physicochemical properties, especially, the electronic structure of the electrocatalyst can affect its surface adsorbing/desorbing characteristics directly for favorable active sites.5,49,50 One effective way of regulating the binding energy is to tune the composition of the electrocatalysts by means, such as metallic or non-metallic hetero-atom doping.51,52 Another way is the introduction of defects,53 such as oxygen vacancies,54 phase boundaries,55 atom distortion,56 strain57 twin crystals,58 grain boundaries,59 stacking defects,60 and exposure of low coordinated surface defects.61

Moreover, many design strategies have been proposed to improve the charge transport by adopting binder-free electrocatalysts,3,7,9 metal (alloy) core electrocatalysts62,63 and highly conductive substrates like Ni foam,64 Cu foam,19 carbon fiber65 and cloth46 to reduce the electric resistance. Those electrocatalyst supports not only have larger surface areas for the growth and dispersion of electrocatalysts, resulting in the utilization efficiency of the active site, but also can enhance the electrocatalyst conductivity effectively, accelerate the rate of electron transfer rate and provide full accessibility to active sites, leading to overpotential reduction due to the electrochemical polarization. In particular, the metal-based supports could directly serve as a metal source to fabricate different morphologies of electrocatalysts.19,67–69
Except for tuning the surface conversion and charge transport, the mass transfer and diffusion issues should also be considered as important. For the water electrolysis process with gas generation, the electrocatalyst wettability with electrolyte and the excessive amounts of gas bubbles formed on the electrode surface for long-term operation cannot be neglected.

This result could greatly increase the resistance of the electrode. Generally, the surface of the electrode has high bubble adhesion ability, the active sites could be covered and the electrolyte diffusion could also be impeded, resulting in a significant voltage increase required for the water electrolysis. In this account, the design of an effective surface structure for the rapid separation of bubbles from the active electrode to improve the electrocatalytic activity should be effective and useful. Thus, it is necessary to fabricate uniform nanostructures with superhydrophilicity/superaerophobicity and rich active sites for favoring the release of gas bubbles and stress accommodation. Herein, the interfaces between the solid/liquid/gas on the superaerophobic surfaces are discontinuous, which could lead to the decrease of the adhesion of the bubble on the surface. Meanwhile, the interfaces between the electrolyte and the active electrode surface on the superhydrophilic surface become richer, which can increase the ability of penetration, thereby improving the electrocatalytic activity. Additionally, some methods (such as the use of magnetic and supergravity fields during water electrolysis) enable the enhancement of the rate of gas bubble separation together with changing the electrolyte environment. Those applied external fields can induce excess convection on the electrolyte, and effectively reduce the bubble accumulation on the surface, thus boosting the electrocatalytic activity.

Up to date, various electrocatalysts for water splitting with outstanding performance have been reported. However, most of them are tested at low current densities (usually <200 mA cm$^{-2}$), rather than high current densities. Notably, almost all of those reported electrocatalysts working at large current density are self-supported transition metal-based electrocatalysts in alkaline media. In comparison with those powder-state electrocatalysts, such electrocatalysts avoid the use of binders (e.g., Nafion) and conducting agents, which can simplify the preparation process of the electrode and decrease the cost. Meanwhile, the electrocatalysts can be anchored on the substrate materials evenly with high loading of the active components. In addition, the intimate contact of the substrate and electrocatalysts can ensure the rapid charge transfer and prevention of electrocatalyst shedding.

To achieve the electrolysis of water at a large current density, the self-supported electrocatalyst should satisfy multiple criteria: (i) The raw electrocatalyst materials should be earth-abundant and inexpensive to meet the needs of industrial production; (ii) The preparation temperature of the electrode should be not too high, in order to reduce the consumption of energy and cost; (iii) It should have excellent intrinsic activity; (iv) The morphology and microstructure should be adjusted so that it can easily contact the reactants with satisfactory wettability to accelerate the detachment of gas bubbles from the surface of the electrodes, and simultaneously promote charge and ion transfer in the external circuit; (v) There is strong adhesion between the current collectors and electrocatalysts in order to prevent the peeling of the electrocatalytic active phase from the current collector under the high current density condition; (vi) It should have steady long-term durability against corrosion at high current density, especially in the presence of strong oxidizing processes. Therefore, engineering low-cost, earth-abundant and self-supported micro/nano electrocatalysts with ultrahigh intrinsic HER/OER activities, excellent electro-conductibility, superhydrophilicity/superaerophobicity for gas bubbles, and high structural stability are worth pursuing for meeting the low-energy consumption and high performance at large current density.

Herein, an overview on the recent progress in the microstructure design, fabrication, and electrocatalytic performances of self-supported transition metal-based electrocatalysts operated stably at large current densities in alkaline electrolytes is given. First, the fundamental mechanisms of HER/OER and kinetics issues in alkaline media for water electrolysis are introduced and analyzed. Then, some representative self-supported transition metal-based electrocatalysts for HER, OER and overall water splitting, including oxides, hydroxides, phosphides, sulfides, nitrides and alloy (as shown in Fig. 2), are summarized. Notably, the synthetic strategies, current density values to achieve the overpotential, stability, the reason for the excellent performance and other aspects are reviewed in detail.

Finally, the existing issues, perspectives and challenges are discussed for the future development of electrocatalysts working at the high current density in the large-scale industrial electrolysis of water for the generation of hydrogen fuel.
2. Fundamentals of alkaline electrocatalytic reactions

In a laboratory-scale experiment, the electrochemical performance of electrocatalysts at high current density is usually evaluated in a three-electrode system. Herein, a carbon rod is usually used as the counter electrode in the HER process to avoid the effect of the slight dissolution of platinum, and the saturated calomel (Hg/Hg2Cl₂) electrode (saturated KCl) as the reference electrode is generally applied in an alkaline electrolyte (usually KOH solution), but the Ag/AgCl electrode (saturated KCl) is utilized in an acidic electrolyte (usually H₂SO₄ solution). For OER, the platinum foil/net is always used as the counter electrode with the Hg/HgO reference electrode (saturated 1.0 M KOH) in KOH electrolyte. At the electrochemical electrolysis temperature of 25 °C, the following equations are applied to determine the potential in different electrolytes:

In alkaline electrolyte for HER:

\[ E_{\text{HER}} = E(\text{Hg/Hg}_2\text{Cl}_2) + 0.0591 \text{pH} + 0.241 \text{ V} \] (1)

In acid electrolyte for HER:

\[ E_{\text{HER}} = E(\text{Ag/AgCl}) + 0.0591 \text{pH} + 0.222 \text{ V} \] (2)

In alkaline electrolyte for OER:

\[ E_{\text{OER}} = E(\text{Hg/HgO}) + 0.0591 \text{pH} + 0.098 \text{ V} \] (3)

In acid electrolyte for OER:

\[ E_{\text{OER}} = E(\text{Ag/AgCl}) + 0.0591 \text{pH} + 0.222 \text{ V} \] (4)

In the following sections, the proposed mechanisms are introduced and discussed.

2.1 Reaction mechanism for the HER

HER occurring on the cathode is a two-electron related reaction, which consists of (i) H₂O molecule adsorption and hydrated proton (H₃O⁺) on the active sites (i.e., the Volmer step); and (ii) subsequent hydrogen molecule desorption from the electrocatalyst surface through either an electrochemical (i.e., Heyrovsky step) route or a chemical path (i.e., Tafel step). Based on the reaction mechanism of HER, the electrocatalytic activity of the electrocatalysts in an alkaline electrolyte should be lower than that in an acidic one, and the reaction is also sensitive to the surface structure. However, due to the strong corrosion of the catalyst material in acidic media, the stability drop sharply in it. Therefore, to date, abundant HER electrocatalysts working in alkaline electrolytes at high current densities with superior activity have been developed. In alkaline media, water dissociation, hydroxyl adsorption (OH_ads) and trade off H_ads occur with the Volmer/Heyrovsky step or Volmer/Tafel step, as described in the following, \(^6\text{,12-14}\)

(1) Due to the lack of protons, a H₂O molecule instead of H⁺ reacts with an electron, generating an adsorbed hydrogen atom (H_ads) species on electrocatalysts.

Volmer step:

\[ \text{H}_2\text{O} + \text{e}^- \rightarrow \text{OH}^- + \text{H}_\text{ads} \] (5)

(2) Then, H_ads couples with the H₂O molecule and an electron to produce a hydrogen molecule.

Heyrovsky step:

\[ \text{H}_2\text{O} + \text{H}_\text{ads} + \text{e}^- \rightarrow \text{OH}^- + \text{H}_2 \] (6)

(3) Or, two H_ads are combined to produce a hydrogen molecule.

Tafel step:

\[ 2\text{H}_\text{ads} \rightarrow \text{H}_2 \] (7)

Differently, in acidic electrolyte, the Heyrovsky and Volmer steps are described as follows, which is related to the protons rather than water as reactants.\(^87\text{-89}\)

(1) Volmer step:

\[ \text{H}_2\text{O}^+ + \text{e}^- \rightarrow \text{H}_\text{ads} + \text{H}_2\text{O} \] (8)

(2) Heyrovsky step:

\[ \text{H}_2\text{O}^+ + \text{H}_\text{ads} + \text{e}^- \rightarrow \text{H}_2 + \text{H}_2\text{O} \] (9)

Notably, based on the above reaction pathway, breaking the strong covalent H–O–H bond is required prior to adsorption of H_ads in the alkaline electrolyte, which is harder to reach than the H₂O⁺ reduction in acid electrolyte. What is more, H₂O adsorption is the first vital step of HER in an alkaline electrolyte, which is more difficult than the weak covalent bond of H₂O⁺ adsorption. Meanwhile, it is well known that four major
factors might have great influence on the HER performance, including water adsorption on the active sites, water dissociation ability, hydrogen binding energy and aqueous OH$^-$ adsorption. Thus, how to rationally design electrocatalysts with improved alkaline HER performance at the high current density should be considered at first from the view of the above four factors. Recently, great efforts have been made to develop highly active HER electrocatalysts with enhanced active site-H$_2$O bond for the effective dissociation of water and binding hydrogen species at the large current densities.

### 2.2 Reaction mechanism for the OER

Compared with the two-electron process of HER, the OER process contains more complex reaction pathways involving multistep multielectron transfer for O$_2$ generation with slow reaction kinetics.$^{84,90,91}$ The development of a highly efficient and stable OER electrocatalyst is therefore more important to promote the overall water splitting performance. Like the HER process, the mechanism of OER is greatly related to the electrocatalyst surface structure, as well as the pH value of the electrolyte. In general, various intermediates (e.g., absorbed hydroxyl (M-OH), adsorbed oxygen (M-O), and adsorbed peroxide species (M-OOH)) could be formed during the OER process, while O$_2$ is evolved via either the direct diffusion reaction of two M-O intermediates or M-OOH species decomposition in either acidic or alkaline electrolytes. The mechanism for the OER in alkaline condition is described as follows.$^{9,92,93}$

1. A M-OH intermediate is formed, which is the first step of the OER process based on OH$^-$ adsorption on the surface of the electrocatalysts.

   \[ \text{M} + \text{OH}^- \rightarrow \text{M-OH} + e^- \quad (10) \]

2. Further reaction with OH$^-$ (eqn [11]) generates the M-O intermediate coupled with H$_2$O and an electron. Thereafter, O$_2$ molecule formation could be through two different pathways: one is directly combining two M-O species to generate O$_2$ and M active sites (eqn [12]).

   \[ \text{M-OH} + \text{OH}^- \rightarrow \text{M-O} + \text{H}_2\text{O} + e^- \quad (11) \]
   \[ 2\text{M-O} \rightarrow 2 \text{M} + \text{O}_2 \quad (12) \]

The other is the combination of M-O with OH$^-$ to produce M-OOH coupled with electron oxidation (eqn [13]), and followed by a proton-coupled electron transfer process to generate O$_2$ and active sites (eqn [14]). Herein, the thermodynamic barrier of reaction (12) is generally higher than those of reactions (13) and (14):

   \[ \text{M-O} + \text{OH}^- \rightarrow \text{M-OOH} + e^- \quad (13) \]
   \[ \text{M-OOH} + \text{OH}^- \rightarrow \text{M} + \text{O}_2 + \text{H}_2\text{O} + e^- \quad (14) \]

According to the above reaction pathway, it is commonly considered difficult to entirely understand the rate-determining steps and confirm the kinetics descriptions of OER due to the existence of the above multiple intermediates. It is also crucial for a detailed comprehension of the interaction between the electrocatalysts surface and reaction intermediates for the overall OER performance. In this case, the DFT calculations are widely used to provide the adsorption energies of intermediates for the individual reaction steps and to explore the reaction mechanism of OER electrocatalysts. To date, great efforts have been made to construct a model of the thermodynamics of the electrochemical reactions.$^{7,13,48,92}$ It was found that the Ru/Ir-based oxides are the most efficient OER electrocatalysts in acid media, while most non-precious electrocatalysts cannot work in acidic electrolytes, let alone at the large current densities, owing to their acid-soluble characteristics. Therefore, the transition metal-based OER electrocatalysts are more favorable in alkaline electrolyte.

### 3. Parameters for the evaluation of the electrocatalytic performance

In order to evaluate the electrocatalytic performances of electrocatalysts toward HER and OER comprehensively, the main parameters, i.e., onset potentials ($E_{\text{onset}}$), overpotentials ($\eta$), $iR$ corrected overpotential, electrochemically active surface area (ECSA), mass or specific activity (MA or SA), Tafel slope, turnover frequency (TOF), stability and faradaic efficiency need to be calculated and discussed in detail.$^{10,15,84,94,95}$

#### 3.1 Onset potentials ($E_{\text{onset}}$), overpotentials ($\eta$) and $iR$-corrected overpotential

The overpotential ($\eta$) is a descriptor to evaluate the electrocatalytic activity, which can be defined as the difference between the actual potential and thermodynamic value under equilibrium condition at a defined current density.$^{15,48,94}$ It can be calculated by eqn (15):

\[ \eta = E_{\text{applied}} - E_0 - iR \quad (15) \]

where $E_{\text{applied}}$ is the actual applied potential, $E_0$ is the theoretical equilibrium value, and $iR$ is the ohmic correction under the same condition.

In particular, to match the photoelectrochemical water-splitting efficiency of 12.3%, a specific current density of 10 mA cm$^{-2}$ ($\eta_{10}$) is regarded as benchmarking one to characterize and compare the electrocatalysts for both HER and OER in various electrolytes.$^{13,96}$ In this review, the performance of the electrocatalysts at high current densities of 500 mA cm$^{-2}$ or higher is emphasized. It is noteworthy that the overpotential is not calculated according to the $iR$ corrected in the real water splitting cell. Therefore, it is necessary to show the $iR$-uncompensated overpotential, and compare it with the $iR$-compensated one at the same current density, especially for the self-supported transition metal-based electrocatalysts at large current density. Unfortunately, only a few researchers provided this particular activity parameter when they reported the overpotentials directly after $iR$ compensation. As an example to display such a strange problem in the $iR$ drop compensation that arose for high-performance electrocatalysts that
could operate under large current density conditions, Kundu et al.\textsuperscript{10} prepared an OER electrode with high-performance by controlling the oxidation of the surface and the simultaneous selective removal of OER-lousy Cr in 304 stainless steel (SS). Fig. 3 displays the same obtained oxidized SS at a sweep rate of 5 mV s\textsuperscript{-1} in 1.0 M KOH with and without 40% and 50% of \(iR\) drop compensations to reach an OER current density of 500 mA cm\textsuperscript{-2}. One can see that the 40% of \(iR\) drop compensation resulted in reasonably lower overpotentials at the same current density, but the compensation of 50% led to a totally unacceptable LSV curve. Hence, the mentioning of the \(iR\) drop compensation percentage is important at different testing conditions in the results. Obviously, the \(iR\) drop uncompensated overpotential would be a more important and valuable activity parameter than the \(iR\) drop-compensated one at a determined current density for either HER or OER at the large current density.

In addition, for the measurement of the overpotential relating to those transition metal-based electrocatalysts grown on the substrates (like CC, CFP and NF working at a large current density), the working area should be exactly determined. It is common to see that "1.0 cm\textsuperscript{2} area was dipped into the electrolyte while conducting electrochemical characterizations" in some published papers.\textsuperscript{97–99} Meanwhile, some other reports claimed to use Teflon tape or epoxy resin to mask other areas of the electrode over 1.0 cm\textsuperscript{2}, which was dipped into the electrolyte even when metal foils and foams were utilized as the substrates.\textsuperscript{100–102} However, these methods are good for masking excessive working electrode areas exposed to the electrolyte, but it cannot completely mask it. Especially, for the electrocatalysts coated on the metal foam, it often tends to become overexposed to the electrolyte due to the capillary action through holes, spaces and pores that are present in it. That is, although the remaining electrode area is covered by the Teflon tape, there is still some inner areas of the electrode that are exposed to the electrolyte so that it is still inefficient in strictly exposing 1.0 cm\textsuperscript{2} area during the electrochemical measurement. In this case, the calculation of the current density value (mA cm\textsuperscript{-2}) still adopting the area of 1.0 cm\textsuperscript{2} should be unreliable. Thus, with greater substrate area, the error of the overpotential at the defined current density will be greater. Therefore, in both HER and OER performance evaluations, it is suggested to introduce the thin substrate for restricting the unwanted interferences from the capillary actions of the foam structure.

![Fig. 3](image)

**Fig. 3.** (a) Surface oxidized SS–304 showing the uniformly grown highly mono-disperse nanocrystals. (b) LSV curves of the surface oxidized SS–304 recorded at a scan rate of 5 mV s\textsuperscript{-1} in 1.0 M KOH electrolyte without and with 40 and 50% of \(iR\) drop compensations. Reprinted with permission from ref. 10, copyright 2018, The Royal Society of Chemistry.

### 3.2 Mass or specific activity (MA or SA) or turnover frequency (TOF)

\(\eta@10\) mA cm\textsuperscript{-2} usually describes the electrocatalytic activity of electrocatalysts. However, it does not always reflect the intrinsic electrocatalytic activity owing to the different active material loadings.\textsuperscript{4,103,104} The excellent performance of the self-supported transition metal-based electrocatalysts in the case with large current density always has a mass loading of 2–4 mg cm\textsuperscript{-2}, which is much higher than those of electrocatalysts prepared by the universal and conventional drop-casting method with \(\sim0.2\) mg cm\textsuperscript{-2} loading. Herein, in order to avoid the mass loading influence, mass activity (MA), specific activity (SA) and turnover frequency (TOF) are suggested to provide more reasonable descriptors for the intrinsic electrocatalytic activity evaluation of the electrocatalysts.

The MA is donated as the current normalization based on the mass loading of the target electrocatalyst at a defined overpotential, which is an important parameter for evaluating noble metal-based materials, but less crucial for non-noble metal-based catalysts.\textsuperscript{4,10} Another key evaluation parameter for the OER/HER electrocatalytic activity is SA, which represents the intrinsic (10) normalization based on the per unit surface area includes the Brunauer–Emmett–Teller (BET) surface area or electrochemically active surface area (ECSA).\textsuperscript{94,105,106} The geometrical area-normalized SA is suitable for planar and smooth surfaces, whereas the BET surface area-normalized SA often results in inappropriate outcomes. The measurement of BET is generally based on \(N_2\) adsorption and desorption, but it does not mean that all of the \(N_2\) molecule-adsorbed and desorbed sites are electrochemically active. Unlike the geometrical surface area, ECSA can evaluate the real active surface area of the self-supported electrocatalyst, that is, those truly active sites exposed to the electrolyte. As such, the SA normalized by ECSA should be more accurate.

The turnover frequency (TOF) (eqn (16)) is another indicator to show the intrinsic activity of the electrocatalyst, which is defined as the number of generated products normalized on the electrochemically active centres number per unit time.\textsuperscript{4,107–109} Although it is difficult to exactly calculate the TOF value for most electrocatalysts, particularly for those nano-catalysts with complex structures, it could still be used to compare the activities of different electrocatalysts within similar systems. Especially, the TOF can serve as a kinetic parameter for 3d-metal-based OER electrocatalysts and noble metal-based HER electrocatalysts, in which the surface of the active center concentration can be calculated by taking the redox active peak.\textsuperscript{10,94,110,111}

\[
\text{TOF} = \frac{jA}{\alpha nF}
\]

where, \(j\) (A cm\textsuperscript{-2}) is the current density at a given overpotential, \(A\) is the geometric surface area of the working electrode, \(F\) represents the Faraday constant (96 485 C mol\textsuperscript{-1}), \(n\) (mol) is the surface concentration of the active sites or number of participating atoms in the electrocatalysts, which could be further analyzed by using the ECSA or ICP-MS (AES or OES).\textsuperscript{112,113} It
should be pointed out that all metal cations in the metal-based electrocatalysts were assumed to be electrocatalytically active, and thus the method of ICP-MS (AES or OES) analysis of the calculated values stands for the lower limit of TOF. \(a\) represents the number of electrons transferred for evolving a molecule of product (for H\(_2\), \(a = 2\) and for O\(_2\), \(a = 4\)).

3.3 Tafel plot

The Tafel slope (\(b\) in eqn (17)) can be determined based on the polarization curve (LSV curve), which can obtain information on the two important kinetic parameters. One is the so-called Tafel slope, which is generally related to the electrochemical reaction mechanism, demonstrating how fast the current density increases with the increase of the overpotential. That is, a lower Tafel slope value indicates a smaller overpotential increase to achieve the same current density, reflecting faster kinetics of electron transfer. When \(\eta = 0\), the corresponding current density is named as the exchange current density (\(j_0\)), which depicts another important kinetic parameter of the electrochemical reaction rate at the equilibrium condition. It is an intrinsic parameter reflecting the charge transfer ability and determining how rapidly the electrode reaction proceeds. A larger exchange current density suggests that the electrocatalyst requires a lower driving force to start the reaction, manifesting that the electrochemical reaction proceeds at a more rapid rate. Actually, when the normalized polarization curves by the double-layer capacitance or ECSA, the obtained normalized exchange current density is a powerful tool for comparing the intrinsic electrocatalytic activities among different electrocatalysts with the similar geometry and structural design.\(^{114,115}\) Consequently, after the normalization, with larger normalized exchange current density, a higher intrinsic activity can be achieved. In essence, a higher \(j_0\) value and a smaller \(b\) value are desirable at the same time for a high-performance electrocatalyst in either OER or HER processes.\(^{10,15,48}\)

\[
\eta = a + b \log|j| \\
(a = 2.303RT \log|j_0|/anF, b = 2.303RT/anF) (17)
\]

where \(b\) stands for the Tafel slope value, \(j\) represents the measured current density, \(j_0\) is the exchange current density, \(R\) is the gas constant (8.3145 J mol\(^{-1}\) K\(^{-1}\)), \(T\) is temperature, \(n\) is the number of transferred electrons in the electrochemical redox reaction, \(F\) is Faraday constant (96 485 C mol\(^{-1}\)), and \(a\) is the charge transfer coefficient.

3.4 Stability

Excellent structural and electrocatalytic stability of an electrocatalyst are crucial indexes for its potential practical application, and can be used to test its long-term durability under applicable conditions. The stability of an electrode is related to not only the robustness of the electrocatalysts, but also the binder capability to endure corrosive conditions. Generally, two effective methods are utilized to characterize the stability or durability of the electrocatalysts under the electrochemical conditions. One method is to compare the LSV curves at the initial cycle and after continuously recycling thousands of CV cycles (Here, the number of cycles should be over 3000 times) at an accelerated sweep rate. The lower potential shift at the specific current density strongly signifies superior stability. The other method is to measure the chronopotentiometry or chronocoulometry, which represents the current density alteration with time under a defined potential (\(i\)-\(t\) curve) or potential variation with time under a certain current density (\(i\)-\(\eta\) curve) (especially, under a current density >10 mA cm\(^{-2}\)) for a long period of time (>10 h). Negligible degradation in the examined current density or potential during the long-term test indicates a robustness of the electrocatalyst.

In addition, the mechanical stability of the self-supported electrocatalysts is another important performance metric to corroborate whether the active components undergo phase transition or peel off from the substrate during the practical long-term operation. There are two efficient means to check its mechanical stability. One is to compare the compositions, morphologies, and structures of the self-supported electrocatalysts, tested by SEM, XRD, XPS and other means before and after the OER/HER long-term electrochemical reaction. If it is almost identical to that of the fresh sample, this suggests that the self-supported electrocatalysts display excellent mechanical stability. The other one is to evaluate the multistep chronocoulometry (CP), which shows the various voltage responses vs. current densities over a long time. The recovery of the overpotential could be realized when the current density of the self-supported electrocatalysts returned to the initial value during the long-term test, which always suggests a good interface between the self-supported electrocatalysts and the substrate with outstanding mechanical robustness.

3.5 Faradic efficiency

Moreover, the faradaic efficiency (FE) is an important parameter to show the selectivity of the electrocatalyst, which is determined by the ratio of the amount of produced gas detected in an experiment to the theoretical amount.\(^{111,116}\) Two well-known methods are usually applied to calculate the FE of OER or HER. The first one is to collect the evolved gas in a special measuring jar by water–gas displacement. The collected gas volume is then changed to moles based on Avogadro’s principle, and the calculated gas molecules moles can be determined from the passed charge using Faraday’s second law of electrolysis.\(^{117,118}\) The second one is to measure the generated gases by gas chromatography (GC) under a constant current density or overpotential. In this case, the evolved gas should have sufficient volume for the evaluation.

4. Electrocatalysts for HER

4.1 Transition metal phosphides

Transition metal phosphides (TMPs) have been receiving wide attention as efficient HER electrocatalysts in alkaline electro-
lyte owing to it possessing analogous active sites in hydroge-
nases with the strong ability of attracting protons and out-
standing conductivity.\textsuperscript{119–121} It is found that the isotropic
structures with more active harmoniously unsaturated surface
atoms could be formed on TMPs.\textsuperscript{111,122} The \textit{in situ} growth of
nanostructured TMPs on conductive supports like NF and CC
has been significantly exploited, and further used practically
with large current density. Herein, the conductive substrate
not only provides a large growth surface area for the active
sites, but also enhances the charge transport of the total elec-
trode. In addition, fabricating the electrode structure with a
porous structure can contribute to dissipating the gaseous
product efficiently and facilitate the exchange of reactants and
products rapidly.

For the preparation of the TMPs-based electrode, transition
metal oxide/hydroxide/oxyhydroxide-based precursors are
always first \textit{in situ} coated on the conductive substrate by elec-
trodeposition or hydrothermal method. Thereafter, the precur-
sors can be transformed into the corresponding TMPs by topo-
tactic phosphidation at low temperature using NaH\textsubscript{2}PO\textsubscript{2} as the
P source. Representative, Huang \textit{et al.}\textsuperscript{123} fabricated NiCoP
nanoflowers on Co foam ((NiCoP/CF) by a low-temperature
phosphidation of the NiCo LDH/CF precursor, as shown in
Fig. 4a. This electrode exhibited good stability in a long-term
test with only a small fluctuation at a large current density of
550 mA cm\textsuperscript{-2} during the 16 h testing period in the alkaline
electrolyte. The excellent performance can be attributed to the
following factors, including the ultrahigh porosity of the CF
support, optimal adsorption energy of the HER intermediate
(H\textsuperscript{*}), facile water dissociation on the NiCoP/NiOOH hetero-
interfaces, and the facilitation of electron transfer from the
interior CF to the exterior NiCoP with the assistance of \textit{in situ}
generated NiOOH on the NiCoP surface. Xu \textit{et al.}\textsuperscript{124} reported a
Co\textsubscript{P}/Co\textsubscript{3}O\textsubscript{4} nanocomposite with a grass-like structure on CF
(denoted as P-Co\textsubscript{3}O\textsubscript{4}/Co\textsubscript{3}O\textsubscript{4}, as shown in Fig. 4b, which was ration-
ally prepared \textit{via} facile hydrothermal synthesis of Co\textsubscript{3}O\textsubscript{4}, fol-
lowed by a sodium hypophosphite-phosphorization process for
the formation of cobalt phosphides. Density functional theory
(DFT) calculations indicated that the phosphorization strategy
could not only improve the conductivity and regulate the elec-
tronic structure of pristine Co\textsubscript{3}O\textsubscript{4}, but also optimize the
adsorption/desorption strength of H\textsuperscript{*}.

Direct phophorization of the available metal substrate was
also developed by sintering or solvothermal condition, which
could avoid the complicated precursor synthesis. However, it is
usually limited by the selection of an appropriate metal sub-
strate, particularly in the cases to synthesize multi-metal phos-
phides. The Yu group\textsuperscript{70} designed and fabricated a Ni\textsubscript{P}
nanoarray electrocatalyst supported on a NF substrate (named
as Ni\textsubscript{3}P/NF) (Fig. 4c), by direct immersion of the NF substrate
in (NH\textsubscript{4})\textsubscript{2}HPO\textsubscript{4} and KOH aqueous solution with a hydro-
thermal reaction to prepare the precursor, followed \textit{via} a low-
temperature topotactic phosphidation process. The self-support-
ated Ni\textsubscript{3}P/NF electrocatalyst exhibited large current densities
of 1000 and 1500 mA cm\textsuperscript{-2} at small overpotentials of 306 and
368 mV, respectively, in 1.0 M KOH solution. The long-term
durability testing showed that the current density as high as 2500 mA cm\textsuperscript{-2}
displayed slight fluctuation after continuous
operating for 10 h. The excellent electrocatalytic activity can be resulted from intimate contacting of nanoarrays and substrate, high intrinsic electrocatalytic activity and fast electron transfer. Especially, the special “superaerophobic” surface characteristics of the Ni3P nanoarrays not only enabled the strong capability to endure internal and external forces, but also released the in situ produced H2 bubbles as fast as possible at high current densities (e.g., >1000 mA cm−2), where the hydrogen generation became vigorous. Wang et al.67 prepared Ni3P/Ni3P nanosheets on a NF substrate by phosphorization of NF with phosphorus vapor at first, and then designed Ni3P/Ni3P nanoparticles coated on Ni3P/Ni3P nanosheets (S-NiP)/NF to provide more active sites by soaking it in a precursor ink, followed by a phosphorizing process with the above phosphorus chemical vapor. This 3D HER electrode showed outstanding durability at a high current density of 1200 mA cm−2 in acidic solution, which has great potential for large-scale application.

For the binary TMPs, the free energy of hydrogen adsorption, which is intensively related to the intrinsic electrocatalytic activity, is generally either too weak or too strong. Notably, it is proved that the incorporation of other elements into the binary TMPs can effectively change the electronic structure and subsequently tune the adsorption free energies of the reaction intermediates, thereby resulting in significant improvement of the electrocatalytic performance.3,4,111 In this regard, Dong et al.125 supported CoFe Prussian blue analogues (PBA) on iron foam (IF) as the precursor to construct the self-supported fluorine-doped cobalt–iron phosphides (P-Co2P/Fe2P/IF), which only required low overpotentials of 229.8, 260.5, 292.2 and 304.4 mV at large current densities of 500, 1000, 2000 and 3000 mA cm−2, respectively, and also displayed excellent HER electrocatalytic stability for 10 h under simulated industrial conditions of 6.0 M KOH electrolyte (Fig. 4d). Yu et al.126 supported ternary Ni–Mo phosphide nanoarrays on NF (denoted Ni3[1–x]Mo2x/P/NF), which delivered low overpotentials of 240 and 294 mV to achieve the high current densities of 500 and 1000 mA cm−2, respectively, in alkaline media (Fig. 4e). DFT calculations revealed that when some Ni atoms in Ni3P were replaced with Mo atoms, the free energy for H* adsorption on the (001) surface of the NiMoP electrocatalyst could be greatly reduced, which was favored for the Volmer–Heyrovsky process. Meanwhile, the metalloid element with P also exerts a synergistic effect in TMPs. For example, the Chen group127 made an amorphous boron phosphates ternary alloy (Co2.90B0.73P0.27/NF) by a facile one-pot electroless method at room temperature, which showed a notable HER electrocatalytic activity with an ultralow overpotential of 384 mV@1300 mA cm−2, and high stability in H2SO4 electrolyte. Another important strategy is to create vacancies with unsaturated sulfur on the crystal surface of the electrocatalyst using special ways. For example, Li et al.133 successfully used the remote hydrogen plasma method to create rich S defects on an amorphous molybdenum sulfide (α-MoS2) loaded on carbon cloth (CC) (Fig. 5b), which not only increased the active site density, but also changed the surface energy of the electrocatalysts, further resulting in the inhibition of bubble trapping on the electrocatalytic surface at high current densities. In comparison with the initial MoS2, a-MoS2 with rich sulfur defects exhibited higher HER electrocatalytic activity with an overpotential as low as 250 mV@500 mA cm−2 in 0.5 M H2SO4 electrolyte.

Meanwhile, it is well known that the engineering of heterojunction structures to improve the electrocatalytic activity with the synergistic effect by two or more factors is an effective method. For example, the Cheng group134 prepared MoS2...
microspheres made of MoS₂ nanosheets, which were further decorated by Mo₂C nanoparticles (MoS₂/Mo₂C). This electrocatalyst possessed the following advantages: (i) The aligned MoS₂ nanosheets had rich exposed active sites to facilitate electron transfer in-plane; (ii) The spherical morphology presented roughness and was crucial for the access of reactants and rapid departure of gas bubbles; (iii) The nanoclusters of Mo₂Ce effectively changed the surface chemistry of the MoS₂ electrocatalyst. Hence, this electrocatalyst delivered the large 1000 mA cm⁻² current density needed for the overpotentials of 227 mV in acidic electrolyte and 220 mV in alkaline media (Fig. 5c), and good durability during the 24 h of testing in both media. Their group further developed a high-throughput scalable method for the production of high-performance MoS₂-based HER electrocatalysts, which also worked well at high current density up to 1000 mA cm⁻². Such electrocatalyst consisted of two-dimensional (2D) MoS₂ modified by Mo₂C nanoparticles on their edges and surfaces (MoS₂/Mo₂C) by a simple thermal treatment, where the 2D MoS₂ nanoflakes were formed by a scalable top-down exfoliation method.¹³⁵ As displayed in Fig. 5d, the MoS₂/Mo₂C electrocatalyst loaded on the high-surface-area Cu foam (HC-MoS₂/Mo₂C) showed notable HER performance with a high current density of 1000 mA cm⁻² at 412 mV and good stability for 24 h under 0.5 M H₂SO₄ electrolyte (Fig. 5e), and good durability during the 24 h of testing in both media. Their group further developed a high-throughput scalable method for the production of high-performance MoS₂-based HER electrocatalysts, which also worked well at high current density up to 1000 mA cm⁻². Such electrocatalyst consisted of two-dimensional (2D) MoS₂ modified by Mo₂C nanoparticles on their edges and surfaces (MoS₂/Mo₂C) by a simple thermal treatment, where the 2D MoS₂ nanoflakes were formed by a scalable top-down exfoliation method.¹³⁵ As displayed in Fig. 5d, the MoS₂/Mo₂C electrocatalyst loaded on the high-surface-area Cu foam (HC-MoS₂/Mo₂C) showed notable HER performance with a high current density of 1000 mA cm⁻² at 412 mV and good stability for 24 h under 0.5 M H₂SO₄ electrolyte. Cheng et al.¹³⁶ fabricated self-supported long and dense Mo₅S₆/Ni₃S₂ co-axial heterostructure nanowires on NF, where the NF is directly used as the Ni source (Fig. 5e). This one only required overpotentials of 182 and 200 mV to obtain the large current densities of 500 and 1000 mA cm⁻², respectively, in alkaline electrolyte, superior to the noble-metal electrocatalyst of Pt/C-NF (281 and 444 mV, respectively), with outstanding durability under the current densities of 500 and 1000 mA cm⁻² for 12 h, indicating that it should have greatly promising for large-scale hydrogen production.

Some investigations also suggest that introducing heteroatoms with stronger electronegativity into catalysts is an efficient approach, which enable the effective substitution of anion sites for modulating the electronic structure and weakening the interaction between metal and anion, resulting in the balance of hydrogen adsorption/desorption behaviors on the surface of the electrocatalyst, and thereby improving the HER activity.⁴,¹¹¹ Inspired by the above viewpoint, Huang et al.¹³⁷ prepared N-doped nickel–molybdenum-based sulfide cuboid arrays on Ni foam (N-NiMoS/NF) via the hydrothermal method with subsequent chemical vapor deposition process. Systematic insights confirmed that the N introduction effectively regulated the electron density and tuned the d-band center of NiMoS, which endowed N-NiMoS to have excellent HER activity with small overpotentials of 250 and 322 mV to reach the current densities of 500 and 1000 mA cm⁻², respectively, in the alkaline electrolyte. Impressively, the N-NiMoS electrode displayed superior durability with a stable current density in 1000 h under the potential of 0.1 V vs. RHE toward HER operation (Fig. 5f).

## 4.3 Transition metal hydroxides

Generally, transition metal hydroxides (TMHs) composed of transition metal cations (such as M²⁺ and M³⁺) and OH⁻ have attracted great attention, owing to their richness on the earth, special 2D-layered structure and dense active sites.¹³,¹³⁸,¹³⁹ It should be mentioned that pure TMHs represent relatively low HER electrocatalytic activity since its could weaken the H₂ adsorption energy. On the other hand, strong OH⁻ adsorption could promote hydroslysis, which is usually the rate-determining step for HER in alkaline water electrolysis.¹⁵,¹³⁸ Various materials can be modified by appropriate methods to achieve better electrocatalytic performance in practical applications. For instance, the Bhattacharyya group¹⁴⁰ wrapped NiCo LDH...
around Cu nanowires (Cu-Ws) coated on the top of Cu mesh (Cu-m) [named as Cu-m/Cu-W/NiCo-LDH] (Fig. 6a), which showed excellent electrocatalytic HER performance with overpotentials of 190 and 246 mV to reach 1000 mA cm\(^{-2}\) current density in alkaline and acidic electrolytes, respectively, along with exceptional 33 h durability at large current densities of 833 and 1112 mA cm\(^{-2}\) in 1.0 M KOH, and 50 h stability at 1000 and 1266 mA cm\(^{-2}\) in 0.5 M H\(_2\)SO\(_4\) electrolyte. Liang et al.\(^{52}\) delicately designed electrocatalysts with a core/shell heterostructure on Ni foam composed of the bimetallic alloy/oxyhydroxide of NiCo/NiCo-OH, which achieved ultralow overpotentials of 184 mV@500 mA cm\(^{-2}\) for HER under basic condition. Wu et al.\(^{52}\) adopted boron (B) doping for modifying the amorphization of crystalline NiCo LDH nanosheets and supported on NF (named as A-NiCo LDH/NF) (as illustrated in Fig. 6b), where it yielded the large current densities at small overpotentials (500 mA cm\(^{-2}\)@286 mV, and 1000 mA cm\(^{-2}\)@381 mV) and high durability in alkaline electrolyte even after 72 h. The amorphization of NiCo LDH was induced to form more oxygen defects by B-doping so that more unsaturated metal atoms were exposed on the surface, thereby boosting its HER performance. Shen et al.\(^{142}\) used metallic Ru to modify (Fe, Ni)(OH)\(_2\) nanosheet arrays supported on a conductive substrate of Ni foam (named as Ru/(Fe, Ni)(OH)\(_2\)/NF), with which a superhydrophilic surface and high conductivity ensured the rapid release of gases and efficient electron transportation and mass transfer at a high current density. This electrode needed an overpotential of only 152 mV to obtain a high 1000 mA cm\(^{-2}\) current density for HER, along with excellent stability over 20 h under a high current density of 500 mA cm\(^{-2}\) in basic electrolyte. Herein, (Fe, Ni)(OH)\(_2\) could enhance the H\(_2\)O dissociation considerably, and the concomitant recombination of adsorbed hydrogen atoms resulted in the formation of H\(_2\) with the assistance of Ru nanoparticles.

### 4.4 Transition metal oxides

Transition metal oxides (TMOs) always show excellent electrocatalytic OER properties. Unfortunately, the inferior water dissociation and undesirable H absorption capacity lead TMOs to be negative for efficient HER. Therefore, considerable attention has been paid to enhance the intrinsic electrocatalytic activity of such electrocatalysts. It is found that the rational anion dopant into TMOs seems to be an attractive strategy by regulating the charge distribution owing to the different atomic radius and electronegativity. Impressively, Ji et al.\(^{143}\) synthesized a nickel-based hollow dendritic self-supported electrode decorated with 2D nanosheets on both internal and external surfaces of a Titanium (Ti) plate by a two-step facile process of electrodeposition and oxidation etching, which simultaneously integrated the F dopant with oxygen vacancies. The obtained electrode achieved an outgoing electrocatalytic activity for HER under alkaline condition with an ultra-low overpotential of 13 mV to drive 10 mA cm\(^{-2}\) current density, and also long-time stability at current density of 500 mA cm\(^{-2}\) for 24 h. The Dong group\(^{144}\) doped phosphorus atoms into Fe\(_2\)O\(_4\) supported on iron foam (P-Fe\(_2\)O\(_4\)/IF) as hydrogen binding sites (as described in Fig. 7a) for alkaline HER, which showed the overpotential of 200 mV@409 mA cm\(^{-2}\) and excellent electrocatalytic stability at a high 500 mA cm\(^{-2}\) current density over 20 h. Herein, such an outstanding HER performance of P-Fe\(_2\)O\(_4\)/IF should be attributed to the inverse spinel Fe–O–P by the phosphorization process, which can provide an octahedral Fe site and O atom, thus enhancing the dissociation of two H\(_2\)O molecules to greatly accelerate the proton supply in the alkaline electrolyte.

Notably, since TMPs or TMSs are great prospective electrocatalysts for HER, they could be integrated with TMOs to create more active sites for the improvement of the electrocatalytic activity with a hierarchical nanostructure. For

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**Fig. 6** (a) Schematic illustration of the fabrication of the Cu-m/Cu-W/NiCo-LDH electrode. HER performance of Cu-m/Cu-W/NiCo-LDH and its HER activity in 1.0 M KOH and 0.5 M H\(_2\)SO\(_4\) electrolyte, respectively, and flexibility studies at different bending angles of the current collector. Reprinted with permission from ref. 140, copyright 2020, The Royal Society of Chemistry. (b) Schematic diagram of the composition, and SEM of the A-NiCo LDH electrocatalyst and HER activity in 1.0 M KOH electrolyte from ref. 52, copyright 2020, Elsevier.

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instance, Dai et al.\textsuperscript{145} developed N-doped MoO\(_2\) grown on conductive substrate of NF (denoted as N-MoO\(_2\)/Ni\(_3\)S\(_2\) NF) by annealing treatment and subsequently via the thermal reaction. Benefitting from the strong coupling interface between N-MoO\(_2\) and Ni\(_3\)S\(_2\), the absorption and dissociation of H\(_2\)O molecules were facilitated. The obtained N-MoO\(_2\)/Ni\(_3\)S\(_2\) NF displayed excellent HER performance in alkaline medium with a small potential of 517 mV at 1000 mA cm\(^{-2}\) and high current density of 500 mA cm\(^{-2}\) over 10 h. Furthermore, A-site Ba-deficient double perovskite PrBa\(_{0.94}\)CoO\(_{2.5}\) (PBO\(_{0.93}\)C) was used as a precursor for fabricating the PBO\(_{0.93}\)C-based double/simple perovskite heterostructure (PBO\(_{0.93}\)C-DSPH),\textsuperscript{146} which delivered a overpotential of 364 mV@500 mA cm\(^{-2}\) in 1.0 M KOH medium toward HER.

### 4.5 Transition metal alloys

Transition metal alloys have aroused great interests as the non-noble-metal HER electrocatalysts in alkaline condition, owing to their high intrinsic electrocatalytic activity.\textsuperscript{9,147} However, their application for the electrolysis of water at high current density has been rarely reported. Feng et al.\textsuperscript{148} first reported a MoNi\(_4\) alloy electrocatalyst embedded in MoO\(_2\) cuboids supported on NF (denoted as MoNi\(_4\)/MoO\(_2\)@Ni) (Fig. 7b) through reducing a NiMoO\(_4\) cuboid precursor at high temperature, where Ni atoms played the role of H\(_2\)O dissociation centres and Mo atoms had excellent H\(_2\) adsorption property. Therefore, the high cathodic current density of 500 mA cm\(^{-2}\) required an overpotential as low as 65 mV in a 5.3 wt\% KOH electrolyte at ambient temperature. Thereafter, a highly crystalline form of MoNi\(_4\) alloy was coated on scarp stainless steel wires (donated as MoNi\(_4\)/SSW)\textsuperscript{62} via a simple thermal decomposition method, which catalyzed the HER with a high current density of 1000 mA cm\(^{-2}\) at \(\eta = 161\) mV under the industrially used 5.0 M KOH electrolyte.

### 4.6 Transition metal nitrides

Currently, transition metal nitrides (TMNs) with high intrinsic activity and high stability have been extensively studied as a promising alternative of platinum due to their Pt-like electronic characteristics.\textsuperscript{149–151} Herein, the N atoms are introduced, which can not only change the d-band electron state density of the corresponding metal, but also reduce the d-band occupation shortages.\textsuperscript{41,151,152} Theoretical and experimental studies revealed that bimetallic nitride electrocatalysts exhibited superior electrocatalytic performance compared to the corresponding single compounds. Jiang et al.\textsuperscript{153} doped N into the MoNi alloy to prepare a Ni\(_{0.2}\)Mo\(_{0.8}\)N electrocatalyst supported on NF (named as Ni\(_{0.2}\)Mo\(_{0.8}\)N/NF) (Fig. 7c), which showed excellent HER electrocatalytic performance with an overpotential of 85 mV@500 mA cm\(^{-2}\) in 1.0 M KOH medium. The Sun group\textsuperscript{154} fabricated carbon-coated nickel molybdenum nitride with porous microrods by nitride treatment of an array of NiMoO\(_3\)xH\(_2\)O microrods supported on NF (NC/Ni\(_3\)Mo\(_3\)N/NF). DFT calculations strongly suggested that the Ni\(_3\)Mo\(_3\)N electrocatalyst possessed suitable \(\Delta G_{\text{H*}}\) values due to the metallic semiconductor structure with special electronic structure. As a result, the fabricated NC/Ni\(_3\)Mo\(_3\)N/NF electrode needed a small overpotential of 954 mV to obtain a high 1500 mA cm\(^{-2}\) current density in 1.0 M KOH solution, and also exhibited superstability at a large current density of 1100 mA cm\(^{-2}\) for 50 h toward HER.

## 5. Electrocatalysts for oxygen evolution reaction

### 5.1 Transition metal hydroxides/oxyhydroxides

Transition-metal-based hydroxide/oxyhydroxides materials have been widely studied for OER electrocatalysis.\textsuperscript{155} Among them, FeNi-based ones have been deeply investigated due to their high intrinsic activity. To meet the requirements of these electrocatalysts working at large current density condition, some strategies including constructing nanostructures and improving hydrophilic characteristics in order to accelerate the fast release of gas bubbles and expose more active sites, and controlling the ratio of Ni/Fe, have been proposed.\textsuperscript{156} For instance, Zhao et al.\textsuperscript{157} prepared amorphous, mesoporous nickel–iron (NiFe) hydroxide nanosheets supported on NF via a facile one-step electrodeposition process, which delivered the current densities of 500 and 1000 mA cm\(^{-2}\) at overpotentials of 240 and 270 mV, respectively. Liu et al.\textsuperscript{158} adopted a simple method to electrochemically deposit NiFe(oxo)hydroxide nanosheets with amorphous structure supported on a 3D partially exfoliated graphite foil substrate (EG). The electrode of NiFe \(2:1/\text{EG}-1.2\) V presented remarkable OER performance with an overpotential of only 251 mV to reach the high current...
density of 500 mA cm$^{-2}$ in alkaline medium, and prolonged to 48 h at the same current density. Especially, Li et al.\textsuperscript{139} prepared Ni/Fe(OH)$_2$ with a molar ratio of Ni(II):Fe(II)=9:1 coated on the stainless steel as the anode, which showed outstanding durability in alkaline electrolyte with no obvious increase in the overpotential at a current density of 1000 mA cm$^{-2}$, even with continuous operation over 10 days under 4.0 M NaOH electrolyte at room temperature. Wang et al.\textsuperscript{160} fabricated Ni(Fe)O$_{x}$ nanodecorated Ni(OH)$_2$ nanosheets array coated on the conductive substrate of a stainless steel mesh (SSM-NCs/Ni(Fe)O$_{x}$) (Fig. 8a), which also showed an outstanding OER performance in alkaline electrolyte. In particular, it only needed overpotentials of 280 and 303 mV to realize the high current densities of 500 and 1000 mA cm$^{-2}$, respectively, and only a slight attenuation in the electrocatalytic activity over 82 h water electrolysis at 500 mA cm$^{-2}$. The Sun group\textsuperscript{161} developed a well-aligned Ni–Fe hydroxide nanosheets array in situ grown on NF (named as NiFe–OH NS/NF) through spontaneous redox reaction (as shown in Fig. 8b). Herein, the tailored highly-oriented amorphous nanosheets with porous structure and the strong electronic interaction between Ni and Fe species endowed the NiFe–OH NS/NF to have high OER activity. Furthermore, a current density as high as 500 mA cm$^{-2}$ was well afforded at 292 mV. The Chen group\textsuperscript{162} synthesized Ni(OH)$_2$ nanosheets on NF by oxidative deposition at first, and then the obtained Ni(OH)$_2$ nanosheet-coated electrode was placed in a solution containing Fe$^{3+}$ to get an Fe-doped Ni(OH)$_2$ nanosheets-covered electrode (Ni(OH)$_2$–Fe/NF) with special nanostructure. This electrode delivered a current density of 1000 mA cm$^{-2}$ at an overpotential of only 330 mV, and maintained its electrocatalytic activity at 1100 mA cm$^{-2}$ stably for at least 10 h toward OER in 1.0 KOH solution.

Other self-supported transition metal hydroxide-based OER electrocatalysts have also been reported. For instance, Huang et al.\textsuperscript{163} prepared NiCoV–LTH (layered triple hydroxide) on NF for efficient OER. By adjusting the molar ratio of Co/V, it is found that the NiCoV–LTH/NF material could realize the conversion from single-crystal nanoneedles to polycrystalline nanosheets (Fig. 8c). In particular, the resultant NiCoV–LTH polycrystalline nanosheets-based electrode (denoted as P-NiCoV–LTH/NF) only needed ultralow overpotentials of 340 and 373 mV to reach the large current densities of 500 and 1000 mA cm$^{-2}$ in alkaline electrolyte, respectively, with strong stability over 20 h under 500 mA cm$^{-2}$. Jiang et al.\textsuperscript{164} constructed Co–Mn carbonate hydroxide (CoMn CH) nanosheet arrays with controllable morphology, as well as composition on NF. The optimized Co$_{3}$Mn$_{2}$CH/NF electrode exhibited unprecedented OER activity with a small overpotential of 462 mV@1000 mA cm$^{-2}$, as shown in Fig. 8d.

To further enhance the electrocatalytic performance of the transition metal-based hydroxide/oxyhydroxides materials, nanocomposite fabricating or cation doping has been used. In this regard, Fan et al.\textsuperscript{39} adopted NiFe–OH alloy nanowires arrays (with ∼2 nm surface NiO/NiFe(OH)$_2$ layer) to improve the reactants transportation. Remarkably, it was found that the high-curvature tips boosted the local electric field by finite element analysis, which induced higher concentration of hydroxide ions (OH$^-$) at the active sites, while the as-prepared electrode with the optimized alloy composition showed a low overpotential of 255 mV@500 mA cm$^{-2}$ (Fig. 9a). Specifically, ultrathin amorphous NiFe oxyhydroxide (shell)-anchored NiFe alloy nanowire (core) arrays (Ni$_1$Fe$_{1-x}$A$^+$H$_{x}$NAs) were further developed by chemical deposition method with the assistance of uniform magnetic field.\textsuperscript{75} Interestingly, it was found that this OER electrode yielded the current densities of 500 and 1000 mA cm$^{-2}$ with stability over 120 h at overpotentials as low as 248 and 258 mV, respectively, which were much lower than the reported ones (as shown in Fig. 9b). Zhao et al.\textsuperscript{165} rationally designed NiFe(oxy)hydroxide on NF-supported NiCo$_2$O$_4$ nanoflakes via hydrothermal method, and followed through an electrodeposition (Fig. 9c). Such an electrode displayed outstanding OER electrocatalytic activity with an overpotential of 340 mV@1200 mA cm$^{-2}$. Meanwhile, our group\textsuperscript{17} also fabricated CoNi (oxy)hydroxide on NF-supported flower-like CoFe$_2$O$_4$, which exhibited excellent OER electrocatalytic activity in alkaline electrolyte with an overpotential of 360 (±5) mV@1000 mA cm$^{-2}$, as presented in Fig. 9d. Furthermore, Zou et al.\textsuperscript{79} also presented amorphous Ni–Fe bimetallic hydroxide film on NF-supported Ni$_3$S$_2$ nanosheet array (denoted as Ni–Fe–OH@Ni$_3$S$_2$/NF) with through an interfacial reaction of Ni$_3$S$_2$.
in Fe$^{3+}$-containing aqueous solution, which showed overpotentials of 369 and 480 mV at 500 and 1000 mA cm$^{-2}$, respectively (Fig. 9e). Additionally, Qiu et al.\textsuperscript{166} demonstrated a highly efficient and robustness OER electrocatalyst with multilayer-stacked hybrid structure, in which vertical graphene nanosheets (VGSs), MoS$_2$ nanosheets, and layered FeCoNi hydroxides (FeCoNi(OH)$_x$) were successively grown on carbon fibers (CF/VGSs/MoS$_2$/FeCoNi(OH)$_x$) as cathode electrode, it only needed the overpotentials of 225 and 241 mV to attain 500 and 1000 mA cm$^{-2}$, respectively. Impressively, a highly crystallized Co-doped FeNi carbonate hydroxide nanosheet array was supported on NF (Co-FeNi CH/NF) (as displayed in Fig. 9f) through a one-step hydrothermal approach,\textsuperscript{167} which required a current density of 500 mA cm$^{-2}$@254 mV. Electrochemical analysis revealed that Co-doped into the trigonal FeNi CH crystal lattice could promote the OER electrocatalytic activity by regulating the electronic structure of the resultant electrocatalyst. Meanwhile, Chen et al.\textsuperscript{168} fabricated amorphous S-incorporated NiFe oxyhydroxide porous nanoclusters/NF composite electrode, which dramatically improved the OER activity with a ultralow overpotential of 260 mV and stably delivered 1000 mA cm$^{-2}$, along with a higher 3000 mA cm$^{-2}$ for OER in 1.0 M KOH medium.

5.2 Transition metal oxides

TMOs have been widely developed as OER electrocatalysts in alkaline environment due to their inexpensive, high abundance and excellent anticorrosion properties.\textsuperscript{169} During the electrocatalytic process, they are usually transformed into a hydroxyl oxide or hydroxide, and thereby show excellent OER performance. Notably, spinel type oxides (AB$_2$O$_4$, A and B are 3d transition metals) have attracted extensive interest for the electrolysis of water at high current density. For example, Ye et al.\textsuperscript{65} constructed the spinel Co$_{3}$Fe$_{3-x}$O$_{4}$ nanosheet/nanowire arrays homogeneously grown on commercial carbon paper for the electrocatalytic OER. It was found that the optimum one (Co$_{3.6}$Fe$_{0.4}$O$_{4}$NSs/CFP) displayed superior OER electrocatalytic activity and long-term stability (100-hours) at 1000 mA cm$^{-2}$ (Fig. 10a). Dong et al.\textsuperscript{170} developed an unique electrochemical corrosion engineering strategy to transform metal solid substrates (e.g., IF and NF) into Ni–Fe oxide films with high OER activity, rather than the direct utilization of metal ions precursors. The obtained film with an ultralow mass loading (0.22 mg cm$^{-2}$) delivered 500 mA cm$^{-2}$ at only 270 mV in 6.0 M KOH electrolyte at the temperature of 60 °C, and fulfilled the requirements (500 mA cm$^{-2}@300$ mV) for practical water splitting. The Zhang group\textsuperscript{171} reported a crystalline multi-metal (Co, Ni, Fe) nanosheets array (NSA) directly grown on NF (CoFeNiO-NSA/NF) enriched with oxygen vacancies by a simple electrosynthesis method, which served as stable and efficient OER electrocatalysts with the high current density of 500 mA cm$^{-2}@281$ mV. Most interestingly, López et al.\textsuperscript{74} prepared highly magnetic electrocatalysts (NiZnFe$_{2}$O$_{4}$), and found that the magnetic enhancement improved the intrinsic activity by about 40% to reach over 1000 mA cm$^{-2}$ at low overpotentials. In this case, the magneto-enhancement appeared to be proportional to the magnetic nature of the catalysts, and was particularly useful for the preparation of highly magnetic iron-nickel oxide electrocatalysts.

More research studies are still necessary for enhancing the activity and stability of these TMOs-based electrocatalysts to realize the commercial application. For example, the construction of hybrid electrocatalysts could synergize the advantages of various active components and satisfy the needs of commercial OER electrocatalysts. Meanwhile, creating nano-interface from hybrid electrocatalysts has also been considered as a
good strategy to boost the electrocatalytic activity of TMOS since the rate of charge transfer could be enhanced between different components at the interface. In this regard, a 3D self-supported NiCeO$_x$@NiFeO$_y$ electrocatalyst with porous network was coated on NF (denoted as NiCe@NiFe/NF-N) through a facile two-step electrodeposition way by the Li group, which required an ultralow overpotential of 359 mV to attain 1000 mA cm$^{-2}$ and also demonstrated excellent stability (Fig. 10b). Furthermore, the introduction of foreign metals could regulate the electronic structure of the electrocatalyst to optimize the adsorption free energy of active sites, and further improved the OER electrocatalytic activity of TMOS. For instance, Zhang et al. prepared S-doped amorphous NiFe$_2$O$_4$/Ni$_x$Fe supported on a Ni wire composite electrode, which showed outstanding OER performance with small overpotentials of 285 mV to achieve long-term stable current density of 500 mA cm$^{-2}$ for 20 h toward OER in an alkaline electrolyte. Li et al. constructed spinel-type ternary multicomponent electrocatalyst with porous hierarchical architecture grown on NF, as shown in Fig. 10c. It displayed good electrocatalytic activity for OER in the practical industrial electrolyte (30 wt% KOH solution), and just required an ultra-small overpotential of 250 mV to reach the large current density of 1000 mA cm$^{-2}$. In particular, this electrode could retain long-term catalytic durability over 100 h at 1500 mA cm$^{-2}$.

5.3 Transition metal phosphides

TMPs have received particular interest as the OER electrocatalysts in alkaline electrolyte due to their noble metal-like electrocatalytic properties. For example, Zhang et al. constructed a Co–Fe Prussian blue analogue grown on NF, and further phosphorized it to synthesize a Fe-CoP electrocatalyst (named as Fe-CoP/NF). It displayed an outgoing OER performance with the current densities of 500 and 1000 mA cm$^{-2}$ at the overpotentials of 295 and 428 mV, respectively. Impressively, unlike in HER, the surfaces of TMPs are usually changed to metal hydroxyl oxides, which can play the role as the active centre under an alkaline solution during the OER process. Meanwhile, because it is difficult to avoid the exposure to air, the oxidation of TMPs often occurs in air. Therefore, the final electrocatalyst is always the metal phosphates covered with oxides layer. As such, the electrocatalysts with multi-component of transition metal oxides and mixed phosphides tend to exhibit higher electrocatalytic activity, when compared with those single component electrocatalysts and are more easily applied in practice. Based on this consideration, Pan et al. designed a novel ternary hybrid electrocatalyst with 3D structure comprising Fe$_2$O$_3$ and Ni$_2$P/Ni (PO$_3$)$_2$ grown on NF (denoted as Fe$_2$O$_3$@Ni$_2$P/Ni(PO$_3$)$_2$/NF), which demonstrated superior OER performance to reach the large electrocatalytic current densities of 500 and 1000 mA cm$^{-2}$ at the small overpotentials of 340 and 370 mV, respectively. In particular, using in situ Raman spectroscopy analysis, it was found that the FeOOH and NiOOH species could be the real active phases for those catalysts (as shown in Fig. 11a). Furthermore, an electrocatalyst of Co$_3$O$_4$/Fe$_{0.33}$Co$_{0.66}$P interface nanowires on NF (named as Co$_3$O$_4$/Fe$_{0.33}$Co$_{0.66}$P/NF) was fabricated. Benefiting from the low oxidation energy barrier by the active Co- and O-sites, this electrode showed an overpotential of merely overpotential of 291 mV@800 mA cm$^{-2}$ for OER in alkaline medium. Meanwhile, Ren et al. reported a robust self-supported OER electrocatalyst consisting of Fe (PO$_3$)$_2$/Ni$_2$P on conductive NF that is commercially available in large scale. From XPS analysis (Fig. 11b), it was found that this electrocatalyst was associated with the in situ generated Ni–Fe oxide/hydroxide and Fe oxyhydroxide on the surface of electrocatalyst during the OER process in alkaline medium. As a result, it yielded current densities of 500 and 1705 mA cm$^{-2}$ at overpotentials of only 265 and 300 mV, respectively, with excellent durability.

5.4 Transition metal sulfides

Similar to TMPs, TMSs also have attracted considerable attention, which are always combined with other compounds or doped by other metal species to enhance the OER activity and applied in the large current density condition. For instance, Sun et al. found that Fe-doped Ni$_3$S$_2$ particles with 11.8%...
Fe-content coated on NF (Fe-Ni3S2/NF) with a hydrothermal way can serve as a highly active and robust OER electrode, which required small overpotentials of 238 and 269 mV to reach the high current densities of 500 and 1000 mA cm$^{-2}$, respectively. The Zhang group$^{179}$ in situ grew CuS-Ni3S2 with CuNi alloy as a precursor on NF (CuS-Ni3S2/CuNi/NF), which only needed low overpotentials of 444 and 510 mV to realize the large current densities of 500 and 1000 mA cm$^{-2}$, respectively. Li$^{180}$ et al. demonstrated a novel, high wettability water-oxidation electrocatalyst composed of amorphous NiFe layer and CoS film on the commercial Ni foam (CoS@NiFe/NF) by a two-step electrodeposition synthetic path. Benefiting from the strong interactions between the NiFe layer and CoS film, enlarged surface active sites and enhanced wettability, the CoS@NiFe/NF electrode exhibited outstanding OER performance at the current density of 1000 mA cm$^{-2}$ and needed merely 330 mV, and excellent water oxidation stability and corrosion resistance for at least 24 h under such current condition in 30 wt% KOH electrolyte.

6. Bifunctional electrocatalysts for overall water splitting

To date, various low-cost HER or OER electrocatalysts with superior performances have been developed. However, there are still many challenges to assemble two-electrode reaction pairs in the same electrolyte for practical application. Notably, exploring bifunctional electrocatalysts that can catalyze either HER or OER effectively is desired to simplify the electrolyzer design, avoiding the detrimental crossover effect of different electrocatalysts, and greatly decreasing the fabrication and operational costs of devices. Therefore, searching self-supported bifunctional electrocatalysts for overall water splitting (OWS) application under the large current density in the commercialization of water electrolyzers has become a hotspot nowadays.

6.1 Transition metal oxides

Owing to the strong hydrolysis ability with various valence states, TMOs have high intrinsic electrocatalytic activity for both HER and OER. In this regard, Yu et al.$^{18}$ hydrothermally grew K$_2$Fe$_4$O$_7$ nanocrystals (nano-KFO) on NF (denoted nano-KFO/NF), which were used as bifunctional electrocatalysts for both cathode and anode to assemble a water electrolyzer (Fig. 12a). It operated over 60 h at 1500 mA cm$^{-2}$ with cell voltages of 2.01 V in 1.0 M KOH solution and 1.89 V in 10.0 M KOH solution, strongly revealing that this bifunctional electrocatalyst had great potential for large-scale hydrogen production. Notably, it should be pointed out that the fabrication of electrocatalysts with a heterostructure could completely exert the performance of each component to obtain outstanding bifunctional electrocatalysts for OWS, especially when operated at a large current density. However, only a few complexes were found to have high stability. From this perspective, Lu et al.$^{181}$ adopted a facile one-step passivator-modulated nickel foam (NF) anodization process with good mixing ability to prepare the NiO/α-Fe$_2$O$_3$@NF electrode. The water electrolytes...
zer using it as both cathode and anode for OWS showed excellent electrocatalytic activity with a low working cell voltage of 1.99 V@500 mA cm$^{-2}$, along with outstanding stability for 24 h continuous operation under this condition. Remarkably, a bifunctional hybrid RuO$_2$–NiO electrocatalyst on NF was prepared by Yang et al., which only required a cell voltage of 1.66 V@500 mA cm$^{-2}$ when assembled in a water electrolyzer. It realized continuous electrolysis for 2000 h@1000 mA cm$^{-2}$, strongly suggesting great potential for practical application. Meanwhile, the Yin group developed a self-supported amorphous CoO$_x$ decorated crystalline RuO$_2$ nanosheet catalyst on NF (CoO$_x$-RuO$_2$/NF) by a hydrothermal method with an annealing process, which showed high performance for both OER and HER with overpotentials of 420 and 215 mV@1500 mA cm$^{-2}$, respectively, and 48 h durability at 1500 mA cm$^{-2}$ in alkaline electrolyte (as displayed in Fig. 12b).

Generally, TMOs are good electrocatalysts for OER in alkaline electrolytes, whereas transition metal-based LDHs and phosphides/sulfides are efficient electrocatalysts for HER. Moreover, the heteroatom-doping of carbon-based materials can avoid the metal dissolution. As such, it is expected to integrate the advantages of HER and OER electrocatalysts for the construction of novel heterostructures to enhance the overall electrochemical water-splitting performance under the large current density. In this regard, Wu et al. prepared a NiFe$_2$O$_4$ nanoparticles/NiFe-LDH nanosheet heterostructure array on NF, and it was used as both the anode and cathode electrocatalysts for OWS. It demanded a small voltage potential of 1.932 V to drive 500 mA cm$^{-2}$. Sun et al. fabricated hierarchical transition bimetal oxides/sulfides heterostructure arrays interacting 2D MoO$_x$/MoS$_2$ nanosheets attached to 1D NiO$_x$/Ni$_3$S$_2$ nanorods by an oxidation/hydrogenation-induced surface reconfiguration strategy on the NF substrate (NiMoO$_x$/NiMoS/NF), as shown in Fig. 12c. It was used to assemble the two-electrode cell with the industrially relevant current densities of 500 and 1000 mA cm$^{-2}$ at low cell voltages of 1.60 and 1.66 V, respectively, at room temperature in alkaline electrolyte. Under these conditions, it achieved notable long-term stability for 500 h continuous operation under 500 mA cm$^{-2}$. Wang et al. prepared a Co$_{0.8}$Ru$_{0.2}$O$_x$@NC composite with the N-doped carbon (NC) shell, which exhibited excellent electrocatalytic activities in an alkaline electrolyte with a small cell voltage of 1.86 V@500 mA cm$^{-2}$. Impressively, the N-doped carbon-coated Ni-MoO$_2$ nanowire heterostructured electrocatalyst...
lyst supported on NF was fabricated to improve both HER and OER activities, which showed low overpotentials for HER (304 mV) and OER (400 mV)@2000 mA cm$^{-2}$ (Fig. 12d), and under a multicurrent-process condition (10–1500 mA cm$^{-2}$) maintained for 340 h without obvious attenuation. Yin et al. also constructed self-supported Ni nanoparticles-encapsulated ultra-thin N-doped-graphene coupling with MoO$_2$ nanosheets on NF. It was used as both cathode and anode, working for over 196 h@1000 mA cm$^{-2}$ with slight changes. Most interestingly, a new approach of 3D-printed Ni (3DPNi) electrode decorated with carbon-doped NiO was reported by the Wu group, which achieved the high current density of 1000 mA cm$^{-2}$ at HER and OER overpotentials of 245 and 425 mV, respectively, in basic electrolyte.

### 6.2 Transition metal hydroxides

Transition metal hydroxides are another a class of advanced OER electrocatalyst, which also exhibited highly efficient performance for catalyzing HER. For example, in situ growing of NiFe-LDH on a 3D hierarchical nickel mesh (NiFe/Ni/Ni) by electrodeposition method as shown in Fig. 13a is a representative example. When it was used as both cathode and anode for alkaline OWS, a current density of 500 mA cm$^{-2}@1.96$ V was achieved. Additionally, the water electrolyzer exhibited superior stability even at 500 mA cm$^{-2}$ over 200 h under industrial environment of 6.0 M KOH electrolyte. Besides LDHs, the bifunctionality of transition metal oxyhydroxides for water splitting was recently reported. For instance, Yu et al. synthesized amorphous mesoporous NiFe (oxy)hydroxide ([Ni, Fe]OOH) coated on the NF as the electrocatalyst for both cathode and anode, by which current densities of 500 and 1000 mA cm$^{-2}$ at the cell voltages of 1.586 and 1.657 V, respectively, were achieved. The Hou group developed crystalline a-Ni (OH)$_2$ with amorphous reduced FeOOH (r-FeOOH) heterostructure grown on NF (r-FeOOH/α-Ni(OH)$_2$/NF). Benefitting from the strong coupling effects between r-FeOOH and α-Ni (OH)$_2$, it delivered the low cell voltages of 1.62 and 1.66 V to obtain 1000 and 1500 mA cm$^{-2}$, respectively, as well as robust stability over 10 h@1500 mA cm$^{-2}$ in alkaline electrolyte. Currently, several effective strategies, mainly including the rational design of architecture and integration with excellent electrical conductivity materials, have been proposed to further promote bifunctional activities of NiFe-based electrocatalysts in the practical electrolysis of water. Along this line, the Yu group fabricated novel 3D bulk electrocatalysts with core-shell nanostructures, in which few-layer NiFe LDH nanosheets were deposited on the Cu nanowire core and further supported on the Cu foam toward OWS. Recently, MXenes have attracted significant attention in vast fields because they have excellent conductivity associated with high electron density of states near the Fermi level, hydrophilicity property and rich surface chemistry enabled by grafted chemical groups. As such, by using the 3D MXene frame, they not only facilitate the mass/charge transportation across the catalyst, but also enhance the water adsorption/activation on the catalyst. An alkaline electrolyzer with NiFe-LDH/MXene/NF as the anode and cathode (Fig. 13b) can be steadily driven at a low cell voltage of 1.75 V@500 mA cm$^{-2}$, while transition metal nitrides are also considered as a class of promising candidates for supporting materials owing to their superior electrical conductivity, good stability, and superior anti-corrosion performance. Pang et al. reported a hybrid bifunctional electrocatalyst with amorphous NiFe LDH nanosheets and metallic Ni$_3$N microsheet arrays on NF for OWS. With the advantage of the intensive coupling and synergistic effect of the NiFe LDH and the Ni$_3$N microsheet arrays with superhydrophilic/superaerophobic properties (Fig. 13c), the alkaline water electrolyzer used as a bifunctional electrocatalyst exhibited a low cell voltage of 1.80 V@500 mA cm$^{-2}$ with at least 100 h durability.

### 6.3 Transition metal phosphides

As discussed above, many TMPs show excellent HER or OER activity at high current density, but only a few can perform well...
for both. Thus, it is desired to fabricate bifunctional TMPs-based electrocatalysts working in the same electrolyte for large-scale applications. A notable example was Co–P film prepared by electrochemical anodization, followed with a thermal annealing process.195 When it was utilized as the bifunctional electrocatalysts for OWS, it only required a cell voltage potential of 1.98 V@1000 mA cm$^{-2}$ and extraordinary stability of 4000 h, indicating a promising application in industrial alkaline water electrolysis. Very recently, there has been a focus on heterogeneous bimetallic phosphides since they exhibited higher activities as the bifunctional electrocatalysts due to their various structural and chemical advantages. Using the straightforward strategy, the NF-supported NiCoP nanorod array electrode (NiCoP/NF) was prepared for HER and OER,196 which showed excellent bifunctional properties with the overpotentials of 180 and 365 mV@500 mA cm$^{-2}$, respectively, at the corresponding cell voltage of only 1.83 V. Wei et al.197 used the CoFe bimetal-organic framework (CoFe-MOF TPAs/Ni) to fabricate macroporous Fe-rich CoFeP triangular plate arrays (macroporous CoFeP TPAs/Ni) for both HER and OER electrocatalysts. Meanwhile, driving HER and OER current densities of 900 and 700 mA cm$^{-2}$ demanded overpotentials of only 263 and 335 mV, respectively. Ren et al.198 constructed iron and dinickel phosphides on NF (FeP/Ni$_2$P/NF), which showed excellent performance for OWS at 500 mA cm$^{-2}$ in alkaline seawater at a cell voltage of 2.004 V, together with robust durability in 40 h. Huang et al.200 prepared a seamless integrated electrode (Fe$_2$P–Co$_3$P/CF), where Co foam (CF) acted as either the collector or the cobalt source. Impressively, when Fe$_3$P–Co$_3$P/CF was used as both anode and cathode at ambient temperature (25 °C) and industrial-like temperatures (65 °C), the operating voltages were as low as 1.87 and 1.71 V@500 mA cm$^{-2}$, respectively, together with over 300 h long-term durability.

For most TMPs, the real active sites could be altered in the HER and OER electrocatalysis. For example, Deng et al.201 embedded Fe-doped Ni$_3$P nanoparticles in carbon nanotubes using the MOF arrays precursor on NF (Fe-doped Ni$_3$P/C–NF) as both OER and HER electrodes, and extraordinary performance was demonstrated for the water electrolysis, which required only a cell voltage potential of 1.66 V@500 mA cm$^{-2}$. Post-elec-

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Fig. 14 (a) Schematic illustration and SEM of the Ni$_3$P–Fe$_2$P electrocatalyst, and its electrocatalytic performance for overall water splitting in 1.0 M KOH and alkaline seawater from ref. 199, copyright 2020, Wiley-VCH. (b) Schematic illustration of the Fe-doped Ni$_3$P/C–NF electrode and its electrocatalytic performance for overall water splitting in alkaline electrolyte, and XRD patterns of post-electrolysis Fe$_2$–Ni$_2$P/C for OER and HER from ref. 200, copyright 2019, American Chemical Society. (c) Schematic illustration of the synthesis of Ni$_3$Co$_3$S$_2$/NiS$_2$/NF and its electrocatalytic performance for OER and HER in 1.0 M KOH from ref. 203, copyright 2017, Elsevier. (d) Schematic illustration of the control of the morphology and phase evolution of the (Ni–Fe)S$_3$/NiFe(OH)$_3$ from ref. 78, copyright 2019, Elsevier.
trosis characterizations and DFT calculations revealed that Fe-doped Ni₃P species were mostly retained after a prolonged HER process, but they were in situ converted to Fe/P-doped \( \gamma \)-NiOOH during the OER process (Fig. 14b), serving as the actual OER active sites with high activity. Thus, the in situ generated transition metal phosphides/transition metal hydroxides heterojunction structure played an important role in superior electrocatalytic activity for both OER and HER. Similarly, Li et al.\(^{202}\) prepared a Ni₃P/MnOOH electrocatalyst grown on 3D NF substrate by electrodeposition, which also displayed high electrocatalytic activity with a small overpotential of 268 mV and 341 mV@1000 mA cm\(^{-2}\) for HER and OER in a simulated industrial environment, respectively.

6.4 Transition metal sulfides

TMSs are also widely investigated HER/OER bifunctional electrocatalysts. It is well known that most TMSs (the representative is the layered MoS₂) show high HER electrocatalytic activity, but poor OER activity. Remarkably, the formation of rich transition metal O/OH species with a phase transformation from the TMSs species have been noticed during the OER process. Therefore, in order to use TMSs for overall water splitting, a common approach of hybridizing 3D transition metal sulfides with oxides and hydroxides has been widely adopted to construct novel bifunctional TMs-based electrocatalysts. In this regard, the Zou group\(^{203}\) decorated Ni₃Co₁₋ₓS₄ nanoparticles on Ni₃S₂ nanosheet arrays grown on NF (Ni₃Co₃₋ₓS₄/Ni₃S₂/NF) via a partial cation exchange reaction between cobalt(II) ions and NF-supported Ni₃S₂ nanosheet arrays, as shown in Fig. 14c. The as-synthesized electrode displayed low overpotentials of 432 and 475 mV@500 mA cm\(^{-2}\) for HER and OER, respectively. The Hou group\(^{68}\) prepared a self-supported 3D ultrasmall zero-valent iron coupled nickel sulfides nanosheets (Fe\(^{0}\)-Ni₃S₂) hybrid on NF (denoted as Fe\(^{0}\)-Ni₃S₂/NF) by a robust one-step gas–solid reaction as a bifunctional electrolyzer for OWS with potentials of 2.4 and 3.0 V to obtain high current densities of 500 and 1000 mA cm\(^{-2}\), respectively. Meanwhile, the Liu group\(^{72}\) coupled micro/nanostructured Co with amorphous Mo/S to achieve CoMoSₓ chalcogel onto NF (CoMoSₓ/NF) with superhydrophilic and superaerophobic properties as the bifunctional electrocatalyst, by which the OWS device delivered 500 mA cm\(^{-2}\)@1.89 V and presented outstanding durability for 100 h. In addition, Li et al.\(^{78}\) fabricated a hierarchically amorphous (Ni-Fe)Sₓ/NiFe(OH)ₓ film on NF via a facile electrodeposited approach, as displayed in Fig. 14d, and used it as the cathode and anode, which only needed 2.2 V@1200 mA cm\(^{-2}\) with excellent 50 h stability at 1000 mA cm\(^{-2}\) under an industrial condition.

Recent studies have demonstrated that element doping (e.g., S, Fe, Sn) could not only effectively alter the electronic structure of TMSs, but also tune the electron density for regulating the H* and O*, OOH* adsorption free energies to achieve high HER and OER performances. Zhang et al.\(^{204}\) synthesized a series of S-doping highly porous Co–S films in situ grown on NF (Co–S/NF), and found that an optimal S doping electrode (denoted as Co–S–50/NF) assembled a water electrolyzer exhibiting superior catalytic activity and robust nature with cell potentials of 2.08 V to reach 500 mA cm\(^{-2}\) in 1.0 M KOH electrolyte, and 1.72 V to achieve 500 mA cm\(^{-2}\) in 30 wt% KOH electrolyte at 353 K for over 150 h. Meanwhile, Yuan et al.\(^{205}\) reported tin (Sn) doped Ni₃S₂ nanosheets grown on NF (Sn–Ni₃S₂/NF) by a simple hydrothermal process, which displayed notably active and excellent durability for OWS with a cell voltage of 1.95 V@500 mA cm\(^{-2}\) for over 14 h.\(^{51}\)

6.5 Transition metal nitrides

Despite the significant progress of TMNs exhibiting satisfactory electrocatalytic activity for either HER or OER with high corrosion-resistance, electrically conductivity, and mechanically strength, their overall water splitting electrocatalytic activities still need to improve, especially for large current density operation. In order to boost the bifunctional catalytic activities, engineering heterostructures containing coupling with functionalized species by synergistic effect has been regarded as a universal route. Along this direction, Chen and co-workers\(^{206}\) prepared a novel superhydrophilic Co₃N–CeO₂ hybrid nanosheet array on a graphite plate (named Co₃N–CeO₂/GP) (Fig. 15a). An alkaline electrolyzer using this binder-free electrode as bifunctional electrocatalysts needed a cell voltage of 1.99 and 2.28 V to reach the high current densities of 500 and 1000 mA cm\(^{-2}\), respectively, for 50 h without conspicuous decay. What is more, it is a big challenge to fabricate bifunctional electrocatalysts for electrolysis of seawater since most of the transition metal-based electrocatalysts during the OER process are not stable in the presence of chloride anions (~0.5 M). Notably, the Yu group\(^{207}\) rationally designed a 3D core–shell TMNs electrode, i.e., NiFeN nanoparticles, which was uniformly decorated on the efficient HER electrocatalyst of NiMoN nanorods grown on NF. The industrial current densities of 500 and 1000 mA cm\(^{-2}\) at low voltages of 1.608 and 1.709 V, respectively, were achieved for overall alkaline seawater splitting at 60 °C. Most significantly, it was found that thin amorphous layers of NiFe oxide and NiFe hydroxide were in situ generated on the outer NiFeN nanoparticles during OER catalysis, as presented in Fig. 15b, which were beneficial for the selective OER electrocatalytic activity, and favored for the resistance to chloride anion corrosion. This is a great finding in the large-scale hydrogen production from seawater electrolysis.

6.6 Transition metal alloy

Recently, transition metal alloys have been widely explored as the active electrocatalysts for both OER and HER under alkaline condition due to the optimized \( \Delta G_{\text{H*}} \) and high intrinsic electrocatalytic activity. Based on the “volcano plot”, designing a multicomponent alloy with optimized surface chemistry is an ideal way to fabricate bifunctional electrocatalysts for OWS. In this regard, the Lu group\(^{208}\) created NiFeMo alloy inverse-opals on NF as both cathode and anode for alkaline OWS, achieving an ultralow cell voltage of 1.75 V@500 mA cm\(^{-2}\) and retaining stable operation for at least 50 h. Such outgoing OWS performance could be ascribed to the increased number of...
active sites by the construction of inverse-opal structure and the enhanced intrinsic activities due to the synergistic effect between the three-constituent elements (as described in Fig. 15c). Kang et al.\textsuperscript{209} synthesized a nanoporous NiMnFeMo alloy (np-NiMnFeMo), which also showed ultrahigh catalytic activity with a large current density of 1000 mA cm\textsuperscript{-2}@290 mV for HER and @570 mV for OER. Recently, the N-doped graphene-decorated NiCo alloy combining with mesoporous NiCoMoO nano-sheet grown on 3D NF (NiCo@C-NiCoMoO/NF) was also prepared as the bifunctional catalyst for OWS, which displayed outstanding electrocatalytic activity and needed a small cell voltage potential of 1.90 V@1000 mA cm\textsuperscript{-2} and maintained stability for 43 h under 6.0 M KOH electrolyte at 60 °C.\textsuperscript{210}

7. Conclusions and outlook

It is particularly desirable to design and fabricate self-supported electrocatalysts with low cost, earth abundance, high activity and robustness for the application of electrocatalytic water splitting at high current density. Unfortunately, most of the reported electrocatalysts are always conducted at a lower current density range (<300 mA cm\textsuperscript{-2}), which hardly satisfy the industrial requirements. In this review, we specially summarized the recently reported results about the self-supported electrocatalysts for HER, OER, and bifunctional electrocatalysts for OWS at large current density, which mainly include transition metal oxides, hydroxides, phosphates, sulfides, nitrides and alloy with excellent durability at large current densities of up to 500 or 1000 mA cm\textsuperscript{-2}, meeting the commercial criteria for alkaline water electrolysis. Those fabrication methods, relevant testing conditions and potential conversion in exploring electrocatalysts suitable for the high current density condition are described in detail. Table 1 compares the electrochemical performances of the corresponding representative HER, OER and OWS electrocatalysts discussed herein.

Generally, the principles and main strategies for the design of effective self-supported transition metal-based electrocatalysts operating at the high current density include: (i) doping...
Table 1 Comparison of the electrocatalytic activities of various self-supported transition metal electrocatalysts for HER, OER, and OWS under high current density

<table>
<thead>
<tr>
<th>Electrocatalysts</th>
<th>Electrolyte</th>
<th>Overpotential (mV) @current density (mA cm(^{-2}))</th>
<th>Stability time (h)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HER</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>NiCoP/CF</td>
<td>1.0 M KOH</td>
<td>281@550</td>
<td>16</td>
<td>123</td>
</tr>
<tr>
<td>Co(P)(_2)O(_4)</td>
<td>1.0 M KOH</td>
<td>—@800</td>
<td>—</td>
<td>124</td>
</tr>
<tr>
<td>Ni(_3)P/NP</td>
<td>1.0 M KOH</td>
<td>368@1500</td>
<td>—</td>
<td>70</td>
</tr>
<tr>
<td>Ni(_3)P/PNiP/(_2)NF</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>—@1200</td>
<td>24</td>
<td>67</td>
</tr>
<tr>
<td>F-Co(_3)P/Fe(_2)P/IF</td>
<td>6.0 M KOH</td>
<td>292.2@2000</td>
<td>10</td>
<td>125</td>
</tr>
<tr>
<td>Ni(<em>{11-\gamma})Mo(</em>{2\alpha})P/(_\gamma)P/NF</td>
<td>1.0 M KOH</td>
<td>294@1000</td>
<td>—</td>
<td>126</td>
</tr>
<tr>
<td>Co(<em>{1.9})Mo(</em>{2.3})P(_{2.7})/NF</td>
<td>1.0 M KOH</td>
<td>165@1000</td>
<td>20</td>
<td>127</td>
</tr>
<tr>
<td>MoS(_2)/CNF</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>450@1000</td>
<td>—</td>
<td>131</td>
</tr>
<tr>
<td>MoSGMoS</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>384@1300</td>
<td>—</td>
<td>132</td>
</tr>
<tr>
<td>a-MoS(_2)/CC</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>250@500</td>
<td>—</td>
<td>133</td>
</tr>
<tr>
<td>MoS(_2)/Mo(_2)C</td>
<td>1.0 M KOH</td>
<td>220@1000</td>
<td>24</td>
<td>134</td>
</tr>
<tr>
<td><strong>OER</strong></td>
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<td></td>
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</tr>
<tr>
<td>NiFe/NF</td>
<td>10.0 M KOH</td>
<td>270@1000</td>
<td>—</td>
<td>157</td>
</tr>
<tr>
<td>NiFe(ox)hydroxide/EG</td>
<td>1.0 M KOH</td>
<td>251@500</td>
<td>48</td>
<td>158</td>
</tr>
<tr>
<td>NiFe(OH)(_2)/SS</td>
<td>4.0 M NaOH</td>
<td>—@1000</td>
<td>240</td>
<td>159</td>
</tr>
<tr>
<td>SSM-NCs/NiFeO(_4)H(_2)</td>
<td>1.0 M KOH</td>
<td>280@500</td>
<td>82</td>
<td>160</td>
</tr>
<tr>
<td>NiFe-OH NS/NF</td>
<td>1.0 M KOH</td>
<td>292@500</td>
<td>—</td>
<td>161</td>
</tr>
<tr>
<td>Ni(OH)(_2)/Fe/NF</td>
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<td>330@1000</td>
<td>—</td>
<td>162</td>
</tr>
<tr>
<td>P-NiCo-V-LDH/NF</td>
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<td>340@500</td>
<td>25</td>
<td>163</td>
</tr>
<tr>
<td>CoMnO(_2)/NF</td>
<td>1.0 M KOH</td>
<td>462@1000</td>
<td>—</td>
<td>164</td>
</tr>
<tr>
<td>NiO/NiFe(OH)(_2)</td>
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<td>—</td>
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<tr>
<td>NiFe(_{0.2})/AHNA</td>
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<td>120</td>
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<tr>
<td>NiFe/NiCoO(_4)/NF</td>
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<td>340@1200</td>
<td>—</td>
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</tr>
<tr>
<td>CoNi/CoFeO(_2)/NF</td>
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<td>360 ± 5@1000</td>
<td>—</td>
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</tr>
<tr>
<td>NiFe-OH@Ni(_{2})S(_2)/NF</td>
<td>30 wt% KOH</td>
<td>469@1000</td>
<td>50</td>
<td>79</td>
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<tr>
<td>CF/VSs/MoS(_2)/FeCoNi(OH)(_2)</td>
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<td>—</td>
<td>166</td>
</tr>
<tr>
<td>CoFeNiCH/NF</td>
<td>1.0 M KOH</td>
<td>254@500</td>
<td>—</td>
<td>167</td>
</tr>
<tr>
<td>S(Ni,Fe)(OH)/NF</td>
<td>1.0 M KOH</td>
<td>250@500</td>
<td>50</td>
<td>168</td>
</tr>
<tr>
<td>Co(<em>{3})Fe(</em>{2})O(_2)/NSs/CFP</td>
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<td>—@1000</td>
<td>—</td>
<td>65</td>
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<tr>
<td>NiFe oxide/NF</td>
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<td>300@500</td>
<td>10</td>
<td>170</td>
</tr>
<tr>
<td>CoFeNiO-NiSA/NF</td>
<td>1.0 M KOH</td>
<td>298@1200</td>
<td>—</td>
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</tr>
<tr>
<td>NiZnFeO(_2)</td>
<td>1.0 M KOH</td>
<td>—@1000</td>
<td>—</td>
<td>74</td>
</tr>
<tr>
<td>NiCeNiFe/NF-N</td>
<td>1.0 M KOH</td>
<td>359@1000</td>
<td>20</td>
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</tr>
<tr>
<td>S-NiFeO(_2)/NiFe</td>
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<td>285@500</td>
<td>30</td>
<td>173</td>
</tr>
<tr>
<td>Co-NiO-Fe(_{2})/NiCoO(_4)</td>
<td>30 wt% KOH</td>
<td>270@1500</td>
<td>100</td>
<td>174</td>
</tr>
<tr>
<td>Fe-CoP/NF</td>
<td>1.0 M KOH</td>
<td>428@1000</td>
<td>30</td>
<td>16</td>
</tr>
<tr>
<td>Fe(_3)O(_3)/NiP/Ni(Po)(_3)/NF</td>
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<td>370@1000</td>
<td>—</td>
<td>175</td>
</tr>
<tr>
<td>Co(<em>3)O(<em>3)/Fe(</em>{0.33})Co(</em>{0.66})/P/NF</td>
<td>1.0 M KOH</td>
<td>291@800</td>
<td>—</td>
<td>176</td>
</tr>
<tr>
<td>Fe(Po)(_3)/NiP/P/NF</td>
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<td>300@1705</td>
<td>—</td>
<td>177</td>
</tr>
<tr>
<td>Fe-Ni(_{2})/NF</td>
<td>30 wt% KOH</td>
<td>269@1000</td>
<td>—</td>
<td>178</td>
</tr>
<tr>
<td>CuS-Ni(_{2})/CuNi/NF</td>
<td>1.0 M KOH</td>
<td>510@1000</td>
<td>—</td>
<td>179</td>
</tr>
<tr>
<td>CoS@NiFe/NF</td>
<td>30 wt% KOH</td>
<td>330@1000</td>
<td>24</td>
<td>180</td>
</tr>
<tr>
<td><strong>OWS</strong></td>
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<td></td>
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</tr>
<tr>
<td>Nano-KFO/NF</td>
<td>1.0 M KOH</td>
<td>2.01 V@1500</td>
<td>&gt;60</td>
<td>18</td>
</tr>
<tr>
<td>Nano-KFO/NF</td>
<td>1.0 M KOH</td>
<td>1.89 V@1500</td>
<td>—</td>
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</tr>
<tr>
<td>NiO/α-Fe(_{2})O(_3)/P/NF</td>
<td>1.0 M KOH</td>
<td>1.99 V@500</td>
<td>24</td>
<td>181</td>
</tr>
<tr>
<td>RuO(_2)/NiO/NF</td>
<td>1.0 M KOH</td>
<td>—@1000</td>
<td>2000</td>
<td>182</td>
</tr>
<tr>
<td>CoO(_2)/RuO(_2)/NF</td>
<td>1.0 M KOH</td>
<td>—@1500</td>
<td>48</td>
<td>183</td>
</tr>
<tr>
<td>NiFe(_2)/NiFeP/LDH</td>
<td>1.0 M KOH</td>
<td>1.93 V@500</td>
<td>20</td>
<td>184</td>
</tr>
</tbody>
</table>
with other heteroatoms to tune the electronic structure and optimize the intermediate absorption energy of materials in the electrochemical process for achieving the synergistic effect with the original elements, thus dramatically improving the intrinsic properties; (ii) introducing defect structures such as lattice defects, interstitial atoms and vacancies to modify the specific surface area, and the quantum size effect of catalysts from an electronic perspective rather than the geometric structures electronically depended on the geometric structures and electronic properties with the particle size makes the identification of their distinct size-dependent functionalities nearly impossible. Therefore, understanding the relationship

<table>
<thead>
<tr>
<th>Electro catalysts</th>
<th>Electrolyte</th>
<th>Overpotential (mV) @current density (mA cm$^{-2}$)</th>
<th>Stability time (h)</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>NiMo$_{13}$/NiMoS/NF</td>
<td>1.0 M KOH</td>
<td>1.60 V@500</td>
<td>—</td>
<td>185</td>
</tr>
<tr>
<td>Co$<em>{0.5}$Ru$</em>{0.2}$O$_{3}$/CF</td>
<td>1.0 M KOH</td>
<td>1.60 V@1000</td>
<td>23</td>
<td>186</td>
</tr>
<tr>
<td>Ni-Mo$<em>{2}$O$</em>{5}$/C/NF</td>
<td>1.0 M KOH</td>
<td>HER: 304@2000</td>
<td>—</td>
<td>187</td>
</tr>
<tr>
<td>Ni@C-MoO$_{2}$/NF</td>
<td>1.0 M KOH</td>
<td>HER: 400@2000</td>
<td>—</td>
<td>187</td>
</tr>
<tr>
<td>3DPNi</td>
<td>1.0 M KOH</td>
<td>HER: 425@1000</td>
<td>—</td>
<td>189</td>
</tr>
<tr>
<td>NiFe/Ni/Ni</td>
<td>6.0 M KOH</td>
<td>1.86 V@500</td>
<td>40</td>
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</tr>
<tr>
<td>[Ni, Fe]OOH/NF</td>
<td>1.0 M KOH</td>
<td>1.65 V@1500</td>
<td>10</td>
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<tr>
<td>Fe$<em>{2}$O$</em>{3}$/Ni(OH)$_{2}$/NF</td>
<td>1.0 M KOH</td>
<td>1.69 V@100</td>
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<td>19</td>
</tr>
<tr>
<td>Cu@NiFe LDH</td>
<td>1.0 M KOH</td>
<td>1.75 V@500</td>
<td>—</td>
<td>193</td>
</tr>
<tr>
<td>NiFe-LDH/MXene/NF</td>
<td>1.0 M KOH</td>
<td>1.98 V@1000</td>
<td>4000</td>
<td>195</td>
</tr>
<tr>
<td>NiFe LDH@Ni$_{2}$N/NF</td>
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<td>1.80 V@500</td>
<td>100</td>
<td>194</td>
</tr>
<tr>
<td>Co-P</td>
<td>1.0 M KOH</td>
<td>1.98 V@1000</td>
<td>—</td>
<td>195</td>
</tr>
<tr>
<td>NiCoP/NF</td>
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<td>1.83 V@500</td>
<td>24</td>
<td>196</td>
</tr>
<tr>
<td>CoFeF TPAs/Ni</td>
<td>1.0 M KOH</td>
<td>HER: 263@900</td>
<td>—</td>
<td>197</td>
</tr>
<tr>
<td>Fe/Co/Ni/NF</td>
<td>1.0 M KOH</td>
<td>OER: 335@700</td>
<td>—</td>
<td>197</td>
</tr>
<tr>
<td>Ni$<em>{2}$P-Fe$</em>{2}$/P/NF</td>
<td>1.0 M KOH</td>
<td>1.72 V@500</td>
<td>40</td>
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</tr>
<tr>
<td>Fe$<em>{2}$/Co$</em>{2}$/P/C</td>
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<td>2.004 V@500</td>
<td>40</td>
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</tr>
<tr>
<td>Fe-Doped Ni$_{2}$/P/C-NF</td>
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<td>1.71 V@500</td>
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<td>200</td>
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<tr>
<td>Ni$_{2}$/P/MnOOH/NF</td>
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<td>1.66 V@500</td>
<td>—</td>
<td>201</td>
</tr>
<tr>
<td>Ni$<em>{2}$/P/Co$</em>{2}$/P/C-NF</td>
<td>1.0 M KOH</td>
<td>1.98 V@500</td>
<td>50</td>
<td>202</td>
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<tr>
<td>Ni$<em>{2}$/S$</em>{2}$/Ni$<em>{2}$/S$</em>{2}$/NF</td>
<td>1.0 M KOH</td>
<td>HER: 432@500</td>
<td>—</td>
<td>203</td>
</tr>
<tr>
<td>Fe$<em>{x}$/Ni$</em>{y}$/S$_{z}$</td>
<td>1.0 M KOH</td>
<td>OER: 475@500</td>
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<tr>
<td>CoMo$_{2}$/NF</td>
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<td>2.4 V@500</td>
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<td>68</td>
</tr>
<tr>
<td>[Ni, Fe]S$<em>{2}$/NiFe(OH)$</em>{2}$/NF</td>
<td>1.0 M KOH</td>
<td>1.89 V@500</td>
<td>100</td>
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<tr>
<td>Co-S/30/NF</td>
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<td>2.12 V@1000</td>
<td>50</td>
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</tr>
<tr>
<td>Sn-Ni$<em>{2}$/S$</em>{2}$/NF</td>
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<td>2.08 V@500</td>
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</tr>
<tr>
<td>Fe$<em>{x}$/Ni$</em>{y}$/S$<em>{z}$/Ni$</em>{2}$/S$_{2}$/NF</td>
<td>1.0 M KOH</td>
<td>1.72 V@500</td>
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<td>—</td>
</tr>
<tr>
<td>279@300</td>
<td>1.0 M KOH</td>
<td>297@300</td>
<td>—</td>
<td>205</td>
</tr>
<tr>
<td>438@500</td>
<td>1.0 M KOH</td>
<td>438@500</td>
<td>60</td>
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</tr>
<tr>
<td>Fe$<em>{x}$/Ni$</em>{y}$/S$<em>{z}$/Ni$</em>{2}$/S$_{2}$/NF</td>
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<td>1.95 V@500</td>
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<td>51</td>
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<tr>
<td>Co$_{3}$/NiCoMoO/GP</td>
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<td>2.28 V@1000</td>
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<td>206</td>
</tr>
<tr>
<td>NiMn$_{2}$/NiFeN/NF</td>
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<td>1.709 V@1000</td>
<td>—</td>
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</tr>
<tr>
<td>NiFeMo/NF</td>
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<td>1.75 V@500</td>
<td>50</td>
<td>208</td>
</tr>
<tr>
<td>np-NiMnFeMo</td>
<td>1.0 M KOH</td>
<td>HER: 290@1000</td>
<td>—</td>
<td>209</td>
</tr>
<tr>
<td>NiCo@C-NiCoMoO/NF</td>
<td>6.0 M KOH</td>
<td>HER: 570@1000</td>
<td>—</td>
<td>209</td>
</tr>
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</table>
between the geometric and electronic structures caused by the varying particle sizes in the catalytic performance toward HER/OER under the large current density is essential to provide guidance for developing new experimental strategies and designing advanced materials with suitable nanostructure for improving electrochemical activity. This is also a grand challenge. To obtain robust self-supported electrocatalysts that can work under the high current density, we should also identify and control the factors to affect the stability like the catalyst composition/phase, substrate material, catalyst–substrate interface, electrode–electrolyte wettability, mechanical property and so on. Although enormous strides and many achievements have been made for the development of electrocatalysts working at high current density, and in-depth investigations of the mechanism behind the reinforcement have been conducted as outlined in this review, there are still many challenges and obstacles to overcome, which require further systematic investigations.

First, the excessive amounts of gas bubbles generated on the surface of electrodes during the electrolysis water process at high current density could rapidly shed off those commercial noble metal based electrocatalysts (e.g., RuO2, Pt/C) and other electrocatalysts combined with binder, leading to the failure of long-term stability. Thus, it is important to develop self-supported electrocatalysts without any binders. For performance comparison of various self-supported electrocatalysts working at the large current density with those noble metal based electrocatalysts, it is necessary to develop some special methods to prepare binder-free noble metal-based electrocatalysts on the conductive substrate.

Second, whether the electrocatalyst is superhydrophilic or superaerophobic requires consideration before fabrication. With the tremendous quantities of bubbles formed on the surface of electrocatalysts at high current densities, the actual contact surface between the electrocatalyst and electrolyte will decrease, which always severely hinders liquid mass transport. Hence, an electrocatalyst with good superhydrophilicity can facilitate the proton transmission and enhance the departure of gas bubbles by superaerophobicity, thereby further improving the overall efficiency and stability of the gas-evolving electrochemical water splitting process.

Third, some self-supported electrocatalysts have been reported to have lower overpotential at large current densities in the laboratory room temperature condition based on the $iR$ compensation or using three-electrode electrolyzer. However, in the actual industrial testing process, the electrochemical parameters of the $iR$–uncompensated overpotential or two-electrode electrolyzer are always used. Meanwhile, the temperature of the electrolyte is usually higher under the industrial testing process, which inevitably affects the potential conversion. Therefore, it is necessary to provide the information on the $iR$–uncompensated overpotential and percentage of $iR$ drop compensation, and the actual potential transformation under different temperatures. In addition, for the electrocatalyst $in situ$ grown on the conductive substrate, the substrate can greatly favor the overall electrocatalytic activity. Hence, it is essential to have an in-depth understanding of the real active sites and real surface area-normalized electrocatalytic activity for the evaluation of an OER or HER electrocatalyst. It is noteworthy that there also exists a problem of the mass transport in the two-electrode traditional electrolyzers being relatively low, which could hamper the overall energy efficiency when operated under large current densities. For the compensation of the mass transfer-controlling phenomenon, flowing the electrolyte to and away from the electrode has been proposed as one solution, which is seldom reported in water electrolysis owing to the limited current densities that have been reported.

Fourth, most currently research studies on the electrocatalytic HER/OER/OWS electrocatalytic activity are usually performed in the laboratory at the large current densities (500 or 1000 mA cm$^{-2}$) with a relatively short-term stability test (<1 week). For practical application, a longer stability test is necessary. Meanwhile, the industrial application conditions need to be simulated for the evaluation of the as-prepared electrocatalysts. For the industrial electrolysis of water, the required electrolyte concentration, environment of temperature, and pressure are often high, in which the migration rate of ions, the conductivity of the electrolyte, and the structural stability of the electrocatalyst materials are significantly different from the lab-scale experiments. Therefore, aiming at the large-scale development of water splitting technology, the electrocatalytic performance of self-supported electrocatalysts should be investigated under a larger current density with an ultra-long stability test under the actual application conditions. Remarkably, it has been confirmed that the surface of the electrocatalysts would undergo severe change, and further greatly influence the electrocatalytic performance under continuous operating, by which the reaction kinetics would be different from those at the lab scale. This might call for another intriguing research study by integrating theoretical simulation and $in situ$ characterization techniques to clarify the electrocatalytic mechanism in detail.

Fifth, to date, most of the self-supported electrocatalysts are fabricated and used in the alkaline solution, and it is rarely reported that the electrocatalysts are applied in acidic and neutral electrolytes for large current density electrolysis of water. Meanwhile, the morphological structure, composition, the valent state of the electrocatalyst, and local environment around the reactive species are dynamically changing under different experimental conditions, which hinders the good identification and research of the real active species/sites, crystal facets, structural morphologies, and chemical compositions during the reaction process, and further impedes the rational design of the electrocatalysts used in different pH ranges of electrolytes. Theoretical analysis and $in situ$ spectroscopic study should be powerful tools to clarify the real electrocatalytic sites, determine the electrocatalytic mechanism, and observe the reaction process, which could provide strong guidance to optimize the performance of a target electrocatalyst. Currently, the $in situ$/$operando$ characterization techniques (e.g., $in situ$ IR, Raman, localized surface plasmon resonance (LSPR), X-ray photoelectron spectroscopy (XPS), and X-ray
absorption spectroscopy (XAS)) have been used to track the surface species in OER or HER. However, due to the high cost and complicated device requirements, they cannot be widely applied in the studies.

Sixth, it is urgent to search for low-cost and highly efficient bifunctional electrocatalysts for OWS application in the large current density. It could not only greatly reduce the cost and save the corresponding time to prepare the OER or HER electrocatalysts, but also decrease the relevant human and the resource material consumption to enable enterprises obtaining greater economic benefits. Unfortunately, to date, those reported self-supported electrocatalysts working at high current density have been only investigated as “catalysts”. A long journey and challenging remains to be taken before realizing them in large-scale devices for the production of hydrogen.

Finally, the developed self-supported electrocatalysts have been widely evaluated in the traditional electrolyzer for alkaline water electrolysis (AWE) in the lab-scale system. However, investigations concerning water electrolysis devices have rarely been reported, making the search and optimization of the electrolyzer configuration an attractive and promising area. Compared to the traditional AWE, currently, the proton exchange membrane water electrolyzer (PEMWE) and anion exchange membrane water electrolyzer (AEMWE) always have compact designs with low ionic resistance and low ohmic loss (iR) of the membrane electrode assembly (MEA), which could significantly lower the energy cost. The OER in PEMWE and AEMWE can be realized in acidic and alkaline conditions, respectively, according to the membrane properties and local pH effect. Although the PEMWE is relatively mature in commercial-scale water electrolysis for long-term operation, the development of durable OER catalysts other than Ir-based noble-metal catalysts in the acidic environment at the large current density remains a great challenge. In contrast, emerging AEMWE technology has the advantage that more OER electrocatalysts are applicable for its local alkaline environment, but the membrane stability and electrolyzer design still need improvement in order to meet long-term electrolysis requirements, including membrane, support, operation conditions local pH effect and bubble effect and so on. Meanwhile, it encouraged more efforts to integrate the novel green energy system with an electrolyzer into a single system, which will decrease the overall cost for hydrogen production in future practical applications.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

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References

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