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Bimetallic Oxyhydroxide as a High-Performance Water Oxidation Electrocatalyst under Industry-Relevant Conditions



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ABSTRACT

Developing high-performing oxygen evolution reaction (OER) electrocatalysts under high-current operation conditions is critical for future commercial applications of alkaline water electrolysis for clean energy generation. Herein, we prepared a three-dimensional (3D) bimetallic oxyhydroxide hybrid grown on a Ni foam (NiFeOOH/NF) prepared by immersing Ni foam (NF) into Fe(NO₃)₃ solution. In this unique 3D structure, the NiFeOOH/NF hybrid was composed of crystalline Ni(OH)₂ and amorphous FeOOH evenly grown on the NF surface. As a bimetallic oxyhydroxide electrocatalyst, the NiFeOOH/NF hybrid exhibited excellent catalytic activity, surpassing not only the other reported Ni–Fe based electrocatalysts, but also the commercial Ir/C catalyst. *In situ* electrochemical Raman spectroscopy demonstrated the active FeOOH and NiOOH phases involved in the OER process. Profiting from the synergy of Fe and Ni catalytic sites, the NiFeOOH/NF hybrid delivered an outstanding OER performance under challenging industrial conditions in a 10.0 mol·L⁻¹ KOH electrolyte at 80 °C, requiring potentials as small as 1.47 and 1.51 V to achieve the super-high catalytic current densities of 100 and 500 mA·cm⁻², respectively.

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1. Introduction

In a context of the development of global power and environmental concerns, electrocatalytic water splitting is a promising renewable and clean energy technology that can convert a large amount of water into hydrogen and oxygen [1,2]. Electrochemical water splitting involves two half reactions; of these, the oxygen evolution reaction (OER) is a four-step electron-transfer reaction [3] that requires a higher overpotential and thus greatly reduces the overall reaction rate, acting as a reaction bottleneck for hydrogen production from electrolyzed water [4,5]. At present, the most efficient OER electrocatalysts are mainly based on noble metal compounds (e.g., RuO₂, IrO₂, and Ir/C) because of their high catalytic activity and high level of stability [6,7]. However, the shortage of these expensive metal compounds limits their wide application [8]. Therefore, it is of great significance to explore

highly competent, stable, and low-cost OER electrocatalysts such as transition-metal (e.g., iron (Fe), cobalt (Co), and nickel (Ni)) oxides [9,10], nitrides [11], borides [12], carbides [13], oxyhydroxides [14], hydroxides [15], chalcogenides [16,17], and phosphorus compounds [18,19]. Among these, Ni-based OER electrocatalysts not only are low in cost and abundant in reserves, but also exhibit good stability for the OER process in alkaline media [20]. However, the poor electronic conductivity of Ni-based OER materials makes their electrocatalytic performance far from satisfactory.

Recently, binary metal-based catalysts with high intrinsic catalytic activity have been employed as efficient OER catalysts for water splitting, instead of single metal-based catalysts [21], due to their enhanced intrinsic catalytic properties [22]. Among the various metals that have been introduced in this area, metallic Fe has become a widely studied material by virtue of its remarkable catalytic performance, strong chemical stability, and low cost [23]. In addition, although a certain amount of progress has been made in the development of highly efficient OER catalysts operating under the conditions of real-world industrial applications

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(10.0 mol·L⁻¹ KOH, 80 °C, and up to 500 mA·cm⁻²), their overall electrocatalytic efficiency remains poor and their synthetic methods are still complicated.

Herein, we prepared a novel three-dimensional (3D) bimetallic oxyhydroxide hybrid consisting of crystalline Ni(OH)₂ and amorphous FeOOH grown on a Ni foam (NF) during a displacement reaction at room temperature, in which the NF was etched by Fe(NO₃)₃ solution. Due to the synergy of the Fe and Ni catalytic sites, the NiFeOOH/NF hybrid exhibited admirable OER activity and stability in alkaline media, reaching the commercially required current densities of 500 and 1000 mA·cm⁻² at 1.51 and 1.55 V, respectively. Importantly, these measured potentials are among the lowest when compared with other reported Ni–Fe based electrocatalysts, as well as the benchmark Ir/C catalyst [24]. The FeOOH and NiOOH phases were specifically OER-active of the NiFeOOH/NF hybrid, as discovered by *in situ* electrochemical Raman spectroscopy. Furthermore, the NiFeOOH/NF hybrid was found to have superior OER activity and corrosion resistance in a widely adopted electrolyte in commercial water–alkali electrolyzers—namely, 10.0 mol·L⁻¹ KOH electrolyte at 80 °C.

2. Material and methods

2.1. Catalyst preparation

To prepare the (NiFeOOH)/NF, commercial NF was immersed in turn in 1.0 mol·L⁻¹ HCl, acetone, ethanol, and then deionized water for 10 min each in an ultrasonic machine. After these treatments, three pieces of NF were dipped into 0.2 mol·L⁻¹ of Fe(NO₃)₃ solution with mechanical shaking for 3 min and then dehydrated at room temperature. The loading amount of NiFeOOH catalyst was approximately 10 mg·cm⁻².

2.2. Physical characterization

The morphologies and microstructures of the samples were surveyed by field-emission scanning electron microscopy (FESEM, Supra 55, Hitachi, Japan) and transmission electron microscopy (TEM) measurements performed on a JEM-2100 electron microscope (JEM-2100, 200 kV, JEOL, Japan) with an expediting voltage of 200 kV. Raman spectra were recorded on a Raman scattering spectroscopy system (LabRAM HR Evolution, Horiba Jobin Yvon, France) with excitation by a diode laser (532 nm) in the backscattering geometry. Rigaku D/Max 2550/PC (Rigaku Corporation, Japan) was used to obtain the X-ray diffraction (XRD) patterns, and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific Inc., USA) was performed using Al K α radiation.

2.3. Electrochemical measurements

Electrochemical tests were performed in a three-electrode cell using 1.0 mol·L⁻¹ KOH as the electrolyte. The NiFeOOH/NF sample, a carbon rod, and an Ag/AgCl electrode acted as the working, counter, and reference electrodes, respectively. The mechanical robustness and stability were studied through multiple-current steps, multiple-potential steps, and amperometric current–time measurements. After the cyclic voltammetry (CV) cycles were stabilized, electrochemical measurements were performed. Linear sweep voltammetry (LSV) was used to acquire the OER catalytic activity with a scan rate of 5 mV·s⁻¹. To ascertain the double-layer capacitance (*C*_{dl}), CV scans between 0.21 and 0.31 V (vs Ag/AgCl) were conducted at 20, 40, 60, 80, and 100 mV·s⁻¹. The potentials versus reversible hydrogen electrode (RHE) in 1.0 mol·L⁻¹ at 25 °C were calculated through the original Nernst equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591\text{pH} + 0.098\text{V}$$

3. Results and discussion

A simple immersion and shocking process was employed to synthesize the 3D NiFeOOH/NF hybrid. The 3D NF sample was introduced into the Fe(NO₃)₃ solution, followed by mechanical shaking for 3 min. NF and Fe³⁺ undergo a redox reaction to form the NiFeOOH/NF hybrid, which consists of crystalline Ni(OH)₂ and amorphous FeOOH [25]. We systematically identified the effects of different Fe(NO₃)₃ concentrations to achieve the highest OER activity; the optimized concentration was 0.2 mol·L⁻¹ (Appendix A Fig. S1). A low-resolution FESEM image of the NiFeOOH/NF material showed that the NiFeOOH hybrid was uniformly grown on the 3D NF sample (Figs. 1(a) and (b)). Moreover, elemental mapping of the NiFeOOH/NF hybrid (Fig. 1(c) and Appendix A Fig. S2) showed that the Fe, Ni, and oxygen (O) elements were homogeneously distributed over the 3D surface area. The NiFeOOH/NF exhibited interplanar spacings of 0.460 and 0.270 nm, which were ascribed to the (001) and (100) planes of Ni(OH)₂ in high-resolution TEM (HRTEM) images (Fig. 1(d) and Appendix A Fig. S3). The corresponding selected-area electron diffraction (SAED) pattern affirmed that the Ni(OH)₂ in the NiFeOOH/NF hybrid was crystalline (Fig. 1(e)). The XRD pattern of the NiFeOOH/NF hybrid showed the existence of crystalline Ni(OH)₂ (Joint Committee on Powder Diffraction Standards (JCPDS) 14–0117) and the Ni substrate (JCPDS 70–0989) (Fig. 1(f)) [26]. No characteristic diffraction peaks of FeOOH species were observed due to its amorphous structural features and high dispersion on the surface of NF [27]. The presence of amorphous FeOOH film in the NiFeOOH/NF hybrid was further revealed by Raman spectroscopy (see below).

Given these findings, it can be concluded that the NiFeOOH/NF hybrid was composed of Ni(OH)₂ with moderate crystallinity and amorphous FeOOH. The cohabiting of the O, Fe, and Ni elements was analyzed by XPS measurements (Appendix A Fig. S4). The high-resolution Fe 2p signals of the NiFeOOH/NF hybrid were located at 711.8 and 724.6 eV, which are related to the Fe 2p_{3/2} and Fe 2p_{1/2} states, respectively, with two satellite peaks at 717.1 and 732.2 eV (Fig. 1(g)) [14,28–30]. The high-resolution Ni 2p XPS spectrum showed the Ni 2p_{3/2} and Ni 2p_{1/2} peaks centered at approximately 855.9 and 873.5 eV, respectively, which were attributed to Ni²⁺ (Fig. 1(h)) [31–34]. The high-resolution O 1s XPS spectrum of the NiFeOOH/NF hybrid exhibited three peaks located at 529.4, 531.4, and 532.8 eV, which were assigned to the Fe–O and Fe–OH bonds in the FeOOH structure and to the H–O–H bonds in the H₂O species, respectively (Fig. 1(i)) [24,35].

The OER electrocatalytic activity of the NiFeOOH/NF hybrid was examined using a three-electrode system in 1.0 mol·L⁻¹ KOH solution. For comparison, commercial Ir/C/NF, NF, and carbon paper (CP) immersed in Fe(NO₃)₃ solution (Fe(NO₃)₃/CP) were also studied (Fig. 2(a)). In contrast to the control samples, the NiFeOOH/NF hybrid exhibited an extraordinary OER activity with low potentials of 1.46, 1.51, and 1.55 V to achieve 100, 500, and 1000 mA·cm⁻², respectively. It is noteworthy that the NiFeOOH/NF hybrid can supply a current density of up to 1400 mA·cm⁻² at a small potential of 1.57 V. This extraordinary catalytic behavior means that the NiFeOOH/NF hybrid satisfies the commercial criteria of OER electrocatalysis under basic electrolyte conditions. The NiFeOOH/NF hybrid clearly exhibited a much smaller potential of 1.51 V in comparison with Fe(NO₃)₃/CP (1.71 V) at 500 mA·cm⁻² (Fig. 2(b)). This potential of the NiFeOOH/NF hybrid is much lower than that of most reported Ni–Fe-based electrocatalysts, as well as that of commercial Ir/C/NF, which is 1.59 V at 500 mA·cm⁻².

The reaction kinetic activity of the NiFeOOH/NF hybrid was further evaluated using its Tafel slope; Fig. 2(c) and Fig. S5 in Appendix A exhibit the Tafel slope of 58.4 mV·dec⁻¹, which is lower than

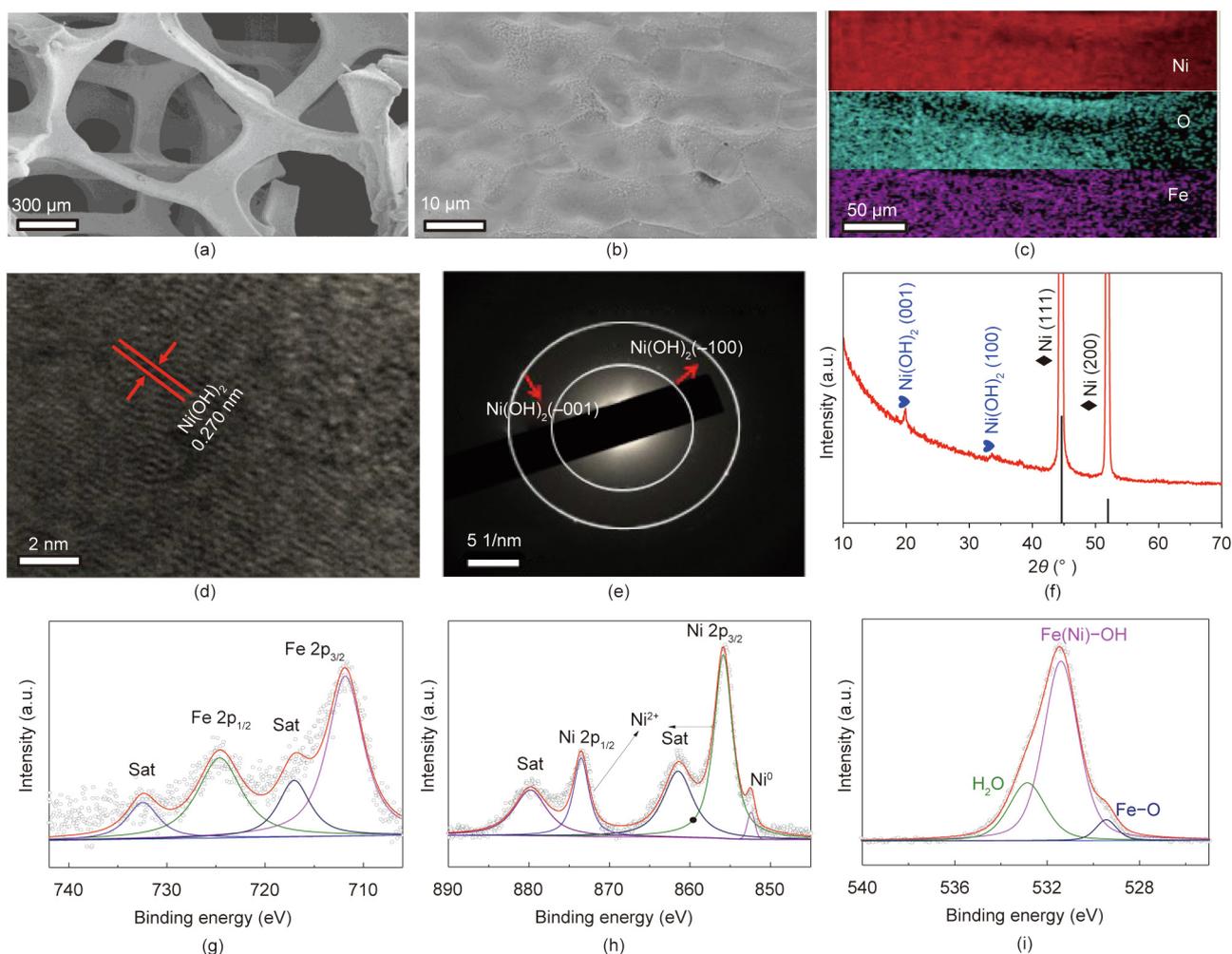


Fig. 1. (a, b) FESEM images of NiFeOOH/NF. (c) Corresponding elemental mapping images of Ni, O, and Fe elements in NiFeOOH/NF. (d) HRTEM image of NiFeOOH/NF. (e) SAED pattern of NiFeOOH/NF. (f) XRD pattern of NiFeOOH/NF. XPS spectra of (g) Fe 2p, (h) Ni 2p, and (i) O 1s for NiFeOOH/NF. Sat: satellite peak.

the $60.9 \text{ mV} \cdot \text{dec}^{-1}$ Tafel slope of Ir/C/NF and the $96.3 \text{ mV} \cdot \text{dec}^{-1}$ Tafel slope of $\text{Fe}(\text{NO}_3)_3/\text{CP}$. This finding implies that the NiFeOOH/NF hybrid possesses fast OER kinetics and inherent outstanding activity toward the OER process. It is notable that the matching Tafel slope and the potential of the NiFeOOH/NF hybrid are almost at the minimum at $100 \text{ mA} \cdot \text{cm}^{-2}$. In addition, the Tafel slope is low in comparison with those of previously reported Ni-Fe-based electrocatalysts (Fig. 2(d) and Appendix A Table S1). These results further demonstrate the outstanding OER performance of the NiFeOOH/NF hybrid. Fig. 2(e) presents the multistep chronopotentiometric curve acquired for the NiFeOOH/NF hybrid under alkaline conditions; with a varying current density from 200 to $1200 \text{ mA} \cdot \text{cm}^{-2}$, the voltage remains constant for the remaining 200 s. These factors confirm the exceptional mechanical robustness and excellent mass transport of the NiFeOOH/NF hybrid [36,37].

Electrochemical durability is a key performance indicator of electrocatalysts. In cyclic voltammogram testing, the polarization curve of the NiFeOOH/NF hybrid after the 500-cycle test remained almost unchanged when compared with the initial one (Fig. 2(f)), indicating the high electrochemical stability of the NiFeOOH/NF hybrid [38]. A chronopotentiometry test over 10 h of continuous reaction further demonstrated the long-term durability of the NiFeOOH/NF hybrid. Notably, the NiFeOOH/NF hybrid also exhibited good stability under $1000 \text{ mA} \cdot \text{cm}^{-2}$ at 2.0 V after chronoamperometry testing for over 10 h (Fig. 2(f) and Appendix A Fig. S6).

To further explore the effect of sample preparation conditions on the OER performance, mechanical shocks were applied for different time intervals during the synthesis process. Electrochemical tests of the NiFeOOH/NF hybrids prepared using mechanical shocks applied with different time intervals were performed. The NiFeOOH/NF hybrid exhibited a larger current density and smaller onset potential than the hybrid samples prepared with the mechanical shocking time intervals of 0.5, 1.0, and 5.0 min (Appendix A Fig. S7). Similarly, the NiFeOOH/NF (3 min) hybrid exhibited the greatest electrochemical double-layer capacitance (C_{dl}) value of $14.61 \text{ mF} \cdot \text{cm}^{-2}$ in comparison with the other control NiFeOOH/NF (0.5, 1.0, and 5.0 min) hybrid samples. These results suggest that the NiFeOOH/NF hybrid featured the most highly exposed active surface areas among all the studied samples (Fig. 3(a) and Appendix A Fig. S8) [39]. Furthermore, electrochemical impedance spectroscopy (EIS) of the NiFeOOH/NF hybrid revealed the minimum charge transfer resistance and the fastest electron-transfer ability among all the studied NiFeOOH/NF hybrid samples (Fig. 3(b)). In the inset of Fig. 3(b), where the R_s is the solution resistance, constant-phase element (CPE1) is related to the double-layer capacitance and R_{ct} is charge-transfer resistance. Importantly, this simple immersion and shocking method were further developed to synthesize a sequence of $\text{Co}(\text{NO}_3)_2/\text{NF}$, $\text{Cu}(\text{NO}_3)_2/\text{NF}$, $\text{Mg}(\text{NO}_3)_2/\text{NF}$, $\text{Ni}(\text{NO}_3)_2/\text{NF}$, and $\text{Zn}(\text{NO}_3)_2/\text{NF}$ compounds. To further identify the effect of the possible synergy between the different metals on OER efficiency, a battery of electrochemical tests was performed. The

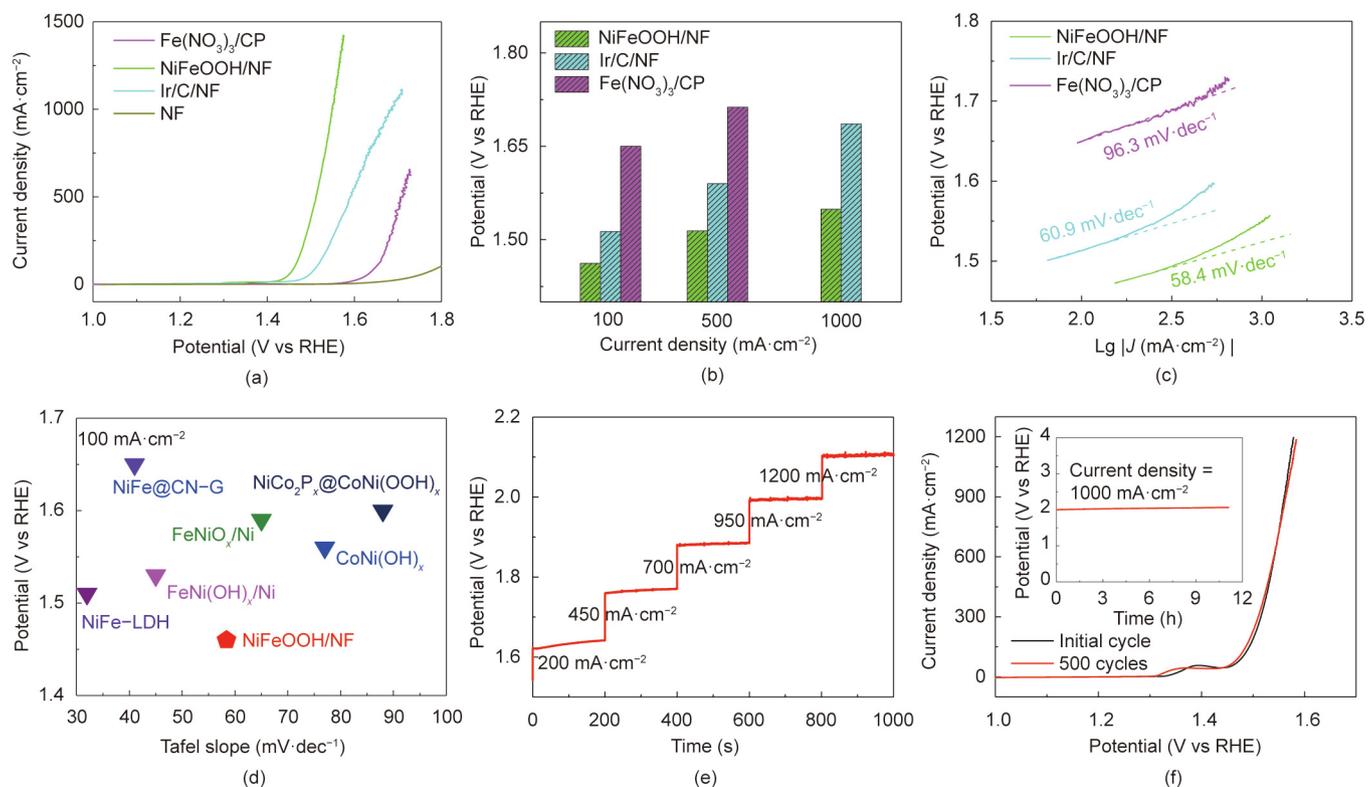


Fig. 2. (a) OER LSV curves of $\text{Fe}(\text{NO}_3)_3/\text{CP}$, $\text{NiFeOOH}/\text{NF}$, $\text{Ir}/\text{C}/\text{NF}$, and NF . (b) Required potentials to achieve 100, 500, and $1000 \text{ mA}\cdot\text{cm}^{-2}$ for $\text{NiFeOOH}/\text{NF}$, $\text{Ir}/\text{C}/\text{NF}$, and $\text{Fe}(\text{NO}_3)_3/\text{CP}$, respectively. (c) Tafel plots for OER over $\text{NiFeOOH}/\text{NF}$, $\text{Ir}/\text{C}/\text{NF}$, and $\text{Fe}(\text{NO}_3)_3/\text{CP}$. (d) Tafel slopes and potentials required for a $100 \text{ mA}\cdot\text{cm}^{-2}$ comparison of $\text{NiFeOOH}/\text{NF}$ and other Ni-based OER electrocatalysts (LDH: layered double hydroxide; CN-G: N-doped graphitic carbon). (e) Multicurrent process curve of $\text{NiFeOOH}/\text{NF}$. (f) OER LSV curves and durability test after 500 cycles for $\text{NiFeOOH}/\text{NF}$ (inset: chronopotentiometric curve for $\text{NiFeOOH}/\text{NF}$ in $1.0 \text{ mol}\cdot\text{L}^{-1}$ KOH at a current density of $1000 \text{ mA}\cdot\text{cm}^{-2}$ (without iR correction)).

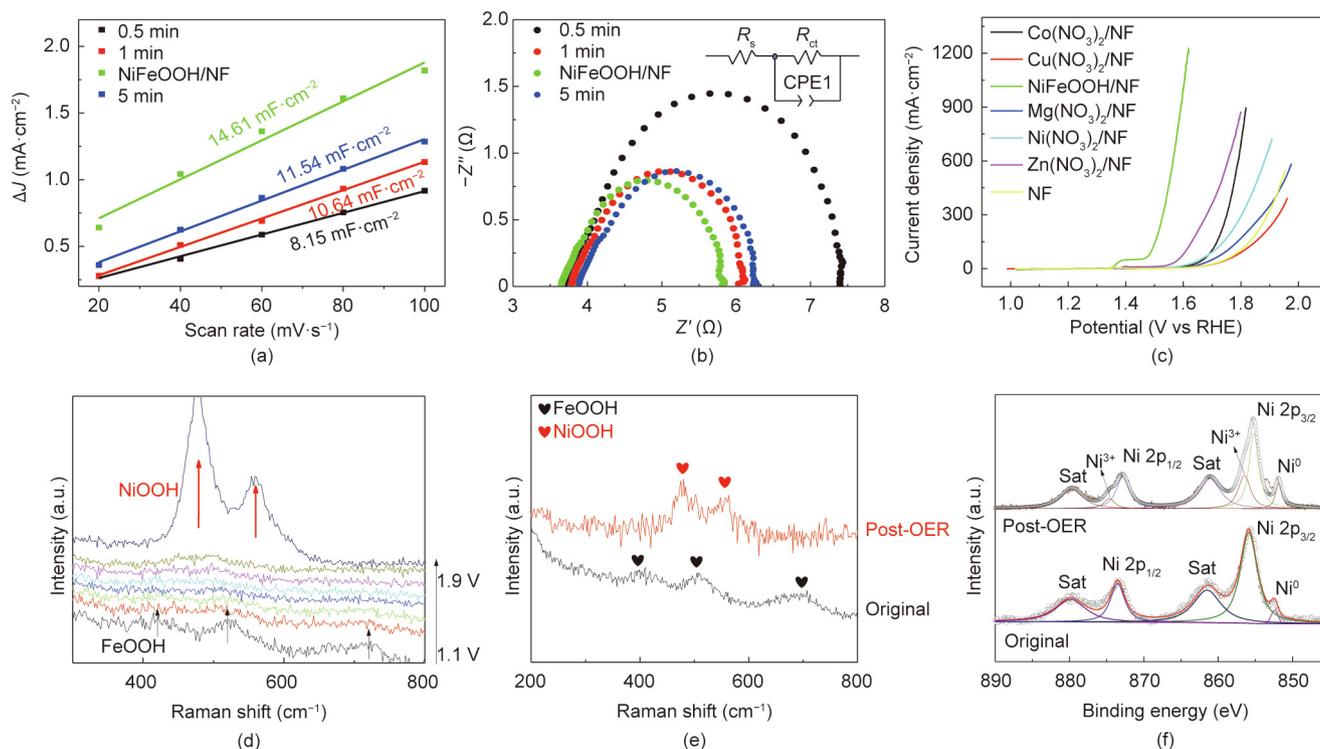


Fig. 3. (a, b) Electrochemical active surface areas (ECSAs) and Nyquist plots of $\text{NiFeOOH}/\text{NF}$ against the shock time. (c) Polarization curves of $\text{Co}(\text{NO}_3)_2/\text{NF}$, $\text{Cu}(\text{NO}_3)_2/\text{NF}$, $\text{NiFeOOH}/\text{NF}$, $\text{Mg}(\text{NO}_3)_2/\text{NF}$, $\text{Ni}(\text{NO}_3)_2/\text{NF}$, $\text{Zn}(\text{NO}_3)_2/\text{NF}$, and NF . (d) Operando Raman spectra of $\text{NiFeOOH}/\text{NF}$ with different applied potentials. (e) Raman spectra of $\text{NiFeOOH}/\text{NF}$ before and after OER tests. (f) High-resolution Ni 2p XPS spectra of $\text{NiFeOOH}/\text{NF}$ before and after the OER test.

results showed that the NiFeOOH/NF hybrid possessed the best OER performance (Fig. 3(c) and Appendix A Fig. S9). In other words, the introduction of the Fe species plays a crucial role in boosting the OER performance, due to the synergistic effect of the Ni and Fe catalytic sites.

In order to evaluate any changes in the composition and structure of the NiFeOOH/NF hybrid throughout the OER operation, *in situ* electrochemical Raman spectroscopy was performed (Fig. 3(d)). At a voltage of 1.1 V, the Raman spectrum presented three main peaks at 422, 520, and 714 cm^{-1} belonging to the FeOOH species. This finding suggests that the active sites were amorphous FeOOH during the initial OER process [2]. As the voltage increased, the peaks of the FeOOH species gradually weakened. When the voltage was increased to 1.5 V, the peaks of the Ni(OH)₂ species gradually appeared at 450 and 500 cm^{-1} [25]. With further gradual increase of the voltage, two main peaks at 479 and 560 cm^{-1} were observed, which were attributed to the typical peaks of NiOOH species. Furthermore, the Ni(OH)₂ structure was transformed into the compound NiOOH species at a potential of greater than 1.7 V. The Raman spectra of FeOOH and NiOOH before and after the OER process were also compared, and the results were in accord with the *in situ* Raman observations (Fig. 3(e)). Therefore, it can be concluded that the amorphous FeOOH and NiOOH phases in the NiFeOOH/NF hybrid are the actual catalytically active phases, which facilitate the high OER efficiency [40].

To further comprehend the conversion behavior of the NiFeOOH/NF hybrid during the OER operation, the XPS proportions of the NiFeOOH/NF hybrid before and after the OER processes were determined. Compared with the XPS spectra before the OER process (Fig. 3(f)), the high-resolution Ni 2p spectra of the NiFeOOH/NF hybrid after the OER process showed three peaks located at

851.9, 855.2, and 872.8 eV, which were attributed to Ni⁰, Ni²⁺ 2p_{3/2}, and Ni²⁺ 2p_{1/2}, respectively [41]. Moreover, the two satellite peaks situated at 856.5 and 874.7 eV were ascribed to Ni³⁺ 2p_{3/2} and Ni³⁺ 2p_{1/2}, respectively [31]. These results reveal that transformation of the oxidation states from Ni²⁺ to Ni³⁺ occurred during the OER process; they also confirm that the NiOOH species act as catalytically active centers for the OER.

Along with the high catalytic activity and good stability of the NiFeOOH/NF hybrid, an industry-relevant electrolyte in an operating environment of 10.0 mol·L⁻¹ KOH at 80 °C is needed by the OER electrode. As shown in Fig. 4(a), the NiFeOOH/NF hybrid presented ultrahigh current densities of 100, 500, and 1000 mA·cm⁻² at 1.47, 1.51, and 1.53 V, respectively. Moreover, the NiFeOOH/NF hybrid delivered a current density of up to 3000 mA·cm⁻² at a low potential of 1.58 V. The NiFeOOH/NF hybrid also exhibited durable stability with a small potential of 1.61 V to achieve 500 mA·cm⁻² in 10.0 mol·L⁻¹ KOH at 80 °C after chronoamperometry testing for over 10 h (Fig. 4(b)). Thus, the NiFeOOH/NF hybrid satisfies the commercial criteria for OER electrocatalysis under harsh industrial conditions. As shown in Fig. 4(c), the NiFeOOH/NF hybrid required the much smaller potentials of 1.51 and 1.53 V to achieve 500 and 1000 mA·cm⁻² in 10.0 mol·L⁻¹ KOH at 80 °C, compared with 1.65 and 1.70 V for Fe(NO₃)₃/CP, and 1.73 and 1.80 V for NF, respectively [27]. This simple method was further applied to commercial stainless steel (Figs. 4(d) and (e)) [42]. The Fe(NO₃)₃/SUS 304 delivered enhanced electrocatalytic activities as compared with SUS 304, which could be attributed to the displacement reaction of a small amount of Ni species contained in stainless steel with Fe³⁺ in the Fe(NO₃)₃ solution. These results demonstrate that the immersion of SUS 304 into Fe(NO₃)₃ solution improved the electrocatalytic activity and corrosion resistance of SUS 304 toward the OER process in a basic electrolyte.

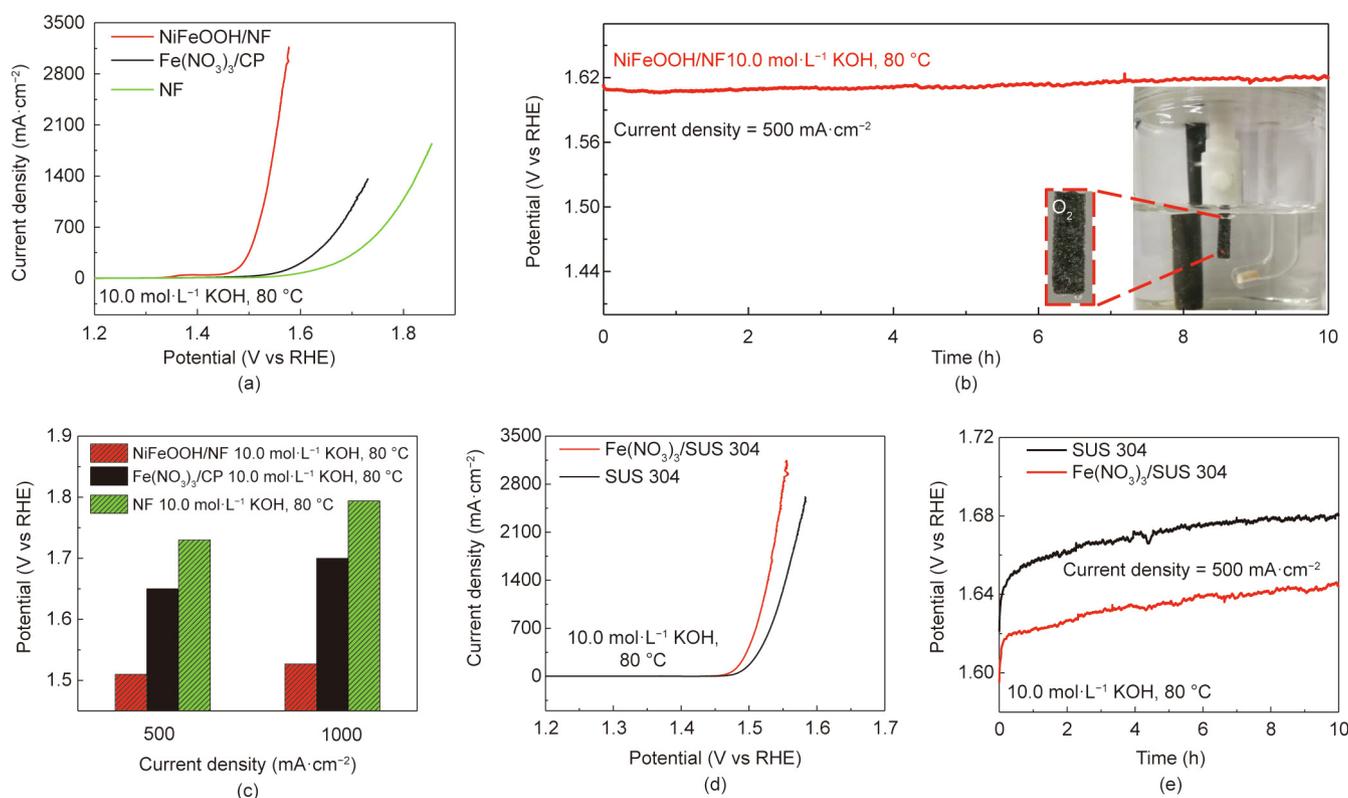


Fig. 4. (a) OER LSV curves of NiFeOOH/NF, Fe(NO₃)₃/CP, and NF in 10.0 mol·L⁻¹ KOH at 80 °C. (b) Chronopotentiometric curve for NiFeOOH/NF at 500 mA·cm⁻² (without *iR* correction); inset: image of the O₂ gas evolution on NiFeOOH/NF. (c) Comparison of the potentials required at 500 and 1000 mA·cm⁻² for NiFeOOH/NF, Fe(NO₃)₃/CP, and NF in 10.0 mol·L⁻¹ KOH at 80 °C. (d) OER LSV curves of Fe(NO₃)₃/SUS 304 and SUS 304 in 10.0 mol·L⁻¹ KOH at 80 °C. (e) Chronopotentiometric curves for SUS 304 and Fe(NO₃)₃/SUS 304 at 500 mA·cm⁻² (without *iR* correction), in 10.0 mol·L⁻¹ KOH at 80 °C.

4. Conclusions

In conclusion, a novel 3D NiFeOOH/NF hybrid electrocatalyst composed of crystalline Ni(OH)₂ and amorphous FeOOH was prepared by means of a simple displacement reaction. The NiFeOOH/NF hybrid showed a strong OER performance, which was evidenced by achieving 500 and 1000 mA·cm⁻² at 1.51 and 1.55 V, respectively, under alkaline conditions. These indicators are superior not only to most reported Ni–Fe-based OER electrocatalysts, but also to the commercial Ir/C catalyst. The achieved OER performance can largely be ascribed to the synergy of the Fe and Ni species. Throughout OER operation, the FeOOH and NiOOH species act as active phases in the NiFeOOH/NF hybrid, as shown by *in situ* electrochemical Raman spectroscopy. In addition, the NiFeOOH/NF hybrid exhibited excellent OER performance under widely adopted harsh electrolyte conditions that are typical for commercial water–alkali electrolyzers. The developed NiFeOOH/NF hybrid introduced here may open an avenue for synthesizing bimetallic oxyhydroxide toward practical applications for clean hydrogen production, along with electrochemical exploration such as CO₂ reduction and O₂ reduction reactions.

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Compliance with ethics guidelines

Jiaxin Yuan, Xiaodi Cheng, Chaojun Lei, Bin Yang, Zhongjian Li, Kun Luo, K.H. Koko Lam, Lecheng Lei, Yang Hou, and Kostya Ken Ostrikov declare that they have no conflict of interest or financial conflicts to disclose.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eng.2020.01.018>.

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