Self-Supporting NiFe Layered Double Hydroxide “Nanoflower” Cluster Anode Electrode for an Efficient Alkaline Anion Exchange Membrane Water Electrolyzer

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Abstract: The development of an efficient and durable oxygen evolution reaction (OER) electrode is needed to solve the bottleneck in the application of an anion exchange membrane water electrolyzer (AEMWE). In this work, the self-supporting NiFe layered double hydroxides (NiFe LDHs) “nanoflower” cluster OER electrode directly grown on the surface of nickel fiber felt (Ni fiber) was synthesized by a one-step impregnation at ambient pressure and temperature. The self-supporting NiFe LDHs/Ni fiber electrode showed excellent activity and stability in a three-electrode system and as the anode of AEMWE. In a three-electrode system, the NiFe LDHs/Ni fiber electrode showed excellent OER performance with an overpotential of 208 mV at a current density of 10 mA cm$^{-2}$ in 1 M KOH. The NiFe LDHs/Ni fiber electrode was used as the anode of the AEMWE, showing high cell performance with a current density of 0.5 A cm$^{-2}$ at 1.68 V and a stability test for 200 h in 1 M KOH at 70 °C. The electrocatalytic performance of NiFe LDHs/Ni fiber electrode is due to the special morphological structure of “nanoflower” cluster petals stretching outward to produce the “tip effect,” which is beneficial for the exposure of active sites at the edge and mass transfer under high current density. The experimental results show that the NiFe LDHs/Ni fiber electrode synthesized by the one-step impregnation method has the advantages of good activity and low cost, and it is promising for industrial application.

Keywords: NiFe layered double hydroxides (NiFe LDHs); oxygen evolution reaction (OER); anion exchange membrane water electrolyzer (AEMWE)

1. Introduction

Water electrolysis is regarded as one of the most promising hydrogen production technologies because of its high catalytic efficiency, high purity, and environmental friendliness [1–3]. Alkaline anion exchange membrane water electrolyzer (AEMWE) has attracted widespread attention because it can use low-cost non-noble metal electrodes to replace the noble metal-based electrodes such as IrO$_2$ and RuO$_2$ [4,5], although its alkaline anion exchange membrane technology needs to be improved [5].

However, the large-scale application of water electrolysis is mainly hindered by the slow oxygen evolution reaction (OER) of the anode [4,6]. Therefore, a key goal is to design and explore OER electrodes with efficient catalytic activity and long stability [7,8]. NiFe-based layered double hydroxide materials have been widely studied because of their low cost, and show excellent performance comparable to noble metal-based OER electrodes in an alkaline medium [9,10].

Since the discovery that NiFe LDHs have high intrinsic OER performance [4,11,12], researchers have made many attempts to improve the catalytic performance of NiFe LDHs, such as optimizing the morphology structure and adjusting the electronic structure [3,4].
Although great progress has been made in the design of NiFe LDHs-based electrodes, there are still some shortcomings that hinder their large-scale commercial application. First, researchers try to design catalysts with low overpotential and pay less attention to stability. So far, it has been reported that NiFe-based nanomaterials are generally not particularly stable and can only run for about 10–12 h in a three-electrode system [2,4], which is far from the needs of industrial production. In addition, constructing self-supporting catalysts and more and more strategies needs to be explored to improve the stability of electrocatalysts at high current density in AEMWE.

In the process of application, precious noble metal-based powder catalysts need to be coated on the collector before the electrocatalytic process. However, the use of the binder will inevitably bury some active centers, increase the electrode resistance, and inhibit charge transfer [13]. In addition, the binder between the collector and the catalyst is weak, so the active centers are easy to peel off from the electrode, resulting in a decline in performance [13]. By comparison, the use of self-supporting electrodes can effectively avoid these problems.

At present, there are many methods for preparing self-supporting NiFe LDHs-based electrodes, such as constant pH coprecipitation, hydrothermal treatment, and electrodeposition [13,14]. However, the methods often use organic precipitant and high temperature and pressurized equipment, which increases the cost and limits the application [15].

Therefore, designing a simpler and energy-efficient method to prepare an efficient and durable OER self-supporting NiFe LDHs electrode can greatly reduce the cost of water electrolysis, and even meet the requirements of industrial hydrogen production [13]. Recently, Yan et al. [14] achieved the simple hydrolysis-promotion-deposition method for the preparation of NiFe LDHs nanosheets electrodes directly on nickel foam substrate at room temperature and ambient pressure. Li et al. [13] reported a simple and energy-efficient synthesis of NiFe LDHs directly growing on nickel foam substrates at room temperature and ambient pressure. These methods are simple and low-cost, and the synthesized NiFe LDHs electrode exhibits good performance in the OER reaction. However, these 2D nanosheets are easy to stack in synthesis, which greatly reduces the exposure of active sites and catalytic efficiency [15].

In this work, we selected nickel fiber felt (Ni fiber) with a relatively flat surface as the substrate, and obtained the self-supporting NiFe LDHs “nanoflower” cluster electrode directly and vertically grown on the Ni fiber substrate by a simple one-step impregnation method at room temperature and ambient pressure (in Figure 1). The results show that the self-supporting NiFe LDHs/Ni fiber electrode not only has remarkable catalytic activity and stability in a three-electrode system, but also serves assemble as the anode for the AEMWE single-cell.

![Figure 1. Schematic preparation of NiFe LDHs/Ni fiber electrode and as the anode of the AEMWE.](image-url)
2. Experimental

2.1. Chemical and Materials

The nickel fiber (Ni fiber felt, Ni \(\geq 99.9\%\), thickness of 0.4 mm) was purchased from Aida, Co., Ltd. (Xinxiang, China). The nickel foam (Ni foam, thickness of 1 mm) was received from Lizhiyuan Co., Ltd. (Shanxi, China). Ferrous chloride (FeCl\(_2\)·4H\(_2\)O, \(\geq 98\%\)), nickel chloride (NiCl\(_2\)·6H\(_2\)O, \(\geq 98\%\)), cobalt chloride (CoCl\(_2\)·6H\(_2\)O, \(\geq 99\%\)), manganese chloride tetrahydrate (MnCl\(_2\)·4H\(_2\)O \(\geq 99\%\)), absolute ethanol (C\(_2\)H\(_5\)OH, \(\geq 99.7\%\)), acetone (C\(_3\)H\(_6\)O, \(\geq 99\%\)), and hydrochloric acid (HCl, 36–38%) were purchased from Bono Chemical Co., Ltd. (Dalian, China). Potassium hydroxide (KOH, \(\geq 99.99\%\)) was purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Pt/C (70 wt%) was purchased from Johnson Matthey Ltd. Iridium oxide (IrO\(_2\), \(99.99\%\)) was provided by Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were used as received without any further purification. Millipore water was used in all experiments.

2.2. Catalyst Synthesis

2.2.1. Synthesis of NiFe LDHs/Ni Fiber

First, Ni fiber (2 \(\times\) 5 cm\(^2\)) was cleaned with C\(_3\)H\(_6\)O, 3 M HCl, C\(_2\)H\(_5\)OH, and deionized water in ultrasound for 5 minutes. In a typical procedure, NiCl\(_2\)·6H\(_2\)O (1.19 g) and FeCl\(_2\)·4H\(_2\)O (0.10 g) were dissolved in 50 mL of deionized water under continuous stirring for 1 h. The obtained solution was light green.

Afterward, the cleaned Ni fiber substrate was immersed in the light green solution for 7 days, and the obtained product was washed with deionized water several times. Finally, the product was continuously dried at 60 \(^\circ\)C for 12 h by vacuum drying and was named NiFe LDHs/Ni fiber electrode.

2.2.2. Synthesis of NiCo LDHs/Ni Fiber

Similarly, Ni fiber (2 \(\times\) 5 cm\(^2\)) was cleaned with C\(_3\)H\(_6\)O, 3 M HCl, C\(_2\)H\(_5\)OH, and deionized water in ultrasound for 5 minutes. In a typical procedure, NiCl\(_2\)·6H\(_2\)O (1.19 g) and CoCl\(_2\)·6H\(_2\)O (0.12 g) were dissolved in 50 mL of deionized water under continuous stirring for 1 h. The obtained solution was red.

Afterward, the cleaned Ni fiber substrate was immersed in the red solution for 7 days, and the obtained product was washed with deionized water several times. Finally, the product was continuously dried at 60 \(^\circ\)C for 12 h by vacuum drying and was named NiCo LDHs/Ni fiber electrode.

2.2.3. Synthesis of NiMn LDHs/Ni Fiber

Similarly, Ni fiber (2 \(\times\) 5 cm\(^2\)) was cleaned with C\(_3\)H\(_6\)O, 3 M HCl, C\(_2\)H\(_5\)OH, and deionized water in ultrasound for 5 minutes. In a typical procedure, NiCl\(_2\)·6H\(_2\)O (1.19 g) and MnCl\(_2\)·4H\(_2\)O (0.10 g) were dissolved in 50 mL of deionized water under continuous stirring for 1 h. The obtained solution was green.

Afterward, the cleaned Ni fiber substrate was immersed in the green solution for 7 days, and the obtained product was washed with deionized water several times. Finally, the product was continuously dried at 60 \(^\circ\)C for 12 h by vacuum drying and was named NiMn LDHs/Ni fiber electrode.

2.2.4. Synthesis of NiFe LDHs/Ni Foam

For comparison, the Ni fiber was replaced with Ni foam (Figure S1). The Ni foam (2 \(\times\) 5 cm\(^2\)) was cleaned with C\(_3\)H\(_6\)O, 3 M HCl, C\(_2\)H\(_5\)OH, and deionized water in ultrasound for 5 minutes. In a typical procedure, NiCl\(_2\)·6H\(_2\)O (1.19 g) and FeCl\(_2\)·4H\(_2\)O (0.10 g) were dissolved in 50 mL of deionized water under continuous stirring for 1 h. The obtained solution was light green.

Afterward, the cleaned Ni foam substrate was immersed in the light green solution for 7 days, and the obtained product was washed with deionized water several times. Finally,
the product was continuously dried at 60 °C for 12 h by vacuum drying and was named NiFe LDHs/Ni foam electrode.

2.2.5. Synthesis of IrO$_2$/Ni Fiber

To prepare the IrO$_2$/Ni fiber electrode, 5 mg of IrO$_2$ was dispersed into 20 µL Nafion (5 wt%) and 980 µL ethanol and water (volume ratio 1:1), and obtained uniform ink through ultrasonic treatment [16]. Then IrO$_2$ ink was dropped on the cleaned Ni fiber substrate and dried at 60 °C.

2.2.6. Preparation of the AEMWE Single-Cell

In a typical procedure, the AEMWE system consists of an anode (NiFe LDHs/Ni fiber, 2 × 2 cm$^2$), a cathode (0.4 mg cm$^{-2}$ of 70 wt.% Pt/C) coated on the anion exchange membrane (A201, Tokuyama, 2 × 2 cm$^2$), and a gas diffusion layer (carbon paper, Toray) [17–19]. Then, the anode, the cathode, an alkaline anion exchange membrane, and carbon paper were hot-pressed at 60 °C and 0.1 MPa for 2 min to obtain membrane electrode assembly (NiFe LDHs/Ni fiber || Pt/C) [20,21]. The AEMWE single-cell was assembled as shown in Figure 1.

2.3. Material Characterizations

The morphology characterization was tested by a scanning electron microscope (SEM, JSM-7800F) instrument produced in Japan, and the microstructure was analyzed with a transmission electron microscope (TEM, JEM-2100F). A Miniflex600 (X-ray diffraction XRD) produced in Japan was used to characterize the object image structure of the material. The X-ray photoelectron spectroscopy (XPS) was measured on the ESCALAB 250Xi spectrometer (Thermo Fisher, Waltham, MA, USA).

2.4. Electrochemical Measurements

The electrochemical measurements were carried out on a Gamry Interface 1000 e electrochemical workstation in 1 M KOH (pH = ~14, O$_2$ saturated) at room temperature. The graphite plate was used as the counter electrode, the standard Hg/HgO electrode was used as the reference electrode, and the prepared self-supported electrodes (1 × 1 cm$^2$) were used as the working electrode. In a three-electrode system, the voltage used in the experiment has been converted to the reversible hydrogen electrode (RHE) based on the Formula (1) [22–25]:

$$E_{RHE} = E_{Hg/HgO} + 0.059pH + 0.098$$  \hspace{1cm} (1)

The calculation of overpotential follows Equation (2) [25,26]:

$$\eta = E_{RHE} - 1.23V$$ \hspace{1cm} (2)

The electrode was activated by cyclic voltammetry (CV). Linear sweep voltammetry (LSV) was used to evaluate the activity of the catalysts between 0–1 V (V vs. Hg/HgO) at a scan rate of 2 mV s$^{-1}$. Electrochemical impedance spectroscopy (EIS) was tested at 0.6 V (V vs. Hg/HgO), with an amplitude of 5 mV in a frequency range from 0.1 Hz to 100 kHz. The chronopotentiometry curves were carried out at different current densities for 10, 50, 100, 200, 300, and 10 mA cm$^{-2}$, respectively. The electrochemically surface area (ECSA) was measured by the CV method at different scan rates in the non-Faradaic region and calculated based on the following (3) [27,28]:

$$ECSA = \frac{C_{dl}}{C_s}$$ \hspace{1cm} (3)

To further test the practical application of the NiFe LDHs/Ni fiber, it was assembled into an AEMWE (2 × 2 cm$^2$). Current–voltage ($I$–$V$) curves were measured at 70 °C. 1 M KOH and the electrolyte were supplied into the anode at a flow rate of 5 mL min$^{-1}$. The stability test was conducted at a current density of 0.5 A cm$^{-2}$ for 200 h. The AEMWE charge
transfer resistance and ohmic resistance were analyzed by measuring EIS at 1.7 V [19]. The amplitude was 10 mV and the frequency range was from 100 mHz to 10 kHz.

3. Results and Discussion

3.1. Structure and Characterization

The morphologies of the Ni fiber electrode and NiFe LDHs/Ni fiber electrode were observed with an SEM. Figure 2a is a bare Ni fiber substrate, which can be seen to be composed of many interlaced fibers. Figure 2b,c are SEM images of NiFe LDHs/Ni fiber electrode under different magnifications. It can be seen that a lot of “nanoflower” clusters grow uniformly on the Ni fiber substrate. The structure is similar to the microstructure of NiFe LDHs reported in the literature [29].

![Figure 2. SEM images of Ni fiber electrode, (a) and NiFe LDHs/Ni fiber electrode (b–d).](image)

Further magnification can show that the nanoflower-like structure is composed of ordered nanowires and extends to the surrounding space as shown in Figure 2d. It can be seen from the further magnification in Figure 2d that the outward extension of each petal of the “nanoflower” cluster petals stretching outward produces the “tip effect”, which is more conducive to the exposure of active sites at the edge and mass transfer under high current density. The results are consistent with the research on the “cluster structure” in recently reported literature [5,30,31].

For comparison, the NiCo LDHs/Ni fiber electrode, the NiMn LDHs/Ni fiber electrode, and the NiFe LDHs/Ni foam electrode were also characterized with an SEM in Figure S2. It can be seen from Figure S2a,b that a dense layer of NiCo LDHs nanosheet is vertically grown on the Ni fiber substrate. Figure S2d–f shows that NiMn LDHs nanosheets are staggered and vertically grown on a Ni fiber substrate. Figure S2g–i shows that NiFe LDHs nanosheets are interlaced or part of the nanosheets form nanoflower balls, which are vertically arranged on the Ni foam substrate. The above results show that the special morphology and structure of NiFe LDHs/Ni fiber electrode are closely related to the substrate of Ni fiber.
To further investigate the microstructure of the NiFe LDHs/Ni fiber electrode, we used ultrasound to exfoliate NiFe LDHs from the Ni fiber framework and observed by the TEM. Figure 3a is the TEM diagram of NiFe LDHs “nanoflowers”. It can be seen that the “nanoflower” cluster petals stretching outward produce the “tip effect”. This result is consistent with the SEM image. The high-resolution TEM image of NiFe LDHs shows the clear lattice fringes are 0.26 nm, matching the (012) crystal planes in Figure 3b.

![TEM Images of NiFe LDHs](image)

**Figure 3.** TEM images of the NiFe LDHs (a,b).

The crystal phase characterization of the Ni fiber electrode and NiFe LDHs/Ni fiber electrode by XRD is shown in Figure 4a. The XRD pattern shows that the strong diffraction peaks at 44.3°, 51.7°, and 76.2° correspond to (111), (200), and (220) crystal planes of metal Ni (PDF#87-0712) fragments from Ni fiber [13,25]. The peaks at 11.4°, 23.1°, 34.3°, 38.8°, 46.3°, 59.8°, and 61.2° correspond to the (003), (006), (012), (015), (018), (110), and (113) crystal planes of NiFe LDHs (PDF#40-0215) [20,32,33]. These results prove the successful formation of the NiFe LDHs phase on Ni fiber substrate.

The surface chemical composition and valence state of the NiFe LDHs/Ni fiber electrode were analyzed by XPS [13]. The survey spectrum further verified the existence of O, Fe, and Ni elements, respectively (in Figure 4b). The XPS spectrum of Ni 2p (in Figure 4c) shows that the peaks located at 855.8 eV and 873.6 eV belong to the Ni 2p3/2 and Ni 2p1/2, respectively, and the two surrounding satellites (abbreviated as “sat.”), indicating that Ni2+ exists in NiFe LDHs/Ni fiber electrode [5,13,25]. As shown in Figure 4d, the Fe 2p XPS spectrum shows that the peaks at 711.6 and 725.3 eV belong to Fe 2p3/2 and Fe 2p1/2, respectively, and the two surrounding satellites (abbreviated as “sat.”), indicating that Fe3+ exists in NiFe LDHs/Ni fiber electrode [34–36]. O 1s spectrum in Figure 4e, the peaks located at 529.2 eV, 530.8 eV, and 532.5 eV are attributed to the metal–oxygen bend (M–O), oxygen in the hydroxide group(M–OH), and chemisorbed water [34,37].

### 3.2. OER Performance in Alkaline Media

The OER electrocatalytic performance of the prepared self-supported NiFe LDHs/Ni fiber electrode was tested with a typical three-electrode system in 1 M KOH solution at 25 °C (oxygen saturated). For comparison, the NiCo LDHs/Ni fiber electrode, NiMn LDHs/Ni fiber electrode and NiFe LDHs/Ni foam electrode, IrO2/Ni fiber electrode, and Ni fiber electrode were also investigated under the same conditions. Figure 5a shows the LSV curves (without iR compensation) of the Ni fiber electrode, NiCo LDHs/Ni fiber electrode, NiMn LDHs/Ni fiber electrode, NiFe LDHs/Ni foam electrode, and IrO2/Ni fiber electrode, respectively. It can be seen that the NiFe LDHs/Ni fiber electrode shows excellent OER catalytic activity in Figure 5a. The NiFe LDHs/Ni fiber at current densities of 10 and 50 mA cm⁻² required overpotentials of 208 and 260 mV, respectively. This result is better than the NiCo LDHs/Ni fiber electrode (286 and 346 mV), NiMn LDHs/Ni fiber electrode (300 and 364 mV), NiFe LDHs/Ni foam electrode (246 and 300 mV), IrO2/Ni fiber electrode (300 and 356 mV), and Ni fiber electrode (340 and 416 mV), respectively (in Figure 5b). In Figure 5c, the NiFe LDHs/Ni fiber electrode shows a smaller Tafel slope of 50 mV dec⁻¹, which is smaller than NiCo LDHs/Ni fiber electrode (69 mV dec⁻¹), NiMn LDHs/Ni fiber electrode (78 mV dec⁻¹), IrO2/Ni fiber electrode (75 mV dec⁻¹), NiFe LDHs/Ni foam electrode...
(60 mV dec$^{-1}$), and Ni fiber (89 mV dec$^{-1}$). The kinetics of the electrodes are measured by EIS. As shown in Figure 5d, the NiFe LDHs/Ni fiber electrode has a smaller semicircle than the NiCo LDHs/Ni fiber electrode, NiMn LDHs/Ni fiber electrode, NiFe LDHs/Ni foam electrode, IrO$_2$/Ni fiber electrode, and Ni fiber electrode, which indicates that it has the lowest charge transfer resistance ($R_{ct}$) [25,38,39]. The results show that NiFe LDHs/Ni fiber electrode has fast charge transfer and ion diffusion. In addition, we evaluated the long-term stability of the NiFe LDHs/Ni fiber electrode through the chronopotentiometry test and studied different current densities (10, 50, 100, 200, 300, and 10 mA cm$^{-2}$) for a total of 60 h (Figure 5e). Figure 5f summarizes the OER performance comparison between NiFe LDHs/Ni fiber electrode and the newly reported non-noble metal-based self-supporting electrodes (see Table 1) [5,6,40–46].

![Figure 4](image-url)

Figure 4. (a) XRD patterns of NiFe LDHs/Ni fiber electrode; (b) the NiFe LDHs/Ni fiber electrode XPS spectra of survey; (c) the NiFe LDHs/Ni fiber electrode of Ni 2p XPS spectra; (d) the NiFe LDHs/Ni fiber electrode of Fe 2p XPS spectra; (e) the NiFe LDHs/Ni fiber electrode of O 1s XPS spectra.
Figure 5. The OER performances were tested in a three-electrode system with 1 M KOH. (a) LSV curves of Ni fiber electrode, NiCo LDHs/Ni fiber electrode, NiMn LDHs/Ni fiber electrode, IrO$_2$/Ni fiber electrode, NiFe LDHs/Ni foam electrode, and NiFe LDHs/Ni fiber electrode with a scan rate of 2 mV s$^{-1}$ at room temperature; (b) the comparison of overpotential at 10, 50, and 100 mA cm$^{-2}$ for NiFe LDHs/Ni fiber electrode; (c) the corresponding Tafel plots; (d) Nyquist plots; (e) chronopotentiometry curves of NiFe LDHs/Ni fiber at various current densities; (f) comparison of the recently reported OER electrode and our work with the density of 10 mA cm$^{-2}$.

Table 1. Summary of various non-noble metal catalysts for OER in alkaline solution (25 °C).

<table>
<thead>
<tr>
<th>Electrocatalysts</th>
<th>Substrate</th>
<th>$\eta$ for OER at Corresponding $j$ (mV@mA cm$^{-2}$)</th>
<th>Tafel Slope (mV dec$^{-1}$)</th>
<th>Stability Tests</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCoFe-NDA</td>
<td>nickel foam</td>
<td>215@10 (iR-compensated)</td>
<td>64.1</td>
<td>100 mA cm$^{-2}$ for 50 h</td>
<td>[6]</td>
</tr>
<tr>
<td>a-LNFBOPO@Ni foam</td>
<td>nickel foam</td>
<td>215@10 (iR-compensated)</td>
<td>37</td>
<td>10 mA cm$^{-2}$ for 300 h</td>
<td>[40]</td>
</tr>
<tr>
<td>V$_{25%}$-Ni$_2$P/NF-AC</td>
<td>nickel foam</td>
<td>221@10 (without iR compensated)</td>
<td>66</td>
<td>50 mA cm$^{-2}$ for 20 h</td>
<td>[41]</td>
</tr>
<tr>
<td>Cr$_1$/FeNi-LDH-SS</td>
<td>stainless steel mesh</td>
<td>202@10 (iR-compensated)</td>
<td>32.5</td>
<td>various current densities for 17 h</td>
<td>[42]</td>
</tr>
<tr>
<td>Cu@CeO$_2$@NFC-0.25</td>
<td>copper foam</td>
<td>231@10 (without iR compensated)</td>
<td>32.7</td>
<td>10 and 20 mA cm$^{-2}$ for 30 h</td>
<td>[43]</td>
</tr>
<tr>
<td>$\gamma$-FeOOH/NF-6M</td>
<td>nickel foam</td>
<td>286@10 (iR compensated)</td>
<td>51</td>
<td>10 and 50 mA cm$^{-2}$ for 48 h</td>
<td>[44]</td>
</tr>
</tbody>
</table>
To further study the catalytic performance of the electrodes, the electrochemical double-layer capacitance ($C_{dl}$) was calculated to evaluate the electrochemical active surface area (ECSA) in Figure 6. As shown in Figure 6f, the $C_{dl}$ of NiFe LDHs/Ni fiber electrode is 5.57 mF cm$^{-2}$, which is significantly higher than that NiFe LDHs/Ni foam electrode (5.02 mF cm$^{-2}$), NiCo LDHs/Ni fiber electrode (4.61 mF cm$^{-2}$), NiMn LDHs/Ni fiber electrode (4.49 mF cm$^{-2}$), and Ni fiber electrode (3.51 mF cm$^{-2}$). The NiFe LDHs/Ni fiber electrode has the largest $C_{dl}$, indicating that it has a large ECSA, which makes it easier to expose the catalytic active sites.
To investigate the changes of NiFe LDHs/Ni fiber electrode after the long-term stability OER test, the morphology structure and element analysis were measured by SEM (Figure S3), and XPS (Figure S4) shows that the morphology of the NiFe LDHs/Ni fiber electrode continues to remain original after the long-term stability test. In addition, the XPS spectra before and after the stability experiment were compared. It can be seen that the chemical components of Ni, Fe, and O still exist. This result proves that the NiFe LDHs/Ni fiber electrode has excellent stability.

The results further prove that the NiFe LDHs/Ni fiber electrode has excellent OER electrocatalytic performance, which is due to the special morphological structure of the “nanoflowers” cluster petal stretching outward to produce the “tip effect”, which is more conducive to the exposure of active sites at the edge and mass transfer under high current density [5,30,31].

3.3. Performance of NiFe LDHs/Ni Fiber Electrode as the Anode of the AEMWE

The application of the NiFe LDHs/Ni fiber electrode as an AEMWE anode under industrial conditions for large currents (>200 mA cm\(^{-2}\)) at alkaline water electrolysis [25,47] was further investigated. The assembly of AEMWE (NiFe LDHs/Ni fiber || Pt/C) (in Figure S6) was tested at 70 °C in 1 M KOH with used a NiFe LDHs/Ni fiber electrode as an anode and commercial Pt/C as a cathode, respectively. As shown in Figure 7a, the AEMWE (NiFe LDHs/Ni fiber || Pt/C) cell current densities were 0.5 and 1 A cm\(^{-2}\), and the cell voltages only 1.68 and 1.87 V (without iR correction), corresponding to the energy efficiency of 88.1 and 79.1%, respectively. This proves that the self-supporting structure of the NiFe LDHs/Ni fiber electrode is beneficial to the gas diffusion of bubbles and the transportation of the electrolytes, resulting in excellent water electrolysis performance under high current density [25]. Figure 7b shows that the long-term stability of the AEMWE was measured at 0.5 A cm\(^{-2}\) for 200 h. In addition, the decrease in voltage is due to the following reasons: (1) after a long-term stability test, some NiFe LDHs catalysts fell off from the Ni fiber substrate; (2) to imitate the start-up and shutdown in the actual application process, the start-up and shutdown are conducted every 12 h, and the newly prepared KOH electrolyte is replaced at the same time; and (3) the in-depth research of Liu et al. on the OER loss mechanism of the layered NiFe LDHs catalyst revealed that the layered structure is not conducive to long-term stability [48]. Ohmic resistance and charge transfer resistance were evaluated by measuring EIS at 1.7 V (about 0.5 A cm\(^{-2}\)) [4]. As shown in Figure 7d, it can be seen that the \(R_\text{ct}\) of the AEMWE is small, which means that the NiFe LDHs/Ni fiber electrode has an efficient charge transfer capability in AEMWE [20]. Figure 7d summarizes the performance comparison between the NiFe LDHs/Ni fiber electrode and the newly reported non-noble metal-based self-supporting electrode as the AEMWEs electrode (see Table 2) [4,17,18,20,21,32,49,50]. The above results reveal that the NiFe LDHs/Ni fiber electrode has excellent catalytic activity and electrochemical stability in AEMWE. In addition, we also enlarged the NiFe LDHs/Ni fiber electrode (20 × 20 cm) as shown in Figure S5. This further proves that the NiFe LDHs/Ni fiber electrode has industrialized application prospects.

| (Anode || Cathode) | Cell Voltage (V @ A cm\(^{-2}\)) | Cell Temperature (°C) | Stability Test (hours @ A cm\(^{-2}\)) | Reference |
|------------------|-----------------------------------|------------------------|----------------------------------------|-----------|
| NiFeCo LDH || NiFeCo phosphide     | 1.75 @ 0.5             | 50                      | 40 @ 0.5                              | [18]      |
| FeOOH/NiFe LDHs@CCH NAs-NF || 70 wt% Pt/C (0.4 mg cm\(^{-2}\)) | 1.68 @ 0.5             | 70                      | 100 @ 0.5                              | [32]      |
| Co(OH)\(_x\)/Ag/Co(OH)\(_2\) || 40 wt% Pt/C (not mention) | 1.8 @ 0.6             | 50                      | 24 @ 0.6                               | [17]      |
| VCoCO\(_x\)@NF || VCoCO\(_x\)@NF     | 2.01 @ 0.2             | 45                      | 12 @ 0.25                              | [21]      |
| CE-COO || 70% wt Pt/C (1 mg cm\(^{-2}\)) | 1.8 @ 1.39             | 45                      | 64 @ 0.5                               | [49]      |
| Ni\(_{90}\)Fe\(_{10}\) (1 mg cm\(^{-2}\)) || 60 wt% Pt/C (1 mg cm\(^{-2}\)) | 1.72 @ 0.8             | 50                      | not mention                            | [50]      |
Table 2. Cont.

| (Anode || Cathode) | Cell Voltage (V @ A cm⁻²) | Cell Temperature (°C) | Stability Test (hours @ A cm⁻²) | Reference |
|-------------------|--------------------------|-----------------------|-------------------------------|-----------|
| M-NiFe-LDH (3 mg cm⁻²) || Pt/C (0.4 mg cm⁻²) | 1.69 @ 1 | 50 | 50 @ 1 | [4] |
| M-NiFe-LDH (3 mg cm⁻²) || Pt/C (0.4 mg cm⁻²) | 1.63 @ 1 | 80 | 50 @1 | [4] |
| NiFe LDH-MoS₂/INF || Pt/C/CP (2 mg cm⁻²) | 1.95 @ 1 | 60 | not mention | [20] |
| NiFe LDHs/Ni fiber || Pt/C (0.4 mg cm⁻²) | 1.68 @ 0.5 | 70 | 200 @ 0.5 | This Work |

Figure 7. (a) Current-voltage curves of the NiFe LDHs/Ni fiber electrode as the anode for AEMWE at 70 °C; (b) stability test at 0.5 A cm⁻²; (c) Nyquist plots were evaluated at 1.7 V; (d) comparison of the NiFe LDHs/Ni fiber || Pt/C AEMWE with that recently reported.

4. Conclusions

In conclusion, the highly efficient and stable self-supporting NiFe LDHs/Ni fiber “nanoflower” cluster electrode was successfully prepared by a facile one-step impregnation method at room temperature and ambient pressure. Benefiting from the synergistic effect between NiFe LDH “nanoflower” cluster petals stretching outward to produce the “tip effect” and the Ni fiber substrate, the NiFe LDHs/Ni fiber electrode has significant inherent activity and structure. The NiFe LDHs/Ni fiber electrode has excellent OER performance with a low overpotential of 208 mV at the current density of 10 mA cm⁻² in 1 M KOH. When the NiFe LDHs/Ni fiber electrode is used as the anode of AEMWE (NiFe LDHs/Ni fiber || Pt/C), it shows high energy conversion efficiency of 88.1% with the cell voltage of 1.68 V at the current density of 0.5 A cm⁻² under industrial conditions of alkaline water electrolysis. In addition, the NiFe LDHs/Ni fiber electrode was tested by stability at 0.5 A cm⁻² for 200 h, indicating that it has good stability. The self-supporting NiFe LDHs/Ni fiber electrode has the advantage of simple, low-cost synthesis method that yields high-efficient catalytic activity and durability.
Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/en15134645/s1, Figure S1: The SEM images of Ni foam. Figure S2: The SEM images of NiCo LDHs/Ni fiber (a–c), NiMn LDHs/Ni fiber (d–f), NiFe LDHs/Ni foam (g–i). Figure S3: The SEM images of NiFe LDHs/Ni fiber after the durability test. Figure S4: The images of NiFe LDHs/Ni fiber after the durability test. XPS spectra of survey (a); Ni 2p XPS spectra (b); Fe 2p XPS spectra (c); O 1 s XPS spectra (d). Figure S5: The optical image of NiFe LDHs grown on large-scale Ni fiber. Figure S6. The digital photo of the AEMWE cell.

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