NiMoCo layered double hydroxides for electrocatalyst and supercapacitor electrode

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ABSTRACT Non-noble-metal electrode materials with high durability and efficiency have become the frontiers of energy conversion and storage fields. However, conventional electrode materials often show high overpotential and low conductivity. To solve this problem, we fabricate a NiMo_xCo_{2-x} layered double hydroxide (LDH)/Ni foam (NF) product through a facile hydrothermal route. The as-prepared NiMoCo-LDH/NF catalyst possesses an overpotential of 123 mV for hydrogen evolution reaction (HER) at 10 mA cm⁻² and 279 mV for oxygen evolution reaction (OER) at 20 mA cm⁻². The as-obtained product exhibits excellent overall water splitting performances. Meanwhile, as the electrode material for supercapacitor, it delivers high specific capacitance and excellent cyclic performance. The asymmetric supercapacitor assembled with NiMoCo-LDH/NF/active carbon exhibits 93% of its initial capacity after 8000 cycles.

Keywords: layered double hydroxide, hydrogen evolution reaction, oxygen evolution reaction, overall water splitting, supercapacitor, energy density

INTRODUCTION

With the rapid development of human society, the demands for energy resources have become very imperative [1–3]. Currently, most of energy comes from traditional fossil fuels [4–6]. However, they might cause serious environmental pollution, and thus it is urgent to seek for alternative clean energy sources to solve the problem. Hydrogen is widely used owing to its unique superiority such as zero carbon emission, abundant reservation and high efficiency [7–9]. Electrochemical water splitting has been identified as one of the most prosperous hydrogen production technologies [10,11]. However, their two reactions exhibit sluggish kinetic processes and high overpotentials [12–14]. It is still a challenge for rational design of catalysts to accelerate their half reaction rates. Gen-

erally speaking, noble metal-based catalysts show fast reaction kinetics. Nevertheless, high cost and scarcity limit their widespread applications [15–17].

Recently, many transition metal hydroxides have been widely investigated as electrochemical catalysts [18,19]. Among them, layered double hydroxides (LDHs) stand out due to their adjustable composition, low cost and high activity [20–22]. Thus far, several high-performance LDH structures have been reported, such as NiFe-LDH arrays, NiCo-LDH and ZnCo-LDH electrocatalysts [23–25]. However, for overall water splitting, they behave with low specific surface area and poor conductivity. These problems can be effectively solved by the reasonable selection and design of electrode materials. For example, Yao *et al.* [26] synthesized Ni/Co/Fe phosphosulfide nanorods through a hydrothermal electrodeposition route. The as-obtained products possess an overpotential of 195 mV (oxygen evolution reaction, OER) and 97.8 mV (hydrogen evolution reaction, HER) at a current density of 10 mA cm⁻². Chanda and coworkers [27] fabricated a Li-doped NiFeCo oxide catalyst with an overpotential of 220 mV at 10 mA cm⁻² for OER. In addition, Xie *et al.* [28] studied the importance of coexistence of ion pairs. They thought that the specific sites of oxygen adsorption (Co²⁺-O-Co³⁺) can improve the catalyst's activity. Inspired from excellent redox activity of molybdenum under mild reaction, nickel, another active transition metal, usually combines with other materials [29]. Fan's group [30] reported that addition of Ni ion into CeO₂ can improve its catalytic performance due to the enhanced redox activity and oxygen storage capacity.

In addition, supercapacitors have attracted extensive attention because they possess excellent cycling stability and fast charge/discharge ability [31–33]. However, the capacitors based on traditional metal oxides still suffer from low energy density, which limits their practical ap-

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plications [34]. Therefore, the design of novel electrodes has become a big challenge. Thereinto, LDH can improve the entire electrode surface and promote the ion adsorption from the electrolyte to increase the energy density. For example, Qiu's group [35] fabricated Ni-CoAl-LDH nanoplates with an energy density of 14.9 W h kg^{-1} at 51.5 kW kg^{-1} . Zhou *et al.* [36] reported $\text{Co}_3\text{O}_4@\text{CoNi-LDH}$ core/shell nanosheet arrays exhibiting a high energy density ($61.23 \text{ W h kg}^{-1}$) at a power density of 750 W kg^{-1} .

In this work, we prepare a series of $\text{NiMo}_x\text{Co}_{2-x}\text{-LDH/Ni foam (NF)}$ catalysts directly grown on NF by a facile hydrothermal route. The NiMoCo-LDH/NF electrode exhibits an overpotential of 123 mV at 10 mA cm^{-2} for HER and excellent OER performance. When used as the electrocatalyst for overall water splitting, it shows a cell voltage of 1.71 V at a current density of 20 mA cm^{-2} and stability for more than 14 h. Meanwhile, as the capacitor electrode material, it delivers high specific capacitance and excellent cyclic performance. The asymmetric supercapacitor (ASC) assembled with $\text{NiMoCo-LDH/NF}/\text{active carbon (AC)}$ exhibits a high energy density at a power density of 2695 W kg^{-1} and 93% of its capacitance retention after 8000 cycles.

EXPERIMENTAL SECTION

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{MoO}_4 \cdot 6\text{H}_2\text{O}$ were obtained from Shanghai Aladdin Bio-Chem Technology Co. Ltd. Urea and NH_4F were purchased from Sigma-Aldrich. All chemical reagents were used as purchased. Before the experiment, a piece of NF ($3 \text{ cm} \times 3 \text{ cm}$) was immersed into 0.5 mol L^{-1} HCl solution. Next, it was washed with ethanol and deionized water under sonication successively, and then dried overnight.

$\text{NiMo}_x\text{Co}_{2-x}\text{-LDH/NF}$ nanosheets were prepared by a facile hydrothermal method. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{MoO}_4 \cdot 6\text{H}_2\text{O}$ with a molar ratio of $2:x:(2-x)$ were dissolved in 50 mL deionized water. Afterwards, 5 mmol urea and equal quantity of NH_4F were added to the above solution under constant stirring. Then a piece of pre-treated NF with the above mixture was transferred into an autoclave and heated at 140°C for 6 h. After being cooled to room temperature, the as-synthesized samples were cleaned with deionized water and dried at 60°C . The loading amounts of $\text{NiMo}_2\text{-LDH}$, $\text{NiMo}_{1.5}\text{Co}_{0.5}\text{-LDH}$, NiMoCo-LDH , $\text{NiMo}_{0.5}\text{Co}_{1.5}\text{-LDH}$ and $\text{NiCo}_2\text{-LDH}$ materials on a substrate of 1.0 cm^2 were about 2.1, 1.9, 1.7, 1.6, and 2.0 mg, respectively.

X-ray diffraction analyzer (XRD, Shimadzu-7000) with a Cu K α radiation ($\lambda = 0.1541 \text{ nm}$, 40 kV) and X-ray

photoelectron spectra (XPS, ESCALAB250) with an Al K α source were used to investigate the phase composition and crystal structure of the samples. The structure and morphology of the products were characterized by using a scanning electron microscope (SEM, Gemini, 300-71-31).

Electrocatalytic performances of the samples were investigated by using a CHI660E electrochemical workstation in a standard three-electrode system. The samples were used as the working electrode. An Ag/AgCl electrode with saturated KCl solution was used as the reference electrode through a double salt-bridge and luggin capillary. And it was calibrated before and after the experiments to ensure accuracy. The Ag/AgCl reference electrode was not directly contacted to the alkaline electrolyte but *via* the salt-bridge full of saturated KCl solution that can eliminate the diffusion potential and maintain its stability. Without this salt-bridge, the accuracy of the Ag/AgCl reference electrode will be reduced because of its corrosion in the alkaline electrolyte. Pt foil was used as the counter electrode for OER (graphite counter electrode for HER) in 1 mol L^{-1} KOH (pH~13.7) electrolyte. All potentials were calculated by using the follow equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V} + 0.059 \text{ V} \times \text{pH}, \quad (1)$$

where E_{RHE} is the potential of the reversible hydrogen electrode (RHE), $E_{\text{Ag/AgCl}}$ represents the experimentally measured potential against the Ag/AgCl reference electrode. All overpotentials (η) of OER were studied through the equation:

$$\eta = E_{\text{RHE}} - 1.23. \quad (2)$$

Linear sweep voltammetry (LSV) polarization curves were measured from 0 to 0.7 V (OER), from -1.45 to -0.9 V (HER) and between 0 and 2.0 V (overall water splitting). Electrochemical impedance spectra (EIS) were evaluated at the open-circuit potential in the frequency range of 10 to 100 mHz. The electrochemical active surface area (ECSA) was analyzed by cyclic voltammetry (CV) curves at various scan rates.

CV measurements, galvanostatic charge-discharge (GCD) curves, and EIS measurements were investigated in a standard three-electrode system in 3 mol L^{-1} KOH electrolytes. The as-prepared samples were used as the working electrode, Pt foil as the counter electrode and Hg/HgO as the reference.

An ASC was constructed by using the NiMoCo-LDH/NF sample as the cathode and AC as the anode. The energy density (E) and power density (P) of the ASC can be calculated by the equations below:

$$E = 1/2CV^2, \quad (3)$$

$$P = 3600E/t, \quad (4)$$

where E (W h kg^{-1}) is the energy density, P (W kg^{-1}) is the power density, C (F g^{-1}) is the specific capacitance, V (V) is voltage range, t (s) is the total discharge time.

RESULTS AND DISCUSSION

The crystal structures of the as-obtained samples were firstly investigated by XRD. The peaks marked with “*” are from NF (Fig. 1a, b). The diffraction patterns of $\text{NiMo}_x\text{Co}_{2-x}\text{-LDH}$ ($x=2$) can be indexed to standard cubic spinel $\text{NiMoO}_4 \cdot x\text{H}_2\text{O}$ phase (JCPDF No. 13-0128) ($\text{NiMo}_2\text{-LDH}$). When the molar ratio of Ni, Mo and Co elements is 1:0:2, the crystal structure changes into $(\text{Co}, \text{Ni})\text{O}(\text{OH})$ phases (JCPDF No. 29-0491), named as $\text{NiCo}_2\text{-LDH}$. In Fig. 1b, with increasing Co content, the characteristic peaks gradually shift to $\text{NiCo}_2\text{-LDH}$ phases.

Surface chemical states and elemental composition of the as-prepared NiMoCo-LDH electrode were analyzed by XPS. In Fig. 1c, the XPS spectrum of Ni 2p consists of four peaks, which include two spin-orbit doublets of Ni 2p_{3/2} and Ni 2p_{1/2} and two shakeup satellites. Two main peaks at 854.5 and 873.1 eV with spin-orbit splitting of 18.6 eV correspond to Ni 2p_{3/2} and Ni 2p_{1/2}. The ones at 854.5 and 873.1 eV can be attributed to Ni^{3+} , and the fitted peaks centered at 853.1 and 871.2 eV correspond to

Ni^{2+} [37,38]. Additionally, the peaks at 860.6 and 879.3 eV can be ascribed to charge-transfer shakeup satellite peaks. From XPS spectra of Co 2p (Fig. 1d), two strong peaks at 778.9 and 795.1 eV correspond to Co 2p_{3/2} and Co 2p_{1/2}. The peaks at binding energies of 771.2 and 795.1 eV could be indexed to Co^{3+} , and the one at 799.1 eV is ascribed to Co^{2+} . Meanwhile, two shakeup satellite peaks are also observed at 783.9 and 801.6 eV [39,40]. Fig. 1e exhibits the Mo 3d spectra. The binding energies of 229.3 and 232.5 eV correspond to Mo 3d_{5/2} and Mo 3d_{3/2}, respectively [41]. O 1s spectra (Fig. 1f) are composed of three main peaks (denoted as O1, O2 and O3), where O1 is metal oxygen bonds, O2 represents oxygen ions and O3 denotes the physicochemically adsorbed water at the surface of active material [42].

Then the morphologies of the as-prepared samples were observed by SEM. In Fig. 2a and b, the $\text{NiMo}_2\text{-LDH}$ electrode presents flower-like shapes and consists of the interconnected nanosheets. The average thickness of the nanosheets is around 20 nm. SEM images of the $\text{NiCo}_2\text{-LDH}$ material also exhibit the morphology of nanosheets, which are closely covered on the surface of NF (Fig. 2d, e). Fig. 2c and f show the corresponding element mappings. Energy-dispersive X-ray spectroscopy (EDS) mappings of $\text{NiMo}_x\text{Co}_{2-x}\text{-LDH}$ samples demonstrate that elements of Ni, Mo, Co and O are uniformly distributed on the sample surfaces.

Figure 1 (a, b) XRD patterns of the as-prepared samples. XPS spectra of the NiMoCo-LDH sample: (c) Ni 2p, (d) Co 2p, (e) Mo 3d, (f) O 1s.

Figure 2 Low- and high-magnification SEM images, and elemental mappings of the NiMo₂-LDH samples (a–c), and the NiCo₂-LDH electrodes (d–f).

Besides, morphology variation of the samples coated on NF was investigated. It is found that the spaces between nanosheets gradually increase and eventually generate individual nanosheets with the content of Mo decreasing (Fig. 3a–c). When the atomic percentage of Mo element is 4.98, the distance between the individual nanosheets is about 500 nm, and they are staggered and vertically grown on the substrate instead of being stacked layer by layer, resulting in full contact of the electrolyte for enhanced available active sites. The nanosheets of the samples are stacked on top of each other when only two elements are present in the materials (Mo 0 at%). The corresponding high-magnification SEM images are shown in Fig. 3d–f.

To study the electrocatalytic performances of the as-prepared samples, HER experiments were conducted in a standard three-electrode system in 1.0 mol L^{−1} KOH at a scan rate of 5 mV s^{−1}. As shown in Fig. 4a, NiMoCo-LDH/NF (η at 10 mA cm^{−2}, η_{10} = 123 mV) is superior to NiMo₂-LDH/NF (η_{10} = 167 mV), NiMo_{1.5}Co_{0.5}-LDH/NF (η_{10} = 149 mV), NiMo_{0.5}Co_{1.5}-LDH/NF (η_{10} = 169 mV) and NiCo₂-LDH/NF (η_{10} = 178 mV) electrodes. To evaluate HER kinetics of the electrodes, Tafel slopes (Fig. 4b) were calculated on the basis of LSV curves. The liner part of Tafel plot was obtained by the following equation [43]:

$\eta = a + b \log j$. η represents the overpotential, b is the Tafel slope and j denotes the current density. The Tafel slopes of NiMo₂-LDH/NF, NiMo_{1.5}Co_{0.5}-LDH/NF, NiMoCo-LDH/NF, NiMo_{0.5}Co_{1.5}-LDH/NF and NiCo₂-LDH/NF electrodes are 191.64, 101.55, 67.39, 157.48 and 159.20 mV dec^{−1}, respectively. The low slope of NiMoCo-LDH/NF catalyst further shows favorable kinetics for HER. From Fig. 4c, the NiMoCo-LDH/NF sample possesses the smallest overpotential.

ECSA was then examined by the electrochemical double layer capacitance (C_{dl}). Large C_{dl} value reveals that electrocatalysts possess plentiful exposed active catalytic sites, which facilitates the adsorption of water molecules [44]. As shown in Fig. 4d, C_{dl} of NiMoCo-LDH/NF (7.45 mF cm^{−2}) electrode is higher than those of NiMo₂-LDH/NF (3.87 mF cm^{−2}), NiMo_{1.5}Co_{0.5}-LDH/NF (5.11 mF cm^{−2}), NiMo_{0.5}Co_{1.5}-LDH/NF (4.93 mF cm^{−2}), and NiCo₂-LDH/NF (3.11 mF cm^{−2}).

EIS reflects the kinetics of the electrode/electrolyte surface. In Fig. 4e, the NiMoCo-LDH/NF possesses larger slope than other electrodes, revealing the rapid electron transfer ability. Meanwhile, the solution resistance (R_s) values of NiMo₂-LDH/NF, NiMo_{1.5}Co_{0.5}-LDH/NF, NiMoCo-LDH/NF, NiMo_{0.5}Co_{1.5}-LDH/NF and NiCo₂-LDH/NF electrodes are 2.14, 2.21, 2.02, 2.32 and 2.59 Ω,

Figure 3 (a–c) Low-magnification SEM images of $\text{NiMo}_x\text{Co}_{2-x}\text{-LDH/NF}$; (d–f) the corresponding high-magnification SEM images and elemental mappings.

respectively. Cycle performance is another critical parameter for an electrocatalyst. As shown in Fig. 4f, the NiMoCo-LDH/NF electrocatalyst still maintains excellent catalytic stability even after 14 h.

OER performances of the electrode materials were investigated at a scan rate of 2 mV s^{-1} in 1.0 mol L^{-1} KOH electrolyte. From the LSV curves shown in Fig. 5a, the NiMoCo-LDH/NF catalyst exhibits an overpotential of 279 mV at a current density of 20 mA cm^{-2} , which is significantly smaller than those of $\text{NiMo}_2\text{-LDH/NF}$ (386 mV), $\text{NiMo}_{1.5}\text{Co}_{0.5}\text{-LDH/NF}$ (305 mV), $\text{NiMo}_{0.5}\text{Co}_{1.5}\text{-LDH/NF}$ (306 mV) and $\text{NiCo}_2\text{-LDH/NF}$ (359 mV) electrodes, respectively. Obviously, bimetallic $\text{NiMo}_2\text{-LDH/NF}$ and $\text{NiCo}_2\text{-LDH/NF}$ show poor OER activity than other ternary electrode materials.

Further evaluation of OER activity was conducted

from the Tafel slopes (Fig. 5b). The Tafel slope of $77.99 \text{ mV dec}^{-1}$ for NiMoCo-LDH/NF sample is much lower than $107.29 \text{ mV dec}^{-1}$ for $\text{NiMo}_2\text{-LDH/NF}$, $99.53 \text{ mV dec}^{-1}$ for $\text{NiMo}_{1.5}\text{Co}_{0.5}\text{-LDH/NF}$, $101.63 \text{ mV dec}^{-1}$ for $\text{NiMo}_{0.5}\text{Co}_{1.5}\text{-LDH/NF}$ and $94.85 \text{ mV dec}^{-1}$ for $\text{NiCo}_2\text{-LDH/NF}$ electrodes. As shown in Fig. 5c, the C_{dl} of 12.8 mF cm^{-2} for NiMoCo-LDH/NF catalyst is higher than those of other electrodes, revealing that increasing the exposed active sites can enhance the electrochemical performance of the electrodes. EIS spectra are shown in Fig. 5d. In the low frequency region, the slope of NiMoCo-LDH/NF is larger than those of other electrodes, indicating its low ion diffusion resistance. To further investigate the diffusion speed of ions in the electrolyte, the diffusion speed was analyzed by the following equation:

Figure 4 HER performances of the electrode samples: (a) LSV curves, (b) Tafel plots, (c) overpotential, (d) double-layered capacitance linear fitting, (e) Nyquist plots, (f) chronoamperometric stability tests.

Figure 5 OER performances of the materials: (a) LSV curves, (b) Tafel plots, (c) double-layered capacitance linear fitting, (d) Nyquist plots, (e) Z' as a function of $\omega^{-1/2}$ plot at the low frequency region, (f) chronoamperometric stability tests.

$$Z = R_s + R_{ct} + \sigma_w \omega^{-1/2}, \quad (5)$$

where σ_w is the Warburg factor, ω represents the angular frequency, R_{ct} represents the charge transfer resistance, and Z denotes the diffusive resistance for OH^- . The slope values of the electrode materials are shown in Fig. 5e. The NiMoCo-LDH/NF catalyst possesses a smaller value than other samples, indicating a quick transmission path for OH^- . As seen from Fig. 5f, the NiMoCo-LDH/NF elec-

trode exhibits excellent stability.

Based on the above catalytic properties of the NiMoCo-LDH/NF electrode for HER and OER, it can be directly used as an electrocatalyst for overall water splitting. Thus, a two-electrode system was constructed using NiMoCo-LDH/NF as anode and cathode, respectively. The system was measured in 1.0 mol L^{-1} KOH at a scan rate of 5 mV s^{-1} . Fig. 6a is a schematic of overall water splitting of the NiMoCo-LDH/NF samples. In Fig. 6b, the voltage

Figure 6 (a) Schematic of overall water splitting; (b) polarization curves of the as-prepared samples for overall water splitting; (c) durability of the NiMoCo-LDH/NF sample; (d) low- and (e) high-magnification SEM images of the NiMoCo-LDH/NF sample after overall water splitting.

of the sample is 1.71 V at 20 mA cm⁻². It indicates that this electrode possesses excellent electrocatalytic performance. Long-term durability of the sample was measured by multiple voltage tests for 14 h. Its current densities do not significantly decrease, as shown in Fig. 6c. Meanwhile, no obvious morphology change is observed from SEM images of the sample (Fig. 6d, e), which further demonstrates the excellent stability.

The excellent overall water splitting performance of the NiMoCo-LDH/NF electrocatalyst might be from the following factors. Firstly, the nanosheet structure shows distinctive advantages with easy electrolyte diffusion and ionic transportation and offers a large surface area with sufficient contact between the electrode and electrolyte. Then, the 3D NF offers a persevering skeleton, which avoids “dead surface” and ensures easy diffusion.

The supercapacitor performances of the samples were studied using 3 mol L⁻¹ KOH solution as the electrolyte. Figs S1a, b and S2a–c show the CV curves of the electrode materials at a scan rate of 5–100 mV s⁻¹. The voltage window of the as-prepared materials is 0–0.5 V. As the scan rate increases, no obvious change in the shape is found, indicating their excellent reversibility. GCD curves of the above mentioned samples are shown in Figs S1c, d and S2d–f, respectively. With increasing current density, the discharge time of the electrode materials gradually decreases.

CV curves of the as-prepared samples at a scan rate of 100 mV s⁻¹ are shown in Fig. 7a. The specific capacitance of the electrode is directly proportional to the curve area. The curve of NiMoCo-LDH/NF shows the largest area, indicating that it possesses the highest specific capacitance among the five electrodes. In Fig. 7b, it is found that NiMoCo-LDH/NF exhibits much longer discharge time than the other electrodes. In addition, the charge and discharge times of the curves are almost the same, demonstrating the reversibility of all electrode materials. As shown in Fig. 7c, the specific capacitance of NiMoCo-LDH/NF reaches 642.1 C g⁻¹ when the current density is 1 A g⁻¹, and the capacitance retention is 85.3% at a current density of 8 A g⁻¹. When the current density increases, the capacitance retentions of the other electrodes are less than 85.3% (77.6% for NiMo₂-LDH/NF, 82.1% for NiMo_{1.5}Co_{0.5}-LDH/NF, 70.3% for NiMo_{0.5}Co_{1.5}-LDH/NF and 72.9% for NiCo₂-LDH/NF).

EIS of the electrodes are shown in Fig. 7d. The curve of NiMoCo-LDH/NF possesses maximum slope and minimum intercept (0.45 Ω), suggesting that the diffusion of redox species in the electrolyte can be revealed from the low frequency range. The diffusion-controlled and pseudocapacitive contributions were calculated from the CV curves (Fig. 7e). The diffusion-controlled charges are about 75.1% of the total charge storage at a scan rate of 5 mV s⁻¹, which indicates an effective diffusion charge

Figure 7 Electrochemical characterizations for supercapacitor performances: (a) CV and (b) GCD curves, (c) specific capacitances, (d) Nyquist plots, (e) contribution ratios between capacitances and diffusion-limited ones, (f) cycling performances.

Figure 8 Electrochemical characterizations of the NiMoCo-LDH/NF//AC ASC. (a) CV curves of AC and NiMoCo-LDH/NF, (b) CV curves at different scan rates, (c) GCD curves, (d) Nyquist plots, (e) cycling performance, (f) Ragone plots.

storage ability of the NiMoCo-LDH/NF electrode. The cycling performances (Fig. 7f) of the as-prepared electrodes were obtained by 8000 charge-discharge cycling at a current density of 10 A g⁻¹. The capacitance retention of the NiMoCo-LDH/NF electrode is 82.7%, much higher than those of the other electrodes. In Fig. S3, the Coulombic efficiency of the electrode materials are close to 100%, indicating that the charging and discharging times of the samples are similar during the cycle.

In order to further study the practical application of the electrode material, an ASC was assembled by using NiMoCo-LDH/NF as the anode and AC as the cathode. CV curves of the NiMoCo-LDH/NF sample and AC electrode are shown in Fig. 8a, within the potential windows of 0–0.5 and –1.0–0 V, respectively. Therefore, the theoretical voltage window of the assembled supercapacitor can reach 1.5 V. Fig. 8b shows the CV curves of the device at scan rates from 5 to 50 mV s⁻¹. The CV curves keep similar shapes when the current density increases by 5 times. Discharge curves from 0 to 1.5 V were also studied at various current densities (Fig. 8c). The specific capacitance reaches 119 C g⁻¹ at a current density of 1 A g⁻¹. In Fig. 8d, it is found that the NiMoCo-LDH/NF//AC ASC shows a low bulk resistance, and the internal resistance is 1.43 Ω. In Fig. 8e, the capacitance retention of the device is 93% after 8000 cycles. According

to the discharge curves, the power densities and energy densities of the NiMoCo-LDH/NF//AC ASC are shown in Fig. 8f. A maximum energy density of 141 W h kg⁻¹ at a power density of 2695 W kg⁻¹ is obtained, which are superior to some previous reports [45–50].

CONCLUSION

In summary, we have synthesized a NiMoCo-LDH/NF electrocatalyst on NF *via* a facile hydrothermal method. The as-obtained sample shows outstanding performances for HER and OER with a lower overpotential. As bi-functional electrocatalyst for overall water splitting, it shows a low voltage. The remarkable electrochemical performance can be attributed to its unique structure. As the electrode for capacitor, it delivers high specific capacitance and excellent cyclic performance. The as-assembled NiMoCo-LDH/NF//AC ASC exhibits high energy density at a power density of 2695 W kg⁻¹ and 93% of its capacitance retention after 8000 cycles.

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Author contributions Liu H and Zhao D did the experiments and wrote the original draft. Liu Y contributed to visualization and investigation. Tong Y helped with software and validation. Wu X supervised, reviewed and edited the manuscript. Shen G supervised the study and gave some advice.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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基于NiMoCo层状双金属氢氧化物的电催化剂和超级电容器电极

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摘要 本文通过调控Ni, Mo, Co三种元素的摩尔比得到一系列高效双功能电催化剂。其中, Co元素特定的氧吸附位点($\text{Co}^{2+}-\text{O}-\text{Co}^{3+}$)可有效提高催化剂的活性。Mo元素在温和反应条件下具有较好的氧化还原能力。Ni是另一种高活性过渡金属。与其他材料结合可有效增强催化剂的氧化还原活性和储氧能力。所制备的NiMoCo层状双金属氢氧化物(NiMoCo-LDH)催化剂在 10 mA cm^{-2} 时析氢反应(HER)过电势为123 mV, 20 mA cm^{-2} 时析氧反应(OER)过电势为251 mV。该材料还表现出优异的全解水性能, 为构筑过渡金属氢氧化物电催化剂提供了崭新思路。同时, 所制备的电极材料用作超级电容器正极时也表现出优异的性能。在 1 A g^{-1} 的电流密度下, NiMoCo-LDH电极拥有 642.1 C g^{-1} 的比容量。组装的NiMoCo-LDH//AC非对称超级电容器在功率密度为 2695 W kg^{-1} 时能量密度为 141 W h kg^{-1} , 经过8000次充放电后仍保持初始容量的93%。