Supporting Information

Ion-exchange synthesis of ternary FeCoNi layered double hydroxide nanocage towards enhanced oxygen evolution reaction and supercapacitor

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1. The Material characterization and measurement instrument

X-ray diffraction (XRD) equipped with Cu Kα radiation (λ = 0.15406 nm) was used to characterize the crystallographic structures of the materials. X-ray photoelectron spectrometer (XPS) analysis was performed using nonmonochromatic, AlKα radiation (1486.6 eV). FTIR spectra were recorded on a Fourier transform infrared spectrometer (JASCOFT/IR-420) in the range of 4000-500 cm⁻¹ using a KBr pellet. The morphology and structure of the materials was recorded on a Tecnai F20 transmission electron microscope (TEM) and a Hitachi S–4800 scanning electron microscope (SEM). All electrochemical measurements were conducted on a CHI-660D electrochemical workstation at room temperature.

2. Chemicals

All the chemicals were used without any further treatment. Nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O), 2-methylimidazole (2-MIM, purity 99%), potassium hydroxide (KOH, AR), were purchased from Sinopharm Chemical Reagent Co. Ltd. Cobalt nitrate (II) hexahydrate (Co(NO₃)₂·6H₂O), ferrous (III) nitrate hexahydrate

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(Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O, AR) was obtained from Aladdin (Shanghai). Polyvinyl pyrrolidone (PVP) was obtained from Sigma Aldrich.

3. Electrochemical measurement

A three-electrode configuration including a glassy carbon electrode (3 mm in diameter) as the working electrode was put into use for the OER activity evaluation with a CHI-660D electrochemical workstation. The catalyst (3.0 mg) and carbon black (1 mg) were dispersed into 1.0 mL of solution (V\textsubscript{ethanol}:V\textsubscript{0.5 wt.\% nafion solution} =97:3) and then followed up with ultrasonic operation for 1 h to prepared catalyst suspension. Subsequently, 5 μL of the suspension was dropped on polished glassy carbon electrode and dried at room temperature. The mercury/mercuric oxide reference electrode (1 M KOH) electrodes (Hg/HgO) and carbon were used as the reference and counter electrode, respectively. The potential was referenced to a reversible hydrogen electrode (RHE):

\[ E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 + 0.059 \times \text{pH} \]  \hspace{1cm} (S1)

The overpotential (\(\eta\)) was calculated by the following formula:

\[ \eta = E_{\text{RHE}} - 1.23 \text{ V} \]  \hspace{1cm} (S2)

The polarization curves were obtained by recording linear sweep voltammetry (LSV) at a scan rate of 5 mV s\textsuperscript{-1} was in 1.0 M KOH. The test of stability was taken by chronoamperometry under \(\eta\) of 0.299 V with constant magnetic stirring. The LSV data presented were all corrected by iR loss. The Tafel plot is commonly used to reflect the kinetics of the active material for OER. The data is shown and the linear regions of the Tafel plots are fitted to the Tafel equation:

\[ \eta = b \log j + a \]  \hspace{1cm} (S3)

where \(\eta\) is the overpotential, \(j\) is the current density, and \(b\) is the Tafel slope. The following equation can be used for calculation the TOF values of the materials as OER.
catalysts:

\[
TOF = \frac{J \times A}{4 \times F \times n}
\]  

(S4)

where \( A \) presents the area of the glassy carbon disk electrode, \( n \) refers to the moles of the active sites deposited onto the glassy carbon disk electrode, \( F \) indicates the faraday constant (96 485 C mol\(^{-1}\)), and \( J \) (A cm\(^{-2}\)) is the current density at overpotential of 0.3 V. The active-site-density \( n \) can be estimated by the equation:

\[
n = \frac{C_{\text{dl}} \times \Delta V}{2F}
\]  

(S5)

where \( C_{\text{dl}} \) and \( \Delta V \) are the double-layer capacitance (\( C_{\text{dl}}, \) F cm\(^{-2}\)) and the voltage window (\( V \)) for CV measurements, and their product (\( C_{\text{dl}} \times \Delta V \)) is the voltammetric charge density (\( Q, \) C cm\(^{-2}\)), and the factor 1/2 is due to the charge-discharge cycles for CV scans.

The electrochemically active surface area (ECSA) of the samples was estimated by determining the double-layer capacitance from CV measurements. The plot of anodic peak current (\( i_a \)) or cathodic peak current (\( i_c \)) vs. scan rate will yield a straight line with a slope vale of \( C_{\text{dl}} \). The ECSA of the catalyst can be calculated by dividing \( C_{\text{dl}} \) by the specific capacitance (\( C_s, 0.04 \text{ mF cm}^{-2} \)) according to the following equation:

\[
ECSA = \frac{C_{\text{dl}}}{C_s}
\]  

(S6)

In the text of overall water splitting, the FeCoNi-LDH is both used as positive and negative electrode for the electrolytic devices in 1 M KOH. The catalyst dispersion is prepared according to the OER testing method, and then the resulting mixture was coated onto the nickel foam substrate (1×1 cm\(^2\)).

The working electrodes for supercapacitors were fabricated as following: First, the mixture of poly (tetrafluoroethylene), carbon black and activity materials (m:m:m=5:20:75) were put and dispersed into ethanol. The mixture was then coated to
the surface of the nickel foam (1×1 cm$^2$). This coated substrate was dried for 12 h under 80 °C in vacuum oven.\textsuperscript{2-5} The investigation of the individual electrode was processed by a three-electrode system in 3 M KOH, in this system Hg/HgO electrodes and Pt were reference and counter electrodes, respectively. Cyclic voltammetry (CV) tests were separately measured from 0 to 0.55 V (vs. Hg/HgO) for CoNi-LDH and FeCoNi-LDH electrodes under various scan rates. Electrochemical impedance spectroscopy (EIS) tests were also performed at open circuit potential in the frequency range from 100 kHz to 0.01 Hz. Galvanostatic charge-discharge (GCD) curves were done from 0 to 0.5 V (vs. Hg/HgO) under different current densities. Based on the galvanostatic charge/discharge curves, the calculation of specific capacitance was obtained as followed formula:

\[
C = \frac{i \Delta t}{m \Delta V}
\]  \hspace{1cm} (S7)

where $i$ was the constant discharge current, $\Delta t$ is the total discharge time, $m$ and $\Delta V$ indicated the mass of the electroactive material in the electrode and discharge voltage, respectively.
**Figure S1.** (a) XRD pattern of ZIF-67. (b-f) EDX spectra of the CoNi-LDH, FeCoNi-LDH, FeCoNi-LDH-1, FeCoNi-LDH-2 and FeCoNi-LDH-3.

**Table S1.** Comparison of the percentage of Fe, Co and Ni in the materials under different reaction time.

<table>
<thead>
<tr>
<th>Reaction time</th>
<th>CoNi-LDH</th>
<th>FeCoNi-LDH-1</th>
<th>FeCoNi-LDH-2</th>
<th>FeCoNi-LDH-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (%)</td>
<td>0</td>
<td>5.1</td>
<td>7.1</td>
<td>10.9</td>
</tr>
<tr>
<td>Co (%)</td>
<td>71.8</td>
<td>67.2</td>
<td>66.4</td>
<td>63.9</td>
</tr>
<tr>
<td>Ni (%)</td>
<td>28.2</td>
<td>27.7</td>
<td>26.5</td>
<td>25.2</td>
</tr>
</tbody>
</table>
Figure S2. Typical SEM images of (a, b) FeCoNi-LDH-1, (c, d) FeCoNi-LDH-2 and (e, f) FeCoNi-LDH-3.
(e, f) FeCoNi-LDH-3.
Figure S3. Typical TEM images of (a) FeCoNi-LDH-1, (b) FeCoNi-LDH-2 and (c) FeCoNi-LDH-3.
**Figure S4.** Typical (a, b) SEM and (c, d) TEM images of the FeCoNi-LDH after 12 h durability test.
Figure S5. (a) XRD pattern and XPS of (b) Co 2p, (c) Ni 2p and (d) Fe 2p of the FeCoNi-LDH after 12h durability test.
Figure S6. Chronoamperometry curves of the FeCoNi-LDH materials with different cation exchange reaction time.
Figure S7. (a) Polarization curve of FeCoNi-LDH//FeCoNi-LDH for overall water splitting in 1 M KOH. (b) Chronoamperometry curves of the FeCoNi-LDH//FeCoNi-LDH. 
**Figure S8.** (a) Specific capacity of the CoNi-LDH and the FeCoNi-LDH materials with different CER time electrodes at various current densities. (b) Cycling performance of the FeCoNi-LDH materials with different CER time electrodes performed at 20 A g⁻¹ after 5000 cycles.
References:


