Design of ZIF-67 MOF-derived Co$_3$O$_4$/NiCo$_2$O$_4$ nanosheets for supercapacitor electrode materials

Jianning Li, Chunyong Zhang, Yingpin Wen, Yuyue Zhao, Yiwen Zhang, Li Shu and Hengfei Qin

Abstract

Binary transition metal oxides exhibit improved properties including good redox potentials and electrical conductivities compared with single metal oxides as electrode materials in energy storage. Herein, ZIF-67 is prepared by a one-step method using Co$^{2+}$ as the central metal ion, 2-methylimidazole as the organic ligand, and methanol as an organic solvent at room temperature. Hollow NiCo$_2$O$_4$ and sheet-like Co$_3$O$_4$/NiCo$_2$O$_4$ derived from bimetallic imidazolate framework precursors were synthesized by adding cobalt and nickel ions in appropriate proportions. A hollow and porous structure is achieved for the reaction between a nickel salt and ZIF-67, and this unique nanostructure provides a high active surface area, which is beneficial to the electrochemical properties. Several samples are prepared and used as electrode materials for electrochemical tests in 6 M KOH. As a result, the Co$_3$O$_4$/NiCo$_2$O$_4$ electrode with a sheet nanostructure showed a high specific capacitance of 846 F g$^{-1}$ at a current density of 0.5 A g$^{-1}$. This Co$_3$O$_4$/NiCo$_2$O$_4$ electrode material is promising for future studies on high-performance supercapacitors to solve emerging energy-related problems.

Keywords

Co$_3$O$_4$/NiCo$_2$O$_4$, electrode materials, nanosheets, supercapacitors, ZIF-67

Date received: 19 April 2021; accepted: 5 August 2021

Introduction

Compared with traditional batteries, supercapacitors exhibiting excellent power density, fast charging and discharging performance, long cycle stabilities, and environmental friendliness are considered to be very promising for energy storage.\footnote{1,2} Although supercapacitors can provide significantly higher power than traditional batteries of the same volume, the small energy density of supercapacitors limits their practical applications.\footnote{3,4} To resolve this problem, it is necessary to research hybrid supercapacitors based on both the energy storage mechanisms of chemical batteries and supercapacitors.\footnote{5}

Transition metal oxides and conductive polymers are typical electrode materials in hybrid supercapacitors. In particular, transition metal oxides are more widely used due to their high stabilities and different valence states.\footnote{6,7} However, for single metal oxides, the limited electron transport between the electrode materials and the electrolyte hinders its electrochemical performance. Classical binary metal oxides such as NiCo$_2$O$_4$,\footnote{8} ZnCo$_2$O$_4$,\footnote{9} and NiFe$_2$O$_4$\footnote{10} have attracted attention because of their numerous active sites that promote the redox reactions of electrode materials, making them suitable candidates for flexible electrode materials.\footnote{11} In previous reports, NiCo$_2$O$_4$ complexes with various morphologies have been synthesized, such as nanosheets, nanoneedles, and yolk-shell nanostructures. Xu et al.\footnote{12} synthesized hierarchical Co$_3$O$_4$/NiCo$_2$O$_4$ core-shell nanosheets as supercapacitors, which showed excellent rate capability and compelling cycling performance. Researchers synthesized a needle-like Ni-Co precursor on Ni foam by using the hydrothermal method and then obtained Ni foam@NiCo$_2$O$_4$ after an annealing process. Besides, carbon nanotubes aerogels are coated on the surface of Ni foam@NiCo$_2$O$_4$ by utilizing van der Waals and viscous forces and exhibit a high specific capacitance at 20 A g$^{-1}$.\footnote{13}

To achieve electrode materials with abundant adsorption
sites, the common way is to expand organic linkers resulting in metal-organic frameworks (MOFs) with ultrahigh porosity.\textsuperscript{14} However, expanded metal links can also cause fragile frameworks and penetration between different lattices, precluding high porosity.\textsuperscript{14,15}

MOFs can be used as support substrates for nanomaterials or as sacrificial templates/precursors for the generation of various nanostructures.\textsuperscript{16} MOFs are coordinated supramolecular materials, composed of coordinated metal ions, nodes, and organic ligands.\textsuperscript{17} Because of their large specific surface areas and abundant oxidation-active sites, they have attracted widespread attention in the field of electrochemical energy storage.\textsuperscript{18,17} MOFs, especially ZIF-67, are a type of promising porous carbon product that can be used as electrode materials in EDLCs (electrochemical double-layer capacitors).\textsuperscript{1} ZIF-67 (a Co-based zeolitic imidazolate framework), with a cubic crystal nanostructure, can be prepared with a metal cobalt ion as the central atom and 2-methylimidazole as the organic ligand under appropriate external conditions.\textsuperscript{20} Sundriyal et al.\textsuperscript{21} prepared nickel-doped ZIF-67 in the presence of rGO, and finally ZIF-67/rGO generated a composition as an electrode, the specific capacitance of which was 304 F g\textsuperscript{−1} at a current density of 1 A g\textsuperscript{−1}. Bimetallic metal oxide materials derived from MOFs possess high stability and conductivity, which provides more active sites and makes them ideal supercapacitor materials.\textsuperscript{10}

The bimetallic mixture derived from an MOF has a more complex structure because metal ions with different functions are concentrated in a MOF framework, and the first type of metal ion may be replaced by the second type leading to provide new functions, which depend on the new metal ion.\textsuperscript{22} In addition, other researchers found that a polyhedron with a hollow structure could be synthesized by selenizing the precursors of Ni-Co bimetallic hydroxides that were derived from ZIF-67, with the generated material showing high specific capacitance and excellent high energy density as a supercapacitor.\textsuperscript{23} This electrode material based on an MOF has a unique structure that can greatly shorten charge transport paths to improve the electron transport and diffusion, thus strengthening the catalytic performance of the electrode materials.\textsuperscript{19}

Inspired by these results, it is of value to develop a facile and effective method to construct materials with high conductivity based on MOFs. In this study, a simple template-assisted method has been employed with ZIF-67 as the precursor, adding cobalt and nickel ions in the appropriate proportions to synthesize products with interesting nanostructures based on coordinating etching and precipitating processes. The combination of ZIF-67 and binary metal oxides shows synergistic effects for capacitance with enhanced performance, such as higher capacitance (846 F g\textsuperscript{−1}) with respect to single ZIF-67 or NiCo\textsubscript{2}O\textsubscript{4}.

**Results and discussion**

The procedure for fabricating ZIF-67, NiCo\textsubscript{2}O\textsubscript{4}, and Co\textsubscript{3}O\textsubscript{4}/NiCo\textsubscript{2}O\textsubscript{4} based on ZIF-67 through the template-assisted method. Figure 2(a) shows the crystalline phases of ZIF-67, NiCo\textsubscript{2}O\textsubscript{4}, and Co\textsubscript{3}O\textsubscript{4}/NiCo\textsubscript{2}O\textsubscript{4} precursors according to X-ray diffraction (XRD) measurements. It shows that NiCo\textsubscript{2}O\textsubscript{4} and Co\textsubscript{3}O\textsubscript{4}/NiCo\textsubscript{2}O\textsubscript{4} before annealing keep the traces of ZIF-67. From Figure 2(b), the XRD pattern types are in agreement with the crystal planes of (110), (111), (220), (311), (400), (422), (511), and (440), respectively, of NiCo\textsubscript{2}O\textsubscript{4} (JCPDS 73-1702) and Co\textsubscript{3}O\textsubscript{4} (JCPDS 80-1535). For ZIF-67, the peaks at 7.4°, 10.4°, 12.7°, 14.7°, 16.4°, 18.0°, 22.1°, 24.5°, 25.5°, 26.6°, 29.6°, 30.5°, 31.4°, and 32.3° are unambiguously assigned to the reported patterns of crystalline ZIF-67.\textsuperscript{24–27} Furthermore, the oxidation states of Ni, Co, and O are explored in the X-ray photoelectron spectroscopy (XPS) spectrum in Figure 3(a). The XPS results in Figure 3(b) show that the oxidation states of Ni belong to Co\textsubscript{2}O\textsubscript{3}/NiCo\textsubscript{2}O\textsubscript{4} with the signals at 853.7 and 870.9 eV conforming with Ni\textsuperscript{2+}. Two other peaks at 855.3 and 872.3 eV are due to the Ni\textsuperscript{3+} species.\textsuperscript{28} As observed in Figure 3(c), two satellite peaks located at 779.2 and 780.6 eV fit well with Co 2p\textsubscript{3/2}, while the other peaks located at 794.4 and 780.6 eV are the satellite peaks of Co 2p\textsubscript{1/2}. Similarly, the O 1s spectrum of Co\textsubscript{3}O\textsubscript{4}/NiCo\textsubscript{2}O\textsubscript{4} is well resolved into three components at 529.3, 531.7, and 533.3 eV.

The morphologies and microstructures of ZIF-67, NiCo\textsubscript{2}O\textsubscript{4}, and Co\textsubscript{3}O\textsubscript{4}/NiCo\textsubscript{2}O\textsubscript{4} were analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Figure 4(a), it is observed that the microstructure of ZIF-67 exhibits a rhombic polyhedron structure with a size in the range of 500 nm. Along with the addition of Co(NO\textsubscript{3})\textsubscript{2} and methanol to 2-MIM, ZIF clusters can be generated by the deprotonation/coordination of imidazoles with Co\textsuperscript{2+}. Next, the ZIF clusters are converted into ZIF-67 polyhedra becoming the skeleton template for NiCo\textsubscript{2}O\textsubscript{4} and Co\textsubscript{3}O\textsubscript{4}/NiCo\textsubscript{2}O\textsubscript{4}. On addition of Ni(NO\textsubscript{3})\textsubscript{2} to the ZIF-67 polyhedron, a hollow structure assembled by nanosheets NiCo\textsubscript{2}O\textsubscript{4} was prepared due to the
etching reaction between released H⁺ (the hydrolysis of nickel ions and cobalt ions) and 2-MIM linkers of ZIF-67. Besides, two metals with different diffusion rates can form inner defects and assist in forming a hollow structure due to the Kirkendall effect. From Figure 4(d), it can be seen that the morphology of NiCo₂O₄ inherits the hollow structure after completing the one-step annealing, but it exhibits larger cavities than the precursor because of decomposition of the organic components and structural reorganization during the calcination process. The SEM images in Figure 4(c) and (e) reveal that the morphology of Co₃O₄/NiCo₂O₄ was changed after adding Ni(NO₃)₂ and Co(NO₃)₂ to ZIF-67, and Co₃O₄/NiCo₂O₄ exhibits an interconnected sheet-like shape. The mechanism
of formation of nanosheets may be interpreted by the following processes. The protons produced by the hydrolysis of Ni\textsuperscript{2+} ions can bind to Co-MOF resulting in liberation of Co\textsuperscript{3+} ions. Meanwhile, part of the liberated Co\textsuperscript{2+} ions are oxidized to Co\textsuperscript{3+} ions by dissolved O\textsubscript{2} and NO\textsubscript{3}\textsuperscript{−} in the solution, which coprecipitate with Ni\textsuperscript{2+} ions to generate nanosheets.\textsuperscript{29,32,33} Besides, more nickel nitrate and cobalt nitrate were added in the process of preparing Co\textsubscript{3}O\textsubscript{4}/NiCo\textsubscript{2}O\textsubscript{4} than the preparation of NiCo\textsubscript{2}O\textsubscript{4}. The reaction system has higher hydrolysis rate because of the lower pH value,\textsuperscript{34} resulting in the formation of Co\textsubscript{3}O\textsubscript{4}/NiCo\textsubscript{2}O\textsubscript{4} nanosheets.

To confirm the presence of Ni, Co, and O in the composites, energy dispersive spectrometer (EDS) full mapping was completed. As shown in Figure 5(b)–(d) and Table 1, O, Co, and Ni are distributed in Co\textsubscript{3}O\textsubscript{4}/NiCo\textsubscript{2}O\textsubscript{4}, and values of 50.47 wt\% (O), 39.18 wt\% (Co), and 10.35 wt\% (Ni) were determined. As revealed by the TEM images, the obtained Co\textsubscript{3}O\textsubscript{4}/NiCo\textsubscript{2}O\textsubscript{4} presents a nanosheet structure, which corresponds to the SEM images. The microstructure of Co\textsubscript{3}O\textsubscript{4}/NiCo\textsubscript{2}O\textsubscript{4} was further analyzed by HRTEM (Figure 6(d)–(f)). The lattice fringes are measured to be 0.20 and 0.29 nm, corresponding to the (400) and (220) planes of NiCo\textsubscript{2}O\textsubscript{4}.\textsuperscript{35,36} Furthermore, the measured lattice fringes of Co\textsubscript{3}O\textsubscript{4} are about 0.24 and 0.47 nm, matching with (311) and (111) crystal plane. Meanwhile, the results of TEM and HRTEM matched the data from XRD.

Figure 7(a) shows the cyclic voltammetry (CV) curves of ZIF-67, NiCo\textsubscript{2}O\textsubscript{4}, and Co\textsubscript{3}O\textsubscript{4}/NiCo\textsubscript{2}O\textsubscript{4} at a constant rate of 5 mV s\textsuperscript{−1} within the work potential window of 0.1–0.35 V. From each CV profile, it can be observed that redox peaks are more obvious in the case of Co\textsubscript{3}O\textsubscript{4}/NiCo\textsubscript{2}O\textsubscript{4} as compared to ZIF-67 and NiCo\textsubscript{2}O\textsubscript{4}, and the CV integrated area of Co\textsubscript{3}O\textsubscript{4}/NiCo\textsubscript{2}O\textsubscript{4} is the largest, indicating that it delivers a better specific capacitance and has higher redox activity than the other electrodes.\textsuperscript{35} The CV curves of ZIF-67, NiCo\textsubscript{2}O\textsubscript{4}, and Co\textsubscript{3}O\textsubscript{4}/NiCo\textsubscript{2}O\textsubscript{4} under different scan rates from 5 to 80 mV s\textsuperscript{−1} are shown in Figure 7(b)–(d). On increasing the scanning speed, the CV curves still maintain a pair of representative redox peaks, while a positive shift of the oxidation peak and a negative shift of the reduction peak are also observed, indicating typical pseudocapacitive characteristics.\textsuperscript{37–39} For anodic and cathodic peaks, the mechanism of energy storage may be ascribed to the surface redox reactions of the Co\textsuperscript{2+}/Co\textsuperscript{3+}/Co\textsuperscript{4+} and Ni\textsuperscript{2+}/Ni\textsuperscript{3+} redox couples in 6 M KOH electrolyte.\textsuperscript{40,41} The reactions can be plausibly suggested as follows\textsuperscript{9,42,43}

\begin{align}
\text{NiCo}_2\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} & \leftrightarrow 2\text{CoOOH} + \text{NiOOH} + e^- \quad (1) \\
\text{Co}_3\text{O}_4 + \text{OH}^- & \leftrightarrow \text{CoOOH} + e^- \quad (2) \\
\text{CoOOH} + \text{OH}^- & \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + e^- \quad (3)
\end{align}

The linear fit is shown in Figure 7(e), which is obtained from the square root of the scan rate versus the current density. The correlation coefficient is $R^2 = 0.9990$ for the cathodic and $R^2 = 0.9989$ for the anodic peaks, suggesting that the obtained electrode system is controlled by a typical diffusion process.\textsuperscript{44}

The galvanostatic charge and discharge (GCD) curves of ZIF-67, NiCo\textsubscript{2}O\textsubscript{4}, and Co\textsubscript{3}O\textsubscript{4}/NiCo\textsubscript{2}O\textsubscript{4} at current densities of
It can be observed that all the electrodes possessed no linear charge and discharge curves with notable discharge platforms, indicating the pseudocapacitance behavior of the charge-discharge process owing to the redox reactions of Co(II) to Co(III), Co(III) to Co(IV), and Ni(II) to Ni(III). The charge curve of the Co$_3$O$_4$/NiCo$_2$O$_4$ electrode exhibits a longer discharge platform among the three samples at a current density of 0.5 A g$^{-1}$, which has a better faradaic redox reversibility and rate capability. The specific capacitance of Co$_3$O$_4$/NiCo$_2$O$_4$ is calculated to be 846 F g$^{-1}$ at 0.5 A g$^{-1}$, which has a better faradaic redox reversibility and rate capability. The specific capacitance of Co$_3$O$_4$/NiCo$_2$O$_4$ was larger than those of ZIF-67 and NiCo$_2$O$_4$. The enhancement of the capacitive performance of Co$_3$O$_4$/NiCo$_2$O$_4$ can be attributed to its better redox reactions and higher electronic conductivity than the monometallic oxides. The valence bond exchange or charge hopping between nickel and cobalt ions can also increase electrochemical performance.

The electrochemical impedance spectroscopy (EIS) of the ZIF-67, NiCo$_2$O$_4$, and Co$_3$O$_4$/NiCo$_2$O$_4$ electrodes are shown in Figure 8(e), which can be simulated by an equivalent circuit. The abscissa of the intersection point of the impedance spectrum and the Z' axis is the series resistance (Rs), describing the internal resistance of the electrodes, the resistance of the electrolyte, and the contact between the electrode and current collector. The Rs values of Co$_3$O$_4$/NiCo$_2$O$_4$, NiCo$_2$O$_4$, and ZIF-67 were 0.687 Ω, 0.724 Ω, and 0.887 Ω, respectively. The slope of the straight line in the low frequency region represents the Warburg resistance (Zw), reflecting the diffusion into the electrode. A higher slope indicates a lower resistance to diffusion, evidently the Co$_3$O$_4$/NiCo$_2$O$_4$ electrode presents a bigger slope than the others. The charge transfer resistance (Rct) value of Co$_3$O$_4$/NiCo$_2$O$_4$ electrode is estimated to be about 3.01 Ω, which is lower than those of NiCo$_2$O$_4$ (3.28 Ω) and ZIF-67 (3.59 Ω). In addition, NiCo$_2$O$_4$ shows a lower charge transfer resistance than ZIF-67, the reason is that its special hollow structure provides more active centers and improves the ion diffusion rate. The lower Rs and Rct value of Co$_3$O$_4$/NiCo$_2$O$_4$ indicates that it
has a better electrochemical performance among the other electrodes. On the contrary, no completed semicircle in the high frequency region is observed in the plot for several electrodes because the electrochemical device is greatly affected by diffusive impedance from OH⁻ ions. The comparison of the Co₃O₄/NiCo₂O₄ electrode in this work with those electrodes previously reported is shown in Table 2.

**Conclusion**

In summary, we have successfully fabricated hollow NiCo₂O₄ assembled by nanosheets and sheet-like Co₃O₄/NiCo₂O₄ through preparing the MOF as a carbon skeleton, which was removed after annealing. Compared with ZIF-67 and NiCo₂O₄, the prepared sheet-like Co₃O₄/NiCo₂O₄ as an electrode material has a maximum specific capacitance. The hollow NiCo₂O₄ surface reveals a porous structure that promotes the surface redox reaction. The accelerated electron migration and diffusion speed are conducive to improving the specific capacitance of the electrode materials. After adding cobalt and nickel ions to the MOF, the specific capacitance of the electrode material (Co₃O₄/NiCo₂O₄) is 846 F g⁻¹ at a current density of 0.5 A g⁻¹, and the transition metal oxide (Co₃O₄/NiCo₂O₄) can increase the electric capacity due to the multi-electron transfer reaction. In addition, Co₃O₄/NiCo₂O₄ has the longest charging and discharging time, showing its good electrochemical performance. Therefore, the Co₃O₄/NiCo₂O₄ prepared in this study has excellent electrochemical properties and can be used as an electrode material in supercapacitors.

**Experimental**

**Chemicals and materials**

Ethanol, methanol, potassium hydroxide, and isopropanol were obtained from Sinopharm Chemical Reagent Co., Ltd. 2-Methylimidazole, nickel nitrate hexahydrate, cobalt nitrate hexahydrate, polytetrafluoroethylene (5 μm), and acetylene black were purchased from Aladdin. All the chemicals are analytically pure and were used without any further purification. All experimental solutions were prepared using deionized water.

**Sample preparation**

2-Methylimidazole (40 mmol) and Co(NO₃)₂·6H₂O (9 mmol) were dissolved in methanol (200 mL) by stirring. The two solutions were mixed thoroughly and aged at room temperature for 24 h. By centrifuging, the precipitates were collected and then dried at 60 °C for 12 h to give ZIF-67.

Ni(NO₃)₂·6H₂O (1 mmol) and ZIF-67 (0.2 g) prepared above were dissolved in ethanol (100 mL) by magnetic agitation for 120 min. The mixture was washed three times with distilled water and ethanol, dried at 60 °C for 12 h, and ground into a powder. Finally, the composites were calcined at 350 °C for 120 min under an air atmosphere with a heating rate of 1 °C min⁻¹ to give NiCo₂O₄. Co₃O₄/NiCo₂O₄ could be acquired in the same step by adding Co(NO₃)₂·6H₂O (2 mmol) and Ni(NO₃)₂·6H₂O (1 mmol).

---

Figure 6. TEM and HRTEM images for (a–c) NiCo₂O₄ and (d–f) Co₃O₄/NiCo₂O₄.
Material characterizations

The morphologies of the synthesized nanomaterials were analyzed by SEM (Zeiss Sigma 300) and TEM (JEOL JEM 2100). The purities and chemical compositions of the samples were determined by XRD using SmartLab 9 kw, operating at 40 kV and 40 mA, and the scanning range of 2θ is 5° to 90°. The states of the elements were analyzed by XPS (Thermo Scientific K-Alpha). Electrochemical measurements including CV, GCD, and EIS were obtained on an electrochemical workstation (CHI760E, China) using a three-electrode system.

Electrode preparation and electrochemical measurements

The catalyst, carbon black, and polyethylene with a mass ratio of 8:1:1 were dispersed ultrasonically for 1 h in isopropyl alcohol (2 mL) to form a mixed solution. Next, the mixed solution was coated onto the surface of nickel foam (1 cm × 1 cm) and dried at 60 °C for 12 h. A typical three-electrode system was composed of a working electrode (nickel foam), a counter electrode (a platinum gauze electrode), and a reference electrode (a saturated calomel electrode) to determine all the electrochemical properties of the samples. The electrolyte is 6.0 M KOH aqueous solution.

The specific capacitance \( C_s \) of several electrode materials can be calculated according to \( C_s = \frac{I \Delta t}{m \Delta V} \), where \( C_s \) (F g\(^{-1}\)) is the specific capacitance, \( I \) (A) is the current, \( m \) (g) is the mass of active materials, \( \Delta t \) (s) is the discharge time, and \( \Delta V \) (V) is the potential range of the charge-discharge. EIS was measured in the range from 100 kHz to 0.01 Hz.

Figure 7. The cyclic voltammograms of (a) ZIF-67, NiCo\(_2\)O\(_4\), and Co\(_3\)O\(_4\)/NiCo\(_2\)O\(_4\) at a scan of 5 mV s\(^{-1}\), (b–d) ZIF-67, NiCo\(_2\)O\(_4\), and Co\(_3\)O\(_4\)/NiCo\(_2\)O\(_4\) at different scan rates, and (e) square root of scan rate versus current density for Co\(_3\)O\(_4\)/NiCo\(_2\)O\(_4\).

The specific capacitance \( C_s \) of several electrode materials can be calculated according to \( C_s = \frac{I \Delta t}{m \Delta V} \), where \( C_s \) (F g\(^{-1}\)) is the specific capacitance, \( I \) (A) is the current, \( m \) (g) is the mass of active materials, \( \Delta t \) (s) is the discharge time, and \( \Delta V \) (V) is the potential range of the charge-discharge. EIS was measured in the range from 100 kHz to 0.01 Hz.
Table 2. Comparison of the electrochemical performance of Co$_3$O$_4$/NiCo$_2$O$_4$ in this work with previously reported studies.

| Sample                  | Test solution | Specific capacitance (F g$^{-1}$) | Current density (A g$^{-1}$) | Ref. |
|-------------------------|---------------|-----------------------------------|------------------------------|------|
| NiCo$_2$O$_4$/NiO/Co$_3$O$_4$ | KOH           | 1693                              | 1.0                          | 28   |
| Co$_2$O$_4$/NiCo$_2$O$_4$/NiO/C&S | 6 M KOH       | 428.24                            | 0.5                          | 51   |
| Co$_2$O$_4$/NiCo$_2$O$_4$   | KOH           | 879.4                             | 0.5                          | 35   |
| Co$_2$O$_4$/NiCo$_3$O$_4$   | 2 M KOH       | 672                               | 0.5                          | 36   |
| Co$_2$O$_4$/NiCo$_3$O$_4$   | 2 M KOH       | 1450                              | 1.0                          | 52   |
| Co$_2$O$_4$/NiCo$_3$O$_4$   | 2 M KOH       | 430                               | 1.0                          | 53   |
| Co$_2$O$_4$/NiCo$_3$O$_4$   | 6 M KOH       | 846                               | 0.5                          | This work |

Figure 8. GCD curves (a) several electrodes at a current of 0.5 A g$^{-1}$; (b–d) ZIF-67, NiCo$_2$O$_4$, and Co$_2$O$_4$/NiCo$_2$O$_4$ in 6.0 M KOH with different current densities; (e) the electrochemical impedance spectra of ZIF-67, NiCo$_2$O$_4$, and Co$_2$O$_4$/NiCo$_2$O$_4$; and (f) the specific capacitance of ZIF-67, NiCo$_2$O$_4$, and Co$_2$O$_4$/NiCo$_2$O$_4$. 
Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of the article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: Financial support from the Postgraduate Research & Practice Innovation Program of Jiangsu University of Technology (XSJCX20.04), the National Natural Science Foundation of China (grant no. 31800495), the Natural Science Foundation of Jiangsu Province (grant no. BK20181040), and the College Student Innovation and Entrepreneurship Training Program of Jiangsu Province (202011463008Z) is gratefully acknowledged.

ORCID iD
Chunyong Zhang https://orcid.org/0000-0002-4177-0795

References

1. Ahmad R, Iqbal N, Baig MM, et al. Electrochim Acta 2020; 364: 137147.
2. Yang K, Yan Y, Chen W, et al. J Electroanal Chem 2019; 851: 113445.
3. González A, Goikolea E, Barrena JA, et al. Renew Sust Energy Rev 2016; 58: 1189.
4. Doan TP, Pham MT, Nguyen VN, et al. J Energy Storage 2020; 33: 102030.
5. Zuo WH, Li RZ, Zhou C, et al. Adv Sci 2017; 4: 1600539.
6. Afif A, Rahman SMH, Tasfiah Azad A, et al. J Energy Storage 2019; 25: 100852.
7. Vlad A, Singh N, Rolland J, et al. Sci Rep 2014; 4: 4315.
8. Saravanakumar B, Priyadharsini T, Ravi G, et al. J Sol-Gel Sci Technol 2017; 84: 297.
9. Zhou SS, Hao C, Wang JJ, et al. Chem Eng J 2018; 351: 74.
10. Pan J, Li SB, Li FB, et al. Colloids Surf A 2020; 609: 125650.
11. Siwatch P, Sharma K and Tripathi SK. Electrochim Acta 2020; 329: 135084.
12. Xu KB, Yang XJ, Yang JM, et al. J Alloys Compd 2017; 700: 247.
13. Gao JS, Li SL, Wang HH, et al. J Alloys Compd 2021; 861: 157963.
14. Furukawa H, Ko N, Go YB, et al. Sci 2010; 329: 424.
15. Xu XT, Tang J, Qian HY, et al. ACS Appl Mater Interfaces 2017; 9: 38737.
16. Yap MH, Fow KL and Chen GZ. Green Energy Environ 2017; 2: 218.
17. Zhang F, Ma JJ and Yao H. Ceram Int 2019; 45: 24279.
18. Zhou HC and Kitagawa G. Chem Soc Rev 2014; 43: 5415.
19. Wang JY, Cui Y and Wang D. Adv Mater 2019; 31: e1801993.
20. Wang GR, Li YB, Xu L, et al. Renew Energy 2020; 162: 535.
21. Sundriyal S, Shrivastav V, Mishra S, et al. Int J Hydrogen Energy 2020; 45: 30859.
22. Sun DR, Sun FX, Deng XY, et al. Inorg Chem 2015; 54: 8639.
23. Qu GM, Zhang XX, Xiang GT, et al. Chin Chem Lett 2020; 31: 2007.
24. Dai P, Yao YC, Hu EZ, et al. Appl Surface Sci 2021, 546: 149128.
25. Lin KY and Chang HA. Chemosphere 2015; 139: 624.
26. Li L, Feng Y, Qiu YR, et al. Microchem J 2020; 155: 104762.
27. Antony R P, Satpati AK, Bhattacharyya K, et al. Adv Mater Interfaces 2016; 3: 1600632.
28. Feng XS, Huang Y, Li C, et al. Chem Eng J 2019; 368: 51.
29. Chen H, Shen ZH, Pan ZH, et al. Adv Sci 2019; 6: 1802002.
30. Feng Y, Xiang D, Qiu YR, et al. Electroanalysis 2019; 32: 571.
31. Han KH, Huang H, Gong QH, et al. J Mater Sci 2018; 53: 12477.
32. Sun CC, Yang J, Rui XH, et al. J Mater Chem A 2015; 3: 8483.
33. Luo H, Wang B, Liu T, et al. Energy Storage Mater 2019; 19: 370.
34. Yang QJ, Liu Y, Yan M, et al. Chem Eng J 2019; 370: 666.
35. Zhu YR, Peng PP, Wu JZ, et al. Solid State Ionics 2019; 336: 110.
36. Gao X, Zhang YX, Huang M, et al. Ceram Int 2014; 40: 15641.
37. Zheng XL, Han X, Zhao XX, et al. Mater Research Bull 2018; 106: 243.
38. Chen HM, Xue CY, Cui DF, et al. Int J Electrochem Sci 2020; 15: 966.
39. Omar FS, Numan A, Duraisamy N, et al. RSC Adv 2016; 6: 76298.
40. Xiang GT, Meng Y, Qu GM, et al. Sci Bull 2020; 65: 443.
41. Umeshbabu E, Rajeshkhanna G and Rao GR. Int J Hydrogen Energy 2014; 39: 15627.
42. Chen DZ, Pang D, Zhang SP, et al. Electrochim Acta 2020; 330: 135326.
43. Raphael Ezeigwe E, Dong L, Wang JY, et al. J Colloid Interface Sci 2020; 574: 140.
44. Packiaraj R, Devendran P, Venkatesh KS, et al. J Energy Storage 2021; 34: 102029.
45. Zhang F, Bao YY, Ma SS, et al. J Mater Chem A 2017; 5: 7474.
46. Qu JI, Bai ZX, Dai EG, et al. J Alloys Compd 2018; 763: 966.
47. Mei BA, Muntehshari O, Lau J, et al. J Physical Chem C 2017; 122: 194.
48. Su L, Zhang CY, Shu L, et al. Nano 2020; 15: 2050082.
49. Zou RY, Zhu L, Luo GL, et al. Int J Electrochem Sci 2020; 15: 484.
50. Hong J, Park SJ and Kim S. Int J Hydrogen Energy 2020; 45: 30859.
51. Mei BA, Muntehshari O, Lau J, et al. J Physical Chem C 2017; 122: 194.