Ni$_3$S$_2$/Zn$_{0.76}$Co$_{0.24}$S for high performance hybrid supercapacitor

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Abstract. Supercapacitors have become a research hotspot in the field of energy storage due to their high-power density, fast charging/discharging ability, long-term stability and safety. Nevertheless, relatively low energy density hindered their application. Herein, Ni$_3$S$_2$/Zn$_{0.76}$Co$_{0.24}$S (NZCS) microsphere were synthesized using a facile two-step hydrothermal process. The polymetallic synergies can improve conductivity and shorten ion transport path. The uniform particle distribution provided numerous active sites for faradaic reactions. The NZCS microsphere showed a large capacity of 571.5 C g$^{-1}$ at 1 A g$^{-1}$ and 87% rate retention when the current increases by 10 times. A hybrid supercapacitor assembled by NZCS cathode and active carbon anode demonstrate a high energy density of 44.1 Wh kg$^{-1}$ (407.0 W kg$^{-1}$) and a stable cycliability of 15,000 cycles with 15% loss. Thus, NZCS is a promising electrode material for high performance supercapacitor.

Keywords: Supercapacitor; Zn$_{0.76}$Co$_{0.24}$S; Ni$_3$S$_2$; hydrothermal.

1. Introduction

Environmental problems and energy shortage have become increasingly serious due to the rapid economic development has led to the huge consumption of coal, oil and other resources. High efficiency, clean energy and related advanced technologies have been put forward higher requirements for energy storage device (EES).[1, 2] Supercapacitors (SCs) has attracted much attention due to its high-power density, ultra-long cycle life and reliable security. However, the relatively low energy density of SCs compared with that of lithium-ion batteries and fuel cells has hindered its further application. Hybrid supercapacitors (HSCs) use a dual charge storage mechanism, both capacitive-controlled and diffusion-controlled, to enable higher operating voltage and higher energy density.[3]

Electrode material is an important factor affecting the supercapacitor, which directly determines the charge storage capacity of the capacitor. Metal sulfides, such as Ni$_3$S$_2$ and Co$_9$S$_8$, have attracted more attention as electrode materials for SCs due to their excellent electrical conductivity and electrochemical activity. However, metal sulfides stored energy by Faraday reaction occurring through the surface of the material with electrolyte ions, and tend to show a poor long-term stable performance in the process of charge and discharge. Designing polymetallic sulfide composites is an effective strategy to improve electrochemical stability due to the high theoretical capacity compared with monometal and more abundant redox reaction.[4] Thus, we prepared Ni$_3$S$_2$/Zn$_{0.76}$Co$_{0.24}$S microsphere by hydrothermal method and exhibit excellent electrochemical properties. The uniform distribution microsphere structure can provide effective active area and has a short ion transport path during energy storage, which can enhance the Faraday reaction between electrolyte ions and the active materials. Moreover, the polymetallic synergies help to enhance electrical conductivity. At the current density of 1 A g$^{-1}$, Ni$_3$S$_2$/Zn$_{0.76}$Co$_{0.24}$S exhibit an large capacity of 571.5 C g$^{-1}$. The NZCS//AC HSC can achieve a high energy density of 44 Wh kg$^{-1}$ at a power density of 407 W kg$^{-1}$ and a long-term cycling stability of 15,000 with 75% capacity retention, which exhibits great application prospect.

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2. Experimental section

2.1 Materials
All the chemical reagents were purchased from Aladdin Biochemical Technology Co., Ltd. and Tianjin iweixin Huagong Technology Co., Ltd. All the chemical reagents were of analytical purity grade, and used without any further purification.

2.2 The synthesis of NZCS
The synthesis of NZCS was displayed in Fig. 1. Typically, 0.49 g Zn(CH₃COO)₂ꞏ2H₂O, 0.49 g Co(CH₃COO)₂ꞏ4H₂O and 0.662 g Ni(CH₃COO)₂ꞏ4H₂O were dissolved in 75 mL deionized water and stirring for 15 min. Then, 0.48 g urea, 0.11 g KOH and 0.38 g C₆H₈O₇ were added in turn to the above solution and stirring until uniform. Furthermore, the above mixture was transferred into a Teflon-lined stainless-steel autoclave and reacted at 160℃ for 6 h to obtain NZCO. For prepared NZCS, NZCO (0.16 g) and Na₂Sꞏ9H₂O (2.8 g) were further processed by hydrothermal method for 8 hours at 120℃.

Fig. 1 Schematic diagram of preparation process of the NZCS

2.3 Materials and electrochemical characterization
X-ray diffraction (XRD, Rigaku D/max-2400) was used for quantitative analysis and macroscopic stress analysis. The molecular structure and valence states were analyzed by XPS. Scanning electron microscope (SEM, Inspect F50) was used to observe the surface morphology of materials.

Cyclic voltammetry (CV), galvanostatic chargedischarge (GCD), and electrochemical impedance spectroscopy (EIS), were characterized by using electrochemical workstation (CHI660E).

The Specific capacity (C, C g⁻¹) can be calculated based on GCD curves, as follow:

\[ C = \frac{I \times \Delta t}{m} \]  

(1)

Where \( I \) (A), \( \Delta t \) (s) and \( m \) (g) are current, discharge time and mass of the active material.

The energy density (\( E \)) and power density (\( P \)) can be calculated as the following equations:

\[ E = \frac{C \times \Delta V}{2 \times 3600} \]  

(2)

\[ P = \frac{E \times 3600}{\Delta t} \]  

(3)

Where \( C \) (C g⁻¹) is the specific capacity of the HSC device, \( \Delta t \) (s) is the discharge time and \( \Delta V \) (V) is the potential window.

3. Results and discussion
NZCS were characterized by XRD, and the results were shown in Fig. 2a. The main diffraction peaks are indexed to (110), (003), (202) of Ni₃S₂ (JCPDS card No. 44-1418) and (111), (220), (311) of Zn₀.₇₆Co₀.₂₄S (JCPDS card No. 47-1656), respectively. There is no other phase, which illustrate the product is composed of Ni₃S₂ and Zn₀.₇₆Co₀.₂₄S. Fig. 2b and Fig. 2c showed the SEM image and the corresponding element distribution of NZCS composite, respectively. It can be seen that NZCS composite is microsphere structure, and the diameter is about 1.6 μm. The uniform distribution of such particles can increase the contact area between the electrode material and the electrolyte during the electrochemical reaction process, providing a good way for electron transfer and ion diffusion.

Fig. 2 (a) XRD pattern, (b) SEM images, and (c) Mapping of NZCS

As shown in Fig. 3a, CV curves of NZCS and NZCO composite electrode materials was measured in a three-electrode system with 2 M KOH as for electrolyte at the scan rate of 10 mV s⁻¹. There are two obvious peaks can be observed, which correspond to the redox process in the charging and discharging process. Compared with NZCO, NZCS has a significantly larger potential window and absolute area, which indicate a higher specific capacity. CV curves of NZCS at different scanning rates was measured in a voltage window of 0 ~ 0.7V as shown in Fig. 3b. The anodic and cathodic peaks can be clearly observed in each curve, which can be interpreted as the following reactions occurring.
Zn_{0.76}Co_{0.24}^{2+}OH ↔ 0.76ZnSOH + 0.24CoSOH + e^- \quad (4)

Ni_3S_2 + 3OH^- ↔ Ni_3S_2(OH)_3 + 3e^- \quad (5)

With the scan rate increasing, the peak current increases gradually and the positions of cathodic and anodic peaks are shifted to negative and positive potentials, respectively, which due to the rapid electronic/ionic transports and good reversibility.

Moreover, in order to further analyze the electrochemical behavior, the capacitance contribution is evaluated according to the Eq. (6), and the results were shown in Fig. 3c.

\[ i(v) = k_1v + k_2v^{0.5} \quad (6) \]

Where \( k_1 \) and \( k_2 \) are constants, \( v \) (mV s\(^{-1}\)) is the scanning rate, and \( i \) (A) is the current. When the scanning rate is 5, 10, 20, 30 and 50 mV s\(^{-1}\), the percentage of capacitance contribution (\( k_1v \)) is 40.0%, 52.0%, 64.0%, 72.2% and 87.2% respectively, which illustrate that the surface capacitive-type behavior and battery-type diffusion-control behavior exist in the process of charge and discharge and the surface-controlled capacitive processes start to be dominant with the increase of scanning rate.

The GCD curves of NZCS at different current densities within a potential range of 0 ~ 0.5 V as shown in Fig. 3d. There is an obvious charging and discharging platform can be observed, which is caused by the reversible redox reactions. The specific capacity of the two electrodes can be calculated by Eq. (1) and the results were showed in Fig. 3e. Compared with NZCO, the NZCS electrode has a larger capacitance. When the current density is 0.5, 1, 2, 4, 6, 8 and 10 A g\(^{-1}\), the capacity of NZCS is 572.8, 571.7, 561.35, 554.4, 531.9, 522.9 and 498.9 respectively, which shows an excellent rate capability of 87% from 1 A g\(^{-1}\) to 10 A g\(^{-1}\). The Nyquist plots of NZCS and NZCO were shown in Fig. 3f. According to the fitting model, the series resistance of NZCO (\( R_s=1.04\Omega \)) and NZCS (\( R_s=1.02\Omega \)) is close, and the charge transfer resistance of NZCS (\( R_{ct}=0.75\Omega \)) is smaller than those of NZCO (\( R_{ct}=1.08\Omega \)), which indicates a relatively fast electron transfer rate of NZCS. In addition, the slope of NZCS curve in the low frequency region is higher than that of NZCO composite electrode, indicating that NZCS composite electrode has a faster ion diffusivity during the energy storage process.

In order to further evaluate the electrochemical performance of NZCS electrodes, the HSC device was assembled with NZCS nanocomposite electrode as positive electrode and AC electrode as negative electrode (NZCS//AC). CV curves of NZCS//AC HSC at different scanning rates was shown in Fig. 4a. When the scanning rate increases gradually, the CV curve remains consistent and the overall appearance is rectangular-like, indicating that NZCS//AC HSC has good capacitance characteristics. The energy density and power density of NZCS//AC HSC can be calculated according to the Eq. (2-3). It shows a maximum power density of 7250.0 W kg\(^{-1}\) (20.7 Wh kg\(^{-1}\)) and a maximum energy density of 44.1 Wh kg\(^{-1}\) (407.0 W kg\(^{-1}\)), respectively, which is higher than that of many supercapacitor devices in literatures as shown in Fig. 4b. When it is packaged into a button battery, it can light up the timer, indicating that NZCS//AC HSC has a good application prospect. The cycling stability of NZCS//AC HSC devices was tested at 4 Ag\(^{-1}\), and the results were shown in Fig. 4c. The specific capacitance of NZCS//AC can maintain 75% of the initial after 15,000 charge-discharge cycles, and the coulomb efficiency can always maintain above 98%, which indicates an excellent long-term stability.

4. Summary

Ni_3S_2/Zn_{0.76}Co_{0.24}S composite was successfully prepared by a two-step hydrothermal method with a following sulfidation method. NZCS electrode exhibits a high specific capacity of 571.5 C g\(^{-1}\) at 1 A g\(^{-1}\), due to the lower charge-transfer resistance and the synergistic of multiple metals, which is more than twice that of NZCO. Moreover, the NZCS electrode was assembled with an AC electrode to assemble an HSC with an energy density of 44.1 W h kg\(^{-1}\) at a power density of 407 W kg\(^{-1}\). After 15,000 charge and discharge cycles, it can still maintain 75% of the initial capacitance value. Therefore, the good electrochemical performance of NZCS composite makes it have a wide application prospect.
References


