Preparation of NiCo$_2$S$_4$-based Electrodes for Supercapacitor Application

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Abstract. Supercapacitors are energy storage devices to deal with problems of oil consumption and environmental pollutions. However, the specific capacitance of pure carbon-based electrodes is too low, and this problem is urgent to solve. The NiCo$_2$S$_4$ is an electrode material which can improve the specific capacitance of the supercapacitor. The NiCo$_2$S$_4$-based electrodes with different carbon-based materials such as carbon black, multiwall carbon nanotube (MWCNT) and graphene foam by slurry method are investigated in this study. The NiCo$_2$S$_4$ electrode with the graphene foam and CNTs demonstrates excellent electrochemical performance, which exhibits the specific capacitance of 2925 F g$^{-1}$ and the area specific capacitance of 5.06 F cm$^{-2}$ at current density of 1 A g$^{-1}$. This result is attributed to that the CNTs can create a conductive network for connection of the NiCo$_2$S$_4$ and porous graphene foam with sponge-like morphology. This structure can facilitate electrolyte into inner portion of the electrode material. It has a high potential to be applied to energy storage devices.

Introduction

Supercapacitor is one of the most significant energy storage devices, which has the advantages of good reliability, long cycle life, fast charge and discharge, and higher instantaneous power [1-3]. Furthermore, it also applies to the energy storage system, which combines with fuel cells, batteries, solar energy and other renewable energy. However, the specific capacitance of pure carbon-based electrodes is too low, and this problem is urgent to solve. In order to enhance the energy density and power density of the supercapacitor, high operating voltage were studied [4]. There are two kinds of storage mechanisms for supercapacitor: one is electric double-layer capacitors (EDLCs), and the other is redox reaction[5]. Electrodes with the EDLC’s mechanism are usually fabricated from materials with high surface area and high electrical conductivity, such as activated carbon, carbon nanofibers, mesoporous carbon, carbon nanotubes, and graphene [6-8], but the specific capacitance is low compared with batteries. Therefore, the electrode materials for pseudocapacitors are the materials to deal with the problem of low specific capacitances by employing surface redox reactions. Electrode materials of pseudocapacitors are transition metal oxygen/sulfide, transition metal hydroxides and their complexes. Researches of supercapacitor materials are currently composed of metal oxides, carbon composites or conductive polymer complex [9-12]. The nickel cobalt sulfide (NiCo$_2$S$_4$) is a pseudocapacitor’s electrode material with excellent optical and conductive properties and has great potential in the application of energy storage device. Compared with NiCo$_2$O$_4$, NiCo$_2$S$_4$ exhibits better performance, because that the electron negativity of sulfur is lower than that of oxygen, and shows a lower energy band gap than the NiCo$_2$O$_4$, and also possesses higher conductivity and higher capacitance performance [13-15]. Several works have been explored about NiCo$_2$S$_4$. Jiang et al. [16] used sacrificial template method to synthesis NiCo$_2$S$_4$ porous nanotubes, which revealed a specific capacitance of 933 F g$^{-1}$ at current density of 1 A g$^{-1}$; Peng et al. [17] developed 3D interconnected NiCo$_2$S$_4$ nanosheets via facile two-step solution-based method, showing high rate capability of 40.3% capacitance retention at 80 mA cm$^{-2}$; Yu et al. [18] prepared sacrificial template method to acquire uniform Ni$_3$Co$_3$S$_4$ hollow nanoprisms with a high specific capacitance of 895 F g$^{-1}$ at 1 A g$^{-1}$ and rate retention 63.3% at 1 to 20 A g$^{-1}$. Carbon-based materials’ supercapacitance is the representative of the double-layer energy storage mechanism, generally activated carbon (ACs), glass carbon, carbon...
nanotubes (CNTs) or activated carbon fiber (ACF) as electrode materials. Among these materials, activated carbon is one of most commonly used materials because of its relatively high specific surface area (2,000-3,000 m$^2$ g$^{-1}$), low cost and high power density [19-20], but there is a drawback of low specific capacitance values and low conductivity [21]. Therefore, graphene is widely used in energy storage materials systems such as supercapacitors, fuel cells, dye-sensitive solar cells and lithium-ion batteries in recent years due to the ultra-high specific surface area and high conductivity. To apply to commercial products and processes, the production process of energy storage materials is mostly slurry process, and the polymer plays an important role in the process to increase the adhesion of the material helping to forming composite materials. The PVDF polymer has mostly been used as a binder, but the performance with PVDF is low. Chou et al. prepared MnO$_2$ supercapacitor with PVDF as a binder, and the specific capacitance value was about 0.2 F cm$^{-2}$ [21]. Lee et al. used PAA to make MnO$_2$ supercapacitor, and the capacitance value was 1.7 F cm$^{-2}$ [22], which can effectively increase per unit area electrode of the material loading, and facilitate to commercial production.

To improve electrochemical properties, NiCo$_2$S$_4$ is synthesized by two-step hydrothermal process to increase the specific capacitance; carbon-based materials such as carbon black, CNT and graphene foam are added to provide high surface area; the polymer PVDF-HFP is a binder helping to mixing above materials by slurry method in this study. Such electrode contains both hard and soft segments to facilitate the transportation of electrolytes and help ions separation which is expected to enhance the electrochemical behavior. The electrode composed of NiCo$_2$S$_4$, PVDF-HFP, acetone, CNTs, and graphene foam achieves the excellent electrochemical performance of high specific capacitance of 2925 F g$^{-1}$ and 5.06 F cm$^{-2}$. It indicates its great potential for application of energy devices.

**Experimental**

**Preparations of NiCo$_2$S$_4$ Powders**

NiCo$_2$S$_4$ was obtained through a two-step hydrothermal method. In the first step, 4 mmol of CoCl$_2$$\cdot$6H$_2$O, 2 mmol of NiCl$_2$$\cdot$6H$_2$O and 24 mmol of urea were totally added into 40 mL deionized water to acquire a clear pink solution. The solution was poured into 50 mL Teflon-lined stainless steel autoclave. Then, the autoclave was sealed and maintained at 120 °C for 4 h and cooled down to room temperature naturally. After that, the pink precipitate was washed with deionized water and ethanol for many times and dried at 65°C for 12 h in vacuum oven. After drying process, (Co,Ni)$_2$CO$_3$(OH)$_2$ powders were collected for the next step. In the second step, the as-obtained powder and Na$_2$S $\cdot$ 9H$_2$O were dissolved in 40 mL distilled water to form a black solution. The solution in 50 mL Teflon-lined stainless steel autoclave was sealed and heated to 165 °C for 5 h and cooled down to room temperature naturally. After that, the black precipitate was rinsed with deionized water and ethanol for many times and dried at 65°C for 12 h in vacuum; the NiCo$_2$S$_4$ powders can be received.

**Preparations of the NiCo$_2$S$_4$ Composites Electrodes by Slurry Process**

Prior to the slurry process, the Ni foam (1 cm x 3 cm) was treated thoroughly in a 3 M HCl solution for 10 min to strip the oxide layer on the Ni foam. Then, it was cleaned with deionized water and ethanol several times and dried at 40°C for 12 h in vacuum oven. As for the graphene-based material, graphene oxide (GO) can be prepared by the improved synthesis method [23]. The graphene foam was synthesized by hydrothermal method [24]. A total of 40 mg of GO was dissolved in a solution containing 40 mL of DI water to form a brown solution (GO aqueous solution = 1 mg/mL). After 6 h stirring, 40 mg sucrose was added into it and the resultant solution was further stirred for 1 h. Here, the carbon source is sucrose and the weight ratio of GO and sucrose is 1:1. Then, the final solution was transferred into the Teflon-lined sealed stainless steel autoclave and maintained at 120 °C under autogenous pressure for 24 h. The process is the hydrothermal polymerization/carbonization of the mixture of GO sheets with sucrose to firstly get the hybrid precursor materials. After reaction, the autoclave was allowed to cool down naturally and the hybrid precursor materials were rinsed with DI
water. Then, the hybrid precursor materials were collected and freezing dried for 2 days; the graphene foam can be received. The as-obtained NiCo$_2$S$_4$ powders via two-step hydrothermal method serve as active materials. PVDF-HFP with the mean molecular weight of 400,000 was chosen as polymer. Carbon black was represented for carbon-based material. The slurry contained NiCo$_2$S$_4$/ PVDF-HFP/ Carbon black with the weight ratio 8:1:1 dissolved in acetone. The 1cm x 1cm as-prepared Ni foam was coated with the slurry and baked at 40$^\circ$C for 1 h in vacuum to complete the preparation of the electrode. For comparison, carbon black in the slurry recipe can be changed by CNTs/carbon black and CNTs/ graphene foam with the weight ratio 1:1 but not deviate from the total ratio of the slurry.

Materials Characterization

The NiCo$_2$S$_4$ was identified by X-ray powder diffraction (XRD) with operation at 30 kV, 20 mA. (D2 phaser system with Cu K$\alpha$ radiation, Bruker) for crystal structure. The surface micro-morphology of the powders can be observed by scanning electron microscope (SEM, Hitachi SU8010) with the extraction voltage of 15 kV and the working current of 10 μA.

Electrochemical Measurement

In this work, the electrochemical performance of the electrode was measured by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) using CHI608 electrochemical analyzer. All the electrochemical measurement was carried out with standard three-electrode system. The NiCo$_2$S$_4$-based composite electrodes served as working electrode with a saturated calomel reference electrode (SCE), a counter electrode of platinum sheet, and electrolyte of 6 M KOH aqueous solution. The values of the specific capacitance (Fg$^{-1}$) can be obtained by the following equation:

$$C = \frac{I \cdot \Delta t}{\Delta V \cdot m}$$

Where C is the specific capacitance of the electrode. $I$ represents the discharge current, $\Delta t$ is the time for a full discharge, $m$ refers to the active material mass loading, and $\Delta V$ is the total width of the potential window.

Results and Discussion

Fig. 1 reveals the XRD pattern of as-prepared NiCo$_2$S$_4$ powders by two-step hydrothermal process. The diffraction peaks at 26.8$^\circ$, 31.6$^\circ$, 38.2$^\circ$, 50.5$^\circ$, and 55.3$^\circ$ can be respectively corresponded to the (220), (311), (400), (511) and (440) planes of the cubic NiCo$_2$S$_4$ with the Fd3m space group (JCPDS No. 43-1477), pointing the synthesis of the cubic NiCo$_2$S$_4$ phase successfully acquired from hydrothermal method.

Figure 1. XRD pattern of the NiCo$_2$S$_4$ prepared by two-step hydrothermal method.
The surface morphologies of the NiCo$_2$S$_4$ powders and powders with carbon-based materials were examined by SEM. Fig. 2(a) indicates the lumps shape of surface morphology of pure NiCo$_2$S$_4$ powders. Carbon black is the spherical shape. Adding some CNTs to replace carbon black can lead the microstructure to build dimensional space connectivity to increase the transport path, shown in Fig. 2(b). As shown in Fig. 2(c), instead of carbon black, using graphene foam can obtain the better separation effect which would create the pathway to facilitate diffusion.

Figure 2. (a) SEM morphology of the NiCo$_2$S$_4$ powder; SEM images of the NiCo$_2$S$_4$ with different carbon-based materials: (b) Carbon black + CNTs, (c) Graphene foam + CNTs.

Fig. 3(a) illustrates CV curves of the NiCo$_2$S$_4$-based electrodes mixed different carbon-based materials at 5 mV s$^{-1}$. The integrated area of CV curve of the electrode using NiCo$_2$S$_4$/Graphene foam + CNTs recipe shows that it has higher area than the other two electrodes (NiCo$_2$S$_4$/Carbon black and NiCo$_2$S$_4$/Carbon black + CNTs), which indicates using graphene foam and CNTs can facilitate transportation path resulting in the better performance. Fig. 3(b) presents CV curves of the electrode at various scan rates varying from 5 to 100 mV s$^{-1}$ in a potential window from -0.1 to 0.5 V. The pseudocapacitive properties of the electrode can be easily found in redox peaks of the CV curve, which can be attributed to the Faradic redox reactions concerned with Ni$^{2+}$/Ni$^{3+}$ and Co$^{2+}$/Co$^{3+}$/Co$^{4+}$ valence state change. The pseudocapacitive behavior in the alkaline electrolyte can be described by the following equations [25-26]:

$$\text{CoS} + \text{OH}^- = \text{CoSOH} + e^-$$

(2)

$$\text{NiS} + \text{OH}^- = \text{NiSOH} + e^-$$

(3)

$$\text{CoSOH} + \text{OH}^- = \text{CoSO} + \text{H}_2\text{O} + e^-$$

(4)

The capacitive property of the electrode is also evaluated by GCD method. Fig. 3(c) shows GCD curves of the electrodes at current density 1 Ag$^{-1}$. The electrode with NiCo$_2$S$_4$/Graphene foam + CNTs can be obtained the larger specific capacitance, which is calculated to be 2925 Fg$^{-1}$, while specific capacitances of the electrodes with carbon black and carbon black + CNTs can be estimated to be 2177 and 2495 Fg$^{-1}$, respectively. Owing that the coating area of Ni foam is 1 cm$^2$, and the mass loading of the electrode with CNTs + graphene foam is 1.73 mg, the area capacitance, 5.06 F cm$^{-2}$, of such electrode can be obtained by converting from its specific capacitance. The CNTs plays the role of conductive network for NiCo$_2$S$_4$. Using some CNTs to replace carbon black can enhance the specific capacitance and the areal capacitance. Furthermore, graphene foam is the porous characteristics, which can bring about loose structure to facilitate electrolyte entering into inner part of the electrode. Substituting graphene foam for carbon black can strongly improve specific capacitance. Fig. 3(d) exhibits GCD curves of the electrode at 1, 2, 5, 10 and 20 A g$^{-1}$, the specific capacitance gradually decreases with the increasing current densities. At the lower current density, ions in electrolyte have sufficient time to entering into internal region of the electrode. However, the
lower specific capacitance can be obtained under higher current density because the ions cannot penetrate into some internal sections, and binder blocks of the polymer also obstruct ion diffusion; only near the external surface of the electrode can react with the electrolyte or ions. Fig. 3(e) displays the specific capacitance changed with current densities. Among these three electrodes, the NiCo$_2$S$_4$ with Graphene foam + CNTs electrode can be found the higher specific capacitance from 1 to 20 A g$^{-1}$. Besides, the electrode of NiCo$_2$S$_4$/graphene foam + CNTs also delivers the better specific capacitance, which can up to 2925 F g$^{-1}$ at 1 Ag$^{-1}$. The result is attributed to that CNTs can create the better conductive network than carbon black and graphene foam can lead to the loose structure to facilitate electrolyte into inner portion of the electrode. Fig. 3(f) demonstrates EIS Nyquist plots of the three electrodes in the frequency sweeping from 100 kHz to 0.1 Hz. The internal resistance $R_s$ which can be observed in real axis closely equal to low value is the resistance including the ionic resistance of electrolyte, and the intrinsic resistance of the active material; while charge-transfer resistance $R_{ct}$ is inversely proportional to the efficiency of electron transfer at the electrode/electrolyte interface. It can be seen that the curve of the electrode of NiCo$_2$S$_4$/carbon black has large semicircle, indicating that $R_{ct}$ is much higher, because this electrode is less conductive network and higher density. The $R_s$ of the NiCo$_2$S$_4$ with carbon black, carbon black + CNTs, and graphene foam + CNTs electrodes are 0.89, 1.01, and 1.41 Ω, respectively. The $R_s$ of the electrodes with CNTs are higher than that with carbon black, indicating that adding CNTs to replace carbon black can make less density body. In addition, the electrode with graphene foam has much higher $R_s$ due to sponge-like morphology of graphene foam.

![Figure 3](image)

Figure 3. (a) CV curves of the NiCo$_2$S$_4$-based composite electrodes at the scan rate 5 mV s$^{-1}$; (b) CV curves of the NiCo$_2$S$_4$ with Graphene foam + CNTs electrodes at different scan rates; (c) GCD curves of the NiCo$_2$S$_4$ mixed with different carbon-based materials electrodes at 1 Ag$^{-1}$; (d) GCD curves of the NiCo$_2$S$_4$ with Graphene foam + CNTs electrodes at various current densities; (e) Specific capacitance vs. current density curves of the NiCo$_2$S$_4$ with different carbon-based materials electrodes; (f) The Nyquist plots of the NiCo$_2$S$_4$ with different carbon-based materials electrodes in of 100 kHz to 0.1 Hz.

**Conclusion**

In summary, the NiCo$_2$S$_4$ powders were successfully synthesized via two-step hydrothermal approach which were characterized by the XRD and SEM analyses. The NiCo$_2$S$_4$-based composite electrodes with graphene foam and CNTs prepared by slurry process exhibited an excellent performance. The specific capacitance was up to 2925 F g$^{-1}$ (5.06 F cm$^{-2}$) at 1 Ag$^{-1}$. It is attributed to a good conducting
network of CNTs and the sponge-like morphology of the graphene foam to facilitate the electrolyte transportation. These results indicate that the designed electrode is appropriate for practical supercapacitor application.

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