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Electrochemical characterization on cobalt sulfide for electrochemical supercapacitors

Feng Tao [b], Yong-Qing Zhao [b], Guo-Qing Zhang [b], Hu-Lin Li [a,b,*]

[a] College of Material Science and Engineering, Nanjing University of Aeronautics and Astronautisc, Nanjing 210013, PR China
[b] College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China

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Abstract

High capacitance at a high charge–discharge current density of 50 mA/cm^2 for a new type of electrochemical supercapacitor cobalt sulfide (CoS_x) have been studied for the first time. The CoS_x was prepared by a very simply chemical precipitation method. The electrochemical capacitance performance of this compound was investigated by cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge–discharge tests with a three-electrode system. The results show that CoS_x has excellent electrochemical capacitive characteristic with potential range $-0.3 \sim 0.35$ V (versus SCE) in 6 M KOH solution. Charge–discharge behaviors have been observed with the highest specific capacitance values of 475 F/g at the current density of 5 mA/cm^2, even at the high current density of 50 mA/cm^2, CoS_x also shows the high specific capacitance values of 369 F/g.

Keywords: Supercapacitors; Cobalt sulfide; High capacitance; Current density; Mechanism

1. Introduction

Recently, electrochemical supercapacitors attract more attentions in the energy storage and conversion systems, which have higher energy density than dielectric capacitors and have higher power density than batteries [1], is being considered for a variety of applications such as in hybrid electric vehicles, uninterrupted power supplies, memory protection of computer electronics and cellular devices [2,3]. The materials studied for capacitor have been mainly of three types: carbon/carbon [4], metal oxide [5–7], and electronically conducting polymer [8]. High-surface-area carbon materials (activated carbon black, carbon aerogel, and carbon nanotubes) are electrochemical double layer capacitors, the charge is a result of electrical charge separation at the interface between electrode and electrolytes. Specific capacitance of 280 and 120 F/g can be achieved in aqueous and non-aqueous electrolytes with the maximum voltages of 1 and 3 V, respectively [9]. Metal oxide and conducting polymer are pseudocapacitors. The electrical charge transport in the redox reaction is the origin of pseudocapacitance. The hydrous ruthenium oxide was reported as the most promising materials with special capacitance value of 863 F/g [10]. Though noble-metal oxides or hydrous oxides yield remarkably large value of capacitance, the high cost of these materials limits its application. Conducting polymer-based electrochemical capacitors represent an interesting class, thanks to the combination of high capacitive energy density and low material cost [11–13]. But, conducting polymer-based material also have some disadvantages that include lower cycle-life and slow kinetics ion transport because the redox sites in the polymer backbone are not sufficiently stable for many repeated redox processes [14,15]. So, it is extreme important to develop alternative electrode material with a combination of low cost and improved performances.

For many years, intense research of new capacitive materials have been the focus of the present study for elec-

* Corresponding author. Address: College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China.
E-mail address: lihl@lzu.edu.cn (H.-L. Li).

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trochemical supercapacitors [16–18]. At present, Jayalakshmi and Mohan Rao [19] have studied the capacitive performance of zinc sulphide nanoparticles in the electrolytes of 0.1 M LiCl, NaCl, NaI, and KI solutions. This work shows a new pathway to identify similar semiconducting materials that can perform as good capacitor electrodes. The value of capacitance (about 200 F/cm^2) was obtained on chalcocite in electrolyte containing 1 M H_2SO_4 and 0.5 M $CuSO_4$, but with unacceptable high leakage current [20]. Cobalt sulfide has been used as negative electrode materials for rechargeable lithium batteries [21], but nobody studies its electrochemical performance. In this work, we synthesized amorphous cobalt sulfide by a very simple chemical precipitation method and study its electrochemical capacitive performance in neutral and alkaline solution, respectively, cobalt sulfide shows good capacitive performance in alkaline electrolyte. According to the cyclic voltammetry (CV) curves of electrodes in this two kinds of solution, we assume the mechanism of electrochemical oxidation of cobalt sulfide consulting the redox mechanism of $Co(OH)_2$ in alkaline electrolyte. Exploring the electrochemical characteristics of this material will direct a new type of supercapacitor materials.

2. Experiment

2.1. Synthesis of cobalt sulfide

Solution A: 0.9633 g $NaS \cdot 9H_2O$ was dissolved in 100 mL deionized water. *Solution B:* 1 g $Co(CH_3COO)_2 \cdot 4H_2O$ was dissolved in 100 mL deionized water. Solution A was dropped into Solution B with vigorous stirring until the black precipitation was formed. Then, the product precipitate was filtered, washed with deionized water several times and dried for 20 h under vacuum at 50 °C.

2.2. Synthesis of the compound electrodes

The working electrodes (20 mg) were prepared by mixing 70 wt.% of cobalt sulfide powder with 15 wt.% of graphite, 12.5 wt.% of acetylene black (>99.9%) and 2.5 wt.% of poly(tetraflouoroethylene) dried powder (PTFE). The first three components were mixed together in an agate mortar until homogeneous black powder was achieved. PTFE was then added to the mixture with a few drops of ethanol. The synthesized paste was pressed at 20 MPa to a nickel gauze, and dried for 10 h under vacuum at 40 °C.

2.3. Characterization of the material

Electrochemical studies were carried out using an electrochemical working station (CHI-660, Chenhua, Shanghai). All the electrochemical measurements were done in a three-electrode arrangement, a platinum gauze and a saturated calomel electrode (SCE) were used as a counter electrode and reference electrode, respectively. All measurements were carried out in 6 M KOH electrolyte. Electrochemical performance was characterized by cyclic voltammetry with a voltage scan rate 10 mV/s. The impedance properties of the electrodes were examined by impedance spectroscopy at applied potential of −0.4 V, −0.3 V, −0.2 V, −0.1 V, 0 V, 0.1 V, 0.2 V, 0.3 V by using a CHI660 electrochemical work station. Data were collected in the frequency range of 10^5–10^{-2} Hz at these applied potential. The galvanostatic charge–discharge of the electrode was evaluated in the certain range of potential at the current of 5 mA, 10 mA, 20 mA, 50 mA.

The state of the cobalt sulfide has been studied with XPS. The cobalt sulfide were kept in nitrogen atmosphere during the transfer for XPS measurement. X-ray photoelectron spectra were acquired on a VG Escalab 210 electron spectrometer, equipped with a hemispherical electron analyzer and an Mg Kα X-ray source (hm = 1253.6 eV). The C1s electron binding energy was referenced at 284.5 eV.

Scanning electron microscopic (SEM) images were recorded with JSM-6380LV microscope. X-ray powder diffraction diagrams were recorded on an X-ray diffractometer (D8 advance-X) using Cu-Kα ($\lambda = 0.154056$ nm) and Sol-X detector, and the scan rate was $1° \min^{-1}$ (step: 0.02°; step time: 1.2 s).

3. Results and discussion

3.1. The morphology and structure of CoS_x

The X-ray powder diffraction patterns of the cobalt sulfide and annealed powders are shown in Fig. 1. We can see that there is no peak in this figure, which demonstrated that the cobalt sulfide powder prepared via the chemical reaction method is amorphous. From many Ref. [22] about preparing cobalt sulfide, we know that the products usually contain several phases of cobalt sulfide, the valence of cobalt in the compound may be 2, 3 or 4, so we named the product in our experiment CoS_x.

The chemical composition of the cobalt sulfide was investigated by XPS in Fig. 2. The position of Co2p region is related to the sulfidation of cobalt. The Co2p spectra of

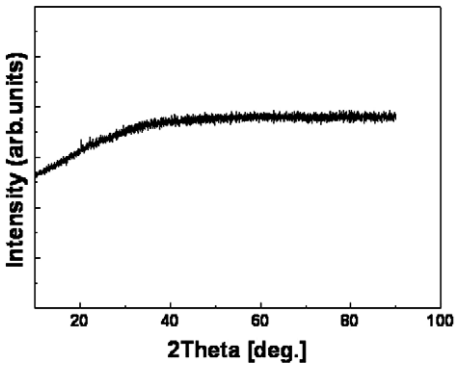

Fig. 1. XRD pattern of the cobalt sulfide.