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Structure variation of nickel cobalt sulfides using Ni foam and nickel salt as the nickel source and the application on the supercapacitor electrode

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ABSTRACT

The nickel cobalt sulfide is one of the promising electroactive materials for energy storage devices. The morphology of the nanomaterial has been widely designed with high surface area and high conductivity to enhance the charge storage ability. Based on the hydrothermal reaction and using the nickel foam which releases nickel ions during the reaction as the substrate, the influences of the nickel source on the morphology of the nickel cobalt sulfide and the pertinent supercapacitor (SC) performance are worthy to be discussed. In this study, the nickel ions are provided by the nickel foam and the nickel salt in the hydrothermal reaction for synthesizing the nickel cobalt sulfide, and the morphology variations as well as the corresponding electrochemical performance are investigated. The aggregation of the nickel cobalt sulfide is obtained at different regions in the nanosheets when different nickel sources are used. The optimized SC electrode shows a specific capacitance (C_F) of 2206 F/g measured by using the galvanic charge/discharge (GC/D) technique at the current density of 4 A/g, and the high-rate charge/discharge capacity is attained with a large C_F value of 1655.8 F/g at the current density of 128 A/g. The excellent cycling stability of the 94.6% retention on the C_F value after 2000 cycles repeated charge/discharge process and the Coulombic efficiency higher than 96% for the entire measurement are also achieved for this system.

1. Introduction

Transition metal oxides [1], hydroxides [2,3] and sulfides [4,5] with their multiple oxidation states for reversible Faradaic redox reactions have been intensively investigated as the supercapacitor (SC) electrode materials. It has been intensively reported that the bimetallic compounds [6–9] can exhibit higher C_F values as compared with those for the single metal-based SC electrodes, owing to the richer redox reactions and higher electronic conductivity attributed from the coupling of two transition metal species [9], among which cobalt and nickel are two of the most studied transition metals due to the high redox activity for their metal ions. Zhang et al. prepared nickel cobalt oxides by co-precipitation and post-annealing methods to obtain a C_F value of 750 F/g for resulting SC electrode [6]. Chen et al. achieve a C_F value of 14.39 F/cm^2 at a current density of 5 mA/cm^2 for the $NiCo_2S_4$ nanotubes-based SC electrode prepared using hydrothermal and anion-exchange methods [8]. Among the bimetallic compounds, the electronegativity of sulfur is lower than that of oxygen. The smaller optical band gap energy and higher conductivity can hence be exhibited by the nickel cobalt sulfides as compared with those for the nickel cobalt oxides and hydroxides [10,11]. It was also reported that the nickel cobalt sulfides have about 2 orders higher electronic conductivity than their oxide counterparts [12]. Therefore, intensive attentions have been paid on the synthesis of the nickel cobalt sulfides and their application on the SC electrodes.

The structure of nickel cobalt sulfide has been widely designed to pursue the high surface area and high conductivity for the charge accumulation and the charge transportation, respectively [13–16]. The hydrothermal reaction is the most commonly used synthesizing method due to the simple and low-cost properties, and the nickel foam was often applied as the substrate for the growth of nickel cobalt sulfide since the electroactive material can directly grow on the nickel foam during the hydrothermal reaction for the better contact between the material and the substrate [8,9]. Li et al. synthesized well aligned Ni–Co sulfide nanowire arrays on

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the nickel foam by a facile two-step hydrothermal method and attained a C_F value of 2415 F/g at a current density of 2.5 mA/cm^2 for the corresponding SC electrode [9]. Chen et al. prepared $NiCo_2S_4$ urchin-like nanostructures by using a facile precursor transformation method and got a superior electrochemical performance with an ultrahigh high-rate capacitance and an excellent cycling stability [10]. Cai et al. prepared $NiCo_2O_4$ nanotube arrays by treating the Ni and Co-precursor with Na_2S solution based on the Kirkendall effect and obtained a C_F value of 15.58 F/cm^2 at a current density of 10 mA/cm^2 for the pertinent SC electrode [17]. On the other hand, the nickel foam was reported to release nickel ions during the hydrothermal reaction, and the nickel salt is not necessary to be added during the hydrothermal reaction for the growth for the nickel cobalt sulfide. Mei et al. synthesized hierarchical mushroom-like Ni_2CoS_4 arrays on a nickel foam via a one-step hydrothermal method to achieve a C_F value of 9.1 F/cm^2 at a scan rate of 5 mV/s without adding any nickel salt in the reaction [18]. However, the effect of the nickel source from the nickel foam and the nickel salt on the morphology of the nickel cobalt sulfide and the corresponding SC performances have never been discussed in the previous reports.

In this study, the nickel source was varied by tuning the reaction time and the ratio of nickel to cobalt in the precursor solution for the hydrothermal reaction. The aggregation of the nanomaterial was found to form at the top and the bottom of the nickel cobalt sulfide nanosheet array depending on the source of the nickel ions. The optimized SC electrode presents a C_F value of 2206 F/g measured by using the GC/D method at the current density of 4 A/g with the nickel cobalt sulfide synthesized in the hydrothermal reaction for 2 h with the Ni to Co ratio of 1–2 in the precursor solution. Moreover, the high-rate capacity with the C_F value of 1656 F/g at the current density of 128 A/g and the excellent cycling stability with a 94.6% retention on the C_F value as compared with the initial C_F value after 2000 cycles repeated charge/discharge process along with the Coulombic efficiency higher than 96% for the entire measurement were also achieved for this optimized SC electrode.

2. Experimental section

2.1. Materials

Nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 99.0%) was purchased from Acros. Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 99.0%) and thiourea (CH_4N_2S) were obtained from Showa. Potassium hydroxide (KOH, analytical reagent grade) was brought from Fisher.

2.2. Synthesis of nickel cobalt sulfide nanostructures and preparation of the supercapacitor electrode

For the preparation of nickel cobalt sulfides, 2 mM of $Ni(NO_3)_2 \cdot 6H_2O$, 4 mM of $Co(NO_3)_2 \cdot 6H_2O$, and 9 mM of thiourea were dispersed in 15 mL de-ionic water (DIW) under stirring at the room temperature for approximately 30 min until a clear and homogeneous solution was obtained. The mixture and the nickel foam (110PPI, thickness = 1.05 mm, Innovation Materials Co., Ltd, Taiwan) was transferred to a 100 mL Teflon-lined autoclave which was then heated in an oven at 180 °C for several hours. After cooling the autoclave to the room temperature, the precipitate was rinsed with DIW and ethanol several times and dried in a vacuum oven at 60 °C for 4 h. The nickel cobalt sulfide was hence obtained. This product is prepared by using the precursor solution containing the Ni to Co ratio of 1–2. The samples prepared using the precursor solution with different ratios of Ni to Co for the hydrothermal reaction were also synthesized for comparison. The reactions for forming the nickel cobalt sulfide were proposed in Eqs. (1)–(6) as follows.

$$S{=}C(NH_2)_{2(s)} + 2H_2O_{(l)} \rightarrow 2NH_{3(aq)} + CO_{2(g)} + H_2S_{(g)} \quad (1)$$

$$Ni^{2+}{}_{(aq)} + 4NH_{3(aq)} \rightarrow [Ni(NH_3)_4]^{2+}{}_{(aq)} \quad (2)$$

$$Co^{2+}{}_{(aq)} + 4NH_{3(aq)} \rightarrow [Co(NH_3)_4]^{2+}{}_{(aq)} \quad (3)$$

$$NH_{3(aq)} + H_2O_{(l)} \rightarrow OH^-{}_{(aq)} + NH_4{}^+{}_{(aq)} \quad (4)$$

$$H_2S_{(g)} + 2OH^-{}_{(aq)} \rightarrow S^{2-}{}_{(aq)} + 2H_2O_{(l)} \quad (5)$$

$$[Ni\ (NH_3)_4]^{2+}{}_{(aq)} + 2[Co(NH_3)_4]^{2+}{}_{(aq)} + 4S^{2-}{}_{(aq)} \rightarrow NiCo_2S_{4(s)} + 12NH_{3\,(aq)} \quad (6)$$

The nickel nitrate and cobalt nitrate were dissociated into nickel and cobalt ions, while the thiourea was dissociated into water to release the hydrogen sulfide. The hydrogen sulfide was then combined with hydroxides to release sulfur ions. Finally, the nickel ions, cobalt ions, and sulfur ions were combined to form the nickel cobalt sulfide.

2.3. Material characterization and electrochemical measurements

The surface morphologies and structures of the cobalt sulfides were investigated using the field-emission scanning electron microscopy (FE-SEM, Nova NanoSEM 230, FEI, Oregon, USA) and the high-resolution transmission electron microscopy (HRTEM) (Philips Tecnai F30 Field Emission Gun Transmission Micro-scope). The composition of the products were determined by X-ray diffraction (XRD) (X'Pert^3 Powder, PANalytical) with Cu Kα radiation (λ = 1.5418 Å). The composition of atoms was analysed by the energy-dispersive X-ray spectroscopy (EDS) in the FE-SEM equipment. The CV and GC/D curves were obtained using a potentiostat/galvanostat (PGSTAT 204, Autolab, Eco–Chemie, the Netherlands) carried out with a three-electrode electrochemical system, where the nickel cobalt sulfides/nickel foam was used as the working electrode, a Pt wire was used as the counter electrode, and an Ag/AgCl/saturated KCl electrode was used as the reference electrode in a 5 M KOH solution.

3. Results and discussion

3.1. Morphology variations for the nickel cobalt sulfide prepared using different hydrothermal times and nickel to cobalt ratios in the hydrothermal solution

An ideal structure of the nickel cobalt sulfide as the electro-capacitive material for the SC electrode should possess the high amount of active sites for charge accumulation and conducting Faradic reactions, the suitable pore size similar to that of the ions in the electrolyte to enhance the ions diffusion into the pore for conducting Faradic reactions, and the low crystallinity to provide the structural disorder and enhance the amount of the defect sites of the nickel cobalt sulfide for proceeding Faradic reactions with ions in the electrolyte.

The hydrothermal time is reported to play an important role on the morphology of the nanostructure [18], and more nickel ions are expected to be released from the nickel foam in the hydrothermal reaction with longer hydrothermal times. To investigate the effects