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Nickel precursor-free synthesis of nickel cobalt sulfide on Ni foam: Effects of the pH value on the morphology and the energy-storage ability

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ABSTRACT

The Ni foam is the most commonly used current collector due to its high conductivity and surface area. It is reported that the Ni foam can release Ni^+ in acid solutions during the hydrothermal reaction, but the influences for the acidity of the solution used in the hydrothermal reaction on the morphology and composition of the nanomaterial as well as the energy-storage ability of the electrode have not been investigated. In this study, the nickel cobalt sulfide is synthesized on the Ni foam via a hydrothermal method respectively using the cobalt nitrate and Ni foam as the cobalt and nickel sources. The pH value of the solution for the hydrothermal reaction is varied for investigating the effects of the acidity on the structure of the nanomaterial and the energy-storage ability of the resulting electrode. The nickel cobalt sulfides synthesized using the precursor solution with different pH values present nanosheet structures with various sizes. A specific capacitance (C_F) of 2.24 F/cm^2 corresponding to the capacity of 0.22 mAh/cm^2 is obtained by using the galvanic charge/discharge technique at a current density of 5 mA/cm^2 for the optimized electrode. Excellent long-term cycling stability with the retention of 86% on the C_F value after 10,000 times charge/discharge cycles is also achieved for this system.

1. Introduction

Bimetallic transition metal sulfides have been widely investigated as the electrocapacitive materials owing to the abundant Faradaic redox reactions and the high electronic conductivity caused by the multiple oxidation states of the transition metal compounds and the coupling of bimetallic transition metal species, respectively [1–6]. Cobalt and nickel are regarded as the most promising species to comprise the bimetallic transition metal compounds due to the high redox activities, among which intensive attentions have been paid on synthesizing the nickel cobalt sulfides for the application on the energy-storage devices due to the lower electronegativity of sulfur as well as the smaller optical band gap energy and higher conductivity for sulfide compounds as compared with those for their oxide counterparts [7,8].

Several methods have been applied for preparing the nickel cobalt sulfide for the electrochemical electrodes as reported in the previous literatures [9–12]. Chen and co-workers applied an one-step electrochemically co-deposition method to prepare the electrode with the nickel cobalt sulfide nanosheets on the conductive carbon and got a specific capacitance (C_F) value of 1418 F/g at a current density of 5 A/g [10]. Liu et al. used a anion exchange reaction to make three-dimensional $NiCo_2S_4$ nanonetworks on the Ni foam and obtained a C_F value of 1501.2 F/g at a current density of 1 A/g for the corresponding electrode [12]. Among the numerous synthesizing methods, the hydrothermal method was considered to be the most promising one due to the simple and low-cost properties [13–15]. Chen et al. used the hydrothermal and anion-exchange methods to synthesize $NiCo_2S_4$ nanotubes on the Ni foam and attended a C_F value of 14.39 F/cm^2 at 5 mA/cm^2 for the pertinent electrode [5]. Li et al. applied a hydrothermal method to obtain the nickel cobalt sulfide on the Ni foam and achieved a C_F value of 2415 F/g at 2.5 mA/cm^2 [6]. On the other hand, the Ni foam has been regarded as the most promising current collector for the nickel cobalt sulfide-based electrode, since the nickel cobalt sulfide can directly grow on the

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surface of the Ni foam during the reaction rather than presenting the powder form which should be deposited on the Ni foam using an extra step. Hence, using the hydrothermal method with the Ni foam incorporated in the reaction as the current collector is the most widely used method to prepare the electrode with the nickel cobalt sulfide as the electrocapacitive material. Lin et al. reported a synthesis of $NiCo_2S_4$ nanosheet arrays with self-decorated nanoneedles on the Ni foam as the electrode by using a two-step hydrothermal approach with the addition of nickel and cobalt nitrates as the bimetal precursors [13]. Kong et al. realized the growth of $NiCo_2S_4$ on the Ni foam through a two-step hydrothermal method using the nickel and cobalt chlorides as the bimetal precursors for the electrode [14]. Nguyen et al. designed $NiCo_2S_4$@MnO_2 core–shell arrays on the Ni foam by applying a hydrothermal method for the electrode using nickel and cobalt nitrates as the bimetal precursors [16]. Cai et al. synthesized $NiCo_2S_4$ nanotube arrays on the Ni foam through a two-step hydrothermal method using the cobalt nitrate and the nickel chloride as the bimetal precursors [17]. It was also reported that the Ni foam cannot only play the role of the current collector but also the source of the nickel ions. Mei et al. synthesized hierarchical mushroom-like $CoNi_2S_4$ arrays on the Ni foam as the electrode by using a one-step hydrothermal method without adding any nickel precursor in the reaction [18]. This concept is very promising on reducing the cost of chemicals and saving the time for preparing the precursors. However, most of the literatures only treated the Ni foam as the substrate for the growth of the nickel cobalt sulfide and the current collector for the electrode, but not the nickel source to participate in the hydrothermal reaction for growing the nanomaterial. Therefore, to realize this promising concept, the electrode with the nickel cobalt sulfide synthesized using the hydrothermal method with the Ni foam participated but without adding the nickel precursor was fabricated in this work.

In this study, the nickel cobalt sulfide nanosheets were synthesized on the Ni foam as the energy-storage electrode using a one-step hydrothermal method using the cobalt nitrate and the Ni foam as the cobalt and nickel sources, respectively. To investigate this concept more deeply, the influences of the pH value of the solution for the hydrothermal reaction on the composition and the morphology of the nickel cobalt sulfide and the resulting electrochemical performances were discussed. The nickel cobalt sulfides were successfully synthesized on the Ni foam and all the samples present sheet-like structures with different sizes and flexibilities. It is verified that the more nickel ions can be released from the Ni foam to participate in the hydrothermal reaction when the solution with the lower pH value was applied to synthesize the nickel cobalt sulfide. A C_F value of 2.24 F/cm^2 corresponding to the capacity of 0.22 mAh/cm^2 was obtained using the galvanic charge/discharge (GC/D) technique at the current density of 5 mA/cm^2 for the nickel cobalt sulfide-based electrode prepared using the solution with the pH value of 2.88 for the hydrothermal reaction. The high-rate capacity and the excellent long-term cycling stability with 86% retention on the C_F value after 10,000 times repeated charge/discharge processes and the Coulombic efficiency higher than 91% for the entire measurement after the activation were also attained for this system. The result confirms the concept that the Ni foam can play the roles of both the current collector and the precursor source for synthesizing the nanomaterials. Also, a new concept was developed that the amount of the dissolved nickel ions from the Ni foam can be easily tuned for synthesizing the nickel cobalt sulfides with different structures on the Ni foam by simply varying the pH value of the solution for the hydrothermal reaction.

2. Experimental section

2.1. Materials

Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, 99.0%) and thiourea (CH_4N_2S) were brought from Showa. Potassium hydroxide (KOH, analytical reagent grade) was obtained from Fisher. Hydrochloric acid (HCl, ACS reagent, 37%) was got from Sigma–Aldrich.

2.2. The nickel cobalt sulfide nanomaterials synthesis and the electrode preparation

The nickel cobalt sulfide nanomaterials were prepared as follows. 6 mM $Co(NO_3)_2{\cdot}6H_2O$ and 9 mM thiourea were dissolved in a 15 mL aqueous solution and then stirred for 30 min at the room temperature to achieve a clear and homogeneous solution. The pH value of the solution was tuned by adding different amounts of HCl. The resulting solution and the nickel foam substrate (110PPI, thickness = 1.05 mm, Innovation Materials Co., Ltd, Taiwan) were then transferred to a 100 mL Teflon-lined autoclave which was heated at 180 °C for 2 h. The autoclave was cooled to the room temperature after the reaction and the electroactive material deposited nickel foam was then rinsed with deionized water (DIW) and ethanol for several times. Finally the sample was dried in a vacuum oven at 60 °C for 4 h. The samples synthesized without adding any cobalt salt in the solution for the hydrothermal reaction were also made with different pH values for comparison. The nickel cobalt sulfide is inferred to be formed via the proposed formulas as follows in Eqs. (1)–(6).

$$S{=}C(NH_2)_2 + 2H_2O \rightarrow 2NH_3 + CO_2 + H_2S \quad (1)$$

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

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

$$NH_3 + H_2O \rightarrow OH^- + NH^{4+} \quad (4)$$

$$H_2S + 2OH^- \rightarrow S^{2-} + 2H_2O \quad (5)$$

$$[Ni\ (NH_3)_4]^{2+} + 2[Co(NH_3)_4]^{2+} + 4S^{2-} \rightarrow NiCo_2S_4 + 12NH_3 \quad (6)$$

2.3. Material characterization and electrochemical measurements

The pH value of the precursor solution was measured by using a pH meter (PH500 Benchtop Laboratory pH Meter). The morphology of the nickel cobalt sulfides was investigated using the field-emission scanning electron microscopy (FE-SEM, Nova NanoSEM 230, FEI, Oregon, USA) and the transmission electron microscopy (TEM, JEM-1230, JEOL, Tokyo, Japan). The composition of atoms was analyzed by the energy-dispersive X-ray spectroscopy (EDS) in the FE-SEM equipment. The structure of the products were determined by X-ray diffraction (XRD, X'Pert^3 Powder, PANalytical) with Cu Kα radiation (λ = 1.5418 Å). The cyclic voltammetry (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. The SC electrode was used as the working electrode, a Pt wire was used as the counter electrode, and an Ag/AgCl/saturated KCl electrode was