Rare Metal Materials and Engineering
Volume 47, Issue 5, May 2018
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2018, 47(5): 1359-1364.

ARTICLE

In-situ Synthesis and Properties of Porous Cobalt Sulfide Nanoneedle Bundles Arrays on Nickel Foam as Electrodes for Supercapacitors

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Abstract: Freestanding porous Co_9S_8 nanoneedle bundles arrays on Ni foam were in-situ synthesized by a facile ion exchange reaction and were directly used as the electrode for supercapacitors. The structure and morphology were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), and transmission electron microscope (TEM). Cyclic voltammetry (CV), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS) were adopted to evaluate the electrochemical property of the porous Co_9S_8 nanoneedle bundles arrays electrode in 3 mol/L KOH solution. The results show that the specific capacitance of the porous Co_9S_8 nanoneedle bundles arrays is 1400 $F \cdot g^{-1}$ at a current density of 4 $A \cdot g^{-1}$ and the arrays exhibit good cycling stability. The excellent electrochemical performance can be ascribed to the porous nanostructure of Co_9S_8 nanoneedle bundles arrays and the 3D conductive nickel foam, which can increase the contact areas between electrode and electrolyte and improve the conductivity of the whole electrode.

Key words: supercapacitors; electrode materials; Co_9S_8; electrochemical performance

Coupled with the critical climate change and energy crises, exploiting environmentally friendly, renewable, low-cost energy storage and conversion systems become very urgent. Supercapacitors and batteries (Li-ion batteries, fuel cells, etc.) are considered as the two most practical and effective devices for electrochemical energy conversion and storage[1-4]. Supercapacitor (SC, also called electrochemical capacitor) has been paid much attention to during the past decade for its advantages such as high rapid charging and discharging rate, high power density and long cycle life[5,6]. Supercapacitor can be classified into pseudocapacitor and electric double layer capacitor (EDLC) based on the mechanism of charge storage[7]. Generally, pseudocapacitors arising from the rapid reversible faradic process of redox-active materials can provide much higher specific capacitances than EDLCs [8, 9]. Although many attempts have been dedicated to explore efficient and inexpensive redox-active materials including transition metal hydroxides[10], oxides[11], sulfides[12], and conductive polymers[13], designing and developing facile methods to produce electrode materials with planned chemical component, unique morphologies and controlled microstructures are still highly desired.

Recently, nanostructured transition metal sulfides have been considered one of the most popular non-noble metals for pseudocapacitor electrode due to their excellent electrochemical properties and high conductivity[14]. Among them, cobalt sulfides with different stoichiometric components, including Co_4S_3, Co_9S_8, CoS, Co_3S_4, Co_2S_3, and CoS_2, make them with different properties meet the requirements for various application[15]. Up to now, various morphologies of cobalt sulfides-based materials including three-dimensional flower-like hierarchical structure [16], nanotubes[17], nanosheet-like films[18], nanoparticles

Received date: May 25, 2017
Foundation item: Fundamental Research Funds for the Central Universities of China (DUT17LK01)
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decorated graphene composite[19] have been prepared and applied in supercapacitors. However, it is still a challenge to optimize the composition and morphology of cobalt sulfides-based electroactive materials, which can dramatically improve their performance to achieve large specific capacitance and long-term stability for supercapacitors.

In this paper, the porous Co_9S_8 nanoneedle bundles arrays on Ni foam have been synthesized by a simple two-step hydrothermal route and directly acted as electrodes for supercapacitors. This binder-free and porous structure can enhance electron and ion transportation, and improve the electrochemical performance. The porous Co_9S_8 nanoneedle bundles arrays exhibited high specific capacitance (1400 $F\cdot g^{-1}$ at a current density of 4 $A\cdot g^{-1}$) and excellent long cycle stability, offering great potential application in supercapacitors.

1 Experimental

1.1 Materials

Cobalt nitrate hexahydrate, urea, ammonium fluoride, sodium sulfide, potassium hydroxide and hydrochloric acid were all analytical grade and used without any further purification. Deionized water was used throughout. Battery-grade Ni foam was purchased from ChangSha Lyrun Material. Co. Ltd (thickness: 1 mm; areal density: 320 g/m^2; PPI (pore/inch): 110; pore size: 0.2~0.6 mm).

1.2 Synthesis of $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ precursor

Typically, 5 mmol of $Co(NO_3)_2\cdot 6H_2O$, 25 mmol of $CO(NH_2)_2$ and 10 mmol of NH_4F were added into 40 mL of deionized water. Then the homogeneous solution was poured into Teflon-lined stainless steel autoclave. After that, a piece of Ni foam (2 cm × 2 cm) was treated with 6 mol/L HCl, washed by deionized water, and then put into the above solution. The top side of Ni foam was uniformly coated with a polytetrafluoroethylene tape to avoid solution contamination. The autoclave liner was heated at 120 °C for 9 h, and then cooled to ambient temperature naturally. The reacted Ni foam was cleaned in deionized water under ultrasonator for 10 min, and then dried in vacuum at 60 °C for 5 h. The reactions involved in this step can be explained as follows:

$$Co^{2+}+xF^-\rightarrow[CoF]^{(x-2)-} \quad (1)$$

$$H_2NCONH_2+2H_2O\rightarrow 2NH_4^++CO_3^{2-} \quad (2)$$

$$[CoF_x]^{(x-2)-}+0.5CO_3^{2-}+OH^-+0.11H_2O\rightarrow Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O+xF^- \quad (3)$$

1.3 Synthesis of porous Co_9S_8 nanoneedle bundles arrays

Typically, 1 mmol Na_2S was dissolved in 40 mL deionized water and transferred into a 50 mL Teflon-line stainless steel autoclave. Then the Ni foam coated with precursor was immersed into the autoclave. The autoclave was heated to 120 °C and kept at this temperature for 5 h and then was allowed to cool to room temperature naturally. The reaction involved in this step can be illustrated as follow:

$$Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O+S^{2-}\rightarrow Co_9S_8+CO_3^{2-}+H_2O \quad (4)$$

The resulting Ni foam was taken out, washed several times with the water and ethanol, and then dried at 60 °C for 4 h. The load mass of Co_9S_8 nanoneedle bundles is about 2.45 $mg\cdot cm^{-2}$.

1.4 Characterization of materials

The XRD patterns of the samples were gained by a Rigaku/Max-3A X-ray diffractometer with CuKα radiation. FE-SEM photos and EDS graphs were performed on a Supra 55 Sapphire apparatus with a system for energy dispersive X-ray analysis. TEM were performed under an accelerating voltage 200 kV on a JEOL-2010 microscope and the TEM images were gained with the selected area electron diffraction (SAED) patterns. The N_2 adsorption-desorption isotherm was determined using the Brunauer-Emmett-Teller (BET) equation by a surface area analyser SSA-4200 (Builder).

1.5 Electrochemical measurements

All electrochemical tests were recorded by employing an electrochemical workstation (CHI 660E, Shanghai, Chenhua). The supercapacitor performance measurements were performed on a three-electrode system at room temperature. The Ni foam (1 cm ×1 cm) loaded with Co_9S_8 nanoneedle bundles arrays, platinum plate, saturated calomel electrode (SCE) and 3 mol/L KOH solution were applied as the working electrode, counter electrode, reference electrode, and electrolyte, respectively. The specific capacitance (C, $F\cdot g^{-1}$) can be calculated by the following equation:

$$C=\frac{I}{M}\frac{\Delta t}{\Delta V} \quad (5)$$

Where I(A), Δt(s), M(g) and ΔV(V) represent the discharge current, discharge time, the mass of active materials and potential window, respectively.

The energy density (E, $W\cdot h\cdot kg^{-1}$) and power density (P, $W\cdot kg^{-1}$) of the electrode materials were evaluated by the following equations:

$$E=\frac{1}{2}CV^2 \quad (6)$$

$$P=E/\Delta t \quad (7)$$

2 Results and Discussion

2.1 Structural characterization

The composition and morphology of the precursor and the as-obtained porous Co_9S_8 nanoneedle bundles arrays were characterized by XRD, SEM and TEM. For the sake of decreasing the impact of the nickel foam substrate on the XRD signals, both precursor and the porous Co_9S_8 nanoneedle bundles arrays powders were scratched from nickel foam substrate. Fig.1a gives the XRD pattern of the precursor, and all of the diffraction peaks can be perfectly suited to