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Ceramics International 40 (2014) 8189–8193
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

One-step electrochemical deposition of nickel sulfide/graphene and its use for supercapacitors

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Received 16 December 2013; received in revised form 3 January 2014; accepted 3 January 2014
Available online 11 January 2014

Abstract

In this current work, the electrochemical co-deposition of nickel sulfide/electrochemically reduced graphene oxide(ERGO) nanocomposites is presented. During the electrochemical process, the graphene oxide nanosheets loose their hydrophilicity and precipitate onto the electrode. In the meantime, nickel sulfide is also electrochemically deposited on the electrode. The porous structure with ERGO covered by nickel sulfide, which facilitates the charge and ion transport in the electrode, has been observed by a scanning electron microscope. The cycle voltammetry curves as well as the galvanostatic charge/discharge curves of the nickel sulfide/ERGO nanocomposites exhibit distinct pseudocapacitive characteristic. The nanocomposites maintain 66.8% of the initial specific capacitance for the first 500 cycles, and only 4.6% loss of the specific capacitance is experienced for the further 1500 cycles, evidently showing a relatively high cycling stability. The results suggest that the nickel sulfide/ERGO is a promising electrode material for supercapacitors.

Keywords: Electrochemical co-deposition; Porous; Pseudocapacitive characteristic; Cycling stability

1. Introduction

Graphene, a single layer of carbon atoms arranged into a honeycomb crystal lattice, is attracting much attention. Owing to its high surface area, excellent flexibility and electrical conductivity, graphene holds great promise for applications in field-effect transistors, solar cells, batteries and supercapacitors [1–8]. Significantly, utilizing graphene as the electrode for the supercapacitor has become the focus of research in the field of energy storage devices [9–11]. Although the supercapacitor displays superior performance such as long cycling life and fast charging–discharging rate at high power density, the energy density of the supercapacitors is relatively low [12]. Integrating graphene with active components such as electrically conducting polymers and metal oxides can be an effective strategy to improve the supercapacitive performance of the graphene based electrode [13–16]. Graphene in composites is used as support for deposition of active components at the nanoscale, which can avoid the aggregation of neighboring components and increase the specific surface area of the active components. It can also provide fast transportation of electron through the entire electrode materials due to the excellent electrical conductivity of graphene. What is more, graphene can restrict the mechanical deformation of the active components during charging–discharging process, and thus lead to better stability because it has unique structural and mechanical properties.

In recent years, much effort has been put into the synthesis of metal sulfides. Among them, nickel sulfides have been widely investigated because of their important applications in catalysis, batteries and supercapacitors [17–20]. Currently, Zhou et al. [21] synthesized Ni_3S_2 nanorod on a three-dimensional graphene network and employed the composites for supercapacitors. The material exhibits a high specific capacitance of 1037.5 F g^{-1} at a current density of 5.1 A g^{-1}.

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0272-8842/$ - see front matter
http://dx.doi.org/10.1016/j.ceramint.2014.01.015

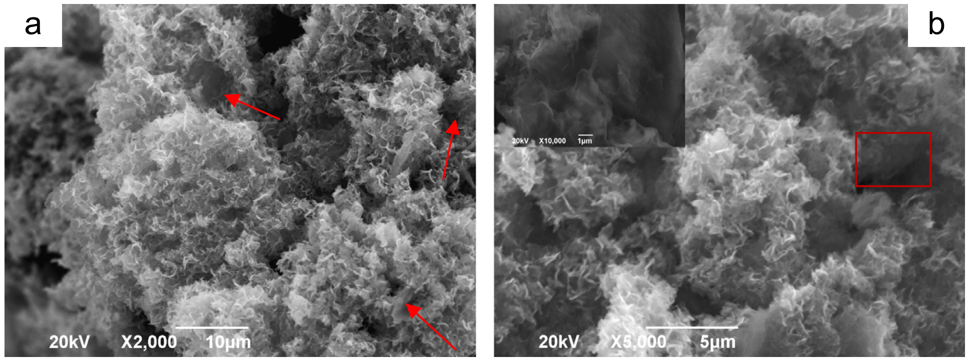

Fig. 1. (a) and (b) Scanning electron microscope (SEM) images of nickel sulfide/ERGO (inset is the enlarged SEM image marked by the red block). For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Sun et al. [22] reported the preparation of nickel sulfides/reduced graphene composites showing a very high specific capacitance of 1169 F g^{-1} at a current density of 5 A g^{-1}. In this paper, nickel sulfide/electrochemically reduced graphene oxide (ERGO) nanocomposites are synthesized by one-step electrodeposition. The nanocomposites serve as the electrode for the supercapacitor and exhibit distinct pseudocapacitive characteristic. Compared with sole nickel sulfides, the nanocomposites behave much better supercapacitive performance, with a high specific capacitance of 1392.2 F g^{-1} at a current density of 2 A g^{-1} and good cycling stability.

2. Experimental section

2.1. Preparation of nickel sulfide/ERGO nanocomposites

Graphene oxide (GO) was synthesized from graphite powder by the modified Hummers′ method [23]. A total of 75 mg GO was mixed with 50 mL de-ionized water and ultrasonicated for 1 h to yield a stable GO suspension. Then $LiClO_4$ (0.05 M), $NiCl_2 \cdot 6H_2O$ (5 mM) and thiourea (0.5 M) were added into the GO solution. A nickel foam (NF) was used as working electrode with Pt foil and Ag/AgCl electrode as counter and reference electrodes, respectively. Prior to electrochemical synthesis, the nickel foam was ultrasonically washed with HCl, acetone, ethanol and deionized water for 20 min, respectively. The potentiodynamic deposition of nickel sulfide/ERGO nanocomposites was performed within the potential range between −1.2 V and 0.2 V at a scan rate of 5 mV s^{-1} for 5 cycles. As-prepared nickel sulfide/ERGO electrode was rinsed with deionzed water and subsequently dried in vacuum at 60 °C for 12 h. For comparison, sole nickel sulfide was also electrochemically deposited on the nickel foam with the deposition bath composed of $NiCl_2 \cdot 6H_2O$ (5 mM) and thiourea (0.5 M).

2.2. Characterization

The surface morphologies and microstructures of as-deposited electrode are characterized by Scanning Electron Microscopy (SEM, JEOL JSM-6360). The electrochemical properties of the nickel sulfide/ERGO electrode are studied using cyclic voltammogram, galvanostatic charge/discharge test and electrochemical impedance spectroscopy (EIS) in 1 M KOH aqueous solution. All the measurements are carried out using a CHI 627D (CH Instrument) electrochemical analyzer in a three-electrode configuration where nickel sulfide/ERGO serves as the working electrode, Pt foil as the counter electrode and Ag/AgCl as the reference electrode. EIS measurements are carried out in the frequency range of 100 kHz–0.01 Hz with an amplitude of 5 mV.

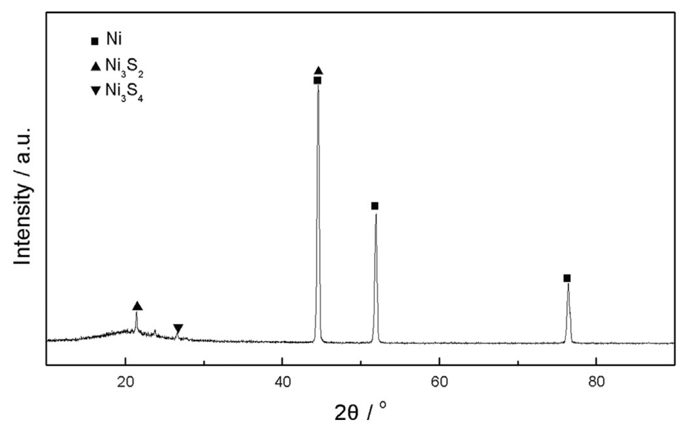

Fig. 2. XRD patterns of nickel sulfide/ERGO.

3. Results and discussion

Fig. 1 shows the typical SEM images of the conformation of nickel sulfide/ERGO nanocomposites. It is illustrated in Fig. 1(a) that ERGO (indicated by red arrows) covered with nickel sulfide is produced. At a higher magnification in Fig. 1 (b), it is clearly seen that nickel sulfide integrate with ERGO, forming a porous structure. Fig. 2 shows XRD pattern of the nickel sulfide/ERGO nanocomposites. The three sharp peaks are indexed to the nickel substrate (JCPDS no. 04-0850). The other minor peaks can be attributed to Ni_3S_2 (JCPDS no. 08-0126) and Ni_3S_4 (JCPDS no. 08-0106), indicating that the nickel sulfides are complicated phases constituted of Ni_3S_2 and Ni_3S_4.

The nickel sulfide/ERGO nanocomposites are further evaluated as the electrode material for the supercapacitor. Fig. 3