



Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem
<http://www.journals.elsevier.com/journal-of-energy-chemistry/>

Hierarchical graphite foil/CoNi₂S₄ flexible electrode with superior thermal conductivity for high-performance supercapacitors

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ARTICLE INFO

Article history:

Received 6 September 2017

Revised 27 October 2017

Accepted 19 November 2017

Available online xxx

Keywords:

Electrode materials
Thermal conductivity
Heat dissipation
Energy storage
Supercapacitors

ABSTRACT

Effective heat dissipation is a crucial issue in electrochemical energy storage devices. Thus, it is highly desirable to develop high-performance electrode materials with high thermal conductivity. Here, we report a facile one-step electrodeposition method to synthesize ternary cobalt nickel sulfide (CoNi₂S₄) flower-like nanosheets which are grown on graphite foil (GF) as binder-free electrode materials for supercapacitors. The as-fabricated GF/CoNi₂S₄ integrated electrode manifested an excellent thermal conductivity of 620.1 W·m⁻¹·K⁻¹ and a high specific capacitance of 881 F·g⁻² at 5 mA cm⁻², as well as good rate capability and cycling stability. Ultimately, the all-solid-state symmetric supercapacitor based on these advanced electrodes demonstrated superior heat dissipation performance during the galvanostatic charge-discharge processes. This novel strategy provides a new example of effective thermal management for potential applications in energy storage devices.

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1. Introduction

Electrochemical energy storage devices (EESDs), including lithium ion batteries (LIBs), supercapacitors (SCs), etc., have recently attracted great attention in both academia and industry because of their wide applications [1,2]. Nevertheless, the increasing demand for better EESDs requires continual innovation, in terms of safety, cost, lifetime, miniaturization, and functionality, among which there are some challenges that still need to be addressed [3–5]. Typically, the temperature of EESDs will increase during the charge-discharge processes on account of Joule heating, which is related to the current and the electrical resistance of the energy storage devices [6,7]. Taking practical applications of EESDs into consideration, for example, wearable electronics as a promising application, require matchable EESDs as power sources [8,9]. The heat generated inside a device must be controlled, which determines the comfort and safety during use, especially for the

large current and/or high power energy storage devices [10–12]. Apparently, the external and internal heat have a critical impact on the safety, reliability and lifetime of energy storage devices, hence limiting their practical applications [12,13]. Therefore, effective thermal management has become extremely crucial to dissipating the large heat flux and ensuring the performance of EESDs [14,15].

Noteworthy, the thermal conductivity of electrode materials plays a major role in the heat dissipation of energy storage devices [16]. Porous materials such as carbon papers, metal foams, graphene aerogel have been used as substrates for the loading of active materials [1,2,17,18]. Although these substrates show good electrical conductivity, most of them suffer from poor thermal conductivity [7]. Moreover, the traditional electrodes prepared by coating a slurry mixture of active materials, conductive agents, and polymer binders onto a metal current collector, also exhibit low thermal conductivity (0.1–2 W·m⁻¹·K⁻¹) [19]. Thus, it is highly desirable to develop high performance electrode materials with high thermal conductivity. Highly thermal conductive materials, mainly including lateral heat spreaders and thermal interface materials (TIMs), have played a significant role in the thermal management for effective heat removal in electronics [20,21]. Graphite foils possess excellent thermal conductivity and electrical

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conductivity, as well as outstanding flexibility, light weight, low cost, chemical stability [21,22]. It is potentially an ideal candidate as thermal management substrates of electrodes in EESDs. More recently, ternary Ni-Co sulfides/oxides/hydroxides compounds have been demonstrated as excellent electrode materials with high electrochemical activity and high electrical conductivity in comparison to monometal compounds [23–30]. To date, few efforts have been focused on the supercapacitors employing highly thermal conductive electrode.

Herein, we report a facile one-step electrodeposition method to synthesize ternary cobalt nickel sulfide (CoNi_2S_4) flower-like nanosheets which are grown on highly thermal and electrical conductivities of commercial graphite foil (GF) as binder-free electrode materials for supercapacitors. The direct growth of active materials on graphite foil forms conductive pathways that not only promote charge transportation, but also minimize the interfacial thermal resistance between substrate and active materials for heat transfer. The as-fabricated GF/ CoNi_2S_4 integrated electrode manifests an excellent thermal conductivity and great electrochemical performance. Furthermore, the flexible all-solid-state symmetric supercapacitors fabricated from these electrodes exhibit superior heat dissipation performance during use. This work provides a new platform to design advanced electrodes for thermal management in high-performance energy storage devices.

2. Experimental

2.1. Electrodeposition of CoNi_2S_4 nanosheets on graphite foil

The CoNi_2S_4 flower-like nanosheets on graphite foil (thickness of 46 μm) was prepared by one-step electrodeposition [26]. Typically, the electrodeposition aqueous solution was prepared with 5 $\text{mmol}\cdot\text{L}^{-1}$ CoCl_2 , 7.5 $\text{mmol}\cdot\text{L}^{-1}$ NiCl_2 and 0.75 $\text{mol}\cdot\text{L}^{-1}$ $\text{CS}(\text{NH}_2)_2$. The electrodeposition was carried out in a three-electrode cell using graphite foil with suitable size (1 $\text{cm} \times 2 \text{ cm}$) as the working electrode, platinum plate (Pt) as the counter electrode, and Ag/AgCl as the reference electrode by cyclic voltammetry at a scan rate of 5 $\text{mV}\cdot\text{s}^{-1}$ within a voltage range of -1.2 to 0.2 V (vs. Ag/AgCl) for 15 cycles. After deposition, the electrode was cleaned by rinsing with deionized (DI) water and dried in a vacuum at 60°C for 12 h. The mass loading of CoNi_2S_4 on GF was about $0.8 \text{ mg}\cdot\text{cm}^{-2}$. In order to compare the heat dissipation performance, Cu foil/ CoNi_2S_4 electrode was fabricated under the same conditions. The mass loading of CoNi_2S_4 on Cu foil was about $0.7 \text{ mg}\cdot\text{cm}^{-2}$.

2.2. Fabrication of flexible all-solid-state symmetric supercapacitors

The PVA/KOH gel electrolyte was prepared by mixing 3 g PVA and 2 g KOH in 40 mL DI water under vigorous stirring at 90°C for 1 h. Before assembly, the as-prepared graphite foil/ CoNi_2S_4 (1 $\text{cm} \times 2 \text{ cm}$) was dipped into the PVA/KOH gel and then dried at room temperature for 2 h. Then, two graphite foil/ CoNi_2S_4 (GF/CNS) electrodes were assembled face-to-face using the PVA/KOH gel and further evaporated the excess of water for 12 h. The solidified PVA/KOH acted as the electrolyte and the separator in the symmetric supercapacitor structure. For comparison, a traditional electrode was also fabricated by mixing active carbon (AC), acetylene black and poly(vinylidene fluoride) with a mass ratio of 8:1:1, and then the slurry was pressed onto nickel foam (NF) current collector (NF/AC). The symmetric supercapacitor based on NF/AC electrodes was prepared by the same method.

2.3. Characterization and electrochemical measurements

Morphologies of the samples were obtained by a field emission scanning electron microscope (SEM, FEI Nova NanoSEM 450). The

crystalline structure was investigated by X-ray power diffraction (Rigaku, D/max-2500 Pc) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.541874 \text{ \AA}$). The chemical states were analyzed using X-ray photoelectron spectroscopy (XPS, ESCALAB 250). The wettability of the electrode surfaces was evaluated by contact angle measurements using a Dataphysics OCA20 contact angle system with 2 $\text{mol}\cdot\text{L}^{-1}$ KOH aqueous solution. The Brunauer-Emmett-Teller (BET) surface areas of the samples were analyzed by nitrogen adsorption apparatus (Micromeritics ASAP 2020, U.S.A.). The electrical properties of the samples were measured by a four-point probe method with an Agilent semiconductor parameter analyzer B1500A. The thermal diffusivities (α) of all the samples were measured using a laser flash apparatus (NETZSCH LFA 467 NanoFlash). The specific heat (C_p) was measured by differential scanning calorimeter (DSC, TA, Q2000) with the sapphire method. The density (ρ) was measured using FA2104J electronic density balance (Hengping, 0.1 mg sensitive quantity) by the Archimedes method. The thermal conductivity (k) was calculated from $K = \alpha C_p \rho$. The surface temperature distributions of the samples were characterized by an infrared thermal image (FTLR-T335) camera.

A three-electrode configuration with a platinum-plate (Pt) counter electrode and a mercury/mercuric oxide (Hg/HgO) reference electrode was used to study the electrochemical behaviors of the individual electrode in 2 $\text{mol}\cdot\text{L}^{-1}$ KOH electrolyte. Cyclic voltammetry (CV)/galvanostatic charge-discharge (GCD) curves, electrochemical impedance spectroscopy (EIS, frequency range: 100 kHz–10 mHz; amplitude: 5 mV), and cycling stability measurements were conducted with an electrochemical workstation (Zennium Zahner, Germany). The mass specific capacitance (C_m) and areal specific capacitance (C_s) were calculated from the galvanostatic charge-discharge curves, using the following equations:

$$C_m = (I\Delta t)/(m\Delta V) \quad (1)$$

$$C_s = (I\Delta t)/(s\Delta V) \quad (2)$$

where, I is the discharge current, Δt is the discharge time, ΔV is the voltage window, s is the area of the active materials, and m is the mass of the active materials. The areal energy density (E) and power density (P) were calculated by

$$E = C_s \times \Delta V^2 / (2 \times 3600) \quad (3)$$

$$P = E \times 3600 / \Delta t \quad (4)$$

3. Results and discussion

As shown in Fig. 1(a), the XRD patterns of GF and GF/ CoNi_2S_4 (GF/CNS) with typical peaks marked with asterisks, originated from graphite. Three characteristic peaks at 26.7° , 31.5° and 38.2° , corresponding to the (220), (311) and (400) diffraction planes, respectively, were indexed to CoNi_2S_4 (JCPDS 24-0334). This result was consistent with that of the previous report by a similar preparation method [26]. The small split peak of GF/CNS at 22° (marked with a black dot) might be attributed to the low amount of Ni_3S_2 impurity, which formed during the electrodeposition process [26,27]. Moreover, XPS analysis was carried out in order to further investigate the elemental composition and chemical state of CoNi_2S_4 (Fig. 1b–d). The high-resolution XPS spectra of Co 2p, Ni 2p and S 2p agreed well with the reported chemical state of ternary cobalt nickel sulfide of CoNi_2S_4 [27–30]. The Co 2p and Ni 2p spectra can be better fitted with two spin-orbit doublets and two shakeup satellites (Sat.). The binding energies at 782.1 and 798.0 eV of the Co 2p peaks were corresponding to Co^{2+} and the binding energies at 779.6 and 794.7 eV to Co^{3+} (Fig. 1b). Similarly, the peak at 854.3 eV was characteristic of Ni^{2+} , the peaks at 856.9 and 874.7 eV

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