Materials Science and Engineering B xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Copper sulfide microspheres wrapped with reduced graphene oxide for high-capacity lithium-ion storage

Yiyong Zhang, Kun Li, Yunhui Wang, Jing Zeng, Panying Ji, Jinbao Zhao*

State Key Lab of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, PR China

ARTICLE INFO

Article history:
Received 19 January 2016
Received in revised form 5 April 2016
Accepted 12 April 2016
Available online xxx

ABSTRACT

In this study, a facile two-step approach was developed to prepare the nanocomposites (Cu_xS/rGO) of copper sulfide (Cu_xS) microspheres wrapped with reduced graphene oxide (rGO). The morphology and structure of Cu_xS/rGO materials were researched by using SEM, XRD and laser Raman spectroscopy. As-prepared Cu_xS/rGO nanocomposites, as an active anode material in LIBs, showed distinctly improved electrochemical characteristics, superior cycling stability and high rate capability. Due to the synergistic effect between the Cu_xS microspheres and the rGO nanosheets, as-prepared Cu_xS/rGO nanocomposites could effectively alleviate large volume changes, provide a 2D conductive network and trap the diffusion of polysulfides during the discharge–charge processes, therefore, the Cu_xS/rGO nanocomposites showed excellent electrochemical characteristics.

1. Introduction

Growing market demands for portable energy storages and environmental issues have triggered significant researches on high-capacity lithium ion batteries (LIBs). The development of next-generation energy-storage devices is of primary importance to meet the challenges in the electronics and automobile industries in the near future [1–9]. In particular, there has been an increasing interest in the development of new multicomponent nanomaterials which can overcome a number of intrinsic limitations of single-component electrode materials for LIBs [10–14]. The performance of batteries depends primarily on the properties of electrode materials, therefore, it is critical to find innovative electrode materials with unique properties to meet these requirements for high-capacity battery development.

Metal sulfides were found to have exceptional electrochemical properties as an alternative material for LIBs electrodes [15,16]. As a new kind of anode electrode materials for LIBs, metal sulfides are known to be promising materials because of their high theoretical capacity [17,18]. Copper sulfides (Cu_xS), in particular, have been attracting high attention since they have such advantages as high theoretical capacity, excellent electrical conductivity and long and flat discharge voltage plateau [19,20]. However, like most other metal sulfides, the Cu_xS suffer from some major drawbacks like serious capacity fading and the loss of active material, which are caused by the pulverization of electrodes during cycling and the formation of polysulfides as Li_2S_x ($2 < x < 8$) [21–25]. The polysulfide intermediates can easily dissolve into the organic electrolytes during the electrochemical reactions and migrate to the anode side leading to the poor capacity retention of LIBs. One of usually accepted strategies to mitigate these drawbacks is to prepare nanometer-sized materials with designed structure [20,26]. For example, Tao et al. [27] already reported the fabrication of CuS/graphene composite by the one-pot hydrothermal method, as anode materials for LIBs, it shows a reversible capacity of 296 $mA\,h\,g^{-1}$ after 25 cycles with a capacity retention rate of 61%. Ren et al. [28] synthesized “double-sandwich-like” CuS@reduced graphene oxide as an anode materials for LIBs, it exhibits a discharge capacity of 710.7 $mA\,h\,g^{-1}$ after 100 cycles at a current density of 0.2C. Feng et al. [29] synthesized copper sulfide nanowires/reduced graphene oxide (CuSNWs/rGO) nanocomposites which exhibit a reversible capacity of 620 $mA\,h\,g^{-1}$ at 0.5C after 100 cycles and 320 $mA\,h\,g^{-1}$ at a high current rate of 4C even after 430 cycles. Our group has successfully fabricated nanorod-like CuS and Cu_2S by a hydrothermal approach without using any template and surfactant. The CuS and Cu_2S nanorod anodes for LIBs reveal that they show high reversible specific capacity, good cycling stability and outstanding rate capability [30]. However, it is still a challenge to find an easy and simple strategy to prepare large-scale nano-structural materials with designed structures and morphologies.

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* Corresponding author. Tel.: +86 592 2186935; fax: +86 592 2186935.
E-mail address: jbzhao@xmu.edu.cn (J. Zhao).

http://dx.doi.org/10.1016/j.mseb.2016.04.004
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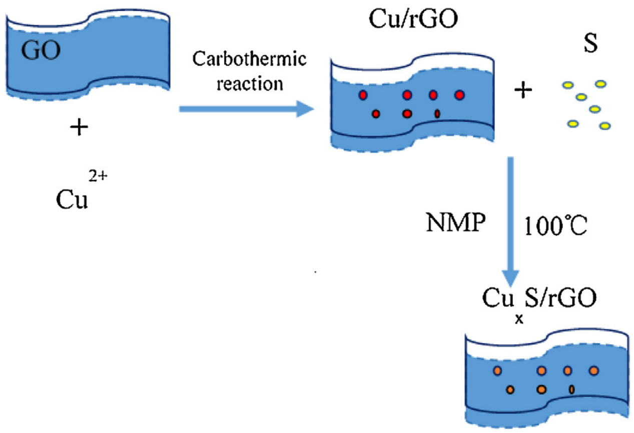

Scheme 1. Synthetic sketch of the Cu_xS/rGO.

Herein, we have developed a facile two-step approach to prepare the nanocomposites (Cu_xS/rGO) of copper sulfide (Cu_xS) microspheres wrapped with reduced graphene oxide (rGO). The rGO nanosheets are porous and elastically strong, which act as a conductive agent and a substrate to produce the Cu_xS/rGO nanocomposites as anode materials. Moreover, the Cu_xS microspheres are wrapped in the interior layers of rGO. These nanocomposites could effectively alleviate large volume expansion and shrinkage, provide a 2D conducting network to enhance the electric conductivity and trap the polysulfides generated during the discharge–charge processes. As-prepared Cu_xS/rGO composites should be a promising candidate for application in high-rate LIBs due to the synergistic effect between Cu_xS microspheres and porous rGO nanosheets.

2. Materials and methods

2.1. Preparation of Cu_xS/rGO

All chemical reagents of analytic grade purity were purchased from Shanghai Chemical Co. Ltd. and used without further purification. First, bulk graphite flakes (~45 μm, 99.99%) were oxidized by a modified Hummer's method to prepared graphene oxide (GO) [31]. Then using an ultrasonicator, as-prepared GO was exfoliated and dispersed in deionized water to gain a stable GO suspension, which concentration is 4.0 mg mL^{-1}. Scheme 1 is the synthetic sketch of Cu_xS/rGO composites. To prepare Cu/rGO, at the desired ratio, copper (II) acetate was dissolved in 30 mL deionized water, then under vigorous stirring, 20 mL GO solution was added. The mass ratio of GO/Cu was 1/1. After sonicating 1 h, the mixed solution was quickly frozen by liquid nitrogen, and evaporated in vacuum at the temperatures below 0 °C for 48 h using the freeze drying equipment. The dry mixed powders were transferred into a tube furnace, and heated from room temperature to 800 °C at a rate of 5 °C min^{-1}, and held at this temperature for 1 h under a flowing argon gas. This intermediate product was denoted as Cu/rGO. The nanocomposites (Cu_xS)/rGO were synthesized from Cu/rGO and nano-sized sulfur powders (China National Medicines Corporation Ltd.). Different mass ratios of the Cu/rGO and the sulfur powders were mixed and dispersed in N-methyl-pyrrolidone (NMP), and heated at 100 °C for 0.5 h before solvent evaporation. The synthetic Cu_xS composites are designated as Cu_xS(2:1)/rGO and Cu_xS(4:1)/rGO, respectively.

2.2. Characterization

The morphologies of as-prepared materials were characterized by using a scanning electron microscope (SEM, HITACHI S-4800) equipped with energy dispersive X-ray spectroscopy (EDX) for elemental analysis. The XRD patterns of the Cu_xS/rGO composites and Cu/rGO were recorded using a Philips X'pert Pro Super X-ray diffract meter and Cu K_α radiation. The laser Raman spectra were recorded at a resolution of 1 cm^{-1} in back scattering (180°) configuration using 532 nm excitation.

2.3. Electrochemical measurements

The slurry with composition of 80 wt% the Cu_xS/rGO active materials, 10 wt% polyvinylidene fluorides (PVDF) and 10 wt% carbon black, which were dissolved in NMP, then casted onto a copper foil to prepare the working electrodes. Afterwards, the electrodes were dried under vacuum at 60 °C for overnight. The electrode loading was in 1 ~ 2 mg cm^{-2}. The CR2016-type coin cells were assembled using the prepared electrodes and lithium metal in an argon-filled glove box. The electrolyte was formed by adding lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 1 M) salt to the mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) at a 1:1 volume ratio. The galvanostatic charge–discharge experiments were measured at different current densities between 1.0 and 3.0 V (vs. Li^+/Li) using a CT2001A cell test instrument (XINWEI Electronic Co.). The electrochemical impedance spectroscopy (EIS) of the Cu_xS/rGO electrodes were recorded by the Autolab PGSTAT 101 cell test instrument in the frequency range of 10 mHz ~ 100 kHz, using two-electrode coin cells with Li metal as the counter electrode. All of the electrochemical tests were performed at room temperature.

3. Results and discussion

The morphology and microstructure of the GO, Cu/rGO and Cu_xS/rGO are shown in Fig. 1a–f, respectively. The SEM image in Fig. 1a shows that the GO with dozens of layers forms a 2D structured network with numerous wrinkles. After reduction, the Cu spheres with diameter of several hundred nanometers coated by the rGO nanosheets are obtained, as shown in Fig. 1b. The SEM images in Fig. 1c and e reveal that as-prepared Cu_xS microspheres are embedded in the rGO nanosheets as expected. Fig. 1d and f further reveals that nano-sized holes are formed on the surface of rGO nanosheets in this process. XRD patterns of samples in Fig. 2a also confirm their structural and compositional differences. Cu_xS(2:1)/rGO can be readily indexed to the hexagonal phase of CuS (JCPDS 001-1281) and there are no metallic copper peaks observed significantly. The XRD pattern of Cu_xS(4:1) shows that it is a mixing phase: one set of the peaks (32.8° and 46.2°) are indexed to Cu_2S (JCPDS 003-1071), the others (43.3°, 50.5° and 74.1°) belong to the unreacted copper powders, and the peak at 48.1° and the broad peaks at about 32.0° and 59.2° indicate the presence of certain amount of CuS.

After chemical oxidation, as-prepared GO shows a strong and sharp peak at 11.6°, indicating that the original sp^2-C bonds of graphite are broken during oxidization [32]. The characteristic peak of GO disappears for the Cu/rGO composites (Fig. 2a), this is due to the considerable reduction capability at high temperature. However, because of its low amount and low diffraction intensity, the characteristic stacking peak of the rGO nanosheets at around 26° cannot be identified from the XRD pattern of the Cu/rGO nanocomposites [27].

The reduction of GO was also analyzed by laser Raman spectroscopy. Fig. 2b shows the Raman spectra of the GO and Cu/rGO. For both spectra, there are two major characteristic peaks at ~1350 cm^{-1} and ~1600 cm^{-1}, respectively. The G band at ~1600 cm^{-1} attributes to the vibration of sp2 carbon atoms in a 2D hexagonal lattice and the D band at ~1350 cm^{-1} corresponds to

Please cite this article in press as: Y. Zhang, et al., Mater. Sci. Eng. B (2016), http://dx.doi.org/10.1016/j.mseb.2016.04.004