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ZnO–SnO_2/graphene composites as high capacity anode materials for lithium ion batteries

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ABSTRACT

A simple hydrothermal method has been developed to synthesize zinc oxide (ZnO)–tin oxide (SnO_2)/graphene composites as anode materials for lithium ion batteries. The ZnO–SnO_2/graphene composite exhibits outstanding electrochemical performance such as high reversible capacities and good cycling stability. The composite delivers a high initial discharge specific capacity of 1287.6 mA h g^{-1} with a reversible specific capacity of 1209.4 mA h g^{-1} at the current density of 1 A g^{-1}. The charge capacity can remain about 1075.3 mA h g^{-1} after 10 cycles. And even after 50 cycles, the charge capacity still remains at 800.9 mA h g^{-1}. Every component of the composite may make a contribution to the enhanced lithium storage capacity and cycling stability.

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1. Introduction

Recently, rechargeable lithium-ion batteries (LIBs) have become promising power sources for a wide range of applications, such as mobile communication devices, portable electronic devices and electrical/hybrid vehicles due to their long cycle life, high voltage and high energy density [1–3]. SnO_2 has been intensively investigated as a promising anode material for LIBs owing to its high capacity, low cost and environmental benignity. However, it suffers from poor cycling performance and low rate capacity because of a large volume change and serious aggregation during cycling processes [4,5]. To overcome these problems, many efforts have been devoted into developing SnO_2-based materials because of their high theoretical specific lithium storage capacities and low potential of lithium-ion intercalations. ZnO has been investigated as an alternative anode material due to it has a high theoretical capacity of 978 mA h g^{-1} [6]. However, it suffers from severe capacity fading upon cycling even at low current densities. There are many reports about the preparation of SnO_2/ZnO composites as anode materials for LIBs. Wang et al. have demonstrated a layer-by-layer approach to synthesize SnO_2/ZnO composite as anode for LIBs. The composite showed high reversible capacity and good cycling stability [7]. Zhu et al. have synthesized a SnO_2/ZnO composite through a two steps hydrothermal method. The composite demonstrated high initial discharge capacity of 1540 mA h g^{-1} with a Columbic efficiency of 68% at a rate of 120 mA h g^{-1} [8]. But so far, there are few reports about the preparation of ZnO–SnO_2/graphene composite.

Herein, we demonstrate a simple hydrothermal method to synthesized ZnO–SnO_2/graphene composite. The composite can possess the advantage of each component and exhibit superior electrochemical performance with large reversible capacity especially at large current density. The existence of the graphene can make a contribution to the large-current charge/discharge capacity because of its extraordinary electronic transport properties, large surface area, and high electrocatalytic activities. Compared with the reported SnO_2/ZnO works, this study can provide a simple, low-cost and effective way to prepare ZnO–SnO_2/graphene composite.

2. Experimental

Preparation of ZnO–SnO_2/graphene composite: All reagents were of analytical grade and were used without further purification. The graphene oxide (GO) employed here was synthesized from natural graphite by a modified Hummers' method [9]. The ZnO–SnO_2/graphene composite was synthesized by a facile hydrothermal method. In a typical preparation process, $SnCl_4 \cdot 5H_2O$, $ZnCl_2$, NaOH and graphite oxide were used as reactants. $SnCl_4 \cdot 5H_2O$ and $ZnCl_2$ were dissolved in 100 mL distilled water to form a transparent solution (the mole ratio of $SnCl_4$:$ZnCl_2$ is 1:2) under magnetic stirring. 3.2 g NaOH was added and immediately reacted with the solution. Then 100 mL graphite oxide suspension (1 mg/mL) was added into the above solution. The mixed solution was then

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transferred into a PTFE-lined autoclave and heated at 200 °C for 24 h. The as-prepared products were washed with deionized water several times and dried at 50 °C.

Sample characterization: The structure and morphology of the as-prepared ZnO–SnO_2/graphene composite were characterized by a Scanning electron microscope (SEM, S-4800) equipped with an energy dispersive X-ray analyzer (EDX), X-ray diffraction (XRD, D/MAX-2500), Raman spectroscopy (In Via Reflex) and Thermogravimetric analysis (TGA, STA 409 PC Luxx®).

Electrochemical measurements: The electrochemical measurements were carried out using the coin-type cell (CR 2032). The working electrodes were prepared by mixing active material with acetylene black and polyvinylidene difluoride (PVDF) binder at weight ratio of 4:4:2 in N-methyl-2-pyrrolidinone (NMP) to form a homogeneous slurry. Then the slurry was pasted onto a copper foil substrate and dried in vacuum oven at 120 °C for at least 12 h. The electrochemical cells used this active material as the working electrode, Li foil as a counterelectrode and reference electrode, and 1 mol L^{-1} $LiPF_6$ in a 1:1 (volume:volume) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as the electrolyte which was assembled in an argon-filled glove box. The calculation of the capacity was based on the ZnO–SnO_2/graphene composite. The cells were galvanostatically charged and discharged in the voltage range 0.01–2.5 V vs. Li/Li^+. Cyclic voltammetry (CV) curves were collected using the Zahner Ennium electrochemical workstation in the potential range 0.01–2.5 V vs. Li/Li^+.

3. Results and discussion

The morphology and structure of the composite were investigated by SEM. Fig. 1a and b illustrates the SEM images of the ZnO–SnO_2/graphene composite. As observed, the surface of hexagonal ZnO is quite rough, which indicates the deposition of SnO_2 and graphene. The hexagonal structures are 800 nm in diameter. Fig. 1c shows EDX spectrum of the as-prepared product. It can be seen that elements Zn, Sn, O exist, which come from the composite.

Fig. 2a shows the XRD patterns of GO and ZnO–SnO_2/graphene composite. The main diffraction peaks of the composite can be indexed to SnO_2 (JCPDS Card no. 41-1445) and ZnO (JCPDS Card no. 36-1451). And some other diffraction peaks can be indexed to Zn_2SnO_4 (JCPDS Card no. 24-1470). Furthermore, no obvious characteristic diffraction peaks of GO were observed, which indicates that the GO was reduced. Significant structure changes occur during the chemical processing from GO to the ZnO–SnO_2/graphene composite in Fig. 2b. The Raman spectrum of GO displays a G band (1590 cm^{-1}) which is related to the vibration of sp^2-bonded carbon atoms in a 2-dimensional hexagonal lattice and a D band (1341 cm^{-1}) corresponding to edge planes and disordered structures. The Raman spectrum of the composite also contains a D band and a G band (1342 cm^{-1} and 1591 cm^{-1}, respectively). However, the D/G intensity ratio of the composites ($I_D/I_G = 1.02$) is larger than that of GO ($I_D/I_G = 0.85$), which indicates a decrease in the average size of the sp^2 domains upon reduction of the exfoliated GO and an increase of edge planes and the degree of disorder in the graphene of the composites. These results suggest that the GO has been successfully reduced to graphene by NaOH [10]. In order to determine the content of each component in the ZnO–SnO_2/graphene composite, TGA was performed in air at the temperature range from room temperature to 800 °C at a rate of 5 °C min^{-1}. TGA curve of the ZnO–SnO_2/graphene is shown in Fig. 2c. An abrupt weight loss that occurs from 240 °C to 500 °C is caused by the oxidization of graphene. After 500 °C, there is no further mass loss, indicating the complete removal of graphene. According to the TGA curve, the content of graphene is about 7.4 wt%.

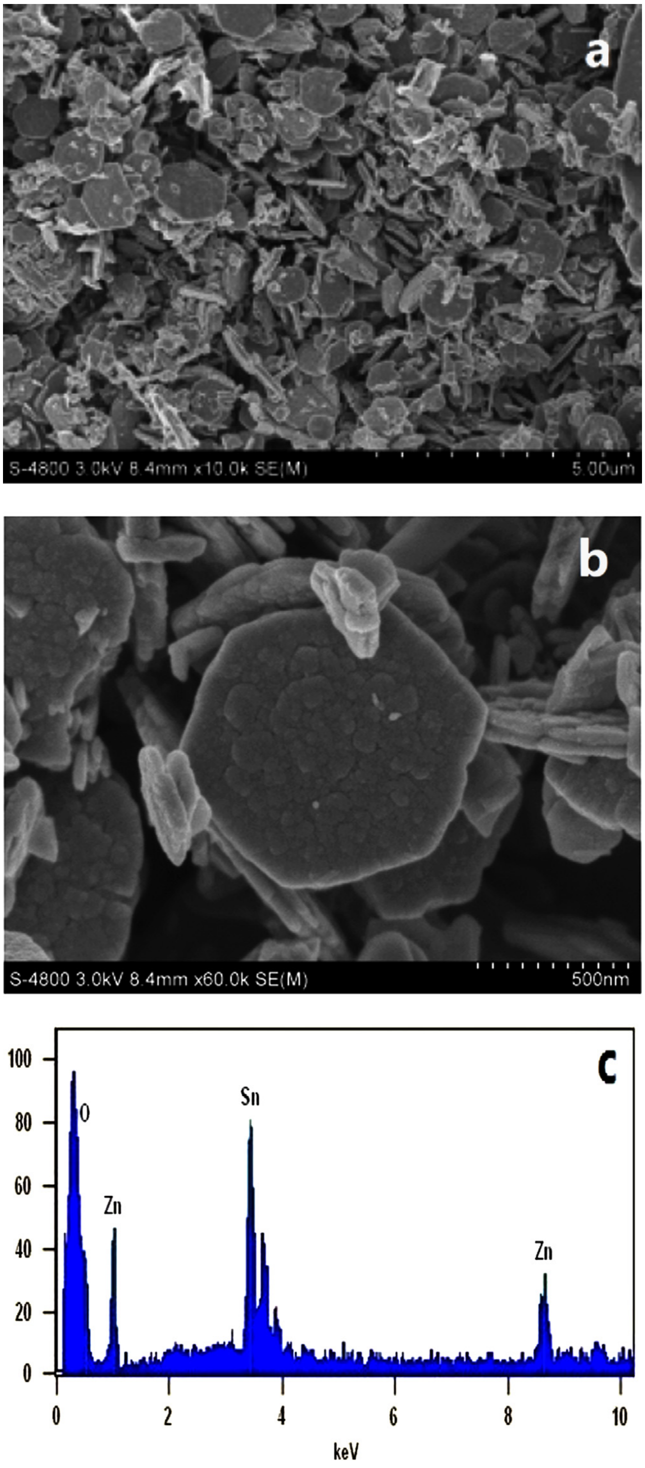

Fig. 1. SEM images (a, b) and EDX spectrum (c) of ZnO–SnO_2/graphene composite.

To evaluate the electrochemical reactivity of the ZnO–SnO_2/graphene composite as anode in lithium-ion batteries, CV was performed in the potential range between 0.01 and 2.5 V. Fig. 3a shows CV curves of the composite in the first two cycles with the scanning rate of 0.2 mV s^{-1}. In the first cycle, two cathodic peaks appeared around 0.38 and 0.78 V. The reduction peak at about 0.78 V can be attributed to the formation of solid electrolyte interface (SEI) layers on the interface of active materials and the reduction of MO_x to M (M is Sn and Zn) as described in Eqs. (1) and

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