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Superior cycle performance of Sn@C/graphene nanocomposite as an anode material for lithium-ion batteries

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ABSTRACT

A novel anode material for lithium-ion batteries, tin nanoparticles coated with carbon embedded in graphene (Sn@C/graphene), was fabricated by hydrothermal synthesis and subsequent annealing. The structure and morphology of the nanocomposite were characterized by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. The size of the Sn@C nanoparticles is about 50–200 nm. The reversible specific capacity of the nanocomposite is $\sim$662 mAh g^{-1} at a specific current of 100 mA g^{-1} after 100 cycles, even $\sim$417 mAh g^{-1} at the high current of 1000 mA g^{-1}. These results indicate that Sn@C/graphene possesses superior cycle performance and high rate capability. The enhanced electrochemical performances can be ascribed to the characteristic structure of the nanocomposite with both of the graphene and carbon shells, which buffer the volume change of the metallic tin and prevent the detachment and agglomeration of pulverized tin.

1. Introduction

Lithium-ion battery is the most widely used rechargeable battery because of its high energy density and excellent service life. However, the energy density and power density of lithium-ion batteries still lies behind the demands of consumers. To improve the electrochemical performances of lithium-ion batteries many new electrode materials have been exploited to obtain such batteries with high energy density, long cycle life, as well as eco-friendliness [1–6]. Among the developed anode materials, metallic tin (Sn) is considered to be a promising anode material because of its high theoretical specific capacity of $\sim$992 mAh g^{-1}, which is much higher than that of the commercial graphite (372 mAh g^{-1}). However, the lithiation and delithiation reactions ($Sn+4.4Li^{+}+4.4e^{-}\leftrightarrow Li_{4.4}Sn$) are accompanied by a large volume change [7–9], which lead to the pulverization of the particles and the electrical disconnection of the electrode. This is the major reason for the poor cycle life of metallic Sn, which hampers the application in lithium-ion batteries [10,11]. Sn particles are usually prepared in nanoscale in order to improve the rate capability, since nanoscale metallic has high activity and short pathway for Li^{+} transport. Nevertheless, aggregation is a general problem for nanoscale materials, especially in charge–discharge process in batteries.

Many efforts have been devoted to improving the electrochemical performance of metallic Sn such as carbon-coating, nanocomposite and porous structure [12–15]. Among the reported approaches, the cycle performance of Sn anode can be considerably improved using carbon matrixes to disperse nanostructure Sn. The carbon matrixes cannot only accommodate the volume change of Sn during charge–discharge process but also provide the electron transport pathways due to the high electronic conductivity of the carbonaceous materials. Various carbon matrixes with different morphologies have been used to prepare Sn/C composites, such as carbon nanotubes [16,17], carbon nanofibers [18], hollow carbon spheres [19,20], and carbon microbeads [21]. All these Sn/C composites show better cycle performance than bare Sn anode material.

Carbon shells coated on the nanoparticles can provide a buffer for the volume change and prevent the aggregation of the particles. However, the metallic Sn with only carbon shell reported previously still exhibited capacity fading [19] because the carbon shell is not elastic enough to compensate the large volume change of Sn. Graphene, a single-atom-thick sheet of honeycomb carbon lattice, was discovered in 2004 and proved to be chemically stable and possess excellent electron conductivity [22]. Graphene nanosheets (GNSs) should be an excellent carbon matrix for dispersing Sn as anodes with good cycle performance and high rate capability because of the natural structure of curly and wrinkled of the disordered stacked GNSs, which create

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substantial void spaces. On the other hand, GNSs are more flexible than carbon shell due to the wide and open porous graphene base. Although the previously reported graphene-based tin anode material without carbon coating improved the cycle performance, the capacity slowly faded from 796 to about 500 mAh g^{-1} even at a small specific current of 55 mA g^{-1} [23]. In order to avoid detachment of the pulverized Sn particles, a novel Sn nanoparticles coating with carbon embedded in graphene (Sn@C/graphene) is proposed. Carbon coated on Sn can wrap up the pulverized Sn particles. Meanwhile, carbon coating is regarded as a conducting bridge between GNSs and Sn particles in the nanocomposite. Moreover, graphene-based Sn was normally prepared by reducing SnO_2/graphene nanoparticles at 800 °C and carbon coating plays a special role, which protects the melting Sn from aggregation while reducing since the melting point of Sn is 232 °C. It can be expected that the as-prepared Sn@C/graphene nanocomposite with characteristic morphology as anode for lithium-ion batteries exhibits large reversible specific capacity, superior cycle performance and excellent rate capability.

2. Experimental

GNSs were prepared through the thermal exfoliation of graphite oxide, which was synthesized by a modified Hummers' method [24]. The detailed preparation process for the GNSs is described in our previous work [25]. SnO_2 nanoparticles aqueous colloid was obtained by fiercely stirring 35 mL of 0.0775 mol L^{-1} $SnCl_4$ aqueous solution while slowly dropping 50 mL of 0.1060 mol L^{-1} NaOH aqueous solution in 12 h. In a typical synthesis of Sn@C/graphene nanocomposite, 0.2499 g of GNSs was dispersed in ethylene glycol by ultrasonication. The dispersion was then mixed with the SnO_2 nanoparticles aqueous colloid by stirring and ultrasonication. The solvent of the suspension was separated away by centrifuging. Then the deposition (SnO_2/graphene) was washed with ethanol for 3 times and dispersed in ethylene glycol again by ultrasonication for 2 h. A hydrothermal process was employed to coat the SnO_2 nanoparticles with carbon using glucose as the carbon source at 180 °C for 12 h, followed by washing with ethanol and drying in vacuum at 55 °C. The obtained powder is SnO_2 nanoparticles coated with carbon and embedded in the graphene (SnO_2@C/graphene). To get Sn@C/graphene nanocomposite, the obtained SnO_2@C/graphene powder was reduced at 800 °C for 12 h within a mixture of N_2 (90%)/H_2 (10%) with a flow rate of 50 mL min^{-1}.

The structure and morphology of the nanocomposites were analyzed by X-ray diffraction (XRD, Bruker D8 ADVANCE), scanning electron microscopy (SEM, Quanta 200 F), and transmission electron microscopy (TEM, FEI, Tecnai G^2 F30 S-Twin). The carbon content was determined by an element analyzer (Vario EL III).

The electrochemical performance was carried out using the CR2025 coin type cells. In a typical cell, metallic lithium sheet was used as the reference and counter electrode with a microporous polymer separator (Celgard 2325) and liquid electrolyte mixtures containing 1 mol L^{-1} $LiPF_6$ and a solvent mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) (Beijing Institute of Chemical Reagents, China). The testing electrodes were prepared by coating the slurry, which consists of Sn@C/graphene nanocomposite, polyvinylidene fluoride (PVDF, Kureha, Japan) and acetylene black with a weight ratio of 75:15:10, onto a copper foil. After drying in a vacuum oven at 100 °C the electrodes were punched into circle and assembled in the cell in a Mikrouna (Super-1220) glove box filled with pure argon. The galvanostatical discharge (Li^+ insertion) and charge (Li^+ extraction) were performed with the voltage between 0.01 and 3.0 V vs. Li/Li^+ at the current densities of 100, 300, 500 and 1000 mA g^{-1} using a Battery Testing System (Neware Electronic Co., China). Cyclic voltammetry curves were measured at a scanning rate of 0.2 mV s^{-1} within the potential range of 0.01–3.0 V vs. Li/Li^+ using an electrochemistry working station (Zahner IM6ex).

3. Results and discussion

XRD patterns of graphene, SnO_2/graphene and the as-prepared Sn@C/graphene are showed in Fig. 1. The characteristic peaks of SnO_2 (JCPDS no. 41–1445) are found at 26.5°, 33.8°, 51.6° and 60.5° in the patterns of SnO_2/graphene. The peaks are weak and wide. The average size of the SnO_2 particles calculated by Scherrer equation is about 3 nm. The peaks of Sn@C/graphene are clearly distinguishable and finely corresponding to the tetragonal Sn phase (JCPDS no. 86-2265), demonstrating that the Sn nanoparticles possess high crystallinity. The elemental analysis indicates that the carbon content of the Sn@C/graphene is about 46.87%, which is much higher than the graphene content (about 18.32%) that we added during the preparation. This result proves that after the hydrothermal process, the glucose converts to disordered carbon and the disordered carbon was successfully coated on the composite [6,26].

Fig. 2 presents the images of SEM and TEM of GNSs, SnO_2/graphene and Sn@C/graphene. Fig. 2a and b presents the representative SEM and TEM images of graphene sheets from the top view, respectively, showing the layered platelets composed of curled nanosheets. This result is in good agreement with that bare graphene sheets showing a weak (0 0 2) diffraction peak in the XRD pattern. The GNSs appear semitransparent and gauze-like, indicating that the GNSs are monolayer or few layers, which is demonstrated by the wrinkled places and the curly edges of the GNSs in the TEM images, as shown in Fig. 2b. Fig. 2c shows that SnO_2 particles are embedded in the GNSs, which are curly and gauze-like. The primary SnO_2 nanoparticles can be observed clearly in Fig. 2e and the size of SnO_2 nanoparticles is about 2–3 nm, which is consistent with the result of XRD. Although some of the primary SnO_2 nanoparticles aggregate to a bigger particle with the size of about 100–200 nm, SnO_2 nanoparticles and the aggregated secondary particles disperse homogeneously on the GNSs (shown in Fig. 2d). After coating with carbon and reduction, the Sn nanoparticles coated with carbon embedded in

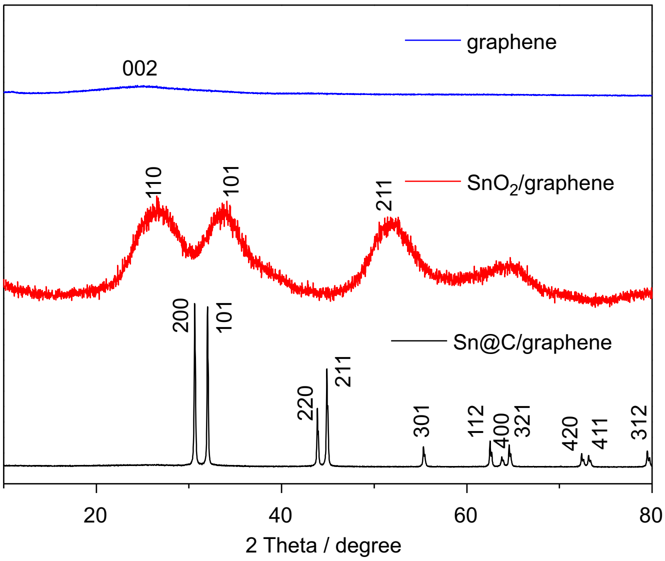

Fig. 1. XRD patterns of graphene, SnO_2/graphene and the as-prepared Sn@C/graphene.