Available online at www.sciencedirect.com

ScienceDirect

Journal of Energy Chemistry 23(2014)338–345

JOURNAL OF ENERGY CHEMISTRY

www.elsevier.com/journals/
journal-of-energy-chemistry/2095-4956
www.elsevier.com/locate/jngc

Dispersing SnO_2 nanocrystals in amorphous carbon as a cyclic durable anode material for lithium ion batteries

Renzong Hu, Wei Sun, Meiqin Zeng, Min Zhu*

School of Materials Science and Engineering, South China University of Technology, Key Laboratory of Advanced Energy Storage Materials of Guangdong Province, Guangzhou 510640, Guangdong, China

[Manuscript received October 2, 2013; revised January 7, 2014]

Abstract

We demonstrate a facile route for the massive production of SnO_2/carbon nanocomposite used as high-capacity anode materials of next-generation lithium-ion batteries. The nanocomposite had a unique structure of ultrafine SnO_2 nanocrystals (~5 nm, 80 wt%) homogeneously dispersed in amorphous carbon matrix. This structure design can well accommodate the volume change of Li^+ insertion/desertion in SnO_2, and prevent the aggregation of the nanosized active materials during cycling, leading to superior cycle performance with stable reversible capacity of 400 mAh/g at a high current rate of 3.3 A/g.

Key words

lithium ion battery; anode; SnO_2 nanocrystals; amorphous carbon; facile strategy

1. Introduction

Lithium ion batteries (LIBs) have been considered as attractive power sources not only for portable consumer electronics but also for upcoming electric/hybrid vehicles and smart grids due to their potential for high power and high energy density [1,2]. To meet the challenges of LIBs with high energy density and long cycle life for use in electric/hybrid vehicles and so forth, great efforts are being made to explore new electrode materials with novel structures and higher specific capacities [3−5]. Accordingly, different kinds of materials, such as transition-metal oxides (Fe_3O_4, Co_3O_4, MnO_2, etc.) [6−8] and alloy-based materials (Si, Sn, Cu_6Sn_5, etc) [9−10] have been studied for the alternative anode materials. Among them, SnO_2-based materials are widely concerned because of their low toxicity, widespread availability, and especially their total theoretical capacity up to as high as 1494 mAh/g (including 711 mAh/g for the conversion reaction and 783 mAh/g for the alloying reaction), which is four times higher than that of the currently used graphite (372 mAh/g) [11−15]. However, the great challenge for practical application of SnO_2 anodes is the severe pulverization and capacity fading problems caused by the extremely large volume change of Sn (about 250% for $Li_{4.4}Sn$ formation) during cycling [16]. To overcome these problems, many methods have been studied to reduce the absolute volume change and cracking of active materials by the nanosize effects, especially via nano-architectured materials, such as nanoparticles, nanowires and nanotubes [17−19]. However, limited cycleability improvement has been obtained by simply nano-modifying the pure SnO_2, because the agglomeration of nanosized SnO_2 and/or Sn is still unavoidable unless there is an extra confining buffer [11−15, 17−19]. In contrast, the nanopainting of SnO_2 with various carbonaceous materials has recently been found effective for improving the cycleability of SnO_2-based anodes [13,19−25], because the carbonaceous materials not only enhance the electrical conductivity but also act as buffering layers for the large volume change of SnO_2. Actually, carbonaceous materials have been widely investigated to enhance performances for different electrode materials for LIBs and other batteries [26−28]. And thus, the SnO_2-carbon composite anodes with various microstructures have been designed and prepared by different strategies. For example, many carbon nanotube-encapsulated SnO_2 composites have been prepared using the wet chemical filling and rapid vacuum absorption [24,25,29]. Yu et al. reported the synthesis of SnO_2@carbon core-shell nanochains by carbonization of a SnO_2@carbonaceous polysaccharide precursor at a relatively high temperature using a new low-flow-rate inert atmosphere strategy [30]. Zhang et al. elevated

---

* Corresponding author. Tel: +86-20-87113924; Fax: +86-20-87111317; E-mail: memzhu@scut.edu.cn

This work was supported by the National Science Foundation of China (Grant No. 51201065 and No. 51231003), the Natural Science Foundation of Guangdong Province (S2012040008050) and the Doctorate Foundation of Ministry of Education (Grant No. 20120172120007 and No. 2014ZZ0002).

doi: 10.1016/S2095-4956(14)60156-X

the electrochemical properties of the carbon-coated SnO_2/graphene nanosheets, whose synthesis processes included first exfoliation of graphene oxide nanosheets from graphite oxide, and then growth of SnO_2, and followed by heating after an addition of glucose [31]. Read et al. prepared a SnO_2-carbon composite by heating a mixture of colloidal SnO_2 (average size of 15 nm) and sugar (sucrose) as carbon precursor, which was finally carbonized to form a hard carbon and acted as a diluent to prevent nanosized SnO_2 agglomeration [32]. Lou et al. designed a novel anode material of coaxial SnO_2@carbon hollow nanospheres which showed a high capacity of about 460 mAh/g and little capacity fading after 100 cycles [23]. Although some properties of these complexly designed SnO_2-carbonaceous anodes far exceed those of the conventional graphitic anode materials and demonstrate very high capacity and good stability, overall performance (especially the output of materials, the electrode loading or the capacity per unit area), as well as those rather complicated production processes of the SnO_2-based anode materials are far from their practical applications.

Therefore, it is still desirable to develop a simple and more efficient way to prepare composites with nanosized SnO_2 stored in the carbon matrix, which not only preserve high-dispersion state of the active SnO_2 but also achieve high capacity together with enhanced cyclic performance. In this work, we develop a facile strategy, which is cost-effective and has a good potential for large scale applications, to synthesize a SnO_2-based carbonaceous nanocomposite anodes for LIBs. And a unique structure with homogeneous dispersion of SnO_2 nanocrystals ($\sim$5 nm) in amorphous carbon matrix is achieved. The origin of the enhanced anode performance of the SnO_2/carbon nanocomposite has been analyzed by microstructure observations combining with electrochemical characterizations.

2. Experimental

2.1. Materials fabrication

Generally, the SnO_2/carbon nanocomposite was fabricated by simply boiling and following heating of Sn together with sugar. In a typical experiment, an aqueous solution consisting of 20 g Sn powders ($\sim$100 mesh, 99.9% purity), 30 g crystal sugar (edible grade) and 180 mL deionized water was put in a stainless steel pot and then boiled in air using an electric oven (2 kW). The solution was heating for 1 h until all the water boiled dry and a brown charred production was achieved (name as charred product). Then, the obtained charred product was transferred to an alumina crucible and kept in a tube furnace at 400 °C (based on the DSC result shown in Figure 1) for 4 h in flowing Ar atmosphere. Finally, brown powders (named as SnO_2/carbon nanocomposite) were obtained and were tested as electrode materials after grinding in a bowl. Pure nanosized SnO_2 (with average diameters of 50 nm) was bought and also characterized as electrode for comparison.

2.2. Materials characterization

The structure and morphology of the samples were characterized using a Philips X-ray diffractometer (XRD) with Cu-K_α radiation, a Carl Zeiss Supra 40 field emission scanning electron microscope (SEM) and a JEOL JEM-2100 transmission electron microscope (TEM) operating at 200 kV. Differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis were made under Ar and/or O_2 on NETZSCH STA409 with a heating rate of 10 °C/min. In order to retain the original morphology of the as-prepared products, the SnO_2/carbon nanocomposite powders were directly dispersed on Cu grids for TEM measurements.

2.3. Electrochemical measurements

The discharge-charge cycling performance of the samples was investigated using a cell test system (LAND-CT2001A) with CR2016 coin-type cells assembled in an argon-filled glove box. The working electrode consisted of 80 wt% of the active material (SnO_2/carbon nanocomposite or pure nanosized SnO_2), 10 wt% conductivity agent (Super-P) and 10 wt% binder polyvinyldifluoride. Lithium foil was used both as a counter electrode and as a reference electrode in the half cells. The electrolyte was $LiPF_6$ (1 mol/L) in a mixture of ethylene carbonate (EC)/diethyl carbonate (DEC)/ethyl methyl carbonate (EMC) with volume ratio of EC/DEC/EMC = 1/1/1 (Shanshan Tech Co., Ltd.). The cells were tested at various current rates between 0.01 and 1.5 V at room temperature. Cyclic voltammetry (CV) over the potential range of 0–2.0 V at a scan rate of 0.3 mV/s, as well as impedance spectroscopy at 5 mV amplitude signal in the 1 MHz to 0.05 Hz frequency range, was performed using a Gamry Interface 1000 Electrochemical System.

3. Results and discussions

The heating conditions of the Sn-sugar composite were set according to the thermal analysis results. Figure 1(a) shows the DSC and TG curves for the charred product of Sn-Sugar composite after boiling. It can be seen that during heating scanning under Ar, there are two endothermic peaks at about 100 °C (peak 1) and 270 °C (peak 2), respectively. In addition, two exothermic peaks appeared among 300$\sim$500 °C (peak 3) and around 750 °C (peak 4). The endothermic peak 1 should be attributed to the evaporation of the residual water, while the sharp peak 2 was induced by the melting of the Sn, suggesting that the Sn particles remained their elemental state even boiling in water and mixing with the charred sugar. With respect to the two exothermic peaks, peak 3 was originated from the following Reaction 1, which involved the decomposition of the sugar and oxidation of Sn to form SnO_2, with weight loss of about 20% as indicated by the TG curve.

$$\begin{gathered}\mathrm{Sn(liquid)} + (\mathrm{C\text{-}H_2O})_n\mathrm{(solid)} \rightarrow \\ \mathrm{SnO_2(s)} + \mathrm{C(s)} + \mathrm{CO_2(gas\uparrow)} + \mathrm{H_2O(g\uparrow)}\end{gathered} \tag{1}$$