Journal of Alloys and Compounds 750 (2018) 220–227

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Synthesis of heterostructure Sn|SnO_2 submicron particles supported by carbon fibers as binder-free anodes for highly reversible lithium storage

Jingjing Ding [a, b], Wenyu Zhu [a], Cong Liu [b], Chao Ma [a], Yang Yang [a], Hongmei Ji [a], Gang Yang [a, b, *]

[a] School of Materials Science and Engineering, China University of Mining and Technology, Xuzhou, 221116, China
[b] Jiangsu Lab of Advanced Functional Material, Changshu Institute of Technology, Changshu, 215500, China

ARTICLE INFO

Article history:
Received 2 January 2018
Received in revised form
28 March 2018
Accepted 29 March 2018
Available online 31 March 2018

Keywords:
Carbon fibers
Tin submicron particles
Binder-free anode electrode
Lithium-ion batteries

ABSTRACT

Tin-based materials are considered to be next-generation anode materials for lithium-ion batteries (LIBs) due to their high theoretical capacity and safety, but their large volume expansion results in rapid capacity fading. In this work, the heterostructure of Sn|SnO_2 submicron particles supported by carbon fibers and amorphous carbon layers (CF/Sn|SnO_2@C) is successfully synthesized by hydrothermal and thermal treatments. Sn|SnO_2 submicron particles are uniformly grown on CF and encased in the CF network. Herein, CF together with a layer of amorphous carbon not only buffers the volume change of Sn|SnO_2 to prevent its pulverization and dissolution but also improves the electric and lithium ionic transportation capabilities during the lithiation/delithiation cycle. The CF/Sn|SnO_2@C film can directly act as a binder-free anode for LIBs, exhibits a stable capacity of 657.6 mAh g^{-1} at a current density of 0.1 A g^{-1} after 50 cycles and presents better rate capacities than the Sn|SnO_2@C comparison sample. Taking advantage of the stabilization and conductive channels of CF, this work demonstrates potential applications in the preparation of CF-based, binder-free anodes for LIBs in which metal oxide submicron particles can be effectively supported by a CF network.

1. Introduction

Lithium-ion batteries (LIBs) have been extensively applied to in the portable electronic devices and electric vehicles (EVs) [1–3]. Graphite, a widely used commercial anode material, cannot satisfy the requirements of high energy storage devices due to its intrinsically low theoretical capacity of 372 mAh g^{-1}. Therefore, it is necessary to develop novel anode materials for high-performance LIBs [4–7]. Tin and its oxide are attractive candidates in view of their low cost, environmental benignity, safety and high lithium storage capacity (theoretical specific capacity of 990 mAh g^{-1} for metallic tin, 782 mAh g^{-1} for SnO_2) [8–18]. Nonetheless, the application of pure SnO_2 as an anode is limited by its low electrical conductivity and severe volume change (~300%) during the lithiation/delithiation process. The pulverization in cycled Sn and SnO_2 electrodes with the unavoidable cracking of the solid electrolyte interphase (SEI) layer leads to serious capacity fading and a limited cycle life.

Compositing tin-based anode materials with carbonaceous materials is considered one of the most effective approaches for enhancing the material properties because carbonaceous materials have the advantages of a natural abundance, high electrical conductivity, and positive effect on volumetric changes in cycled tin electrodes [19,20]. Alcoutlabi's group reported a comparative study on the performance of binary SnO_2/NiO/C and Sn/C composite nanofibers as alternative anode materials for LIBs. The flexible composite nanofibers were directly used as working electrodes in LIBs without a current collector, conductive additives and polymer binder. The SnO_2/NiO/C and Sn/C composite fiber anodes delivered approximately 675 mAh g^{-1} after 100 cycles [21]. Qin et al. reported a sandwiched C@SnO_2@C hollow nanostructure that exhibited reversible specific capacities of ~1011 and ~933 mA h g^{-1} at a current density of 0.1 A g^{-1} at the 2nd and 50th cycles, respectively [22]. Xia et al. synthesized SnO_2@N-CNF films, which showed a

---

* Corresponding author. School of Materials Science and Engineering, China University of Mining and Technology, Xuzhou, 221116, China.
E-mail address: gyang@cslg.edu.cn (G. Yang).

https://doi.org/10.1016/j.jallcom.2018.03.395
0925-8388/© 2018 Elsevier B.V. All rights reserved.

reversible capacity of 754 mAh g^{-1} at 1 A g^{-1} after 300 cycles [23]. An increasing number of studies have revealed that carbonaceous materials play an important role in high-performance Sn-based anode materials for LIBs [24–26]. In our previous work, we synthesized tin nanoparticles encased in carbon fibers (Sn/C) that present a high specific capacity and long cyclic life because the composite structure of metallic tin nanoparticles encased in carbon fibers is advantageous for decreasing the volume change and aggregation of particles during the charge and discharge process [27]. Carbon fiber (CF), as an important kind of carbonaceous material, can be easily produced by electrospinning and carbonization. CF has the advantages of flexible, low cost, scalable preparation in comparison with graphene and carbon nanotubes [28–30]. Moreover, CF networks with abundant conductive channels can be used as excellent substrates to support inorganic compounds and improve their electrochemical properties. However, the composite of CF/Sn|SnO_2@C in which Sn|SnO_2 submicron particles are ex situ grown in a CF network has rarely been reported, and the structural change in CF/Sn|SnO_2@C after charging/discharging cycles is unknown.

In this work, Sn|SnO_2 submicron particles are ex situ grown on and encased in a CF network to obtain a highly reversible lithium storage capability. The CF/Sn|SnO_2@C composite film can be directly used as a binder-free anode. The CF in this work has important roles, such as decreasing the aggregation of metallic tin, buffering the volume change of Sn|SnO_2 submicron particles during the lithiation/delithiation cycle, providing a high electrical conductivity and Li^+ transportation channels, and significantly enhancing the reversible capacity and cycle stability.

2. Experimental

2.1. Preparation of CF/Sn|SnO_2@C and Sn|SnO_2@C samples

The carbon fiber (CF) was prepared according to previous research [27–31]. $SnCl_2 \cdot 2H_2O$ (2 mmol), $Na_3C_6H_5O_7 \cdot 2H_2O$ (5 mmol) and NaOH (1 mmol) were dissolved and mixed in distilled water (50 mL) under magnetic stirring for 20 min to form a milky solution. The solution and CF film were transferred into a 100 mL Teflon-lined autoclave and heated in an oven at 180 °C for 6 h. After cooling to room temperature naturally, the CF@SnO_2 intermediate was obtained after washing the product with distilled water and drying at 60 °C. In the subsequent step for the carbon coating, 1 g of glucose was dissolved in 50 mL of distilled water under magnetic stirring for 20 min. A clear solution of glucose and the CF@SnO_2 film were transferred together into a 100 mL Teflon-lined autoclave and heated in an oven at 180 °C for 4 h. After cooling down to room temperature naturally, carbon-coated samples (CF@SnO_2@C) were obtained after washing the product with distilled water and drying at 60 °C (here, the symbol "@" represents the coating interface among CF, SnO_2 and C, which was confirmed by the morphology and elemental distribution of CF@SnO_2@C in the SEM image as follows). Finally, the CF@SnO_2@C sample was heat-treated at 700 °C for 3 h in an N_2 atmosphere, and it was reduced to CF/Sn@C via a carbothermic reduction with the Sn submicron spherical particles remaining in the CF network. Because a thin passivation oxide layer was grown on tin submicron particles by natural oxidation for 6 h, the final product is CF/Sn|SnO_2@C (herein the symbol "/" represents the interface between the tin particles and CF, which was confirmed by the following morphology and elemental distribution in the SEM images). The film parameters of CF/Sn|SnO_2@C are 100 ± 5 μm in thickness and 2.8 ± 0.1 mg cm^{-2}. Sn|SnO_2@C was prepared as a reference sample by the same process as CF/Sn|SnO_2@C but without adding the CF film in the hydrothermal process.

2.2. Characterizations

The crystal structures of the samples were analyzed by X-ray powder diffraction (XRD, Rigaku Cu-Kα radiation). X-ray photoelectron spectroscopy (XPS, Thermo Scientific, Escalab250Xi, Al-Kα as X-ray source) measurements were performed to evaluate the composition and valence of the elements. The surface morphologies, elemental mapping and microstructures of the samples were evaluated using a field emission scanning electron microscope (FE-SEM, SIGMA, ZEISS 20 kV) equipped with X-ray energy dispersive spectroscopy (EDX, Oxford Instruments Analytical) and a high-resolution transmission electron microscope (HRTEM, JEOL JEM-200CX, 200 kV). Thermogravimetric analysis (TGA/DTA851E) was carried out in an oxygen atmosphere at a heating rate of 5 °C min^{-1} from room temperature to 900 °C.

2.3. Electrochemical measurements

All electrochemical data were collected using CR 2016 coin-type cells, which were assembled in an Ar-filled glove box. Lithium metal disks and Celgard 2400 microporous polypropylene films were used as the counter electrode and separator, respectively. The electrolyte was 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC (1:1 by volume). The flexible CF/Sn|SnO_2@C film was directly applied as a binder-free anode, and the mass of each electrode was 2.8 ± 0.1 mg cm^{-2}. For the comparison electrode, Sn|SnO_2@C powder was the active material and was mixed with acetylene black and poly(vinylidene fluoride) (PVdF) according to a weight ratio of 8: 1: 1. The mixture was stirred for 6 h in N–methyl-2-pyrrolidone (NMP), and then, the mixture slurry was painted onto copper foil and dried in a vacuum at 100 °C for 12 h.

The electrochemical performances with varying current densities (vs Li/Li^+) were investigated in the voltage range of 0.001–3.0 V using a LAND CT2001A battery testing system (Wuhan, China) at room temperature. The mass of the active material used to calculate the specific capacity was the total mass of the composite electrode, and the net capacity from the composite electrode did not remove the contribution from carbon fiber. The cycle voltammetry (CV) profiles were collected at a scan rate of 0.1 mV s^{-1} using a CHI660E electrochemical workstation (Shanghai, China). The electrochemical impedance spectra (EIS) of the electrodes at the state of the 50th discharge were collected on a PARSTAT2273 electrochemical workstation (Princeton Applied Research, USA) between 10^{-2} Hz and 10^5 Hz at an AC voltage amplitude of 5 mV.

3. Results and discussion

CF@SnO_2@C is the important intermediate sample synthesized using the hydrothermal method, and the SnO_2 crystallites and porous carbon homogeneously grew around the carbon fibers, as shown in Fig. 1. The XRD patterns of the CF film present a typical amorphous carbon structure characterized by a broad peak centered at 22° (2θ). The hydrothermal products of CF@SnO_2 and CF@SnO_2@C present the pure phase of SnO_2 corresponding to tetragonal SnO_2 (JCPDS No. 41-1445). Fig. S1 (Supporting Information) shows the SEM image and histograms of the pure carbon fibers. Most fibers are 300–400 nm in diameter. CF@SnO_2@C retains a fibrous morphology, but the fiber diameter increases to 400–600 nm (Fig. 1b). Sn and O are homogeneously distributed on the carbon fiber, as shown in the elemental mapping images (Fig. 1c–e).

To produce tin submicron particles supported on carbon fibers, CF@SnO_2@C was heat-treated at 700 °C for 3 h in an N_2 atmosphere. Herein, SnO_2 nanosheets were reduced to Sn submicron particles