Energy xxx (2015) 1–8

Contents lists available at ScienceDirect

Energy

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

Novel three-dimensional tin/carbon hybrid core/shell architecture with large amount of solid cross-linked micro/nanochannels for lithium ion battery application

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ARTICLE INFO

Article history:
Received 17 March 2014
Received in revised form
15 January 2015
Accepted 30 January 2015
Available online xxx

Keywords:
Tin/carbon core/shell nanofibers
Three-dimensional architecture
Encapsulation of tin/carbon nanocrystals
Lithium-ion battery

ABSTRACT

Uniform Sn/C hybrid core/shell nanocomposites were synthesized by a combination of electrospinning and subsequent thermal treatment in a reducing atmosphere. The particular three-dimensional architecture, consisting of a Sn@C nanoparticle core and porous hollow carbon nanofiber shell, is characterized by many micro/nanochannels, enhanced mechanical support from the three-dimensional hollow carbon shell, and the abundant porous carbon matrix. The as-prepared Sn/C core/shell nanomaterials exhibit excellent electrochemical performance. They display a reversible capacity of 546.7 $mAhg^{-1}$ up to 100 cycles at the current density of 40 mAg^{-1} and good rate capability of 181.8 $mAhg^{-1}$ at 4000 mAg^{-1}. These results indicate that the composite could be a promising anode candidate for lithium ion batteries.
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1. Introduction

Much interest has been focused on lithium rechargeable batteries with high energy density and high power density because of their potential applications in powering different electrical devices [1–8]. Many potential anode materials with high theoretical capacity, such as Si [9–13] and Sn alloys [14] and SnO_2-containing composites [15], have been explored to replace the current graphite anode materials. Nevertheless, practical implementation of those metal/alloys and composites is usually hampered by the large initial irreversible capacity loss owing to the Li_2O formation and the poor capacity retention because of the pulverization that occurs during extended charge/discharge cycling [2].

Feasible strategies to improve the Li^+ storage capacity and cyclability of those electrode materials are enhancing the Li^+ transport and mechanical performance via formation of a one-dimensional (1D) nano-architecture [16,17], employing Si [18–20], Sn [21–23], or other alloys instead of their oxides, and introducing some dispersed materials with little volume variation during the charge/discharge process, such as TiO_2 [24], Cu [25,26], or some buffer matrix material such as carbon [27–30], which would mitigate volume expansion during cycling. It would be a more effective way to improve the Li^+ transport and mechanical performance of Sn-based materials if we could combine the advantages of the one-dimensional nano-architecture and of the Sn metal electrode materials with that of the buffer matrix to form one-dimensional materials with core/shell architecture. Up to now, however, only a few one-dimensional Sn-based nanomaterials with all the advantages mentioned-above, apart from Sn/C/CNT [23], Sn/SnO_x/C nanofibers [31], Co–Sn@C nanofibers [32], and Sn/C nanofibers [33], have been reported as anode materials for the lithium ion battery. This is possibly due to their complicated synthesis procedures, high preparation costs, or the nature of Sn metal, which is inclined to evaporate at high temperature, greatly limiting the Sn

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http://dx.doi.org/10.1016/j.energy.2015.01.105
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Please cite this article in press as: Yang Z, et al., Novel three-dimensional tin/carbon hybrid core/shell architecture with large amount of solid cross-linked micro/nanochannels for lithium ion battery application, Energy (2015), http://dx.doi.org/10.1016/j.energy.2015.01.105

content in the target product that is obtained from these common synthesis routes. It is still a challenge to synthesize one-dimensional Sn/carbon core/shell nanomaterials with the "cushioning effect" of a carbon matrix, especially by a cheap and simple technique. Electrospinning is a simple method used to form continuous one-dimensional nanofibers under the electrostatic force of the charges on the surface of a liquid droplet in a sufficiently high electric field, which is applied between the capillary nozzle and the metal collector [22,34–37].

Herein, this paper presents a relatively simple and low-cost approach to obtain novel three-dimensional (3D) Sn/C core/shell nanostructures with cross-linked micro/nanochannels by a combination of electrospinning and subsequent thermal treatments, which can effectively reduce the evaporation loss of Sn at high temperature because of the protective function of the carbon coating during the additional glucose-hydrothermal process. This three-dimensional Sn/C core/shell nanocomposite has unique advantages, such as nanoporosity, mesoporosity, three-dimensional architecture, the special core/shell structure, and large surface-to-volume ratio. In the 3D hybrid nanostructure, the carbon acts as a mechanical support and buffer matrix, which can effectively buffer the volume changes of the tin during lithium ion intercalation/deintercalation. In addition, the carbon in the composite could effectively prevent the tin crystals from agglomerating during cycling and simultaneously improve the electrical conductivity of the composite. The three-dimensional Sn/C core/shell composite has been explored here in a preliminary way for potential use as an anode material for the lithium battery and has exhibited excellent cycling stability and rate capability.

2. Experimental

2.1. Synthesis of three-dimensional Sn/C core/shell hybrid nanomaterials

The procedures for preparing the electrospinning solution are similar to those in our previously reported experimental results [34–37]. Simply, 0.7 g polyacrylonitrile (PAN, MW = 150,000, Aldrich) was dissolved in 5.6 g N,N-dimethylformamide (DMF, 99.8%, Aldrich) at 80 °C with vigorous stirring for 2 h (solution **No. 1**), and then, 0.8 g tin(II) 2-ethylhexanoate (95%, Aldrich) was mixed with 2.4 g anhydrous ethanol and 3.1 g acetic acid (solution **No. 2**). Afterwards, the **No. 2** solution was added dropwise to the **No. 1** solution at 80 °C with vigorous stirring. The mixed solution was then stirred again at room temperature for 3 h. The polymer solution was transferred into a 10 ml syringe with a capillary tip (0.8 mm diameter). For spinning, the set-up was similar to that described previously [34,36–38]. Typically, the collector was placed 9.5 cm from the spinneret to collect the nanofibers. A high voltage of 13.3 kV was applied between the spinneret and the collector by a direct-current power supply (DW-P303-5ACCD, Tianjin Dongwen High Voltage Power Supply Co., China.). The solution was pushed out of the spinneret by a syringe pump (TS2-60, Baoding Lange Constant Flux Pump Co., China) at the rate of 0.3 ml/h. The collector was kept at 180 °C during the electrospinning process to evaporate the solvent. After spinning for more than 20 h, the nanofiber films were easily peeled off. The electrospun nanofibers were slowly decarbonized in an air environment (heating rate: less than 1 °C min^{-1}), or used directly as the precursor in the following glucose-hydrothermal procedure (see Table 1), respectively. Subsequently, 0.30 g pure SnO_2 nanofibers (the precursor for **TC1** as defined in Table 1) or tin composite/PAN nanofibers (the precursor for **TC2** as defined in Table 1) were completely immersed in 15 ml 0.8 M glucose solution (see Table 1), respectively. These suspensions were transferred to different 30 ml Teflon-lined autoclaves, respectively, which were then heated in an oven at 180 °C for at least 4 h. The products were harvested by centrifugation and washed with deionized water and ethanol, respectively, at least five times. After drying at 50 °C, the resulting brown products were carbonized and simultaneously reduced into three-dimensional Sn/C composites at 750 °C for 4 h under 5% H_2/Ar atmosphere, according to the TGA (thermogravimetric analysis) results (Supporting Information (S) Fig. S1). Finally, black films (the three-dimensional Sn/C core/shell nanocomposites, **TC1** and **TC2**) were obtained, respectively.

2.2. Materials characterization

The compositions and crystal structures of the as-prepared Sn/C hybrid core/shell nanomaterials were obtained by XRD (X-ray diffraction) analysis (MMA, GBC, Australia). TGA (Thermogravimetric analysis) of the as-prepared hybrid nanomaterials in samples **TC1** and **TC2** was carried out with a TGA/DSC1 type instrument (METTLER TOLEDO, Switzerland) at a heating rate of 10 °C min^{-1} from 25 to 1000 °C in air, respectively. The morphology of the as-synthesized nanomaterials was evaluated using a JEOL 7500FA field emission scanning electron microscope (FE-SEM, JEOL, Tokyo, Japan) and a JEOL 2011F TEM (transmission electron microscope, JEOL, Tokyo, Japan). EDX (Energy dispersive X-ray spectroscopy, JEOL 7500FA) was used to confirm the respective contents of carbon and Sn. XPS (X-ray photoelectron spectroscopy) experiments were carried out on a VG Scientific ESCALAB 220IXL instrument, using aluminum Kα X-ray radiation during XPS analysis.

2.3. Electrochemical characterization

Electrochemical properties were measured on electrodes prepared by compressing a mixture of the as-prepared Sn/C hybrid nanomaterials, carbon black (Super P, MMM, Belgium), and PVDF (poly(vinyl difluoride)) binder in a weight ratio of 70:15:15 and pasting the mixture on copper foil. Pure lithium metal foil was used for the counter and reference electrodes. The electrolyte was $LiPF_6$ (1 M) in a mixture of EC (ethylene carbonate) and DMC (dimethyl carbonate) (1:1 v/v; MERCK KgaA, Germany). Coin cells were assembled in a high-purity argon-filled glove box (Mbraun, Unilab, Germany). A LAND-CT2001A instrument was used with a charge–discharge current density of 40 mAg^{-1} to measure the electrochemical capacity of those electrodes at room temperature by the galvanostatic method. Rate capability tests of the electrodes were then carried out systematically. The cut-off potentials for charge and discharge were set at 3.0 and 0.01 V versus Li^+/Li, respectively. CV (Cyclic voltammetry) was performed on a PARSTAT@2273 electrochemical workstation.

3. Results and discussion

3.1. Composite composition and morphology

The powder XRD (X-ray diffraction) patterns of the as-prepared Sn/C hybrid nanomaterials (**TC1** and **TC2**) clearly proclaim their morphology and elemental composition (see Fig. 1). When the material is heat-treated in air followed by heat-treatment in 5% H_2/Ar atmosphere, there are sharp characteristic peaks of tin in the X-ray diffraction patterns, possibly because of the high crystallinity of the Sn/C hybrid core/shell nanomaterials (**TC1**) and the high percentage of tin metal in the composite, in spite of some interference from the carbon in the hybrid core/shell nanomaterials, according to the TGA results (see Supporting Information Fig. S1(a)), which is mainly attributable to the tetragonal tin metal (JCPDS 86-2264) in the Sn/C hybrid core/shell nanomaterials obtained from the as-

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