Carbon nanofibers with highly dispersed tin and tin antimonide nanoparticles: Preparation *via* electrospinning and application as the anode materials for lithium-ion batteries

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ABSTRACT

One-dimensional carbon nanofibers with highly dispersed tin (Sn) and tin antimonide (SnSb) nanoparticles are prepared by electrospinning in the presence of antimony-doped tin oxide (denoted as ATO) wet gel as the precursor. The effect of ATO dosage on the microstructure and electrochemical properties of the as-fabricated Sn-SnSb/C composite nanofibers is investigated. Results indicate that ATO wet gel as the precursor can effectively improve the dispersion of Sn nanoparticles in carbon fiber and prevent them from segregation during the electrospinning and subsequent calcination processes. The as-prepared Sn-SnSb/C nanofibers as the anode materials for lithium-ion batteries exhibit high reversible capacity and stable cycle performance. Particularly, the electrode made from Sn-SnSb/C composite nanofibers obtained with 0.9 g of ATO gel has a high specific capacity of 779 mAh·g^{-1} and 378 mAh·g^{-1} at the current density of 50 mA·g^{-1} and 5 A·g^{-1}, respectively, and it exhibits a capacity retention of 97% after 1200 cycles under the current density of 1 A·g^{-1}. This is because the carbon nanofibers can form a continuous conductive network to buffer the volume change of the electrodes while Sn and Sn-SnSb nanoparticles uniformly distributed in the carbon nanofibers are free of segregation, thereby contributing to electrochemical performances of the electrodes.

1. Introduction

Lithium ion batteries (LIBs) have been widely used in portable electronic devices, due to their distinctive merits such as high energy density and long cycle life [1,2]. However, currently available commercial LIBs are often used for low order power demand, which is attributed to the low specific capacity of the anode and cathode active materials. This means that researchers need to further improve the energy and power densities of LIBs so as to satisfy the demands of electric vehicles and power grids. Unfortunately, currently used commercial graphite anode material for LIBs offers a low theoretical capacity (372 mAh·g^{-1}) [3,4], and it is imperative to develop alternative anode materials with increased reversible and rate capacities as well as long-term cyclic stability.

Tin (Sn) based anode materials are often regarded as promising candidate anode materials for LIBs, due to their high theoretical capacity associated with the formation of Li$_{4.4}$Sn species (Li$_{4.4}$Sn; 994 mAh·g^{-1}). Nevertheless, the practical application of Sn-based anode materials is greatly hindered by their large volume changes (up to 300%) during the repeated charge-discharge processes [5,6]. The reason lies in that the large volume changes can cause cracking and pulverization of the electrode materials, consequent loss of interparticle electrical contact and particle-current collector in-between electrical contact, as well as the repeated formation of solid-electrolyte interface (SEI) films, thereby resulting in rapid capacity decay and poor cyclability [7].

To overcome the volume expansion issue of the anode materials for LIBs, researchers have established two representative strategies. One is to reduce the particle size of Sn to nanoscale thereby minimizing the strain during volume expansion [8,9]. Another is to integrate electrode material with other matrices such as carbonaceous matrix or metallic matrix [10–12]. Carbonaceous matrix is of particular significance,

because the carbon coating layer, in some sense, can act as a volume buffer to reduce the stress concentration caused by lithium insertion; and it can also prevent the agglomeration of Sn nanoparticles and enhance the interparticle electrical conductivity [13,14]. Metallic matrices like SnSb alloys are also interesting, because they can alleviate the volume change upon the lithium insertion/extraction reactions of Sn and Sb occurring at different potentials. Namely, the unreacted phases of SnSb alloys can act as the buffer matrices to accommodate volume change yielded by their reacted phases, thereby increasing the structural stability of the whole anode electrode [7,15–19].

Electrospinning technique is a simple and versatile method for preparing electrode active materials/C composite nanofibers has been extensively focused on [20,21]. The one-dimensional (1D) nanofibers can buffer the volume change of the active materials and form a stable SEI film. In addition, the electrospun carbon nanofibers (CNFs) can effectively prevent the aggregation of electrode active materials and increase the surface area [14]. In electrospinning process, soluble inorganic salt precursors (e.g., $SnCl_2$) or SnO_2 nanoparticles dispersed in polymer solution are often used for preparing Sn/C composite nanofibers. When soluble inorganic salt precursor is used as the precursor for electrospinning, CNFs containing uniformly distributed Sn nanoparticles are usually obtained; but Sn nanoparticles are prone to forming micron-sized Sn spheres on the surfaces of CNFs, due to the high molecule mobility and low melting point of Sn. As a result, the aggregate of micron-sized Sn spheres can cause a decrease in the reversible discharge/charge capacities of LIBs [22–26]. When SnO_2 nanoparticles are used as the precursors for electrospinning, Sn nanoparticles with a lowered mobility can be encapsulated in the fibers and prevented from precipitation owing to the restriction by the carbon matrix [27,28]. This strategy, however, faces a key challenge in realizing the homogeneous distribution of the Sn nanoparticles confined in the carbon matrix [29,30].

In the present research, therefore, we adopt highly dispersed antimony-doped tin oxide (ATO) wet gel as the precursor to fabricate Sn-SnSb/C nanofibers by electrospinning, hoping to construct high performance Sn/C anode material for LIBs. The ATO wet gel with a high content of water can be uniformly dispersed in the solution, which is beneficial to the homogeneous distribution of Sn and SnSb nanoparticles in CNFs, and ATO wet gel also can help to prevent the agglomeration and precipitation of the nanoparticles on the surface of CNFs. As a result, the as-prepared Sn-SnSb/C nanohybrids exhibit excellent rate capability and long-term cyclability, showing great potential as the anode material with long cycle life and high-energy density for LIBs.

2. Experimental

2.1. Materials

Polyvinylpyrrolidone (PVP, $M_W = 1,300,000$) was purchased from Aladdin. Tin powder (99.5%, 200 mesh) was purchased from Sinopharm Chemical Reagent Co., Ltd. Antimony oxide was purchased from Tianjin Kermel Chemical Reagent Co., Ltd.

2.2. Fabrication of wet ATO precursor slurry

The as-received Sn powder and antimony oxide were added into distilled water; and then nitric acid was slowly dripped into the distilled water until all the tin and antimony oxide were dissolved to form a transparent solution. Upon completion of nitric acid addition, H_2O_2 was dropwise added into the transparent solution within 30 min, followed by the addition of ammonium hydroxide to afford a precipitate. The as-obtained precipitate was washed with distilled water and filtered to provide the ATO precursor slurry. Corresponding X-ray diffraction (XRD) pattern (Figure S1) indicates that the raw materials are mainly transformed to SnO_2 after the reaction. Relevant transmission electron microscopic (TEM) image (Figure S2) shows that the ATO gel has a size of about 5–10 nm and exhibits a uniform size distribution. Moreover, the as-prepared ATO wet gel precursor was not dried in order to keep its good dispersibility.
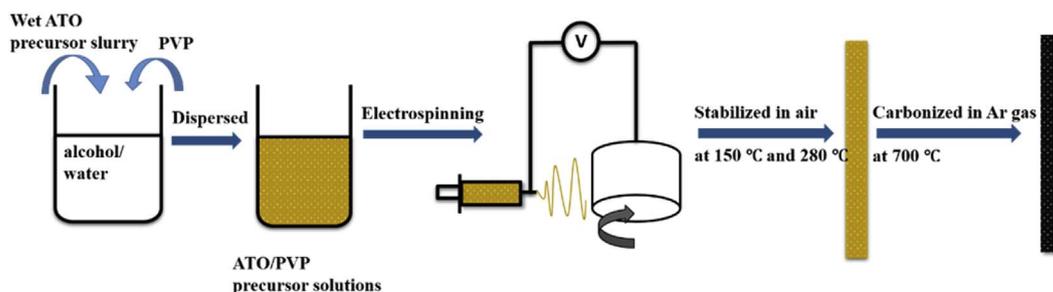
2.3. Fabrication of Sn-SnSb/C nanofibers

A proper amount of the wet ATO precursor slurry (0.3 g, 0.6 g, 0.9 g, and 1.2 g) was separately dispersed in 20 mL of the mixed solvent of ethanol/distilled water (3:1) and sonicated for 30 min. Then 2.4 g of PVP was added into the ATO precursor solutions under magnetic stirring for 24 h to obtain homogeneous solutions. The resultant homogeneous solutions were separately inhaled into a 5-mL syringe with a 21-gauge stainless steel needle. A 15 kV direct current (DC) voltage was applied between the needle and the stainless steel meshwork (the needle was kept 20 cm away from the stainless steel meshwork) while the mixed solution was fed at a rate of 0.25 mm min^{-1} to conduct electrospinning. The electrospun ATO/PVP nanofibers were stabilized at 150 °C in air for 24 h and then stabilized at 280 °C in air for 2 h, followed by carbonization at 700 °C in Ar atmosphere to form Sn-SnSb/C hybrid nanofibers. As-prepared Sn-SnSb/C nanofibers are denoted as P-ATO-0.3, P-ATO-0.6, P-ATO-0.9 and P-ATO-1.2, respectively (the numeral suffixes refer to the weight of ATO in gram). The experimental procedure for fabricating Sn-SnSb/C hybrid nanofibers is shown in Scheme 1.

For a comparative study, we also fabricated Sn-C hybrid nanofibers with $SnCl_2$ as the precursor. The details about the fabrication of Sn-C hybrid nanofibers are described in supporting information, where P-ATO-0.9 is cited as the example. In other words, P-$SnCl_2$-0.9 was prepared with 0.9 g of $SnCl_2$ precursor (the content of active materials used is the same as that of P-ATO-0.9) and used for the comparative study.

2.4. Characterizations

The morphology of various as-prepared nanofibers was observed with a transmission electron microscope (TEM; JSM-2010, JEOL Ltd., Japan), a field emission transmission electron microscope (FETEM; Tecnai G2 F20, FEI Company, USA) and a scanning electron microscope (SEM; Nova NanoSEM 450, FEI Company, USA). The crystallographic structure of the as-prepared products was identified by X-ray diffraction (XRD; Bruker, D8 Advanced; Germany, Cu-$K\alpha$ radiation, wavelength

Scheme 1. Schematic illustration of the fabrication of Sn-SnSb/C nanofibers by electrospinning.