Nanostructured Antimony/carbon Composite Fibers as Anode Material for Lithium-ion Battery

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ABSTRACT

Antimony/carbon (Sb/C) composite fibers with Sb nanoparticles uniformly dispersed in carbon matrix have been successfully fabricated by a facile spinning approach and the subsequent calcination in argon flux. As the anode materials of lithium-ion battery, experimental results reveal that the increase of Sb concentration enhanced the lithium-ion storage capacity and worsened the cycling performance. Carbon matrix could efficiently buffer the volume change and maintain the integrity of electrode during the lithiation/delithiation, improving the cycling capability. Among the Sb/C composite fibers, the sample (Sb5) with appropriate carbon content of ca. 50.1 wt% achieves a reversible capacity of 315.9 mAh g^{-1} after 100 cycles at a current density of 100 mA g^{-1} and the capacities of 464.4, 395.4, 328, 246.2 and 149.8 mAh g^{-1} at 100, 200, 400, 800 and 1600 mA g^{-1}, respectively. Electrochemical impedance spectroscopy (EIS) results indicate that Sb5 shows more superior charge transfer rate and Li-ion diffusion ability than the samples with high Sb concentration (Sb6) or carbon concentration (Sb4), finally resulting in better capacity retention and rate performance.

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1. Introduction

Lithium-ion batteries (LIBs) have attracted considerable attention as environment friendly power sources for removable electronic devices. Although graphite (LiC$_6$: 372 mAh g^{-1}) is used as the anode material for Li-ion secondary batteries, the search for higher-capacity materials is being actively pursued to meet the fast-growing requirements of high-power Li-ion batteries [1–4]. A large number of studies are focusing on IV main group (Si, Ge, Sn) and V main group (Sb, Bi) elements because of their larger theoretical lithium storage capacity than graphite [5–9]. Their commercial utilization, however, is still hindered by the poor capacity retention during cycling, which exhibits rather huge capacity loss at the first charge/discharge cycle as well as fading capacity upon cycling [10–12]. The main reason is attributed to the severe volume expansion/contraction that accompanies the lithium insertion/extraction process, besides the resulting pulverization and aggregation of electrode materials [8,13–16].

Recently, downsizing materials with nanoscale is one of most popular approaches for improving the electrochemical performance of these electrodes [17–19]. It is supposed that the nanostructured materials could provide a series of better properties including (i) the larger specific surface area, which results in a decrease of charge/discharge capacity loss; (ii) a shorter diffusion length for Li-ion transport, which leads to a faster rate capability; and (iii) combating the stress of lithium insertion/extraction, which causes the increase of cycling life [8,10,17]. However, the nanosized metals are much easy to aggregate into larger particles and then pulverize again [3,5,11,20]. To solve this problem, the use of active/inactive nanocomposite, in which the active one reacts with lithium and the inactive one serves as a buffer, is extensively accepted [8,21–23]. Among them, composites of metal and carbon (amorphous or graphite) have been widely investigated since carbon not only served as a buffer to cushion the stress from volume expansion of active materials and maintained the structural integrity of anode materials during cycling, but also prevented the aggregation of metal particles [24–27]. Many studies have presented that the Sb/C composites showed an enhanced electrochemical performance comparing with no matter the unsupported antimony or carbon, for combining the high capacity of antimony and the stability of carbon [28–30]. Metallic antimony could react with lithium-ions to form the alloyed Li$_3$Sb, consequently the gravimetric capacity of Sb is 660 mAh g^{-1} as high as about twice of the capacity of graphite, improving the reversible capacity of LIBs [16,31,32]. More recently, the composites of antimony and carbon nanotubes (Sb/CNT), antimony and graphite

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(Sb/graphite), and morphology controlled antimony and carbon (Sb/C) have also been fabricated and exhibited good lithium-ion storage performance [6,24,28]. Inspired by the above researches, it is anticipated that the superior lithium-ion storage performance could be realized from Sb/C composite fibers since the fiber morphological carbon matrix can not only buffer the volume expansion and hinder the aggregation of Sb nanoparticles, but also provides a long-distance pathway for electrons transport and supports numerous active charge-transfer sites [25,33–35].

In this work, nanostructured Sb/C composite fibers were prepared from the lab-made antimony chloride ($SbCl_3$)/polyvinyl butyral (PVB) precursor fibers by carbonizing PVB in argon to form carbon matrix and reducing $SbCl_3$ to form Sb nanoparticles by carbon. The electrochemical measurements demonstrate that the as-prepared Sb/C composite fibers exhibit superior cycling and rate performances.

2. Experimental

2.1. Materials

Antimony chloride ($SbCl_3$) was purchased from Sinopharm Chemical Reagent Co. Ltd. And polyvinyl butyral (PVB, Mw = 170,000–250,000) was supplied by Aladdin Chem. Co. Ltd. Methanol (CH_4O) is used as solvent. All chemicals are of analytical grade and were used as received without further purification.

2.2. Preparing of Sb/C composite fibers

In a typical synthesis, 4 g PVB were dissolved in 40.0 mL absolute methanol under magnetic stirring at 60 °C to obtain a clear solution and further concentrated at 40 °C to reach an adaptive viscosity for spinning into continuous fibers. Then, 5 g $SbCl_3$ were added into the above viscous solution and the $SbCl_3$/PVB precursor fibers were fabricated by spinning using our lab-made spinning apparatus. The precursor fibers were dried in an oven at 60 °C for 12 h to remove the solvent (methanol). The final Sb/C composite fibers were obtained by carbonizing the dried $SbCl_3$/PVB fibers at 600 °C for 2 h in argon with a heating rate of 3 °C min^{-1}, and designated as Sb5. For comparison, the products with other $SbCl_3$/PVB mass ratios of 4:4 and 6:4 were also prepared under the same experimental conditions as those of Sb5, and assigned as Sb4 and Sb6, respectively.

2.3. Characterization

The structure of the resultant products was determined by X-ray powder diffraction (XRD) on a Rigaku D/Max-RC X-ray diffractometer with Ni filtered Cu Kα radiation (λ = 0.1542 nm, V = 40 kV, I = 40 mA) in the range of 10–80° at a scanning rate of 4° min^{-1}. Raman spectra were obtained by a Renishaw confocal Raman microspectroscopy (Renishaw Co. Ltd. Gloucestershire, U. K.) with a laser excitation wave length of 780 nm. In order to examine the morphology and microstructure of samples, A JSM-6700F field emission scanning electron microscope (FE-SEM) at an accelerating voltage of 15 kV and an electric current of 1.0×10^{-10} A and a JEOL JEM-2100 high-resolution transmission electron microscopy (HR-TEM) with an accelerating voltage of 200 kV were used. X-ray photoelectron spectra (XPS) were recorded on a Kratos Analytical spectrometer, using Al Kα ($h\nu$ = 1486.6 eV) radiation as the excitation source, under a condition of anode voltage of 12 kV and an emission current of 10 mA. Thermogravimetric (TG) analysis was performed from ambient temperature to 800 °C in air at a heating rate of 5 °C min^{-1} using a SDT thermal-microbalance apparatus to evaluate the carbon content.

2.4. Electrochemical Measurement

To prepare the working electrode, the active material, carbon black, and polyvinylidene fluoride (PVDF) with a weight ratio of 8:1:1 were mixed in N-methyl-2-pyrrolidinone (NMP) to form a homogenous slurry, which was coated on a copper foil substrate, followed by drying in a vacuum oven at 120 °C for 12 h. The CR2025-type cells were assembled using Li foil as counter and reference electrode, Celgard 2300 as separator, and 1 M LiPF$_6$ (dissolved in ethylene carbonate, dimethyl carbonate, and ethylene methyl carbonate with a volume ratio of 1:1:1) as electrolyte. The assembly was performed in a glove box filled with argon atmosphere. The performance of the cells was evaluated galvanostatically in the voltage range from 0.02 to 3 V at various current densities on a LAND CT2001A battery test system.

Cyclic voltammogram (CV) was obtained by an IVIUMSTAT electrochemistry workstation with a scanning rate of 0.1 mV s^{-1} and the potential vs. Li/Li$^+$ ranging from 0.01 to 3 V. Electrochemical impedance spectra were tested on the same instrument with AC signal amplitude of 10 mV in the frequency range from 100 kHz to 0.01 Hz. The data were adopted to draw Nyquist plots using real part Z′ as X-axis, and imaginary part Z″ as Y-axis.

3. Results and Discussion

3.1. Characterizations of Sb/C composite fibers

The phase and purity of Sb5 are investigated by XRD. As shown in Fig. 1, all diffraction peaks can be well indexed to the rhombohedral Sb (JCPDS 35–0732), and no other diffraction peak was detected, indicating that Sb^{3+} ions in the precursor fibers have been completely reduced to Sb by carbon. The diffraction peaks of carbon were not found in the XRD pattern, suggesting that the polymer PVB has been transformed into amorphous carbon during the carbonization process. Finally, the Sb/C composite fibers were obtained. The carbon form of Sb5 is determined by Raman spectroscopy. As shown in Fig. 2, the broad peak located at 1324 cm^{-1} is assigned to the D band of carbon materials, confirming the existence of amorphous carbon. The other peak of G band at ca. 1580 cm^{-1} represents graphitic carbon [36,37]. The intensity ratio of the two peaks (I_D/I_G) could be used to evaluate the disordered degree of carbon materials. The I_D/I_G ratio of ca. 1.0 for Sb5 demonstrates the low graphitization degree of the carbon matrix, which will be favorable to the electrochemical performance [38,39].

To evaluate the carbon content in the samples, TG analysis have been carried out and the TG curves of products Sb4, Sb5 and Sb6 were given in Fig. 3. The slight weight loss below 300 °C is mainly associated to the evaporation of water absorbed on the surface of samples. The dominant weight loss after 400 °C, which is
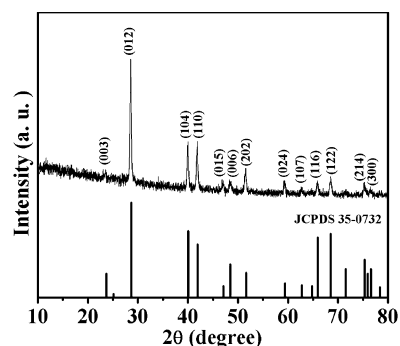

Fig. 1. XRD pattern of product Sb5.