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Synthesis and characterization of Sb/CNT and Bi/CNT composites as anode materials for lithium-ion batteries

Yanna NuLi *, Jun Yang, Mingshan Jiang

Dpartment of Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China

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Abstract

Sb/CNT and Bi/CNT composites were prepared by a heating treatment method. SEM imaging showed that the metal particles were uniformly deposited on the CNTs exterior and in the CNTs web. It was found that the composites showed improved cyclability than unsupported Sb and Bi and higher reversible capacities than CNTs. The improvement may be attributed to the small-scale dimension and high dispersion of the metal particles and the conductivity and ductility of the CNTs matrix. Moreover, the first reversibility was also increased comparing to CNTs, resulted from the lower surface of the composites.

Keywords: CNTs; Sb and Bi; Composites; Anode; Lithium-ion batteries

1. Introduction

Carbonaceous materials are commonly commercialized anodes in lithium-ion batteries, but higher capacity alternatives such as Al, Si, Sn, Bi and Sb that could alloy lithium, have shown a renewal interest as potential replacements for developing high performance lithium-ion batteries [1]. The major hindrance to their application is the poor cyclability and the mechanical instability caused by mechanical cracking due to the volume change occurring during lithium insertion and removal. In order to counteract the mechanical degradation, small particle size materials and composite materials containing active/inactive or less active phases have been investigated [2,3]. On the other hand, intermetallic lithium insertion compounds and mixed active material composites have also been proposed as alternative anodes [4–6]. Processes have further been developed to incorporate metal particles in a conductive matrix capable of reversible insertion/removal of lithium like carbon or graphite, which provides not only mechanical and conductivity support for the dispersed phase but also allows to add to the overall capacity of the composite material [7,8]. CNTs, duo to its particular morphology, structure, physical and chemical properties, are of great interest for much potential application [9]. As the host for the intercalation of Li, CNTs can exhibit good cycle stability but large irreversible capacity loss in the first cycle [10]. It has been reported active anode material-CNT such as SnO–CNT composite prepared by a sol–gel method showed an enhanced electrochemical performance compared with the unsupported SnO and CNTs, resulted from the conductivity and ductility of the CNTs matrix and the high dispersion of the SnO [11]. It has been proposed that CNTs play an important role for nanoparticles' nucleation, growth and coagulation processes in a novel nanosized SnO_2/CNTs composite prepared by homogeneous precipitation [12]. Nanocomposites of CNTs with Sb particles prepared by chemical reduction also exhibited improved cyclability compared to unsupported Sb particles and higher reversible specific capacities than CNTs [13]. Investigation by Ajayan et al. showed bismuth could be successfully filled the nanotube in the presence of oxygen by heating closed tubes with Bi metal in air at ~850 °C [14] and C-h. Kiang examined the feasibility to produce bismuth-filled CNTs by heating solid bismuth nanoparticles with single-walled CNTs [15]. However, the electrochemical performance of the composites was not studied. In this work, composites of CNTs with Sb and Bi particles were prepared by simple heating-treatment method, and their

* Corresponding author. Tel.: +86 21 5474 5887; fax: +86 21 5474 1297.
E-mail address: nlyn@sjtu.edu.cn (Y. NuLi).

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Table 1
Comparison of performance for Li insertion (discharge) and extraction (charge) reactions between 0 and 1.5 V at 25 mAh g^{-1} (capacity in mAh g^{-1}) for the materials in this work

Electrode	1st discharge	1st charge	1st coulombic efficiency (%)	50th charge	R50/1 (%)
CNT	469.3	226.2	48.2	221.7	98.0
Sb	844.5	523.6	62.0	255.2	48.7
Bi	565.7	339.4	60.0	117.9	34.7
Sb/CNT	796.7	448.6	56.3	277.4	61.8
Bi/CNT	570.1	308.4	54.1	170.6	55.3

R50/1 is defined as the fiftieth/the first charge capacity.

predominance to unsupported Sb, Bi or CNTs in Li^+ insertion and extraction reactions were examined (shown in Table 1).

2. Experimental

2.1. Material preparation

Two grams of Bi powder, Sb powder and fifteen stainless steel grinding balls were placed in a 80 ml stainless steel grinding bowl in an argon-filled glove box, respectively, and milling was performed at 250 rpm for 2 h in a planetary ball mill. Bi/CNT composite was prepared by heating ball-milled Bi powder and CNTs with 60:40 wt.% at 850 °C for 5 h in air. After cooling automatically, the precursor was then gradually heated to 450 °C under Ar/H_2 (5% H_2) for 2 h to remove the oxidation group. Sb/CNT composite was prepared by heating ball-milled Sb powder and CNTs with 60:40 wt.% in air at 850 °C for 5 h, subsequently heat-treating at 700 °C in Ar/H_2 for 2 h. The resulting composite samples were ball-milled at 250 rpm for 2 h. Ball-milled CNTs were also obtained by milling CNTs with ethanol at 250 rpm for 2 h. The samples were characterized by XRD using a Philips 3100E diffractometer with Cu Kα radiation and SEM with a scanning electron microscope (Hitachi S 2150).

2.2. Cells assembling and electrochemical test

The electrochemical behaviors were measured via CR2025 coin-type test cells assembled in an argon-filled glove box. Electrodes were prepared by drying slurry (85 wt.% active material, 5 wt.% acetylene black and 10 wt.% polyvinylidene fluoride dissolved in N-methyl-2-pyrrolidinone) on a copper foil at 120 °C under vacuum. Lithium sheet acted as the counter electrode and Celgard 2700 membrane the separator. The electrolyte was 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in weight ratio). Discharge–charge measurements of the coin cells were carried out at 25 mA/g with voltage cut-off of 0/1.5 V vs. Li/Li^+.

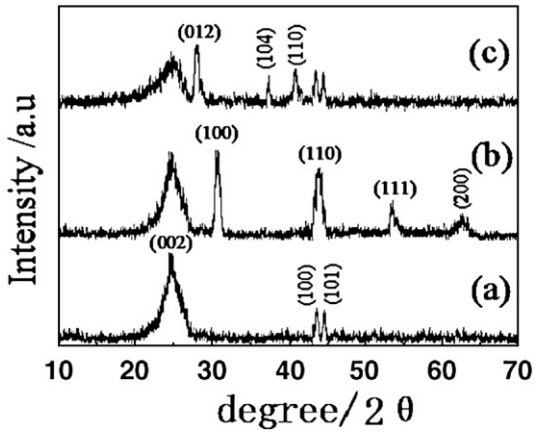

Fig. 1. The XRD patterns of (a) CNTs, (b) Sb/CNT composite and (c) Bi/CNT composite.

3. Results and discussion

Several composites with different metal/CNT weight ratios have been studied and better performance can be obtained for the composites

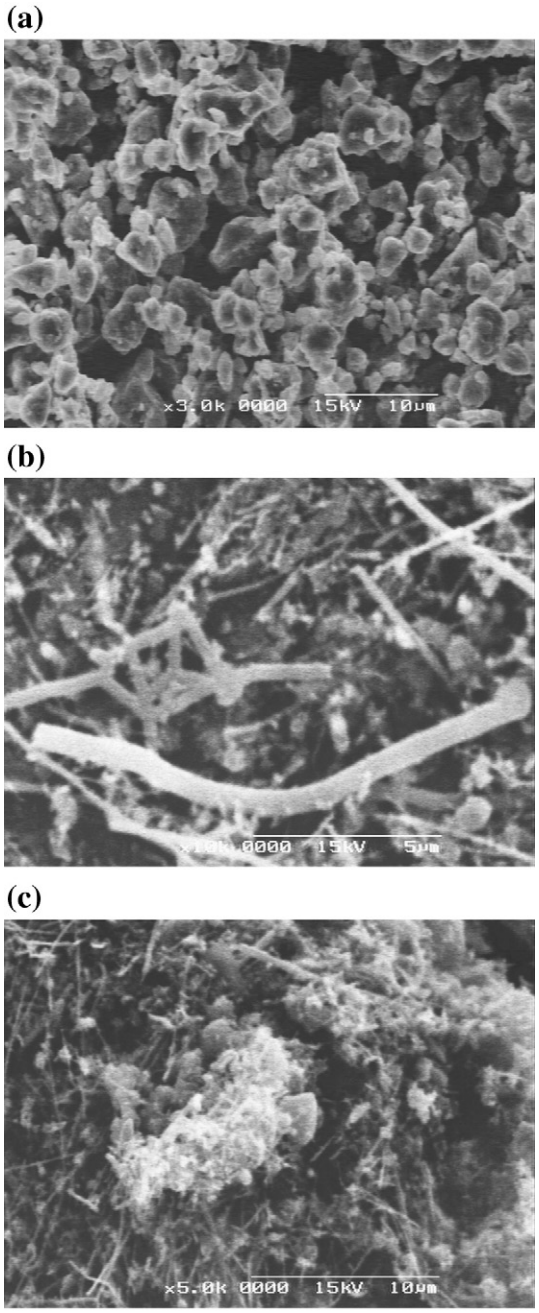

Fig. 2. SEM image of (a) Bi, (b) CNTs and (c) Bi/CNT composite.