



Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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



Carbon embedded SnSb composite tailored by carbothermal reduction process as high performance anode for sodium-ion batteries

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ARTICLE INFO

Article history:

Received 25 May 2017

Received in revised form 13 November 2017

Accepted 18 November 2017

Available online xxx

Keywords:

SnSb composite with carbon
Carbothermal reduction
Anode material
Sodium ion battery
Reaction mechanism

ABSTRACT

We report a facile and mass-producible carbothermal reduction process to synthesize a SnSb/C composite with enhanced conductivity through the small grains by restricting their size and aggregation. As-synthesized SnSb material consists of crystalline SnSb without residual oxide, and appears as a homogeneously distributed phase with carbon by XRD and TEM analysis. SnSb/C anode for Na-ion batteries exhibits outstanding electrochemical performances, showing a sodiation/desodiation capacity of 650/490 mAh·g⁻¹, 265 mAh·g⁻¹ at 4C rate, and 70% of capacity retention at 0.2C (100 mA·g⁻¹) over 200 cycles. SEM images of the after-cycled electrode does not show a significantly different morphology from the fresh electrode, indicating that the as-prepared SnSb electrode is free of pulverization caused by repeated sodiation/desodiation reactions. The electrochemical reaction mechanism of SnSb/C anode is suggested by ex-situ XRD measurements and high-resolution TEM analysis of fully sodiated and desodiated electrodes.

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Introduction

Lithium-ion batteries (LIBs) are widely used as the primary power sources for various portable devices such as cellular phones, laptop and tablet computers because of their high gravimetric/volumetric energy densities and superior long-term cyclabilities [1–4]. Worldwide energy and environmental concerns, and the growth of industries related to electric vehicles (EVs) and energy storage systems (ESSs), have greatly increased interest in LIBs. Large-scale secondary battery systems with high energy densities and excellent durabilities are urgently required to meet the increasing demands of EV and ESS applications. Among the rechargeable batteries, LIBs are considered as the leading candidates because of their many commercially successful applications in mobile electronic devices and some hybrid electrical vehicles [5,6]. However, lithium resources are constrained geographically over the earth and their costs are expected to increase dramatically because of the globally increasing demand for LIBs [7–10].

Among the other rechargeable batteries, the Na-ion battery (NIB) is also of interest because of unlimited sodium resources and its chemical similarity to the LIB [7,11]. An NIB has the same operating principle as an LIB: both are based on the reversible movement of alkali ions (Li⁺, Na⁺) between the anode and cathode. Furthermore, sodium belongs to the same group as lithium, indicating that the two elements have similar physical and chemical properties. These attributes suggest that NIB and LIB developments could follow similar paths. Hence, cathode materials for NIBs have been introduced in several forms, such as a layered structure [9,12,13], phosphate-type [14,15], and prussian analog [16,17]. Anode materials suitable for NIBs, however, are very challenging to develop because graphite with its typical interlayer spacing of 0.335 nm has too high energy barrier for the sodium intercalation process [18]. As an alternative to graphite, hard carbon has an improved electrochemical reversibility for sodium and a relatively high capacity of 300 mAh·g⁻¹ [19–21]. However, the limited capacity (<300 mAh·g⁻¹) and safety issues involved with the major reaction near the Na-metal plating potential are seriously concerned [22–25]. The high cost of hard carbon is also seen as barriers to the commercialization of NIBs. To address the drawbacks of hard carbon, alloy-able elements such as Sn, Sb, Se, and P with Na have received the attention; these alloys have much higher reversible capacities and safer reaction potentials [25–30].

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<https://doi.org/10.1016/j.jiec.2017.11.032>

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Unfortunately, as with LIBs, the huge volume expansion caused by the alloying reaction with sodium causes electrode pulverization, resulting in poor cyclic durability [30]. To overcome these obstacles, binary compounds such as SnSb, SnS₂, and Sb₂S₃, in which both elements can react with sodium electrochemically at different potentials, have been introduced [31–35]. They provide improved capacity and electrochemical performance, including stable cyclic durability and outstanding kinetic properties for the conversion reactions because of the buffering and conductive effects of the second element.

Among these binary compounds, SnSb has received particular attention as an anode material. The SnSb electrode has several advantages: (1) high theoretical capacity (752 mAh g⁻¹) compared with hard carbon (2) volume expansion can be suppressed by a ductile Sn phase; and (3) through the conversion and reconstruction reactions, the different reaction potentials of metallic Sn and Sb provide an electrically conductive network within the electrode that is maintained by residual unreacted Sn or Sb from the alloying reaction forming Na–Sn and Na–Sb during sodiation/desodiation. Previously, an SnSb composite synthesized by ball milling with carbon or TiC, and a reduced graphene oxide (RGO)-loaded SnSb prepared by hydrothermal and subsequent thermal reduction processes, have shown limited electrochemical performances induced by uncontrolled microstructure [31,32,36,37]. Besides, the above-mentioned synthetic processes are very complicated and energy-intensive, resulting in low yields and difficulty in scaling up.

We report here a simple, environmentally friendly, cost-effective and mass-producible carbothermal reduction process to prepare a SnSb/C composite with enhanced conductivity through the small grains by restricting their size and aggregation, besides creating a reducing atmosphere [38,39]. Its electrochemical performances were evaluated, from which related reaction mechanism was correlated for sodium-ion chemistry. A carbothermal reduction reaction of SnO₂ and Sb₂O₃ with polyvinylpyrrolidone (PVP) provided crystalline SnSb uniformly dispersed within a carbon matrix. The as-synthesized SnSb/C composite electrode exhibited superior electrochemical performance with a high reversible capacity of 490 mAh g⁻¹ at the 0.1C rate (1C = 500 mA g⁻¹), stable cycle performance over 200 cycles, and an outstanding rate capability, delivering 265 mAh g⁻¹ at 2 A g⁻¹ corresponding to 4C. Ex situ X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HR-TEM) analyses indicated that the SnSb/C composite reacted reversibly with sodium ion during sodiation and desodiation. Cyclic voltammetry (CV) also supported the reversible reaction mechanism with Na.

Experimental

Preparation of the SnSb/C composite

The SnSb composite with carbon was prepared by the following carbothermal reduction process. The precursor powders of Sb₂O₃ (Aldrich, 99.9%, <250 nm particle size), SnO₂ (Aldrich, 99.9%, -325 mesh), and polyvinylpyrrolidone (PVP) solution by dissolving PVP in distilled water at a weight ratio of 2:8, were mixed homogeneously. Super P as reducing agent for carbothermal reduction process was added to the above mixture at a molar ratio of Sb₂O₃(1): SnO₂(2): Super P(7). As-obtained mixture was heat-treated at 900 °C for 2 h under an Ar atmosphere to get the final SnSb/C composite. For the comparison, highly crystalline SnSb powder was also synthesized through the high energy mechanical milling (HEMM, Pluertes-5) of stoichiometric amounts of Sn (Aldrich, >99%) and Sb (Aldrich, >99.9%) powders for 10 h at 350 rpm under an Ar atmosphere and subsequent heat treatment at 300 °C for 2 h.

Material characterization

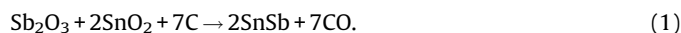
The as-fabricated SnSb and SnSb/C composites were characterized using XRD and HR-TEM. Ex situ XRD patterns of the SnSb/C composite electrode were used to observe structural changes at the fully sodiated and desodiated potentials. The powder collected from fully sodiated and desodiated electrodes was also examined by HR-TEM to clarify the reaction mechanism. Field-emission scanning electron microscopy (FE-SEM; HITACHI S-4800) was used to observe morphological changes of the electrode.

Electrochemical measurements

For the electrochemical evaluation, a slurry consisting of 70 wt% as-prepared SnSb/C, 15 wt% conducting agent (Super P), and 15 wt% polyacrylic acid dissolved in *N*-methylpyrrolidone as a binder was pasted on a copper foil substrate at a thickness of 10 μm. The as-coated electrodes were dried overnight at 120 °C in a vacuum oven. The mass loading of the electrodes was controlled at approximately 3–4 mg cm⁻². Coin-type (2032) electrochemical cells were assembled in an Ar-filled glove box using a glass microporous fiber having a thickness of 200 μm as the separator, Na metal as the counter and reference electrodes, and 1 M NaClO₄ dissolved in a mixture of ethylene carbonate and propylene carbonate (1:1 v/v) with 5 wt% fluoroethylene carbonate additive (Panaxetec Co., Ltd., Busan, South Korea). Galvanostatic charge/discharge tests were carried out at a potential window of 0.005–2.0 V (vs. Na/Na⁺) at various current densities (50–2000 mA g⁻¹) using a Maccor tester (Series 4600A) at room temperature. CV measurements were conducted at a sweep rate of 0.1 mV s⁻¹ at a potential ranging from 0.005 to 2.0 V (vs. Na/Na⁺) using a Biologic VMP3 instrument. Electrochemical impedance spectroscopy (EIS) was conducted with a frequency response analyzer (Biologic, VMP3) at frequencies ranging from 10 mHz to 1 MHz with an amplitude voltage of 5 mV.

Results and discussion

Simply heating the Sb₂O₃ and SnO₂ precursors at 900 °C led to the formation of highly crystalline SnSb according to Eq. (1):



The thermal energy supplied by the heat treatment was sufficient to break the Sn–O and Sb–O bonds in SnO₂ and Sb₂O₃, respectively, and form SnSb. Further heat treatment with PVP provided enhanced electrical conductivity and a buffering matrix during the electrochemical reaction with sodium. A highly

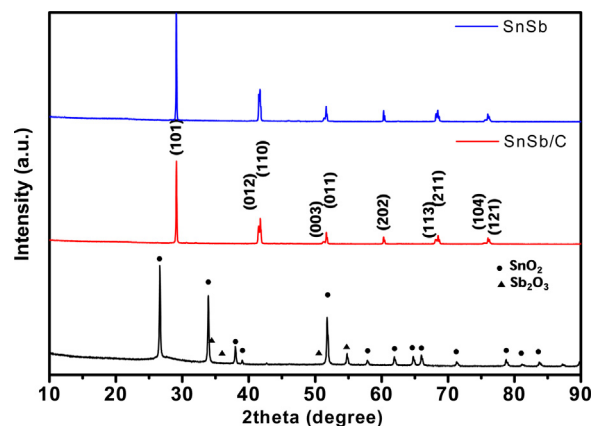


Fig. 1. XRD patterns of SnSb and the SnSb/C composite.

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