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Electrochemical investigation of SnSb nano particles for lithium-ion batteries

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ABSTRACT

The nanosized SnSb alloy was synthesized by a reductive co-precipitation method using $NaBH_4$ as a reducing agent. In order to get fine powder with uniformly distributed particles, the final product was sonicated and stirred for 48 h with isopropyl alcohol, dried at 100 °C and characterized by various techniques. Galvanostatic cycling results showed initial reversible capacities of 1300 and 1500 mA h g^{-1} respectively for Cu foil and Ni mesh current collector, at a constant current density of 60 mA g^{-1} in the potential range of 0.005–1.5 V. Upon increasing the potential window from 1.5 to 3 V, the initial reversible capacity of Cu foil increased to 1400 mA h g^{-1} whereas for Ni mesh, the same capacity of 1500 mA h g^{-1} is obtained. However, the capacity fading is found to be significantly lower in the Ni mesh compared to Cu foil. The coulombic efficiency of the Cu foil and Ni mesh current collector is better maintained at 99% in the potential window between 0.005–1.5 V in comparison with 0.005–3 V. The electrochemical impedance studies imply that the kinetic properties of Li^+ are very fast even after 50 cycles.

1. Introduction

Presently, lithium ion batteries (LIB's) play an important role in portable electronic devices such as cameras, laptops etc., because of their high energy density and long cycle life. In order to meet these requirements new anode materials have emerged to replace commercially used carbonaceous anodes [1–4]. The Sn, Si and Sb based anode materials have been widely studied due to their superior Li-storage and high specific gravimetric and volumetric capacities ($Li_{4.4}Sn$, 990 mA h g^{-1} Li/Sb: 660 mA h g^{-1} and $Li_{22}Si_5$: 4200 mA h g^{-1} [5–8]. However, alloy anodes have not been commercialized because of their high volume change during alloying and de-alloying reactions with Li^+. Continuous volume change during cycling will cause the mechanical pulverization of the electrode resulting in poor cyclability and cracking of the electrode. In order to overcome this problem, next generation anodes of intermetallic compounds [9], active/inactive nano-composite materials [10] and single phase instead of multiphase materials [11] have been widely studied. It is to be noted that nano-composite materials can reduce the volume change during a cycling process due to their small particle size and uniform particle distribution of the compound, which can alleviate the mechanical disintegration of the electrode and thus lead to low capacity fading with good cycling behavior.

Hence, in this article, we report SnSb nano-material that was prepared by a reductive co-precipitation method using $NaBH_4$ as a reducing agent. To obtain fine particle size with uniform particle distribution, the final product was ultrasonicated and stirred for 48 h with isopropyl alcohol. In order to improve the stability of the electrode and ensure a good electrical contact during volume expansion and contraction upon cycling, the electrode materials were coated on two different current collectors of Cu foil and Ni mesh. Electrochemical properties of SnSb nano material coated on Cu foil and Ni mesh were studied at two different potential ranges and the results are discussed here.

2. Experimental details

Nanosized SnSb powders were fabricated by reductive co-precipitation of the metal chloride salts as follows: raw materials (Merck, AR grade) taken for solution A were 1 mol of $SnCl_2 \cdot 2H_2O$, 1 mol of $SbCl_3 \cdot H_2O$ and 0.5 mol of $C_6H_5Na_3O_7$ (sodium citrates) and solution B is made of 1.5 mol of each NaOH and $NaBH_4$ respectively, as reducing agents. These two solutions were titrated

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(i.e. the solution A is slowly mixed with solution B under continuous stirring). The resultant precipitate was filtered and washed with distilled water, 0.35 M HCl and acetone several times before being dried at ambient temperature. After that, the final products were dissolved in isopropyl alcohol using ultrasonicator and magnetic stirrer for 48 h and then dried at 100 °C for 24 h. The final product was characterized by various techniques.

The structure and morphology of the samples were examined by X-ray diffraction (XRD,–SHIMAZDU-6000) using Cu-Kα radiation source and transmission electron microscope (TEM, –PHILIPS TECNAI-FE12), respectively. Raman studies were carried out using a Renishaw micro Raman spectrometer (Model-INVIA, λ=514 nm-Ar ion laser). The slurry was prepared using 70 wt% of SnSb, 15 wt% of super P carbon and 15 wt% of PVDF dispersed in appropriate amount of NMP (N-methyl pyrrolidinone) and the slurry was coated on Cu foil and Ni mesh (16 mm circular diameter). Then the electrodes were kept in vacuum oven for drying at 70 °C for overnight. The batteries were assembled in an Argon filled glove box by using active materials as an anode, Li metal as counter electrode and 1 M $LiPF_6$ in EC/DMC (1:1) as electrolyte. The fabricated coin cells were studied electrochemically by using galvanostatic cycling (GC) (Bitrode battery tester (model SCN, Bitrode, USA)), cyclic voltammetry (CV) (MacPile II, Biologic, France) and electrochemical impedance spectroscopy (EIS). The GC test was carried out at two different potential ranges of 0.005–1.0 V and 0.005–3.0 V vs. Li, at a current density of 60 mA g^{-1} and CV was carried out in the potential range of 0.005–3.0 V. The electrochemical impedance measurements were carried out using Solartron/Gain-phase analyzer (model SI 1255) and the plots are recorded by applying an AC signal of 10 mV amplitude over the frequency range from 0.18 MHz to 3 mHz at room temperature and the data was analyzed by Z-view software.

3. Results and discussions

XRD pattern of Fig. 1(a) can be indexed to the well-known rhombohedral β-SnSb phase (JCPDS 33-0118) [10,12] with the space group, R-3m (Space Group: 166). No discrete oxide peak and impurity phases (except a minor peak at 40°) were detected in the sample indicating that the elemental Sn and Sb had been completely reduced from their chlorides to form single phase SnSb alloy by a solution reduction method. All the diffraction peaks are sharp, which is an indication of good crystallinity and shows low crystallite size of ~11 nm. For further confirmation of SnSb alloy, Raman spectroscopy was carried out. Raman spectrum of Fig. 1(b) shows two specific emission peaks at 440 cm^{-1} and 680 cm^{-1} indicating the formation of SnSb nano alloy [13]. TEM image (Fig. 1(c)) shows the agglomerated particles of SnSb. The aggregated particles are spherical and uniformly distributed with lower dimension around 20 nm in diameter.

A few selected galvanostatic charge (de-lithiation)–discharge (lithiation) cycling profiles of SnSb nanoparticles are shown in Fig. 2(a and b). Lithium ion insertion–extraction for all potential ranges and coulombic efficiency vs. cycle number are shown in Fig. 2(c–f), respectively. To study the effect of operating voltage on electrochemical properties, the SnSb material was tested in two different potential ranges of 0.005–1.5 V (CSLV) and 0.005–3 V (CSHV) for Cu foil and 0.005–1.5 V (NSLV) and 0.005–3 V (NSHV) for Ni mesh at a constant current density of 60 mA g^{-1}, respectively. For both potential ranges the Cu foil and Ni mesh electrodes show a first cycle intercalation potential plateau of nearly 1 V. Comparing both potential ranges at after 50 cycles, very mild intercalation potential differences of 0.6–0.8 V is observed in Cu foil and Ni mesh electrodes. This indicates higher stability of SnSb alloy electrodes during the cycling process [14]. The initial reversible capacity of 1500 mA h g^{-1} is observed for both potential ranges of Ni mesh, whereas Cu foil shows slightly lower capacity of 1300–1400 mA h g^{-1} for both the ranges. The increased initial reversible capacity of Ni mesh electrode might be due to the increased surface area of the mesh which would contain a higher quantity of active material (20–22 mg), suggesting more solid electrolyte interface (SEI) film formation in Ni mesh electrode than the Cu foil (3–4 mg). The SEI film formation is mainly due to the decomposition of the electrolyte

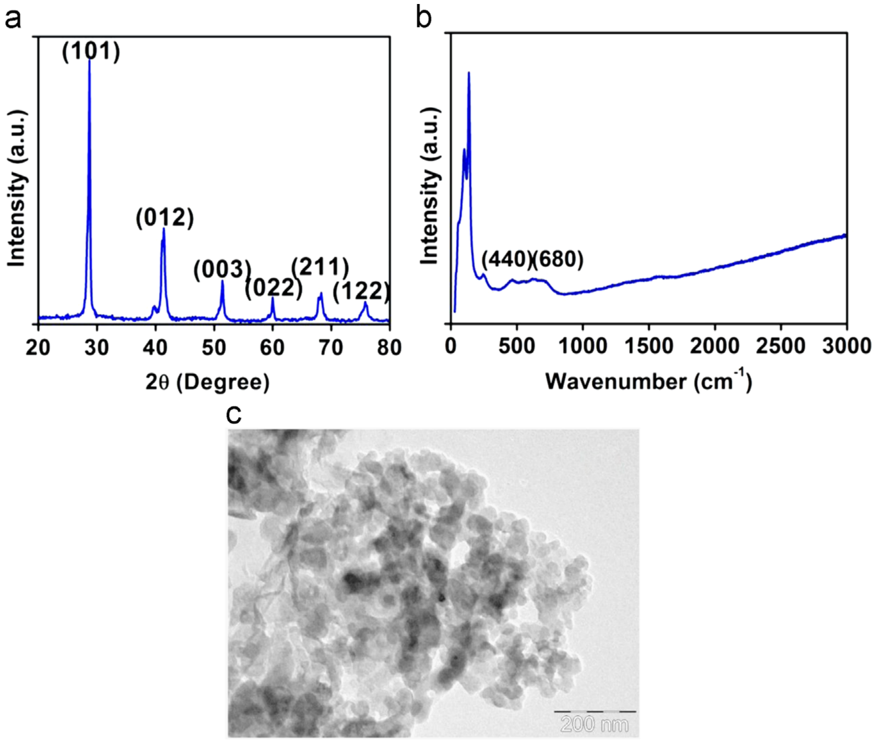

Fig. 1. (a) XRD diffraction, (b) Raman spectrum and (c) TEM microscope of SnSb alloy, scale bar 200 nm.