International Journal of NanoScience and Nanotechnology.
ISSN 0974-3081 Volume 2, Number 3 (2011), pp. 217-224

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The Best Route to Synthesis SnSb Nanoparticle with Low Distribution of Size

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Abstract

Nano-sized particles of Sn-Sb alloy powders were synthesized by three kinds of reductive precipitation methods: rapid mixing, slow (solution) titration and slow titration with microwave assistance. The structure and morphology of synthesized Sn-Sb alloy powders were evaluated by X-ray diffraction (XRD), scanning electron microscope (SEM), and transmission electron microscope (TEM). Slow, rapid mixed Sn-Sb alloy powders exhibit trace of parent materials and relatively large particle size (average) of 100-250 nm. In contrast, the microwave assisted Sn-Sb shows almost negligible influence from the parent material and a narrow size distribution (40-70nm). The particle size characterization through SEM, TEM and Dynamic Light Scattering in dispersed fluid agreed well with each other.

Keywords: Sn-Sb alloy; Nanoparticle; Microwave assisted synthesis; XRD; TEM; Lithium-ion Battery.

Introduction

In recent years, there has been a renewed interest in tin-based alloy materials as promising alternative anodes for graphite in Li-ion secondary batteries. Rechargeable lithium-ion batteries are widely used in various electronic devices, for the reason of ease in forming different shapes, possess low self discharge rate [1] and absence of any memory effect. Currently much attention has been paid on nano-sized powders and nanostructured materials such as nanowires [2], nanotubes [3], and nanocomposites [4] because of the increased surface area that provides more room for better lithiation and delithiation process.

Sn-Sb alloy exhibits excellent electrochemical properties as both Sn and Sb can be alloyed with lithium ($Li_{22}Sn_5$:994mAh/g, Li_3Sb:660mAh/g), and thus attracted attention of scientists [5, 6]. Since both the components of Sn-Sb alloy are active for lithium storage, the theoretical Li storage capacity of Sn-Sb alloy anode is very high and is expected to approach pure metals. In the literature, microsized Sn_2Sb alloy powder prepared by precipitation (rate of mixing not reported) when carbonized through mechanical milling has resulted in 5-10μm particle size, however the specific capacity fading is observed [7]. Li et al., [8] reported that dispersing nano-sized SnSb alloy on the surface of Hard Carbon Spherules (HCS) is an effective way and is prepared by reductive co-precipitation method and has to enhance the dimensional stability of nano-alloy particles during Li insertion and extraction. The pristine Sn-Sb [9] particle prepared by reductive co-precipitation method has resulted in high initial irreversible capacity due to the particle size of 200nm. Wang et. al., [10] reported that ultrafine Sn-Sb alloy anode materials synthesized by hydrogen plasma-metal reaction, showed the particle size of 100-300nm and has fading capacity. It is expected that the preparation method and the reduction in particle size would improve the characteristic of the electrode thus providing better performance. Discrepancy among the charge capacity versus size of the particle may be due to wide range of size distribution and the non-uniformity in morphology of the alloy employed. According to our knowledge there is no article for nano-sized SnSb alloy prepared by microwave assisted synthesis method. As these factors very much depend on the growth kinetics, this work focuses on the rate of precipitation of the particle obtained thereof.

Experimental

Two aqueous solutions were prepared with appropriate gram molecular weights for the synthesis of Sn-Sb powder, namely solution 1 formed by $SnCl_2.2H_2O$, $SbCl_3.H_2O$, and sodium citrates; and solution 2 constituted of NaOH and $NaBH_4$. The two solutions prepared were mixed together to obtain the required Sn-Sb alloy. In the process of mixing, one was titrated rapidly (resulting in sample A) [11], another was mixed slowly (resulting in sample B) and also another was subjected for microwave heating for few minutes followed by slow titration (resulting in sample C). Microwave heating was done for various durations and found that the results of the particle size were identical after 1minute and 30 seconds of heating. During the preparation of all the samples, the solutions were continuous by stirred for ensuring homogeneity. The precipitates thus obtained was filtered and subsequently washed with distilled water, 0.35 M HCl, and acetone followed by drying at 120°C in vacuum. The phase compositions and particle morphologies of synthesized Sn-Sb powders were characterized by X-ray diffraction (XRD) (SHIMADZU-XRD 6000), scanning electron microscopy (SEM) (JEOL-6390), Transmission electron microscope (TEM) (PHILIPS TECNAI-FE12) and particle size analyzer (Dynamic Light Scattering (DLS) (Metrohm-Nanotrac NPA253) respectively and the results are discussed further.

Results and Discussion

The XRD patterns of synthesized Sn-Sb alloy powders A, B and C are shown in Fig.1. The assignments of XRD patterns are made using ICDD data (card Number #33-0118 for of SnSb alloy, #650296 for Sn and #851234 for Sb) for sample C (microwave assisted SnSb alloy) and also assignments are made using the hexagonal formula $1/d^2 = 4/3[(h^2+hk+k^2)/a^2]+l^2/c^2$ for all the samples the a and c vales are almost same and is given in Table 1. The rapid titrated sample A showed minor parental traces of Sn whereas the slow titration (sample B) resulted in prominent peaks corresponding to Sn and Sb [11]. In sample C, peaks correspond to the complete formation of hexagonal phase of Sn-Sb [12]. The formation of nanosized particle and also the best formation of the alloy without residual parent material are accomplished due to the microwave heating process. In addition, the peak broadening in XRD peaks of microwave assisted preparation indicate size reduction in the crystallites than those of Fig. 1 (A) and (B). Using Scherrer equation,

$$t = 0.9\ \lambda/\beta\ \cos\theta$$

where, t is the average crystallite size in (Å), λ is the wavelength of the X-ray radiation (1.5416 Å), β is the full width at half maximum intensity of the peak and θ is the diffraction angle. The estimated average crystallite size for the slow and rapid mixing of Sn-Sb alloys (samples A&B) are 20-40 nm and microwave assisted Sn-Sb alloys are 14-15nm.

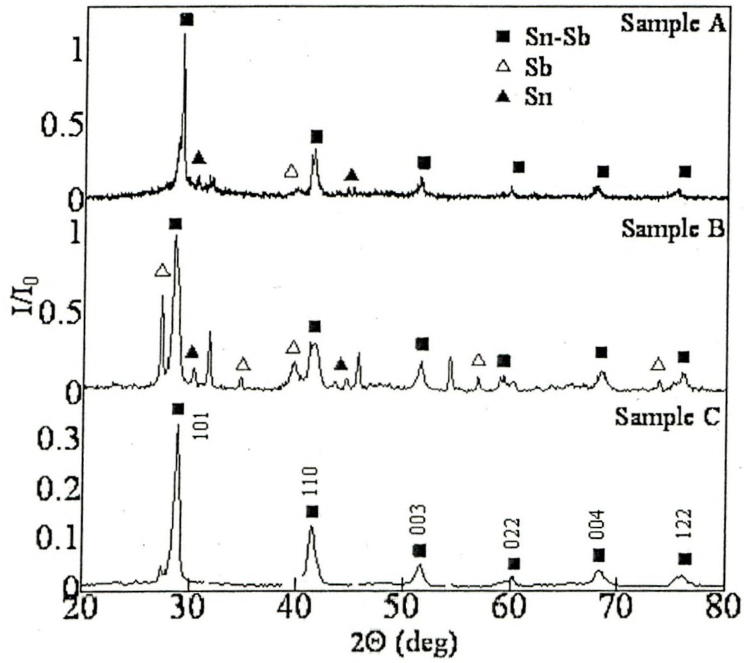

Figure 1: XRD pattern of Sn-Sb alloy powders prepared by rapid mixing (A), slow titration (B), and microwave assisted slow titration for 1min 30 secs (C).

Table 1: XRD data with assignments of hkl values using lattice constant 4.325Å, 5.346Å and hexagonal structure for sample C (microwave assisted SnSb alloy).

$d_{observed}$	$d_{calculated}$	I/I_0	hkl values	$2\theta_{observed}$	$2\theta_{calculated}$
3.10347	3.067576	100	101	28.7428	28.769
2.17447	2.1625	41	110	41.4947	41.777
1.77323	1.782	14	003	51.4948	51.274
1.53785	1.533788	5	202	60.1183	60.44
1.35998	1.3365	4	004	69	70.1
1.25403	1.251058	7	122	75.796	75.9

As a preliminary exercise, all the three samples were subjected for SEM analysis and the Fig. 2 illustrates the morphology of Sn-Sb alloy powders prepared by rapid mixing (A) slow titration (B), and microwave assisted slow titration (C) for 1minute and 30 seconds. Sample (A) shows more agglomerated spherical particle of size ~150 nm (average) and Sample (B) shows larger spheres of size ~ 250 nm (average) but with low agglomeration than sample (A) is observed through cleavages in the SEM picture, Fig 2 (B). Zhong Wang [10] reported that SnSb alloy prepared by hydrogen plasma-metal reaction have the particle size of 100-300 nm and Chaoli Yin [11] reported that SnSb alloy prepared by rapid and slow titration process and the particle size was ~350 nm. Also Fei Wang [9] reported that the particle size of SnSb is 200 nm prepared by co-precipitation method. On the contrary, SEM images of sample (C) showed the least particle size of 60 nm (average) and agglomeration is also reduced due to microwave processing. Hence, microwave assisted slow titration method is the best for obtaining the very low particle size. The histogram, Fig 2(D), shows a narrow distribution of microwave assisted Sn-Sb nanoparticles. Eventhough the agglomeration was minimal with microwave assisted preparation, minor agglomeration effects were observed locally at few spots.

In Fig. 3 TEM picture of synthesized Sn-Sb alloy powder by microwave assisted slow titration, the particle distribution is uniform and the size distribution is 50-80 nm and average particle size around 60 nm is obtained which is in very good agreement with the observed SEM results. Zhong Wang [13] reported hydrothermally prepared Sn-Sb alloy to possess particle size ranging between 50-200 nm. It is to be noticed here that the change in method to microwave with slow titration has resulted in more uniform and smaller particle size in Sn-Sb alloys.

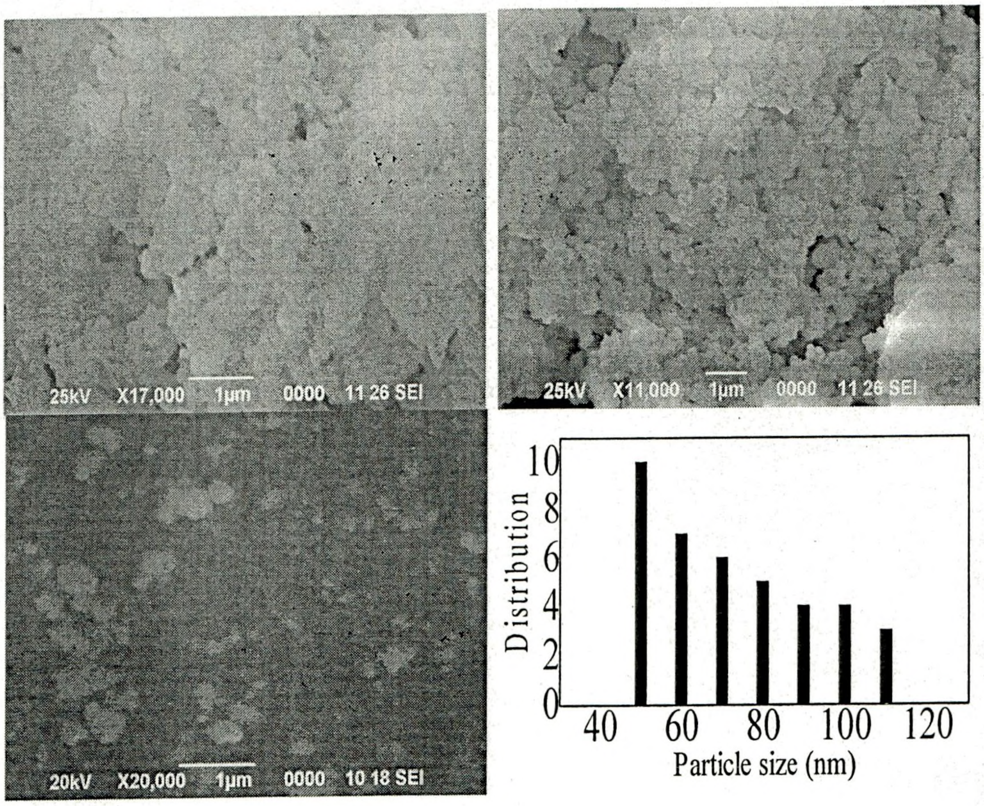

Figure 2: SEM images of Sn-Sb alloy prepared by A) rapid mixing, B) Slow titration, C) microwave assisted for 1min 30 secs, Fig 2(D) Distribution of microwave assisted Sn-Sb particle.

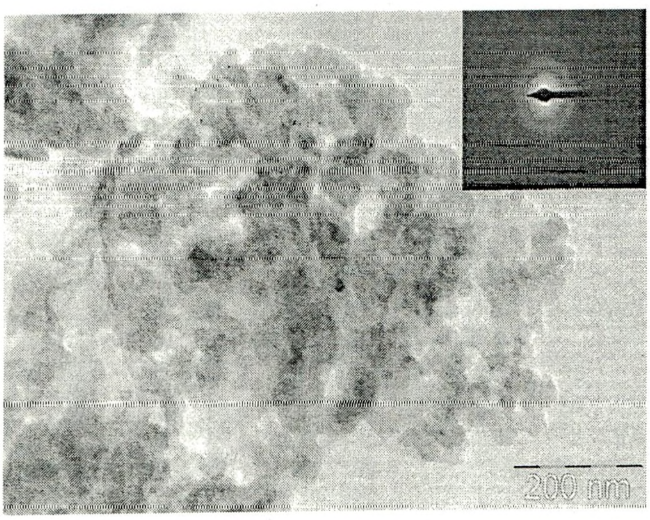

Figure 3: TEM images of Sn-Sb alloy prepared by microwave assisted slow titration.

For better perusing to view the particle size and to avoid agglomeration effects. Hence the result was crosschecked using the particle size analyzer in liquid medium using the particles are suspended and unfoliated in Carboxy methyl cellulose (CMC) medium and DLS is employed. Since, CMC has been reported as the best dispersant for many particles [14] have been chosen. Fig. 4 (a) and (b) shows the particle size analysis of microwaved Sn-Sb and Carbon Nanotube (CNT) dissolved in CMC. Carboxymethyl cellulose (0.4g) was added in 100 ml of ultrapure (distilled) water. CMC dispersed in water was found to contain particles of higher size (~ 500nm) which was observed using particle size analyzer which would result in around 500 nm, high background in a particle size measurement. Hence the medium was filtered through 200 nm Nylon filter. The filtered CMC was checked once again to ensure that there were no suspensions of CMC at all. The filtered CMC is used for suspending Sn-Sb alloy particles. As the viscosity of the dispersion medium is a highly influencing factor in particle size measurement in DLS technologies. The dispersant viscosity values of CMC - 3.60 cps at 26.5 deg C is measured using brookfeld viscometer is used in the instrument. With the CMC (50ml) solution, 20 mg of microwave assisted Sn-Sb sample C is added and homogenized by ultrasonication for 80 minutes and subjected for analysis. Fig 4 (a) shows the particle size distribution (30 – 80nm) of sample C obtained. Very few particles with 120 nm dimension, higher than 80nm, were observed. The average particle size of 54 nm (maximum in Fig.4a) agrees well with other measurements. The histogram width at 54nm shows a width of 0.05 indicating the occurrence of closely sized particles. It is to be noted that the particle size distribution is quite narrow (30 – 80nm).

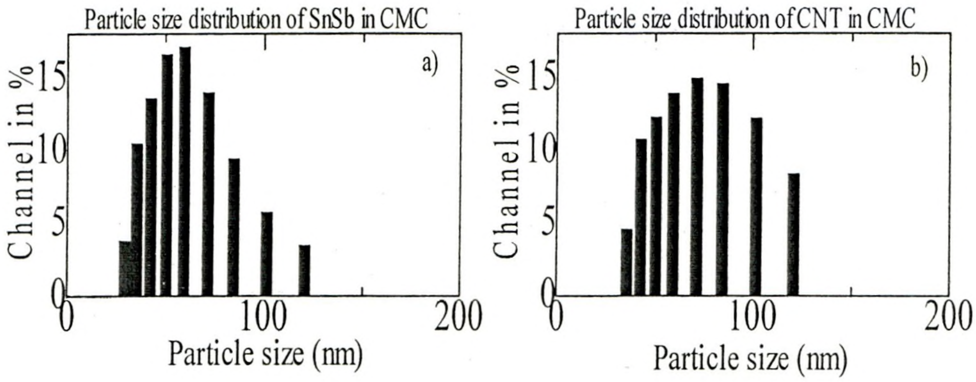

Figure 4: (a) Particle size analysis of microwaved Sn-Sb and (b) Particle size analysis of Carbon Nanotube (CNT)

For crosschecking the reliability of the analysis, CNT (Techno-korea) with CMC (Fig 4b) (0.4% CMC in water and sonicated for 80 mins similar to the previous preparation) is made as CNT would commonly have very lower particle size (≈20-40nm). The nanotubes possessed larger diameter distribution from 40 – 120 nm in the unfoliated condition. Hence the particle size distribution of microwave assisted Sn-Sb (sample C) and that of commercial Carbon Nanotube matches well with the analysis adding reliability to the data. It is confirmed that the size of the produced microwave assisted Sn-Sb alloy is narrow and nearly a uniform distribution of particle size exist. Therefore, the surface area of Sn-Sb may be equal to surface area of CNT. The Sn-Sb thus prepared by microwave assistance would be of greater expectation when employed in lithium battery anodes and is in the future scope.

Acknowledgement

The authors would like to acknowledge Dr.V.Saravanan, Defence metallurgical research laboratory (DMRL) Hyderabad for the TEM analysis. Also the authors acknowledge the suggestions rendered by Metrohm India Limited.

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