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Contributed Paper

Solution Route Preparation and Characterization of Dendrite InSb Powders, Anode Material for Lithium-ion Batteries

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ABSTRACT

Solution route method can be used to synthesize InSb compound, potential anode material for lithium-ion batteries. Stoichiometric amount of $InCl_3$, $SbCl_3$, and Zn powders were reacted in ethylene glycol to receive intermetallic InSb powders. The characterization of the as received product by XRD technique indicated 48% InSb volume fraction and some other impurities. From SEM results, the morphology of the product was observed to have dendritic structure. The selected area diffraction (SAD) pattern obtained from TEM technique verified the dendrite particles as InSb phase. High crystallinity InSb dendrite was also confirmed by TEM micrograph and its single crystal SAD pattern.

Keywords: Electron microscopy, indium antimonide, intercalation compound, lithium-ion battery, synthesis.

1. INTRODUCTION

The binary semiconducting compound InSb, with zinc-blende type structure (space group F43m (216)) exhibits interesting properties as a negative insertion material for lithium-ion batteries replacing graphite electrode for safety reasons [1-3]. Crystallographically, the zinc-blende framework also contains three dimensional interstitial sites suitable for lithium ion intercalation [3]. It was reported that InSb electrode prepared by ball-milling method provides approximately 340 mAh g^{-1}, which was relatively high compared to carbon based electrode [2]. However, the material produced by ball-milling process may introduce some residual stresses as well as particle agglomeration, which potentially reduce the cell performance [4]. Chemical route approach then came into attention and was proposed [5] with the objective to minimize these problems and more importantly the production cost. The theory concerning this method was reported elsewhere, which is analogous to the synthesis of Cu_6Sn_5 and Cu_2Sb compounds [5-7]. From those preliminary results, the intermetallic compounds were observed to precipitate out having a dendritic morphology. This morphology appeared to compose of nanometer-sized particles, which had very high surface area. Consequently, this experiment explored the synthesis of InSb compound by carrying the reaction out using the same condition as for the synthesis of Cu_6Sn_5 and Cu_2Sb compounds, which were ethylene glycol solvent, zinc powder (45mm particle size) reducing agent, and reacted at

room temperature. X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) techniques were employed for phase identification and morphological studies.

2. Materials and Methods

The preparation of InSb was conducted by dissolving stoichiometric amounts (equation (1)) of $InCl_3$ (Fluka, purity 98.0%) and $SbCl_3$ (Aldrich Chemical, purity 99.0%) in ethylene glycol (EG, JT. Baker, purity 99.0%) at room temperature. Zinc powder (Fluka, 45μm particle size) was gradually added to the solution. The reaction was continuously stirred for over 1 hour before it was filtered and washed by methanol (Merck, commercial grade). Finally, it was dried in the oven at 65°C for 30 minutes.

$$InCl_3 + SbCl_3 + 3Zn \rightarrow InSb + 3ZnCl_2 \quad (1)$$

As received product powder was characterized for the phases present by powder X-ray diffraction (XRD, siemen D500/D501, Cu Kα (λ1.54) Ni filter, 2θ = 10-80°, step:0.02°, step time: 1s) technique. A Scanning Electron Microscope (SEM) equipped with Energy Dispersive Spectroscopy (EDS) (JEOL JSM-6335F) technique was used to observe morphology of the product powder. Finally, nanometer scale morphology which is directly related to the crystallography of the phase present was determined by a Transmission Electron Microscope (TEM) equipped with Energy Dispersive Spectroscopy (EDS) (JEOL JEM-2010).

3. Results and Discussion

The XRD pattern of the product powder was presented in figure 1. There were three phases present; InSb, Sb metal (space group R-3m), and In metal (space group I4/mmm). By applying direct comparison method, the volume fractions of those phases were calculated using the integrated intensities of InSb (111), Sb (012), and In (101) peaks [8]. The product was found to consist of 48% InSb, 34% Sb and 18% In, by volume. Small fraction of InSb phase present may be explained by the insufficient electrons energy due to low reaction temperature, resulting in the presence of additional metallic phases. However, annealing the product powder at

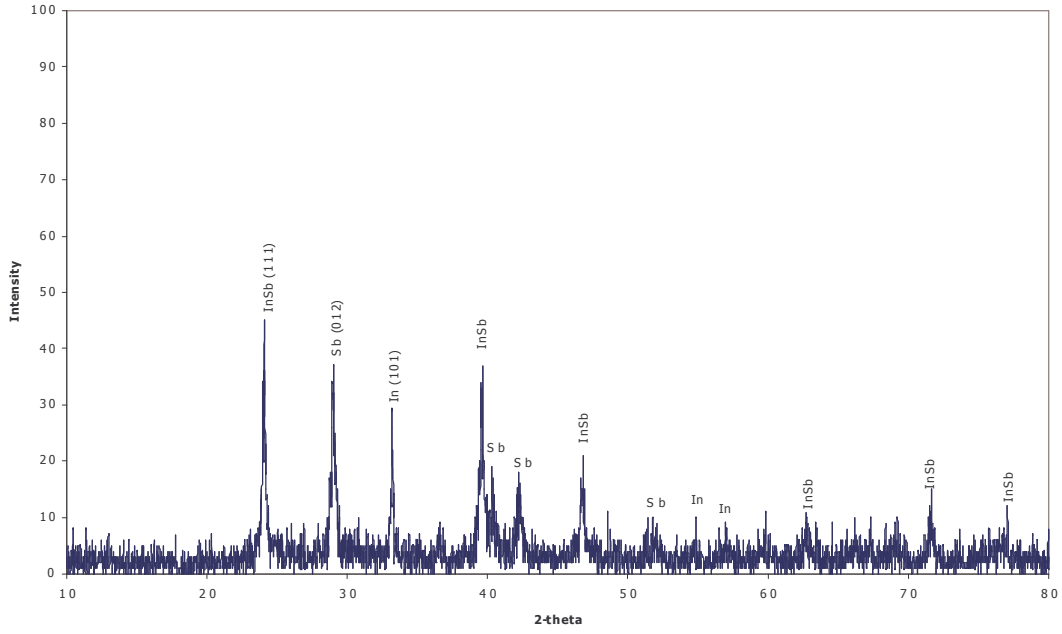

Figure 1. Powder XRD pattern of the as received product.

400°C under argon atmosphere can improve the formation of desired phase and the product was found to consist approximately 82% InSb, 16% Sb, and 2% In_2O_3 [5,7]. The existence of In_2O_3 was considered as due to the reaction between indium metal and the unremoved ethylene glycol solvent [5].

The morphology of the as received product observed by SEM technique was shown in figure 2. A dendritic structure with an average of 0.84-2.00 μm primary arms, 0.16-0.40 μm secondary arms, and 40-100nm ternary arms was discovered. Because of individual nano-particles attached to each other creating a specific dendritic structure, the surface area was assumed to be relatively high. This property is one of the key parameters needed for fast cell reaction and good capacity retention as well as long charge-discharge cycle life due to proportional of the particle size to the absolute dimensional changes [9-10]. The identification of dendrites was confirmed by TEM studies. The selected area diffraction (SAD) pattern taken from the dendrite particle as indicated in figure 3 was indexed as zinc-blende InSb compound. From the preliminary study, dendrites with lighter color were further determined as antimony metal [5]. It is interesting that high crystallinity in the intermetallic InSb dendrites can occur at this low temperature, indicating an advantage over other method by lowering the manufacturing cost of electrode material. It was also important to note that the growth of secondary arms was determined to be 60° angle from primary arms as well as between ternary and secondary arms. The crystallographic growth direction of the primary arm was measured to be (220) direction. The mechanism of dendrite formation was proposed [5-6] to involve a nucleation of the intermetallic compounds on the reducing agent particles and finally growing into dendrites. After zinc metal powder had all transformed into ions, detached dendrite particles were found to disperse in the solution.

The electrochemical properties of the annealed material were reported previously [7] to provide approximately 400 mAh g^{-1} in the first cycle and drop to 350 mAh g^{-1} in the second cycle followed by slow capacity fading in the subsequence cycles. The large irreversible capacity in the first cycle and capacity fading were assumed as due to Sb and In_2O_3

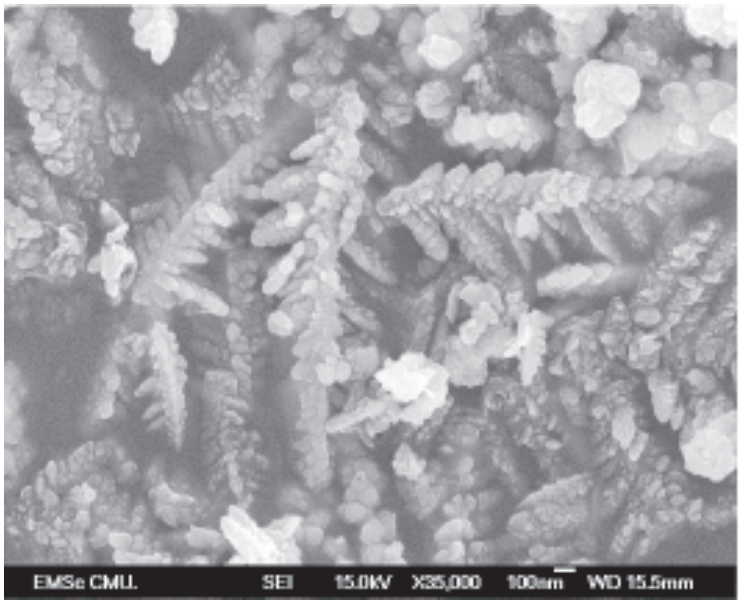

Figure 2. SEM micrograph of the as received product powder showing a dendritic morphology.

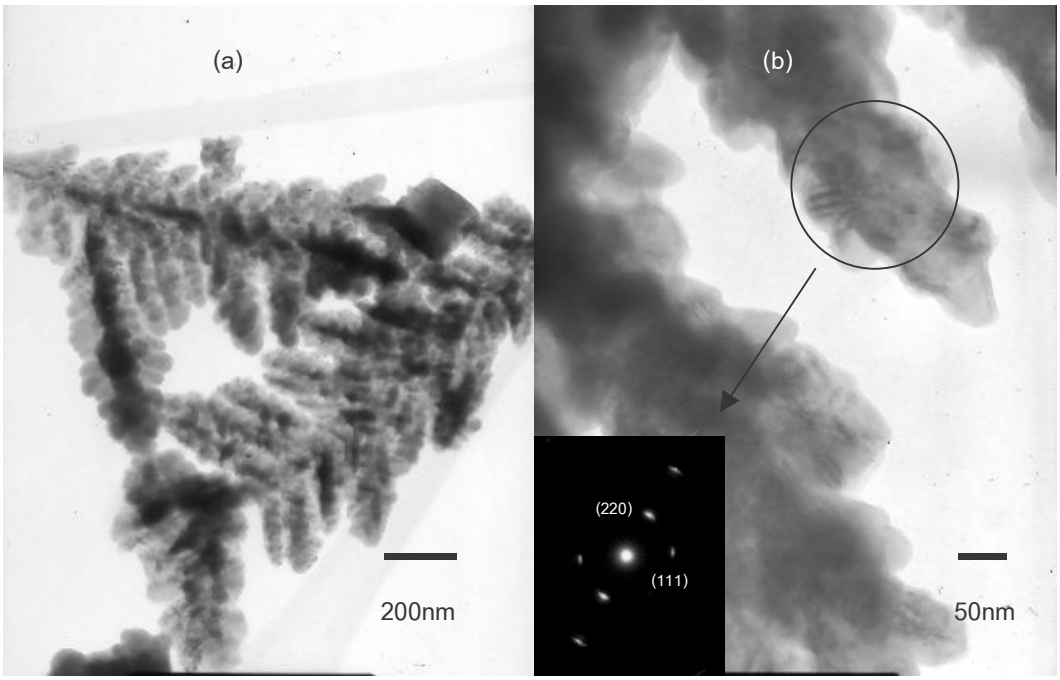

Figure 3. TEM micrographs showing (a) the dendrite particles and (b) the dendrite tip with the inserted single crystal SAD pattern corresponding to InSb phase.

impurities. The electrochemical performance of this material can be improved by minimizing these impurities. Processing parameters, such as solvent type, reducing agent, reaction temperature, and more importantly atmospheric conditions are all necessary parameters that need to be controlled in order to obtain the most suitable mean to produce high purity InSb compound.

4. Conclusion

The binary semiconducting compound, InSb, can be synthesized by the solution route method although with In and Sb impurities. Crystalline dendritic morphology observed in InSb powder was obtained using this method. It was considered to provide high surface area suitable for making negative electrode for lithium-ion batteries. However, the presented small amount of impurities adversely affected the cell performance. Thus, improvement of this synthesis method is necessary to minimize these contamination.

Acknowledgements

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