Processing Parameter Studies on Solution Route Synthesis of Dendrite InSb Powders, Anode Material for Lithium-ion Batteries

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ABSTRACT

Intermetallic InSb compound with dendrite morphology was preliminary prepared by redox reaction at room temperature between $InCl_3$, $SbCl_3$ and Zn powder in ethylene glycol solvent. The characterization of the as-received product by XRD technique indicated 48% InSb volume fraction and other impurities. To obtain more intermetallic phase, the effect of processing parameters on the formation of InSb needs to be considered. Therefore, this experiment reports on the consequence of processing parameters such as solvent, reducing agent, reducing agent particle size and reaction temperature to the formation of dendritic crystalline InSb powder. From XRD results, it was observed that the formation of InSb compound depended on the type of solvent and reducing agent whereas no change had been observed by varying reducing agent particle size and reaction temperature. Dendritic morphology, which was verified by TEM patten as InSb phase, was observed by SEM studies in all conditions, using ethylene glycol solvent and zinc reducing agent.

Key words: Electron microscopy, Indium antimonide, Lithium-ion battery, Solution route synthesis

INTRODUCTION

Intermetallic InSb compound has been introduced as a potential anode material for high energy lithium-ion batteries (Thackeray et al, 1999; Johnson et al., 2000; Vaughey et al., 2000) The InSb electrochemical cell can provide approximately 340 mAh g^{-1} in the first cycle and slowly fades in the subsequent cycles. Developing more crystallinity in InSb compound is one possibility to improve the cell performance. The solution route method which was proposed as an alternative way to produce intermetallic compounds such as Cu_6Sn_5, Cu_2Sb, and InSb (Sarakonsri et al, 2006) was considered. The InSb powder synthesized by this method was reported to have crystalline dendrite structure. Unfortunately, there were In and Sb metal impurities observed in the product. Processing parameters such as solvent type, reducing agent type, reducing agent particle size and reaction temperature which affect InSb dendrite formation, therefore, were investigated in this experiment (shown in Table 1) in order to receive the most suitable mean to produce high-purity InSb compound. Various viscosity and polarity solvents such as ethylene glycol (EG, JT. Baker, purity 99.0%), dimethyl

sulfoxide (DMSO, Sigma Chemical) and dimethyl formamide (DMF, Labscan Asia, 99.8% v/v) were chosen. Different reducing agents (zinc, magnesium, and iron) were also studied. Size of Zn reducing agent particle (Fluka, 10 and 45μ particle size) may involve in kinetic process and affect the size of dendrite particles. Finally, thermodynamic factor, which was reaction temperature was examined at 0, room temperature and 50°C.

MATERIALS AND METHODS

The preparation of InSb was conducted and coded according to the processing parameters shown in Table 1. The detail of the preparation for the first experimental condition is described by dissolving stoichiometric amounts (Equation (1)) of $InCl_3$ (Fluka, purity 98.0%) and $SbCl_3$ (Aldrich Chemical, purity 99.0%) in EG 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.

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

Products from all synthesis conditions were 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. Scanning Electron Microscopy (SEM) equipped with Energy Dispersive Spectroscopy (EDS) (JEOL JSM-6335F) technique was used to observe morphology of the product powders. Finally, nanometer scale morphology which was directly related to the crystallography of the phase present was determined by Transmission Electron Microscopy (TEM) equipped with Energy Dispersive Spectroscopy (EDS) (JEOL JEM-2010) technique.

Table 1. Processing parameters for the synthesis of InSb compound.

	Reaction code	Solvent	Reducing agent	Reducing agent particle size (μm)	Reaction Temperature (°C)
1	EGZn45TR	EG	Zn	45	R
2	EGZn10TR	EG	Zn	10	R
3	DMFZn10TR	DMF	Zn	10	R
4	DMSOZn10TR	DMSO	Zn	10	R
5	EGMgTR	EG	Mg	Unknown	R
6	EGFeTR	EG	Fe	Unknown	R
7	EGZn45T0	EG	Zn	45	0
8	EGZn10T0	EG	Zn	10	0
9	EGZn45T50	EG	Zn	45	50
10	EGZn10T50	EG	Zn	10	50

RESULTS AND DISCUSSION

The powder XRD patterns of products synthesized by DMFZn10TR, DMSOZn10TR and EGMgTR conditions are presented in Figure 1. The powder XRD patterns of the products synthesized by EGZn10T0, EGZn45T0 and EGZn45TR conditions are shown in Figure 2 as well as by EGZn10T50, EGZn45T50 and EGZn10TR conditions in Figure 3.

There was no XRD result from EGFeTR condition due to no precipitation occurred in this experiment. Iron metal, which is classified as diamagnetic material, was affected by a magnetic force from a magnetic bar and lost no electrons for the redox reaction. It was observed in the XRD pattern in Figure 1 that there was an unidentified amorphous phase present in the synthesis condition, using Mg as a reducing agent (EGMgTR). Magnesium metal has more negative value of the standard reduction potential than zinc and iron metals or higher kinetic overpotential for the oxidation-reduction reaction to occur in high rate (Shriver and Atkins, 1999). However, the organometallic formation by the reaction between Mg and ethylene glycol solvent was more preferably to occur (Sharpe, 1986). The conditions using DMSO and DMF solvents (DMSOZn10TR and DMFZn10TR, Figure 1) produced relatively low InSb phase compared with the conditions using EG solvent (EGZn10TR) and with other conditions. The polarity of DMSO and DMF are lower than EG which results in the better dissolution of salts in EG. Moreover, the dipole of DMSO and DMF are higher than EG. The stable solvation process of In and Sb ions by DMSO and DMF molecules occurred. The consequence was less intermetallic compound observed in these synthesis conditions. Among all synthesis conditions, the EGZn45TR condition was observed to have relatively high InSb(111) peak compared with Sb(012) peak, indicating relatively high InSb compound fraction in the product.

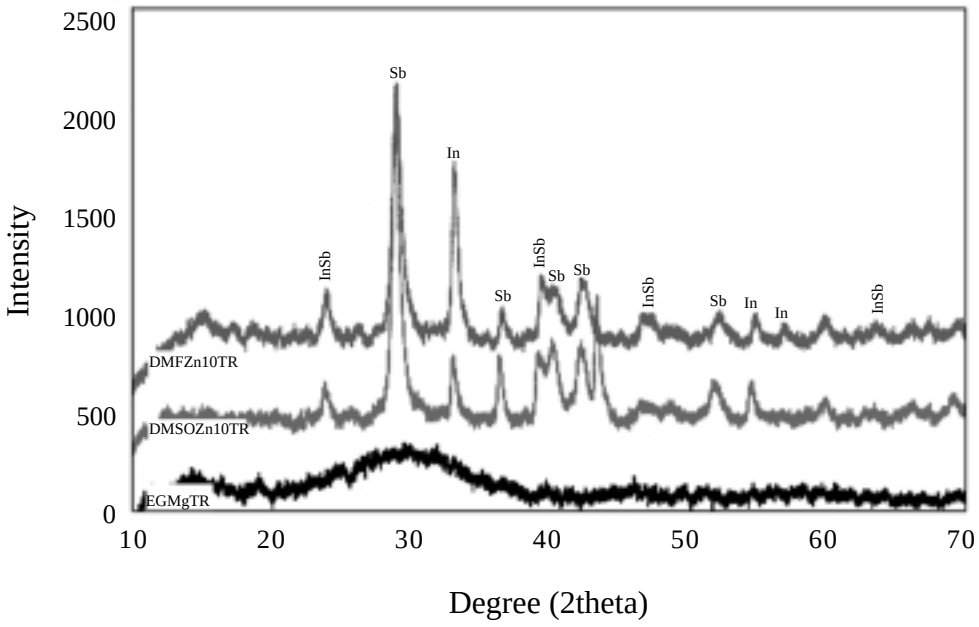

Figure 1. Powder XRD patterns of the as-received product from DMFZn10TR, DMSOZn10TR and EGMgTR conditions.

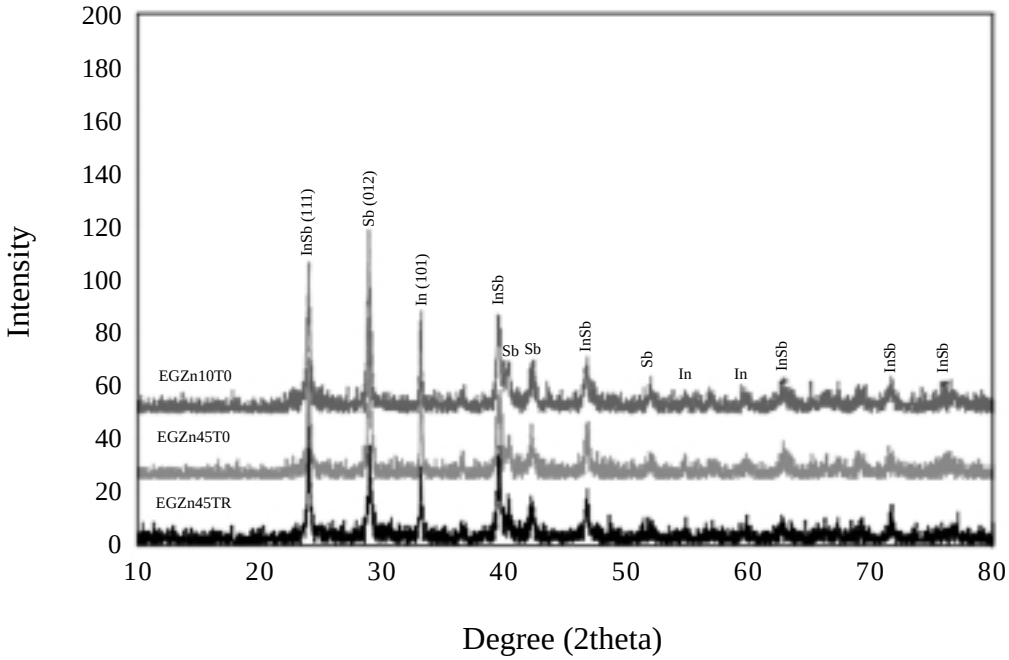

Figure 2. Powder XRD patterns of the as-received product from EGZn10T0, EGZn45T0 and EGZn45TR conditions.

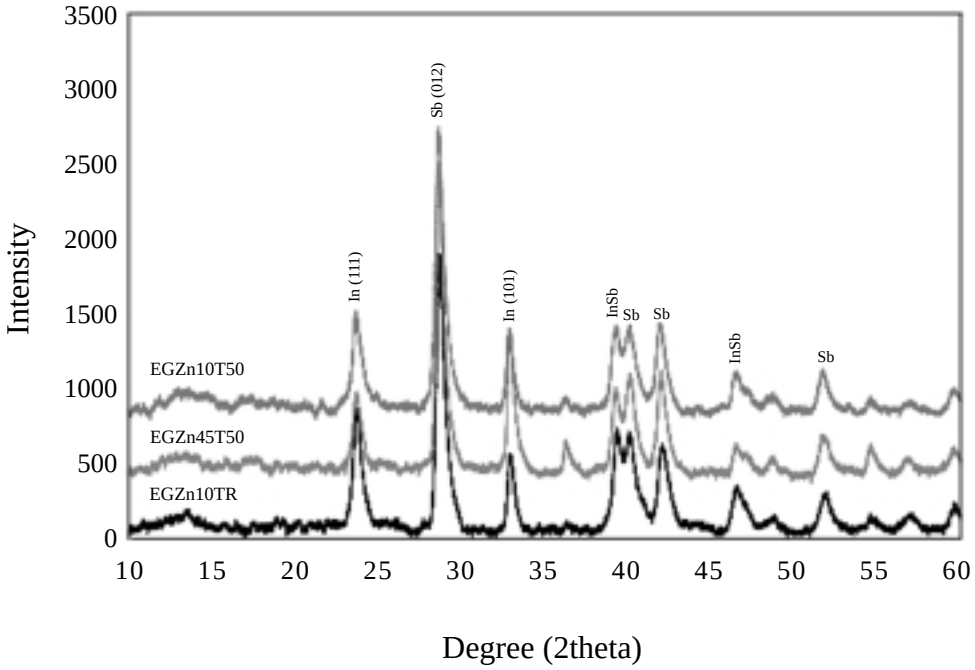

Figure 3. Powder XRD patterns of the as-received product from EGZn10T50, EGZn45T50 and EGZn10TR conditions.

For the SEM studies, the SEM images of products synthesized by EGZn45TR, EGZn10TR, DMSOZn45TR, DMFZn45TR, EGZn45T0, EGZn10T0, EGZn45T50 and EGZn10T50 are presented in Figure 4a- 4h, respectively. It was revealed in the SEM micrographs that the dendritic morphology, which was confirmed by TEM pattern (Figure 5) as InSb phase, appeared in all synthesis conditions except the conditions using DMSO and DMF solvents. There were a number of small particles precipitating out of the large spherical particles indicating that annealing at high temperature might introduce more intermetallic

phase. Due to large distribution of dendrite particle sizes in conditions using EG solvent and Zn reducing agent, as illustrated in Figure 4a-b and 4c-4h, the effect of reducing particle size and reaction temperature to dendrite formation were too difficult to be measured accurately. Therefore, no significant effect was observed by varying reducing agent particle sizes (10 and 45 μm) and reaction temperature from 0-50°C to the formation of dendrite InSb compound. However, it was noticed that crystalline dendrites observed in these conditions composed of number of nanometer particles which corresponded to high-surface-area material.

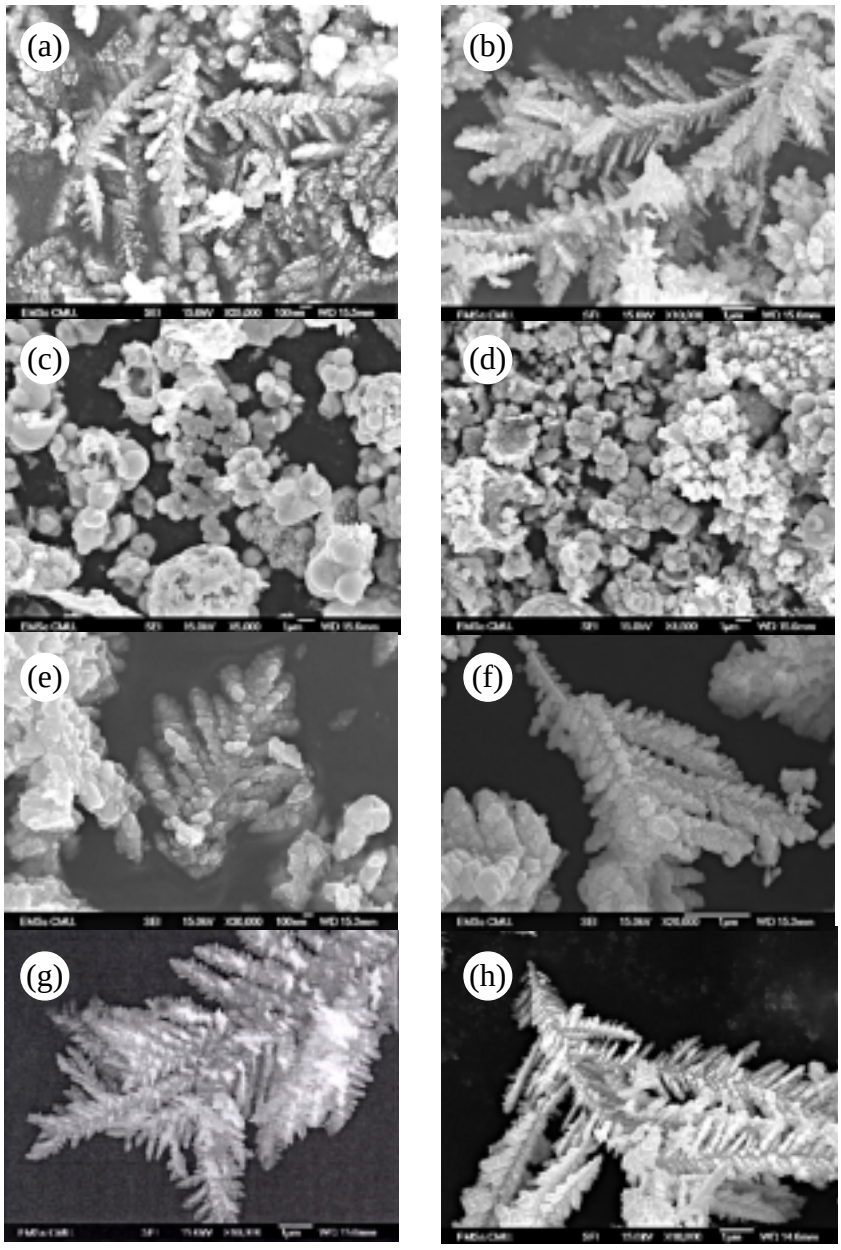

Figure 4a-4h. SEM micrographs of the as-received product powders from EGZn45TR (a), EGZn10TR (b), DMSOZn45TR (c), DMFZn45TR (d), EGZn45T0 (e), EGZn10T0 (f), EGZn45T50 (g) and EGZn10T50 (h).

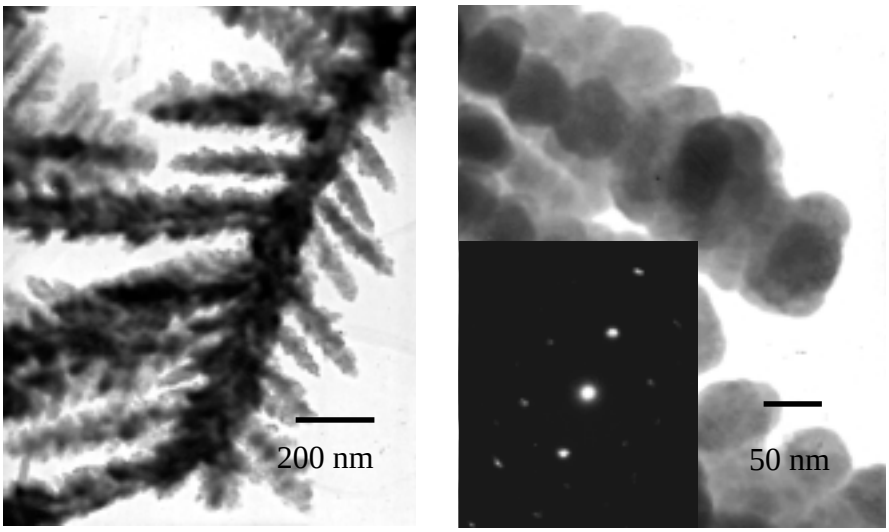

Figure 5. TEM micrographs of the product from EGZn45T0 condition showing the dendrite particles (a) and the dendrite tip with the inserted single crystal SAD pattern corresponds to InSb phase (b).

CONCLUSION

The suitable mean to synthesize intermetallic InSb compound by solution route method was by using ethylene glycol solvent, Zn reducing agent with particle size of 45 and 10 microns, and reaction temperature from 0–50°C. However, there may be other conditions that are more suitable than the conditions conducted here which need to be further investigated.

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REFERENCES

Johnson, C. S., J. T. Vaughey, M. M. Thackeray, T. Sarakonsri, S. A. Hackney, L. Fransson, K. Edstrom, and J. O. Thomas. 2000. Electrochemistry, and in-situ X-ray diffraction of InSb in lithium batteries. Electrochemical Communications 2: 595–600

Sarakonsri T., K. Choksawatpinyo, S. Seraphin, and T. Tunkasiri. 2006. Solution route preparation and characterization of dendrite InSb powders, anode material for lithium-ion batteries. Chiang Mai Journal of Science, (In press)

Sharpe, A. G. 1986. Inorganic Chemistry. 2nd ed. Longman, Singapore

Shriver, D. F., and P. W. Atkins. 1999. Inorganic Chemistry. 3rd ed. Oxford University Press, New York

Thackeray, M. M., C. S. Johnson, A. J. Kahaian, K. D. Kepler, J. T. Vaughey, Y. Shao-Horn, and S. A. Hackney. 1999. Composite electrodes for lithium batteries. ITE Battery Letters 1(1): 26

Vaughey, J. T., J. O'Hara, and M. M. Thackeray. 2000. Intermetallic insertion electrodes with zinc blende-type structure for Li Batteries: A study of Li_xInSb (0 x 3). Electrochemical and Solid State Letters 3: 13