Study on Alloy Anode with Composite Structure for LIB Prepared via Electrodepositing Method

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Abstract: A composite structure anode for lithium ion battery (LIB) was investigated. The composite anode was prepared by electrodepositing Sn-Sb alloy on a template-like electrode which was obtained by forming a spange-like micro-porous membrane on a copper foil via a mixed phase inversion process, and then annealing in the atmosphere of N_2. SEM and XRD results showed that composite structure of the anode was consisted of electrodeposited Sn-Sb alloy dispersing in a PAN-pyrolyzed conjugated conducting polymer gridding, which was connected with the Cu foil through transition alloy layer formed by heat-treatment. By comparison, the composite anode presented more reasonable microcosmic structure, better cycling performance and higher C-rate Performance than that obtained via directly electrodeposited Sn-Sb alloy on a Cu foil and then heat-treatment .

Keywords: lithium ion batteries; Alloy anode; Electrodeposition; Micro-porous membrane electrode; Sn-Sb alloy

1. Introduction

Lithium-ion batteries are the power sources of choice for popular mobile devices, such as cellular phones and computers. However, to meet the increasing demand for lithium ion batteries with higher energy density, many research attempts have been made to explore new anode materials or design novel nanostructures of electrode materials, because, generally, the performance of any device depends intimately on the properties of the materials of which it is formed. In this respect, one of the attractive candidates is the alloying metal with Lithium, such as Sn, Si, and Sb. Indeed, these metals which store lithium can provide very high theoretical specific capacity as the anode. For instance, the lithium–tin alloy has, in its fully lithiated composition, $Li_{4.4}Sn$, a theoretical specific capacity of 994 mAh g^{-1}, that is, a value almost three times larger than that of conventional graphite (372 mAh g^{-1}). A major drawback, however, affects these materials, that is, the large volume expansion–contraction that accompanies the lithium alloying–dealloying process. These volume variations result in severe mechanical strains that greatly limit the cycling life of the lithium-alloy electrodes. The use of nanostructures is a popular approach for improving the electrochemical response of these electrodes.

The use of nanostructures, however, is not the ultimate solution because they still have some drawbacks; these include: i) a low tap density, associated with the large surface-to-volume ratio, which results in a low energy density; ii) a high surface reactivity; iii) the nanoparticles tend to aggregate upon cycling, ultimately reducing the cycling life of the electrode. In addition, Some proposal, such as alloying with another metallic element, usage of very thin layers, and introduction of porous structure, have been reported to improve the electrochemical performance of alloy material electrodes. Recently，researches on porous-structure alloy/C composite anode materials are becoming more and more being focused on because of the following facts: (a) the open pores that allow easy transport of liquid electrolyte; (b) the continuous network that is expected to improve electrical conductivity; (c) a lot of interspaces and excess pores between alloy microparticles and support medium that can buffer the volume change caused by disintegration of the alloy structure; and (e) suitable microporous network that may block the reaggregation of the superfine particles.

We ever reported the synthesis of the porous-structure alloy/C composite anode materials. Herein, another novel preparing method for the composite anode material will be proposed.

2. Experimental

The polymer PAN used in this study was synthesized by suspension polymerization. As-prepared polymer PAN was dissolved in N, N-dimethylformamide in

which some graphite powder was contained under the mechanical agitation to form a homogenous casting solution at a PAN concentration of 3–5 wt.% at ambient temperature. After complete dissolution and having been left still for a certain time, the resulting viscous solution was cast by a homemade blade with an about 30 μm gap onto a rimmed Cu foil (thickness, 30–40 μm), which was treated in corrosive hydrochloric acid solution in advance. After exposed to an atomization steam generated by ultrasonic spray machine for appropriate time at ambient temperature to obtain desirable microporous superficial layer, the Cu foil was immediately immersed in a deionized water bath for at least 4 h to further perform phase inversion. After the exchange of solvent and water by phase inversion, a microporous film layer hard coated on the Cu foil were formed. The resultant was washed, rinsed, and dried at 80 °C under vacuum for 24 h, successively. In the end, a white, opaque membrane was firm adhered to the Cu foil, and thus a template-like microporous membrane electrode was obtained.

The composite anode material for LIB was prepared by pre-plating Cu and electrodepositing Sn–Sb alloy into the as-obtained micro-porous membrane electrode through membrane pores in it, then heat-treatment under the protection of nitrogen gas. The pre-plating Cu, aiming at strengthening connect between membrane layer and Cu current collector, was conducted in an almost pH-neutral bath containing 25 g/L of $Cu_2P_2O_7$, 130 g/L of $K_4P_2O_7 \cdot 10H_2O$, 60 g/L of $Na_2HPO_4 \cdot 12H_2O$ and suitable additives under a constant current density of 5 mA/cm^2 for sess than 10min at room temperature. SnSb alloy was electrodeposited in a pH 8.5 electroplating bath containing 30 g/L of $SnCl_2 \cdot 2H_2O$, 2 g/L of $SbCl_3 \cdot 2H_2O$, 130 g/L of $K_4P_2O_7 \cdot 10H_2O$, 7 g/L of $C_4H_6O_6$, and suitable additives under a constant current density of 3.5mA/cm^2 for less than 1.5h, where the membrane electrode was used as working electrode and a pure Sn plate as counter electrode. All electrodeposition runs were carried out at 30–50 ℃ without agitation.

After electro-deposition, heat-treatment and preparation of tested anode foil were done as follows: the as-electrodeposited composite electrode foil as well as unelectrodeposited micro-porous membrane electrode were cut into circular sheets of diameter 1cm and then put them into a quartz tube furnace. The heat-treatment was performed under the protection of nitrogen gas at appropriate temperature. Different temperature and time of heat-treatment were tried to optimize parameter of heat-treatment. Based on electrochemical performance and conduction of pyrolytic PAN, the proper temperature for heat-treatment of the electrode foils was carried out in the range of 250–350 ∘C under the atmosphere of N2 for 14 h. Electrochemical tests were performed on 2032-type coin cells with lithium metal (0.5mm thick foil) as a counter electrode. The electrolytes used were 1M LiPF6 EC + DEC +DMC (1:1:1, v/v/v). The separa-

tor of cell was Celguard 2400. The cell assembly was performed in a glove box filled with argon gas (less than 2ppm of water). The charge–discharge cycling of the coin cell was galvanostatically performed at different current densities with cut-off voltages of 0.02–2.0V at room temperature. Cycle test was conducted using Land Battery Test System made by Wuhan Land Electronic Co. Ltd. In this study, the charging and discharging processes represent Li-de-insertion and Li-insertion processes, respectively.

The amount of active materials in sample was calculated as follows. Amount of active materials = total weight of anode sheet−weight of corresponding copper current collector or copper substrate, where corresponding copper current collector or copper substrate was the same treatment processes as that of the composite anode foil or unelectrodeposited micro-porous membrane electrode sheet. For the sake of conveniene, the composite electrode and the electrodeposited Cu-Sn electrode on the bare copper foil are coded as E_C and E_B, respectively, hereafter.

Crystal structures of samples were characterized by an X-ray diffractometer (XRD: D/max-RB) using Cu Ka radiation. For the cross-section observation, the microporous membrane electrode foils were put in liquid nitrogen and were then cut with a lancet to obtain their cross-section. Before passing through a scanning electron microscope (SEM), the membrane electrode foil samples had to go through the carbon coating process. After that, the samples were imaged and photographed by employing a SEM (JSM6301, Hitachi) with energy dispersion X-ray spectroscopy (EDS; EDXS, ATW Link Isis300) with potentials of 15 kV in achieving magnification ranging from 500× to 50,000× to examine the membrane cross-section and the surface.

3. Results and discussion

2.1 Physical characterization

Fig.1 shows secondary electron images of the surface of the composite electrode materials before or after heat-treatment.It can be observed that there are abundant spongy micro-pore structures in the surface of them and the sizes of these micro-pores obviously augment after heat-treatment. In the fig.1b, The Sn-Sb alloys consisted of submicron crystallites may be clearly seen coming out from membrane pores in microporous membrane, while many empty micropores distribute around the pillar-like alloy. Apparently, these empty micrpores should play an important role in allowing easy transport of liquid electrolyte and buffering the large volume charge caused by Li-insertion of the alloy structure.

Fig.2 shows the electron back scattered SEM images of cross-section of composite electrode before (a) or after (b) heat-treatment. In Fig.2a, one can notice that electrodeposited SnSb alloys seem to distribute in all

membrane layer structure of the composite electrode and the distribution is even dispersive,on the whole. In the nethermost membrane layer approaching copper substrate, a fuscous trip-like thin layer can be distinctly observed. Obviously, the thin layer is assuredly pre-electroplated Cu layer, in which microporous meshworks of PAN membrane seem to be very clear and root themselves here, accordingly boosting up the connect between the meshworks and Cu substrate. In Fig. 2b, because Sn was excessive in the electroplating alloy layer, in the course of heat-treatment, the excessive Sn would melt partially and Cu would disperse up from the Cu substrate, resulting in change of membrane layer

structure to form layered structure, here, ① for Cu substrate, ② for Cu_3Sn alloy layer formed in and nearby pre-electroplated Cu layer on account of combination between dropped molten Sn and the dispersed Cu from the Cu substrete, ③ for composite layer of SnSb alloy dipersing in pores of the microporous membrane layer. In the composite layer, partial drop of molten Sn caused appearance of many new empty pores in the born microporous composite layer, offering rather advantageous conditions for buffering volume change of alloy materials during charge/discharge and making separation or isolation of alloy materials more evidance.
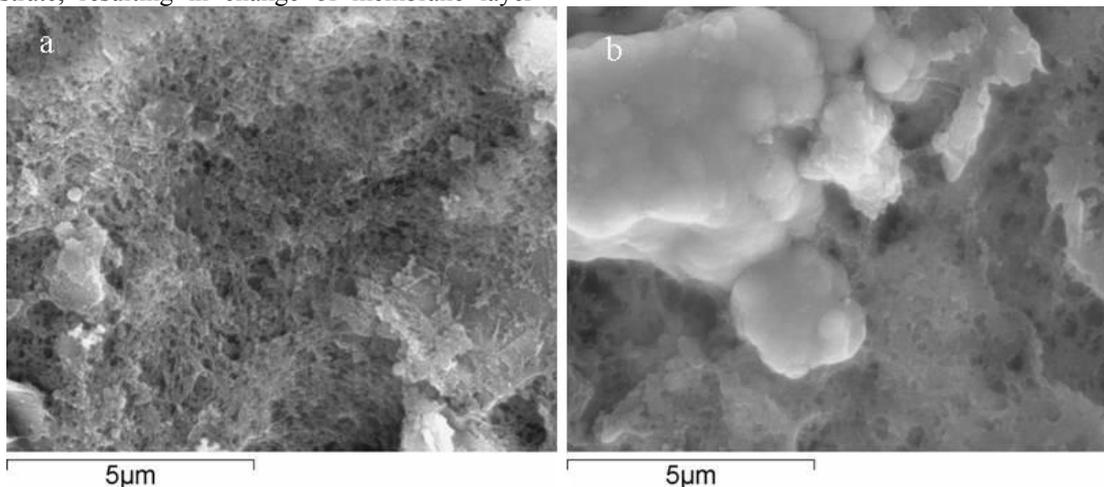
Fig.1 Secondary electron images of surface morphology of E_C electrode materials before (a) or after(b) heat-treatments
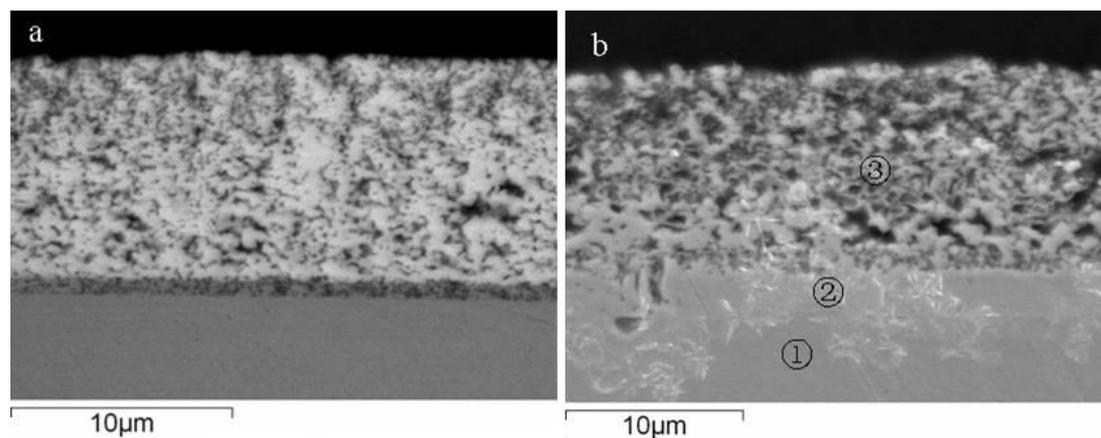
Fig.2 electrons back scattered images of surface morphology of the cross-section of E_C electrode materials before (a) or after(b) heat-treatments

Fig.3 and Fig.4 Show the X-ray diffraction (XRD) patterns for composite anode material E_C before and after heat-treatment. In the former, one can observe that diffraction peaks of β-Sn (JCPDS no. 65-2631) are also very evidence besides graphite and SnSb alloy with clear diffraction peaks for composite material before heat-treatment, which indicates that alloys in the microporous membrane electrode are SnSb composite ones with excess Sn. As for diffraction peaks of Cu, it should

attribute to diffraction of Cu in Cu substrate. In the latter, Composition in heat-treated composite anode materials has varied. The pattern shows that besides graphite and SnSb alloy, though the diffraction peaks of Sn exist all the same, strength of them seem to weak a lot. It can be explained that because partial drop of molten Sn when heat-treating reduced comtent of Sn in the composite material layer and the droped Sn combined with Cu diffusing from Cu substrate and pre-electroplating Cu layer

to form Cu$_3$Sn alloy. In Fig.4, we can also notice diffraction peaks of SnO besides abovementioned alloys, Sn and graphite. Normally, these ones should not appear.

The result shows that protection of N$_2$ rose problems in the couse of heat-treating materials, resulting in that Sn in the composite materials was oxidized
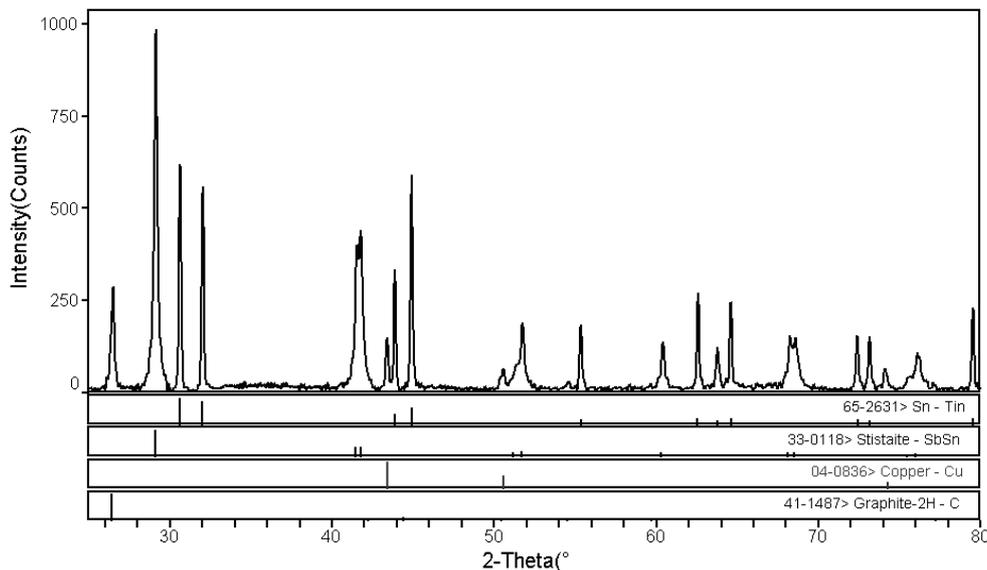
Fig.3 XRD patterns of E$_C$ electrode materials before heat-treatment
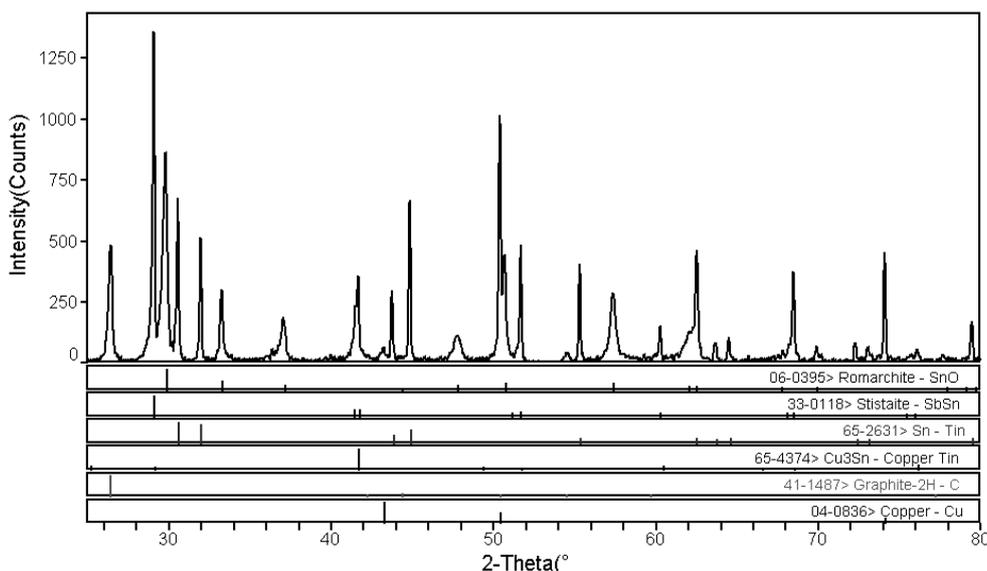
Fig.4 XRD patterns of E$_C$ electrode materials after heat-treatment

2.2 Electrochemical properties of electrode materials

The charge/discharge curves of E$_C$ and E$_B$ are showed in Fig.5. Two kind of different curves can be clearly observed. The one of E$_B$ electrode presents distinct charge/discharge curve figure with ladder-like form of SnSb alloy, in which every plateau indicates intercalating-Li /deintercalating-Li state at different phases.The curve is almost like as that of Sn/SnSb shown in references[2,7]. However, in the curve of E$_C$ electrode, the

curve takes on continuous leaning form without obvious ladder-like one, especially above 0.2V, which indicates that PAN conducting polymer is influential on charge/discharge performances of the composite material because it can also by itself electrochemically insert and release lithium. To evaluate the extent of this contribution, we have separately prepared a sample by using the same procedure of synthesis used to prepare the composite, however, without electrodepositing SnSb alloy. This alloy-free sample, tested as an electrode in a cell totally similar to that used for the characterization of the com-

posite, displayed a specific capacity limited to 30 mAh g−1, that is, a small fraction of the total capacity delivered by the composite.
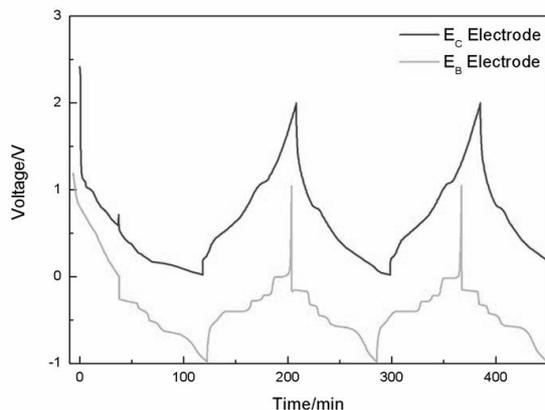
Fig.5 Contrast of typical charge–discharge voltage profiles of E_C and E_B electrodes

Fig.6 presents cycling performances of E_C and E_B electrodes when charging. Here, charging rates of the both are different. The former is 0.6C while the latter is o.25C. The performance of E_B electrode obtaining high initial charging capacity (approaching theoritical specific capacity of SnSb) starts to deteriorate sharply from 8th cycles, and at the same time the curve of it also starts to declines nearly at the form of diagonal line. This indicates that after initial cycles, due to the larger morphological changes of the alloys during Li ion insertion/extraction, which cause pulverization of alloy materials and loss of electrical contact between inter-particles, and particle and the current collector, sharp decline of their electrochemical performance comes into being. However, although charge rate of E_C electrode is nearly double that of E_B electrode, the former excel the latter a lot in the cycling performance. As for fluctuation of the curve, it seems to result from change of room temperature during testing of electrochemical performance of the cells.
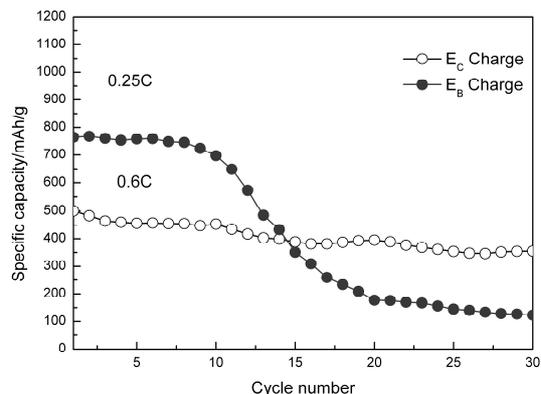
Fig.6 Contrast of cycling performances of E_C and E_B electrodes at room temperature

Fig.7 shows cycling performance at diverse rates of the E_C composite anode. From Fig.7, during charging and discharging at a low rate, E_C composite electrode demonstrates a good cycling stability and specific capacity retention. When charging and discharging at 1.5C rate, cycling performance of the composite electrode is still desirable and impressible. At the same time, it can be deduced that coulombic efficiencies of its following cycles except for first cycle have been kept higher values. Under the condition of charging and discharging at 3C rate, it can be observed that the composite electrode presents some cycling stability. It is considered that good cycling performance of the composite material can be attributed to two factors. First, amorphous carbon membrane formed by pyrolysis of PAN in the composite material serves as a supporting medium, which would both buffer the volume expansion of Sn–Sb alloy and prohibit the aggregation of Sn or Sb micro-particles and maintain the conduction path between Sn or Sb particles and amorphous carbon. Second, electrodeposited Sn–Sb alloy phases in membrane layer are surrounded by some empty micrpores, which would relax the mechanical stress resulting from phase transition structure and volume expansion during Li insertion processes.
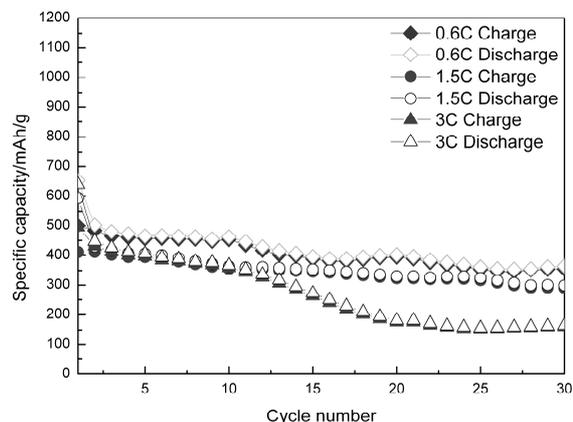
Fig.7 Cycling performance at various rates of E_C electrode at room temperature

Fig.8 takes on cycling performance at diverse rates of the E_B electrode. In the picture, one can clear observe that cycling performances of the E_B electrode are all rather awful whether it was tested at low rate or at high rate. It is obvious that in contrast with E_C electrode, electrochemical performance of E_B electrode is all worse. In addition, sa far as overlaping extent of charging and discharging curves, it is easy to find that E_B electrode is far inferior to E_C electrode, which shows that coulombic efficiency of E_B electrode is a lot worse than that of E_C electrode. All in all, E_B electrode fails effectively to buffer the volume expansion of Sn–Sb alloy, thus, re-

sulting in bad electrochemical performance.
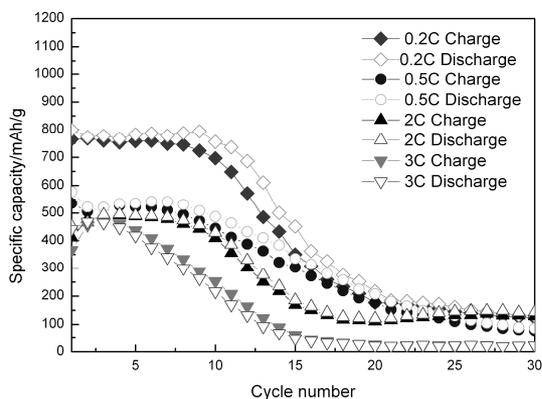
Fig.8 Cycling performance at various rates of E$_B$ electrode at room temperature

3. Conclusions

A composite material anode for LIB using a novel templatelike-directed electrodepositing SnSb process can be prepared successfully. The template-like PAN microporous membrane electrode may be prepared by forming a spange-like micro-porous membrane on a copper foil via a mixed phase inversion process induced by both water vapor atmosphere and nonsolvent water coagulating bath. The composite material anode have a novel characteristic structure, i.e. coexistence of alloy microparticles dispersedly isolated by meshwork of conducting polymer deriving from low temperature pyrolysis of PAN and some empty meshwork pores. The characteristic structure was beneficial to inhibit the aggregation between SnSb microparticles, to relax the volume expansion during cycling and to improve the cycleability of electrodes. Electrochemical test results of the composite electrode showed a much improved cycle performance compared to the electrode prepared by electrodepositing SnSb alloy on a bare Cu foil. Therefore, we believe that it is a very promising method to use the tem-

plate-like-directed electrodepositing alloy process so as to obtain composite material anode for LIB. But then, it is necessary to further research on the process to the effect that higher initial coloumbic efficiency can be achieved at the same time that improved cycle performance reaches desirable results. In fact, some correlative studies are underway.

4. Acknowledgements

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