

[Article ID] 1003- 6326(2001) 06- 0852- 04

Lithium ion storage behaviours of CoSb_3 intermetallic compound and effects of some carbonaceous additives^①

JIANG Xiao-bing(蒋小兵), ZHAO Xin-bing(赵新兵), ZHANG Xiao-bin(张孝彬),
ZHANG Lir-juan(张丽娟), CAO Gao-shao(曹高劭), ZHOU Bang-chang(周邦昌)

(Department of materials science and Engineering, Zhejiang University,
Hangzhou 310027, P. R. China)

[Abstract] Intermetallic compound CoSb_3 powders were prepared by vacuum melting and ball milling. It is found that the reversible capacity of the CoSb_3 electrode is about $470 \text{ mA}\cdot\text{h/g}$ at the first cycle with the potential plateaus from 0.8 V to 1.0 V against the pure lithium electrode. 10% mesocarbon microbead (MCMB) (mass fraction) additives can improve both capacity and cycling life of CoSb_3 , while the effect of carbon nanotube (CNT) additives is not visible.

[Key words] lithium ion battery; anode materials; CoSb_3 ; intermetallic compound; electrochemical property

[CLC number] TQ 152

[Document code] A

1 INTRODUCTION

Lithium ion cells currently represent the state-of-the-art in small rechargeable batteries due to their high voltage, high energy density, and long life, compared with conventional rechargeable batteries. The technology is based on the use of suitably chosen lithium intercalation compounds for the electrodes such as the various carbonaceous materials for the anode. But the researches^[1,2] found that large energy loss and low performances at the large current density were the shortcomings of the carbonaceous materials. And the first irreversible capacity caused by the production of solid electrolyte interface (SEI) in the organic electrolyte was also large. Because the potential of Li^+ insertion is very closed to that of metal lithium, it easily causes the sediment of the metal lithium on the surface of the electrodes when the cell is charged too deeply. Most researchers focused on finding a new type anode material whose potential must be higher than that of the carbonaceous material to improve its safety. In recent years, there has been great interest in the study of alloys and compounds with the aim of finding new materials for the anode of lithium ion cell, such as SnO_2 ^[3], SnSb ^[4], Cu_6Sn_5 ^[5], SnFe_3C ^[6-8], Fe_2O_3 ^[9], Mg_2Ni ^[10], Mg_2Ge ^[11], Zn_4Sb_3 ^[12,13] and nano-particle CoO ^[14].

In our previous study^[15] on the electrochemical reaction of some metal antimonides with lithium-ions, it was found that antimony was the active element which alloys or decays with lithium reversibly during the electrochemical cycling. It was also found that some metal antimonides seemed to be very attractive as the candidate anode materials for lithium-ion bat-

teries. In the present work the electrochemical characteristics of an intermetallic compound, CoSb_3 , are investigated, and the effects of carbonaceous additives, mesocarbon microbead (MCMB) and carbon nanotube (CNT), on the electrochemical behaviours of the compound is experimentally analyzed.

2 EXPERIMENTAL

The stoichiometric amounts of the element powders of commercial pure cobalt and antimony were molten in a sealed $d 15 \text{ mm} \times 100 \text{ mm}$ quartz tube under vacuum of about 10^{-2} Pa at 1100°C for 6 h. After solidification, the ingot was annealed at 600°C for 240 h. The obtained intermetallic compound was milled to powders with a ball-miller for 120 h under the protection of ligroin with the mass ratio of the steel balls to powders being 20:1 and the rotation rate of 150 r/min. About 10% MCMB (mass fraction) or CNT additives were mixed into the powders using the same milling condition.

The structures of the compound were characterized by X-ray diffraction (XRD) analysis using a $\text{CuK}\alpha$ radiation. The morphologies of the CoSb_3 -MCMB and -CNT hybrids were analyzed with a Philip CM2000 ultra-high resolution transmission electron microscope (UHRTEM).

All testing electrodes were prepared by coating slurry of 80% active powders, 10% carbon black and 10% polytetrafluoroethylene (PTFE) binder (mass fraction) on a porous nickel substrate with the size of $d 11 \text{ mm} \times 1.5 \text{ mm}$. The electrodes were pressed between two steel plates at 18 MPa for 1 min and then dried at 100°C for 24 h in the vacuum drier. Pure

① **[Foundation item]** Project (59771032) supported by the National Natural Science Foundation of China; project (97033518) supported by Research Fund of Doctoral Program of the Education Ministry of China

[Received date] 2000- 12- 20; **[Accepted date]** 2001- 02- 26

lithium (99.9%) was used as the against electrode. The organic electrolyte was prepared by dissolving 1 mol/L vacuum-dried LiPF₆ in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with volume ratio being 1:1. All cells were assembled in an argon glove box. The cells were charged and discharged between 0.05 and 1.5 V under the constant current density of 20 mA/g. All capacities were calculated over the total mass of the dried electrode slurry containing the alloy powders, carbon black additives and the PTFE binder.

3 RESULTS AND DISCUSSION

Fig. 1 illustrates the XRD patterns of the CoSb₃ sample before ball-milling. The patterns show that a single phased skutterudite CoAs₃(T_h⁵) structure has been obtained after 600 °C/240 h annealing of the vacuum molten sample. The calculation from Fig. 1 leads to a crystal lattice parameter of the cubic unit cell of $a = 9.0274 \text{ \AA}$ which is a little larger than the value reported by Alcántara et al^[16] ($a = 9.0114 \text{ \AA}$), but the difference is in the range of experimental errors.

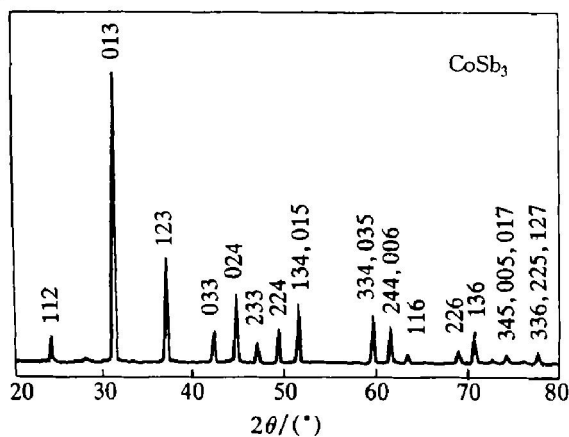


Fig. 1 XRD patterns of annealed CoSb₃ intermetallic compound

Fig. 2 shows the charge and discharge curves of the CoSb₃ electrode. It can be seen that, after the first charge (Li⁺-insertion), the charge and discharge (Li⁺-extraction) plateaus of the CoSb₃ electrode are very stable at about 0.8 and 1.0 V respectively with a small potential hysteresis of about 0.2 V. The charge and discharge potentials of the CoSb₃ electrode are very close to those of other antimonides found in our previous work^[15]. This means that antimony is the active element reacting with lithium. The first charge and discharge capacities of the CoSb₃ reach 627 mA·h/g and 470 mA·h/g respectively. The reversible capacity in the first cycle (470 mA·h/g) is about 30% higher than that of the carbon materials. Although the reversible capacity de-

creases to about 394 mA·h/g in the fifth cycle, it is well comparable to the carbon based materials. Considering the high densities of the CoSb₃ compound (about 7.65 g/cm³), the volume capacity of the cobalt antimonides would be as high as three times that of carbon based materials.

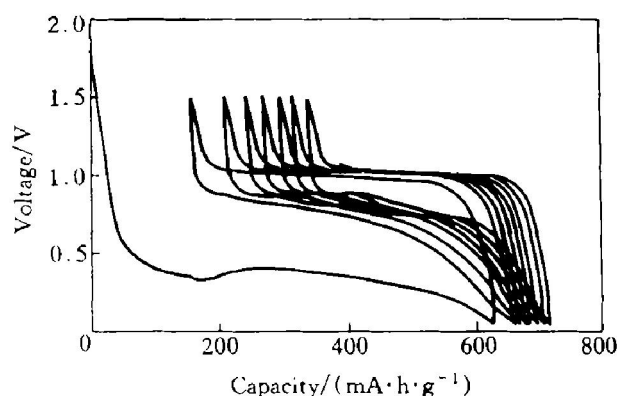


Fig. 2 Cycling profiles of CoSb₃ using pure lithium as against electrode

The capacity decreases of CoSb₃ may be due to the fragmentation of the intermetallic powders, since as many as a dozen of lithium-ions could insert into one CoSb₃ molecular, which leads to a violent volume change of the powders during cycling. As some broken materials could be out of electric contact with the electrode, they become inactive in the succeeding cycles and make the capacities of the electrode decrease during cycling. Considering the fact that many carbonaceous materials have excellent flexibility, deformability and electric conductivity, MCMB and CNT are blended into the powders.

The carbon nanotubes (CNTs) were prepared by CVD catalytic method from ethyne using cobalt as the catalyst. The TEM morphology of the CoSb₃-CNT hybrid (Fig. 3(a)) shows that the CNTs are central hollow cylinders with an average diameter of about 13 nm. The electrochemical properties of similar CNTs have been studied by Wu et al^[17] as anode materials for lithium-ion batteries. They found that the reversible capacity of CNTs with diameters of about 12 nm is about 200~250 mA·h/g. Commercial MCMBs with the average diameter of about 10 μm, special surface of about 1 m²/g and density of about 2.18 g/cm³ have been used in the present work. As been reported, the reversible capacity of MCMB are about 340 mA·h/g^[18]. Fig. 3(b) shows the morphology of the CoSb₃-MCMB hybrid. Because of the relative large sizes of the MCMBs, one can only see some graphite fragments in the picture.

Fig. 4 shows the cycling profiles of the CoSb₃-CNT and CoSb₃-MCMB electrodes against pure lithium. No obvious difference in the potential plateaus between the hybrids and pure CoSb₃ can be seen from Fig. 4 in comparison with Fig. 2. The reversible ca-

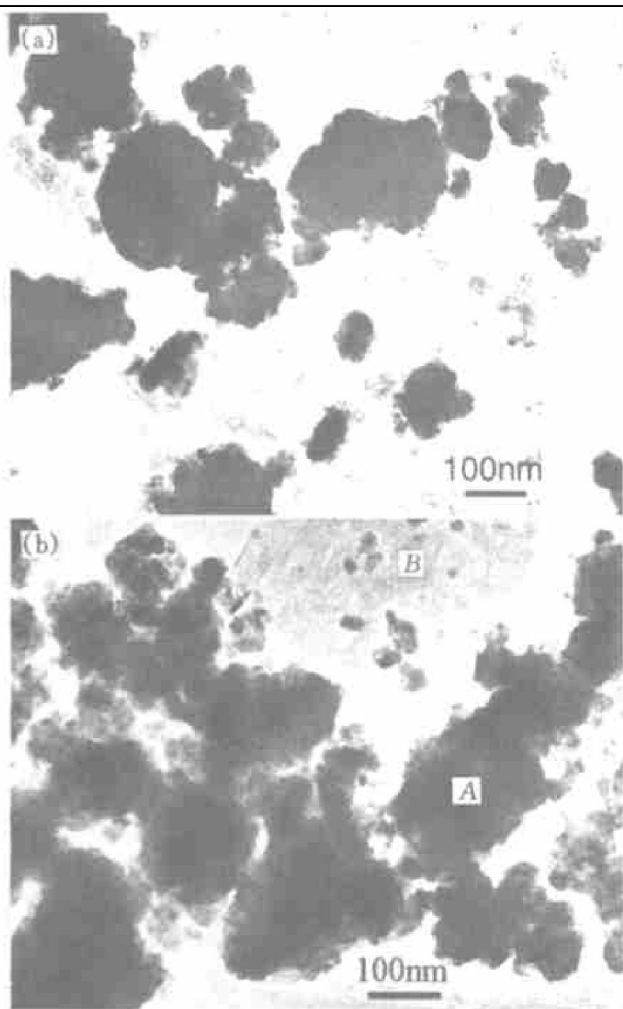


Fig. 3 TEM micrographs of hybrids
(a) $-\text{CoSb}_3\text{-CNT}$; (b) $-\text{CoSb}_3\text{-MCMB}$

capacities of both samples are about $410\text{mA}\cdot\text{h/g}$ for $\text{CoSb}_3\text{-CNT}$ and $586\text{mA}\cdot\text{h/g}$ for $\text{CoSb}_3\text{-MCMB}$ in the first cycle, and decrease to about $342\text{mA}\cdot\text{h/g}$ and $550\text{mA}\cdot\text{h/g}$ for $\text{CoSb}_3\text{-CNT}$ and $\text{CoSb}_3\text{-MCMB}$ samples respectively. This seems that the CNT additives decrease while the MCMB additives increase the capacities of a CoSb_3 electrode. The unexpected difference between both carbonaceous additives are not considered to be due to the capacity difference of about $100\text{mA}\cdot\text{h/g}$ between CNT and MCMB, since most carbonaceous materials have a potential against lithium at about 0.1V and no corresponding plateaus near 0.1V can be found in both cycling profiles in Fig. 4(a) and Fig. 4(b). This suggests that neither CNT nor MCMB has taken part in the electrochemical reaction with lithium during cycling in our experiments. It can be easily understood that the lithium electrode has been used in the same time as the referring electrode to control the charge/discharge cycling in the present work. Due to the surface polarization of the lithium electrode during charge (Li^+ insertion), the cell voltage will be higher than the potential of the CoSb_3 , $\text{CoSb}_3\text{-CNT}$ or $\text{CoSb}_3\text{-MCMB}$ electrode against pure lithium. In other words, the cut-off potential during charge could be

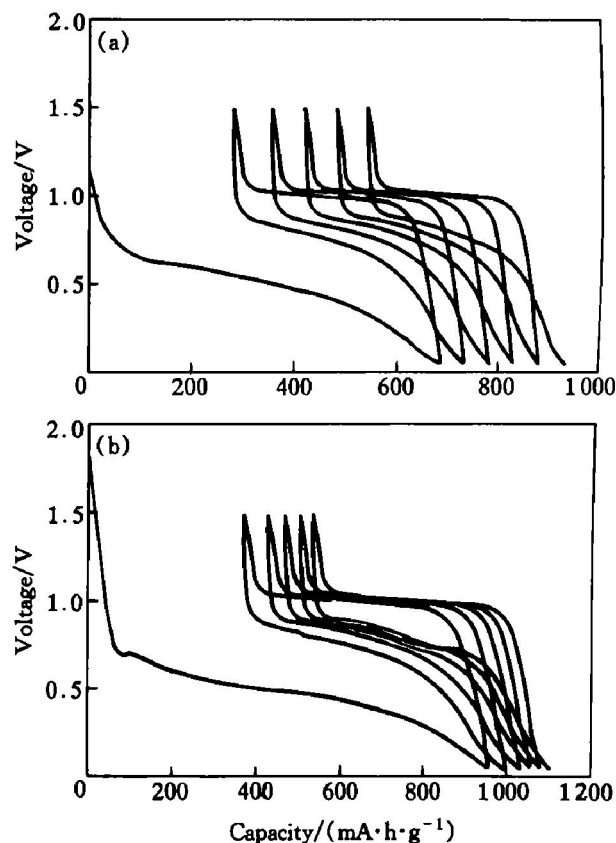


Fig. 4 Cycling profiles of hybrids
using pure lithium as against electrode
(a) $-\text{CoSb}_3\text{-CNT}$; (b) $-\text{CoSb}_3\text{-MCMB}$

significantly higher than 0.05V and therefore lithium-ions would not insert into CNTs or MCMBs in the present experimental conditions.

In spite of this, the carbonaceous additives have effects on the electrochemical properties of CoSb_3 electrodes. From Fig. 3, it can be seen that the CoSb_3 powders assemble together to form large granules (eg. the large cluster marked "A" in Fig. 3(b)). The UHRTEM picture (Fig. 5) shows that the grains in the granules could be very small, with the sizes from a few nanometers to about 20nm . The fracture of the powder granules during the charge/discharge cycling makes some grains or fragments be out of electric contact with the electrode and leads to a capacity decrease directly. Thus some soft and well electric conductive additives are needed. The MCMBs will be easily broken, because of their relative large size, into graphite flakes after ball-milling (denoted as "B" in Fig. 3(b)), so that the MCMBs (or graphite flakes) can act as some adhesive agents and connect the CoSb_3 grains or fragments with each other and also to the electrode effectively. Conversely, CNTs are very strong and in a thin-long fibre form. They are almost not deformable during milling and contact with the CoSb_3 powders only in a few "points" due to their high rigidity (as shown in Fig. 3(a)), and therefore CNTs can not improve the electrochemical properties of the powders.

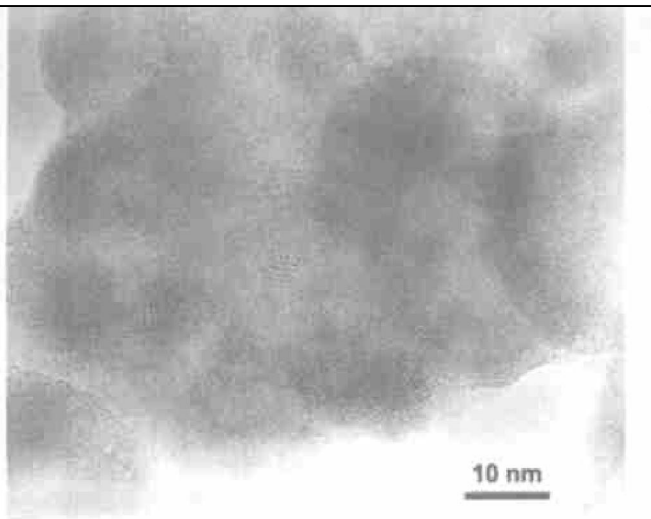


Fig. 5 UHRTEM of CoSb₃ powders showing small grains in large granule

4 CONCLUSIONS

1) The reversible capacity of skutterudite structured intermetallic compound CoSb₃ can reach 470 mA·h/g in the first cycle. With a relative high potential of about 1.0 V against metal lithium, the cell safety could be improved if CoSb₃ were used as the anode material instead of carbonaceous anode materials.

2) The capacities of CoSb₃ decrease during cycling because the fracture of the CoSb₃ powders or granules make some CoSb₃ fragments be electrochemically inactive.

3) The reversible capacity and cycling property can be significantly improved by MCMB additives due to the adhesive and connective effect of the graphite flakes from MCMBs. The CNT additives have little effect on the improvement of the electrochemical properties of the CoSb₃ powders under the present conditions.

[REFERENCES]

- [1] Dahn J R, ZHENG Tao, LIU Ying-hu, et al. Mechanisms for lithium insertion in carbonaceous material [J]. *Science*, 1995, 270: 590– 593.
- [2] QIU Wei-hua, ZHANG Gang, LU Shi-gang, et al. Correlation between the structure and electrochemical properties of carbon materials [J]. *Solid State Ionics*, 1999, 121: 73– 77.
- [3] Idota Y, Kubota T, Matsufuji A, et al. A high capacity ion-storage material [J]. *Science*, 1997, 276: 1395– 1399.
- [4] Yang J, Takeda Y, Imanishi N, et al. Ultrafine Sn and SnSb_{0.44} powders for lithium storage matrices in lithium ion batteries [J]. *J Electrochem Soc*, 1999, 146: 4009 – 4013.
- [5] Wang G X, Sun L, Bradhurst D H, et al. Lithium storage prosperities of nanocrystalline η -Cu₆Sn₅ alloys prepared by ball-milling [J]. *J Alloys Comp*, 2000, 299: L12– L15.
- [6] Ou Mao, Dunlap R A, Dahn J R. Mechanically alloyed Sn-Fe(-C) powders as anode materials for Li-ion batteries—The Sn₂Fe system [J]. *J Electrochem Soc*, 1999, 146: 405– 413.
- [7] Ou Mao, Dahn J R. Mechanically alloyed Sn-Fe(-C) powders as anode materials for Li-ion batteries—The Sn-Fe system [J]. *J Electrochem Soc*, 1999, 146: 414 – 422.
- [8] Ou Mao, Dahn J R. Mechanically alloyed Sn-Fe(-C) powders as anode materials for Li-ion batteries—The SnFe₃C system [J]. *J Electrochem Soc*, 1999, 146: 423 – 427.
- [9] LI Hong, HUANG Xue-jie, CHEN Li-quan. Anode based on the oxide materials for lithium rechargeable batteries [J]. *Solid States Ionics*, 1999, 123: 189– 197.
- [10] Kim H, Park B, Sohn H J, et al. Electrochemical characteristics of Mg-Ni alloys as anode materials for secondary Li batteries [J]. *J Power Sources*, 2000, 90: 59 – 63.
- [11] Sakaguchi H, Honda H, Esaka T. Synthesis and anode behavior lithium storage intermetallic compounds with various crystallinities [J]. *J Power Source*, 1999, 81– 82: 229– 232.
- [12] LU Chun-ping, ZHAO Xin-bing, CAO Shao, et al. Effects of graphite on ZrSb alloys as anode materials for lithium-ion batteries [J]. *Trans Nonferrous Met Soc China*, 2000, 10(2): 204– 208.
- [13] Zhao X B, Cao G S. A study on the behaviours of lithium-ion inserting in Zn₄Sb₃ anode [J]. *Electrochimica Acta*, 2001, 46(6): 891– 896.
- [14] Polzot P, Laruollo S, Grugoon S, et al. Nanosized transition-metal oxide as negative electrode material for lithium-ion batteries [J]. *Nature*, 2000, 407: 496 – 499.
- [15] Zhao X B, Cao G S, Lv C P, et al. Electrochemical properties of some Sb or Te based alloys for candidate anode materials of lithium-ion batteries [J]. *J Alloys Comp*, 2001, 315(1– 2): 265– 268.
- [16] Alcántara R, Fernández-Madrigal F J, Lavela P, et al. Electrochemical reaction of lithium with the CoSb₃ skutterudite [J]. *J Mater Chem*, 1999, 9: 2517– 2521.
- [17] Wu G T, Wang C S, Zhang X B, et al. Structure and lithium insertion properties of carbon nanotube [J]. *J Electrochem Soc*, 1999, 146: 1696– 1701.
- [18] Kim J S, Park Y T. Characteristics of surface films formed at a mesocarbon microbead electrode in a Li-ion battery [J]. *J Power Sources*, 2000, 91: 172– 176.

(Edited by YANG Bing)