

Electrochemical properties of $\text{CoFe}_3\text{Sb}_{12}$ as potential anode material for lithium-ion batteries^{*}

ZHAO Xin-bing (赵新兵)[†], ZHONG Yao-dong (钟耀东), CAO Gao-shao (曹高劭)

(Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China)

[†]E-mail: zhaoxb@zju.edu.cn

Received Jan. 19, 2003; revision accepted Dec. 22, 2003

Abstract: A skutterudite-related antimonide, $\text{CoFe}_3\text{Sb}_{12}$, was prepared with vacuum melting. XRD analysis showed the material contained Sb, FeSb_2 , CoSb_2 and CoSb_3 phases. The electrochemical properties of the ball-milled $\text{CoFe}_3\text{Sb}_{12}$ -10 wt% graphite composite were studied using pure lithium as the reference electrode. A maximal lithium inserting capacity of about 860 mAh/g was obtained in the first cycle. The reversible capacity of the material was about 560 mAh/g in the first cycle and decreased to *ca.* 320 mAh/g and 250 mAh/g after 10 and 20 cycles respectively. *Ex-situ* XRD analyses showed that the antimonides in the pristine material were decomposed after the first discharge and that antimony was the active element for lithium to insert into the host material.

Key words: $\text{CoFe}_3\text{Sb}_{12}$, Anode materials, Lithium-ion batteries, Electrochemical properties

Document code: A

CLC number: TQ150.9; O646.5; X783

INTRODUCTION

Binary skutterudites have cubic $Im\bar{3} (T_h^5)$ structure and the chemical form of AB_3 , where A represents a metal atom and B represents a pnico-gen atom. There are eight formula units per cubic unit cell, in which there are additionally two structural voids with the radii varied from 1.63 Å for CoP_3 to 2.040 Å for IrSb_3 . The void is large enough for an alkaline earth or rare earth atom to insert into it and to form ternary compounds called filled skutterudites. In these compounds, the inserting loosely bound atoms can move or bounce around inside the voids due to the relative large-void room compared to the sizes of the filling atoms. This

property makes filled skutterudites have very low thermal conductivity and therefore be of interest in the development of advanced thermoelectric materials (Tritt, 1999).

Considering that the lithium ions could insert into the voids in a skutterudite, the authors have studied the electrochemical properties of CoSb_3 (Jiang *et al.*, 2001) as a candidate for anode materials of lithium-ion batteries. Similar earlier work was reported by Alcántara *et al.* (1999). These works showed that CoSb_3 had large reversible capacities although the structural voids held little significance for the storage of lithium ions, and that even the crystal structure itself would be decomposed irreversibly during the first cycle when lithium ions were inserted into the material. However, these works, and also the experimental results found in another antimonide Zn_4Sb_3 (Zhao *et al.*, 2000; Zhao and Cao, 2001; Cao *et al.*, 2001), showed that antimony is an attractive lithium ions storage element.

^{*} Project supported by the National Natural Foundation of China (No. 59771032) and the RFDP of the Education Ministry of China (No. 20010335045)

A high lithium antimonide, Li_3Sb , can be formed at about 0.8 V vs Li^+/Li and decomposed at about 1.0 V vs Li^+/Li (Alcántara *et al.*, 1999; Zhao and Cao, 2001). In the present work, the electrochemical and structural behaviours of a skutterudite related antimonide, $\text{CoFe}_3\text{Sb}_{12}$, were studied.

EXPERIMENTS

$\text{CoFe}_3\text{Sb}_{12}$ alloy was prepared by vacuum melting from stoichiometric amounts of pure cobalt, iron and antimony (all purity of $\geq 99\%$) in a sealed silica tube at 1100 °C for six hours. The as-solidified alloy was further ball-milled for 120 hours with 10 wt% pure graphite in a conventional planetary ball miller under the protection of ligroin with the rotation rate of 150 rpm and the ball-to-material mass ratio of 20:1.

A two-electrode test cell model (Zhao *et al.*, 2000) was used to measure the electrochemical properties of the material, where the $\text{CoFe}_3\text{Sb}_{12}$ -10 wt%C electrode worked as the cathode and pure lithium (99.9%) was used as the anode in the test cell model. The organic electrolyte was prepared by dissolving 1 mol/L vacuum dried LiClO_4 in 1:1 volume ratio mixture of ethylene carbonate (EC, Merck Schuchardt, 99.5% pure) and diethyl carbonate (DEC, Fluka Chemie AG, 99.5% pure). All cells were assembled in an argon glove box. The electrochemical properties of the materials were measured with a computer-controlled measuring instrument in constant-current mode at 30.0 ± 0.1 °C under a dried atmosphere. The cells were charged/discharged between 0.005 V and 2.500 V, with constant current of 20 mA/g or 100 mA/g. To calculate the capacities, we already considered the masses of both $\text{CoFe}_3\text{Sb}_{12}$ and graphite additives of an electrode. XRD analyses were taken with $\text{Cu } K_\alpha$ radiation at a scanning step of 0.02°.

RESULTS AND DISCUSSION

The XRD patterns of the as-solidified $\text{CoFe}_3\text{Sb}_{12}$ alloy are given in Fig.1 showing the dominant

reflection bands of Sb and FeSb_2 with a minor component of CoSb_2 reflection. Since lithium ions do not insert into the voids of the skutterudite structure, we did not try making skutterudite structure by long time annealing the $\text{CoFe}_3\text{Sb}_{12}$ alloy in the present work.

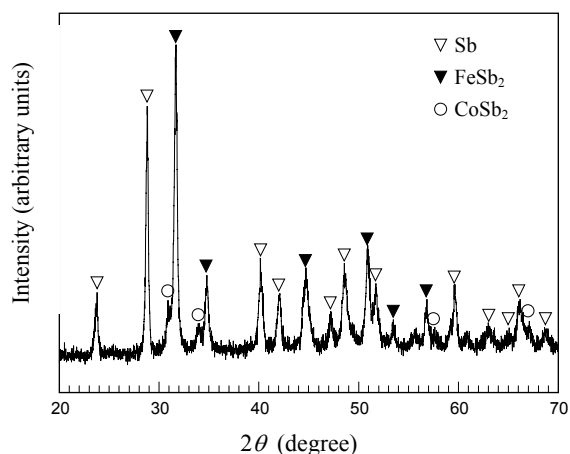


Fig.1 XRD patterns of the as-solidified $\text{CoFe}_3\text{Sb}_{12}$ alloy

Fig.2 shows the cycling profiles of the $\text{Li} | \text{LiClO}_4(\text{EC}+\text{DEC}) | \text{CoFe}_3\text{Sb}_{12}$ -10 wt%C cells using a charge/discharge current of 20 mA/g (sample I-20) in the first 10 cycles. The maximal discharge (Li^+ insertion) and charge (Li^+ extraction) capacities of the $\text{CoFe}_3\text{Sb}_{12}$ -10 wt%C electrode in the first cycle were about 860 mAh/g and 580 mAh/g respectively, which means there was an irreversible capacity of

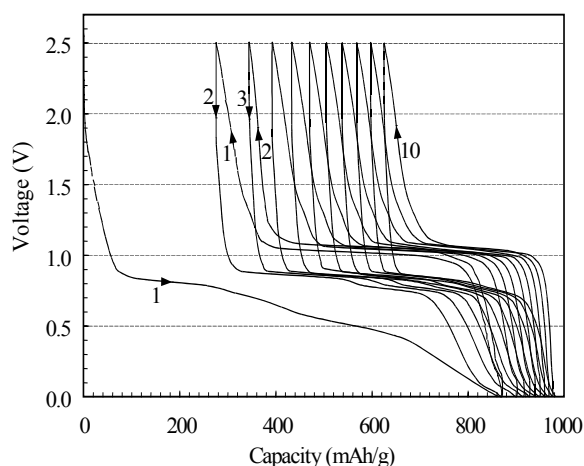


Fig.2 Cycling profiles of $\text{Li} | \text{LiClO}_4(\text{EC}+\text{DEC}) | \text{CoFe}_3\text{Sb}_{12}$ -10 wt%C cell in the first 10 cycles using a constant current of 20 mA/g. The arrows and numbers indicate the directions of charge/discharge and the cycle numbers

ca. 280 mAh/g (about 30% of the total Li^+ inserting amount) in the first cycle. The origin of this irreversible capacity was considered to be mainly due to the formation of a passivating film by electrolyte decomposition on the alloy surface as suggested by Alcántara *et al.*(1999).

Fig.2 shows that the charge voltage plateaus were near 1.05 V and that the discharge plateaus after the first cycle were between 0.75 V and 0.85 V, which were very close to that in CoSb_3 (Alcántara *et al.*, 1999), and also very close to the potential of Li_3Sb against pure lithium of about 0.95 V at 25 °C reported by Wang *et al.*(1986). The near-constant lithium-ion extracting potential of about 1.05 V vs metallic lithium shown in Fig.2 means that a lithium-ion battery using metal antimonides as the anode and lithium cobaltates as the cathode would have a very steady working voltage of about 3 V. Such a battery would have some advantages in comparison with the traditional lithium-ion batteries using carbon based anodes. Firstly, the possible deposition of metallic lithium on the anode surface could be minimized due to a more noble potential of the anode than that of metallic lithium. Secondly, a 3 V lithium-ion battery could meet the demand for lower voltage of portable appliances such as mobile phones and notebook computers. Owing to a higher density of $\text{CoFe}_3\text{Sb}_{12}$, the volume power output of the lithium-ion cell with a $\text{CoFe}_3\text{Sb}_{12}$ -C anode will be still larger than that with a carbon based anode, even though the battery output power is reduced because of the lower working voltage.

The reversible capacities of the $\text{Li} | \text{LiClO}_4(\text{EC}+\text{DEC}) | \text{CoFe}_3\text{Sb}_{12}$ -10 wt%C cells are plotted in Fig.3 vs the cycle number. The reversible capacity of sample I-20 decreased from about 580 mAh/g in the first cycle to about 350 mAh/g in the 10th cycle. These are significantly higher than that obtained by Alcántara *et al.*(1999). Another sample, sample I-100, tested with a higher charge/discharge current, 100 mA/g, was measured till the 20th cycle. The reversible capacity of sample I-100 was 370 mAh/g in the first cycle and 210 mAh/g in the 20th cycle respectively, which are also compatible to the results of CoSb_3 (Alcántara *et al.*, 1999).

Fig.4 gives the *ex-situ* XRD patterns of CoFe_3 -

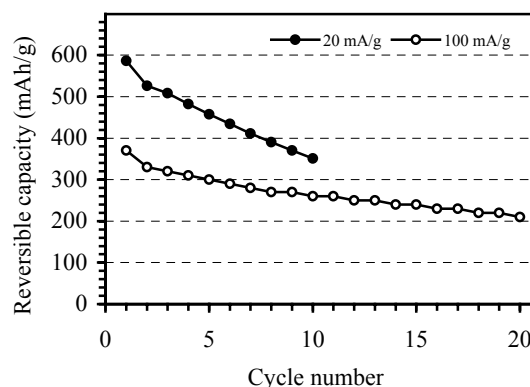


Fig.3 Cycling capacities of $\text{Li} | \text{LiClO}_4(\text{EC}+\text{DEC}) | \text{CoFe}_3\text{Sb}_{12}$ -10 wt%C cells using currents of 20 and 100 mA/g

Sb_{12} -10 wt%C electrodes before cycling (a), after the first discharge (b), after the first charge (c) and after 5 cycles (d). The electrodes were covered with polymer films to avoid oxidation after removal from the cells in the argon glove box. Because of the relative small amount of the testing material in an electrode, the XRD patterns showed very strong reflections of nickel substrate as well as that of the polymer films. Despite all this, we could still see the reflections of Sb and FeSb_2 in the sample before cycling. There is no visible line from the small amount of graphite additives in Fig.4 due to the sm-

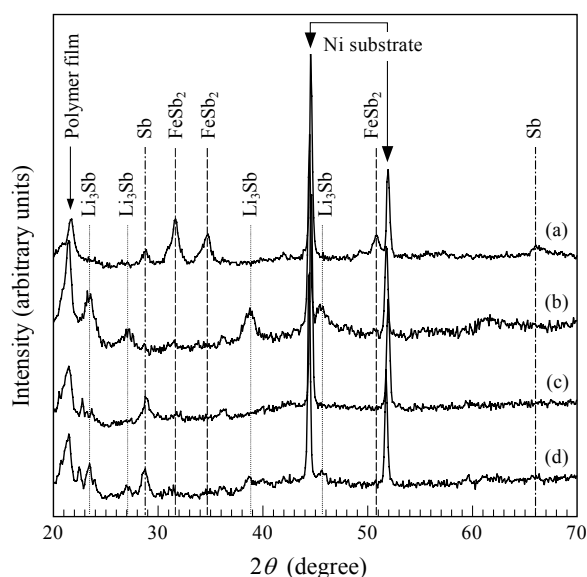


Fig.4 XRD patterns of the electrodes before cycling (a), after the 1st discharge (b), after the 1st cycle (c) and after 5 cycles (d)

all amount. Note some important phenomena from the XRD patterns in Fig.4. Firstly, no metal antimonides such as FeSb_2 , CoSb_2 and CoSb_3 exist after the first discharge, and they are not restored after the lithium ions were extracted in the succeeding charge. This means that the original antimonide structures had been destroyed irreversibly in the first discharge. Since it needs some energy for the decomposition of the metal antimonides during the first discharge, the insertion of lithium ions into the electrode is hindered, which leads to the delay of the first discharge process, or a voltage drop, compared with the later cycles in Fig.2. Secondly, a remarkable reflection of Li_3Sb found in pattern (d) after 5 cycles indicated that some Li_3Sb clusters or crystallites remained un-reacted in spite of the fully charged the cell. This is thought to be the cracking of the material from the volume change during the charge/discharge cycling. Therefore, some Li_3Sb fragments fell out, became electrically isolated from the electrode and did not participate in the succeeding electrochemical reactions, causing the capacity decrease of the material during the cycling.

CONCLUSION

The skutterudite-related compound, $\text{CoFe}_3\text{-Sb}_{12}$, shows good properties of high reversible capacity and high energy density. These make $\text{CoFe}_3\text{-Sb}_{12}$ a potent candidate as anode material for lithium-ion batteries. The *ex-situ* XRD results showed that the metal antimonide phases in the pristine ma-

terial were decomposed irreversibly into non-crystalline iron, cobalt and antimony when lithium-ions inserted into the electrode in the first discharge. As the material cracking caused by the volume change is considered to be the main cause of the capacity decrease of the material during the cycling, it is thus suggested that further reduction of the particle sizes and the improvement of the binder and additives should be helpful for the increase of the cycling properties.

References

- Alcántara, R., Fernándezmadrigal, F.J., Lavela, P., Tirado, J.L., Jumas, J.C., Olivierfourcade, J., 1999. Electrochemical reaction of lithium with the CoSb_3 skutterudite. *J. Mater. Chem.*, **9**:2517.
- Cao, G.S., Zhao, X.B., Li, T., Lü, C.P., 2001. Zn_4Sb_3 (-C₇) powders as a potential anode materials for lithium-ion batteries. *J. Power Source*, **94**:102.
- Jiang, X.B., Zhao, X.B., Zhang, X.B., Zhang, L.J., Cao, G.S., Zhou, B.C., 2001. Lithium-ion-storage behaviours of CoSb_3 intermetallic compound and effects of some carbonaceous additives. *Trans. Nonferrous Met. Soc. China*, **11**:852.
- Tritt, T.M., 1999. Thermoelectric materials: holey and unholey semiconductors. *Science*, **283**:804.
- Wang, J., Raistrick, I.D., Huggins, R.A., 1986. Behavior of some binary lithium alloys as negative electrode in organic solvent-based electrolytes, Electrochemical reaction of lithium with the CoSb_3 skutterudite. *J. Electrochem. Soc.*, **133**:457.
- Zhao, X.B., Cao, G.S., Li, T., 2000. Electrochemical properties of Zn_4Sb_3 as anode materials for lithium-ion batteries. *J. Mater. Sci. Lett.*, **19**:851.
- Zhao, X.B., Cao, G.S., 2001. A study of Zn_4Sb_3 as a negative electrode for secondary lithium cells. *Electrochimica Acta*, **46**:891.