ANTIMONY-BASED INTERMETALLICS AS NEW ANODE MATERIALS FOR LITHIUM BATTERIES

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Introduction

Recently, there has been great interest in the study of lithium alloys with the aim of finding new materials for the negative electrode of lithium batteries, as an alternative to carbonous materials. Tin-based alloys (or intermetallics) have received prominence due to the large reversible capacities. In particular, Fe-Sn[(1)] and Fe-Sn-C[(2)], Cu-Sn[(3)] systems have been the subject of study as lithium strage materials for lithium batteries. Here, we evaluate the galvanostatic cycling behavior of antimony-based intermetallics, $CoSb_3$.

Experimental

The $CoSb_3$ anode materials were synthesized at 600~800°C for 100 h under argon, using Co and Sb powder as starting materials. The galvanostatic cycling behavior of $CoSb_3$ electrodes has been studied in 1 mol/L $LiPF_6$ / ethylene carbonate (EC) / dimethyl carbonate (MEC) (1:2), and 1 mol/L $LiPF_6$ / EC / diethyl carbonate (DEC) (1:2). The structures of some samples during cycling were analyzed by ex-situ X-ray diffraction (XRD) with Cu-Kα radiation.

Results and Discussion

Fig.1 shows the charge and discharge curves of $CoSb_3$. The capacity of about 700 mAh/g (with respect to the mass of active material) was obtained at the first discharge (lithium insertion), which showed a plateau at about 0.5V. After further charge and discharge processes took place at about 1.2V and 0.8V, respectively. The reversible capacity is about 600 mAh/g for the first 20 cycles. The mechanism of the charge and discharge reaction was studied by X-ray diffraction (Fig.2). At the first discharge, $CoSb_3$ is decomposed to non-crystalline cobalt and Li-Sb alloy, and this reaction is irreversible. Further cycling, the reversible extraction-insertion of lithium occurred in the antimony alloy. The cycle life is longer than that of pure antimony electrodes, probably which due to the dispersion of the non-crystalline metal caused by the decomposition of $CoSb_3$. This non-crystalline metal buffers the stress and strain by phase transformation of Li-Sb, so that the pulverization of the electrode material is restrained and the cycle life is improved.

The cycle life of $CoSb_3$ was influenced by the electrolyte (Fig.3). In the DEC-based electrolyte, the observed coulombic efficiencies were slightly higher and the cycle life was longer than that in the MEC-based one. The irreversible capacity is related with the formation of a passivated film on the surface of the electrode material. For the DEC based electrolyte, dense and stable SEI (Solid Electrolyte Interface) is formed, so that the cycle life is longer.

Antimony-based intermetallics electrode have superior properties relative to a pure antimony electrode. And the intermetallics are considered to be a candidate for new anode materials of lithium batteries.

References

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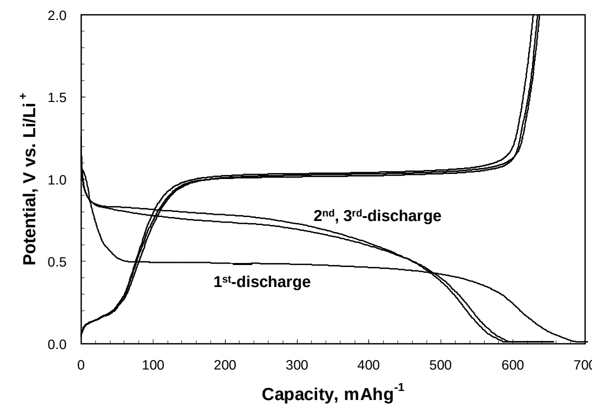

Fig.1 : Charge and discharge curves of $CoSb_3$.

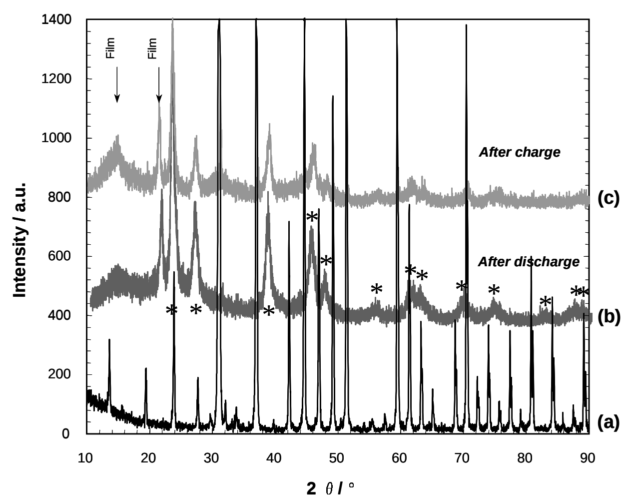

Fig.2 : XRD patterns of the pristine $CoSb_3$(a), the electrode discharged to 0.01V(b), and charged to 2V(c). ; (*) symbols indicate the peeks of Li_3Sb.

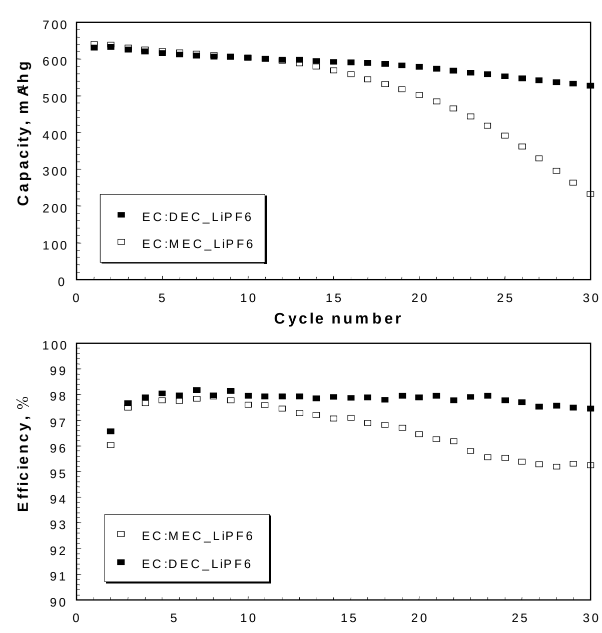

Fig.3 : Charge-discharge cycle characteristics of $CoSb_3$.