

## Study on Some Li Alloy Anodes for Lithium Secondary Batteries

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### Introduction

Recently, the demand for lithium ion batteries as a power supply for portable electric devices has steadily increased, and their capacity requirement has become larger. However, the capacity of graphite has already approached the theoretical limit of  $C_6Li$  ( $372 \text{ mAhg}^{-1}$ ).

Many studies have been conducted on Li-alloy anodes<sup>1)</sup> like Li-Sn, Li-Al and Li-Si, though the achievements are not enough because of their limited charge-discharge reactions which are necessary for heavy pulverization and followed by severe capacity decay.

In this work, some Li alloy anode under the full charge-discharge condition with theoretical capacity was investigated, focusing on Li-Sn alloy anodes<sup>2,3)</sup>.

### Experimental

An electrodeposited tin layer on electrolytic copper foil was fabricated from an aqueous solution of  $\text{SnSO}_4$ ,  $\text{H}_2\text{SO}_4$  and formalin. The thickness of this tin layer was  $2 \mu\text{m}$ . In order to investigate the effects of heat treatment, an electrodeposited tin anode with heat treatment was also fabricated by annealing the as-deposited anode at  $200^\circ\text{C}$  for 24h in vacuum.

The electrochemical characteristics were measured using a three-electrode test cell. Lithium metal was employed as a counter electrode and a reference electrode. The electrolyte was EC/DMC=1/1 containing  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6$ . In order to use the full capacity of the active material, the test cell was charged (lithium intercalation) to 0V versus  $\text{Li/Li}^+$  at three successive steps of decreasing current density, 0.25, 0.13 and  $0.05 \text{ mAcm}^{-2}$ , and was discharged to 2V versus  $\text{Li/Li}^+$  at the same steps of current density.

The structures of these anodes were investigated by backscattered electron images (BEI), X-ray diffractometry (XRD) and X-ray microanalyzer (XMA).

### Results and discussion

The charge-discharge curves of the as-deposited and the annealed anodes in the first cycle are shown in Fig. 1. In the full charge-discharge condition, the first charge capacity of  $940 \text{ mAhg}^{-1}$  of the as-deposited anode and  $905 \text{ mAhg}^{-1}$  of the annealed anode were close to the theoretical limit ( $994 \text{ mAhg}^{-1}$ ), and were 2.5 times as large as that of graphite. The coulomb efficiency in the first cycle was 93% and 90% respectively, which was almost equal to that of graphite.

Fig. 2 shows the cycle performance of the as-deposited and the annealed anodes in the full charge-discharge condition. Although the discharge capacity of the as-deposited anode in the first cycle was  $940 \text{ mAhg}^{-1}$ , it decreased to almost  $200 \text{ mAhg}^{-1}$  in the second, and never recovered in the following cycles. In contrast to this, the cycle performance of the annealed anode was significantly improved, and the retention capacity ratio after the first 10 cycles was improved from 20% to 94%. According to BEI, XRD and XMA, it was observed that this annealing induced the formation of two different Sn-Cu intermetallic compound layers between the tin layer and the copper current collector. It is considered that introducing copper in the tin phase and its concentration gradient by heat treatment enhanced the interface strength between the active material and the current collector, and thus the cycle

performance was improved.

Some Li-Si anodes under the full charge-discharge condition will be discussed as well.

### References

- 1) M. Winter, J. O. Besenhard, *Electrochimica Acta*, 45 (1999) 31-50
- 2) N. Tamura et al., The 41st Battery Symposium in Japan, Nagoya, 2000, p.540.
- 3) S. Fujitani, Proceedings of HBC2001 : The 3rd Hawaii Battery Conference, 2001, p210-214.

Fig.1 Initial charge-discharge curves of the electrodeposited anodes; solid line: the annealed anode, dotted line: the as-deposited anode.

Fig. 2 Cycle performance of the electrodeposited anodes; closed dots: the annealed anode, open dots: the as-deposited anode.

