

New a-Si Alloy Thin Film Anode with Self Organized Micro Columnar Structure

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INTRODUCTION

Li alloys like Li-Sn, Li-Si and so on have gathered many attentions because of their large specific capacity for an anode of lithium secondary batteries. However, large volume expansion from discharged state to charged state so heavily pulverizes the alloy particles in electrode as to degrade electronic conductivity and cycle performance.

We have shown that a amorphous Si (a-Si) anode formed on moderately roughened surface copper foil by a sputtering process can solve the above problem and achieve virtually 100% reversibility over a large capacity larger than 3000mAh/g.

In this work, the a-Si thin film anodes are discussed in terms of the stress relaxation mechanism through micro columnar structure self-organized by the first charge and discharge, and its phase structural change. Also, performances of experimental Li-ion cells are described.

EXPERIMENTAL

a-Si thin film electrodes were prepared by depositing Si on the electro-plated Cu foil with moderate surface roughness in micrometer scale irregularities. Argon RF sputtering process was employed for the deposition. The electrochemical performance was examined by using a tri-polar test cell with 1mol/L of LiPF_6 in EC/DEC=3:7 electrolyte. Experimental cells of 300-400mAh class were fabricated for combinations of a commercially available LiCoO_2 cathode with the a-Si thin film anode and a commercially available carbon anode, where the same capacity in unit square was given to the both anode.

The cells were charged at a constant current (1C) up to 4.2V followed by a constant voltage at 4.2V down to 20mAh and then, were discharged to 2.75V at a constant current (1C).

RESULTS AND DISCUSSION

The a-Si electrode ($5\mu\text{m}$) exhibited an initial discharge capacity of 3590mAh/g in the tri-pole test cell. The initial charge-discharge efficiency was 96%. The Si films as deposited was observed to uniformly cover the surface of the copper along with the irregularities and after first charge, grow to $17\mu\text{m}$ thickness at the fully charged state as shown in figure. 1. After the first charge and discharge, the Si thin film was divided into micro columns. However, each column remained adhering on the copper foil.

This is partly because the adhesion of the Si was enhanced by enlarged contact area of the roughened copper foil surface and partly because an intermixed layer of active mass and the underlying copper was formed during the sputtering process. The self-organized micro columnar structure was formed by microscopic anisotropy of the deposited a-Si density along with the irregularities.

The a-Si active mass remain substantially in amorphous state in a whole range. Thus, SiLi_x solid solution with an amorphous structure is considered to be the only phase in the reaction system.

Figure 2 shows thickness change of the

experimental cells. The total change of the cell thickness was almost the same, which indicate that volume increase of carbon and Si per unit Li occlusion be the same. The volumetric energy density of the cell using the Si anode was about 1.3 times as large as that using graphite. Cycle performance of these cells is shown in Fig. 3. After 50 cycles, the retained capacity using the Si anode was 92%. Further investigation on extended cycle performance is to be discussed.

REFERENCES

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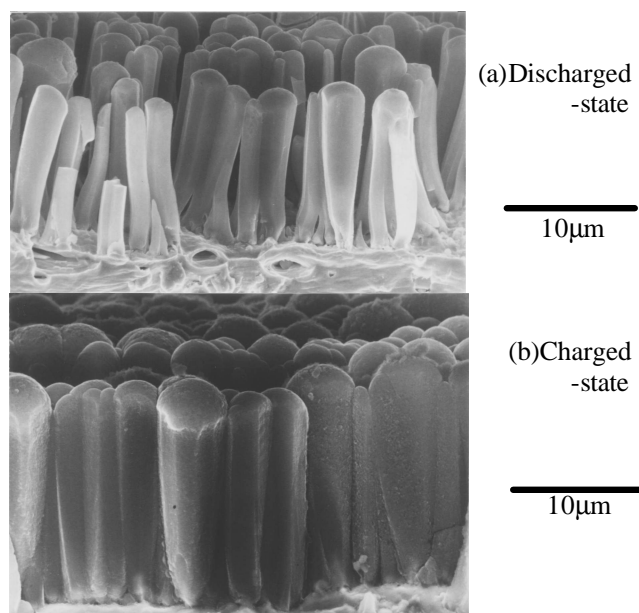


Fig. 1. Cross-sectional SEM images of a-Si thin film electrode for (a) discharged and (b) charged state.

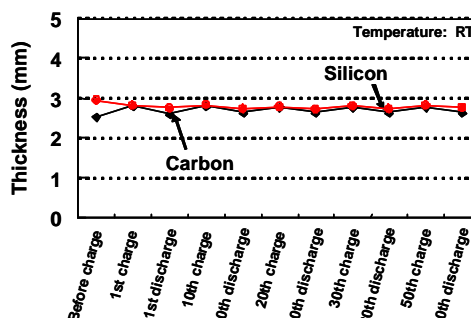


Fig. 2. The thickness change of batteries with the thin-film Si and conventional graphite anode.

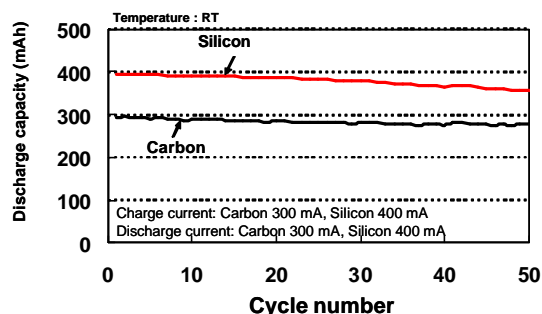


Fig. 3. Cycle characteristics of the cell using a LiCoO_2 cathode and the Si thin film anode.