

Anode behavior of electroplated rough surface Sn thin films for lithium-ion batteries

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Available online 24 May 2005

Abstract

Electroplated Sn thin films with a rough surface were prepared on a Cu foil by using an electroplating bath consisting of SnSO₄, sulfuric acid, thiourea, and non-ionic surface-active agent (polyoxyethelen(8)octylphenylether) at room temperature. The apparent density of the thin film increased as increasing amounts of the non-ionic surface-active agent were added and it exhibited its maximum value at about 1 mM. This suggests that the apparent density of the thin film was controlled by the amount of added non-ionic surface-active agent. In addition, the rough surface Sn thin films worked as negative electrode materials for lithium-ion batteries. The discharge capacities of the thin film electrodes exhibited high values of over 700 mAh g⁻¹ but their cycle performance was poor. In contrast, Sn-based alloy thin film electrodes, containing intermetallic compounds of Cu₆Sn₅ and Cu₃Sn, obtained by the heat treatment of the electroplated rough surface Sn thin films on the Cu foil, improved the cycle life of the Sn thin film electrodes compared with that prior to heat treatment. Intermetallic compounds of Cu₆Sn₅ and/or Cu₃Sn formed into thin films should limit any great volume change caused by lithium insertion and extraction.

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Keywords: Porous Sn thin film; Electroplating; Lithium-ion battery; Negative electrode material; Surface-agent

1. Introduction

Lithium-ion (LiC₆/LiCoO₂) batteries with a high energy density have been developed for use with mobile electronic devices such as cellular phones and notebook PCs. However, the capacity of graphite as a negative electrode has already approached the theoretical limit of LiC₆ (372 mAh g⁻¹). Many researchers are now studying potential new negative electrode materials. A large number of these researchers have focused on Sn metal because the theoretical capacity is 994 mAh g⁻¹ (Li_{4.4}Sn). For example, electroplated Sn thin films on a current collector exhibited a high capacity when evaluated as negative electrode materials for lithium secondary batteries. However, the cycle performance was very poor. This was believed to be because the large volume change that occurs with the expansion and/or contraction of the thin film during charge–discharge cycling destroys the conductive path in the thin film and causes exfoliation from the thin film cur-

rent collector. Therefore, it is very important to prevent this large volume change during lithium insertion and extraction. Recently, electroplated Sn-based alloy thin films [1–6] and mesoporous Sn thin films [7] were prepared with a view to overcoming this problem during charge–discharge. However, there have been no other detailed studies of porous Sn thin films as negative electrodes.

We therefore attempted to prepare electroplated porous Sn thin films on a copper foil current collector by using an electroplating bath containing a non-ion surface-active agent and to form Cu–Sn alloy in electroplated Sn thin films by using heat treatment. Then we estimated the charge–discharge properties of the thin film electrodes before and after heat treatment.

2. Experimental

Copper foil was electroplated (thickness: 4–6 μm) by using an electroplating bath containing SnSO₄, sulfuric acid, thiourea, and a non-ionic surface-agent such as 10 wt.% poly-

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Table 1
Composition of the electroplating bath

Components	Concentration
SnSO ₄	0.2 M
H ₂ SO ₄	2.0 M
Thiourea	0.2 M
Surface-active agent	<10 mM

oxyethylene(8)octylphenyl ether solution (Triton X 114), described in Table 1, under a constant current density of 20 mA cm⁻² at room temperature. In this experiment, the amount of added non-ionic surface-active agent was changed to prepare porous Sn thin films. In addition, the thin films were heat treated after electroplating at around 200 and 220 °C for 10 h in a vacuum. X-ray diffraction (XRD) measurements and scanning electron microscope (SEM) observations were carried out for the thin films both before and after heat treatment to examine their crystalline structure and morphology, respectively.

The electrode characteristics were tested in an electrochemical cell using a lithium sheet (approximately 500 μm thick) as a counter and a reference electrode. The electrolyte was 1 mol dm⁻³ LiPF₆ in an organic liquid mixture consisting of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (3:7 volume ratio). A simple two-electrode cell was fabricated in a dry Ar-filled glove box. The electrode properties at room temperature were tested by charge-discharge measurements in the 0.01–1.0 V potential range (versus Li⁺/Li).

3. Results and discussion

Regardless of the amount of non-ionic surface-active agent added to the electroplating bath, XRD measurements (Fig. 1) revealed that the crystalline structure of the electroplated thin films is attributed to the β-Sn phase. Fig. 2 shows the relationship between the apparent density of the thin film electrodes prepared by the electroplating method and the amount of added non-ionic surface-active agent. The apparent den-

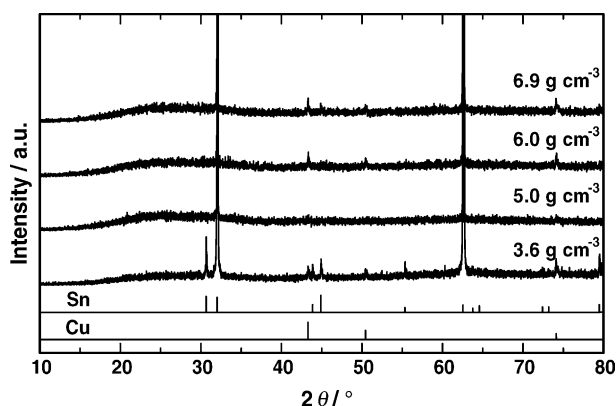


Fig. 1. X-ray diffraction patterns of electroplated thin films on Cu foil.

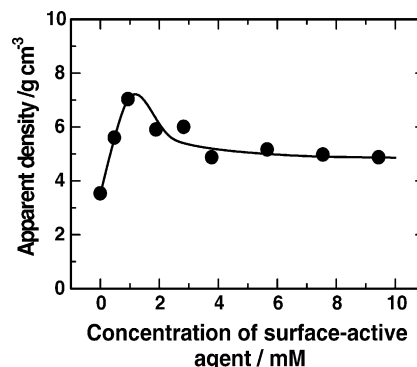


Fig. 2. Relationship between the apparent density of the thin film electrodes prepared by the electroplating method and the amount of added non-ionic surface-active agent.

sities were calculated from the electroplated weight and thin film thickness. The apparent density of the thin film prepared without the addition of the non-ionic surface-active agent was about 3.5 g cm⁻³. The apparent densities of the thin film increase as the added amount increases and decrease after that. In this case, the apparent density exhibited its maximum value when the amount of added surface-active agent was about 1 mM. Such thin film has a relatively high density (about 6.9 g cm⁻³) because the density of β-Sn is 7.2 g cm⁻³. By contrast, the apparent densities have a constant value of about 5.0 g cm⁻³ when the amount of added surface-active agent is above 4 mM. These results mean that we should be able to control the density by adding very small amounts of non-ionic surface-active agent. In addition, SEM observations showed that the surface area of the thin film was uneven. Therefore, we believe it is possible to control the density of the thin film prepared by electroplating by controlling the surface roughness under these experimental conditions.

Fig. 3 shows the first charge–discharge curve of Sn thin film with an electrode density of about 5.0 g cm⁻³ without heat treatment. The thin film works as a rechargeable negative electrode material for lithium-ion batteries. The irreversible capacity during the first charge–discharge is about 23%. The discharge capacity (lithium extraction) over 700 mAh g⁻¹

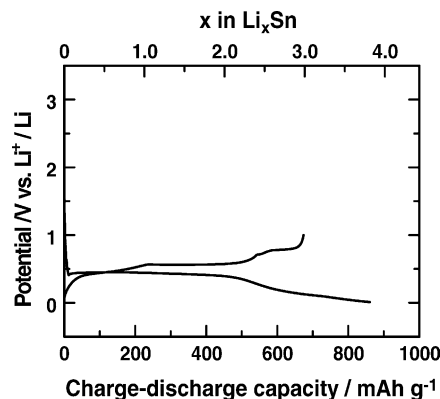


Fig. 3. First charge–discharge curve of Sn thin film with an electrode density of about 5.0 g cm⁻³ without heat treatment.

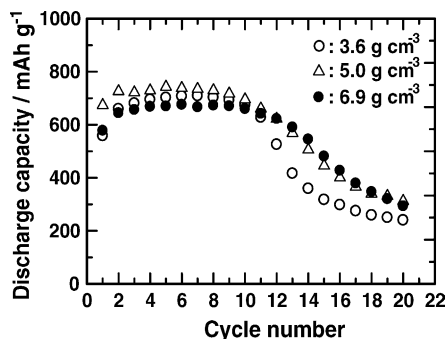


Fig. 4. Cycle performance of thin films with apparent electrode densities of 3.5, 5.0, and 6.9 g cm^{-3} before heat treatment.

was about two times that of carbon negative electrodes in conventional lithium-ion batteries.

Fig. 4 shows the cycle performance of thin films with apparent electrode densities of 3.5, 5.0, and 6.9 g cm^{-3} before heat treatment. Their discharge capacities degrade rapidly after about the 12th cycle during the charge–discharge test. The cycle performance of Sn thin films with electrode densities of 5.0 and 6.9 g cm^{-3} was slightly better than that for an apparent electrode density of 3.5 g cm^{-3} . However, the performance was still poor.

We used heat treatment to improve the cycle performance of electroplated Sn thin films with a rough surface on Cu foil. Fig. 5 shows XRD patterns for thin films with an apparent electrode density of 6.0 g cm^{-3} before and after heat treatment at 200 and 220 °C for 10 h in a vacuum. The thin film heat treated at 200 °C shows the same patterns before and after treatment. On the other hand, by using XRD measurements we confirmed that Cu_3Sn and Cu_6Sn_5 are mainly formed with heat treatment at 220 °C. Peaks attributed to Sn alloys were also detected for other thin films after heat treatment at 220 °C. The Sn alloy thin films were simply prepared from electroplated Sn thin films with a rough surface on Cu foil.

Fig. 6 shows the cycle behavior of the thin films after the heat treatment of electroplated Sn thin films with various

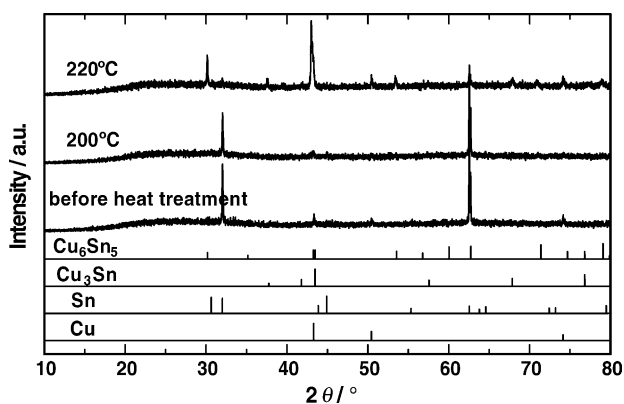


Fig. 5. X-ray diffraction patterns before and after heat treatment of the thin films with an apparent electrode density of 6.0 g cm^{-3} at 200 and 220 °C for 10 h in a vacuum.

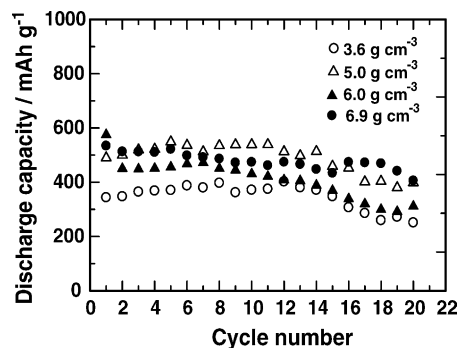


Fig. 6. Cycle behavior of the thin films after heat treatment of the electroplated Sn thin films with various electrode densities (3.6, 5.0, 6.0, and 6.9 g cm^{-3}).

electrode densities (3.6, 5.0, 6.0, and 6.9 g cm^{-3}). Although there was almost no difference in the charge–discharge characteristic at each electrode density, all the electrodes exhibited relatively better cycle performance after heat treatment as shown in Fig. 4. Therefore, the Cu–Sn alloy electrodes obtained by the heat treatment of Sn thin films with low or high densities provide improved cycle performance. Intermetallic compounds of Cu_6Sn_5 and/or Cu_3Sn formed in the Sn thin films as starting materials should prevent any great volume change during lithium insertion and extraction.

At present, we are investigating high rate performance, the relationship between cycle properties and the morphology or expansion of thin film electrodes after a charge–discharge cycle, and the basis of the irreversible capacity of porous Sn thin film negative electrodes.

4. Conclusions

Electroplated Sn thin films with a rough surface on Cu foil were prepared by using an electroplating bath consisting of SnSO_4 , sulfuric acid, thiourea, and a non-ionic surface-active agent (polyoxyethylene(8)octylphenyl ether) at room temperature. The apparent densities (3.5–6.9 g cm^{-3}) of the electroplated Sn thin film were controlled by the amount of added non-ionic surface-active agent. The density is controlled by the surface roughness under these experimental conditions. In addition, thin film electrodes consisting of intermetallic compounds of Cu_6Sn_5 and/or Cu_3Sn that were obtained by heat treating the electroplated Sn thin films with a rough surface on the Cu foil improved the cycle life of the thin film electrodes.

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