

Irreversible capacity of electrodeposited Sn thin film anode

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Abstract

Tin thin film anodes for lithium-ion cells were prepared by electroplating and morphology changes of the surface during alloying and de-alloying were investigated by in situ AFM to understand the origin of large irreversible capacity on Li–Sn alloy anodes. The results of cyclic voltammetry (CV) revealed that an irreversible reduction peak, which is assigned to solvent decomposition, was observed in the range 1.0–1.4 V not in the first cycle, but in the second cycle and later. AFM observation during CV revealed that surface roughening by alloying and de-alloying occurred significantly in the first and second cycles. This surface roughening destroyed existing surface film and brought about a large area of active surface, and therefore is the reason for the appearance of large irreversible capacities in the second and third cycles in constant current charge and discharge tests.

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1. Introduction

Lithium alloys such as Li–Sn and Li–Si have attracted much attention because they have high specific capacities than graphite electrodes now used in commercially available lithium-ion cell [1–3]. However, capacity retention of lithium alloys is poor and should be improved for commercial application. It is widely known that large volume expansion and contraction occur during charging and discharging to cause particle fracture and electrochemical pulverization, which results in significant capacity loss upon cycling. Another problem is the presence of a large irreversible capacity [4,5]. It is reasonable to consider that protective surface film, called solid electrolyte interphase (SEI), is formed on these alloy electrodes as have been reported for graphite negative electrodes [6–8]. However, there have been few reports concerning decomposition of electrolyte and the resulting SEI formation on lithium alloy anodes, and therefore the SEI formation should be clarified to understand the origin of the large irreversible capacity. Thick SEI layer may be another reason for the poor capacity retention of lithium alloy electrodes.

In the present study, tin thin film anodes were prepared by electroplating, and their electrochemical properties were tested. Morphology changes of the surface during alloying and de-alloying were investigated by in situ AFM [6–8] to understand the origin of the large irreversible capacity on Li–Sn alloy anodes.

2. Experimental

Tin thin films were electrodeposited on copper substrates from a sulfate bath [3]. The copper substrates were polished with 1 μm diamond slurry to a mirror finish (roughness: ca. 30 nm). The sulfate bath contains SnSO_4 (27 g L^{-1}), H_2SO_4 (100 mL L^{-1}), Stannolume 161 makeup (33 mL L^{-1} , Atotech Japan) and Stannolume 161 collective (5 mL L^{-1} , Atotech Japan). Sn thin films were deposited at 2.0 mA cm^{-2} for 10 min using an Sn plate (99.9% purity) counter electrode. The calculated thickness of the resulting thin films was about 1 μm . The Sn thin films were washed with distilled water and dried at 60 $^\circ\text{C}$ in an electric oven.

Electrochemical measurements were carried out using three-electrode cells. The counter and reference electrodes were lithium metal. The electrolyte solution was 1 M LiClO_4

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dissolved in propylene carbonate (PC, Kishida Chemical Co., Lithium Battery Grade). Cyclic voltammetry (CV) was conducted at 0.5 mV s^{-1} between 2.0 and 0.0 V using a potentiostat (Hokuto Denko, HSV-100). Charge and discharge tests were carried out at a constant current of $56 \mu\text{A cm}^{-2}$ ($12/C$ rate) between 2.0 and 0.0 V using a battery test system (Hokuto Denko, HJ1001SM8). For AFM observation, the thin film sample was mounted at the bottom of a laboratory-made electrochemical AFM cell [6,7]. In situ electrochemical AFM observation was carried out with an AFM system (Molecular Imaging, PicoSPM[®]) equipped with a potentiostat (Molecular Imaging, PicoStat[®]). Cyclic voltammetry was performed at 0.5 mV s^{-1} between 2.0 and 0.0 V, and AFM images were continuously obtained during the CV measurements. All measurements were carried out at 30°C in an argon-filled glove box (Miwa, MDB-1B+MM3-P60S) with a dew point lower than -60°C .

3. Results and discussion

Fig. 1 shows typical cyclic voltammograms at 0.5 mV s^{-1} of the Sn thin film prepared by electroplating. A cathodic peak at 0.25 V and an anodic peak at 0.75 V were observed, which are assigned to lithium alloying and de-alloying, respectively [3,9]. The peaks were broadened and the peak current gradually decreased upon cycling. The poor cycleability generally has been attributed to a large volume changes during alloying and de-alloying [1]. In addition to these reversible peaks, an irreversible peak was seen in the range of 1.4–0.9 V in Fig. 1 (see the inset). This peak is most probably assigned to solvent decomposition and SEI formation [4,5] because the alloying reaction occurs at potential more negative than 0.7 V. Surprisingly, the peak was not observed in the first cycle, but appeared in the second cycle. The peak current became the maximum in the third cycle and decreased in the fourth

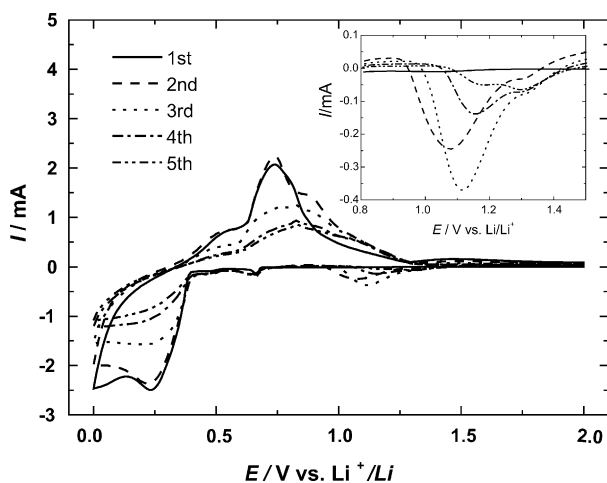


Fig. 1. Cyclic voltammograms of electrodeposited Sn thin film in 1 M LiClO_4/PC . Scan rate: 0.5 mV s^{-1} . The inset show magnified voltammograms in the range of 0.8–1.6 V.

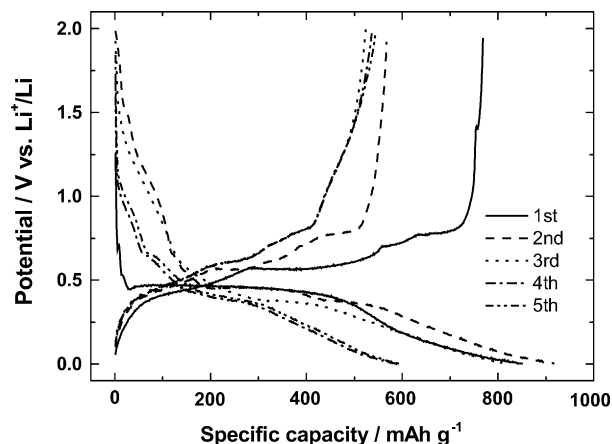


Fig. 2. Charge and discharge curves of electrodeposited Sn thin film at $56 \mu\text{A g}^{-1}$ ($12/C$ rate) in 1 M LiClO_4/PC .

and fifth cycles. In the case of graphite negative electrodes, the irreversible peak, which is assigned to reductive decomposition of electrolyte and SEI formation, appears only in the first charging process [6–8]. This curious phenomenon on the electrodeposited Sn thin films originated from the large volume change during cycling as will be discussed later.

Fig. 2 shows charge and discharge curves of the tin thin film at a constant current of $12/C$. The first discharge capacity was 780 mAh g^{-1} , but decreased in the range $500\text{--}600 \text{ mAh g}^{-1}$ in the following cycles. The irreversible capacity was small in the first cycle (81.2 mAh g^{-1}). However, large irreversible capacities appeared in the second and third cycles (349 and 291 mAh g^{-1} , respectively). In the fourth cycle and later, the irreversible capacity greatly decreased to $50\text{--}60 \text{ mAh g}^{-1}$. On the second and third charge curves, an additional capacity is seen in the potential range of $1.5\text{--}1.0 \text{ V}$, which is the major reason for the large irreversible capacities in the second and third cycles. The presence of the additional capacity in this potential range is in agreement with the results of CV in Fig. 1.

To clarify the abnormal appearance of the irreversible capacity in the second and third cycles, cyclic voltammetry was carried out and surface morphology changes were observed simultaneously by in situ AFM. Panel (a) in Fig. 3 shows a cyclic voltammogram of Sn thin film electrode at 0.5 mV s^{-1} obtained in the electrochemical AFM cell. The voltammogram was very similar to that of the first cycle in Fig. 1. Fig. 3(b–f) show AFM images obtained simultaneously during the CV. Before CV, the surface was flat and grooves made by polishing of the substrate were clearly seen. The roughness of the surface before CV was about 60 nm . During the cathodic sweep, nearly no morphology change was observed down to 0.3 V , though a small reduction peak was observed at about 0.7 V . At around 0.3 V (Fig. 3(c)), expansion of surface was observed, which was due to an increase in volume by the alloying reaction with lithium in the range $0.4\text{--}0.0 \text{ V}$ in the CV. At lower potentials (Fig. 3(d)), surface expansion be-

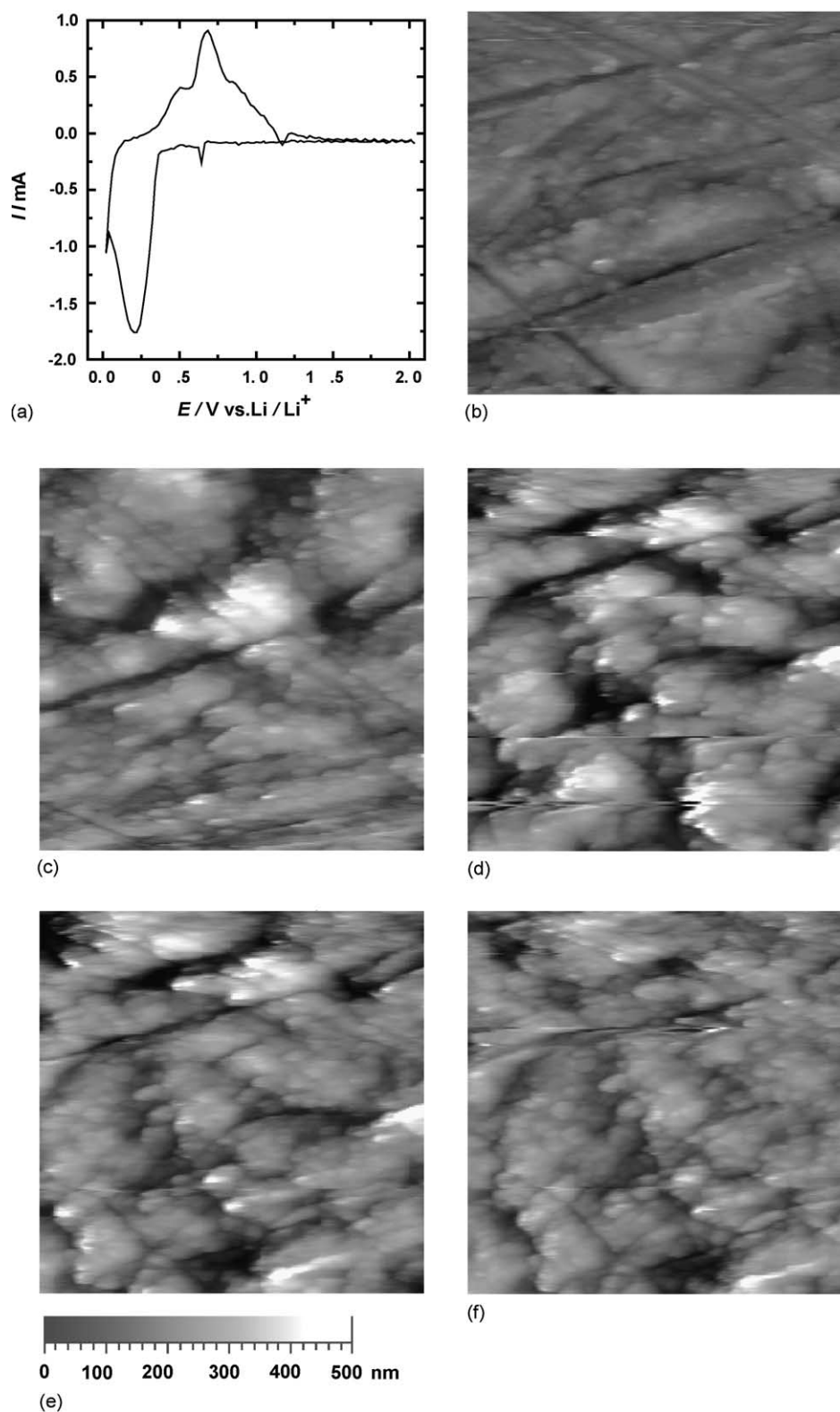


Fig. 3. Cyclic voltammogram (a) and AFM images (b–f) ($1 \mu\text{m} \times 1 \mu\text{m}$) of electrodeposited Sn thin film obtained (b) before CV (2.0 V), in the potential ranges of (c) 0.35–0.20 V, (d) 0.20–0.05 V, (e) 0.70–0.85 V during CV and (f) after CV (2.0 V) in 1 M LiClO_4/PC . Scan rate: 0.5 mV s^{-1} .

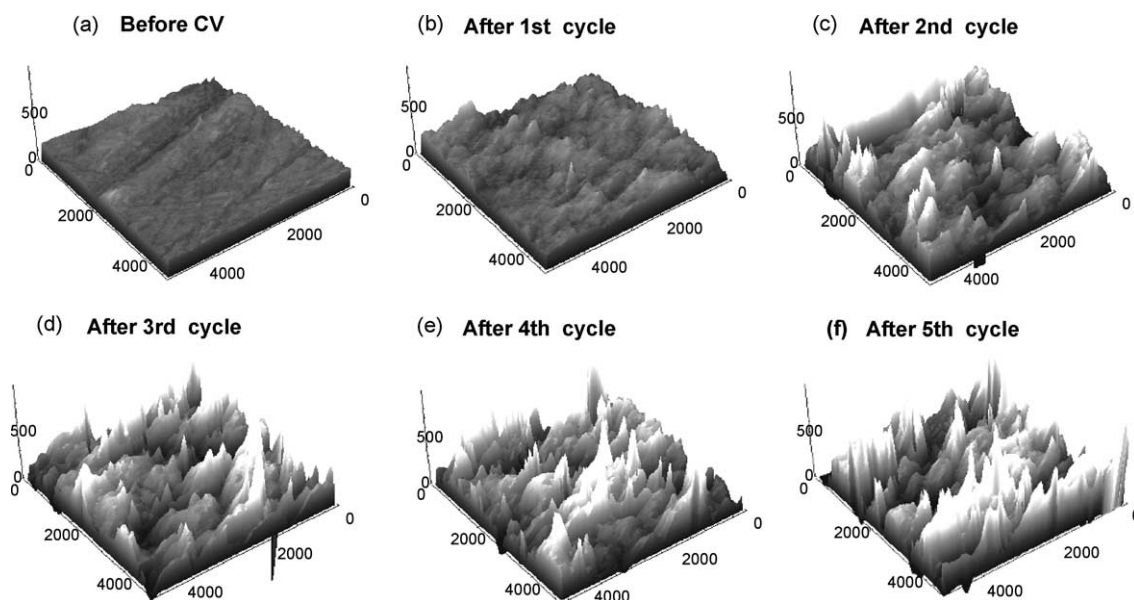


Fig. 4. Three-dimensional AFM images of electrodeposited Sn thin film (a) before and (b–f) after CV in 1 M LiClO₄/PC. Scan rate: 0.5 mV s⁻¹.

came more significant, and the surface roughness increased to 400 nm. During the anodic sweep, dramatic contraction of the surface was observed at about 0.7 V (Fig. 3(e)), which corresponded to the de-alloying peak in the CV. After the first cycle of CV (Fig. 3(f)), surface roughness decreased to 200 nm, but was still much larger than that before CV.

Fig. 4 shows the variation of surface morphology up to the fifth cycle. Surface roughening occurred drastically in the first and in second cycle, but in the third cycle and later, surface morphology did not change significantly. The appearance of the large irreversible capacity in the second and third cycles therefore can be attributed to a large change in surface roughness in the first and second cycles. Tin film electrode as prepared by electroplating had an inert surface presumably because of the presence of an oxide layer, and therefore only a negligible amount of solvent decomposition occurred in the first cathodic sweep. However, the alloying and de-alloying reactions caused surface roughening, especially in the first and second cycles, as shown in Fig. 3, and thereby existing SEI layer was destroyed and a large area of active surface was formed on the thin film. In addition, the oxide layer was probably reduced to metallic surface at lower potentials, which also activated the surface. Consequently, in the following charging process, vigorous solvent decomposition occurred in the potential range of 1.0–1.4 V on the surface activated, which resulted in the appearance of large irreversible capacities in the second and third cycles in Fig. 2. On the other hand, in the third cycle and later, further surface roughening did not occur as shown in Fig. 4(d–f). Hence, stable SEI layer was hence formed on the surface and solvent decomposition decreased significantly, which resulted in a decrease in irreversible capacity as shown in Fig. 2. Beaulieu et al. investigated the electrochemical reactions of Sn thin film

prepared by sputtering, and reported that a large irreversible reaction occurred at about 1.6 V in the first charging process [4]. They reported that their thin film did not contain oxygen at all from the results of energy dispersive spectroscopy (EDS) measurements. The presence of oxide layer may play an important role in surface reactivity to solvent decomposition.

4. Conclusions

Sn thin films were prepared by electroplating and morphology changes of the surface during charging and discharging were investigated by in situ AFM to understand the origin of the large irreversible capacity on Li–Sn alloy anodes. The results of CV revealed that an irreversible reduction peak, which is assigned to solvent decomposition and SEI formation, appeared in the range 1.0–1.4 V not in the first cycle, but in the second cycle and later. Similarly, in the constant current charge and discharge tests, large irreversible capacities (~ 300 mAh g⁻¹) were observed in the second and third cycles.

AFM observation during CV revealed that volume expansion and contraction of the Sn film and the resulting surface roughening occurred significantly in the first and second cycles. This surface roughening destroyed existing SEI layer and brought about a large area of active surface, and therefore is the reason for the appearance of large irreversible capacities in the second and third cycles. Unfortunately, the surface of the Sn thin film became too rough during alloying to observe SEI layer itself in the present study. Much thinner and flatter film is needed to observe how SEI layer is formed on Sn.

Acknowledgment

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