Multilayered Sn-Zn/Zn/Cu Alloy Film Electrode Prepared by Electroplating Method for Lithium Secondary Batteries

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Received May 29, 2003 ; Accepted October 8, 2003

A multilayered Sn-Zn/Zn/Cu film electrode was prepared by an electroplating method and the electrode performance was investigated. The heat-treated electrode showed an excellent charge-discharge performance; a discharge capacity of around 300 mAh g⁻¹ was maintained even after 100 cycles. The electrode was mainly composed of a Cu₆Sn₅ phase due to interdiffusion of Sn and Cu during heat-treatment process. At the same time, two Zn enriched layers were formed. This optimized electrode structure would relax volume expansion and phase transition during cycling, resulting in an enhanced electrode performance.

Key Words : Sn-based Alloy Electrode, Electroplating Method, Multilayer Film

1 Introduction

Sn-based alloys have been studied as negative electrode materials for lithium secondary batteries. Although they have larger theoretical capacity than that of graphite, they generally don't have an enough cyclic life to be used as commercial products. One of the serious problems is that large volume expansion and structure transition in the electrode occurs during charge-discharge process, which cause cracks, at last, resulting in a capacity decay. Many attempts have been made for the purpose of practical applications by forming various Sn-based alloys/intermetallic compounds and composites with inorganic and organic agents.¹⁻⁷⁾

An electroplating method has been used to prepare Sn-based alloy electrodes.^{1, 8-10)} In this preparing process, any binder and conducting agents are not needed, and therefore a compact electrode with low cost could be prepared. In our previous work, Sn and Sn-Zn films on a Cu foil (Sn/Cu and Sn-Zn/Cu electrodes) have been developed using the electroplating method, and its performance has been reported.^{9, 10)} It was found that these electrodes with heat-treatment at appropriate conditions showed a high electrochemical capacity and a good cycle life because of the formation of Cu₆Sn₅ due to interdiffusion of Sn in the plated film and Cu from the Cu foil. In this work, a multilayered Sn-Zn/Zn/Cu film electrode has been prepared using the electroplating method. We expect that a Zn layer would strengthen an adhesion between an active material and a Cu foil, resulting in a better cyclic performance than that of the Sn-Zn/Cu electrode. The structure and performance of the multilayered Sn-Zn/Zn/Cu electrode have been investigated in detail.

2 Experimental

A Zn film was electroplated on a Cu foil (current col-

lector), and then a Sn-Zn alloy film was electroplated on the top of that to produce a multilayered Sn-Zn/Zn/Cu film electrode. A Zn plating solution was composed of 0.16 M (= mol dm⁻³) Zn²⁺ and 0.65 M Sulfosuccinic acid, and pH was adjusted to 2-5. In the case of a Sn-Zn alloy plating, a solution composition was 0.18 M Sn²⁺, 0.04 M Zn²⁺, and 0.5 M Sulfosuccinic acid, and pH was adjusted 3-6. The current density of the Zn and Sn-Zn alloy plating was 10-50 mA cm⁻² and 5-20 mA cm⁻², respectively. The content of Zn in the Sn-Zn film was around 10 wt %. The thickness of the plated Zn and Sn-Zn films was around 0.5 and 5 μm, respectively. In order to improve the performance of the electrode, heat-treatment has been carried out at 200°C for 17 hours under vacuum.

Electrode structures were characterized by X-ray diffraction analysis (XRD) using a M06XCE diffractometer with Cu radiation source (MAC science), scanning electron microscopy (SEM) (HITACHI, S-2150) and energy dispersion X-ray spectroscopy (EDX) (HORIBA, EMAX-7000).

Charge-discharge tests were conducted using a screw type stainless cell composed of the multilayered Sn-Zn/Zn/Cu film electrode as working electrode (φ 11), a Li metal sheet as counter electrode (φ 18) and a separator. Electrolyte was 1 M LiPF₆ in EC and DMC (1 : 2 by volume). All cells were assembled in an argon atmosphere globe box. Cyclic tests were carried out at constant current density; the current density was 0.2 mA cm⁻² for 1st charging (Li insertion) and 0.2 mA cm⁻² for 1st discharging (Li extraction), and was 0.4 mA cm⁻² for charging and 1.0 mA cm⁻² for discharging after following cycles. The potential range was 0-1.0 V vs. Li/Li⁺.

3 Results and Discussion

Figure 1 shows the first cycle profiles of the as-plated

and heat-treated multilayered Sn-Zn/Zn/Cu film electrodes. It can be seen that these curves were very different; there was an obvious plateau about 0.4 V vs. Li/Li^+ on charging process and several plateaus on discharging process for the as-plated electrode. On contrast, a plateau at about 0.2 V was present on charging process and a smooth curve was observed on discharging process for the heat-treated electrode. It was suggested that a main component of the as-plated electrode was different from that of the heat-treated one.

Figure 2 presents the cyclic behaviors of the as-plated and heat-treated electrodes. An initial capacity of the as-plated electrode was very high, but the cycleability was poor. A discharge capacity of the as-plated electrode was high around 700 mAh g^{-1} within first 10 cycles. During the following 10 cycles, the discharge capacity drastically decayed to below 100 mAh g^{-1} . On contrast, the heat-treated electrode showed an excellent cyclic performance though the capacity fade for initial several cycles was significant. A discharge capacity of about 300 mAh g^{-1} was maintained even after 100 cycles.

In order to investigate the effect of these electrode structures on the performances of these electrodes, the structure difference between the as-plated and heat-treated electrode was investigated. Figure 3 presents the XRD patterns of the as-plated and heat-treated electrodes. Peaks attributed to Sn and Cu (foil) were observed for the as-plated electrode, but there was no peak for Zn due

Fig. 1 First charge-discharge curves of the as-plated and heat-treated multilayer Sn-Zn/Zn/Cu film electrodes.

Fig. 2 Cyclic behaviors of as-plated and heat-treated multilayer Sn-Zn/Zn/Cu film electrodes.

to lower Zn content. In the case of the heat-treated electrode, it was found that a Sn phase decreased, and Cu_6Sn_5 intermetallic compound was formed and became a main component because of interdiffusion of Sn and Cu during heat-treatment process.

Figure 4 shows distributions of Sn, Cu and Zn elements on cross-section of the as-plated and heat-treated electrodes. For the as-plated electrode, the electroplated Zn film was observed clearly between the plated Sn-Zn film and the Cu foil. The result also shows that the content of Zn in the plated Sn-Zn film is low, so it cannot be observed by XRD analysis. In the case of the heat-treated electrode, the figure shows the trend that Cu diffused from Cu foil toward the plated film, resulting in the formation of Cu_6Sn_5 during heat-treatment. On the other hand, Zn between the plated Sn-Zn film and Cu foil separated into two parts; one was a center of the Cu_6Sn_5 layer and the other was a interface between the Cu_6Sn_5 layer and Cu foil. As a result, a multilayered structure electrode composed of Cu_6Sn_5 and Zn enriched layers was formed by heat-treating an as-plated Sn-Zn/Zn/Cu film electrode, as shown in Fig. 5.

Based on the relations between the electrode structures and charge-discharge curves or cyclic behaviors of the as-plated and heat-treated electrodes, the formation of Cu_6Sn_5 layer could contribute to a good performance

Fig. 3 XRD patterns of as-plated (a) and heat-treated (b) multilayer Sn-Zn/Zn/Cu film electrodes.

Fig. 4 Distributions of Sn, Cu, and Zn elements on cross-section of as-plated and heat-treated multilayer Sn-Zn/Zn/Cu film electrodes.

Fig. 5 Electrode structure model of multilayer Sn-Zn/Zn/Cu film electrode heat-treated at 200°C for 17 hours.

Fig. 6 Surface morphology of heat-treated electrodes before cyclic test and after 1 cycle and after 100 cycles.

of the heat-treated electrode. It was suggested that during the charge process of the heat-treated electrode, Li reacted with Cu_6Sn_5 to yield a Li_2CuSn -type phase firstly, and further lithiation of Li_2CuSn proceeded to yield $\text{Li}_{4.4}\text{Sn}$ and extracted Cu.^{2, 4)} At the same time, extracted Cu was used as a binder and matrix in the electrode, which would relax volume expansion of the electrode during charge-discharge process.²⁾ On the other hand, the Zn enriched layer sandwiched between two Cu_6Sn_5 layer could also relax volume expansion and the other Zn enriched layer at interface between Cu_6Sn_5 layer and Cu foil would strengthen an adhesion of the interface. So the good performance of the heat-treated electrode was obtained by forming the optimized multilayer structure, composed of Cu_6Sn_5 intermetallic and Zn enriched layers.

The surface morphology of the heat-treated electrode before and after charge-discharge cycles have been shown in Fig. 6. The surface of the electrode before test looks like wrinkle but evenly. After 1st cycle, it was observed that the surface morphology has been changed drastically and cracks emerged. As charge-discharge cycle proceeded further, for example after 100 cycles, the active material broke to fine particles. It suggests the capacity decay of the electrode can be attributed to the loss of the contact between the active material particles, and the adhesion between the active material layer and the Cu foil due to the formation of cracks, resulted from the volume expansion and phase transition during charge-discharge process. In order to use Sn-based alloys in Li secondary batteries, this problem should be solved.

4 Conclusion

In this work, we prepared the multilayered Sn-Zn/Zn/Cu film electrode by the electroplating method and its performance as negative electrode for lithium secondary batteries has been investigated. Experimental results showed that the heat-treated electrode was composed of Cu_6Sn_5 and Zn enriched layers, and showed an excellent cyclic performance; a discharge capacity of about 300 mAh g^{-1} was maintained even after 100 cycles. The multilayered Sn-Zn/Zn/Cu film electrode would be a promising negative electrode material for lithium secondary batteries.

Acknowledgement

This work is a part of "Regional Consortium Research Development Work" supported by METI.

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