Deformation Behavior of Copper Foil Collectors with Ni_3Sn_4 Film During the Charge-Discharge of Lithium Ion Secondary Cells on the Basis of an Optical Cantilever Method

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Received November 30, 2009 ; Accepted February 4, 2010

The deformation behavior of copper foil collectors electrodeposited with Ni_3Sn_4 during the charge-discharge cycle was observed in situ using an optical cantilever method. It was found that in the high yield strength copper foil, cyclical deformation due to charge-discharge were observed, while in low yield strength copper foil, the deformation which occurred during the first charge period remained. The former is elastic deformation and the latter is plastic deformation. As plastic deformation promotes deterioration through peeling and shedding of the active material during sequential cycles, the high yield strength copper should be adopted. For example, 3 μm Ni_3Sn_4 film requires a 31 μm pure copper foil collector with a yield strength of 350 MPa or a 18 μm Corson copper alloy foil collector with the yield strength of 700 MPa.

Key Words : Copper Foil Collector, Ni-Sn Alloy, Li-ion Battery, Deformation

1 Introduction

Lithium alloying metal based anode materials such as Sn, Si, Sb have been extensively investigated for high energy density Li-ion batteries. However, they have poor cyclability because of their larger volume change compared to conventional carbon base anodes during the charge-discharge cycle. The large volume change causes a peeling and shedding of anode material from the copper foil as well as collector or breakage into fragments. As the copper foil collectors suffer a large stress from the anode materials expanding, the mechanical properties of the copper foil is a major factor related to the degradation of electrode performance. However, although there are some reports available on the electrochemical characteristics of copper foil collectors, there are no reports regarding the influence of the mechanical properties.^{1,2)}

In our study, we firstly investigated the relation between the mechanical properties and the transformational behavior of copper foil during charge-discharge cycles. The *in-situ* deformation measurement was achieved using the optical cantilever method with a set of Ni_3Sn_4 film and a copper foil regarded as a bimetal.³⁾

2 Experimental

Table 1 shows the mechanical properties of the copper foils used in the experiment. The copper-foil samples have different thicknesses and a 0.2% yield strength. Samples Nos. 1 to 6 are rolled copper foil (Hitachi Cable, Ltd.). Nos. 1, 2 and 3 are pure copper called TPC (Tough Pitch Copper). No. 4 is a solid-solution-hardened copper alloy, and Nos. 5 and 6 are precipitation-hardened copper alloys. No.6 is a kind of Corson copper alloy. Samples Nos. 7 and 8 are general types of electrolyte copper foils. The thickness and the 0.2% yield strength are measured

values. It is known that 0.2% yield strengths of Nos. 2 and 3 change to that of No. 1 with annealed at 150 °C for 30 min and Nos. 4, 5 and 6 are stable at 400 °C for 60 min.

The active material was electrodeposited onto the copper foil at 50 °C in a pyrophosphoric acid bath (Nihon Kagaku Sangyo, Pyroalloy® SN). The active material thickness was 0.1, 1.0 or 3.0 μm , as controlled by the time of electrodeposition under a constant current density of 10 mA cm^{-2} .

The *in-situ* displacement measurements were made using the method given in Ref. 4. Figure 1 shows the cell structure. The active material was electroplated onto one side of the copper foil. While the copper foil was

Table 1 Mechanical properties of copper foil collectors.

No.	Copper Foils ^{a)}	Chemical composition /mass%	Thickness $t_{\text{Cu}}/\mu\text{m}$	0.2% Yield strength $\sigma_{\text{Cu}}/\text{MPa}$
1	R TPC (annealed)	Cu : > 99.9	16	70
2	R TPC		16	350
3	R TPC		31	350
4	R HCL02Z	Zr : 0.02 Cu : balance	18	390
5	R HCL64T	Cr : 0.25 Sn : 0.25 Zn : 0.20 Cu : balance	25	540
6	R HCL305	Ni : 2.5 Si : 0.5 Zn : 1.5 Cu : balance	18	700
7	E A	Cu : > 99.9	12	270
8	E B		30	190

a) R : Rolled Copper E : Electrodeposited Copper

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Fig. 1 Schematic view of measurement cell.

lithium-inert and did not show a volume change due to charge and discharge, the active material showed volume expansion and contraction due to lithiation and delithiation, and so the electrode warped and returned to its original shape. A laser beam was placed incident to the copper side surface, and the reflection was detected with a laser displacement meter (Keyence, LK080). Two lithium plates were used as reference and counter electrodes. A solution of 1 M LiClO_4 in a 1:1 (v/v) mixture of ethylene carbonate (EC) and propylene carbonate (PC) was used as the organic solvent (Tomiya Yakuin Kogyo, LIPASTE®). A galvanostatic charge-discharge tests (Hokuto Denko, HJ1001SM8J) was used with a current density 0.4 mA cm^{-2} for the samples of thickness 0.1 and $1.0 \text{ }\mu\text{m}$, and 1.2 mA cm^{-2} for the samples of thickness $3.0 \text{ }\mu\text{m}$.

3 Results and Discussion

The electrodeposited active material was Ni-57atm% Sn or Ni_3Sn_4 . Figure 2 shows a typical time change of voltage and displacement in the electrode; (a) in $18 \text{ }\mu\text{m}$ HCL305 foil with a $1 \text{ }\mu\text{m}$ Ni_3Sn_4 , the displacement in the copper foil varied cyclically between 0 and 3.5 mm in accordance with the voltage change due to charge and discharge; (b) in annealed $16 \text{ }\mu\text{m}$ TPC foil with a $1 \text{ }\mu\text{m}$ Ni_3Sn_4 , the displacement in the initial charge remained, and the foil did not return to the initial state.

Figure 3 shows the deformation of $18 \text{ }\mu\text{m}$ HCL305 foil with a $1 \text{ }\mu\text{m}$ Ni_3Sn_4 in the first cycle. As charging proceeded, the displacement began to increase due to the volume expansion of the active material. In the discharge period, the displacement swiftly decreased to almost zero, and then began to increase rapidly again. This was very probably because cracks in the active material caused by volume contraction released the plating stress that had been there from the start.

In the second cycle onward, the displacement rose steadily as charging began. This behavior resembled that of the first cycle, but the displacement was smaller. This was very probably because the volume change of the active material became small due to the evolution of cracks in the active material, and with that, the effect on the copper foil was reduced. Figure 5 shows the SEM

Fig. 2 In-situ measurement of electrode displacement in the charge-discharge cycle for the samples: (a) $18 \text{ }\mu\text{m}$ HCL305 with $1 \text{ }\mu\text{m}$ Ni_3Sn_4 deformed cyclically and (b) $16 \text{ }\mu\text{m}$ TPC with $1 \text{ }\mu\text{m}$ Ni_3Sn_4 deformed permanently and did not return to the initial state.

images of $3 \text{ }\mu\text{m}$ Ni_3Sn_4 electrodeposited on $18 \text{ }\mu\text{m}$ HCL305 copper foil. These indicate the one charge-discharge which caused the Ni_3Sn_4 to crack.

Stoney's equation (1) between film stress and strain:

$$\sigma_{\text{NiSn}} = E t_{\text{NiSn}}^2 / 6 r t_{\text{Cu}} \quad (1)$$

is well known.⁵⁾ Assuming $t_{\text{NiSn}} \ll t_{\text{Cu}}$, the neutral plane is $2/3$ apart from the interface with the Ni_3Sn_4 film, and using the geometric similarity condition

$$d / r = \Delta d / (2 t_{\text{Cu}} / 3) \quad (2)$$

we have:

$$t_{\text{NiSn}} \sigma_{\text{NiSn}} = 0.25 \sigma_{\text{Cu}} t_{\text{Cu}} \quad (3)$$

Here, t_{NiSn} is the film thickness of Ni_3Sn_4 ; σ_{NiSn} is the stress of the active material; t_{Cu} , σ_{Cu} , E are the thickness, stress, and Young's modulus of copper foil; r is the radius of curvature of warpage; d is the perimeter at the neutral plane; and Δd is the displacement at the lateral surface.

Equation (3) is to be valid in elastic deformation, and it

Fig. 3 Interpretation of the electrode deformation in Fig. 2 (a) during the 1st cycle.

Fig. 4 SEM images of 3 μm Ni_3Sn_4 electrodeposited on 18 μm HCL305 copper foil (a) in the initial and (b) after 1 cycle of charge-discharge.

indicates that plastic deformation occurs under the condition of $t_{\text{NiSn}} \sigma_{\text{NiSn-charge}} > 0.25 \sigma_{\text{Cu-y}} t_{\text{Cu}}$, and elastic deformation occurs under the condition of $t_{\text{NiSn}} \sigma_{\text{NiSn-charge}} \leq 0.25 \sigma_{\text{Cu-y}} t_{\text{Cu}}$. Here, $\sigma_{\text{NiSn-charge}}$ is the stress of active material at expansion, and $\sigma_{\text{Cu-y}}$ is 0.2% yield strength of copper foil.

Table 2 classifies the deformation behavior of copper foil based on the experiment. By using the value in the table for 31 μm TPC ($\sigma_{\text{Cu}} = 350 \text{ MPa}$) with a Ni_3Sn_4 plating layer of 3 μm presumed to have an elastic deformation limit value, Eq. (3) gives $\sigma_{\text{NiSn}} = 897 \text{ MPa}$. By using this value of σ_{NiSn} , the experimental data are plotted in Fig. 5, where the horizontal axis shows $\sigma_{\text{Cu}} t_{\text{Cu}}$ and the vertical axis $t_{\text{NiSn}} \sigma_{\text{NiSn}}$. The Δ symbols show electrodes with plastic deformation, and the O symbols show electrodes with elastic deformation. Clearly, a linear curve, which has a gradient of 0.25 as shown in Eq. (3) passes through the point of origin, and separates the two zones for plastic and elastic deformation.

As the above discussions clearly indicate, the displacement behavior of an electrode is decided by the magni-

Table 2 Deformation behavior of copper foil collectors.

No.	Thickness $t_{\text{Cu}} / \mu\text{m}$	0.2% Yield strength $\sigma_{\text{Cu}} / \text{MPa}$	Ni_3Sn_4		
			Thickness	$t_{\text{NiSn}} / \mu\text{m}$	
			0.1	1	3
1	16	70	E	P	P
2	16	350	E	E	P
3	31	350	E	E	E
4	18	390	E	E	P
5	25	540	E	E	E
6	18	700	E	E	E
7	12	270	E	P	P
8	30	190	E	E	P

E : Elastic strain P : Plastic strain

Fig. 5 Classification of deformation behavior of copper foil collectors. The Δ symbols show electrodes with plastic deformation, and the O symbols show electrodes with elastic deformation.

tude relation between two factors: “active material thickness times stress in the charge period” and “copper foil collector thickness times 0.2% yield strength.” Once plastic deformation occurs, the volume change of the active material during and after the second cycle is not influential; When plastic deformation is experienced, the life of an electrode is degraded because the active material comes off. We will see a greater stress when using an active material comprising Sn, Sb or Si, and then it is desirable to use copper foil with a higher yield strength, or thicker copper foil.

4 Conclusion

By examining to what extent the 0.2% yield strength of copper foil collector affects deformation of the electrode during the charge-discharge cycle, conclusions were obtained as follows. When the active material was

on one side of the copper foil, a copper foil with a low yield strength showed plastic deformation in the first charge period. In the case a copper foil with a high yield strength, a cyclic elastic deformation was observed. This returned to its initial shape after the discharge ended. As plastic deformation will promote peeling and shedding of the active material during the sequential cycles, high yield strength copper should be adopted. For example, a 3 μm Ni_3Sn_4 film would require a 31 μm pure copper foil collector with a yield strength of 350 MPa or 18 μm Corson copper alloy foil collector with a yield strength of 700 MPa. The minimum yield strength and minimum thickness of copper foil are decided depending on the type and composition of the active material. It is also assumed that the copper foil should have a high yield strength if high-capacity active material comprising such elements as Sn, Sb or Si, in which the volume change is large, is to be adopted.

Acknowledgement

The authors thank to Professor T. Osaka, Associate Professor T. Momma, and Dr. H. Mukaibo at Waseda University for many discussions.

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