Charge–discharge characteristics of a layered-structure electroplated Cu/Sn anode for Li-ion batteries

JungWon Park, JiYong Eom*, HyukSang Kwon**

Department of Materials Science & Engineering, KAIST, 373-1, Guseong-dong, Yuseong-gu, Daejeon, 305-701, Korea

A R T I C L E   I N F O

Article history:
Received 21 September 2009
Received in revised form 28 October 2009
Accepted 28 October 2009
Available online 6 November 2009

Keywords:
Sn anode
Cu anode
Electroplating
High-voltage irreversible capacity
Li-ion battery

A B S T R A C T

An electroplated copper/tin (Cu/Sn) anode with a layered structure is described that minimizes the high-voltage irreversible capacity observed in an electroplated Sn anode at a potential over 1 V. The high-voltage irreversible capacity is caused by the electrolyte decomposition at the catalytic site of the Sn anode. In the electroplated Cu/Sn anode, the upper Cu layer effectively suppresses the exposure of the newly formed Sn surfaces, resulting in the absence of the high-voltage irreversible capacity. Therefore, the electroplated Cu/Sn anode exhibits a higher cycle performance than the electroplated Sn anode.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Tin (Sn) is well-studied as an anode material for lithium (Li)-ion batteries because of its high Li storage capacity (theoretical limit of Li4.4Sn is 994 mAh g⁻¹) [1–3]. Beatti and Dahn reported a strange phenomenon in the Sn anode, called 'anomalous high-voltage irreversible capacity' [4]. This event occurs during lithiation of the Sn anode at the high voltage region over 1 V, causing a considerably larger amount of irreversible capacity and a significantly lower cycle performance [4–5]. Similar results were also observed in the nanometric Bi anode system [6].

The high-voltage irreversible capacity is caused by electrolyte decomposition at the catalytic site of the Sn anode [7]. Pure Sn is assumed to have a crystal face (or faces) that acts as a catalyst for the electrolyte decomposition, and severe decomposition of the electrolyte occurs at high potential (around 1.5 V). Therefore, the electrolyte decomposes until a thick layer is built up, thus blocking the catalytic surface and preventing subsequent decomposition. This thick layer also serves to inhibit the diffusion of Li, thereby decreasing the overall capacity in subsequent cycles. In addition, new Sn surfaces appear due to cracking during the first cycle, which provide more ‘fresh’ Sn surfaces. In addition, if there is SnO impurity, it will be removed in the first cycle by Li₂O formation. Therefore, the high-voltage irreversible capacity is mostly observed in the second cycle.

If it is possible to cover the fresh Sn surface, then the high-voltage irreversible capacity should be avoided. In this work, an electroplated Cu/Sn anode was designed to cover the Sn layer with a thin Cu layer, and its charge–discharge characteristics were examined.

2. Experimental

The Sn and Cu/Sn anodes with 1-μm thickness were prepared by electroplating method onto 18-μm-thick Cu substrates. The Sn and Cu/Sn electroplating was done galvanostatically in a bath after removing the surface oxide film by soaking in a 100 g dm⁻³ H₂SO₄ solution and subsequently rinsing with deionized water. The plating conditions are illustrated in Table 1. The Cu/Sn anodes were prepared by Sn electroplating followed by Cu electroplating, as shown in Fig. 1. After electroplating, each Sn and Cu/Sn electrode was cut to about 1 cm² and dried in a vacuum for 12 h.

The Li/Sn and Li/(Cu/Sn) cells were assembled using a 2016 coin-type cell in an Ar-filled glove box. A polypropylene separator soaked with liquid electrolyte (provided by Merck©), which consisted of 1 M LiPF₆ dissolved in a 1:1 v/v ratio of ethylene carbonate (EC) and dimethyl carbonate (DMC), was placed between the anode and the Li foil in the cell. The charge/discharge tests of the Li/Sn and Li/(Cu/Sn) cells were performed in galvanostatic mode. The cells were charged (lithiation) and discharged (delithiation) at a constant current of 100 mA g⁻¹ between 0.02 and 1.5 V.

* Corresponding author. Present address: Development 1 Team, Energy Business Division, Samsung SDI Co., Ltd., 508, Sungdong-dong, Cheonan, Chungcheongnam-do, 330-300, Korea. Tel.: +82 70 7125 0387; fax: +82 41 560 3696.
** Co-corresponding author. Tel.: +82 42 350 3326; fax: +82 42 350 3310.
E-mail addresses: jyeom74@gmail.com (J. Eom), hskwon@kaist.ac.kr (H. Kwon).

© 2009 Elsevier Ltd. All rights reserved.

doi:10.1016/j.electacta.2009.10.074
3. Results and discussion

Fig. 2 shows the charge/discharge curves of the electroplated Sn and Cu/Sn anodes. Contrary to the Sn anode, the high-voltage irreversible capacity was not observed in the Cu/Sn anode, indicating that the Cu layer covering the Sn layer effectively suppressed the electrolyte decomposition reaction.

In order to verify the effects of the Cu layer, the surface morphologies of the Sn and Cu/Sn anodes at the same charge/discharge stage were compared, as shown in Fig. 3. Several cracks were observed on the surface of the Sn anode after the first cycle (Fig. 3(c)), and precipitated β-Sn was observed after the second cycle (Fig. 3(e)), which is believed to be the result of a structurally collapsed active Sn layer. Contrary to this, no crack was observed in the Cu/Sn anode after the first cycle (Fig. 3(d)), and only a few cracks appeared after the second cycle (Fig. 3(f)). These results indicated that the Cu/Sn anode is mechanically more stable than the Sn anode. In addition, due to the coverage of the Sn layer by the Cu layer, the fresh Sn surface was not exposed, and hence the high-voltage irreversible capacity was suppressed.

Notably, the lithiation profiles between the Sn and Cu/Sn anodes are different, as shown in Fig. 2. During lithiation, the Sn anode, which was reacted with Li at 0.75 V, exhibited a plateau at 0.4 V, and the potential decreased gradually. However, the first lithiation profile of the Cu/Sn anode was different. In the profile, the voltage decreased rapidly to around 0.1 V without any plateau, and then exhibited a plateau at 0.4 V. Since this profile was significantly different from that of the Sn anode, we investigated whether the Sn anode was properly lithiated. Although the lithiation profile of the Cu/Sn anode was different from that of the Sn anode, delithiation profiles of the two anodes were almost same, suggesting that the state of lithiation of each anode was very similar.

In order to confirm the lithiation, structural changes of the Cu/Sn anode during the first lithiation/delithiation were examined by X-ray diffraction (XRD) analysis, as shown in Fig. 4. The XRD results show that the Sn and Cu$_6$Sn$_5$ peaks decreased with lithiation, due to amorphization of the Sn and Cu$_6$Sn$_5$ phases, and the peaks were recovered after delithiation. These results provide evidence that the Cu/Sn anode was properly lithiated and delithiated. Therefore, a kinetic explanation was likely for the strange lithiation profile. The specific current of this charge/discharge test was not slow enough to achieve equilibrium at any point. In addition, the Cu layer covering the Sn layer acted as a resistance of Li diffusion, so the measured voltage was shifted.

According to Dahn's mechanism, the high-voltage irreversible capacity is due to the film formation, which acts as a barrier of Li diffusion and results in diminished cycle performance of the Sn anode. Since the high-voltage irreversible capacity was absent in the Cu/Sn anode, it was expected to achieve better cycle performance. Fig. 5 shows the reversible (discharge) capacity and Coulombic efficiency of the Sn and Cu/Sn anodes during the charge/discharge tests for 20 cycles. Although the first reversible capacity of the Cu/Sn anode (308 mAh g$^{-1}$) was less than that of the Sn anode (656 mAh g$^{-1}$), the second reversible capacity of the Cu/Sn anode (398 mAh g$^{-1}$) was considerably higher than that of the Sn anode (290 mAh g$^{-1}$). The first reversible capacity of the Cu/Sn anode was less than that of the Sn anode, likely because the Cu layer covering the Sn layer acted as a resistance of Li diffusion. From the second cycle, the reversible capacity of the Cu/Sn anode was increased because the upper Cu layer effectively suppressed the structural collapse of the active Sn layer. Therefore, the fresh Sn surface was not exposed, and thus the high-voltage irreversible capacity was suppressed.

The enhanced cycle performance of the Cu/Sn anode was due to the absence of the high-voltage irreversible capacity, which is displayed in the Coulombic efficiency plot shown in Fig. 5(b). Although the first Coulombic efficiency of the Cu/Sn anode (60%) was less than that of the Sn anode (85%), the second Coulombic efficiency of the Cu/Sn anode (91%) was significantly higher than that of the Sn anode (53%), due to the absence of the high-voltage irreversible capacity. In the following cycle, the Cu/Sn anode exhibited better cycle performance than the Sn anode. The reversible capacity of the Cu/Sn anode was higher than that of the Sn anode by 150 mAh g$^{-1}$ (in the fifth cycle) and by 100 mAh g$^{-1}$ (in the 20th cycle).

---

Table 1

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>Sn plating</th>
<th>Cu plating</th>
</tr>
</thead>
<tbody>
<tr>
<td>WE</td>
<td>Sn plating</td>
<td>Cu plating</td>
</tr>
<tr>
<td>RE</td>
<td>Sn plating</td>
<td>Cu plating</td>
</tr>
</tbody>
</table>

The Sn and Cu/Sn electroplating conditions used in this work (the chemical agents are provided by Aldrich$^a$).

<table>
<thead>
<tr>
<th>Chemical Agents</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn$_2$P$_2$O$_7$ + 120 g dm$^{-3}$ K$_2$P$_2$O$_7$ + 0.15 g dm$^{-3}$ additive</td>
<td>Sn$_2$P$_2$O$_7$ + 120 g dm$^{-3}$ K$_2$P$_2$O$_7$ + 0.15 g dm$^{-3}$ additive</td>
</tr>
<tr>
<td>CuSO$_4$ + 60 g dm$^{-3}$ H$_2$SO$_4$</td>
<td>CuSO$_4$ + 60 g dm$^{-3}$ H$_2$SO$_4$</td>
</tr>
</tbody>
</table>

Fig. 3. SEM images on the surfaces of the electroplated Sn and Cu/Sn anodes ((a), (b): as-plated, (c), (d): after the 1st cycle, (e), (f): after the 2nd cycle, respectively). The lithiated samples were disassembled and inserted into the transfer jig in the glove box, and then transferred into the scanning electron microscope.

Fig. 4. XRD patterns of the electroplated Cu/Sn anode at different voltage stages during the first lithiation/delithiation.
4. Conclusions

To reduce the high-voltage irreversible capacity observed in the electroplated Sn anode, the electroplated Cu/Sn anode was successfully formed by Sn electroplating followed by Cu electroplating. Although several cracks were observed on the surface of the Sn anode after the first cycle, no crack was observed in the Cu/Sn anode, because the upper Cu layer effectively suppressed the structural collapse of the active Sn layer. Therefore, the fresh Sn surface was not exposed, and hence the high-voltage irreversible capacity was suppressed in the Cu/Sn anode. Although the first reversible capacity and Coulombic efficiency of the Cu/Sn anode were less than those of the Sn anode, the second reversible capacity and Coulombic efficiency of the Cu/Sn anode were considerably higher than those of the Sn anode. The enhanced cycle performance of the Cu/Sn anode was due to the absence of the high-voltage irreversible capacity.

Acknowledgements

This work was supported by the Growth Engine Technology Development Program (Project No. 10016472) and the BK21 program funded by Korea Ministry of Knowledge Economy.

References