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Effects of substrate morphology and ageing on cycle performance of a Sn-anode fabricated by electroplating

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Abstract

The effects of Cu substrate morphology and ageing on the cycle performance of a Sn-anode electroplated on a smooth, a pyramid and a nodule-type Cu substrate and aged at 200 °C for 0, 1, 5, 20 h in a vacuum were examined. The Sn-anode electroplated on the nodule-type Cu substrate and aged for 1 h exhibited the highest reversible capacity (up to ∼600 mAh g^{-1}) and a stable cycle performance, which resulted from the enhancement in adhesion and electrical contact properties between the Sn layer and the Cu substrate by the mechanical interlocking effect of the nodule-type Cu substrate and also by the buffering effects of an intermetallic compound formed by the ageing process. However, when aged for longer than 1 h at 200 °C, the reversible capacity of the Sn-anode decreased significantly due to the formation of an inactive Cu_3Sn phase, irrespective of the morphology of the Cu substrate.
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Keywords: Tin; Electroplating; Anode; Cycle life; Ageing; Li battery

1. Introduction

The preparation of Sn-based anodes for Li-ion batteries is a viable, advantageous process, for the following reasons: First, the electroplating process is simpler than the currently-used powder process because there is no need for any binder or conductive agents (Fig. 1). Second, owing to their low impurity, a comparatively high initial coulombic efficiency can be obtained. However, a Sn-anode has the intrinsic problem of crumbling due to the large amount of volume expansion (up to about 300%) during Li insertion, resulting in the electrical isolation of the Sn-anode from the Cu substrate with a significant decrease in the charge/discharge capacity of cell. To overcome this problem, several methods have been suggested. One possible method is the alloying of Sn with other metals such as Zn, Cu and Co, all of which form a stable structure and suppress the volume expansion during the reaction [1–3]. However, when the applied potential is lower than its specific potential, the alloy structure is ruined, which causes a large volume change as well. On the other hand, the deposition of Sn on a Cu substrate with a high level of roughness has received attention due to the improved adhesive properties between the substrate and the Sn layer. Tamura et al. suggested that a pyramid-type Cu substrate significantly improved the cyclic properties of a Sn-anode [4]. Takamura et al. used a Ni substrate made rough by sandpaper and chemical etching for a vacuum evaporated Si-anode and this considerably increased the cycle performance of the electrodes [5].

In addition to these studies, the forming by ageing of an intermetallic phase between the active layer and the substrate was suggested as beneficial. Wang et al. showed that an electroplated Sn–10Zn anode exhibited higher cyclic properties after ageing was performed [1]. Moreover, the Sn electrode electroplated on the pyramid-type Cu substrate showed higher cyclic properties when aged at 200 °C for 20 h [4].

From the studies mentioned above, it is suggested that a properly roughened substrate and an ageing at proper conditions are indispensable processes necessary to improve both the high capacity and the high cycle performance of electroplated Sn-based anodes. In this investigation, we attempt to use a nodule-type Cu substrate which was developed to improve

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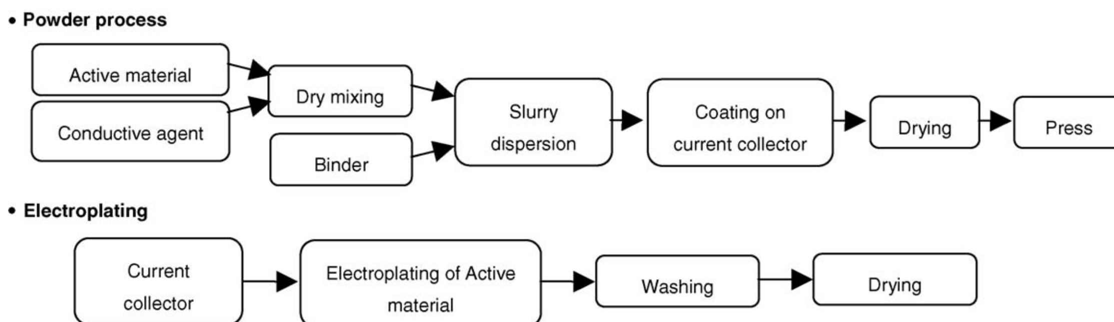


Fig. 1. Comparison between a powder process and an electroplating process for the fabrication of anode in Li-ion battery.

the adhesion strength of the Cu layer in a PCB (printed circuit board), by a mechanical interlocking effect by the nodules. Therefore, it is expected to obtain a high reversible capacity due to its high adhesion strength when the nodule-type Cu substrate is used as the substrate for Sn-anode. The objective of this present study is to explore the possibility of using a nodule-type Cu substrate and to determine the proper aging condition to improve the cycle performance of the Sn-anode.

2. Experimental

2.1. Preparation of Sn-anode

Sn-anodes with a 1 μm thickness were prepared by electroplating Sn on to 18 μm Cu substrates with three different types of surface morphologies—smooth, pyramid-type and nodule-type (Fig. 2). The smooth and pyramid-type Cu substrates were produced by an electroplating process onto the surface of a titanium drum under different plating conditions with different additives and the nodule-type Cu substrate was produced by a subsequent surface treatment followed by pyramid-type Cu plating process. The Sn electroplating was done galvanostatically in a bath after removing a surface oxide film by soaking in 100 g L^{-1} H_2SO_4 solution and subsequent rinsing with de-ionized water. This plating condition is illustrated in Table 1.

After electroplating, each Sn electrode was cut to about 1 cm^2 and aged in a vacuum preheated at 200 °C for 1, 5 and 20 h.

2.2. Chage/discharge test and structural analysis of the Sn-anode

The Li/Sn cells were assembled using a coin-type cell in an Ar-filled glove box. A glass fiber filter soaked with a liquid electrolyte (provided by Merck©), which was 1 M of $LiClO_4$ dissolved in a 1:1 volume ratio of ethylene carbonate (EC) and dimethyl carbonate (DMC), was placed between the anode and the Li-cathode in the cell.

Table 1
Sn electroplating condition used in this work

Bath	30 g L^{-1} $Sn_2P_2O_7$ + 120 g L^{-1} $K_4P_2O_7$ + 0.15 g L^{-1} additive
Current density	10 mA cm^{-2}
Anode	Rb-oxide

The charge/discharge test of the Li/Sn cells was performed for 20 cycles in a galvanostatic mode. The cells were charged (lithiation) and discharged (delithiation) in the galvanostatic mode at a constant current of 100 mA g^{-1} between 0.02 and 1.5 V. The structure of each Sn-anode was analyzed by X-ray diffractometry (XRD). The surface morphologies and the cross-sectional images of the Sn electrodes were observed by secondary electron microscopy (SEM) before and after the charge/discharge tests for 20 cycles. All the potentials are referring to Li/Li^+.

3. Results and discussion

3.1. Effects of surface morphology of Cu substrates on the structure and cycle performance of Sn-anodes

Fig. 3 shows the SEM images on the surface morphology of the Sn electrodes electroplated on the smooth, pyramid-type and nodule-type Cu substrates, respectively. Although they were plated on Cu substrates with different morphologies, the deposit looks very similar.

The XRD pattern of the as-plated Sn electrode on the smooth Cu substrate is presented in Fig. 4. The XRD pattern shows the peaks of the Cu substrate, Sn and small amount of η-Cu_6Sn_5. From these results, we found that the Sn electrode was composed mostly of Sn and that a thin η-Cu_6Sn_5 phase formed between the electroplated Sn layer and the Cu substrate.

Fig. 5 shows the cycle performance of the as-plated Sn-anode on the three Cu substrates. The initial reversible capacity of the Sn-anode plated on the smooth Cu substrate was 655 mAh g^{-1}, which is a much higher capacity than that of graphite (about 350 mAh g^{-1}) and the initial coulombic efficiency was up to ∼85%. However, after the first cycle, the reversible capacity decreased sharply to 283 mAh g^{-1} in the second cycle and finally decreased to 212 mAh g^{-1} in the twentieth cycle. Such poor cycle performances are primarily due to the crumbling of the Sn-anode brought on by the severe volume change during lithiation/delithiation and also due to the poor adhesion properties between the electroplated Sn and the Cu substrate.

To improve the cycle performance of the Sn electrode, two rough Cu substrates with different surface morphologies—pyramid and nodule-type were used. The appearance of each electrode is not very different from the other, as seen in Fig. 3; however, the cycle performances were considerably different, as

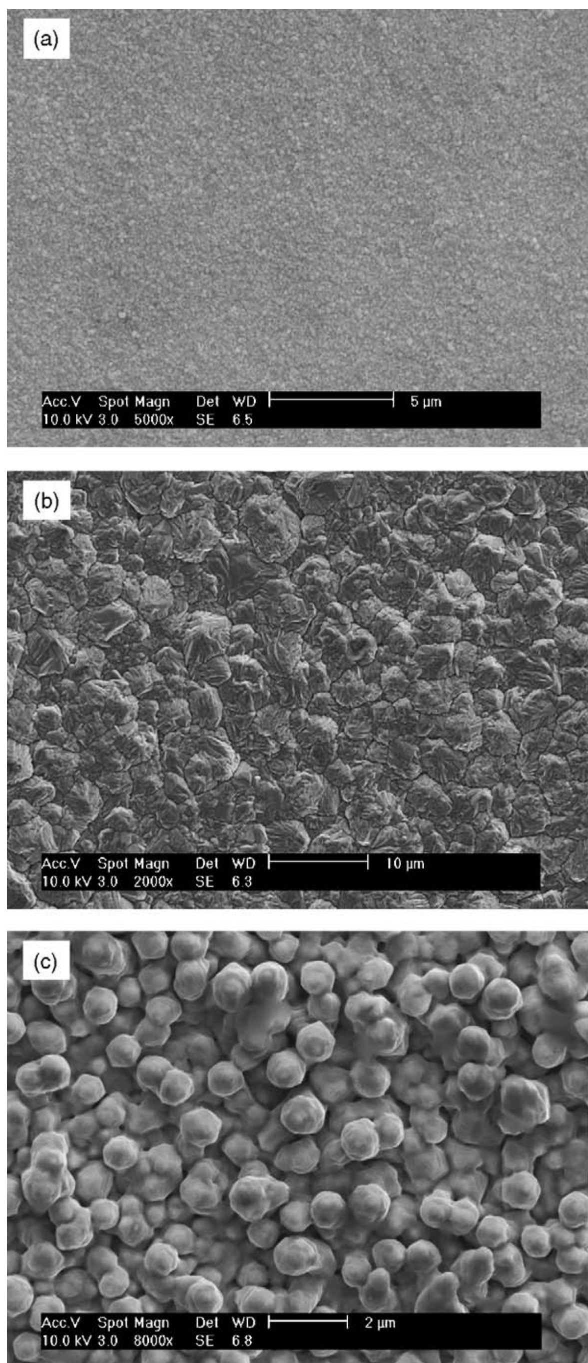


Fig. 2. SEM images on the surface morphology of: (a) smooth; (b) pyramid-type; (c) nodule-type Cu substrates used in this work.

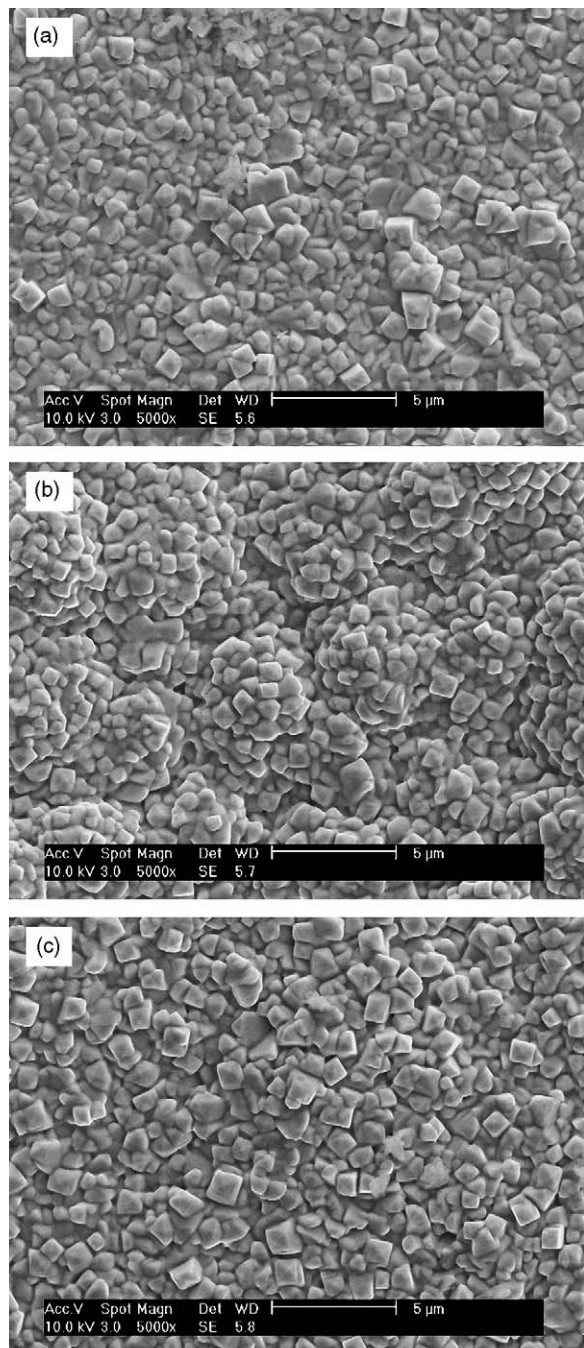


Fig. 3. SEM images on the surfaces morphology of Sn deposit electroplated on: (a) smooth; (b) pyramid; (c) nodule-type Cu substrate.

shown in Fig. 5. The Sn electrode electroplated on the pyramid-type Cu substrate exhibited a reversible capacity of around 650 mAh g^{-1} (1st cycle), around 280 mAh g^{-1} (2nd cycle) and 200 mAh g^{-1} (20th cycle), which is very similar to the Sn-anode electroplated on the smooth Cu substrate. Contrary to these performances, the Sn-anode electroplated on the nodule-type Cu substrate showed 700 mAh g^{-1} (1st cycle), 450 mAh g^{-1} (2nd cycle) and 377 mAh g^{-1} (20th cycle), which are significantly higher values compared to those of the other Sn electrodes.

As mentioned above, the nodule-type Cu substrate was developed to improve the adhesion strength of the Cu layer in a PCB by the mechanical interlocking effect by the nodules. Fig. 6 shows schematic models of the structure of the Sn-anodes plated on the three Cu substrates. Considering the structure, it is believed that the excellent adhesion strength of the Sn layer is obtained when the Sn was plated on the nodule-type Cu substrate. Therefore, the high cycle performance of the Sn electrode formed on the nodule-type Cu substrate probably appears due to the improvement in both the adhesion strength and the electrical contact between the Sn layer and the nodule-type Cu substrate which

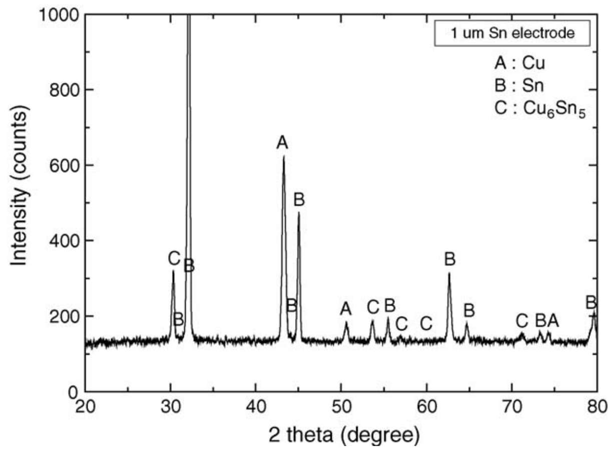


Fig. 4. XRD pattern of Sn electrode electroplated on the smooth Cu substrate.

resulted from the interlocking of the nodules similar to that in a PCB.

3.2. *Effects of ageing on the cycle performance of Sn-anodes*

The representative intermetallic compounds of Sn and Cu are η-Cu_6Sn_5 and Cu_3Sn. Of these two, the former is able to react with Li and forms $Li_{13}Cu_6Sn_5$ [6], but the latter is generally

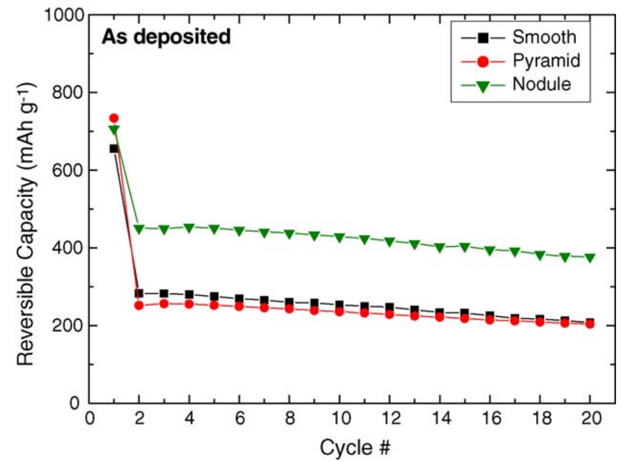


Fig. 5. Cycle performance of the Sn electrodes electroplated on the smooth, pyramid and nodule-type Cu substrates, respectively.

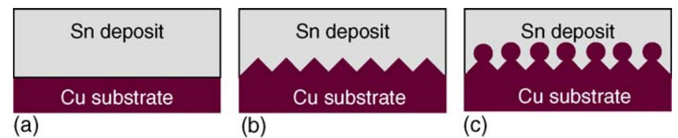
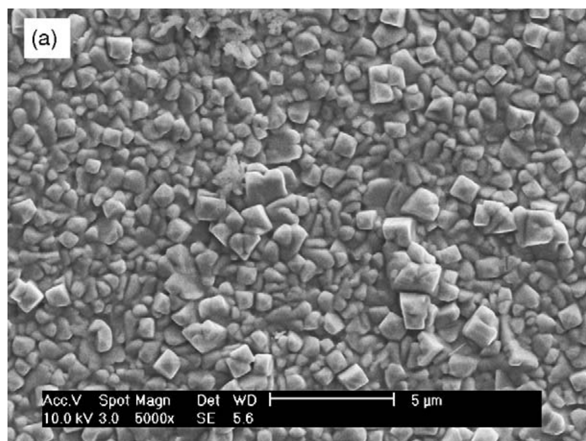
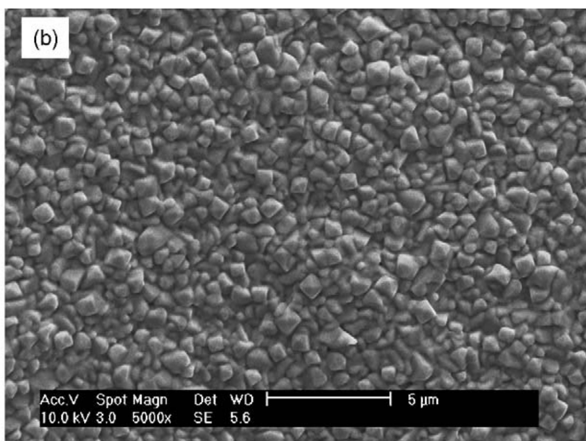
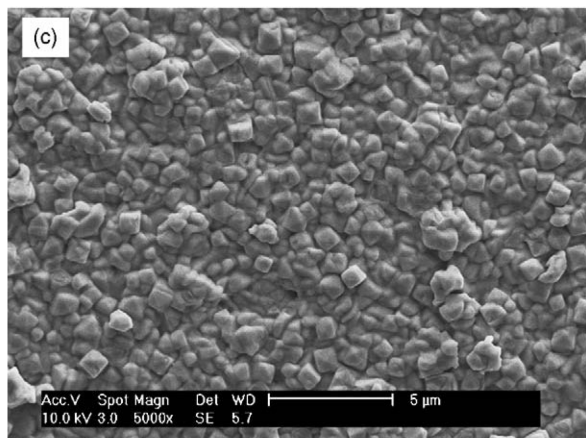


Fig. 6. Schematic models of the structures of the Sn-anodes plated on: (a) the smooth Cu substrate; (b) pyramid-type Cu substrate; (c) nodule-type Cu substrate.







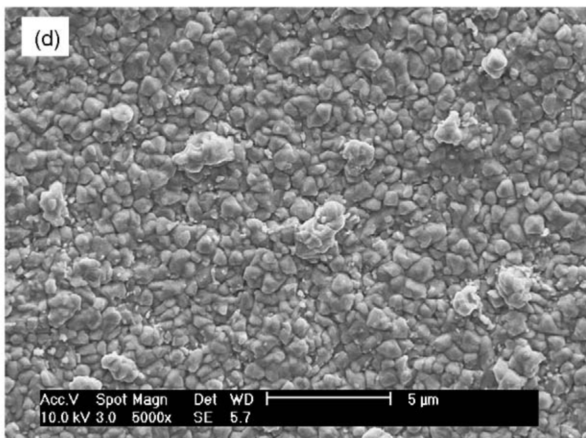


Fig. 7. SEM images on the surface morphology of: (a) as-plated Sn electrode, aged Sn electrode; (b) for 1 h; (c) for 5 h; (d) for 20 h at 200 °C.

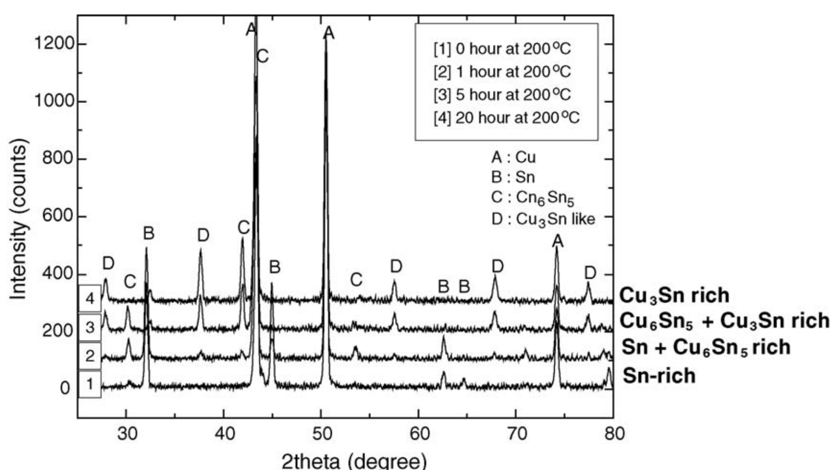


Fig. 8. XRD patterns of the as-plated Sn-anode and the Sn-anodes subsequently aged for 1, 5 and 20 h, respectively, at 200 °C.

regarded as not reactive with Li, as demonstrated by the XRD analysis performed on a Sn-anode before and after the cycle tests [7].

Fig. 7 displays the SEM images on the surface morphology of the as-plated Sn-anode and the Sn-anodes aged for 1, 5, 20 h at 200 °C, respectively. The appearance of each electrode is not very different from the others except the aged Sn-anode for 20 h. In Fig. 7(d), small particles were observed on the surface of the Sn-anode aged for 20 h, which demonstrates that new phase was formed on the surface of the Sn-anode by the ageing for 20 h.

The XRD patterns of the as-plated Sn-anode and the Sn-anodes aged for 1, 5, 20 h at 200 °C are listed in Fig. 8. The XRD patterns show that the active layer is Sn-rich with a small amount of η-Cu_6Sn_5 in as-plated condition, Sn- and η-Cu_6Sn_5-rich with a small amount of Cu_3Sn when aged for 1 h, η-Cu_6Sn_5-rich when aged for 5 h and Cu_3Sn-rich when aged for 20 h.

Fig. 9 shows the effects of the ageing on the cycle performance of the Sn electrodes electroplated on the smooth Cu substrate. The first and second reversible capacities of an unaged electrode were 655 and 283 mAh g^{-1}, respectively. After ageing for 1 h at 200 °C, the initial reversible capacity was slightly decreased from 655 to 593 mAh g^{-1}. However, the second reversible capacity was significantly increased from 283 to 482 mAh g^{-1}. The twentieth reversible capacity was 489 mAh g^{-1}, which is almost same value as was recorded for the second reversible capacity. After ageing for 5 h at 200 °C, the first, second and twentieth reversible capacities were 121, 106 and 104 mAh g^{-1}, respectively. After ageing for 20 h at 200 °C, the electroplated Sn electrode exhibited an extremely low reversible capacity, which is probably due to the formation of an inactive Cu_3Sn phase throughout the Sn-anode, as confirmed by the XRD results shown in Fig. 8.

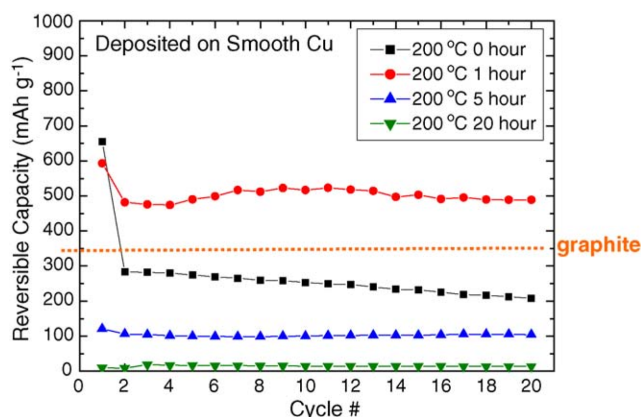
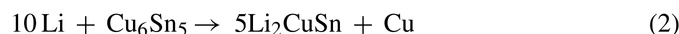


Fig. 9. Cycle performance of the as-plated Sn-anode and the subsequently aged Sn-anodes for 1, 5 and 20 h, respectively, at 200 °C.

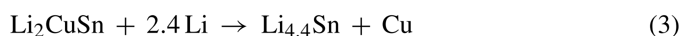
It is well known that Sn reacts with Li following a reaction (1) and its volume change is up to ∼300%.

$$4.4\,\text{Li} + \text{Sn} \rightarrow \text{Li}_{4.4}\text{Sn} \quad (1)$$

The η-Cu_6Sn_5 phase reacts with Li by a reaction (2) and (3) as follows and their volume change are 64 and 120%, respectively:



$$10\,\text{Li} + \text{Cu}_6\text{Sn}_5 \rightarrow 5\text{Li}_2\text{CuSn} + \text{Cu} \quad (2)$$



$$\text{Li}_2\text{CuSn} + 2.4\,\text{Li} \rightarrow \text{Li}_{4.4}\text{Sn} + \text{Cu} \quad (3)$$

When the two phases—Sn and η-Cu_6Sn_5—react with Li in an electrode, the reaction between Sn and Li is not completed before the η-Cu_6Sn_5 begins to react with Li. Li starts to react with Sn at 0.75 V versus Li and with η-Cu_6Sn_5 at around 0.4 V. At around 0.4 V, formed Li–Sn alloy is LiSn which is larger than Sn by only 50%. In the voltage region from 0.4 to 0 V, the Sn and the η-Cu_6Sn_5 phases react with Li at the same time, which may lower the relative volume mismatch and therefore reduce the mechanical stress between the layers.

In addition, it was reported that formed Cu_3Sn phase between the Cu and the Sn-based solder joint increased the shear force, required to fracture the Sn based solder joint, by about 20% [8], which demonstrates that the Cu_3Sn phase improves the adhesion strength between the Sn-based active layer and the Cu substrate.

Therefore, it is believed that the high reversible capacity of the Sn-anode aged for 1 h is due to following three reasons: First, when aged, Cu and Sn diffuse into each other and form intermetallic compounds such as the η-Cu_6Sn_5 and the Cu_3Sn, therefore, the amount of the Sn phase which is very easily crumbled due to its severe volume change became less than as-plated

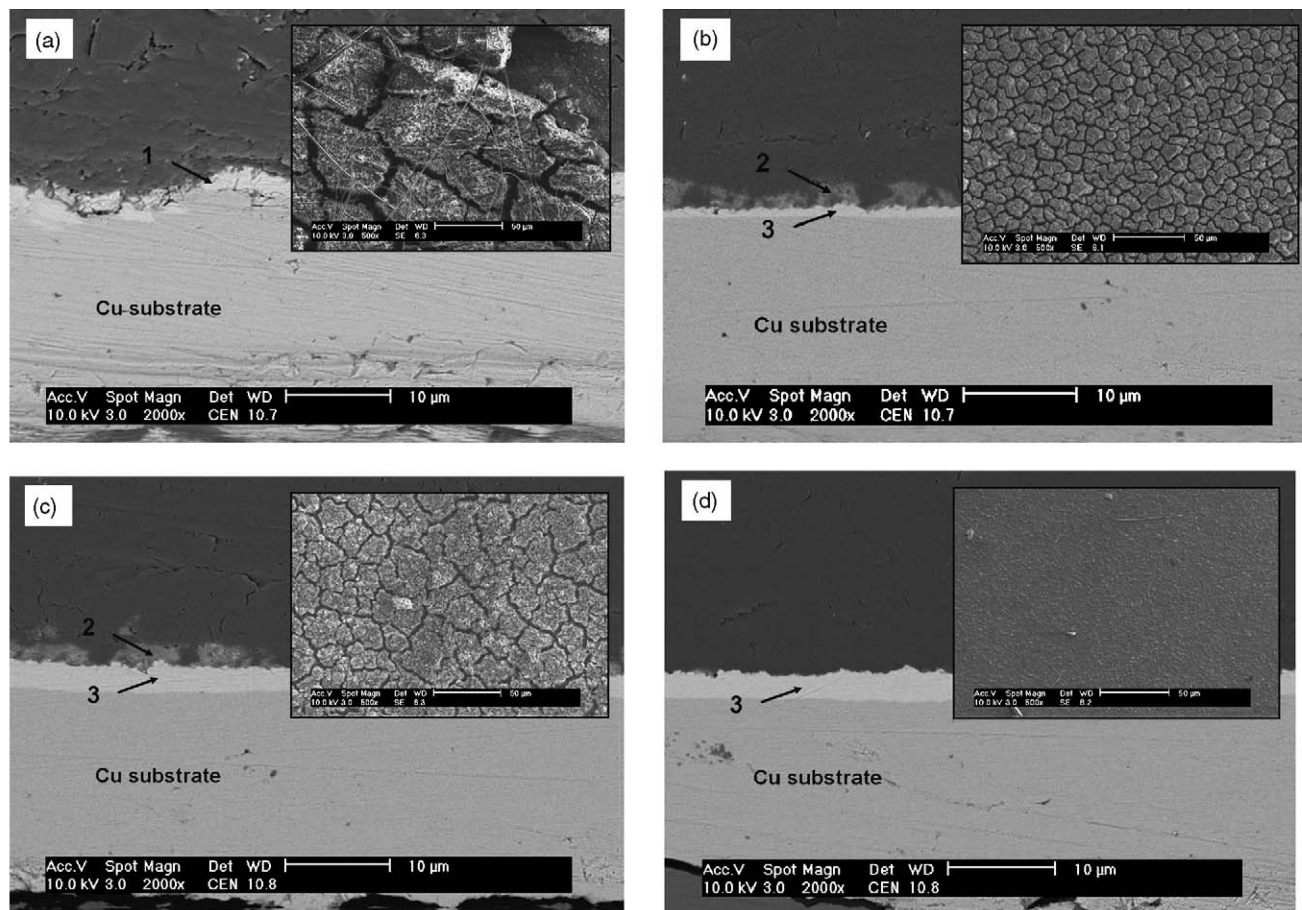


Fig. 10. SEM images on the cross-section and surface of Sn electrodes after cycle test for 20 cycles. The Sn electrodes were electroplated on the smooth Cu substrate and then aged. (a) As-plated; (b) aged for 1 h; (c) aged for 5 h; (d) aged for 20 h in vacuum at 200 °C.

Sn. Second, the intermetallic layer formed between the Sn layer and the Cu substrate acts as a buffering layer by reducing the mechanical stress between the layers. And third, the Cu_3Sn phase formed between the η-Cu_6Sn_5 layer and the Cu substrate increases the adhesion strength.

Fig. 10 shows the SEM images on the cross-section and the surface of the Sn-anode electroplated on the smooth Cu sheet, aged for 1, 5, 20 h at 200 °C and finally subjected to 20 cycles of charging/discharging. According to energy dispersive spectroscopy (EDS) data, the active layer in the as-plated/aged Sn-anode consisted of pure Sn (phase 1), Cu:Sn = 6:4 (phase 2) and Cu:Sn = 3:1 (phase 3). Comparing the EDS data with the XRD result, we can conclude that the phase 2 and 3 are η-Cu_6Sn_5 and Cu_3Sn, respectively. The as-plated Sn electrode is composed mostly of Sn and a thin η-Cu_6Sn_5 layer between the Sn and the Cu substrate, as confirmed in Fig. 8. In this case, horizontal cracks were observed between the plated Sn layer and the Cu substrate after the cycle test and some sections of the Sn deposit were able to be peeled off, which is probably a reason of the poor cycle performance. The Sn electrodes aged for 1 and 5 h are composed of two phases, namely η-Cu_6Sn_5 and Cu_3Sn. The upper phase corresponding to η-Cu_6Sn_5 reacted with Li; following this vertical cracks due to the volume change during the reaction were observed. Conversely, the lower phase corresponding to Cu_3Sn did not react with Li and thus did not crack. The Sn electrode, after ageing for 20 h, for the most part did not react with Li due to the large formation of the Cu_3Sn phase and consequently no crack was observed.

From these results, we can conclude that the intermetallic compounds formed by the ageing acted as a buffering layer and for this reason the active layer is adhered in spite of its volume change. However, the Cu_3Sn phase formed when aged for longer than 1 h reduces the reversible capacity due to its immunity to Li.

3.3. *Optimization of Cu substrates and ageing conditions*

To optimize the Cu substrates and ageing condition for the purpose of improving both the capacity and cycle performance of the Sn-anode, the Sn electrodes plated on the three different Cu substrates were aged for 1, 5 and 20 h and then charge/discharge tests were performed, as shown in Fig. 11. All the Sn electrodes electroplated on the three different Cu substrates exhibited the maximum value in reversible capacity when aged for 1 h. This value was lower when aged for 5 h and became negligible when aged for 20 h (as mentioned in Section 3.2). Comparing the Sn electrodes plated on the three Cu substrates, the Sn electrode electroplated on the nodule-type Cu substrate showed the highest reversible capacity, up to $\sim$600 mAh g^{-1} (aged for 1 h) and $\sim$250 mAh g^{-1} (aged for 5 h)

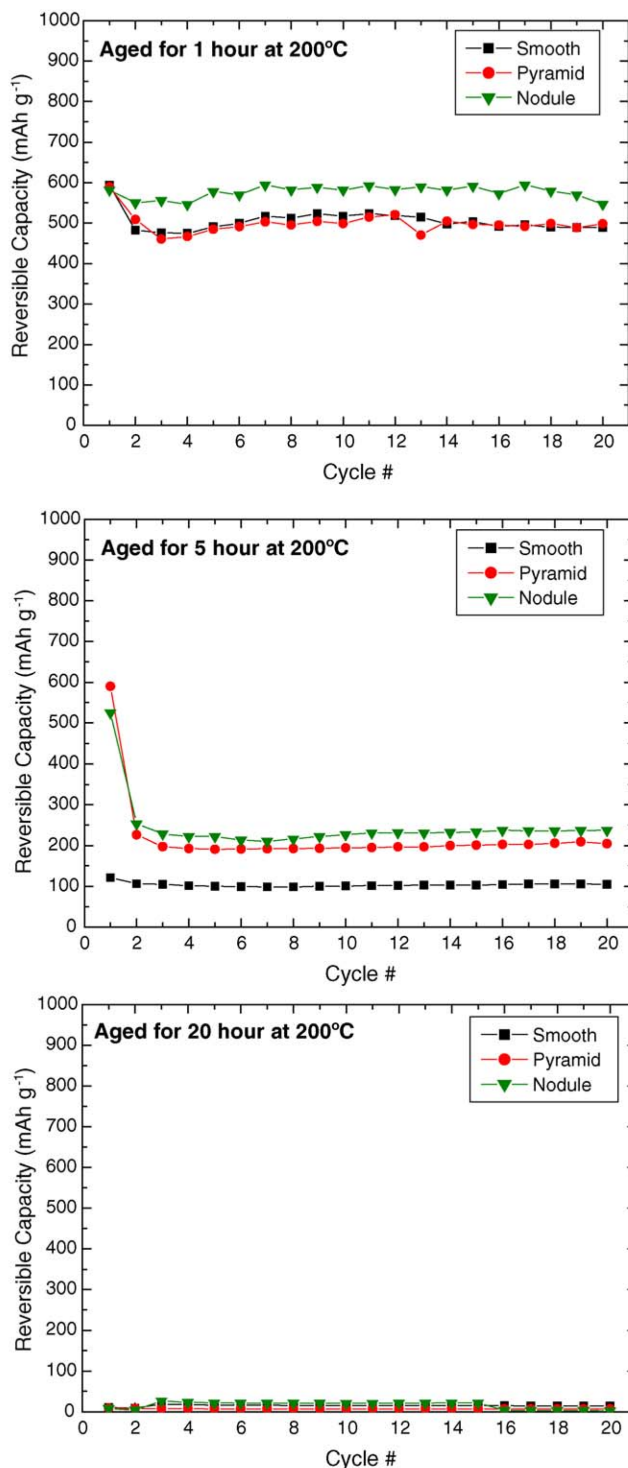


Fig. 11. Cycle performance of the Sn electrodes electroplated on the smooth, pyramid and nodule-type Cu substrates. The Sn electrodes were aged for 1, 5 and 20 h at 200 °C.

throughout the aging time, similar to the as-plated Sn electrode (Section 3.1). This demonstrates that the high adhesion strength and good electrical contact brought on by the mechanical interlocking effect is still effective when the electrode is aged. From the results of the charge/discharge tests, the Sn electrode electroplated on the nodule-type Cu substrate and aged for 1 h exhibited the best performance in both reversible capacity and cycle life.

4. Conclusions

The Sn electrodes with a 1 μm thickness were successfully formed by electroplating on Cu substrates with three different surface morphologies—smooth, pyramid and nodule-type and their structure and cycle performance were examined by SEM, XRD and by a cycle test. Conclusions drawn from the results are as follows:

- Comparing the cycle performance of the Sn electrodes electroplated on the three different Cu substrates, the Sn electrode electroplated on the nodule-type showed the highest reversible capacity (700 mAh g^{-1} (1st cycle), 450 mAh g^{-1} (2nd cycle) and 377 mAh g^{-1} (20th cycle), which demonstrates that the nodule-type Cu substrate enhanced the adhesion and electrical contact properties between the Sn and the Cu.
- Sn-anode electroplated and aged for 1 h at 200 °C exhibited a high reversible capacity and cycle performance, which is due to the decrease of the Sn content in the active layer, the buffering effects of the intermetallic compounds formed between the Sn layer and the Cu substrate and the enhanced adhesion strength by formation of the thin Cu_3Sn phase. However, when aged for longer than 1 h at 200 °C, the reversible capacity decreased due to the thickening of the inactive Cu_3Sn phase.
- The best performance of the Sn-anode was obtained when the Sn-anode was electroplated on the nodule-type Cu substrate and aged for 1 h at 200 °C.

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References

[1] L. Wang, S. Kotamura, T. Sonoda, D.-H. Kim, K. Obata, S. Tanase, T. Sakai, The 43rd Battery Symposium in Japan, 2002, p. 26.
[2] T. Sonoda, T. Fujieda, T. Sakai, et al., The 43rd Battery Symposium in Japan, 2000, p. 532.
[3] N. Tamura, M. Fujimoto, M. Kamino, S. Fujitani, Electrochim. Acta 49 (2004) 1949.
[4] N. Tamura, R. Ohshita, M. Fujimoto, S. Fujitani, M. Kamino, I. Yonezu, J. Power Sources 107 (2002) 48.
[5] T. Takamura, IMLB 12 (2004) 241.
[6] K.D. Kepler, J.T. Vaughey, M.M. Thackeray, Electrochem. Solid-State Lett. 2 (1999) 307.
[7] N. Tamura, R. Ohshita, M. Fujimoto, M. Kamino, S. Fujitani, J. Electrochem. Soc. 150 (2003) A679.
[8] S.F. Dirnfeld, J.J. Ramon, Weld. J. Suppl. (1990) 373.