Contents lists available at ScienceDirect

Journal of Power Sources

Short communication

Effects of Cu substrate morphology and phase control on electrochemical performance of Sn–Ni alloys for Li-ion battery

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ARTICLE INFO

ABSTRACT

The influence of substrate morphology and ageing on the charge–discharge performance of a Sn–Ni alloy anode electrodeposited on a Cu substrate are examined. The Sn–Ni alloy (Sn 82 at.%–Ni 18 at.% anode) shows a high capacity of around 480 mAh g^{-1} up to 12 cycles, but its capacity rapidly fades with cycling. The initial capacity and the cyclic properties of the alloy electrode are significantly improved when the surface morphology of the Cu substrate is changed from smooth-type to nodule-type. Optimized ageing treatment leads to further enhancement in the charge–discharge performance of the anode. The increase in the capacity and better cyclic properties are attributed to stronger adhesion between the Si–Ni anode and the Cu substrate. This is induced by inter-locking of the nodule-type Cu substrate and a buffering effect of Cu–Sn intermetallic compounds formed during ageing.

1. Introduction

Tin, one of the most promising candidates for high-capacity anode materials for lithium-ion secondary battery, has received attention due to its high theoretical capacity (995 mAh g^{-1}). There is, however a serious problem in that the volume variation of Sn reaches to 400% during Li$^+$ insertion/extraction. This results in electrical isolation of Sn particles from the Cu substrate, followed by rapid capacity fading. The cyclic properties of Sn can be improved when alloyed with elements such as Ni, Zn, and Fe, which are inactive towards Li and hence function as a matrix, that buffers the volume expansion [1–5].

For fabrication of electrodes, the electrodeposition process is more simple compared with the conventional slurry process, in which active materials are used in powder form. In addition, the exclusion of binder and conductive agents may prevent some undesirable phenomena such as the isolation of Li$^+$ [6]. Several researchers have studied the effects of the composition and morphology of electrodeposited Sn–Ni alloy on its cyclic properties [1–3]. This study attempts to elucidate the effects of Cu substrate morphology and ageing on the cyclic properties of an electrodeposited Sn–Ni alloy anode.

It has been reported that the adhesion between the active material and the substrate can have a critical effect on the electrochemical properties of the active material [6,7]. Furthermore, since the intermetallic compounds that are formed between the Cu substrate and the active material during ageing may buffer the volume change of the electrode, as well as improve adhesion, it is necessary to control the phase produced by the reaction between the active material and the Cu substrate. An examination is made of this requirement.

2. Experimental

Sn–Ni alloy electrodes with different composition were electrodeposited on Cu substrates to a thickness of 1 μm and with varying Sn concentration in pyrophosphate electrolytic baths, each of which contained SnCl$_2$·2H$_2$O (0.175, 0.135, 0.090, and 0.068 M), NiCl$_2$·6H$_2$O (1.262 M), K$_4$P$_2$O$_7$ (0.5 M), glycine (0.125 M), NH$_4$OH (5 ml l^{-1}). The Sn–Ni alloy electrodes were electrodeposited galvanostatically at the same current density (5 mA cm^2) for 5 min. The cutting edge of the electrodeposit was observed by scanning electron microscopy (SEM) to confirm its thickness. Two types of Cu substrate with different surface morphologies – smooth- and nodule-type – were used. Ageing was undertaken at 200 °C

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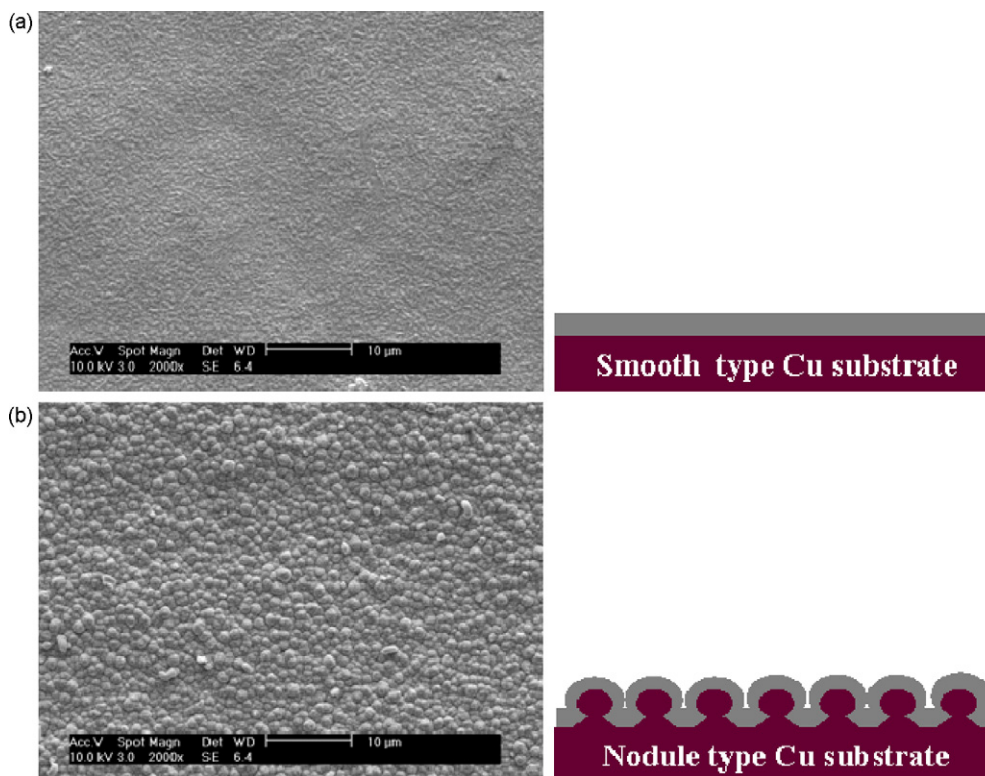hskwon@kaist.ac.kr (H.-S. Kwon).

Fig. 1. Surface morphology of Sn 82 at.%–Ni 18 at.% alloy electrode electrodeposited on (a) smooth-type Cu substrate and (b) nodule-type Cu substrate.

for 2, 5 and 10 min under vacuum. The composition, morphology and structure of Sn–Ni alloy electrodeposits were analyzed by energy dispersive spectroscopy (EDS), SEM, and X-ray diffraction (XRD).

The electrochemical characteristics of the Sn–Ni electrodes were examined in a galvanostatic mode at a constant current of $50\,mA\,g^{-1}$. Lithium metal was used as a counter electrode, and 1 M $LiClO_4$ was dissolved in a 1:1 volume ratio of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as an electrolyte. The cells were charged (lithiation) to 0.01 V vs. Li/Li$^+$ and discharged (delithiation) to 1.2 V vs. Li/Li$^+$.

3. Results and discussion

Sn–Ni alloys with various compositions (Sn 90 at.%–Ni 10 at.%, Sn 82 at.%–Ni 18 at.%, Sn 69 at.%–Ni 31 at.%, Sn 58 at.%–Ni 42 at.% and Sn 48 at.%–Ni 52 at.% alloys) were electrodeposited on smooth-type Cu substrates. When these electrodes are subjected to galvanostatic charge–discharge cycling, a higher amount of Sn incorporation in the alloys tends to deteriorate their cyclic properties. On the other hand, a smaller amount of Sn incorporation is followed by a very low capacity even lower than that ($372\,mAh\,g^{-1}$) of commercialized anode material, graphite. Hence, the Sn 82 at.%–Ni
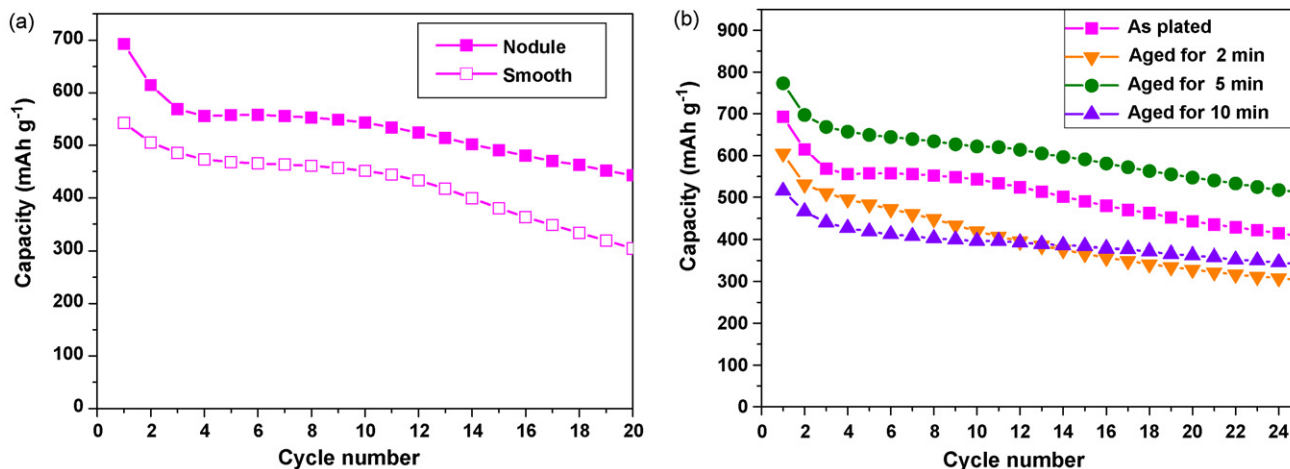

Fig. 2. (a) Effect of Cu surface morphology on cyclic properties of Sn 82 at.%–Ni 18 at.% electrode. (b) Effect of ageing time on cyclic properties of Sn 82 at.%–Ni 18 at.% electrode electrodeposited on nodule-type Cu substrate.
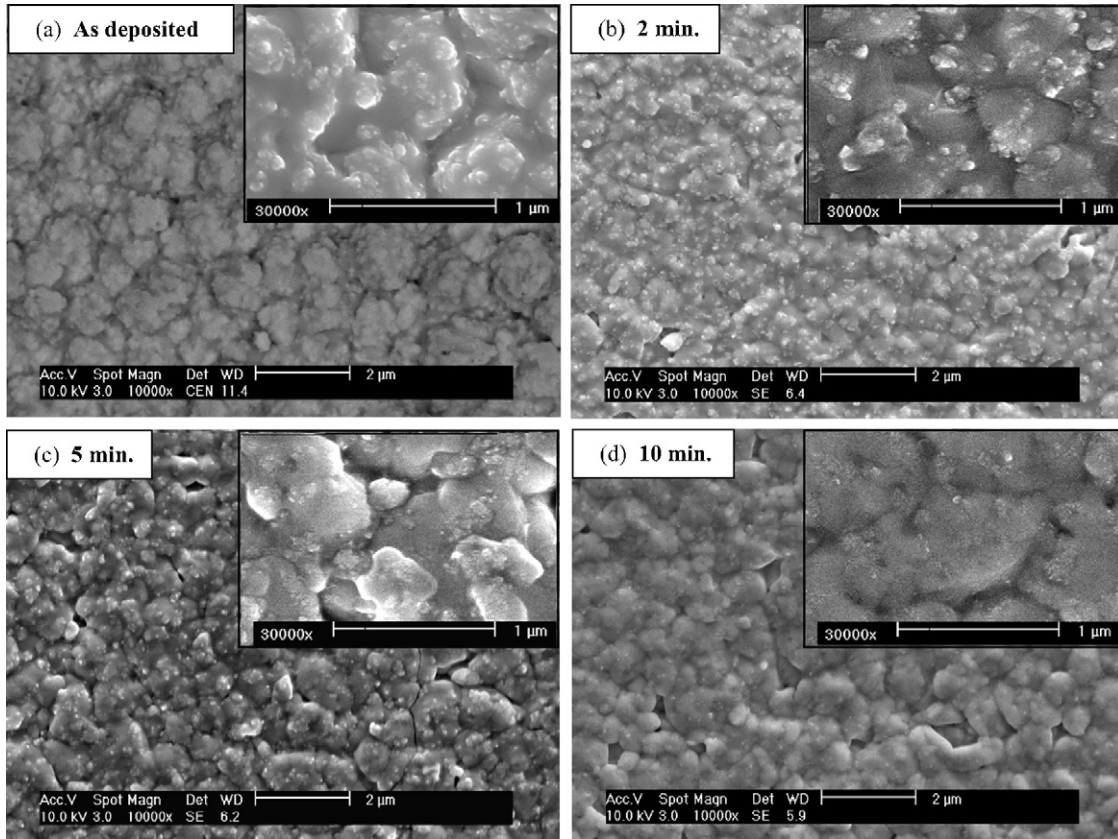
Fig. 3. Surface morphology of Sn 82 at.%–Ni 18 at.% electrode electrodeposited on nodule-type Cu substrate (a) as deposited, and aged at 200 °C for (b) 2 min, (c) 5 min, (d) 10 min.
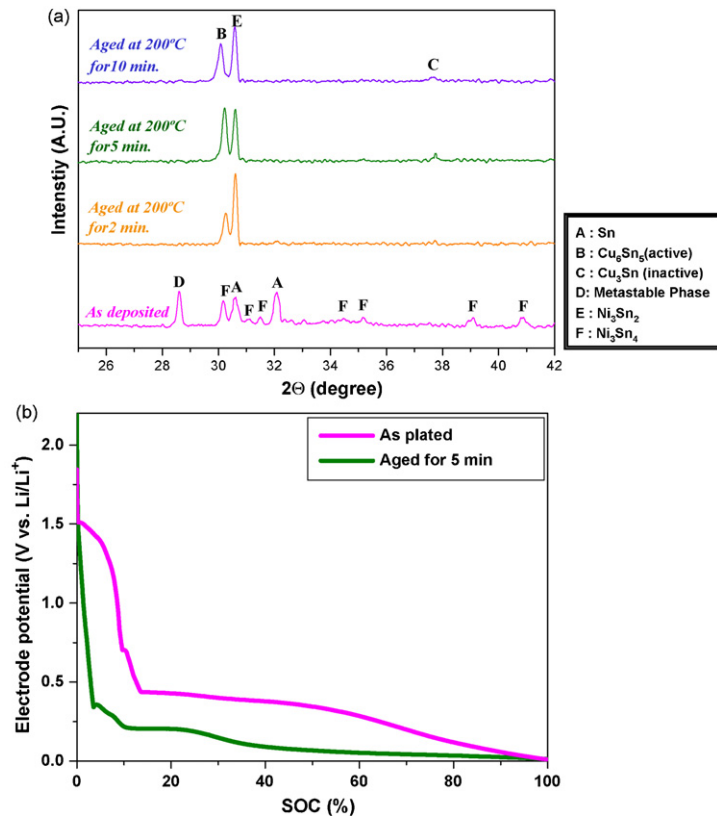

Fig. 4. (a) XRD patterns of Sn 82 at.%–Ni 18 at.% electrode electrodeposited on nodule-type Cu substrate; as deposited, and aged at 200 °C for 2 min, 5 min, 10 min. (b) Effect of ageing on polarization of Sn 82 at.%–Ni 18 at.% electrode electrodeposited on nodule-type Cu substrate during 1st charge.
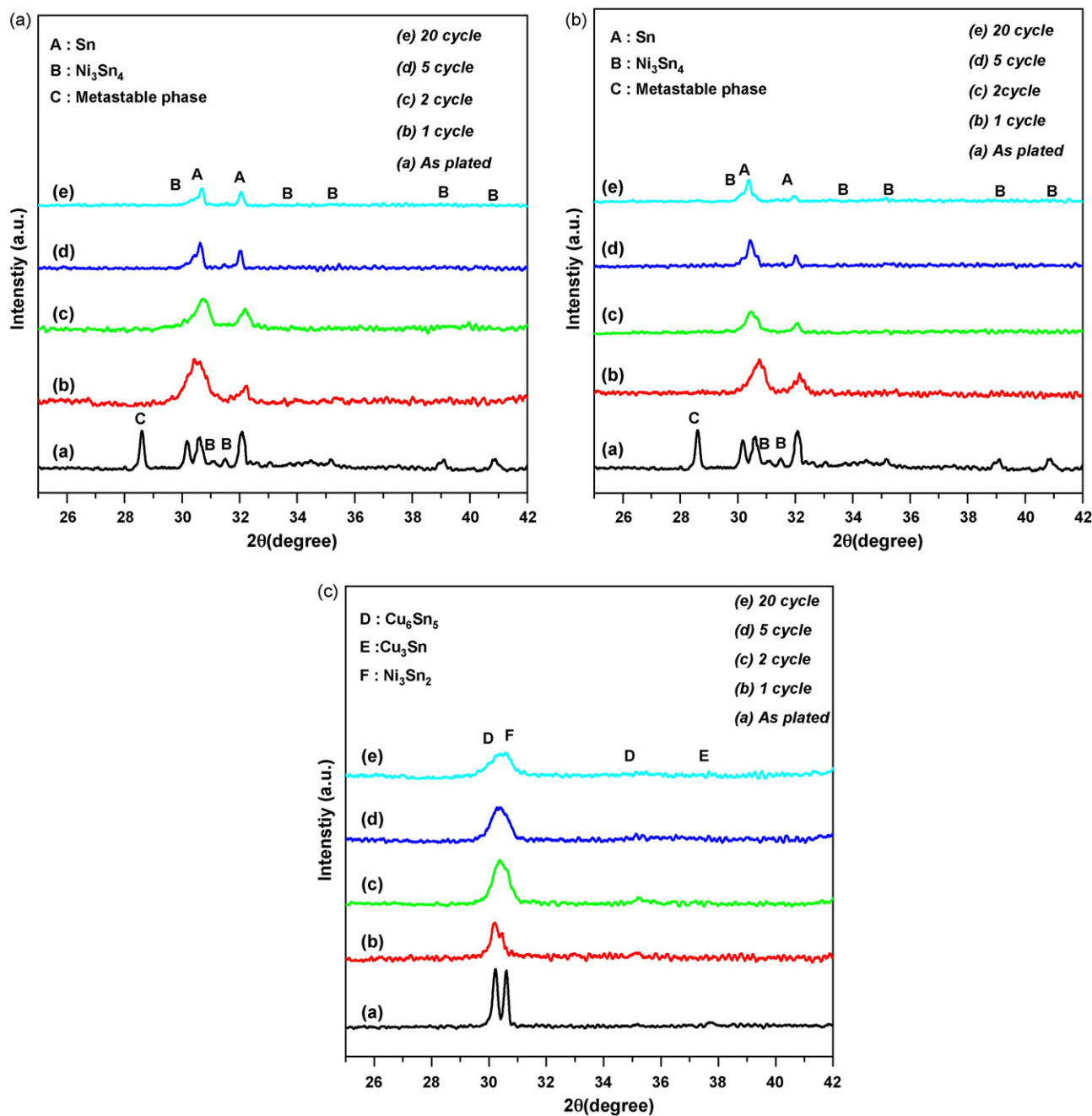
Fig. 5. Effects of Cu substrate morphology and ageing on after-cycle phase transition of Sn 82 at.%–Ni 18 at.% alloy electrode electrodeposited on (a) smooth-type Cu substrate, (b) nodule-type Cu substrate, (c) nodule-type Cu substrate and aged for 5 min.

18 at.% alloy electrode with a high capacity of about 480 mAh g^{-1} and good capacity retention up to 12 cycles, was selected from among the various compositions, despite the fact that its capacity rapidly faded after 12 cycles.

3.1. Effects of Cu substrate morphology

In order to improve the cyclic properties of the Sn 82 at.%–Ni 18 at.% alloy electrode, a nodule-type Cu substrate was substituted for the smooth-type Cu substrate. The morphology of the Sn 82 at.%–Ni 18 at.% alloy electrode electrodeposited on the smooth-type Cu substrate is compared with that on the nodule-type Cu substrate in Fig. 1. The Sn–Ni alloy on the smooth-type Cu substrate has a relatively smooth morphology, whereas that on the nodule-type Cu substrate has many spherical grains. The charge–discharge results for these electrodes are shown in Fig. 2a and demonstrate that the electrode on the nodule-type Cu substrate exhibits a higher capacity of around 560 mAh g^{-1} together with improved cycle behaviour.

It is well known that the nodule-type Cu substrate is very effective in increasing the adhesion strength of the Cu layer in the PCB (Printed Circuit Board) by an mechanical inter-locking effect [6]. Therefore, the enhanced adhesion strength between the Sn–Ni alloy electrode and the Cu substrate may contribute to the observed improvement in cycle performance.

3.2. Effects of ageing on cyclic performance

Sn 82 at.%–Ni 18 at.% alloy electrodes on nodule-type Cu substrates were aged for 2, 5 and 10 min at 200 °C under vacuum to strengthen the electrode-substrate adhesion. The surface morphologies of the electrodes with ageing are shown in Fig. 3. There is no significant change in the morphology, there is a distinct variation in their electrochemical performance. As shown in Fig. 2b, the Sn–Ni alloy electrode aged for 5 min shows the highest capacity, 650 mAh g^{-1}, and the best cycle performance (Fig. 2b). In case of the electrode aged for 2 min, a low capacity, 400 mAh g^{-1} and a deteriorated cyclic property are observed. Although the cyclic property of the electrode aged for 10 min is outstanding, its capacity is also low compared with the electrode aged for 5 min.

To examine the reason why the electrode aged for 5 min shows the best cyclic property, XRD analysis was conducted. As shown in Fig. 4, the as-deposited Sn 82 at.%–Ni 18 at.% alloy electrode consists of Sn, Ni$_3$Sn$_4$ and a metastable phase [1], but after ageing, the peaks of Sn, Ni$_3$Sn$_4$ and the metastable phase disappear with the evolution of Cu$_6$Sn$_5$, Cu$_3$Sn and Ni$_3$Sn$_2$ phases. This phenomenon can be simply attributed to the diffusion of Cu from the substrate into the electrode and its reaction with Sn. Since the Cu$_6$Sn$_5$ phase reacts with Li, as expressed by reactions (1) and (2), its volume expansion is less than half of that of pure Sn during Li$^+$ insertion [6].

$$10Li + Cu_6Sn_5 \rightarrow 5Li_2CuSn + Cu \tag{1}$$

$$Li_2CuSn + 2.4Li \rightarrow Li_{4.4}Sn + Cu \tag{2}$$
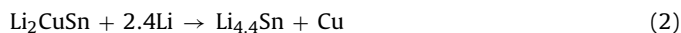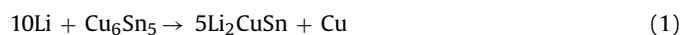
Up to 5 min, the longer the ageing time, the greater is the amount of the Cu$_6$Sn$_5$ phase that is formed. Further ageing diminishes the Cu$_6$Sn$_5$ phase with augmentation of the Ni$_3$Sn$_2$ phase. Even if the Cu$_3$Sn phase can improve the adhesion property between the electrodeposited alloy and Cu substrate, it may decrease the reversible capacity because of its inactivity with Li$^+$. As shown in Fig. 4a, the ageing time is proportional to the amount of Cu$_3$Sn phase.

Given the above findings, the superiority of the Sn 82 at.%–Ni 18 at.% alloy electrode aged for 5 min in terms of electrochemical performance can be attributed to the formation of intermetallic compounds such as Cu$_6$Sn$_5$ and Cu$_3$Sn in an optimized ratio. It seems that the electrode aged for 2 min incorporates too small an amount of Cu$_6$Sn$_5$ and Cu$_3$Sn to compensate for the disappearance of Sn and Ni$_3$Sn$_4$, which restrains the volume expansion during Li$^+$ insertion into the as-deposited Sn–Ni alloy electrode. The reduced capacity of the electrode aged for 10 min can be explained by augmentation of the inactive phase, Cu$_3$Sn.

The first charge curve of the Sn 82 at.%–Ni 18 at.% alloy electrode aged for 5 min is compared with that of the as-deposited Sn 82 at.%–Ni 18 at.% alloy electrode in Fig. 4b. After ageing, the high-voltage irreversible capacity disappears, and hence the reaction potential is lowered below 0.4 V vs. Li/Li$^+$. Assuming that Sn reacts with Li, the successive phase transition including Li$_7$Sn$_3$, Li$_6$Sn$_2$, Li$_{13}$Sn$_5$, Li$_5$Sn$_2$ and Li$_{22}$Sn$_{52}$ would develop a potential plateau around 0.4 V vs. Li/Li$^+$ [8]. The 1st charge curve of the as-deposited Sn–Ni alloy electrode shows this typical reaction. On the other hand, a large over-potential is observed during the 1st charge of the electrode aged for 5 min [9,10]. This is because Li reacts not with Sn but with Cu$_6$Sn$_5$. Because Li$^+$ initially intercalates into the hexagonal lattice (NiAs-type structure, $P6_3/mmc$) of the Cu$_6$Sn$_5$ alloy to form the phase Li$_x$Cu$_6$Sn$_5$ (an iso-structure of the cubic symmetry phase Li$_2$CuSn (Cu$_2$MnAl-type, $Fm/3m$)), it appears that the Cu–Sn intermetallic compounds can buffer the volume expansion that may occur during Li$^+$ insertion [11].

Fig. 5 presents XRD patterns for the Sn 82 at.%–Ni 18 at.% alloy electrode electrodeposited on the smooth-type Cu substrate, on the nodule-type Cu substrate, and on the nodule-type Cu substrate and aged for 5 min after cycling. In the as-deposited electrode, it is shown that the peak intensity of the Sn phase is weakened with the disappearance of metastable phase. This phenomenon occurs irrespective of the morphology of the Cu substrate. By contrast, some phases such as Cu$_6$Sn$_5$, Cu$_3$Sn and Ni$_3$Sn$_2$ are almost retained in the Sn–Ni alloy electrode aged for 5 min. This implies that, with ageing, the Sn–Ni alloy electrode experiences a type of topotactic reaction [11,12]. Thus, it can be concluded that the adoption of a notch-type Cu substrate with ageing is a very effective method to improve the electrochemical performance of Sn-based materials.

4. Conclusions

In order to improve the cyclic properties of Sn–Ni alloy electrodes, the morphology of the Cu substrate as well as the ageing conditions have been optimized. As a result of using a nodule-type Cu substrate, the reversible capacity of a Sn 82 at.%–Ni 18 at.% alloy electrode is increased to 560 mAh g^{-1} and its cyclic property is also improved. The enhancement in electrochemical performance can be attributed to an increase in the adhesion strength between the active material and the Cu substrate.

For further improvement in the electrochemical properties, a Sn 82 at.%–Ni 18 at.% alloy electrode electrodeposited on the nodule-type Cu substrate is aged to incorporate an optimum amount of inactive phase. At its optimum condition (ageing for 5 min), the Sn–Ni alloy electrode exhibits the highest capacity, 650 mAh g^{-1} and a good cyclic property. Finally, structural and electrochemical analyses demonstrate that intermetallic compounds such as Cu$_6$Sn$_5$ and Cu$_3$Sn form during ageing and can not only improve the adhesion strength between active material and Cu substrate, but also buffer the volume expansion during cycling.

Acknowledgements

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