**Improved cyclability of Sn–Cu film electrode for sodium secondary battery using
inorganic ionic liquid electrolyte**

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ABSTRACT

Thin films of Sn–Cu alloys with various compositions were prepared by annealing tin-coated copper foils at 463 K for 0–45 h. Their charge–discharge behaviors as negative electrodes for sodium secondary batteries were investigated using an inorganic ionic liquid electrolyte, *i.e.*, NaFSA–KFSA (FSA = bis(fluorosulfonyl)amide), at 363 K. A Sn–Cu film annealed for 4 h exhibited a stable reversible capacity of approximately 100 mAh (g-Sn)⁻¹. The improvement in the cyclability is discussed based on X-ray diffraction, X-ray photoelectron spectroscopy, and field-emission scanning electron microscopy results.

Keywords: Sodium secondary battery; Ionic liquid; Sn–Cu alloy; Negative electrode; Cyclability

1. Introduction

Urgent global energy issues require the development of sustainable energy supply systems, including renewable energy resources and electrical energy storage (EES) devices. Currently, lithium-ion batteries are widely used in mobile electronic devices, such as mobile phones and PC laptops. However, for the use of these batteries in large-scale stationary EES devices or electric vehicles, there are concerns about the limitations and uneven distribution of lithium resources, which could cause supply instability and steep price rises. In the past decade, sodium secondary batteries have been attracting increasing attention as alternatives to lithium-ion batteries, because sodium is more abundant than lithium [1–5]. In previous studies, sodium secondary batteries have been classified into two types, according to their operating temperatures. The first class consists of sodium–sulfur and sodium–nickel chloride batteries [6–9] operated at temperatures as high as 573 K. Although these batteries have been used in stationary EES devices, their high operating temperatures cause problems, because complicated temperature control systems are required and liquid sodium metal is highly reactive at high temperatures. The second class includes batteries operated at room temperature, using organic solvents as electrolytes [10–13]. However, there are safety issues in the construction of large-scale batteries, because of the flammability and

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3 volatility of organic solvents.
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6 For the construction of intrinsically safe sodium secondary batteries, the authors
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8 have developed alkali metal amide-based ionic liquids that can deposit sodium metal at
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10 intermediate temperatures [14–19]. In particular, the NaFSA–KFSA ionic liquid (x_{NaFSA}
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12 $= 0.56$, $x_{\text{KFSA}} = 0.44$, m.p. = 334 K; FSA = bis(fluorosulfonyl)amide) exhibits not only
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14 high safety, because of its non-flammability and negligible volatility, but also a
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16 sufficiently wide electrochemical window of ca. 5 V and thermal stability [19].
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18 Furthermore, the production cost of this ionic liquid is expected to be low, because it
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20 consists entirely of inorganic ions, and expensive synthetic processes such as
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22 electrolytic fluorination are not required. In our previous study, excellent cycling and
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24 rate properties were achieved for NaCrO_2 and $\text{Na}_2\text{FeP}_2\text{O}_7$ positive electrodes in
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26 NaFSA–KFSA ionic liquid at 353–363 K [19–21]. However, with regard to the negative
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28 electrode, with conventional sodium metal, there is a potential risk of forming highly
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30 reactive liquid sodium, because the operating temperature is close to the melting point
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32 of metallic sodium (371 K).
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51 On the basis of this background, the authors focused on tin as an alternative negative
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53 electrode material. Tin has a high theoretical capacity of $847 \text{ mAh (g-Sn)}^{-1}$ for the
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55 sodium-richest phase $\text{Na}_{15}\text{Sn}_4$ [22]. Moreover, the higher melting points of tin (505 K)
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3 and $\text{Na}_{15}\text{Sn}_4$ (681 K) solve the problems of safety and the operating temperature range.
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6 Previously, Chevrier et al. calculated the volumetric energy densities of alloy
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9 compounds (Na_xM ; M = Si, Ge, Sn, and Pb) using density functional theory calculations,
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12 and predicted that tin and lead have the highest volumetric energy densities [23]. The
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15 authors have already investigated the sodiation/desodiation behaviors of tin thin films
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18 electrodeposited on an Al current collector in NaFSA–KFSA ionic liquid at 363 K, and
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21 shown the feasibility and mechanism of the sodiation/desodiation process [24,25]. Here,
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24 tin thin films were selected because conducting agents and binders are not necessary for
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27 the fabrication of electrodes unlike powder active materials and the increase of energy
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30 density can be realized. Although the initial reversible capacity was as high as 729 mAh
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33 $(\text{g-Sn})^{-1}$, the capacity decreased because of the large volume changes during
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36 alloying/dealloying ($\Delta V = 430\%$ for $\text{Na}_{15}\text{Sn}_4$) and the resulting pulverization of the
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39 active materials.
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44 Recently, there have been increasing numbers of reports on the sodiation of
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47 tin-based negative electrodes, such as pure tin [26–28], SnO_x [29–31], Sn–C [32,33],
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50 Sn–SnS–C [34], Sn–Co–C [35], SnSb [36,37], and Sn–Cu [38–40] in organic solvents at
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53 room temperature. Among these materials, Sn–Cu nanocomposite exhibited an
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56 interesting cycling performance, *i.e.*, 400 mAh $(\text{g-Sn})^{-1}$ for 100 cycles [40]. Sn–Cu
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composites have been widely studied as negative electrodes for lithium-ion batteries [41–46]. It is worth noting that Tamura et al. reported improved reversibility of an electrode made of a Sn–Cu film prepared by annealing tin-coated copper foil at 473 K. It was concluded that annealing strengthened the Sn/Cu interface by forming buffer layers of Sn–Cu alloy [43,44].

Similar improvements in cyclability are expected for the sodiation/desodiation of Sn–Cu alloy films prepared by annealing tin-coated copper foils, in the present study, we therefore investigated the charge–discharge behaviors of Sn–Cu films (ca. 1 μm thick) in NaFSA–KFSA ionic liquid at 363 K. We adopted the electrodeposition method for the preparation of tin-coated copper foils. By utilizing the electrodeposition method, a clear interface between tin and copper is achieved, which is important for the succeeding alloying process. Various Sn–Cu films were analyzed, using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and field-emission scanning electron microscopy (FE-SEM), before and after charge–discharge tests. The cyclability improvements are discussed based on these results.

2. Experimental

2.1. Reagents and their handling

NaFSA (99+%) and KFSA (99+%) were purchased from the Mitsubishi Materials Electronic Chemicals Co., Ltd. The salts were dried under vacuum at 353 K for 48 h prior to use. The NaFSA–KFSA eutectic salt (NaFSA:KFSA = 56:44 (mol%) [17]) was prepared by grinding the two salts in a mortar.

Tin-coated copper foils were prepared by electrodeposition of tin on copper foils. The loading mass was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Before electrochemical measurements, these Sn–Cu films were dried in a vacuum at 363 K for 48 h, and then annealed at 463 K under vacuum. The annealing time was 2, 4, 10, 25, or 45 h.

2.2. Electrochemical measurements and analysis

Galvanostatic charge–discharge tests were performed in an argon atmosphere, using a VSP electrochemical measurement apparatus (Bio-Logic Co.) with a two-electrode cell (Tomcell Japan Co., Ltd.). Two sheets of glass-fiber filter paper (Whatman, GF-A, 260 μm), used as a separator, were vacuum impregnated with the electrolyte prior to the tests. Based on the ICP-AES results, Sn–Cu alloy films with tin loading masses between 0.88 and 1.07 mg cm^{-2} (corresponding to tin thicknesses between 1.21 and 1.46 μm) were used as the working electrode. The counter electrode consisted of sodium metal

(99.85%; Sigma-Aldrich, Inc.). The charge–discharge rates were set at current densities of 84.7–847 mA (g-Sn)⁻¹, which correspond to rates of C/10–1C. The cut-off voltages were 0.005 and 1.200 V, and the operating temperature was 363 K for all the tests in the present study. The two-electrode cell was heated using a mantle heater, and the temperature of the cell was monitored using a thermocouple, and maintained at 363 K.

The film phases in the Sn–Cu alloy films before and after the charge–discharge tests were identified by XRD, using an Ultima IV or SmartLab diffractometer (Rigaku Co.; Cu-K α radiation, $\lambda = 0.15418$ nm) equipped with a one-dimensional high-speed detector (D/teX Ultra, Rigaku Co.) with a nickel filter. The elemental compositions and chemical states of the Sn–Cu alloy films were investigated using XPS (JPS-9010, JEOL) combined with argon-ion etching. The surfaces and cross-sections were observed using FE-SEM (SU-8020, Hitachi, or JSM-7600F, JEOL). Before the cross-sectional observations, a cross-section polisher (SM09010, JEOL) was used to cut the Sn–Cu alloy films. Prior to analysis of the samples after the charge–discharge tests, the NaFSA–KFSA salts were removed using dehydrated and deoxidized tetrahydrofuran (water content < 10 ppm, oxygen content < 1 ppm; Wako Pure Chemical Industries, Ltd.), and the samples were transferred to the XRD and FE-SEM instruments without air exposure, using transfer vessels.

3. Results and discussion

3.1. Characterization of annealed Sn–Cu films

[Fig. 1](#) shows the XRD patterns of the annealed Sn–Cu alloy films. The unannealed film (denoted by 0h-annealed film) consists of β -Sn, Cu_6Sn_5 , and the Cu current collector. The presence of the Cu_6Sn_5 phase is explained by alloying of tin and copper at room temperature, which has previously been reported by several research groups [\[43,47\]](#). For the 2h- and 4h-annealed films, peaks attributable to the Cu_3Sn phase are observed, and the intensities of the Cu_6Sn_5 peaks are stronger than those of the β -Sn, in contrast to the 0h-annealed film. This corresponds to progress in alloying at 463 K. For the 10h- and 25h-annealed films, the β -Sn phase almost disappears and two intermetallic compounds, *i.e.*, Cu_6Sn_5 and Cu_3Sn phases, become dominant. The peak intensity ratio of Cu_6Sn_5 to Cu_3Sn indicates that the amount of Cu_6Sn_5 in the 10h-annealed film is larger than that in the 25h-annealed film. The 45h-annealed film is completely transformed into the Cu-richest phase, Cu_3Sn .

XPS depth profiles of the 0h-, 4h-, and 10h-annealed Sn–Cu alloy films are shown in [Fig. 2](#). For all the films before argon-ion etching, the binding energies of Sn $3d_{5/2}$ peaks are observed at around 487 eV, corresponding to SnO (486.5 eV) or SnO_2 (486.9

eV). This is explained by an oxide film covering the surface. After etching for 3 s, the Sn 3d_{5/2} peaks shift to the position of the Sn⁰ state (484.9 eV), as a result of removal of the oxide film, and their intensities decrease with increasing annealing time. Cu 2p_{3/2} peaks are clearly observed at approximately 933 eV, corresponding to the Cu⁰ state (932.9 eV), for the 4h- and 10 h-annealed films after etching for 3 s. For the 0h-annealed film, a weak Cu 2p_{3/2} peak is detected, which is consistent with the formation of the Cu₆Sn₅ phase detected by XRD. Moreover, the longer the annealing time, the stronger the Cu 2p_{3/2} peak becomes. It is therefore suggested that the formation of Sn–Cu alloys proceeds from the original Sn/Cu interface toward the top surface of the Sn.

Selected cross-sectional FE-SEM images of the Sn–Cu films are presented in Figs. 3a–3f. As shown in Fig. 3a, the 0h-annealed film mainly consists of β-Sn (light-gray region), Cu₆Sn₅ (gray region), and the Cu current collector (dark-gray region). The β-Sn and Cu₆Sn₅ domains are mixed in the surface layer to a depth of ca. 1 μm. A magnified image (Fig. 3b) shows a thin Cu₃Sn layer of thickness ca. 100 nm between the Cu₆Sn₅ and Cu layers, which is too thin to be detected by XRD analysis. In the 4h-annealed film (Figs. 3c and 3d), the Cu₆Sn₅ and Cu₃Sn areas increase, and micron-sized β-Sn domains are localized on the surface. In the 10h-annealed film (Fig. 3e), the β-Sn region

has almost disappeared, which is consistent with the XRD results (see Fig. 1). For the 25h-annealed film (Fig. 3f), a thinner Cu_6Sn_5 film and thicker Cu_3Sn film, respectively, are observed than in the 10h-annealed film; this is in agreement with the XRD results.

3.2. Charge–discharge behaviors of annealed Sn–Cu films

Fig. 4a shows the initial charge–discharge curves of Sn–Cu films with different annealing times at a current density of $84.7 \text{ mA (g-Sn)}^{-1}$. The 0h-annealed film exhibits an initial discharge (dealloying) capacity of ca. $400 \text{ mAh (g-Sn)}^{-1}$, corresponding to half of the theoretical capacity. In our previous report, an initial reversible capacity of over $700 \text{ mAh (g-Sn)}^{-1}$ was obtained when tin-coated Al foils were used [24]. This difference is caused by the lower reactivities of Sn–Cu alloys [38]. For the Sn–Cu films with longer annealing times, smaller initial capacities are obtained; values of approximately 150 and $100 \text{ mAh (g-Sn)}^{-1}$ are observed for the 2h- and 4h-annealed films, respectively. The 10h-, 25h-, and 45h-annealed films have small discharge capacities, less than $10 \text{ mAh (g-Sn)}^{-1}$. It is found that films without a $\beta\text{-Sn}$ phase exhibit considerably lower capacities than those containing this phase. It is therefore concluded that the capacity is mainly contributed by $\beta\text{-Sn}$.

Fig. 4b shows the cycling characteristics of these Sn–Cu films. The discharge

capacity of the 0h-annealed film remains at around 400 mAh (g-Sn)⁻¹ until the third cycle, but decreases to approximately 120 mAh (g-Sn)⁻¹ after 20 cycles. This degradation is caused by the enormous volume change during sodiation/desodiation ($\Delta V = 430\%$ for Na₁₅Sn₄) [24,25]. After 40 cycles, however, the capacity gradually increases and reaches ca. 165 mAh (g-Sn)⁻¹ at the 100th cycle. The reason for this behavior is discussed in the next paragraph. The 2h-annealed film retains a discharge capacity of 150–200 mAh (g-Sn)⁻¹ for the initial five cycles, and then stabilizes at a lower capacity of ca. 110 mAh (g-Sn)⁻¹. For the 4h-annealed film, although the capacities of the initial 10 cycles are small, ca. 120 mAh (g-Sn)⁻¹, a stable reversible capacity of around 110 mAh (g-Sn)⁻¹ is obtained for 100 cycles. In the case of the 10h-annealed film, an increase in capacity from 10 to 50 mAh (g-Sn)⁻¹ is observed in the initial 20 cycles. This is explained by an increase in the effective surface area by micro-crack formation during the charge–discharge cycles (see also Fig. 8f). The 25h- and 45h-annealed films show small initial capacities of 5 and 1 mAh (g-Sn)⁻¹, respectively. The XRD and cross-sectional FE-SEM results show that almost no β -Sn phase is present in the 10h-, 25h-, and 45h-annealed films, and the ratios of Cu₆Sn₅/Cu₃Sn are higher than those for the films with shorter annealing times. In particular, the 45h-annealed film has almost no Cu₆Sn₅ phase. It is therefore considered that the Cu₆Sn₅ phase is slightly active with

sodium, but the Cu_3Sn phase is inactive.

In Fig. 4b, the 0h-annealed film shows the highest capacity of ca. $165 \text{ mAh (g-Sn)}^{-1}$ at the 100th cycle among all the Cu-Sn alloy electrodes. The main features in the cycle property are the large decrease of capacity during initial 10 cycles and the gradual recovery of capacity after 40 cycles. As shown in Figs. 1–3, the 0h-annealed film consists of $\beta\text{-Sn}$, Cu_6Sn_5 , and the Cu current collector. The Cu_6Sn_5 phase is formed by alloying of tin and copper at room temperature [43,47]. Considering that the alloying reaction occurs in some degree even at room temperature, further alloying between tin and copper would proceed during the charge-discharge tests at 363 K. However, the rate of alloying would be much slower compared to that at the annealing temperature of 463 K. Moreover, such further alloying at 363 K would not practically proceed for the other Cu-Sn alloy films already annealed at 463 K. Since the 0h-annealed film possesses the largest amounts of $\beta\text{-Sn}$ phase, it shows the highest capacity in the beginning in the charge-discharge tests. During the initial 10 cycles, the capacity rapidly decreases due to falling-off of pulverized $\beta\text{-Sn}$. Meanwhile, the alloying of $\beta\text{-Sn}$ and Cu current collector also gradually proceeds during the cycles and some portions of the fallen $\beta\text{-Sn}$ become active again. As the result, the capacity gradually recovers and reaches the highest capacity at the 100th cycle among all the Cu-Sn alloy electrodes.

Since the 4h-annealed film exhibits the best capacity retention, the charge–discharge test was continued up to 1000 cycles. Figs. 5a and 5b, respectively, show the charge–discharge curves, and cycling properties of the specific capacity and coulombic efficiency of the 4h-annealed Sn–Cu film. Stable reversible capacities greater than 100 mAh (g-Sn)⁻¹ are obtained for 1000 cycles. No noticeable changes in the charge–discharge profiles are observed between the 100th and 1000th cycles. Moreover, at the 1000th cycle, the reversible capacity and coulombic efficiency are 105 mAh (g-Sn)⁻¹ and 99.5%, respectively. This stable cyclability can be explained as follows. In the 4h-annealed film, as shown in Figs. 3c and 3d, active β -Sn regions are randomly dispersed in less-active Cu₆Sn₅ regions. In such domain structure, the strain generated from the active β -Sn regions can be absorbed by the less-active regions, which effectively suppresses pulverization of the active β -Sn. Furthermore, to achieve stable cyclability, delamination of active material layer from current collector must be prevented. In the 4h-annealed film, Cu₆Sn₅ and Cu₃Sn layers play a role of buffer layer and prevent the delamination, as in the case of tin negative electrodes for lithium-ion batteries [43,44].

The rate properties were also investigated using another 4h-annealed Sn–Cu film. As shown in Fig. 6, a reversible capacity of ca. 130 mAh (g-Sn)⁻¹ is observed at 84.7

mA (g-Sn)⁻¹ at the 20th cycle. This value is slightly higher than the results shown in Figs. 4 and 5, and can be attributed to differences among the amounts of β-Sn in different 4h-annealed films, *i.e.*, slight differences among the β-Sn thicknesses of these films before annealing, as stated in the experimental section. At a high current density of 847 mA (g-Sn)⁻¹, the Sn-Cu film still maintains a reversible capacity of 70 mAh (g-Sn)⁻¹, which is more than half the capacity at 84.7 mA (g-Sn)⁻¹. Moreover, the capacity recovers to the initial value when the rate returns to 84.7 mA (g-Sn)⁻¹. The domain structure of β-Sn and Cu₆Sn₅ therefore effectively supports sustainable sodiation/desodiation, even at even high rates.

3.3. Analysis of annealed Sn-Cu films after charge-discharge tests

Figs. 7a–7f show XRD patterns of the 0h-, 4h-, and 10h-annealed films before and after the charge-discharge tests. For the 0h-annealed film (Figs. 7a and 7b), the same β-Sn and Cu₆Sn₅ phases are observed before and after the charge-discharge test. Before the charge-discharge test, the diffraction peaks of the β-Sn (200) and (301) planes (2θ = 32.02° and 55.33°) are strong, indicating preferred orientation of the (100) plane. After the test, however, the observed pattern agrees well with the reported powder pattern. It is considered that the preferred orientation was destroyed by the sodiation/desodiation

process. In addition, the peaks for Cu_6Sn_5 are weaker after the test; this is also explained by alloying/dealloying with sodium. For the 4h-annealed film (Figs. 7c and 7d), $\beta\text{-Sn}$, Cu_6Sn_5 , and Cu_3Sn phases are detected before and after the charge–discharge test. Similar changes to those for the 0h-annealed film are observed for the $\beta\text{-Sn}$ and Cu_6Sn_5 patterns after the test. In contrast, the peak intensities of Cu_3Sn are almost unchanged, indicating that the Cu_3Sn phase is inactive with sodium. For the 10h-annealed film (Figs. 7e and 7f), a similar phenomenon is observed. The peak intensities of Cu_6Sn_5 become weak and those of Cu_3Sn are unchanged.

Figs. 8a–f show representative surface FE-SEM images of the 0h-, 4h-, and 10h-annealed films before and after charge–discharge tests. Before the charge–discharge tests (Figs. 8a, 8c, and 8e), all the films have flat, smooth surface morphologies. After the tests, however, a rough morphology with some large pores is seen for the 0h-annealed film (Fig. 8b); this is caused by the severe volume changes during sodiation/desodiation. For the 4h-annealed film after 1000 cycles (Fig. 8b), a denser morphology with smaller amount of pores is observed, indicating that the original framework is preserved, because of the domain structure of active $\beta\text{-Sn}$ and less-active Cu_6Sn_5 . Because of this stable film structure, there is no noticeable deterioration, even after 1000 cycles (see Fig. 5). For the 10h-annealed film after the test (Fig. 8f), a

smooth surface with minor cracks is observed. The Cu_6Sn_5 phase at the surface hardly reacts with sodium, therefore the film does not undergo serious volume changes.

4. Conclusions

Sn–Cu alloy films were prepared by annealing tin-coated copper foils at 463 K for 0–45 h, and their charge–discharge behaviors were investigated in the inorganic ionic liquid NaFSA–KFSA at 363 K. The major findings of the present study are summarized as follows.

1. XRD and cross-sectional FE-SEM analyses revealed that the 0h-, 2h-, and 4h-annealed films consisted of β -Sn, Cu_6Sn_5 , and Cu_3Sn phases. For the 10h- and 25h-annealed films, β -Sn disappeared as alloying progressed. For the 45h-annealed film, the Sn–Cu alloys were completely transformed into the Cu_3Sn phase.
2. In the charge–discharge tests, the films without a β -Sn phase exhibited much smaller capacities than those containing this phase. For the films with the β -Sn phase, the discharge capacities mainly originated from the β -Sn phase. Moreover, it was found that Cu_6Sn_5 reacted slightly with sodium, and that Cu_3Sn was almost inactive.

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3 3. Among the Sn–Cu films with different annealing times, the 4h-annealed film
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6 exhibited the best capacity retention, and maintained a stable reversible capacity
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9 of ca. 100–120 mAh (g-Sn)⁻¹ for 1000 cycles. The XRD and FE-SEM analyses
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12 suggested that the stable cyclability was mainly attributable to an appropriate
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15 domain structure of active β-Sn and less-active Cu₆Sn₅.
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Figure captions

Fig. 1. X-ray diffraction patterns of annealed Sn–Cu alloy films; annealing temperature: 463 K, annealing time: 0–45 h.

Fig. 2. X-ray photoelectron spectroscopy depth profiles of annealed Sn–Cu alloy films; annealing time: 0–10 h.

Fig. 3. Selected cross-sectional field-emission scanning electron microscopy images of annealed Sn–Cu alloy films. (a) and (b) 0h-annealed film at different magnifications, (c) and (d) 4h-annealed film at different magnifications, (e) 10h-annealed film, and (f) 25h-annealed film. (b) and (d) show enlarged views of the red rectangular areas of (a) and (c), respectively.

Fig. 4. (a) Initial charge–discharge curves of annealed Sn–Cu alloy film electrodes at a current density of $84.7 \text{ mA (g-Sn)}^{-1}$ and (b) cycling characteristics of these Sn–Cu films during 100 cycles.

Fig. 5. (a) Charge–discharge curves and (b) cycling properties of specific capacity and

coulombic efficiency of 4h-annealed Sn–Cu film at current density of 84.7 mA (g-Sn)⁻¹.

Fig. 6. (a) Charge–discharge curves and (b) rate properties of specific capacity and coulombic efficiency of 4h-annealed Sn–Cu film at current densities of 84.7–847 mA (g-Sn)⁻¹. The values of 84.7, 169, 424, and 847 in the figure represent the current densities in mA (g-Sn)⁻¹.

Fig. 7. Comparison of X-ray diffraction patterns of Sn–Cu film electrodes before and after charge–discharge tests. (a) 0h-annealed, before, (b) 0h-annealed, after, (c) 4h-annealed, before, (d) 4h-annealed, after, (e) 10h-annealed film, before, and (f) 10h-annealed film, after.

Fig. 8. Representative field-emission scanning electron microscopy images of surface morphologies of Sn–Cu alloy films before (a, c, and e) and after (b, d, and f) charge–discharge tests. Annealing time: 0 h (a, b), 4 h (c, d), and 10 h (e, f).

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