

A study on tin-based negative electrode materials
for sodium secondary batteries
using Na[FSA]–K[FSA] inorganic ionic liquid

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Chapter 1

General introduction

1.1 Electrical energy storage devices

In the last several decades, considerable efforts have been devoted to create a new energy supply system for establishment of low carbon society (LCS), in order to overcome environmental problems, such as global warming and climate change. The realization of LCS requires us to make a fundamental shift from traditional fossil fuel power generation towards utilization of renewable energy resources such as solar and wind power. However, since these renewable energies have the intermittent nature, it is difficult to balance supply and demand of electricity. Hence, large-scaled electrical energy storage (EES) systems utilizing stationary EES devices and electric vehicles (EVs) are indispensable for electric load-leveling.

Lithium-ion battery (LIB) is one of the potential candidates for the EES device because LIBs possess high energy densities and have been widely spread for portable devices such as PC laptops and smartphones. Nevertheless, for construction and spread of large-scaled LIBs, two major problems are remaining.

Firstly, lithium and cobalt resources are unevenly distributed in the world, which leads to concerns about unstable supply and steep increase in price depending on the political situations of the resource-producing countries. Thus, it is desirable to construct EES devices using more ubiquitous resources. Sodium secondary battery is a promising candidate as an alternative device because of abundant sodium resources in the crust and sea water, and its similar chemical nature with lithium (See **Table 1-1**). Moreover, the standard redox potential of Na^+/Na couple is close to that of Li^+/Li couple, which leads to the practically high energy densities of sodium secondary

batteries. Lastly, the inexpensive aluminum metal can be used as a current collector of negative electrodes for sodium secondary batteries because aluminum is inactive with sodium [1]. In contrast, aluminum forms intermetallic compounds with lithium [1], and copper is commonly used as a current collector of negative electrodes for LIBs. This is the hidden advantage of sodium secondary batteries. Based on these backgrounds, the number of papers on sodium secondary batteries is rapidly increasing in the last decade [2–12].

Secondly, current LIBs utilize highly-volatile and flammable organic solvent-based electrolytes, which leads to the safety concerns such as over charge and thermal runaway especially when their large-scaled battery systems are put into practical use. Thus, though in the R&D stages, there are many studies on safer electrolytes such as ionic liquids and solid electrolytes. Details are presented in the later sections.

1.2 Brief overview of sodium secondary batteries

In this section, the author briefly introduces the history of sodium secondary batteries. Although sodium secondary batteries have gathered much attention in the last decade, they have longer history of fundamental research since the last half of 1960's.

1.2.1 Electrolytes

In the earlier stage of research, Na/S [13–18] and Na/NiCl₂ [19] batteries operating at high temperatures of around 573 K were reported. These batteries utilize solid electrolyte β'' -alumina ($\text{Na}_2\text{O} \cdot x\text{Al}_2\text{O}_3$, $5 \leq x \leq 7$) which exhibits high sodium ion conductivities at high temperatures. The high temperature operation enables the high charge–discharge rates due to the high electrode reaction rates. However, to ensure sufficient performance, these batteries require heating systems as well as heat insulators to maintain the high operating temperature, which leads to an increase

in the size and weight of the battery system. In addition, Na/S battery has a relatively high lower limit temperature due to high melting points of sodium sulfides (558 K for Na_2S_4) and a low conductivity of sulfur. Accordingly, energy consumption by the heaters decreases the energy density of the total battery system. There is also a potential risk related to the highly reactive liquid sodium metal because the mechanically fragile β'' -alumina easily breaks when the physical impact is applied from the outside.

Since 1980's, the organic solvent electrolytes emerged as the second class of electrolytes which enabled battery operation at lower temperatures. As typical literatures, there are reports on organic solvents [20–28] and polymers [29,30]. At lower operating temperatures, handling of batteries is much easier, heaters for maintaining the operation temperature are not necessary, and a wide variety of component materials are available. However, the use of organic solvents is highly disadvantageous for the construction of safe and high-performance batteries due to the flammability and volatility of the organic solvents.

In the recent decade, solid electrolytes have been revisited because of their high safety. There are several reports on solid electrolytes [31–33] operating at temperatures of lower than 100°C. However, the rate performances of batteries are still insufficient due to low conductivities ($< 1 \text{ mS cm}^{-1}$) of these electrolytes compared to liquid electrolytes. In addition, aqueous solutions have also been utilized by some groups [34–36], but the narrower electrochemical windows of these electrolytes limit the energy densities of the batteries. Very recently, ionic liquid electrolytes also emerged as a new class of safer electrolytes because ionic liquids possess nonflammability and negligible volatility [37–39]. The optimization of the ionic liquids has realized practically high conductivities over 5 mS cm^{-1} at ambient temperatures. Details of the ionic liquid electrolytes are presented in the **Section 1.4**.

1.2.2 Positive electrodes

As mentioned in the previous section, since 1970's, charge–discharge properties of sulfur were investigated as the positive electrode material of Na/S battery operating at around 573 K [13–18]. After 1980's, sodium batteries operating at ambient temperatures were explored. In 1980, the electrochemical behavior of TiS_2 at ambient temperatures was reported, in which a 1.5 M sodium triethyl(*N*-pyrrolyl)borate ($\text{Na}[(\text{C}_2\text{H}_5)_3\text{B}(\text{NC}_4\text{H}_4)]$)–dioxolane solution was used as an electrolyte [20]. Although other chalcogenide compounds, MX_2 ($\text{M} = \text{Ti, V, Cr, Nb, Ta}$; $\text{X} = \text{S, Se}$), were studied, their average operating potentials were lower than 2.0 V vs. Na^+/Na [40]. At around the same time, new sodium intercalated compounds appeared as positive electrodes exhibiting higher average charge–discharge potentials at around 3.0 V vs. Na^+/Na . For example, in 1981, Delmas *et al.* [21] found layered oxides, O3-, O'3-, P3-, and P2-type Na_xCoO_2 that exhibited electrochemical intercalation/deintercalation of sodium. In 1982, reversible structural transitions of other layered oxides, O3- NaCrO_2 and O'3- NaNiO_2 , was reported [22]. In 1985, charge–discharge behaviors of O'3-type NaMnO_2 and P2-type Na_xMnO_2 were evaluated [23]. Since then, a variety of layered oxides were explored, such as O3- NaFeO_2 [41,42], P2- $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ [43], O3- $\text{Na}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ [43], O3- $\text{Na}[\text{Fe}_{1/2}\text{Co}_{1/2}]\text{O}_2$ [44], P2- $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ [45,46], O3- $\text{Na}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ [47], and so on. It is worth noting that the first Na-ion cell without using sodium metal was reported in 1988 [24], in which Na_xCoO_2 positive electrodes and a composite negative electrode of poly(*p*-phenylene) and Na–Pb alloys was operated in a 1 M NaPF_6 -dimethoxyethane (DME) solution.

In 2000's, diverse polyanionic compounds appeared as positive electrode materials for sodium batteries. Generally, polyanionic compounds possess open structure, and realize fast diffusion of sodium, leading to better charge–discharge characteristics. Phosphates are the most widely investigated compounds, and they are categorized into some groups such as $\text{Na}_3\text{M}_2(\text{PO}_4)_3$ ($\text{M} = \text{V}$ [37,48], Fe [48]), $\text{Na}_x\text{MPO}_4\text{F}$ ($\text{M} = \text{V}$ [49], Mn [50,51], Fe [50,52], Co [53]),

$\text{Na}_3\text{M}_2(\text{PO}_4)_2\text{F}_3$ ($\text{M} = \text{V}$ [54,55], Fe , Ti [55]), NaMPO_4 ($\text{M} = \text{Mn}$ [56], Fe [57,58]), $\text{Na}_2\text{MP}_2\text{O}_7$ ($\text{M} = \text{Mn}$ [59], Fe [60,61], Co [62]), and $\text{Na}_4\text{M}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ ($\text{M} = \text{Fe}$ [63], Co [64]). Among them, fluorophosphates ($\text{Na}_x\text{MPO}_4\text{F}$ and $\text{Na}_3\text{M}_2(\text{PO}_4)_2\text{F}_3$) and mixed phosphates ($\text{Na}_4\text{M}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$) containing vanadium and cobalt show high average redox potentials at around 4 V vs. Na^+/Na [49,53–55,64], and are attractive as positive electrode materials. Recently, sulfate [65,66] and silicate [67] compounds have also been explored. Especially, an alluaudite-type sodium iron sulfate, $\text{Na}_2\text{Fe}_2(\text{SO}_4)_3$, exhibited the highest redox potential (ca. 3.8 V vs. Na^+/Na) among iron-based positive electrode materials whose components are abundant in earth's crust.

In addition, electrochemical behaviors of fluoride compounds such as MF_3 ($\text{M} = \text{Ti}$, Mn , Fe , Co) [68] and NaMF_3 ($\text{M} = \text{Mn}$, Fe , Ni) [69] were investigated, in which iron-based fluorides showed higher capacities. However, a problem of large potential hysteresis between charging and discharging processes still remains.

1.2.3 Negative electrodes

Generally, materials operating at a potential of lower than 1.5 V vs. Na^+/Na are categorized into negative electrodes. Since the first study fifty years ago, several studies were conducted to explore negative electrodes for sodium batteries. However, there is no extensive research until the last decade. In this subsection, the author introduces a brief history of the research on negative electrodes.

1.2.3.1 Early studies

In the early days, sodium metal was utilized as a negative electrode material of Na/S and Na/NiCl_2 batteries, as stated in the **Subsection 1.2.1** [13–19]. Although metallic sodium possesses high energy densities, it is highly reactive with moisture and oxygen. Thus, there is a serious danger in the case of leakage of liquefied sodium metal. In 1983, the electrochemical

behavior of a titanium-based layered oxide, O₃-NaTiO₂, was reported [25], in which 0.3 Na was reversibly deintercalated below 1.6 V vs. Na⁺/Na in a NaClO₄-propylene carbonate (PC) electrolyte. In 1987, charge-discharge behaviors of Na-Pb alloys prepared by a metallurgical process were investigated in a 1 M NaPF₆-dimethoxyethane (DME) solution, and the phase transition mechanism of Na-Pb alloys was estimated [26]. As mentioned in the previous subsection, the first Na-ion cell was constructed by the same group [24].

At around the same time, Delmas *et al.* reported reversible electrochemical intercalation of sodium into NaTi₂(PO₄)₃ in a NaClO₄-PC electrolyte [27,28]. NaTi₂(PO₄)₃ is one of NASICON-type compounds (NASICON = sodium (Na) Super Ionic CONductor) that possess open frameworks and realize fast sodium diffusion. However, its operating potential is higher than 1.5 V vs. Na⁺/Na, which is not suitable for a negative electrode.

1.2.3.2 Carbon materials

In 1988, electrochemical intercalation of sodium into graphite was reported utilizing a Na[CF₃SO₃]-PEO (PEO = polyethylene oxide) polymer electrolyte operating at 80°C [29]. In contrast to lithium batteries, only small amount of sodium was intercalated into graphite to form NaC₆₄ even at a slow rate of C/200 (C/200 = a current density that takes 200 hours to make full charged or discharged state). In 1993, a carbeneous material after heat treatment of petroleum coke showed a higher reversible capacity corresponding to the composition of NaC₃₀ utilizing the above-mentioned polymer electrolyte at 86°C [30]. In 2000, Dahn *et al.* prepared hard carbons by pyrolysis of glucose at 1000 or 1150°C, and reported that these hard carbons gave high reversible capacities around 300 mAh g⁻¹ in a 1 M NaClO₄/EC-DEC solution at 30°C [70]. Hard carbon consists of ordered layered graphene parts and interstitial spaces (pores) between graphene domains. According to the detailed analyses of sodiation/desodiation mechanism [71-73], charge-discharge profiles are divided into two regions, *i.e.*, a sloping potential region above 0.2

V vs. Na^+/Na and a plateau region below 0.2 V vs. Na^+/Na . The former corresponds to the intercalation of sodium into graphene layers and the latter is ascribed to sodium insertion into pores. Recently, reversible sodium insertion into graphite was reported [74–76]. Co-intercalation of solvated Na^+ ion occurs when ether-based electrolytes containing diethylene glycol dimethyl ether (DEGDME), tetraethylene glycol dimethyl ether (TEGDME), and dimethoxyethane (DME). The reported reversible capacity was ca. 150 mAh g^{-1} .

1.2.3.3 Titanium-based compounds

In 2011, titanium compounds were revisited. Charge–discharge behavior of $\text{Na}_2\text{Ti}_3\text{O}_7$ was reported [77], in which this material showed an extremely low $\text{Ti}^{4+}/\text{Ti}^{3+}$ redox potential of 0.3 V vs. Na^+/Na as compared with the potential for the lithium counterpart (1.5 V vs. Li^+/Li [78,79]). Moreover, 2 moles of Na can be inserted into $\text{Na}_2\text{Ti}_3\text{O}_7$, resulting in a high reversible capacity of 178 mAh g^{-1} . Although $\text{Na}_2\text{Ti}_6\text{O}_{13}$ [80] and $\text{Na}_4\text{Ti}_5\text{O}_{12}$ [81] were also explored, both of them showed reversible capacities of lower than 50 mAh g^{-1} . In the case of $\text{Na}_4\text{Ti}_5\text{O}_{12}$, the obtained charge–discharge performance was much poorer than $\text{Li}_4\text{Ti}_5\text{O}_{12}$ that exhibits stable reversible capacities of ca. 150 mAh g^{-1} with the redox potential of 1.5 V vs. Li^+/Li [82]. This was explained by the fact that the prepared trigonal $\text{Na}_4\text{Ti}_5\text{O}_{12}$ has different structural properties from cubic $\text{Li}_4\text{Ti}_5\text{O}_{12}$ that possesses a three-dimensional lithium diffusion network. Electrochemical behavior of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was also investigated. It was found that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ reversibly separates into two titanates, $\text{Li}_7\text{Ti}_5\text{O}_{12}$ and $\text{Na}_6\text{LiTi}_5\text{O}_{12}$ [83].

Electrochemical insertion of sodium was also studied for several TiO_2 polymorphs such as anatase [84–86], hollandite [87], bronze [88], and rutile-type [89,90] structures. In the first report on TiO_2 [84], amorphous TiO_2 nanotube exhibited reversible capacities of ca. 140 mAh g^{-1} in the potential range of 0.9–2.5 V vs. Na^+/Na , and anatase TiO_2 nanotube showed extremely small capacities below 10 mAh g^{-1} in the potential range of 0.5–2.5 V vs. Na^+/Na . However, in later

reports [85,86], anatase TiO_2 nanocrystal and nanorods showed a high reversible capacity of 150–200 mAh g^{-1} with deep charging toward 0.01 V vs. Na^+/Na . Charge–discharge profiles after the 2nd charging are different from those for the 1st charging, suggesting the structural changes due to conversion reactions. Recently, a new titanium phosphate, $\text{Na}_3\text{Ti}_2(\text{PO}_4)_3$, was reported to exhibit two redox potentials of 2.1 V for $\text{Ti}^{4+}/\text{Ti}^{3+}$ and 0.4 V for $\text{Ti}^{3+}/\text{Ti}^{2+}$ [91]. Moreover, layered oxides utilizing $\text{Ti}^{4+}/\text{Ti}^{3+}$ redox, such as $\text{P2-Na}_{0.66}[\text{Li}_{0.22}\text{Ti}_{0.78}]\text{O}_2$ [92], $\text{P2-Na}_{2/3}[\text{Co}_{1/3}\text{Ti}_{2/3}]\text{O}_2$ [93], $\text{P2-Na}_{0.6}[\text{Cr}_{0.6}\text{Ti}_{0.4}]\text{O}_2$ [94] and $\text{P2-/O3-Na}_x[\text{Ni}_{x/2}\text{Ti}_{1-x/2}]\text{O}_2$ [95–97], were revealed to show good cycling properties,.

1.2.3.4 Alloy compounds

In the past few years, alloy compounds were also revisited owing to their higher theoretical capacities than aforementioned negative electrode materials. Sodium forms alloy compounds with silicon (Si), phosphorous (P), germanium (Ge), tin (Sn), antimony (Sb), lead (Pb), bismuth (Bi), *etc.* [1,98]. **Table 1-2** summarizes their densities, Na-richest phases, gravimetric and volumetric theoretical capacities at discharging conditions, and volume expansion ratios.

In 2011, Chevrier *et al.* [99] calculated the volumetric energy densities of silicon, germanium, tin, and antimony by density functional theory (DFT) calculation, and concluded that tin and lead have the highest volumetric energy densities. In that year, the magnetron sputtered Sb_2O_4 thin film was reported to show high reversible capacities over 700 mAh g^{-1} at a rate of C/70 [100]. However, there was a large potential hysteresis of approximately 1 V between charging and discharging profiles.

In 2012, several reports on silicon, tin, antimony, lead, and SnSb alloy appeared [101–104]. Komaba *et al.* [101] investigated cycling properties of silicon, tin, lead electrodes combined with poly(acrylic acid) (PAA) binder. They found that a Sn/PAA composite electrode delivered the highest reversible capacity of ca. 500 mAh g^{-1} at a rate of 50 mA g^{-1} , and that a Si/PAA

composite electrode showed an extremely small capacity below 50 mAh g⁻¹ at the same rate. Qian *et al.* [102] reported that a Sb/C nanocomposite electrode exhibited stable capacities of ca. 600 mAh g⁻¹ at a rate of 100 mA g⁻¹. Since the average operation potential of a Na–Sn alloy electrode (< 0.5 V vs. Na⁺/Na) is lower than that of a Na–Sb alloy electrode (> 0.5 V vs. Na⁺/Na), tin is preferable in terms of energy densities of a Na-ion battery.

Since 2013, various materials which form alloy with sodium have been reported, such as phosphorus [105,106], germanium [107,108], bismuth [109,110], and SiO [111]. Among them, red phosphorous showed high reversible capacities over 1500 mAh g⁻¹. However, both red phosphorus and the formed Na₃P are flammable, leading to the inevitable safety issues. Moreover, as shown in **Table 1-2**, the theoretical volumetric capacity of phosphorus is lower than that of tin, because phosphorus possesses a much lower density than tin.

Therefore, considering the safety and the installation space for practical batteries, tin is one of the promising materials as a high capacity negative electrode material. Details of tin-based negative electrodes are presented in the next section.

1.3 Tin-based negative electrode materials

1.3.1 Lithium batteries

In 1970's, for lithium secondary batteries, alloy compounds received attention as alternative negative electrodes to lithium metal, because the utilization of lithium metal negative electrodes led to dendritic lithium formation and critical electrode failure [112–114]. Firstly, aluminum [115–121], silicon [122–126], tin [127–131], and antimony [132,133]-based compounds were investigated at high and low operation temperatures, and their thermodynamic properties and cycling behaviors were revealed. As the results, in the case of lower operation temperatures below 100°C, the fatal and intrinsic issues of large volume changes were recognized. That is, the

pulverization and electrical isolation of active materials resulted in the capacity fade [117,118,120,121].

To improve such poor cycleability, four major countermeasures were proposed for tin negative electrodes, *i.e.*, the utilization of (1) tin oxides [134–136], (2) Sn–M₁ system (M₁: inactive metals with lithium; Ni, Fe, etc.) [137–140], (3) Sn–M₂ system (M₂: active metals that form Li–M₂ binary alloys; Si, Cd, Sb, etc.) [141–144], (4) Sn–M₃ system (M₃: metals that form Li–Sn–M₃ ternary alloys; Cu, Ag, etc.) [145–148]. The concepts of these systems are explained as follows:

(1) Tin oxides

In the 1st charging, tin oxides separate into Li–Sn alloys and Li₂O, and generally Li₂O is inactive with lithium. Hence, after the 1st charging, only Li–Sn alloys contribute to the reversible capacity, and Li₂O play a role as a matrix to relieve the strain generated by the volume expansion/contraction cycles of Li–Sn alloys. However, the capacity loss in the 1st cycle due to irreversible Li₂O formation was inevitable, and the formed Li₂O possesses low electrical conductivity and impedes the electrochemical reaction.

(2) Sn–M₁ system (M₁: inactive metals with lithium)

As is the case with tin oxides, in the 1st charging, Sn–M₁ alloys separate into Li–Sn alloys and M₁ metal, and M₁ is inactive with lithium. After the 1st charging, since M₁ exists in the active material layer, M₁ acts as a conductor and buffer matrix for the large volume change, and prevents the capacity fade. In addition, some Sn–M₁ alloys are kinetically inactive with lithium, due to the low thermodynamic activities of tin in the Sn–M₁ alloys. So, the Sn–M₁ alloys also play the same role as M₁ metal.

(3) Sn–M₂ system (M₂: active metals that form Li–M₂ binary alloys)

This system was proposed in 1981, as a “mixed conductor matrix” for the Sn–Si system operating at 410°C [141]. In 1988, electrochemical behavior of the Sn–Cd system at ambient

temperatures was reported [142]. Generally, in the 1st charging, the potentials of Li–Sn alloy formation are different from those of Li– M_2 alloy formation. In other words, the formation of Li–Sn alloys and Li– M_2 alloys does not occur at the same time. Therefore, Li–Sn alloys play a role as a conductor and buffer matrix during the Li– M_2 alloy formation, and vice versa. Compared with tin oxides and Sn– M_1 systems, the Sn– M_2 system has the advantage that M_2 metal can contribute to the reversible capacity, leading to the increase of battery energy densities. However, the final volume change ratio is higher than the above-mentioned systems. In addition, after the 1st charging, lithiation/delithiation of Sn and M_2 metal usually occurs independently. If the alloying potentials of Sn and M_2 metal with Na are different, a “mixed conductor matrix” lasts for a long time, leading to the better cycleability.

(4) Sn– M_3 system (M_3 : metals that form Li–Sn– M_3 ternary alloys)

This system is related to both the Sn– M_1 and Sn– M_2 systems. For example, in the case of M_3 = Cu, Cu–Sn alloys (Cu_6Sn_5 and Cu_3Sn) first transform into Li_2CuSn , Li–Sn alloys and Cu). Then, at the end of charging, the final products are $Li_{4.4}Sn$ and Cu, which is similar to the Sn– M_1 system [145,146]. In contrast, the Sn–Ag system undergoes more complicated reactions [147,148]. For example, when Ag_3Sn phase is utilized, this phase transforms into Ag_2LiSn and metallic Ag during the initial stage of lithiation. Further lithiation leads to the formation of $AgLi_2Sn$ and Li–Sn alloys. At the end of charging, $AgLi_2Sn$ phase separates into Li–Ag and Li–Sn alloys. In this case, a matrix is formed owing to the presence of Li–Sn–Ag ternary alloys. However, such repeated phase separation may bring about electrode failure during cycling.

Based on these backgrounds, to achieve the ultimate goal of longer operating life for sodium secondary batteries, the present study mainly focuses on Sn– M systems in which M does not form binary alloys with sodium, *i.e.*, (2) Sn– M_1 system or a part of (4) Sn– M_3 system. Details are presented in the next subsection.

1.3.2 Sodium batteries

Figure 1-1 shows a phase diagram of the Na–Sn system [1]. According to this phase diagram, tin forms eight intermetallic compounds with sodium below 371 K: NaSn₆, NaSn₄, NaSn₃, NaSn₂, α -NaSn, Na₉Sn₄, Na₃Sn, and Na₁₅Sn₄. The formation of Na₁₅Sn₄ phase gives the high theoretical capacity of 847 mAh (g-Sn)⁻¹.

In the early studies on the Na–Sn system, several groups reported thermodynamic properties of Na–Sn alloys [149–152]. Although most of the studies focused on liquid alloys, the formation potentials of solid Na–Sn alloys at 393 K were reported by Baker *et al.* in 1990 [152].

Since 2011, several pioneering works on Na–Sn alloys appeared, aiming at the development of negative electrode materials for sodium batteries. For example, Chevrier *et al.* [99] predicted the formation potentials for the limited number of Na–Sn alloys by DFT calculations, and Slater *et al.* [6] observed several potential plateaus corresponding to the formation of Na–Sn alloys in organic solvent-based electrolytes at ambient temperatures. Komaba *et al.* [101] reported the cycleability of a tin powder composite electrode using a PAA binder. They obtained a high reversible capacity of 500 mAh (g-Sn)⁻¹ in an FEC-added NaClO₄/PC electrolyte at ambient temperatures. In addition, the formation of Na₁₅Sn₄ phase was confirmed by *ex situ* X-ray diffraction (XRD) analysis. Ellis *et al.* [153] also investigated the phase transitions of Na–Sn alloys in a NaPF₆/EC-DEC electrolyte at 303 K by *in situ* XRD analysis.

Recently, many Sn–M systems have been investigated to improve the electrode performance. Since 2011, Sn–Sb system has been reported [104,154,155]. Although Sb is active with sodium, the electrochemical formation of ternary Na–Sn–Sb phases has not been confirmed yet. Thus, this system is tentatively categorized into (3) Sn–M₂ system (M₂: active metals that form Na–M₂ binary alloys). As mentioned in the **Subsection 1.2.3.4**, the average operation potentials of tin and antimony are different from each other, which is an ideal “mixed conductor matrix”. In 2013, Sn–Cu system was reported, in which Sn–Cu nanocomposites exhibited reversible capacities of

ca. 400 mAh g⁻¹ for 100 cycles [156]. Other studies revealed that Cu₆Sn₅ phase has extremely low activity with sodium [157,158]. Moreover, in contrast to the case of lithium batteries, the formation of Na–Sn–Cu ternary alloys has not been confirmed. Thus, Sn–Cu system presumably belongs to the (2) Sn–M₁ system (M₁: inactive metal with sodium). Similarly, Sn–Ni [159] and Sn–Fe [160] systems were investigated, and both systems were classified into the same Sn–M₁ system. Other systems, such as Sn–O [161–164], Sn–S [165–167], Sn–P [168–172], and Sn–Co [173,174], were also reported.

1.4 Ionic liquid electrolytes

1.4.1 Overview

Ionic liquids are liquids composed of only cations and anions, and usually possess lower melting points than 100°C [175]. Historically, room temperature ionic liquids were discovered in the first half of the 20th century [176]. Most of the ionic liquids exhibit high safety of nonflammability and negligible volatility. Moreover, some of them show also wide electrochemical windows, reasonably high ionic conductivities, and thermal stabilities. These physicochemical properties are suitable as electrolytes for electrochemical devices.

In 1970's, the studies on lithium secondary batteries utilizing molten salts started [177–184]. In the most reports, molten LiCl–KCl systems were applied and the operating temperatures were higher than 673 K [177–181]. Although other studies explored new molten salts containing bromides to decrease the melting points, their operating temperatures were still higher than 473 K [182–184]. From the late 1990's, room temperature molten salts (ionic liquids) containing imidazolium, piperidinium, pyrrolidinium, ammonium-based organic cations were applied to electrolytes of lithium-ion batteries [185–191]. In the field of sodium batteries, Okada and Yamaki *et al.* constructed a Na₃V₂(PO₄)₃/Na₃V₂(PO₄)₃ symmetric cell utilizing an

imidazolium-based ionic liquid [37]. Recently, the pyrrolidinium-based ionic liquids have also been investigated as promising electrolytes [38,39].

1.4.2 Alkali metal amide-based ionic liquids

In such circumstances, Hagiwara *et al.* have explored a new class of ionic liquids containing no organic cations. They investigated the physicochemical and electrochemical properties of single salts, binary and ternary mixtures of alkali metal bis(trifluoromethylsulfonyl)amides ($M[TFSA]$; $M = Li, Na, K, Rb,$ and Cs ; $TFSA = bis(trifluoromethylsulfonyl)amide$) [192–196], and alkali metal bis(fluorosulfonyl)amides ($M[FSA]$; $M = Li, Na, K, Rb,$ and Cs ; $FSA = bis(fluorosulfonyl)amide$) [197–202]. The structures of $TFSA$ and FSA anions are shown in **Figure 1-2**.

1.4.2.1 $M[TFSA]$ ionic liquids

$M[TFSA]$ single salts show the melting points in the range of 390–530 K, and their binary or ternary mixtures melt at lower temperatures. For instance, the melting points of $Li[TFSA]$ and $Na[TFSA]$ are 506 and 530 K, respectively, and these temperatures are too high for practical applications. However, the melting points are able to be lowered by mixing other $M[TFSA]$ s. For instance, the $Li[TFSA]$ – $K[TFSA]$ – $Cs[TFSA]$ ternary system ($x(Li[TFSA]) = 0.20$, $x(K[TFSA]) = 0.10$, $x(Cs[TFSA]) = 0.70$) [195] and the $Na[TFSA]$ – $Cs[TFSA]$ binary system ($x(Na[TFSA]) = 0.10$, $x(Cs[TFSA]) = 0.90$) [196] exhibit the lower melting points of 419 K and 390 K, respectively. Here, the $Li[TFSA]$ – $K[TFSA]$ – $Cs[TFSA]$ melt enables the reversible electrodeposition of lithium, and has a high ionic conductivity of 14.2 mS cm^{-1} and a wide electrochemical window of 5.0 V at 423 K. A $Li/LiFePO_4$ battery was reported to exhibit stable cycling behavior for 50 cycles at 423 K [195]. In the case of the $Na[TFSA]$ – $Cs[TFSA]$ melt, the reversible electrodeposition of sodium, a high ionic conductivity of 12.4 mS cm^{-1} , and a wide

electrochemical window of 4.9 V were confirmed at 423 K. Moreover, a Na/NaCrO₂ battery was reported to give excellent cycle and rate performances at 423 K [196].

1.4.2.2 M[FSA] ionic liquids

Further lowering of the operating temperature was realized by applying M[FSA] salts. Although the melting points of M[FSA] single salts lie in the range of 360–410 K, their binary or ternary mixtures have lower melting temperatures, as in the cases of M[TFSA] salts. For example, Na[FSA] and K[FSA] single salts melt at 379 K and 375 K, respectively, and the Na[FSA]–K[FSA] eutectic mixture ($x(\text{Na[FSA]}) = 0.56$, $x(\text{K[FSA]}) = 0.44$) melts at 334 K [198]. A phase diagram of the Na[FSA]–K[FSA] system is shown in **Figure 1-3**. The reversible electrodeposition of sodium is possible in the eutectic melt. Moreover, it possesses a reasonably high ionic conductivity of 3.3 mS cm^{-1} and a wide electrochemical window of 5.2 V at 363 K [200]. It is worth noting that M[FSA] salts are composed of entirely inorganic ions, and that their production processes do not require an expensive electrolytic fluorination process unlike M[TFSA] salts. So far, Na/NaCrO₂ and Na/Na₂FeP₂O₇ batteries showed good cycling properties and rate capabilities at 353–363 K [200–202]. Operation at this intermediate temperature range is able to reduce the energy loss by the temperature control as compared to the high temperature operation of Na/S and Na/NiCl₂ batteries, and to enhance the battery performance as compared to the room temperature operation owing to the improved kinetics of electrode reactions and ion transfer. However, although in the solid state in this temperature range, the use of metallic sodium has the potential risk in safety. Thus, the development of safer negative electrodes is necessary.

From this background, the author focused on tin as a promising negative electrode material for sodium secondary batteries using Na[FSA]–K[FSA] inorganic ionic liquid.

1.5 Aims of this study

With the aim to develop a sodium secondary battery utilizing the new inorganic ionic liquid, the electrochemical formation of Na–Sn alloys and charge–discharge behaviors of various tin-based negative electrode materials were investigated in Na[FSA]–K[FSA] ionic liquid electrolyte ($x(\text{Na[FSA]}) = 0.56$, $x(\text{K[FSA]}) = 0.44$). A brief summary of the aims in each chapter is given below:

In Chapter 3, tin-coated aluminum foils (Sn–Al films) were prepared by electroplating of tin, and the electrochemical formation of Na–Sn alloys was evaluated by cyclic voltammetry. Then, the reversibility of Na–Sn alloying and dealloying processes was examined by galvanostatic charge–discharge tests under various conditions.

In Chapter 4, the formation potentials of Na–Sn alloy phases were investigated by GITT (Galvanostatic Intermittent Titration Technique) and *ex situ* XRD analysis. Based on these results, thermodynamic data of Na–Sn alloy phases were calculated.

In Chapter 5, tin-coated copper foils (Sn–Cu films) were prepared by electroplating of tin, and their charge–discharge characteristics were investigated. The improved cycleability of Sn–Cu films was also discussed based on the results of XRD and SEM analyses.

In Chapter 6, charge–discharge characteristics of electrodeposited tin film on nickel foils (Sn–Ni films) were examined, and the mechanism on their cycleability was elucidated by XRD and SEM analyses.

In Chapter 7, electrochemical behaviors of tin-coated iron foils (Sn–Fe films) were investigated, and the effects of the alloying degree on cycleability were evaluated. Sodium activities of some Fe–Sn alloys were also discussed.

Table 1-1 Abundances of Li and Na in Earth's crust and seawater and their standard redox potentials in water.

Element	Abundance		Standard redox potential in water / V vs. SHE [205]
	Crust [#] / mg kg ⁻¹ [203]	Sea water ^{##} / mg kg ⁻¹ [204]	
Li	2.0×10 ¹	1.8×10 ⁻¹	-3.040
Na	2.9×10 ⁴	1.1×10 ⁴	-2.714

[#] Compositions of the upper crust (to the depth of 10 km underground). The composition of sodium was calculated from the value for Na₂O (3.89 wt%).

^{##} The values are shown by two significant digits for convenience.

Table 1-2 Comparison of the densities, Na-richest phases, gravimetric and volumetric theoretical capacities at discharging condition, and volume expansion ratio for various alloy negative electrodes. [1,98]

M	Densities / g cm ⁻³	Na-richest phase	Theoretical capacity		Volume change ΔV / %
			mAh (g-M) ⁻¹	mAh (cm ³ -M) ⁻¹	
Si	2.33	NaSi	954	2223	144
P [#]	2.16	Na ₃ P	2596	5607	299
Ge	5.33	NaGe	369	1967	126
Sn	7.29	Na _{3.75} Sn	847	6172	424
Sb	6.69	Na ₃ Sb	660	4418	293
Pb	11.34	Na _{3.75} Pb	485	5501	387
Bi	9.81	Na ₃ Bi	385	3774	253

[#] In case of red phosphorus

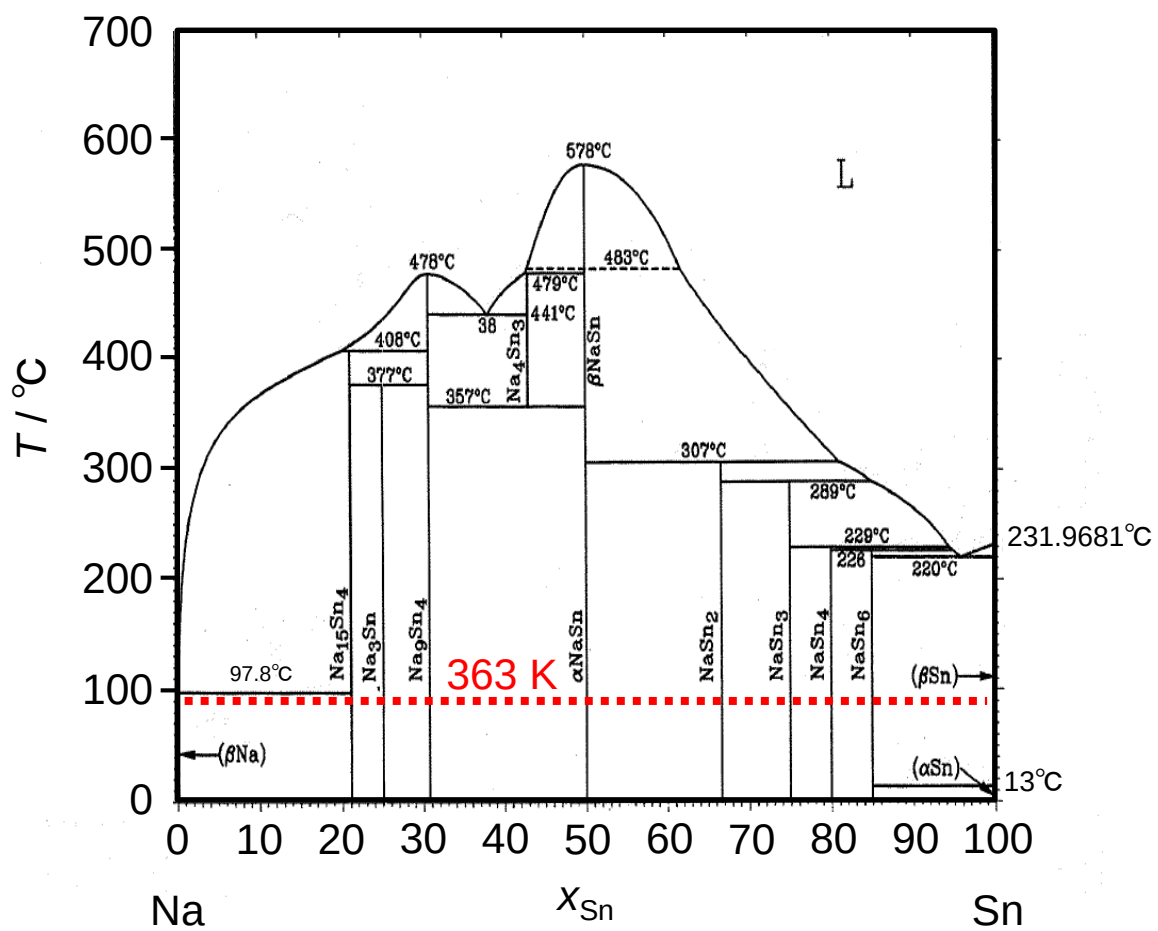


Figure1-1 A phase diagram of the Na–Sn system [1].

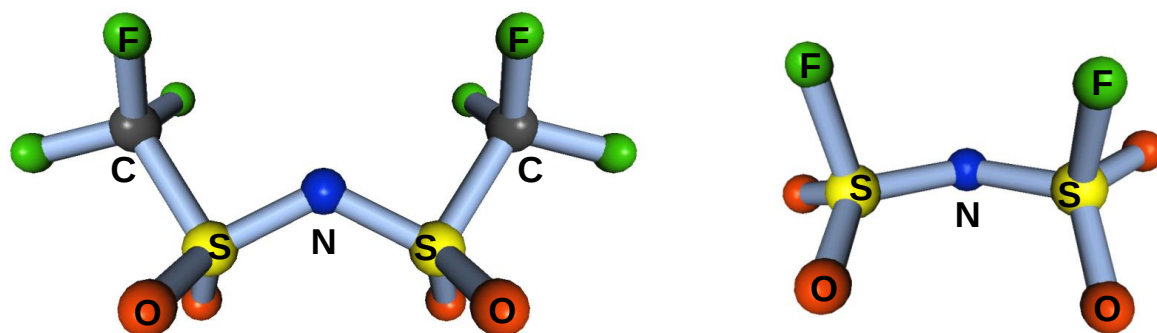


Figure 1-2 Structures of TFSA (left) and FSA (right) anions.

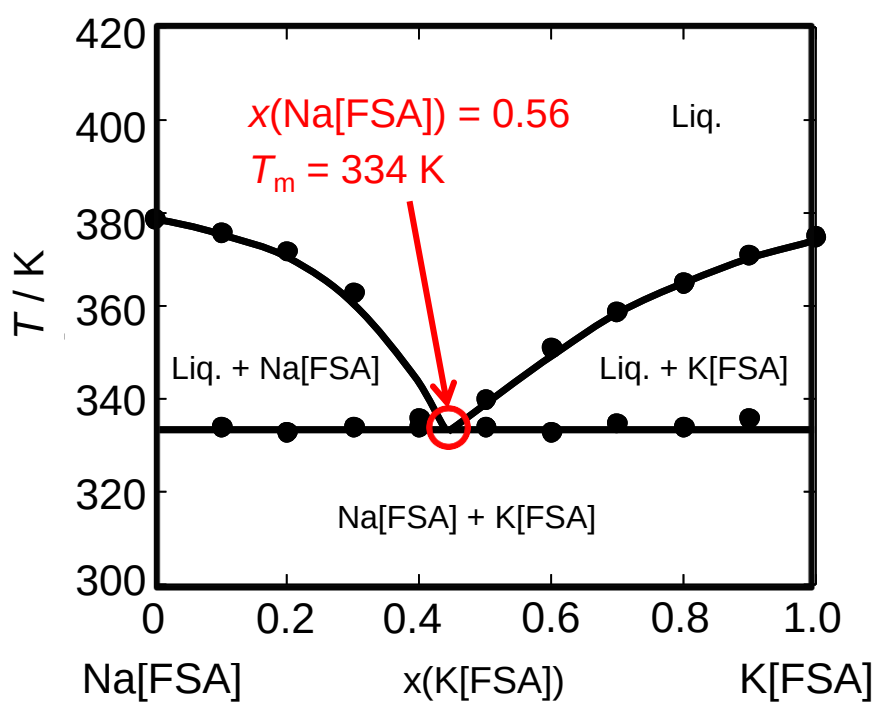


Figure 1-3 A phase diagram of the Na[FSA]–K[FSA] [198].

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Chapter 2

Experimental

2.1 Apparatus

2.1.1 Glove box

Glove boxes combined with gas purification systems (Miwa Manufacturing Co., Ltd., DBO-2LKH-O, DBO-2LKH-HNBR or DBO-1KH-HNBR2), a glove box (Hoei Industries, Ltd., NP-002) connected with a gas purification system (Miwa Manufacturing Co., Ltd., MM3-H80S-S) or a glove box (Miwa Manufacturing Co., Ltd., 1ADB-3-O) connected with a gas purification system (Miwa Manufacturing Co., Ltd., MS3-P60S-N) were used to handle air- and moisture-sensitive reagents. All glove boxes were filled with dry argon gas (99.998%). The concentration of water in all glove boxes was monitored by a dew point meter (GE Panametrics Ltd., MTS5-311-10; or GE Sensing & Inspection Technologies, VeriDri-12R-11-000-0-0) and the dew points of the glove boxes were kept below 213 K. The concentration of oxygen in the glove box (Miwa Manufacturing Co., Ltd., DBO-2LKH-HNBR) was also checked by an oxygen analyzer (GE Sensing & Inspection Technologies Co., Ltd., DF-150ε).

2.1.2 Vacuum line

A vacuum line was used for the drying of various reagents prior to use. **Figure 2-1** shows a schematic drawing of the vacuum line. The main body of the vacuum line was made of stainless steel tubes (1/2 inch o.d.; o.d. = outer diameter; SUS304 or SUS316) and PFA tubes (1/2 inch o.d., PFA = tetrafluoroethylene-perfluoroalkylvinylether copolymer), and these tubes were connected with joints, SUS316 needle valves partly made of a Kel-F tip (Swagelok[®] Co.). A PFA tube (1/4

inch o.d.) was used to connect the main body with a drying vessel (See also **Figure 2-2**). The temperature of the drying vessel was controlled by an oil bath filled with silicone oil. A stirrer bar was put at the bottom of the oil bath, and the silicone oil was stirred by using a magnetic stirrer to make the temperature gradient of the bath as small as possible. An oil-sealed rotary vacuum pump (Shibaura Eletec Corp., RP-602; or ULVAC KIKO, Inc., GLD-136C) was connected to this reaction line. In addition, a cold trap made of Pyrex[®] glass was set up just before the pump to prevent water and solvents from entering the pump. The degree of vacuum was below 2 Pa. Pressure in the vacuum line was constantly monitored by a Pirani gauge (Shimadzu Corp., PM-32A; or ULVAC, Inc., GP-1G).

2.2 Reagents and their handling

All manipulations and reactions were performed under argon atmosphere using dry and deoxygenated solvents. All chemicals used in this study were of analytical grade.

Na[FSA] (99+%) and K[FSA] (99+%) were purchased from Mitsubishi Materials Electronic Chemicals Co., Ltd. The salts were dried under vacuum at temperatures of 333–353 K for 48 h prior to use. The Na[FSA]–K[FSA] eutectic salt (mol% Na[FSA]:K[FSA] = 56:44 [11]) was prepared by grinding the two salts in a mortar. FSA salts were weighed by an electronic scale balance (Sartorius Mechatronics Japan K.K., CP423S, CPA224S or CPA225D).

Various kinds of Sn films, which were supplied from Sumitomo Electric Industries, Ltd., were used for electrochemical measurements. Sn films were prepared by electrodeposition of tin onto several substrates (Al, Cu, Ni or Fe foils). The thickness of electrodeposited tin was determined based on the results of inductively coupled plasma atomic emission spectroscopy (ICP-AES; Thermo Fisher Scientific, Inc., iCAP6300). Sn films were weighed by an electronic scale balance (Sartorius Mechatronics Japan K.K., CPA224S, CPA225D; or Shimadzu Corp., AEL-40SM).

Details of handling of Sn films are presented in each chapter.

2.3 Electrochemical measurements

Electrochemical measurements were conducted using a VSP multi-channel potentiostat-galvanostat (Biologic Co.) or a 580-type battery cycler (Toyo Co.). All tests were performed at 363 K in the present study. Electrochemical cells were heated by a mantle heater, and their temperature was monitored by a thermocouple and maintained at 363 K.

2.3.1 Cyclic voltammetry

Cyclic voltammetry was conducted using a three-electrode system. Schematic drawings of a three-electrode beaker cell and electrodes for the beaker cell are shown in **Figures 2-3** and **2-4**, respectively. The working electrode was made of a Sn film on Al foil (hereinafter, a Sn–Al film) or an Al plate (Nilaco Corp., 99+%, 0.1 mm thickness). The reference and counter electrodes were both Na metals (Sigma-Aldrich, Inc., 99.85%). Cyclic voltammograms were collected at scan rates of 0.1 mV s^{-1} for the Sn–Al film and 10 mV s^{-1} for the Al plate electrode.

2.3.2 Charge–discharge test

Galvanostatic charge–discharge tests were performed using a two-electrode cell. A schematic drawing of the two-electrode cell (Tomcell Japan Co., Ltd.) is shown in **Figure 2-5**. Various Sn films were used as working electrodes. The counter electrode was composed of Na metal. Two-, three- or four-ply glass fiber filter papers (Whatman, GF-A, $260 \text{ }\mu\text{m}$ thickness per sheet) were used as a separator. The separator was vacuum-impregnated with the Na[FSA]–K[FSA] melts at 363 K for two days prior to the test. Detailed conditions are shown in each chapter or section.

2.3.3 Galvanostatic intermittent titration technique (GITT)

Equilibrium potentials for Na–Sn alloys were investigated by galvanostatic intermittent titration technique (GITT). Repeating the cycle of the galvanostatic electrolysis and the open circuit potential measurement gives the correlation of the quantity of electricity and the equilibrium potential, which was proposed by Weppner and Huggins [2]. The two-electrode cell was also used for this measurement. The setup of the cell was the same with the case of charge–discharge tests. Details are presented in **Chapter 4**.

2.3.4 Preparation of Na–Sn alloy samples

The Na–Sn alloy samples were prepared by a combination of galvanostatic and potentiostatic electrolysis using the aforementioned two-electrode cell. After electrolysis, the open circuit potentials were monitored and the potentials just before cooling the cells were regarded as the potentials of Na–Sn alloy samples. Detailed procedures are described in **Chapter 4**.

2.4 Analysis

All the Sn film electrodes after electrochemical measurements were treated in the argon atmosphere, and their surfaces were washed by dehydrated and deoxidized tetrahydrofuran (Wako Pure Chemical Industries, Ltd., water content < 10 ppm, oxygen content < 1 ppm) to remove the Na[FSA]–K[FSA] salt before analyses. Finally, these samples were transferred to the XRD and FE-SEM apparatuses without air exposure by air-tight transfer vessels.

2.4.1 X-ray diffraction (XRD)

The components of various Sn film electrodes were investigated using an X-ray diffractometer (Rigaku Co., Ultima IV or SmartLab; Cu-K α radiation ($\lambda = 0.15418$ nm); 40 kV

and 40 mA for Ultima IV, 40 kV and 30 mA for SmartLab) equipped with a one-dimensional high-speed detector (Rigaku Co., D/teX Ultra for Ultima IV, D/teX Ultra 250 for SmartLab) with a nickel filter. Some of the obtained XRD patterns were corrected by a standard specimen of mica, and analyzed by DICVOL program [3] or RIETAN-FP/VENUS program [4].

2.4.2 X-ray photoelectron spectroscopy (XPS)

The elemental compositions and chemical states of Sn film electrodes were investigated by X-ray photoelectron spectroscopy (XPS; JEOL, JPS-9010, Mg K α source). Depth profiles of these electrodes were obtained by a combination with argon-ion etching apparatus. The accelerating voltage and current of etching were fixed at 800 V and 19.0 mA, respectively.

2.4.3 Field emission-scanning electron microscope (FE-SEM) and energy dispersive X-ray spectroscopy (EDX)

The surfaces of Sn film electrodes were observed by a field emission scanning electron microscope (FE-SEM; Hitachi, SU-8020) with energy dispersive X-ray spectrometer (EDX; Horiba, X-max).

Prior to the cross-sectional SEM observation, some of Sn film electrodes were cut with a focused ion beam (FIB) system (FEI Co., Quanta 3D FEG) combined with air-tight transfer system (Gatan, Inc., C1010). To reduce the damage of the samples, tungsten was vapor-deposited on their surfaces in advance. This FIB system is also equipped with scanning electron microscope (SEM) that was used for the cross-sectional observation. Other Sn film electrodes were cut with a cross-section polisher (CP; JEOL, IB090-20), and the cross-sections were observed by an FE-SEM (JEOL, JSM-7600F) with an energy dispersive X-ray spectrometer (Oxford Instruments, X-max^{N80}).

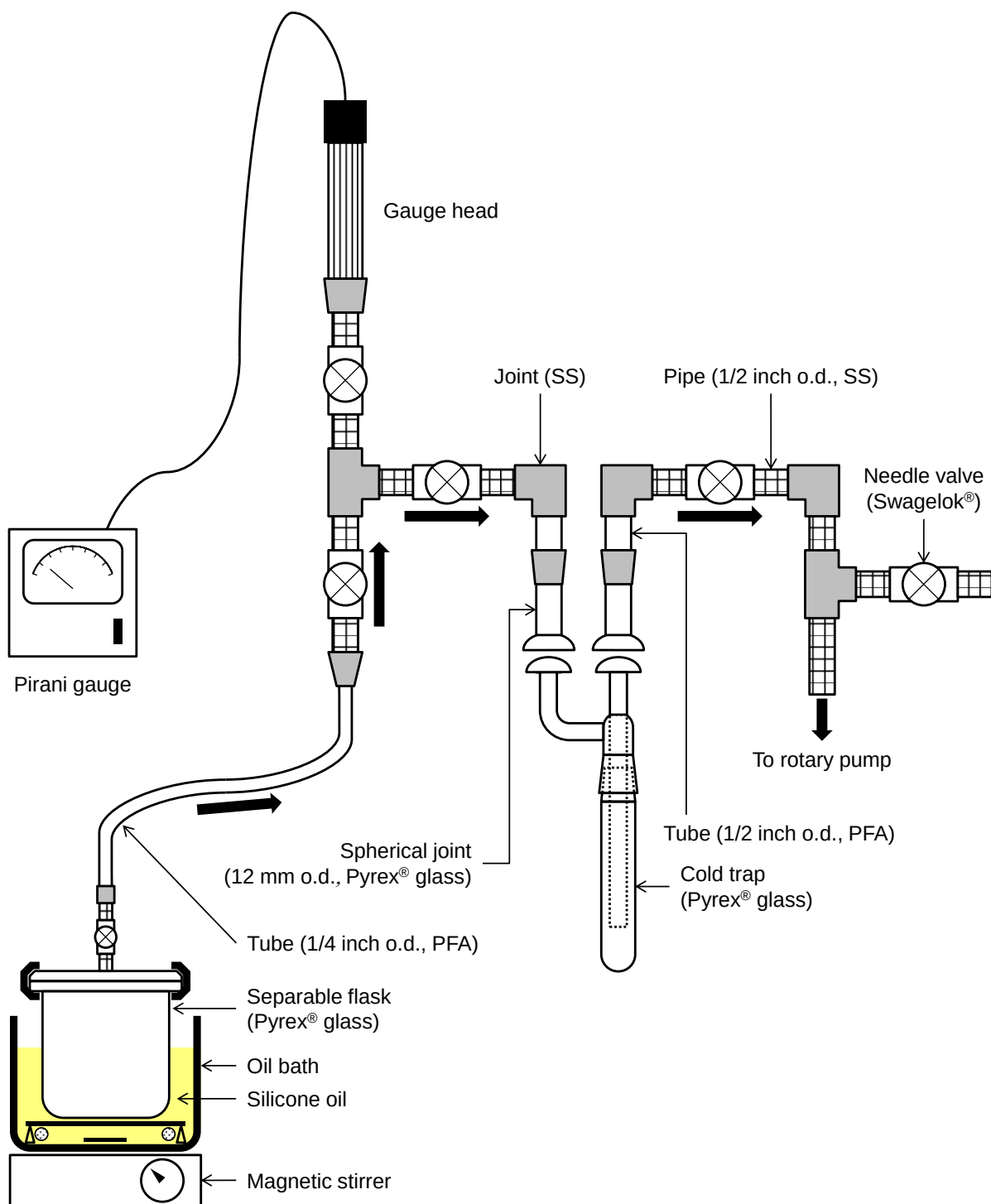


Figure 2-1 A schematic drawing of a vacuum line.

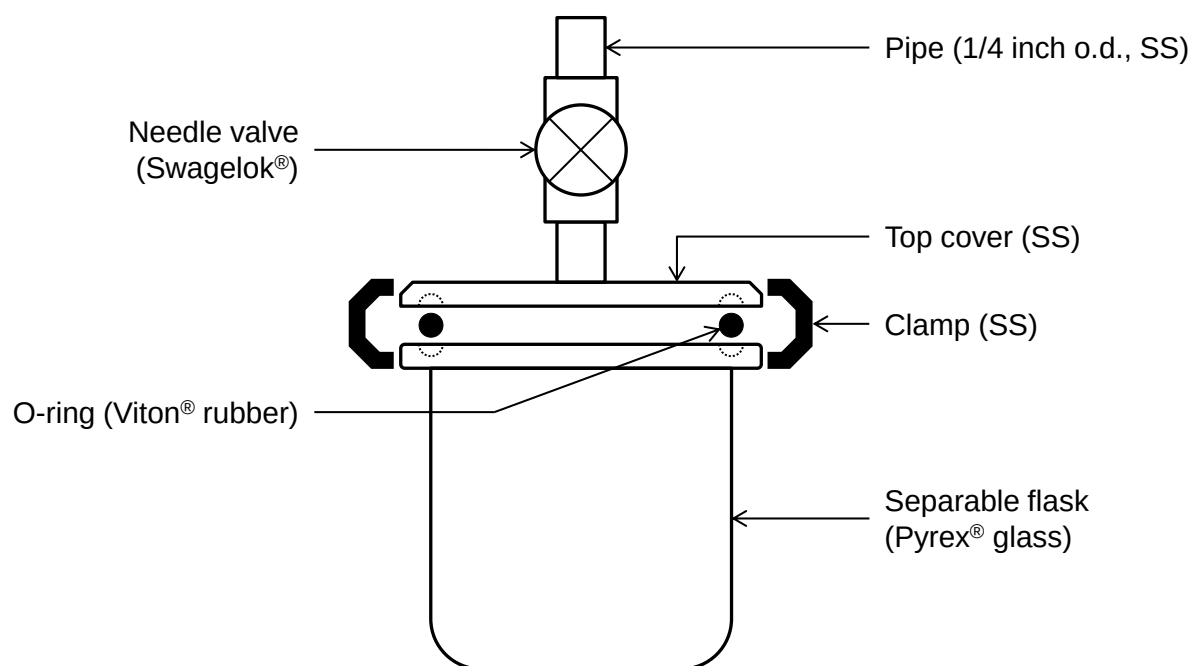


Figure 2-2 A schematic drawing of a drying vessel.

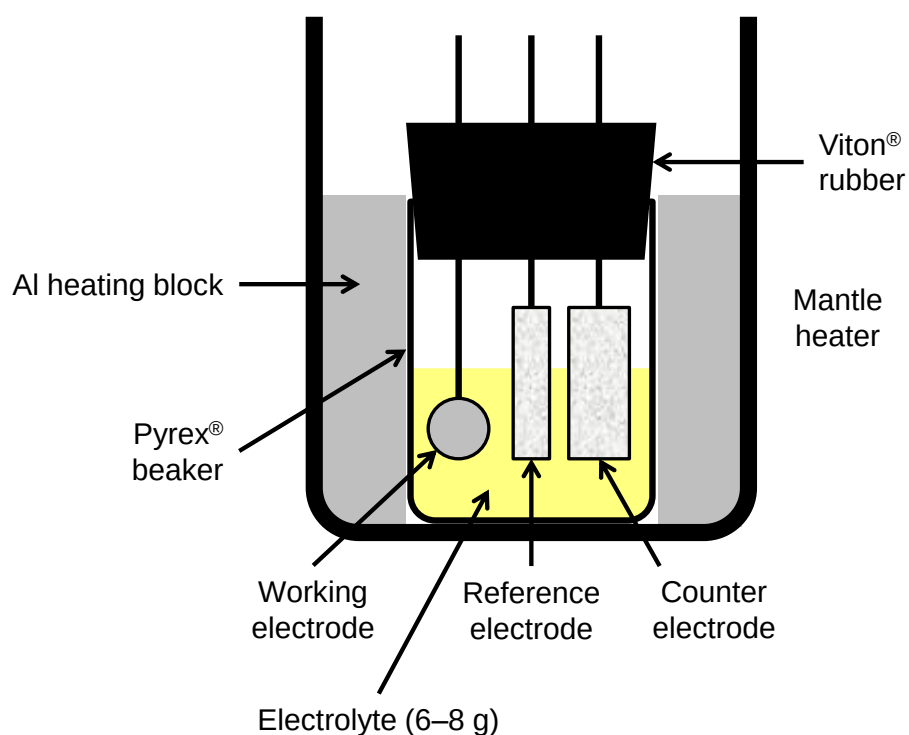


Figure 2-3 A schematic drawing of a three-electrode beaker cell for cyclic voltammetry.

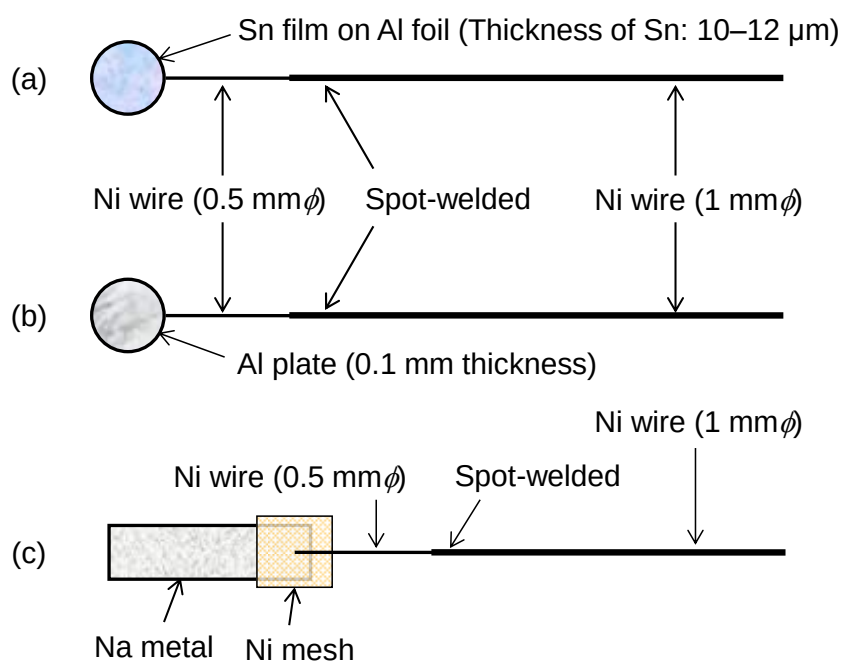


Figure 2-4 Schematic drawings of (a) Sn film electrode, (b) Al plate electrode, and (c) Na electrode for the three-electrode beaker cell.

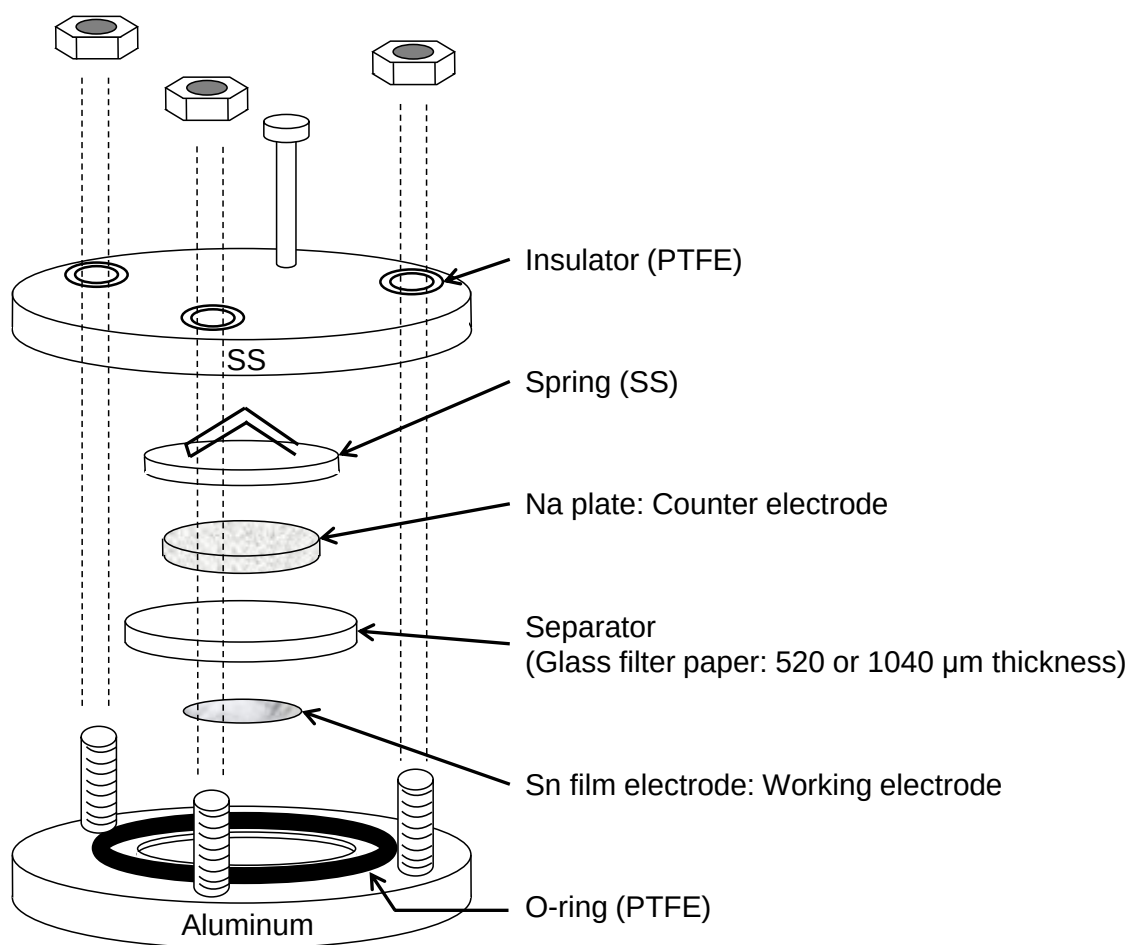


Figure 2-5 A schematic drawing of the two-electrode cell for charge–discharge test and galvanostatic intermittent titration experiment.

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Chapter 3

Charge–discharge behavior of Sn–Al film

3.1 Introduction

Alloy compounds are attractive as negative electrodes for secondary batteries due to their high theoretical capacities. Since 1970's, there have been numerous number of studies on alloy negative electrode materials for lithium secondary batteries, such as aluminum [1–4], silicon [5–9], tin [10–14], and antimony [15,16]. However, there have been few studies on alloy negative electrodes for sodium secondary batteries until 2000's [17,18].

As described in **Chapter 1**, sodium has been known to form alloy compounds with elements which mainly belong to Groups 14 and 15 of the periodic table, such as silicon (Si), phosphorous (P), germanium (Ge), tin (Sn), antimony (Sb), lead (Pb), bismuth (Bi) [19,20]. Most of them possess higher theoretical capacities than carbonaceous materials or oxide-based materials. According to the phase diagram of the Na–Si system, sodium and silicon form a sodium-richest NaSi phase, corresponding to a high theoretical capacity of $954 \text{ mAh (g-Si)}^{-1}$. However, pure silicon was reported to give a small practical capacity below $200 \text{ mAh (g-Si)}^{-1}$ [21]. Germanium and bismuth are less abundant, and antimony or lead-based compounds are usually toxic. On the other hand, tin exhibits a high theoretical capacity of $847 \text{ mAh (g-Sn)}^{-1}$ for $\text{Na}_{15}\text{Sn}_4$. Chevrier *et al.* [22] calculated the volumetric energy densities of alloy compounds by density functional theory (DFT) calculation, and revealed that tin and lead have the highest volumetric energy densities. Moreover, tin is less expensive and has high safety. Therefore, tin seems to be the best candidate for a negative electrode among these elements.

There have been an increasing number of reports concerning Na–Sn alloy negative electrodes

especially over the last few years. Some of the pioneering works are summarized as follows. Chevrier *et al.* predicted formation potentials for several Na–Sn alloys by DFT calculations [22]. Slater *et al.* reported that several potential plateaus, suggesting coexisting states of Na–Sn alloys, were observed in an organic solvent based electrolyte at ambient temperatures [23]. Komaba *et al.* investigated the cycleability of Sn powder electrodes with a polyacrylate binder [21]. They obtained a high reversible capacity of 500 mAh (g-Sn)⁻¹ in an FEC-added NaClO₄/PC electrolyte at 298 K (FEC = fluoroethylene carbonate). They also confirmed the formation of Na₁₅Sn₄ phase by *ex situ* X-ray diffraction (XRD). Ellis *et al.* observed the electrochemical formation of Na–Sn alloys in an NaPF₆/EC-DEC electrolyte at 303 K using *in situ* XRD analysis [24].

The aim of this chapter is to evaluate the basic charge–discharge behavior of tin-coated aluminum foils (hereinafter called “Sn–Al films”) with 10 μm thickness of tin using Na[FSA]–K[FSA] ionic liquid at 363 K.

3.2 Experimental

A glove box (Miwa Manufacturing Co., Ltd., DBO-2LKH-O) under dry argon atmosphere was used to handle ionic liquids and assemble all of the electrochemical cells used for the experiments in this chapter. The dew points of the glove box were kept below 213 K. Na[FSA] and K[FSA] used for the experiments in this chapter were dried under vacuum at 353 K (Na[FSA]) or 333 K (K[FSA]) for 48 h prior to use.

All electrochemical measurements in this chapter were performed under argon atmosphere using a VSP electrochemical measurement apparatus (Bio-Logic Co.). Tin-coated aluminum foils (Sn–Al films) was used as received from Sumitomo Electric Industries, Ltd. The thickness of tin was estimated to be 10–12 μm based on the results of inductively coupled plasma atomic emission spectroscopy (ICP-AES; Thermo Fisher Scientific, Inc., iCAP6300). For calculation of

the current density, the electrode area of the Sn–Al film electrode was assumed to be that of only tin-coated area.

The scan rates of cyclic voltammetry were 0.1 and 10 mV s⁻¹ for the Sn–Al film and the Al plate, respectively. The current density of galvanostatic charge–discharge tests was fixed at 0.619 mA cm⁻², which corresponds to the C/10 rate for a Sn–Al film with 10 μm thickness of tin. The numbers of sheets of glass fiber filter paper (Whatman, GF-A, 260 μm thickness per sheet) used for the charge–discharge tests were two (Test Nos. 1–4), three (Test No. 6), and four (Test No.5), respectively.

3.3 Results and discussion

3.3.1 Cyclic voltammetry

Figure 3-1 shows cyclic voltammograms for the Al plate and the Sn–Al film in Na[FSA]–K[FSA] at 363 K. The sweep directions are indicated by arrows in the figure. No prominent current is detected between 0 and 2.0 V vs. Na⁺/Na for the Al plate electrode. In contrast, steep increases of the cathodic currents are observed at 0.5 V, 0.3 V, and 0.1 V vs. Na⁺/Na for the Sn–Al film. In the sweep to positive potential, a large anodic current peak is observed around 0.9 V vs. Na⁺/Na. These cathodic and anodic currents are ascribed to the formation of Na–Sn alloys and the dissolution of Na from the alloys, respectively.

3.3.2 Cycleability of Sn–Al films under various conditions

3.3.2.1 Charge–discharge behavior between 0.005 and 1.200 V

Charge–discharge curves of a Na/Na[FSA]–K[FSA]/Sn cell between 0.005 and 1.200 V at 363 K (Test No.1) are shown in **Figure 3-2a**. The charge (alloying) and discharge (dealloying) capacities for the 1st cycle are 790 and 729 mAh (g-Sn)⁻¹, corresponding to 93% and 86% of the

theoretical capacity, respectively. Three potential plateaus are observed in both the charge and discharge curves, which presumably correspond to the coexisting states of Na–Sn alloy phases. The plateau potentials occur at: (a) 0.26 V, (b) 0.10 V, and (c) 0.04 V for the charge process, and (a') 0.57 V, (b') 0.22 V, and (c') 0.12 V for the discharge process. Plateaus (a), (b), and (c) in the charge process may be associated with the same coexisting phase states (a'), (b'), and (c'), respectively, in the discharge process. However, based on the phase diagram, there is the possibility that several other potential plateaus may appear. In addition, there are relatively large potential differences between the plateaus in the charge process and those in the discharge process, especially between plateau (a) and (a'). Thus, more-detailed analysis is required to confirm the precise correlation between the plateaus in the charge and discharge processes. **Figure 3-2b** shows the specific capacities and coulombic efficiencies versus the cycle number for 30 cycles. A high discharge capacity of ca. 700 mAh (g-Sn)⁻¹ is maintained during the initial three cycles. However, the capacity decreases rapidly to 204 mAh (g-Sn)⁻¹ in the 5th cycle and further to 121 mAh (g-Sn)⁻¹ in the 10th cycle. The coulombic efficiency of 92% in the 1st cycle decreases to 52% in the 5th cycle and remained a low value of 74% in 10th cycle. This decrease in the capacity and coulombic efficiency are presumably explained by the deterioration of the electrode due to the large volume change during the alloying and dealloying process, as is often observed for the Li–Sn system [25].

3.3.2.2 Volume change at each potential plateau

Here, the volume change of the Sn–Al film is estimated during the 1st discharge process in **Figure 3-2a**. The capacities corresponding to the plateaus (a'), (b'), and (c') are approximately 200, 250, and 300 mAh (g-Sn)⁻¹, respectively. **Table 3-1** lists the theoretical capacities and molar volumes of the Na–Sn alloy phases reported in the phase diagram of the Na–Sn system. When compared the measured capacities with the theoretical capacities, it is rational to assign the

plateau (a') to the phase transformation from α -NaSn to β -Sn with a theoretical capacity of 226 mAh (g-Sn)⁻¹. Similarly, the plateau (b') corresponds to the phase transformation from Na₉Sn₄ to α -NaSn with a theoretical capacity of 282 mAh (g-Sn)⁻¹, and plateau (c') is equivalent to the transformation of Na₁₅Sn₄ to Na₉Sn₄ with a theoretical capacity of 339 mAh (g-Sn)⁻¹. The calculated values of the corresponding ratios of the volume contraction for each plateau are as follows: (a') 0.45 (= 16.29/35.81), (b') 0.63 (= 35.81/56.74), and (c') 0.66 (= 56.74/85.39). Incidentally, when the fully charged alloy, Na₁₅Sn₄, is completely discharged, the volume contraction ratio becomes as small as 0.19 (= 16.29/85.39). It is hypothesized that if electrode deterioration occurs mainly by the volume change, a charge–discharge test utilizing only one plateau should give better cycleability. Moreover, considering the contraction ratio, plateau (c) is expected to show the better cycleability.

3.3.2.3 Cycleability at each plateau

In order to confirm the hypothesis stated above, three additional charge–discharge tests (Test Nos. 2–4) were performed by changing the cut-off voltages based on the three plateaus. The detailed experimental conditions are summarized in **Table 3-2**.

(1) Plateau (a)

Figure 3-3a shows the charge–discharge curves of a Na/Na[FSA]–K[FSA]/Sn cell with cut-off voltages of 0.200 and 1.200 V (Test No.2). In the first charge, plateau (a) is observed at around 0.25 V and the charge capacity is 90 mAh (g-Sn)⁻¹. Increasing the cycle number results in the appearance of a new plateau (x) at around 0.45 V, and the charge capacity increases to ca. 167 mAh (g-Sn)⁻¹ at the 10th cycle. More detailed investigation on the correlation between the charge and discharge plateaus, including phase identification by X-ray diffraction, will be presented in **Chapter 4**. **Figure 3-3b** shows the cycling properties of specific capacity and coulombic efficiency for the Na/Na[FSA]–K[FSA]/Sn cell. From the initial cycle to the 9th cycle, both the

charge and discharge capacities increase to the highest discharge capacity of ca. 140 mAh (g-Sn)⁻¹. This increase is explained by the formation of sodium diffusion paths and the enhanced rate of Sn utilization. The highest coulombic efficiency of 95% is recorded at the 3rd cycle. After the 9th cycle, however, there is a rapid decline in both the charge and discharge capacities, indicating the degradation of the electrode due to the volume change.

(2) Plateau (b)

The charge–discharge curves for Test No.3 (cut-off voltages: 0.075 and 0.300 V) are plotted in **Figure 3-4a**. In the first cycle, the charge capacity and discharge capacity reach ca. 500 mAh (g-Sn)⁻¹ and ca. 260 mAh (g-Sn)⁻¹, respectively. The large difference between the charge and discharge capacities is ascribed to the charge capacity from plateau (a) because the first charge is initiated from the rest potential of the Sn–Al film. The charge–discharge curves for the 2nd and 10th cycles overlap completely in the figure, indicating good cycleability for the initial 10 cycles with a discharge capacity of ca. 250 mAh (g-Sn)⁻¹. **Figure 3-4b** shows the cycling properties of the specific capacity and coulombic efficiency for the Na/Na[FSA]–K[FSA]/Sn cell. Although good cycleability is observed until the 10th cycle, the charge and discharge capacities gradually decrease with increasing the cycle number, indicating electrode degradation. At the 20th cycle, there is a precipitous decline in the capacity to less than 20 mAh (g-Sn)⁻¹, which is ascribed to the almost total delamination of the Sn film from the Al current collector as in the case of tin negative electrodes for lithium-ion battery [25].

(3) Plateau (c)

Figures 3-5a and **3-5b** show the charge–discharge curves and cycling properties of the specific capacity and coulombic efficiency for Test No.4 (cut-off voltages: 0.005 and 0.200 V). The first charge capacity and discharge capacity are ca. 830 mAh (g-Sn)⁻¹ and 320 mAh (g-Sn)⁻¹, respectively. The discrepancy is explained in the same manner as in the case of Test No.3, with additional capacities corresponding to plateaus (a) and (b) in the charge process. A stable

discharge capacity of around 300 mAh (g-Sn)⁻¹ is observed until the 15th cycle with a coulombic efficiency of larger than 90%. After the 15th cycle, the capacity gradually decreases down to ca. 200 mAh (g-Sn)⁻¹ at the 30th cycle, suggesting that the electrode degradation by volume change is not completely suppressed.

The discharge capacities during the cycles for Test Nos. 1–4 are compared in **Figure 3-6**. The best cycleability is obtained in the Test No.4, which utilizes the lowest potential plateau (c). As explained before, the volume change of tin in the plateau (c) is the smallest among the three plateaus. This result is consistent with our hypothesis: the degradation of the tin negative electrode occurs by volume change, and a smaller volume change gives better cycleability.

3.3.3 Self-repairing effect

In the previous section, the cycleability of a tin negative electrode was evaluated within the theoretical capacity of Na₁₅Sn₄ (847 mAh (g-Sn)⁻¹). In this section, the author describes a new interesting cycling behavior for the tin negative electrodes in the case that the charge capacity is set to deposit metallic sodium. Under such charging condition, although the capacity once decreases in the initial few cycles, it drastically recovers in the following cycles. The mechanism of the recovery is also discussed in this section.

3.3.3.1 Charge–discharge behavior with an upper cut-off voltage at 1.200 V

A new charge–discharge condition is set as follows (Test No.5). In the charging (alloying) process, a constant capacity is fixed to 889 mAh (g-Sn)⁻¹, which corresponds to 105% of the theoretical capacity of tin. A cut-off voltage in the discharge (dealloying) process is set at 1.200 V. **Figures 3-7a** and **3-7b** show the charge–discharge curves and cycling properties for Test No.5, respectively. In the first cycle, a new pairs of plateaus (d and d') appear. These plateaus correspond to the coexisting state of Na₁₅Sn₄ and metallic sodium. Although a high discharge

capacity of $835 \text{ mAh (g-Sn)}^{-1}$ is observed in the first cycle, the capacity drastically decreases during the initial 5 cycles. This is a typical capacity fade as explained in the previous section. However, the discharge capacity gradually recovers after the 5th cycle to reach $800 \text{ mAh (g-Sn)}^{-1}$ in the 12th cycle. Then, a high average capacity over $820 \text{ mAh (g-Sn)}^{-1}$ and an average coulombic efficiency over 90% are observed until 30th cycles, suggesting a highly reversible reaction.

According to the enlarged discharge curves (**Figure 3-7c**), the plateau potentials of (c') and (d') are observed at around 0.02–0.03 and 0.12–0.14 V, respectively. Thus, the obtained discharge capacities can be divided into two components, *i.e.*, a dealloying capacity (above 0.05 V) and a metallic dissolution capacity (below 0.05 V). The discharge capacities for these two regions are plotted as a function of cycle number in **Figure 3-7d**. In the initial 3 cycles, the dealloying capacity maintains high values over $700 \text{ mAh (g-Sn)}^{-1}$, and the metallic dissolution capacity exhibits low values below $30 \text{ mAh (g-Sn)}^{-1}$. However, in the 5th cycle, the former decreases to $356 \text{ mAh (g-Sn)}^{-1}$, and the latter increases to $54 \text{ mAh (g-Sn)}^{-1}$. Afterwards, the dealloying capacity gradually rises again to reach ca. $430 \text{ mAh (g-Sn)}^{-1}$ in the 15th–30th cycles. On the other hand, the metallic dissolution capacity drastically increases to $400 \text{ mAh (g-Sn)}^{-1}$ during the 5th–30th cycles. Unlike the result of Test No.1, the drastic fade of dealloying capacity is effectively suppressed. The mechanism of this phenomenon should be related to the metallic sodium deposition.

Figure 3-8 depicts a proposed mechanism of cycling behavior of a tin negative electrode for the charge–discharge test above. During the initial cycles, microcracks are generated on the surface of the Sn–Al film due to the large volume changes (Step 1). In the extended cycles (Step 2), the Sn–Al film undergoes serious pulverization and a part of tin becomes electrically isolated, especially in the discharging process that involves the volume contraction of the alloy. The loss of electrical contact leads to a serious capacity fade. However, during the following charging

process, the electrical contact between pulverized fragments (tin or Na–Sn alloys) and deposited sodium metal are regenerated owing to interdiffusion of sodium and tin atoms (See red ellipses shown in **Figure 3-8**). This interdiffusion is likely to be facilitated by the elevated operating temperature of 363 K, because the melting points of sodium and tin are as low as 371 K and 505 K, respectively. Such “self-repairing effect” to recover the electrical contact proceeds in the successive cycles, which results in the gradual increase of the discharge capacity. However, since the metallic dissolution capacity is still too large, which is not desirable from a view point of safety, more appropriate charge–discharge condition should be explored to reduce the quantity of metallic sodium deposition.

3.3.3.2 Charge–discharge behavior with an upper cut-off voltage at 0.200 V

Based on the above result, a new charge–discharge test was conducted in the following condition (Test No.6). Constant charge capacities are set to 889 and 339 mAh (g-Sn)^{−1} for the 1st cycle and the following cycles, respectively. The latter value corresponds to 40% of the theoretical capacity of tin, and almost equals to the sum capacity of plateaus (c) and (d). In accordance with this setting, a cut-off voltage in the discharge process is fixed to 0.200 V. **Figures 3-9a** and **3-9b** show the charge–discharge curves and cycleability for Test No.6. During the initial 10 cycles, stable discharge capacities of ca. 320 mAh (g-Sn)^{−1} are observed. Then, the capacity decreases to ca. 250 mAh (g-Sn)^{−1} after 30 cycles. Afterwards, as in the case of Test No.5, the discharge capacity recovers and stable reversible capacities of approximately 320 mAh (g-Sn)^{−1} are retained until the 80th cycle.

Figure 3-9c shows the discharge capacities for the two regions as a function of cycle number. During the initial 10 cycles, the dealloying capacity retains approximately 300 mAh (g-Sn)^{−1}. Then, although it gradually decreases during the 15th–30th cycles, an average capacity of ca. 260 mAh (g-Sn)^{−1} is maintained after 80 cycles. On the other hand, the metallic dissolution capacity

shows a low value less than 30 mAh (g-Sn)⁻¹ within the initial 30 cycles except for the 1st cycle. Afterwards, it slightly increases to 60 mAh (g-Sn)⁻¹, and keeps this value after 80 cycles. Thus, the quantity of deposited sodium metal is largely suppressed compared with Test No.5.

Figure 3-10 depicts a possible charge–discharge mechanism for Test No.6. When compared with Test No.5, the volume contraction of tin is milder and less amount of tin becomes electrically isolated. Moreover, since pulverized fragments mostly consist of Na-rich Na–Sn alloys at the discharged state (0.200 V) and exist in a dense state (Step 2 in **Figure 3-10**), the recovery of electrical contact occurs even with a smaller amount of sodium metal deposition, which leads to the lower metallic dissolution capacity in the extended cycles.

3.4 Conclusions

Electrochemical behaviors of Sn–Al films with 10 μm thickness of tin for sodium secondary battery were evaluated in Na[FSA]–K[FSA] ionic liquid electrolyte at 363 K. The major findings in this chapter are summarized as follows:

Cycleability of a tin negative electrode within the theoretical capacity of the Na–Sn system

1. Various Na–Sn alloy phases were formed during the charge–discharge process at 0.619 mA cm⁻² with cut-off voltages of 0.005 and 1.200 V, evidenced by three potential plateaus in the charge process (a, b, and c) and discharge process (a', b', and c').
2. Based on a comparison of the capacity at each plateau with the theoretical value in the first cycle, the three observed discharge plateaus were tentatively assigned as follows: (a') α-NaSn/β-Sn (observed capacity: ca. 200 mAh (g-Sn)⁻¹, theoretical capacity: 226 mAh (g-Sn)⁻¹, volume contraction ratio: 0.45), (b') Na₉Sn₄/α-NaSn (observed capacity: ca. 250 mAh (g-Sn)⁻¹, theoretical capacity: 282 mAh (g-Sn)⁻¹, volume contraction ratio: 0.63), and (c') Na₁₅Sn₄/Na₉Sn₄ (observed capacity: ca. 300 mAh (g-Sn)⁻¹, theoretical capacity: 339 mAh

$(\text{g-Sn})^{-1}$, volume contraction ratio: 0.66) under the afore-stated conditions.

3. A better cycleability was obtained when a lower potential plateau is used, which is consistent with the hypothesis that the degradation of the tin negative electrode occurs by volume change, and a smaller volume change gives better cycleability.

Cycleability of a tin negative electrode with the condition of sodium metal deposition

4. When the 1st charge capacity was set to $889 \text{ mAh } (\text{g-Sn})^{-1}$, which is 105% of the theoretical capacity of tin, a pair of new plateaus (d) and (d') was observed, which corresponds to the coexisting state of $\text{Na}_{15}\text{Sn}_4$ and metallic sodium. In Test No.5, although the discharge capacity once rapidly decreased from 835 to $411 \text{ mAh } (\text{g-Sn})^{-1}$ in the initial 5 cycles, it recovered and maintained at high values over $800 \text{ mAh } (\text{g-Sn})^{-1}$ after 30 cycles. Moreover, the obtained discharge capacities were divided into two regions, *i.e.*, the dealloying capacity and the metallic dissolution capacity. After 30 cycles, the dealloying capacity kept over $400 \text{ mAh } (\text{g-Sn})^{-1}$, however, the metallic dissolution capacity also reached as large as $400 \text{ mAh } (\text{g-Sn})^{-1}$, which is unfavorable in terms of safety.
5. In Test No.6, only two plateaus (c) and (d) were used except 1st charging process, which resulted in the better cycleability. The dealloying capacity retained approximately $260 \text{ mAh } (\text{g-Sn})^{-1}$ after 80 cycles. Moreover, the metallic dissolution capacity was effectively suppressed below ca. $60 \text{ mAh } (\text{g-Sn})^{-1}$.
6. This phenomenon was explained by “self-repairing effect” in which the deposited sodium metal reconstructed the electrical contact between the pulverized particles of tin or Na-Sn alloys.

Table 3-1 Theoretical capacities and molar volumes of Na–Sn alloy phases.

Phases	Capacity / mAh (g-Sn) ⁻¹	Molar volume / cm ³ (mol-Sn) ⁻¹
β-Sn	0	16.29 [19]
NaSn ₆	37.6	N/A ^a
NaSn ₄	56.4	N/A ^a
NaSn ₃	75.3	N/A ^a
NaSn ₂	113	26.12 [26]
α-NaSn	226	35.81 [27]
Na ₉ Sn ₄	508	56.74 [28]
Na ₃ Sn	677	N/A ^a
Na ₁₅ Sn ₄	847	85.39 [28]

^a Crystal structure has not been reported.

Table 3-2 Conditions of charge–discharge tests.

Test No.	Plateaus	Cut-off voltages
1	(a), (b), and (c)	0.005 and 1.200 V
2	(a)	0.200 and 1.200 V
3	(b)	0.075 and 0.300 V
4	(c)	0.005 and 0.200 V

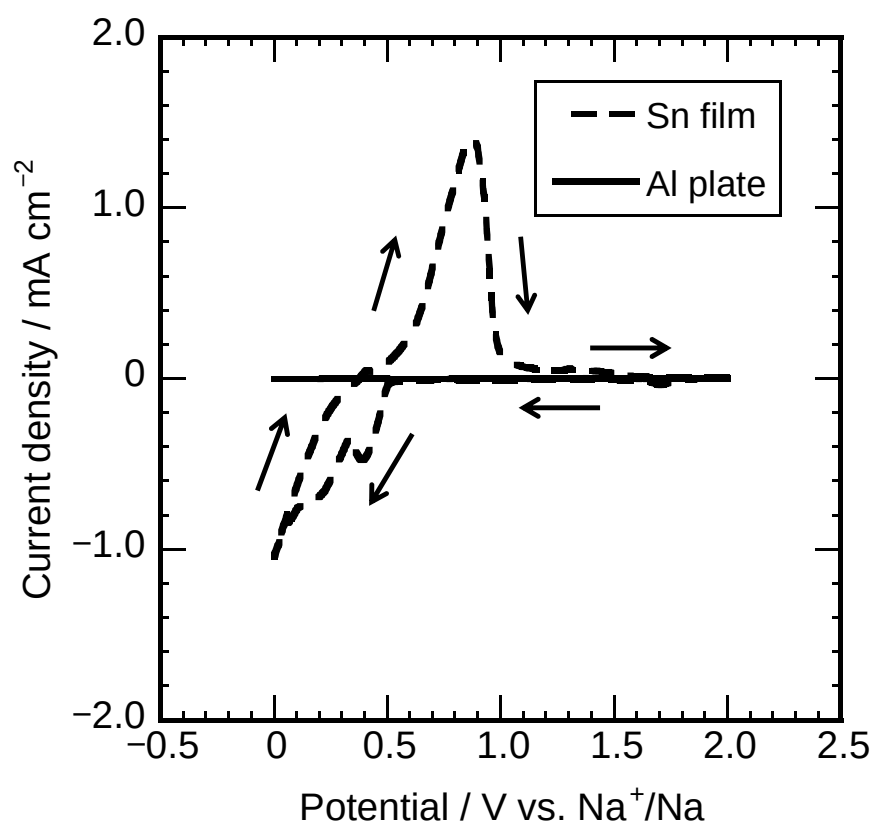


Figure 3-1 Cyclic voltammograms for the Sn–Al film and the Al plate in Na[FSA]–K[FSA] at 363 K. Counter and reference electrodes: Na metal. Scan rate: 0.1 mV s⁻¹ (Sn–Al film) and 10 mV s⁻¹ (Al plate).

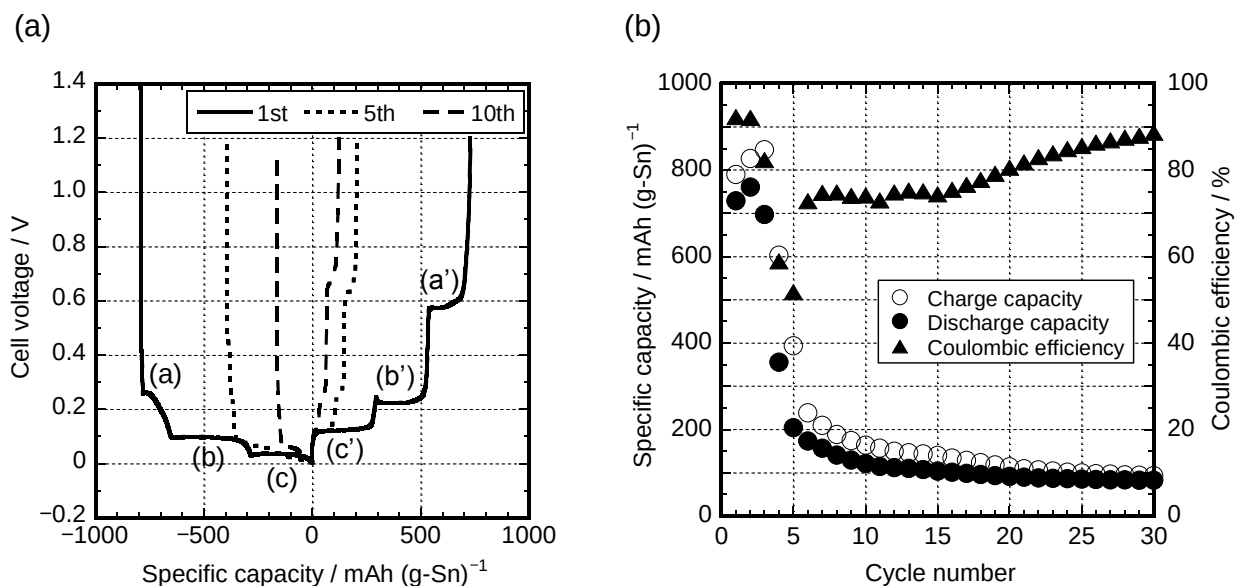


Figure 3-2 (a) Charge–discharge curves and (b) cycling properties of specific capacity and coulombic efficiency of a Na/Na[FSA]–K[FSA]/Sn cell at 363 K. Cut-off voltages: 0.005 and 1.200 V. Current density: 0.619 mA cm^{-2} .

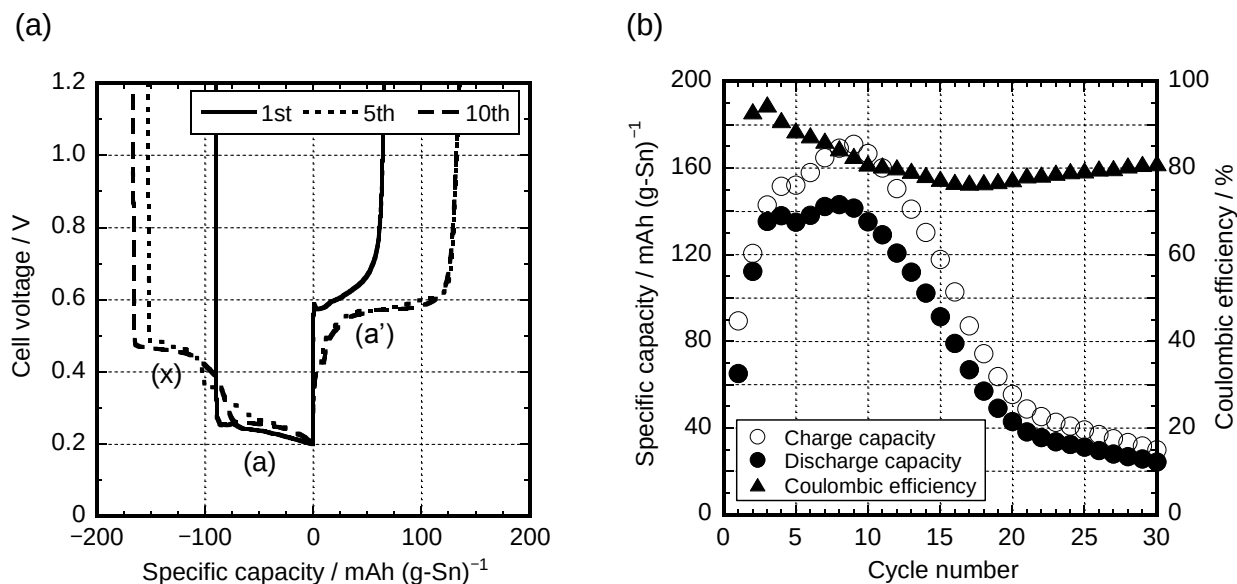


Figure 3-3 (a) Charge–discharge curves and (b) cycling properties of specific capacity and coulombic efficiency of a Na/Na[FSA]–K[FSA]/Sn cell at 363 K. Cut-off voltages: 0.200 and 1.200 V. Current density: 0.619 mA cm^{-2} .

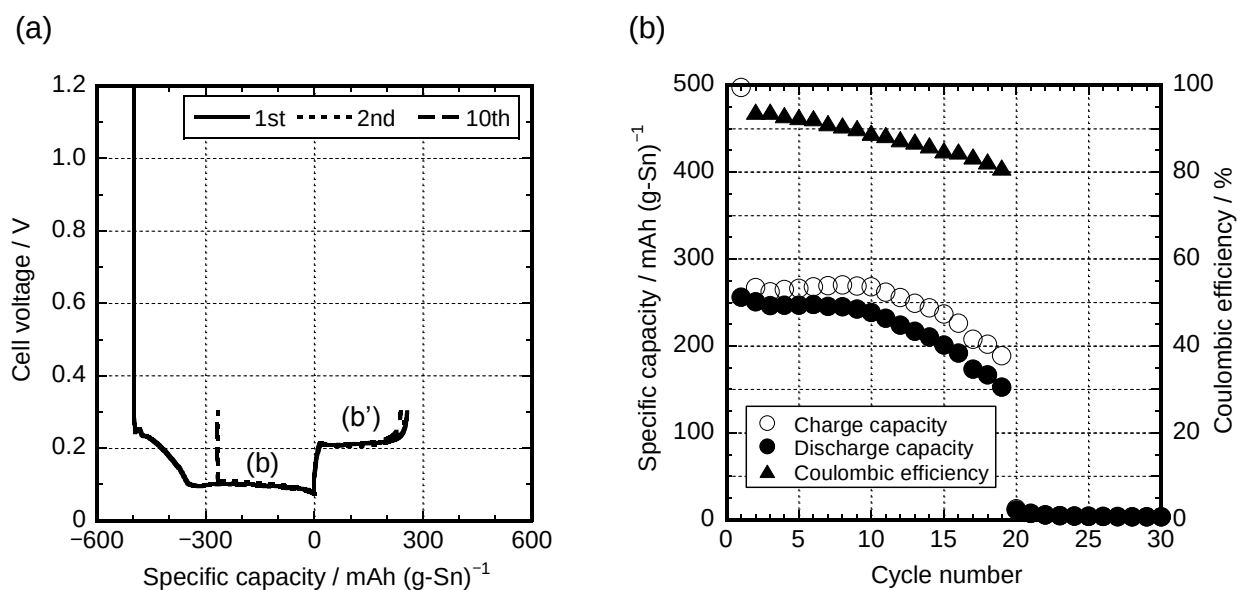


Figure 3-4 (a) Charge–discharge curves and (b) cycling properties of specific capacity and coulombic efficiency of a Na/Na[FSA]–K[FSA]/Sn cell at 363 K. Cut-off voltages: 0.075 and 0.300 V. Current density: 0.619 mA cm^{-2} .

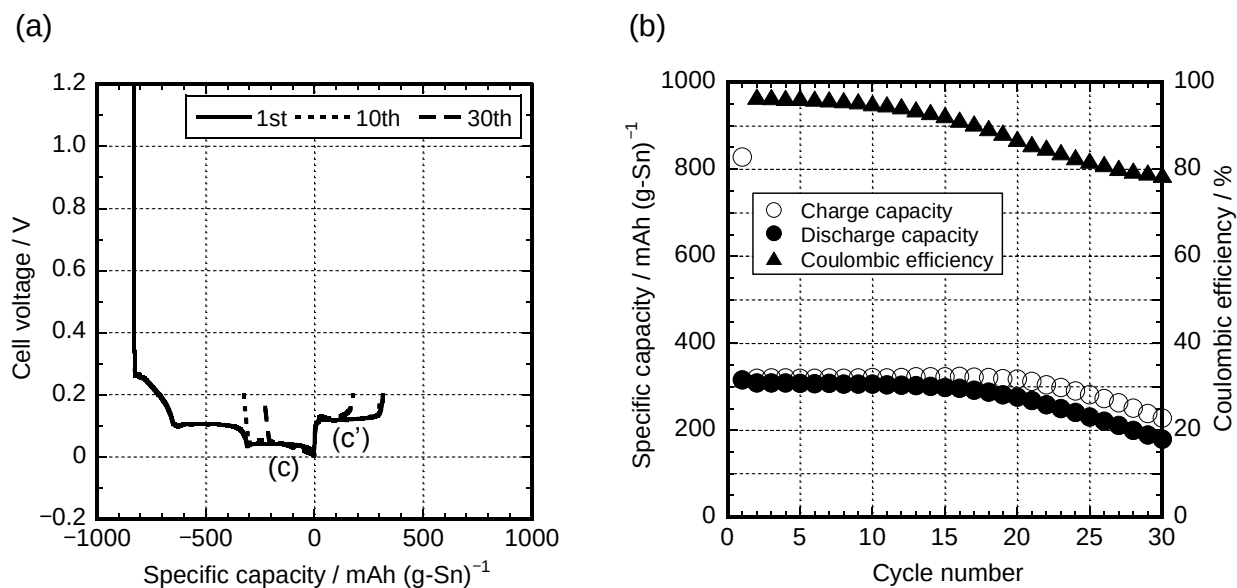


Figure 3-5 (a) Charge–discharge curves and (b) cycling properties of specific capacity and coulombic efficiency of a Na/Na[FSA]–K[FSA]/Sn cell at 363 K. Cut-off voltages: 0.005 and 0.200 V. Current density: 0.619 mA cm^{-2} .

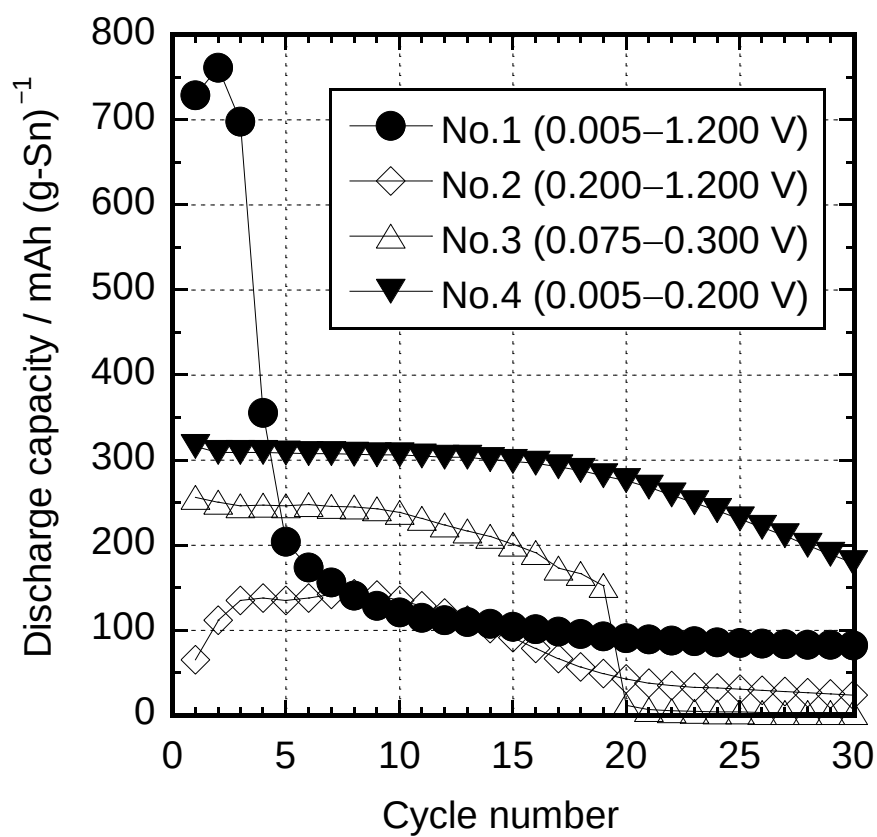


Figure 3-6 Summary of discharge capacities of the four charge–discharge tests No.1: 0.005–1.200 V, No.2: 0.200 V–1.200 V, No.3: 0.075–0.300 V, No.4: 0.005–0.200 V.

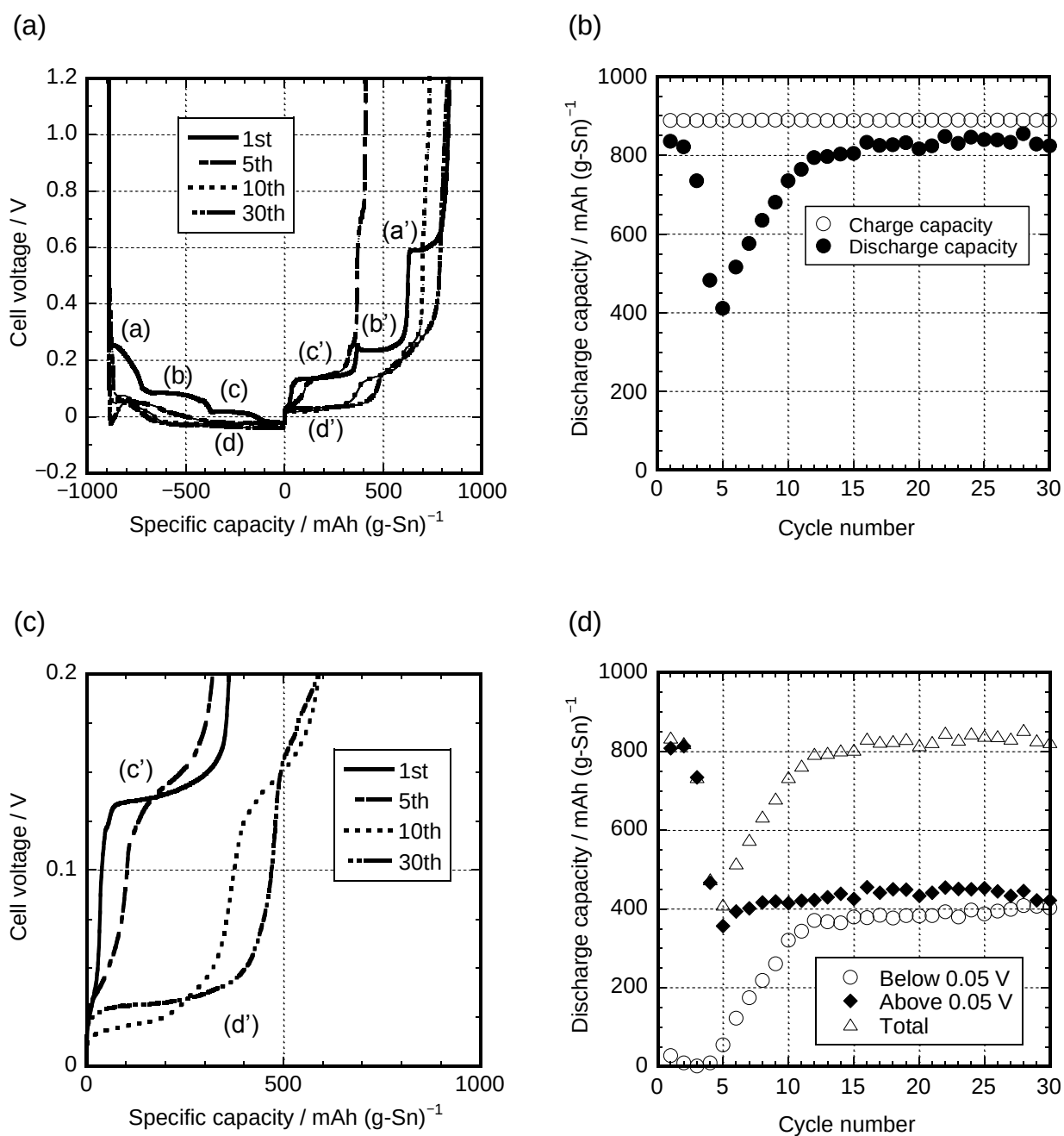
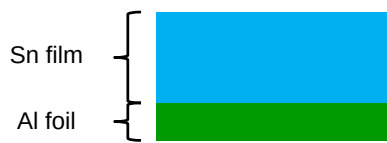
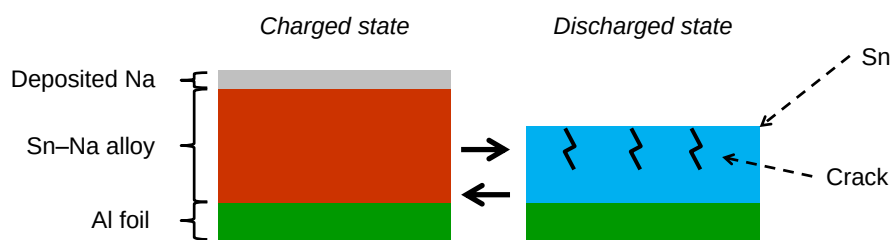


Figure 3-7 (a) Charge–discharge curves, (b) cycling properties of specific capacity, (c) magnified discharge curves, and (d) discharge capacities of the two regions for a Na/Na[FSA]–K[FSA]/Sn half cell at 363 K. Current density: 0.619 mA cm⁻². Constant charge capacity: 889 mAh (g-Sn)⁻¹. Cut-off voltage (discharge): 1.200 V.

Before test (Step 0)



Initial cycles (Step 1)



Extended cycles (Step 2)

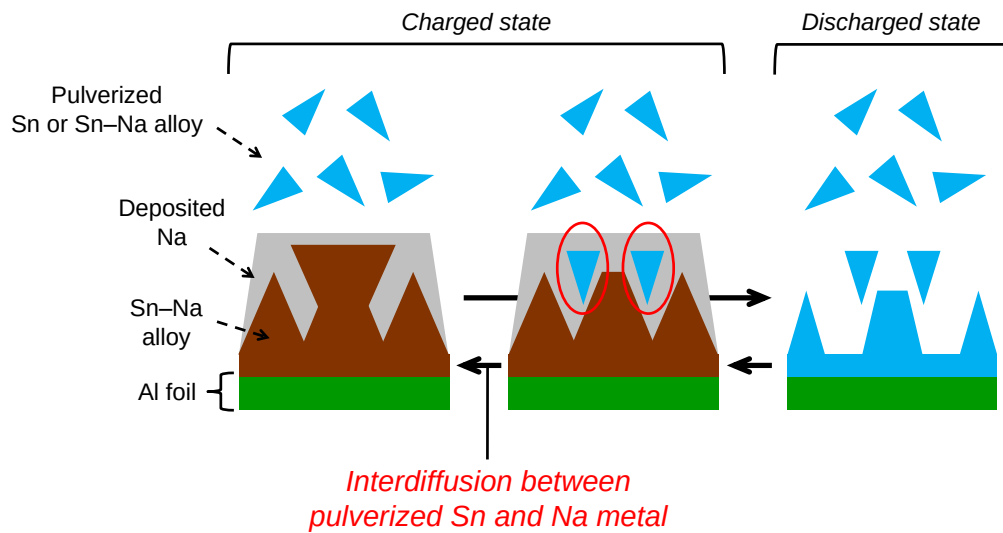


Figure 3-8 A schematic drawing of “self-repairing effect” for Test No.5.

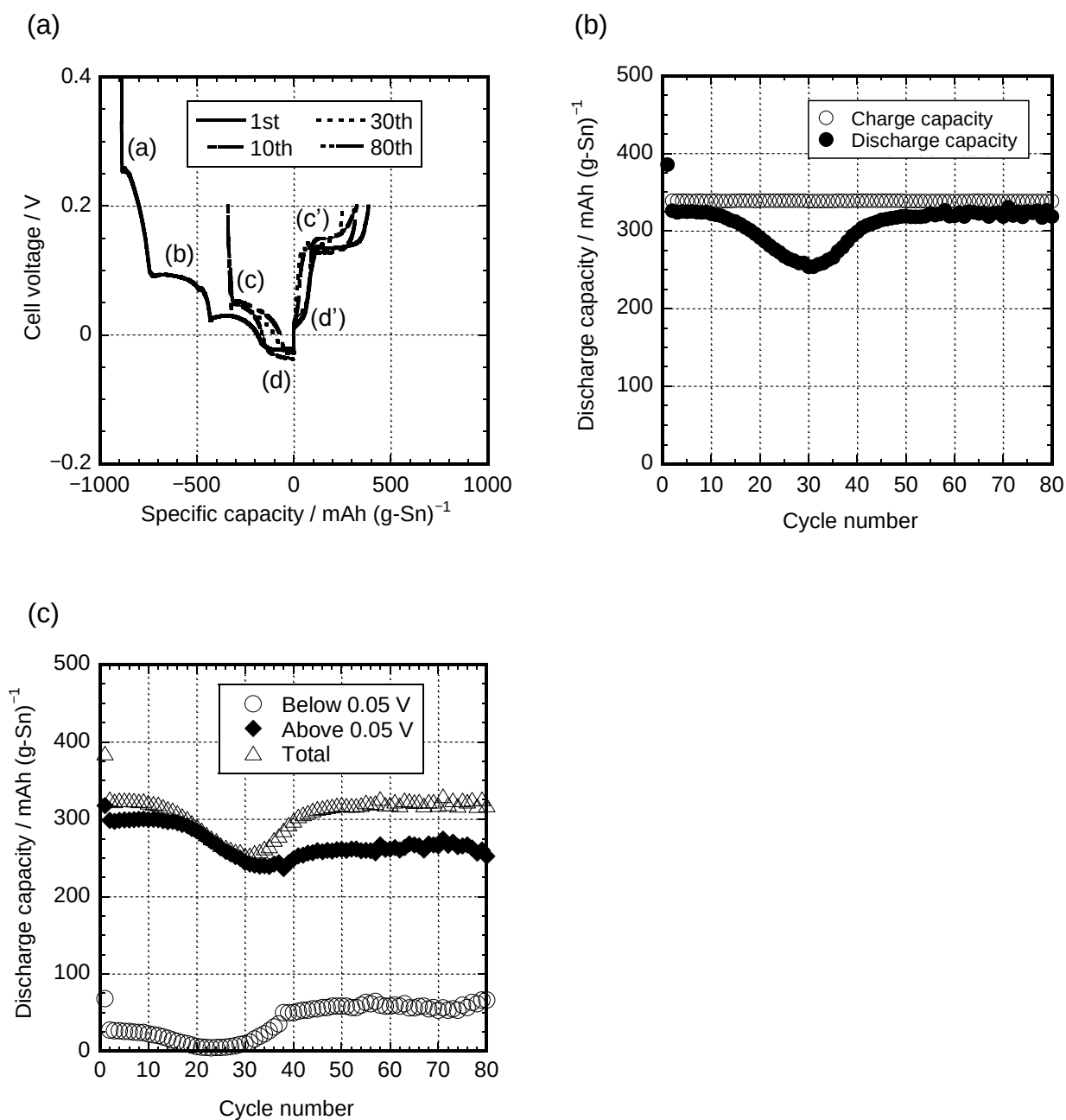
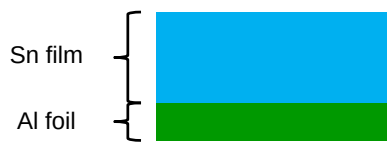
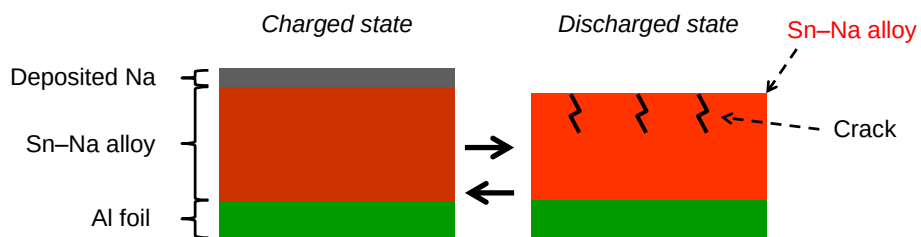


Figure 3-9 (a) Charge–discharge curves, (b) cycling properties of specific capacity, (c) discharge capacities of the two regions for a Na/Na[FSA]–K[FSA]/Sn half cell at 363 K. Current density: 0.619 mA cm^{-2} . Constant charge capacity: $339 \text{ mAh (g-Sn)}^{-1}$. Cut-off voltage (discharge): 0.200 V.

Before test (Step 0)



Initial cycles (Step 1)



Extended cycles (Step 2)

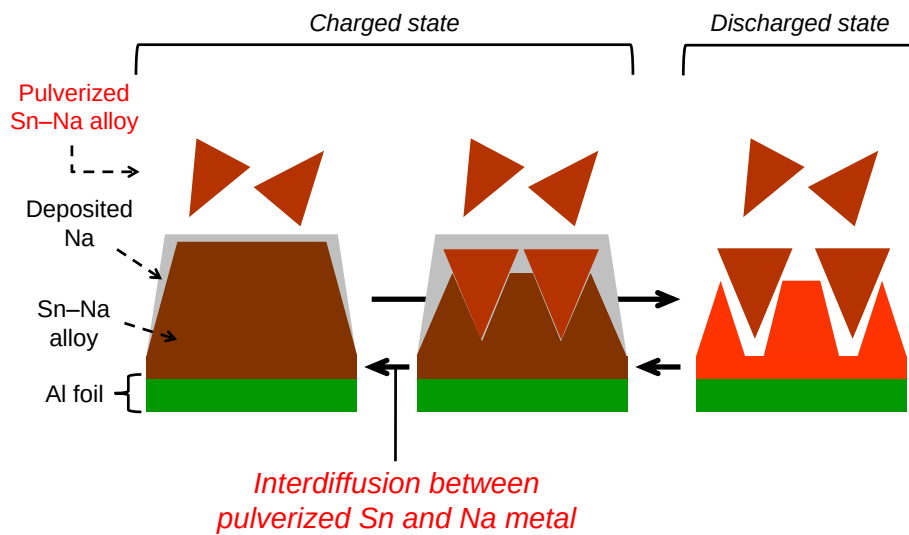


Figure 3-10 A schematic drawing of “self-repairing effect” for Test No.6.

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Chapter 4

Thermodynamic studies on Na–Sn alloys

4.1 Introduction

In the previous chapter, charge–discharge behaviors of Sn–Al films with 10 μm thickness of tin were evaluated in Na[FSA]–K[FSA] ionic liquid at 363 K. However, the formation of Na–Sn alloys was not directly confirmed by any analyses such as X-ray diffraction (XRD). The investigation of formation potentials for Na–Sn alloys is important as fundamental data to discuss the charge–discharge behaviors of tin negative electrodes. Incidentally, there have been few reports on structural analyses of electrochemically-formed Na–Sn alloys or thermodynamic properties of Na–Sn alloys until 2011 [1–4], unlike the case of Li–Sn alloys [5–12].

Preceding studies for Na–Sn alloys are summarized as follows. Since 1970's, several groups have reported the formation potentials or thermodynamic data of Na–Sn alloys [1–4]. Most of them, however, focused on liquid alloys [1–3]. Although Crouch-Baker *et al.* [4] reported the equilibrium potentials for some of the Na–Sn alloys at 393 K, no detailed investigation was conducted on the whole Na–Sn alloy phases, and any phase identification of Na–Sn alloys was not given by XRD analysis. In 2012, Komaba *et al.* [13] investigated the cycleability of Sn powder electrodes with a poly(acrylic acid) (PAA) binder, and confirmed the formation of $\text{Na}_{15}\text{Sn}_4$ phase by *ex situ* XRD analysis. Ellis *et al.* [14] conducted a study on the structure changes during alloying/dealloying of tin with sodium in a $\text{NaPF}_6/\text{EC-DEC}$ electrolyte at ambient temperatures by *in situ* XRD analysis. Most of the obtained patterns, however, did not correspond to any of the reported Na–Sn alloy phases. In 2013, Baggetto *et al.* [15] prepared Na–Sn alloys in a NaClO_4/PC electrolyte at 298 K, and newly reported that one of the

unidentified XRD patterns in the previous report [14] was identified as a new metastable phase of trigonal Na_5Sn_2 by Rietveld refinement. In 2014, however, Baggetto *et al.* [16] reported that the exact composition of the trigonal phase was Na_7Sn_3 , which is still remaining as a controversial issue. Du *et al.* [17] also investigated the electrochemical formation of Na–Sn alloys in a $\text{NaPF}_6/\text{EC-DEC-FEC}$ electrolyte at 333 K, and identified the trigonal Na_5Sn_2 phase and Na_4Sn_4 phase (identical to $\alpha\text{-NaSn}$) by X-ray diffraction. Thus, it is worth investigating the Na–Sn system in detail over the entire compositional range in intermediate temperature ionic liquids.

Galvanostatic intermittent titration technique (GITT) combines transient and steady-state measurements, and is an effective way not only to obtain the direct relation between equilibrium potentials and compositions but also to determine diffusion coefficients. This technique was firstly introduced by Weppner and Huggins [18], and has been applied for various materials including alloys and oxides [19–23].

The purpose of the study in this chapter is to determine the thermodynamic properties of Na–Sn alloys using GITT and *ex situ* XRD analysis.

4.2 Experimental

Glove boxes combined with gas purification systems (Miwa Manufacturing Co., Ltd., DBO-2LKH-O or DBO-2LKH-HNBR) and a glove box (Hoei Industries, Ltd., NP-002) connected with a gas purification system (Miwa Manufacturing Co., Ltd., MM3-H80S-S) under dry argon atmosphere was used to handle ionic liquids and assemble all of the electrochemical cells used for the experiments in this chapter. The dew points of the glove box were kept below 213 K. The concentration of oxygen in the glove box (Miwa Manufacturing Co., Ltd., DBO-2LKH-HNBR) was checked by an oxygen analyzer (GE Sensing & Inspection Technologies Co., Ltd., DF-150ε) and was kept below 2 ppm. Na[FSA] and K[FSA] used for the experiments in this chapter were dried under vacuum at 353 K (Na[FSA]) or 333 K (K[FSA]) for

48 h prior to use.

All electrochemical measurements in this chapter were performed under argon atmosphere using a VSP electrochemical measurement apparatus (Bio-Logic Co.) and the two-electrode cell (Tomcell Japan Co., Ltd.). Tin-coated aluminum foils (Sn–Al films) was used for electrochemical measurements as received from Sumitomo Electric Industries, Ltd. The thickness of tin was estimated to be 10.9–12.0 μm based on results of inductively coupled plasma atomic emission spectroscopy (ICP-AES; Thermo Fisher Scientific, Inc., iCAP6300).

Galvanostatic intermittent titration technique (GITT) was employed according to the following procedure:

1. Galvanostatic electrolysis was conducted at a current of C/20 rate for 80 min (*i.e.*, 56.4 mAh (g-Sn)⁻¹, 1/15 of full charge (847 mAh (g-Sn)⁻¹)).
2. The open circuit potential was monitored; when the rate of potential change became less than 1.0 mV h⁻¹, the potential was regarded as the equilibrium value.
3. Steps 1 and 2 were repeated 18 times in total.

The Na–Sn alloy samples were prepared by a combination of galvanostatic and potentiostatic electrolysis. After electrolysis, the open circuit potentials were monitored and the potentials just before cooling the cells were regarded as the potentials of Na–Sn alloy samples. Na–Sn alloy phases were identified by an X-ray diffractometer (Rigaku Co., Ultima IV; Cu-K α radiation (λ = 0.15418 nm); 40 kV and 40 mA) equipped with a one-dimensional high-speed detector (Rigaku Co., D/teX Ultra) with a nickel filter. Prior to XRD measurements, the Na[FSA]–K[FSA] salt was removed by soaking in dehydrated and deoxidized tetrahydrofuran (Wako Pure Chemical Industries, Ltd., water content < 10 ppm, oxygen content < 1 ppm), and the samples were transferred to the XRD apparatus by transfer vessels without exposing to air. Some of the obtained XRD patterns were corrected by a standard specimen of mica, and analyzed by DICVOL program [24] or RIETAN-FP/VENUS program [25].

4.3 Results and discussion

4.3.1 Equilibrium potentials and Na compositions for Na–Sn alloys

According to the phase diagram of the Na–Sn system [26], as shown in **Figure 1-1**, eight intermetallic compounds exist at 363 K: $\text{Na}_{15}\text{Sn}_4$, Na_3Sn , Na_9Sn_4 , $\alpha\text{-NaSn}$, NaSn_2 , NaSn_3 , NaSn_4 , and NaSn_6 .

Figure 4-1 shows the relation between the equilibrium potentials and the Na compositions of the Na–Sn alloys, as determined by GITT in Na[FSA]–K[FSA] ionic liquid at 363 K. The Na composition, x , is defined as the atomic ratio of sodium to tin. In the negative potential region below 0.2 V vs. Na^+/Na , three distinct potential plateaus are observed. The capacities of the plateaus at 0.16 V ($1.0 < x < 2.0$), 0.08 V ($2.25 < x < 3.25$), and 0 V ($3.5 < x < 4.5$) naturally lead to the following estimation: these equilibrium states correspond to $\text{Na}_9\text{Sn}_4/\alpha\text{-NaSn}$, $\text{Na}_{15}\text{Sn}_4/\text{Na}_9\text{Sn}_4$, and $\text{Na}_{15}\text{Sn}_4/\text{Na}$, respectively. The potential reaches 0 V at $x = 3.5$, which is smaller than the theoretical value for the full charge of $x = 3.75$ ($\text{Na}_{15}\text{Sn}_4$); this is probably due to the slow diffusion of sodium in the Na–Sn alloys. A gently sloped region is also observed at ca. 0.5 V vs. Na^+/Na and $0 < x < 1.0$. According to the phase diagram of the Na–Sn system, several potential plateaus should appear within this Na composition range. However, in the present measurement, the resolution of the Na composition is insufficient to distinguish the plateaus between $0 < x < 1.0$.

4.3.2 Preparation of Na–Sn alloy samples

On the basis of the results from GITT, Na–Sn alloy samples were prepared by a combination of galvanostatic and potentiostatic electrolysis. **Table 4-1** lists the final Na compositions and the corresponding potentials of Na–Sn alloy samples. The final Na compositions are calculated from

the total quantity of electricity assuming 100% current efficiency. The potential values are the open circuit potentials just before cooling the cells. It should be noted that, for sample 1, tin was first alloyed to the composition of $\text{Na}_{0.24}\text{Sn}$ by galvanostatic electrolysis, and then dealloyed by successive potentiostatic electrolysis at 0.600 V, 0.800 V and 1.200 V; the open circuit potential was then monitored and confirmed to be stable at 0.557 V vs. Na^+/Na . The other samples were prepared by only the alloying process.

4.3.3 XRD analysis

Figure 4-2 shows the XRD pattern of sample 1 (potential: 0.557 V vs. Na^+/Na). The pattern is identified as $\beta\text{-Sn}$, which confirms that the Na–Sn alloy returns to $\beta\text{-Sn}$. On the assumption of 100% current efficiency, the final Na composition, x (in Na_xSn), of sample 1 is calculated to be 0.03, *i.e.*, very close to zero, which is consistent with the XRD result. The XRD pattern of sample 2 (potential: 0.225 V vs. Na^+/Na) is shown in **Figure 4-3** and shows the evidence of $\alpha\text{-NaSn}$, which is consistent with the calculated Na composition of $x = 1.04$. The diffraction peak of $\alpha\text{-NaSn}$ 321 ($2\theta = 31.23^\circ$) is exceptionally intense, which is explained by the preferred crystal orientation of the sample.

Since sample 3 (potential: 0.122 V vs. Na^+/Na) possesses a Na composition of $x = 2.30$, its predicted phase is Na_9Sn_4 ; however, the obtained XRD pattern shown in **Figure 4-4** does not match the previously reported pattern for the Na_9Sn_4 phase. Actually, this XRD pattern is also reported by other groups [14–17], and Baggetto *et al.* [15] tentatively identified this pattern as trigonal Na_5Sn_2 phase by Rietveld refinement. The Rietveld refinement was also conducted for the sample 3, as shown in **Table A-1** and **Figure A-5**, and the obtained result is agree with the previous reports. It should be noted that, according to the later report from Baggetto *et al.* [16], the occupancies of Na sites were slightly revised with the analyses of Na–Sn alloys that were metallurgically formed at around 450 K for 24 h, and the correct composition of the trigonal

phase is Na_7Sn_3 . However, the metallurgical formation of Na–Sn alloys at higher temperatures is likely to involve the evaporation of metals with low melting points, such as sodium (371 K) and tin (505 K). Moreover, the obtained sample was the mixture with Na_9Sn_4 phase, which led to the difficulty of determining the accurate Na occupancy by the Rietveld refinement. So far, this phase should be denoted as $\text{Na}_{5-y}\text{Sn}_2$, in which the value of y corresponds to the defects in Na sites. In the case of the present study, as shown in **Table 4-1**, the Na composition x in Na_xSn of sample 3 is 2.30, which is close to the composition of the already-identified Na_9Sn_4 phase ($x = 2.25$). Therefore, the Na composition of the trigonal $\text{Na}_{5-y}\text{Sn}_2$ phase was tentatively determined as Na_9Sn_4 ($y = 0.5$).

The XRD pattern of sample 4 (potential: 0.007 V vs. Na^+/Na) corresponds to the $\text{Na}_{15}\text{Sn}_4$ phase, as shown in **Figure 4-5a**. However, upon magnification of the profile (**Figure 4-5b**), the peaks are evidently at lower angles than in the reference pattern. An analysis of the XRD pattern using the DICVOL program reveals that the crystal system of this alloy corresponds to a cubic system with a slightly larger lattice parameter ($a = 13.24(1) \text{ \AA}$) than that of the reference ($a = 13.14 \text{ \AA}$). **Table 4-2** lists the d values and indices of the pattern. The discrepancy in the lattice parameters is likely to be due to the larger Na composition ($x = 4.14$) than that of the $\text{Na}_{15}\text{Sn}_4$ phase ($x = 3.75$). Despite $\text{Na}_{15}\text{Sn}_4$ being considered as a line compound in the phase diagram of Na–Sn system, the results of the present study suggest that it has a compositional range.

4.3.4 Thermodynamic data for Na–Sn alloys

Based on the GITT and XRD results, the equilibrium potentials of Na–Sn alloys are summarized in **Table 4-3**. Although information on the gently sloped region at $0 < x < 1.0$ is not sufficient, a closer look at the Sn-rich side of the potential–Na composition plots leads to the following assignments: The plots at 0.53 V ($x = 0.25$) and 0.46 V ($x = 0.75$) correspond to coexisting $\beta\text{-Sn}/\text{NaSn}_2$ and $\text{NaSn}_2/\alpha\text{-NaSn}$ states, respectively, as indicated by the broken curve in

Figure 4-6.

Thermodynamic data for the Na–Sn alloys are obtained as follows: firstly, relative partial molar Gibbs free energies of sodium are obtained from the equilibrium potentials; then, relative partial molar Gibbs free energies of tin are calculated using the Gibbs–Duhem equation [27]; and finally, standard Gibbs free energies of formation (ΔG_f^0) of -17.0 , -23.9 , -20.6 , and -16.6 kJ (mol-atom) $^{-1}$ at 363 K are obtained for NaSn₂, α -NaSn, Na₉Sn₄, and Na₁₅Sn₄, respectively. The detailed calculations are documented in **Appendix A.1**.

These values are compared with previously reported thermodynamic data for Na–Sn alloys. According to Crouch-Baker *et al.* [4], the equilibrium potentials are 0.44 V (Sn/ α -NaSn), 0.16 V (α -NaSn/Na₉Sn₄), and 0.08 V (Na₉Sn₄/Na₁₅Sn₄) at 393 K, which corresponds to ΔG_f^0 values of -21.2 , -19.0 , and -15.4 kJ (mol-atom) $^{-1}$ for α -NaSn, Na₉Sn₄, and Na₁₅Sn₄, respectively. Rivier *et al.* [1] collected the equilibrium potentials of Sn-rich liquid Na–Sn alloys at different temperatures. Thus, ΔG_f^0 values for liquid Na–Sn alloys can be calculated by integrating the Gibbs–Duhem equation using Darken’s method [28]. Details of these calculations are also documented in **Appendix A.1**. Considering the Sn-rich side of the Na–Sn phase diagram (**Figure 1-1**) in the range 580–756 K, the activities of tin and sodium of the Na–Sn alloys at the liquidus line are equal to those of α -NaSn. Therefore, it is possible to calculate ΔG_f^0 values for α -NaSn at 580–756 K. **Figure 4-7** shows the plots of the ΔG_f^0 values for α -NaSn calculated using the data from both the previous and present studies as a function of temperature. The ΔG_f^0 values at 583–633 K calculated using the data of Rivier *et al.* are plotted at intervals of 10 K, and a solid fitting curve is drawn on the assumption that the ΔH_f^0 and ΔS_f^0 values are independent of temperature except for the fusion of tin and sodium. The slope of the fitting curve was calculated from the thermodynamic data on enthalpies and entropies of fusion for tin and sodium (**Table 4-4**). Thus, the ΔG_f^0 value of α -NaSn is calculated to be -22.4 kJ (mol-atom) $^{-1}$ at 363 K, which agrees with the value determined in the present study (-23.9 kJ (mol-atom) $^{-1}$). For reference, the

ΔG_f^0 value reported by Crouch-Baker *et al.* is $-21.2 \text{ kJ (mol-atom)}^{-1}$ at 393 K [4]. Thus, the data obtained in the present study is consistent with that reported previously.

4.4 Conclusions

Thermodynamic studies were conducted for Na–Sn alloys in Na[FSA]–K[FSA] ionic liquid at 363 K. The major findings in this chapter can be summarized as follows:

1. Using GITT, the equilibrium potential–Na composition plot was obtained. Plateaus at 0.08 and 0.16 V vs. Na^+/Na corresponded to the coexisting states of $\text{Na}_{15}\text{Sn}_4/\text{Na}_9\text{Sn}_4$ and $\text{Na}_9\text{Sn}_4/\alpha\text{-NaSn}$, respectively. It is proposed that the gently sloped region at around 0.5 V vs. Na^+/Na was a combination of two plateaus.
2. XRD results were consistent with the equilibrium potential–Na composition plot. The stable phases at 0.557 V, 0.225 V, and 0.007 V vs. Na^+/Na were identified as $\beta\text{-Sn}$, $\alpha\text{-NaSn}$, and $\text{Na}_{15}\text{Sn}_4$, respectively. The obtained $\text{Na}_{15}\text{Sn}_4$ sample possessed a slightly larger lattice than the reference one, which indicates that $\text{Na}_{15}\text{Sn}_4$ has a compositional range. The XRD pattern of the alloy at 0.122 V vs. Na^+/Na was identified as trigonal $\text{Na}_{5-y}\text{Sn}_2$ phase by Rietveld refinement, and the Na composition was tentatively determined as Na_9Sn_4 from the quantity of charge.
3. The equilibrium potentials for several Na–Sn alloys were clarified. Thermodynamic calculations revealed that the ΔG_f^0 value of $\alpha\text{-NaSn}$ is $-23.9 \text{ kJ (mol-atom)}^{-1}$ at 363 K, which is in agreement with previously reported data.

Table 4-1 A summary of procedure of electrolysis, final Na compositions and the corresponding potentials for Na–Sn alloy samples. (Time in brackets shows amount of time spent for each step)

Sample No.	1	2	3	4	
Procedure	<i>a</i>	ca. C/21 rate (1 h 20 min)	ca. C/21 rate (5 h 20 min)	ca. C/21 rate (12 h)	ca. C/21 rate (20 h)
	<i>b</i>	0.600 V (13 h)	0.200 V (17 h)	0.120 V (10 h)	0.005 V (24 h)
	<i>c</i>	OCP (3 h)	OCP (30 min)	OCP (3 h)	OCP (3 h)
	<i>d</i>	0.600 V (17 h)	0.200 V (13 h)	0.120 V (3 h)	0.005 V (18 h)
	<i>e</i>	OCP (2 h)	OCP (1 h)	OCP (1 h)	OCP (1 h)
	<i>f</i>	0.800 V (8 h)	—	—	—
	<i>g</i>	OCP (2 h)	—	—	—
	<i>h</i>	1.200 V (12 h)	—	—	—
	<i>i</i>	OCP (38 h)	—	—	—
Final composition (<i>x</i> in Na _{<i>x</i>} Sn)	0.03	1.04	2.30	4.14	
Final potential / V vs. Na ⁺ /Na	0.557	0.225	0.122	0.007	

*C/21 rate = Alloying process at C/21 rate (the current density that takes 21 h for full charge)

**OCP = Monitoring open circuit potential

Table 4-2 The observed and calculated d values and indices for sample No.4.

h	k	l	$d / \text{\AA}$	
			obs.	calc. [#]
2	1	1	5.399	5.407
2	2	0	4.686	4.683
3	1	0	4.180	4.188
3	3	2	2.825	2.824
4	2	2	2.704	2.704
5	1	0	2.598	2.597

[#] $a = 13.24(1) \text{\AA}$.

Table 4-3 Equilibrium potentials for Na–Sn alloys in Na[FSA]–K[FSA] at 363 K.

Formation reaction	Potential / V vs. Na^+/Na
$2 \beta\text{-Sn} + \text{Na}^+ + \text{e}^- \rightleftharpoons \text{NaSn}_2$	0.53
$\text{NaSn}_2 + \text{Na}^+ + \text{e}^- \rightleftharpoons 2 \alpha\text{-NaSn}$	0.46
$4 \alpha\text{-NaSn} + 5 \text{Na}^+ + 5 \text{e}^- \rightleftharpoons \text{Na}_9\text{Sn}_4$	0.16
$\text{Na}_9\text{Sn}_4 + 6 \text{Na}^+ + 6 \text{e}^- \rightleftharpoons \text{Na}_{15}\text{Sn}_4$	0.08

Table 4-4 Enthalpies and entropies of fusion for tin and sodium [29].

M	Fusion enthalpy / kJ (mol-M)^{-1}	Fusion entropy / $\text{J (mol-M)}^{-1} \text{K}^{-1}$	Melting point / K
Sn	7.195	14.245	505.12
Na	2.598	7.003	371.01

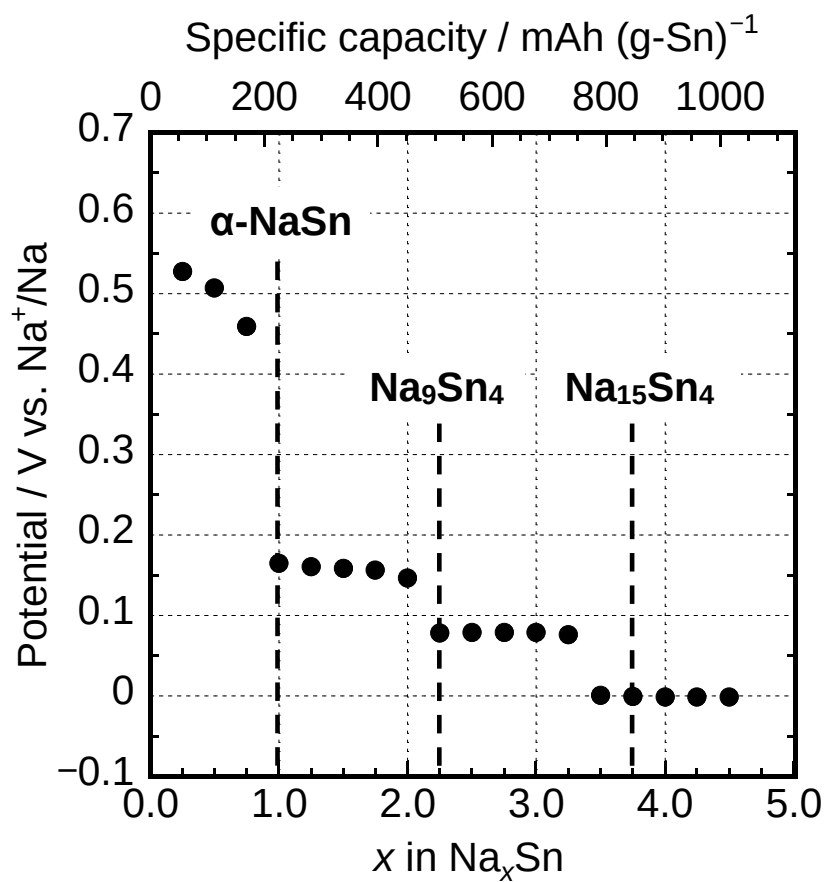


Figure 4-1 The relation between equilibrium potentials and Na compositions for Na–Sn alloys determined by GITT using a Na/Na[FSA]–K[FSA]/Sn cell at 363 K.

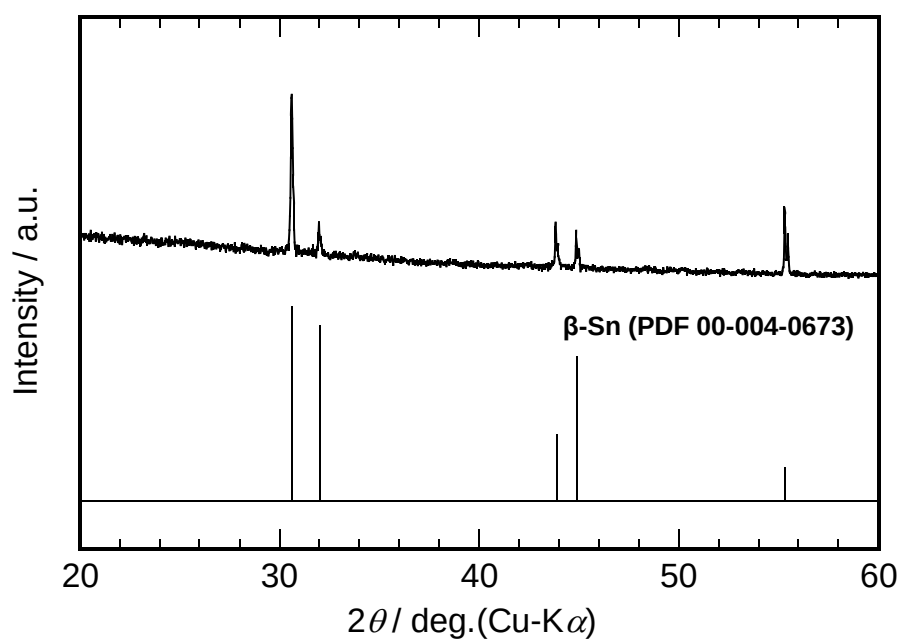


Figure 4-2 An XRD pattern of the sample No.1 (Potential: 0.557 V vs. Na^+/Na).

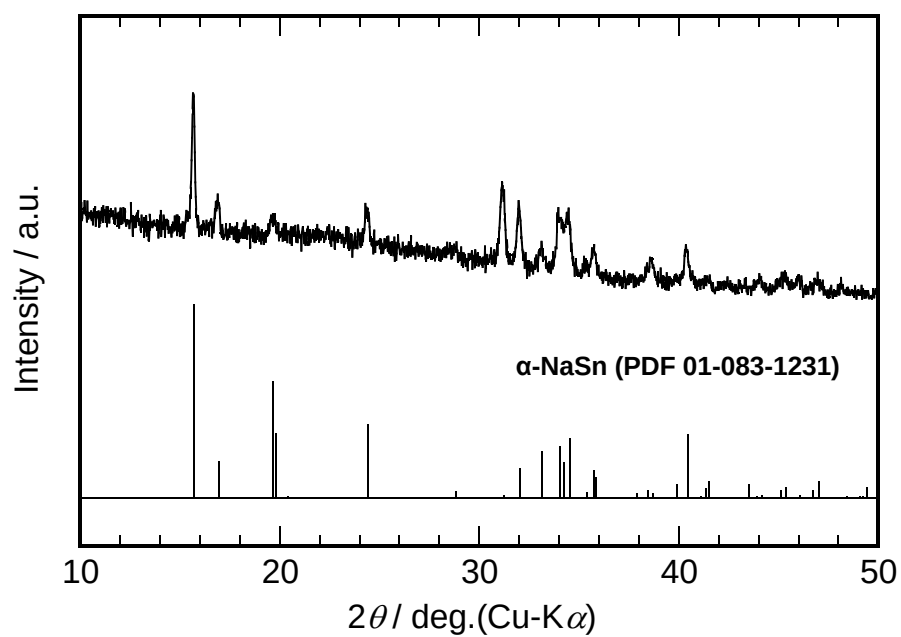


Figure 4-3 An XRD pattern of the sample No.2 (Potential: 0.225 V vs. Na^+/Na).

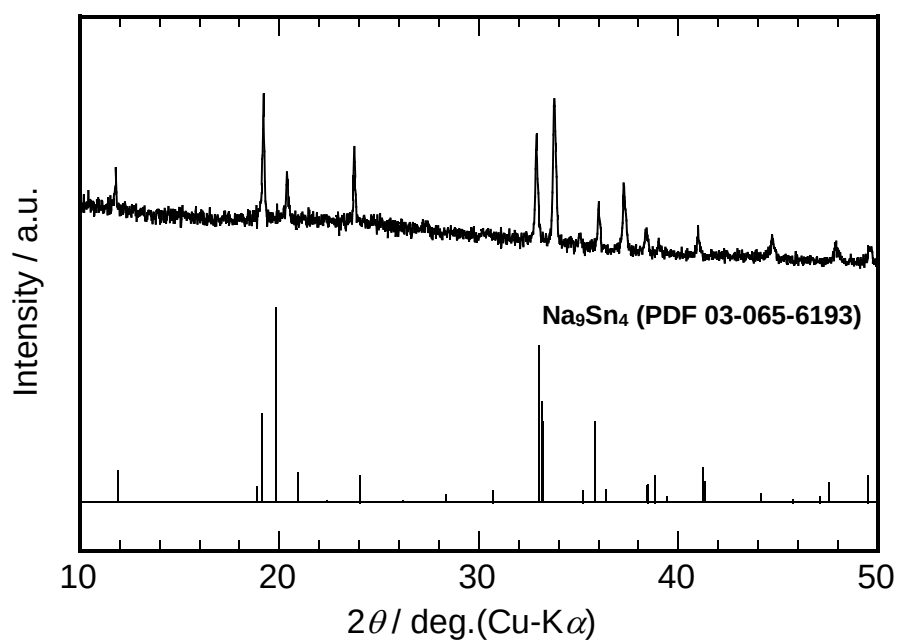


Figure 4-4 An XRD pattern of the sample No.3 (Potential: 0.122 V vs. Na⁺/Na) compared with the previously reported Na₉Sn₄.

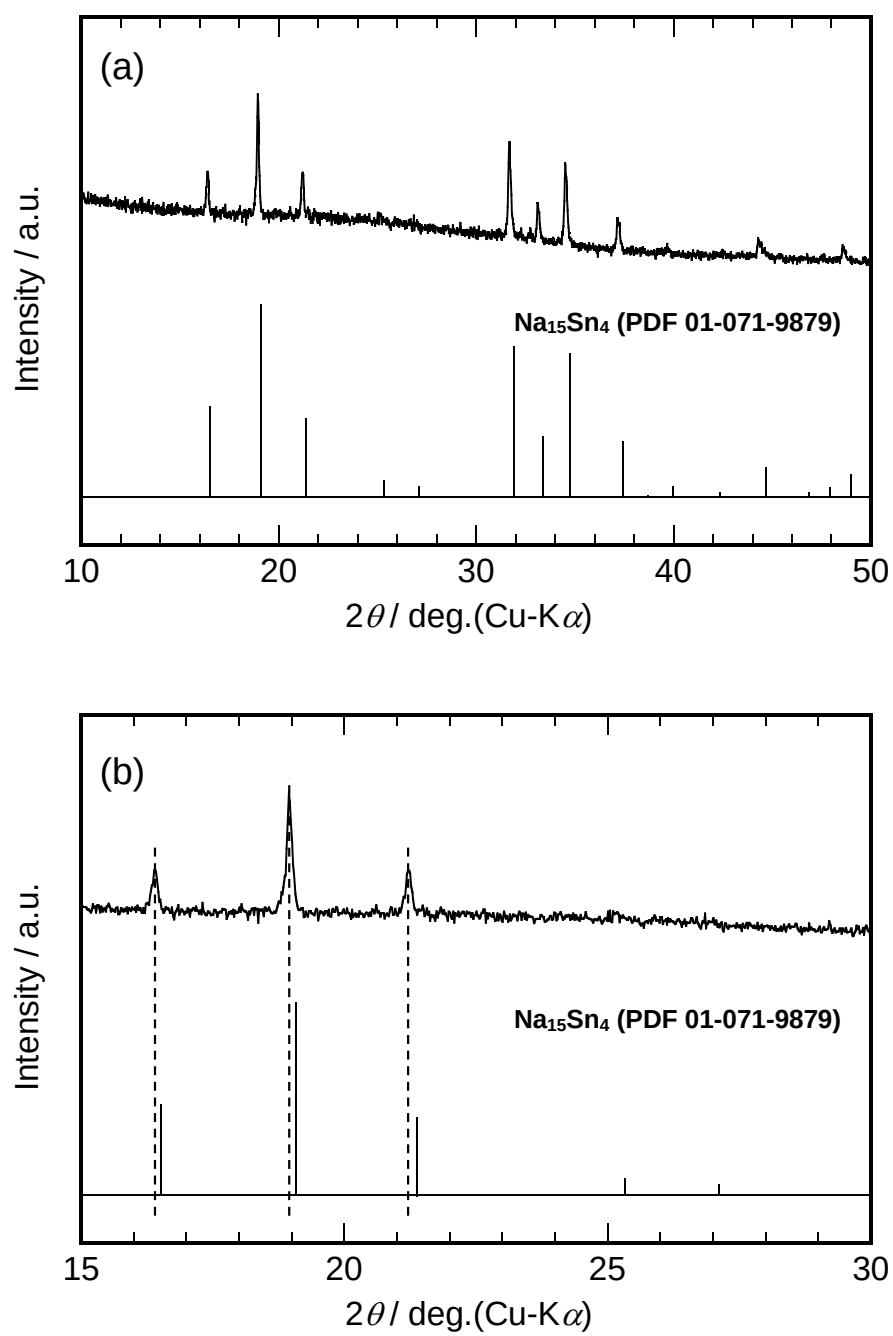


Figure 4-5 XRD patterns of the sample No.4 (Potential: 0.007 V vs. Na⁺/Na): (a) full-scale and (b) magnified part.

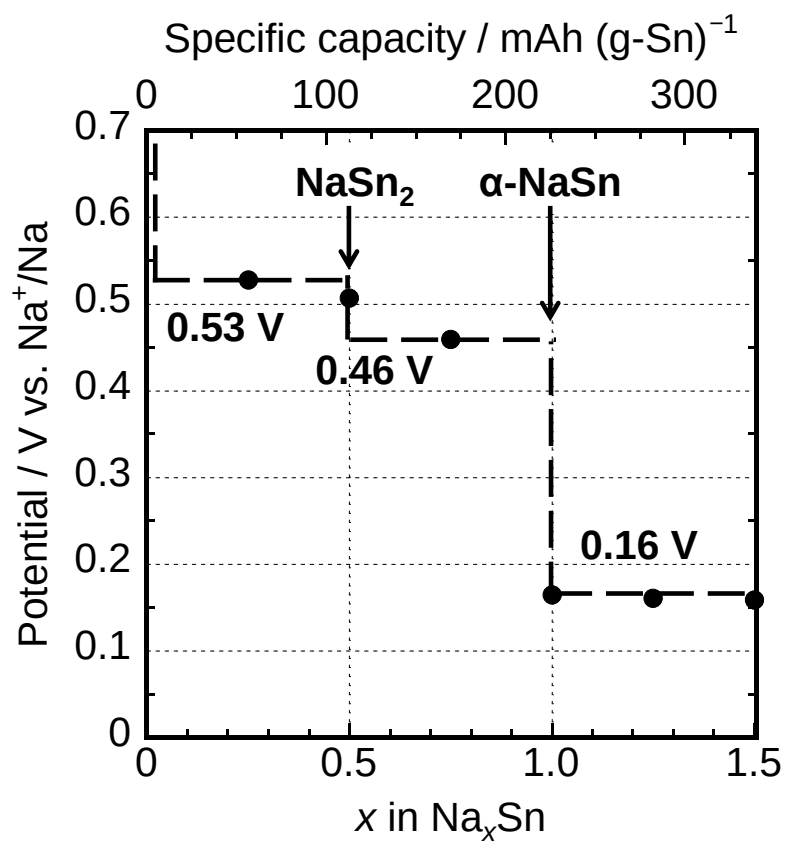


Figure 4-6 The relation between equilibrium potentials and Na compositions for Na-Sn alloys determined by GITT using a Na/Na[FSA]-K[FSA]/Sn cell at 363 K. (A magnified plot for the Sn-rich side of **Figure 4-1**)

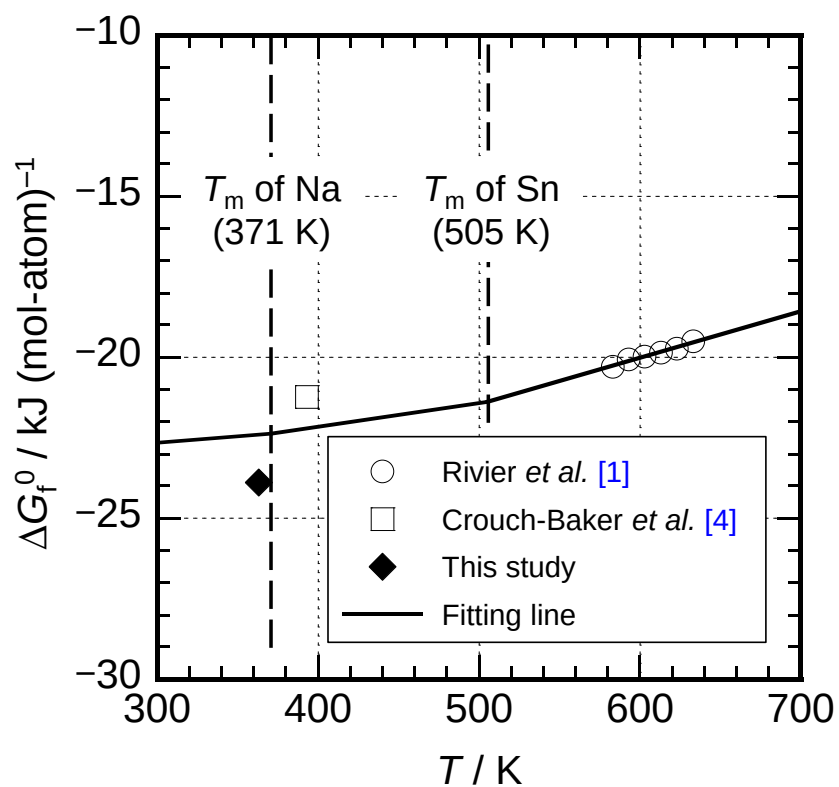


Figure 4-7 Comparison of standard Gibbs free energies of formation for α -NaSn calculated from previous studies [1,4] and this study. The solid fitting curve is drawn based on the report by Rivier *et al.* [1] and thermodynamic data of tin and sodium [29].

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Chapter 5

Charge–discharge behavior of Sn–Cu film

5.1 Introduction

In **Chapter 3**, the basic charge–discharge behaviors of Sn–Al films with 10 μm thickness of tin were investigated, and it was found that the capacity rapidly decreased from 729 to 121 $\text{mAh} (\text{g-Sn})^{-1}$ in initial 10 cycles with cut-off voltages of 0.005–1.200 V. This is explained by the large volume change during alloy/dealloying process. Although the limitation of cut-off voltages led to better capacity retention especially by utilizing a pair of the lowest potential plateaus (c and c'), the capacity decline was unavoidable after 30 cycles. In the case of sodium deposition during charging process, the capacity once decreased in initial cycles and recovered in the following cycles. However, this charge–discharge condition is involved with the sodium deposition/dissolution, which intrinsically poses the safety problem. Therefore, the improvement of cycleability without sodium metal deposition is the most desirable goal.

In lithium-ion batteries, there have been the large amounts of reports on better cycleability for tin negative electrodes. As mentioned in **Chapter 1**, so far, four major countermeasures were proposed, *i.e.*, the utilization of (1) tin oxides [1–3], (2) Sn– M_1 system (M_1 : inactive metals with lithium; Ni, Fe, etc.) [4–7], (3) Sn– M_2 system (M_2 : active metals that form Li– M_2 binary alloys; Si, Cd, Sb, etc.) [8–11], (4) Sn– M_3 system (M_3 : metals that form Li–Sn– M_3 ternary alloys; Cu, Ag, etc.) [12–15]. Among them, the author focused on the (2) Sn– M_1 system and a part of (4) Sn– M_3 system. Since Sn–M alloys shows smaller volume changes or they are sometimes almost inactive with lithium, these alloys play a role as a buffer for the volume change of tin and consequently reduce the generated strain of the tin film electrode, leading better cycling

characteristics. There have been many studies on better cycleability of tin negative electrodes by utilizing Cu–Sn alloys [12,13,16–19]. For example, Tamura *et al.* applied the electrodeposited tin film on copper foil with 2 μm thickness of tin (denoted as “Sn–Cu alloy thin-film electrode”) for negative electrodes of lithium-ion batteries [13,17]. According to the previous study [13], various kinds of Sn–Cu alloy thin-film electrodes were prepared by electrodeposition of tin on copper foils and the following annealing at 473 K for 24 h. A Sn–Cu alloy thin-film without annealing showed the sudden capacity decrease in the 2nd cycle from 940 to 200 mAh g^{-1} . In contrast, an annealed film exhibited improved capacity retention (20 $\rightarrow$ 94%) and retained a reversible capacity over 800 mAh g^{-1} after 10 cycles, which was explained as follows. Since the annealed film possessed less active Cu–Sn alloys such as Cu_6Sn_5 and Cu_3Sn , the interface strength between the active material and the current collector was improved and the delamination of active material was prevented. In sodium-ion batteries, some reports on Sn–Cu alloy negative electrodes in organic solvents at room temperature [20–22]. Among these materials, Sn–Cu nanocomposite exhibited an interesting cycling performance, *i.e.*, 400 mAh g^{-1} for 100 cycles [22].

Similar improvements in cycleability are expected for the sodiation/desodiation of Sn–Cu films prepared by annealing tin-coated copper foils. Therefore, the aim of this chapter is to investigate the charge–discharge behaviors of Sn–Cu films (ca. 1 μm thickness of tin) in Na[FSA]–K[FSA] 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. In addition, it is useful to utilize such electrodeposited tin films for evaluation of their fundamental charge–discharge characteristics, because the contribution of conductive agents to the capacity can be avoided unlike in the case of composite electrodes. 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

cycleability improvements are discussed based on these results.

5.2 Experimental

Glove boxes (Miwa Manufacturing Co., Ltd., DBO-2LKH-HNBR or DBO-1KH-HNBR2) or a glove box (Miwa Manufacturing Co., Ltd., 1ADB-3-O) connected with a gas purification system (Miwa Manufacturing Co., Ltd., MS3-P60S-N) under dry argon atmosphere were used to handle ionic liquids and assemble all of the electrochemical cells used for the experiments in this chapter. The dew points of the glove box were kept below 197 K. The concentrations of oxygen in the glove box (Miwa Manufacturing Co., Ltd., DBO-2LKH-HNBR) were also checked by an oxygen analyzer (GE Sensing & Inspection Technologies Co., Ltd., DF-150ε), and were maintained below 2 ppm. Na[FSA] and K[FSA] used for the experiments in this chapter were dried under vacuum at 353 K for 48 h prior to use. Tin-coated copper foils (Sn–Cu films) were prepared by electrodeposition of tin on copper foils. The loading mass of tin was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Thermo Fisher Scientific, Inc., iCAP6300). Before electrochemical measurements, these Sn–Cu films were dried in 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.

All electrochemical measurements in this chapter were performed under 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 thickness per sheet), used as a separator, were vacuum-impregnated with the electrolyte prior to the tests. Sn–Cu 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 electrodes. The counter electrode consisted of sodium metal (Sigma-Aldrich, Inc., 99.85%). The charge–discharge rates

were set at current densities of $84.7\text{--}847\text{ mA (g-Sn)}^{-1}$, 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 this chapter.

The phases in the Sn–Cu 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, $\lambda = 0.15418\text{ nm}$) equipped with a one-dimensional high-speed detector (Rigaku Co.; D/teX Ultra for Ultima IV, D/teX Ultra 250 for SmartLab) with a nickel filter. The elemental compositions and chemical states of the Sn–Cu films were investigated by XPS (JEOL, JPS-9010) combined with argon-ion etching. The surfaces and cross-sections were observed using an FE-SEM (Hitachi, SU-8020, or JEOL, JSM-7600F). Before the cross-sectional observation, a cross-section polisher (CP; JEOL, SM09010) or a focused ion beam (FIB) system (FEI Co., Quanta 3D FEG) was used to cut the Sn–Cu films. The damage associated with FIB processing was alleviated by the vapor-deposited tungsten coated on their surfaces. This FIB system is also equipped with an air-tight transfer system (Gatan, Inc., C1010) and a scanning electron microscope (SEM). Prior to analysis of the samples after charge–discharge tests, the Na[FSA]–K[FSA] salt was removed by soaking in dehydrated and deoxidized tetrahydrofuran (Wako Pure Chemical Industries, Ltd., water content $< 10\text{ ppm}$, oxygen content $< 1\text{ ppm}$), and the samples were transferred to the XRD and FE-SEM apparatuses by transfer vessels without exposing to air.

5.3 Results and discussion

5.3.1 Characterization of annealed Sn–Cu films

5.3.1.1 XRD

Figure 5-1 shows the XRD patterns of the annealed Sn–Cu films. The unannealed film (denoted as “0h-annealed film”) consists of β -Sn, Cu₆Sn₅, 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 been previously reported by several research groups [13,23]. 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 $\beta\text{-Sn}$, in contrast to the 0h-annealed film. This corresponds to the progress in alloying at 463 K. For the 10h- and 25h-annealed films, the $\beta\text{-Sn}$ 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 .

5.3.1.2 XPS

XPS depth profiles of the 0h-, 4h-, and 10h-annealed Sn–Cu films are shown in **Figure 5-2**. 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 SnO₂ (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 the length of the 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 Cu_6Sn_5 phase detected by XRD. Moreover, the Cu $2p_{3/2}$ peak intensities increase with the length of the annealing time. It is therefore suggested that the formation of Sn–Cu alloys proceeds from the original Sn/Cu interface toward the top surface of the tin film.

5.3.1.3 Cross-sectional FE-SEM

Selected cross-sectional FE-SEM images of the Sn–Cu films are presented in **Figures**

5-3a–5-3f. As shown in **Figure 5-3a**, the 0h-annealed film mainly consists of β -Sn (light-gray region), Cu_6Sn_5 (gray region), and the Cu current collector (dark-gray region). The β -Sn and Cu_6Sn_5 domains are mixed in the surface layer to a depth of ca. 1 μm . A magnified image (**Figure 5-3b**) shows a thin Cu_3Sn layer of thickness ca. 100 nm between the Cu_6Sn_5 and Cu layers, which is too thin to be detected by XRD analysis. In the 4h-annealed film (**Figures 5-3c and 5-3d**), the Cu_6Sn_5 and Cu_3Sn areas increase, and micron-sized β -Sn domains are localized on the surface. In the 10h-annealed film (**Figure 5-3e**), the β -Sn region has almost disappeared, which is consistent with the XRD results (See also **Figure 5-1**). For the 25h-annealed film (**Figure 5-3f**), a thinner Cu_6Sn_5 film and thicker Cu_3Sn film are observed, as compared to the 10h-annealed film. This is in agreement with the XRD results.

5.3.2 Charge–discharge behaviors of annealed Sn–Cu films

5.3.2.1 Initial charge–discharge curves

Figure 5-4a 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 **Chapter 3**, an initial reversible capacity over $700 \text{ mAh (g-Sn)}^{-1}$ was obtained when tin-coated aluminum foils were used. This difference can be explained by the lower reactivities of Cu–Sn alloys. 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 Sn–Cu films without β -Sn phase exhibit considerably lower capacities than those containing this phase. It is therefore concluded that the capacity is mainly contributed by β -Sn.

5.3.2.2 Cycleability

Figure 5-4b 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 3rd 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 ($\Delta V = 424\%$ for Na₁₅Sn₄) as shown in **Chapter 3**. 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 5 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 as small as approximately 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 microcrack formation during the charge–discharge cycles (See also **Figure 5-8f**). 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 Cu₃Sn phase is almost inactive.

In **Figure 5-4b**, the 0h-annealed film shows the highest capacity of ca. 165 mAh (g-Sn)⁻¹ at the 100th cycle among all the Sn–Cu films. The main features in the cycling property are the large decrease of capacity during initial 10 cycles and the gradual recovery of capacity after 40 cycles. As shown in **Figures 5-1–5-3**, the 0h-annealed film consists of β -Sn, Cu₆Sn₅, and the Cu current collector. The Cu₆Sn₅ phase is formed by alloying of tin and copper at room temperature [13,23]. 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 Sn–Cu films already annealed at 463 K. Since the 0h-annealed film possesses the largest amounts of β -Sn, it shows the highest capacity in the beginning of the charge–discharge tests. During the initial 10 cycles, the capacity rapidly decreases due to falling-off of pulverized β -Sn. Meanwhile, the alloying of β -Sn and Cu current collector also gradually proceeds during cycling and some portions of the fallen β -Sn become active again. As a result, the capacity gradually recovers and reaches the highest capacity at the 100th cycle among all the Sn–Cu films.

5.3.2.3 Cycleability and rate property of the 4h-annealed film

Since the 4h-annealed film exhibits the best capacity retention, the charge–discharge test was continued up to 1000 cycles. **Figures 5-5a** and **5-5b**, 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 $100 \text{ mAh (g-Sn)}^{-1}$ are obtained for 1000 cycles. No noticeable changes in the charge–discharge profiles are observed between the 100th and the 1000th cycles. Moreover, at the 1000th cycle, the reversible capacity and coulombic efficiency are $105 \text{ mAh (g-Sn)}^{-1}$ and 99.5%, respectively. This stable cycleability can be explained as follows. In the 4h-annealed film, as shown in **Figures 5-3c** and **5-3d**, active β -Sn regions are randomly dispersed in less-active Cu_6Sn_5 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 the pulverization of the active β -Sn. Furthermore, to achieve stable cycleability, the delamination of the active material layer from the current collector must be prevented. In the 4h-annealed film, Cu_6Sn_5 and Cu_3Sn layers act as a buffer layer and prevent the delamination, as in the case of tin negative electrodes for lithium-ion batteries [13,17].

The rate properties were also investigated using another 4h-annealed Sn–Cu film. As shown in **Figure 5-6**, 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 **Figures 5-4** and **5-5**, which can be attributed to a slight difference in the amounts of β -Sn for different 4h-annealed films, *i.e.*, a slight difference in the β -Sn thickness 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 a rate of 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.

5.3.3 Analysis of annealed Sn–Cu films after charge–discharge tests

5.3.3.1 XRD

Figures 5-7a–5-7f show XRD patterns of the 0h-, 4h-, and 10h-annealed films before and after the charge–discharge tests. For the 0h-annealed film (**Figures 5-7a** and **5-7b**), 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 β -Sn 200 and 301 ($2\theta = 30.65^\circ$ 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 Cu₆Sn₅ are weaker after the test; this is also explained by alloying/dealloying with sodium. For the 4h-annealed film (**Figures 5-7c** and **5-7d**), β -Sn, Cu₆Sn₅, and Cu₃Sn phases are detected before and after the charge–discharge test. Similar changes to those for the 0h-annealed film are observed for the β -Sn and Cu₆Sn₅ patterns after the test. In contrast, the peak intensities of Cu₃Sn are almost unchanged, indicating that the Cu₃Sn phase is inactive with sodium. For the

10h-annealed film (**Figures 5-7e and 5-7f**), a similar phenomenon is observed. The peak intensities of Cu_6Sn_5 become weak and those of Cu_3Sn are unchanged.

5.3.3.2 Surface FE-SEM

Figures 5-8a–5-8f 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 (**Figures 5-8a, 5-8c, and 5-8e**), 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 (**Figure 5-8b**); this is caused by the severe volume changes during sodiation/desodiation. For the 4h-annealed film after 1000 cycles (**Figure 5-8d**), 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 . Owing to this stable film structure, there is no noticeable deterioration, even after 1000 cycles (see also **Figure 5-5**). For the 10h-annealed film after the test (**Figure 5-8f**), 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.

5.3.3.3 Cross-sectional FE-SEM

Figures 5-9a–5-9c depict selected cross-sectional FE-SEM images of the 0h-, 4h-, and 10h-annealed films after charge–discharge tests. For the 0h-annealed film (**Figure 5-9a**), the thickness of the active material layer including $\beta\text{-Sn}$ and Cu_6Sn_5 above Cu current collector increase to more than $10\text{ }\mu\text{m}$ (See also **Figure 5-3a**). Moreover, large pores are observed in the active material layer, which reflects harsh volume changes during alloying/dealloying process of 100 cycles. In addition, white region at the top surface of the film corresponds to the deposited tungsten during FIB processing. As shown in **Figure 5-9b**, the 4h-annealed film retains denser

morphology even after 1000 cycles. The Cu_3Sn layer lies between the active material layer and Cu current collector, and keeps unreacted. This is consistent with XRD results (See also **Figure 5-7**). As shown in **Figure 5-9c**, the 10h-annealed film undergoes milder electrode expansion, corresponding to the lower reversible capacities than the 0h- and 4h-annealed films (See also **Figure 5-4**).

5.4 Conclusions

Sn–Cu 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 Na[FSA]–K[FSA] at 363 K. The major findings in this chapter are summarized as follows.

1. XRD and cross-sectional FE-SEM analyses revealed that the 0h-, 2h-, and 4h-annealed films consisted of $\beta\text{-Sn}$, Cu_6Sn_5 , and Cu_3Sn phases. For the 10h- and 25h-annealed films, $\beta\text{-Sn}$ 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 $\beta\text{-Sn}$ phase exhibited much smaller capacities than those containing this phase. For the films with the $\beta\text{-Sn}$ phase, the discharge capacities mainly originated from the $\beta\text{-Sn}$ phase. Moreover, it was found that Cu_6Sn_5 slightly reacted with sodium, and that Cu_3Sn was almost inactive.
3. Among the Sn–Cu films with different annealing times, the 4h-annealed film exhibited the best capacity retention, and maintained a stable reversible capacity of ca. 100–120 mAh $(\text{g-Sn})^{-1}$ for 1000 cycles. The XRD and FE-SEM analyses suggested that the stable cycleability was mainly attributable to an appropriate domain structure of active $\beta\text{-Sn}$ and less-active Cu_6Sn_5 .

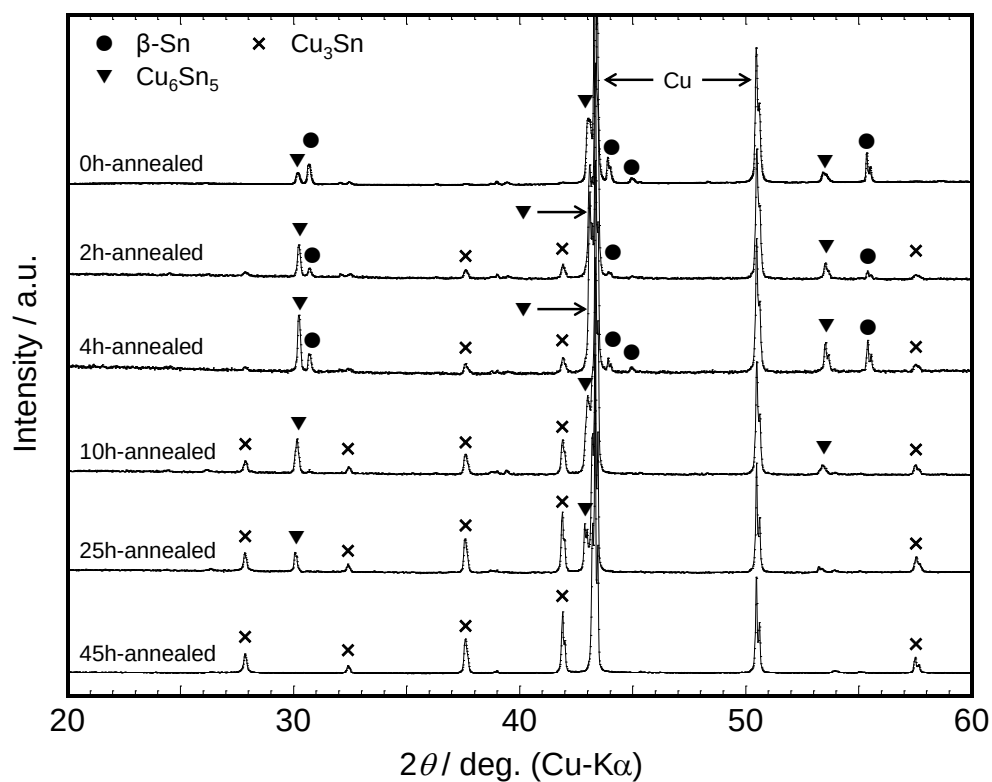


Figure 5-1 X-ray diffraction patterns of annealed Sn–Cu films; annealing temperature: 463 K, annealing time: 0–45 h.

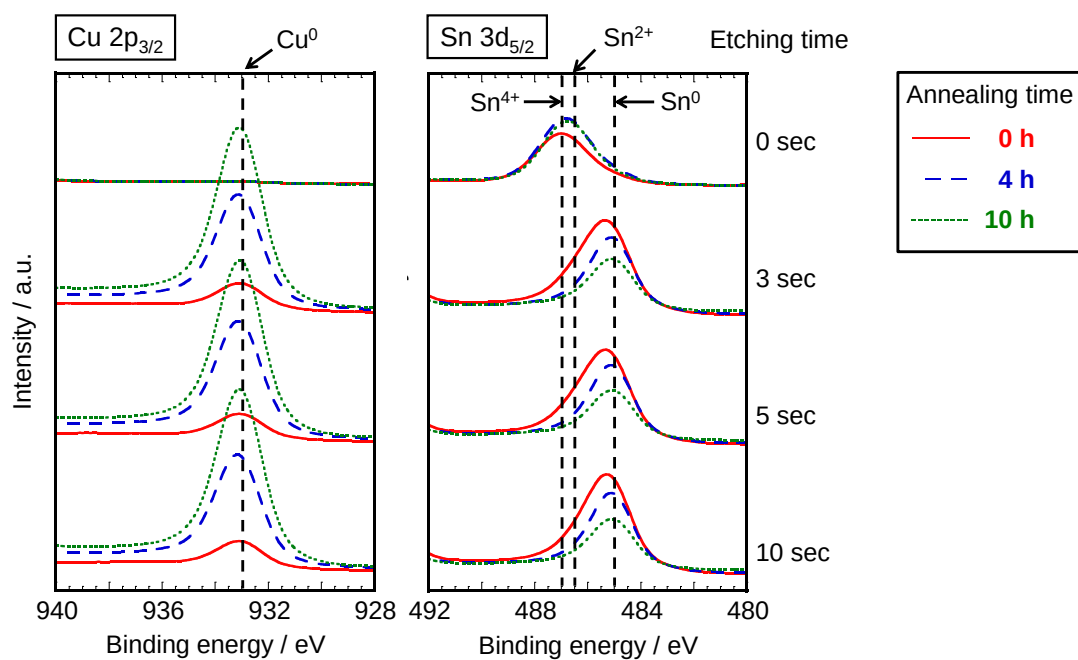


Figure 5-2 X-ray photoelectron spectroscopy depth profiles of annealed Sn–Cu films; annealing time: 0–10 h.

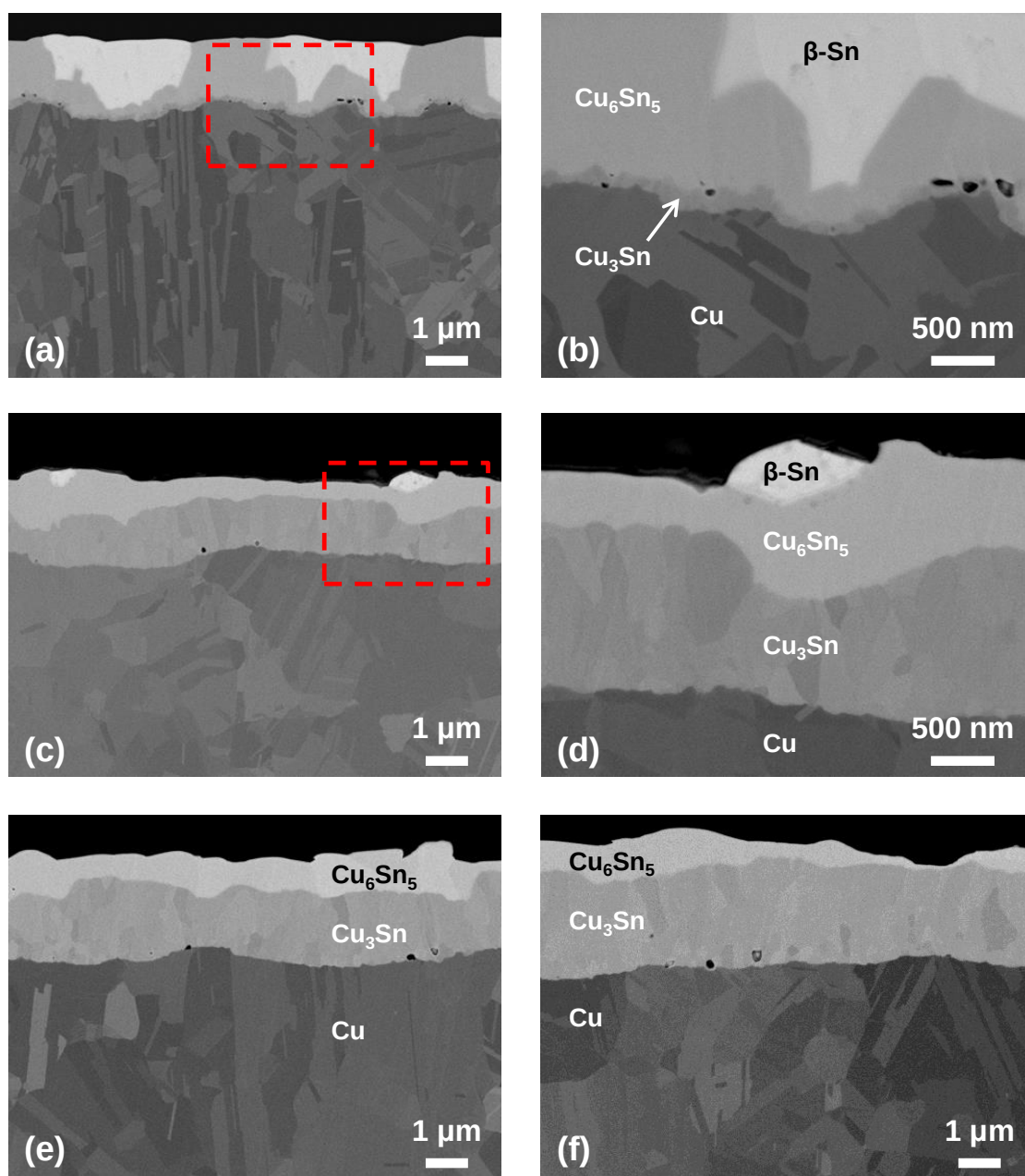


Figure 5-3 Selected cross-sectional field-emission scanning electron microscopy images of annealed Sn-Cu films. (a) and (b) 0h-annealed film at different magnifications, (c) and (d) 4h-annealed film at different magnifications, (e) 10h-annealed film, and (f) 25h-annealed film. (b) and (d) show enlarged views of the red rectangular areas of (a) and (c), respectively.

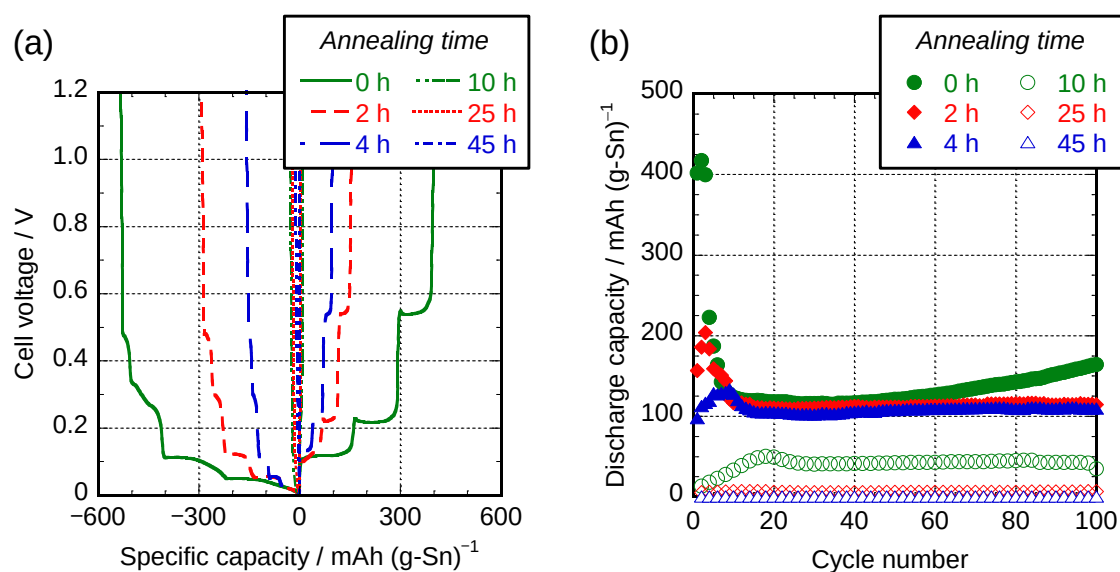


Figure 5-4 (a) Initial charge–discharge curves of annealed Sn–Cu films at a current density of $84.7 \text{ mA (g-Sn)}^{-1}$ and (b) cycling characteristics of these Sn–Cu films during 100 cycles.

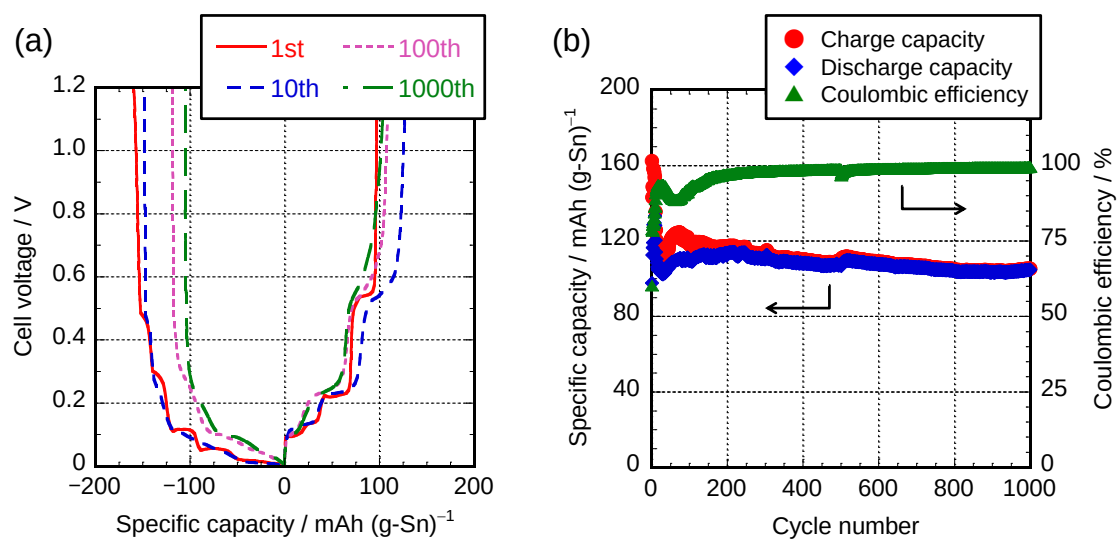


Figure 5-5 (a) Charge–discharge curves and (b) cycling properties of specific capacity and coulombic efficiency of the 4h-annealed Sn–Cu film at current density of $84.7 \text{ mA (g-Sn)}^{-1}$.

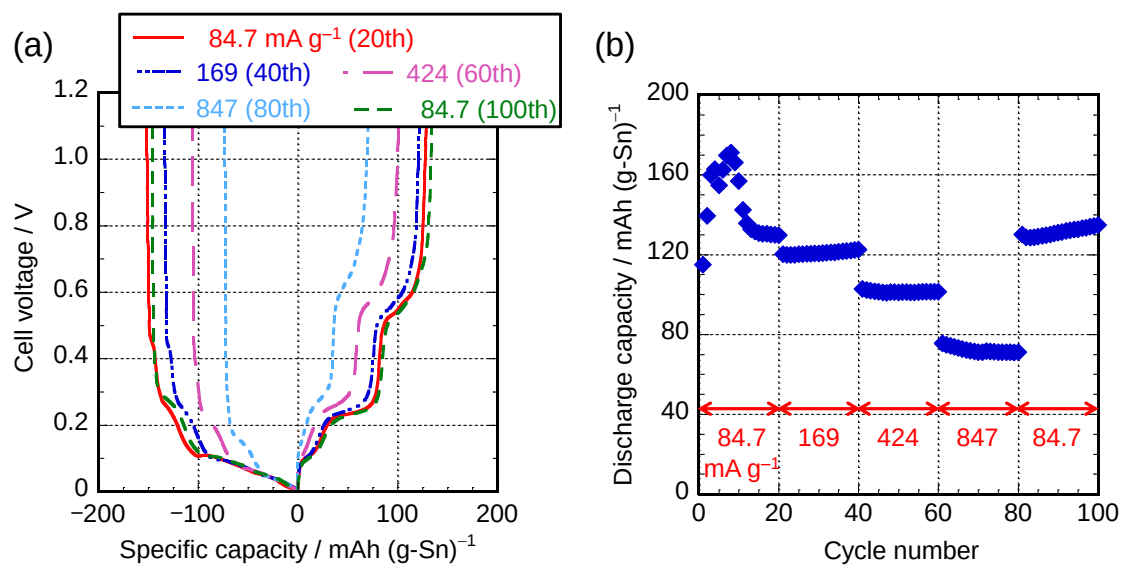


Figure 5-6 (a) Charge–discharge curves and (b) rate properties of specific capacity and coulombic efficiency of the 4h-annealed Sn–Cu film at current densities of 84.7–847 mA (g-Sn)⁻¹. The values of 84.7, 169, 424, and 847 in the figure represent the current densities in mA (g-Sn)⁻¹.

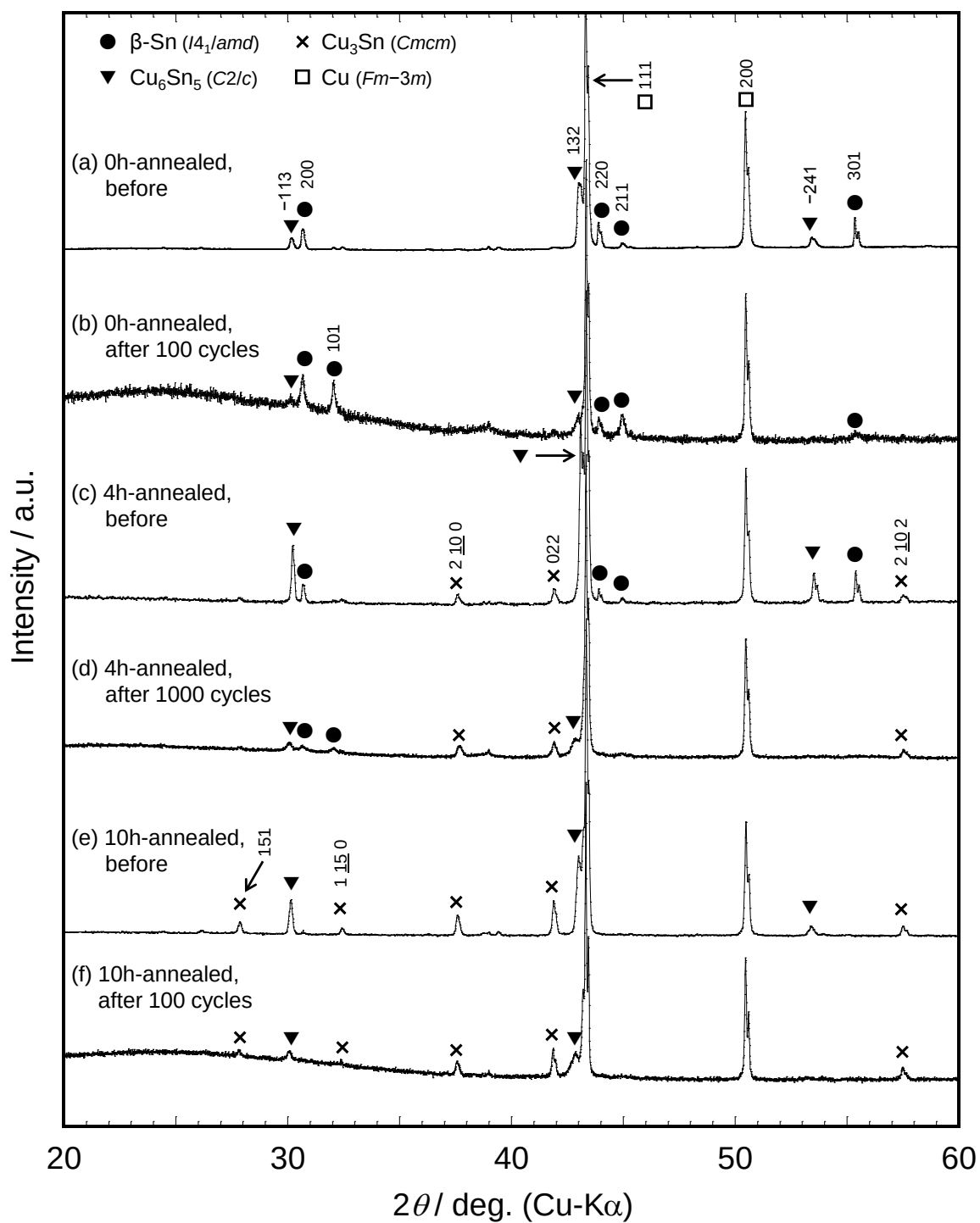


Figure 5-7 Comparison of X-ray diffraction patterns of Sn–Cu films before and after charge–discharge tests. (a) 0h-annealed, before, (b) 0h-annealed, after, (c) 4h-annealed, before, (d) 4h-annealed, after, (e) 10h-annealed film, before, and (f) 10h-annealed film, after.

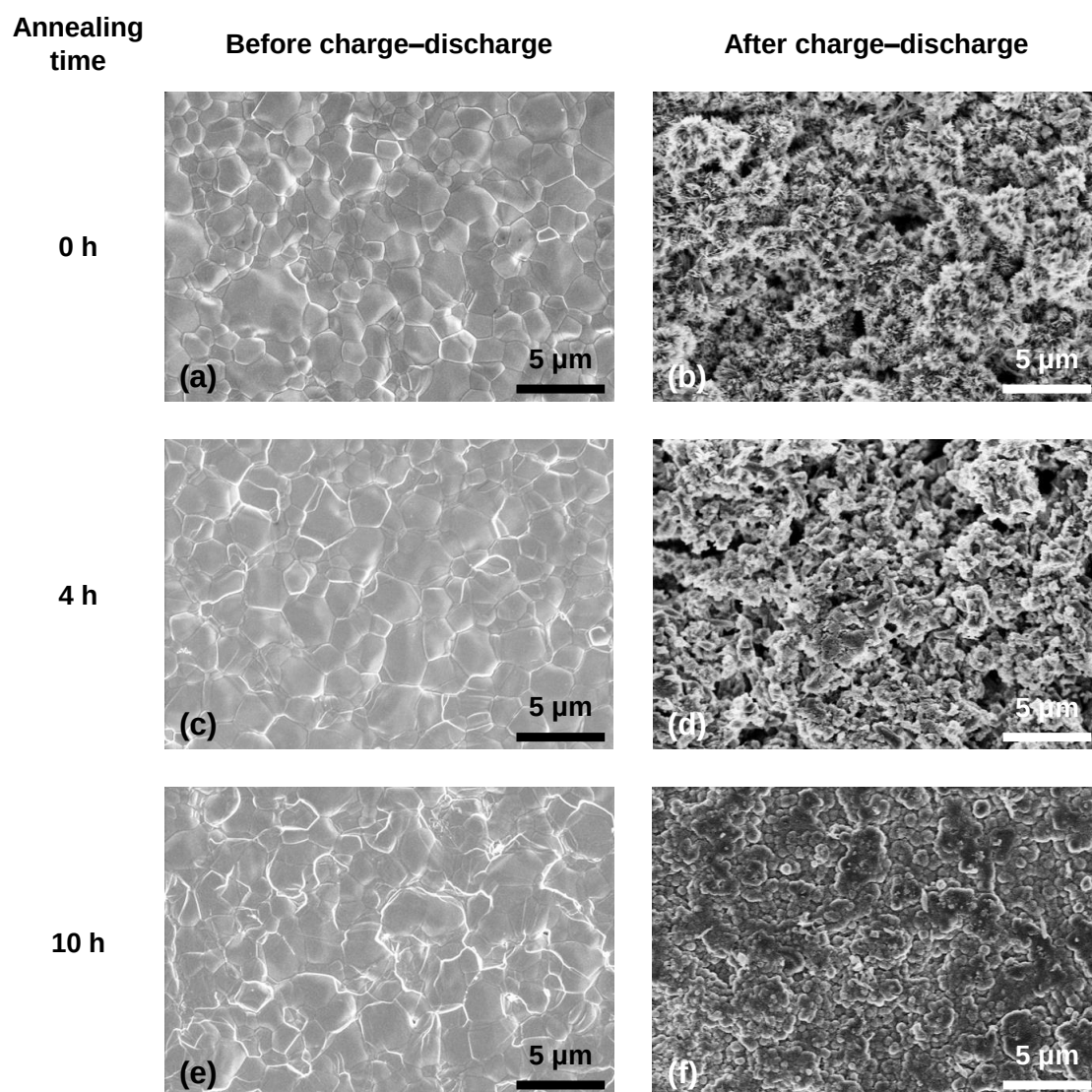


Figure 5-8 Representative field-emission scanning electron microscopy images of surface morphologies of Sn–Cu films before (a, c, and e) and after (b, d, and f) charge–discharge tests. Annealing time: 0 h (a, b), 4 h (c, d), and 10 h (e, f).

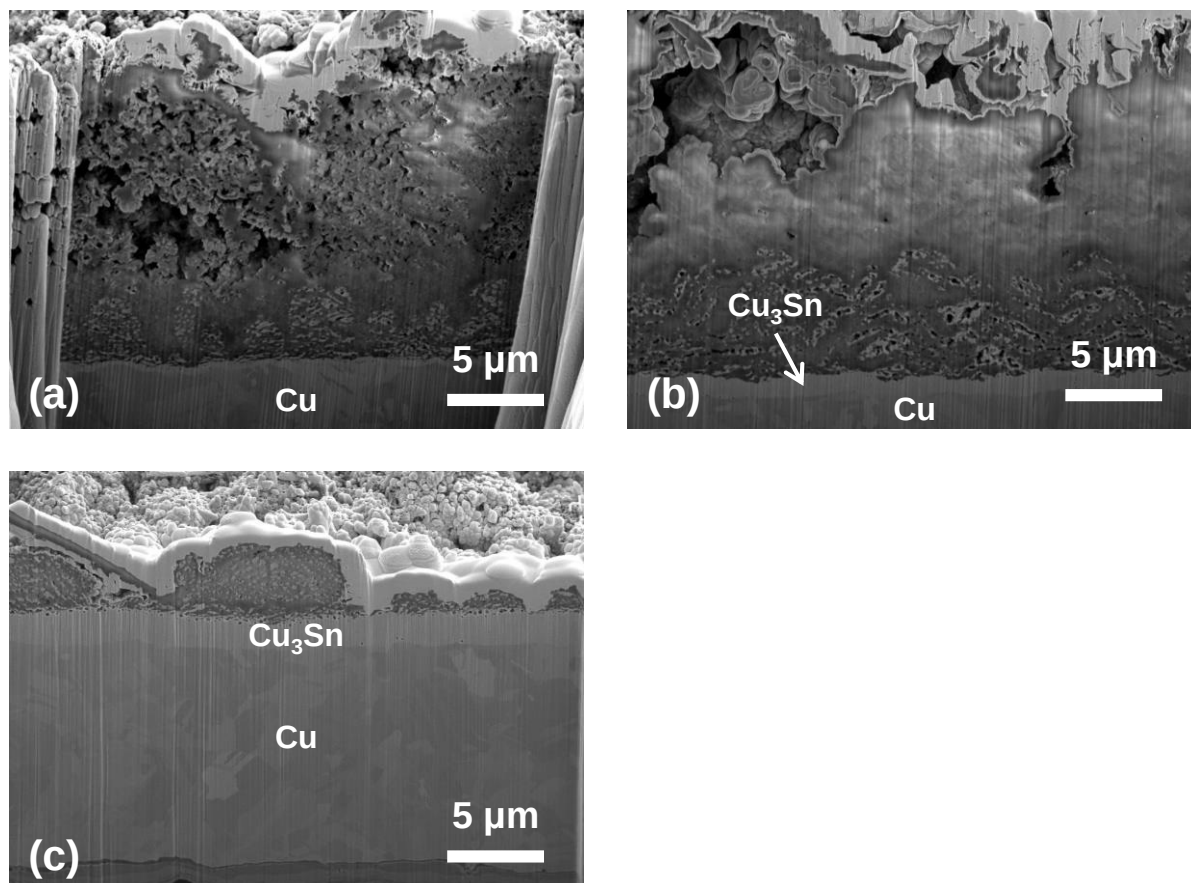


Figure 5-9 Selected cross-sectional field-emission scanning electron microscopy images of Sn-Cu films after charge-discharge tests. (a) 0h-annealed film after 100 cycles, (b) 4h-annealed film after 1000 cycles, and (c) 10h-annealed film after 100 cycles.

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Chapter 6

Charge–discharge behavior of Sn–Ni film

6.1 Introduction

In the previous chapter, with an aim to improve cycleability of a tin negative electrode, charge–discharge behaviors of annealed Sn–Cu films were evaluated. As a result, the 4h-annealed Sn–Cu film exhibited the best capacity retention and a stable reversible capacity of 100–120 mAh (g-Sn)⁻¹ for 1000 cycles. However, these capacities were lower than the theoretical capacity of tin (847 mAh (g-Sn)⁻¹), and thus, it is necessary to explore other Sn–M systems.

In this chapter, the author focuses on the Sn–Ni system. In lithium-ion batteries, several studies on Ni–Sn alloy negative electrodes have been conducted [1–9]. Some of them reported improved cycle performances of co-electrodeposited Sn–Ni alloy thin films [5,6]. In sodium-ion batteries, it was recently reported that Ni₃Sn₂ nanocomposite electrodes delivered a stable capacity of 270 mAh g⁻¹ at 1C rate after 300 cycles [10]. However, to clarify the mechanism for improving cycleability, it is better to utilize a simplified material. A promising candidate material is the Sn–Ni alloy film prepared by annealing treatment of electrodeposited tin film on nickel substrate. It is expected to elucidate the role of Ni–Sn alloys by the examination of this material, as in the case of Sn–Cu films.

The aim of this chapter is to investigate cycle performances of Sn–Ni films that were prepared by annealing tin-coated nickel foils, as negative electrodes for sodium secondary battery applying Na[FSA]–K[FSA] ionic liquid as an electrolyte at 363 K. Sn–Ni films with different annealing times from 0 to 25 h were prepared in order to evaluate the effects of the alloying degree on the charge–discharge performance. The electrodes before and after the charge–discharge tests were analyzed by X-ray diffraction (XRD) and field-emission scanning

electron microscopy (FE-SEM), and the mechanism of their cycleability was also discussed.

6.2 Experimental

A glove box (Miwa Manufacturing Co., Ltd., DBO-1KH-HNBR2) or a glove box (Miwa Manufacturing Co., Ltd., 1ADB-3-O) connected with a gas purification system (Miwa Manufacturing Co., Ltd., MS3-P60S-N) under dry argon atmosphere was used to handle ionic liquids and assemble all of the electrochemical cells used for the experiments in this chapter. The dew points of the glove box were kept below 197 K. Na[FSA] and K[FSA] used for the experiments in this chapter were dried under vacuum at 353 K for 48 h prior to use. Tin-coated nickel foils were prepared by electrodeposition of tin on nickel foils. The loading mass of tin was determined via inductively coupled plasma atomic emission spectroscopy (ICP-AES; Thermo Fisher Scientific Inc., iCAP6300). Before electrochemical measurements, these Sn–Ni films were dried in vacuum at 363 K for 48 h, and some of them were annealed at 463 K under vacuum. Annealing time was set at 2, 10 or 25 h.

All electrochemical measurements in this chapter were performed under argon atmosphere using electrochemical measurement apparatuses (Bio-Logic Co., VSP, or Toyo Co., 580-type battery cycler) with a two-electrode cell (Tomcell Japan Co., Ltd.). Two sheets of glass-fiber filter paper (Whatman, GF-A, 260 μm thickness per sheet), used as a separator, were vacuum-impregnated with the electrolyte prior to the tests. Sn–Ni films with tin loading masses between 0.67 and 0.85 mg cm^{-2} (corresponding to the thicknesses of tin between 0.92 and 1.16 μm) were selected and used as the working electrodes. The counter electrode consisted of sodium metal (Sigma-Aldrich, Inc., 99.85%). The charge–discharge rate was set at a current density of 84.7 mA (g-Sn)^{-1} that corresponds to C/10 rate. Cut-off voltages were 0.005 and 1.200 V, and the operating temperature was 363 K for all the tests in this chapter.

To characterize Sn–Ni films before and after charge–discharge tests, XRD analysis was applied to identify phases of the films using an X-ray diffractometer (Rigaku Co., SmartLab, Cu-K α radiation ($\lambda = 0.15418$ nm)) equipped with a one-dimensional high-speed detector (Rigaku Co., D/teX Ultra 250) with a nickel filter. The elemental compositions and chemical states of Sn–Ni alloy film were investigated by X-ray photoelectron spectroscopy (XPS; JEOL, JPS-9010) combined with argon-ion etching. The surfaces and cross-sections were observed by an FE-SEM (Hitachi, SU-8020, or JEOL, JSM-7600F). Before the cross-sectional SEM observation, a cross-section polisher (CP; JEOL, IB090-20) was used to cut the Sn–Ni films. Prior to analysis of the samples after charge–discharge tests, the Na[FSA]–K[FSA] salt was removed by soaking in dehydrated and deoxidized tetrahydrofuran (Wako Pure Chemical Industries, Ltd., water content < 10 ppm, oxygen content < 1 ppm), and the samples were transferred to the XRD and FE-SEM apparatuses by transfer vessels without exposing to air.

6.3 Results and discussion

6.3.1 Characterization of Sn–Ni films before charge–discharge tests

6.3.1.1 XRD

Figure 6-1 shows XRD patterns of Sn–Ni films before charge–discharge tests. A Sn–Ni film without annealing at 463 K (hereinafter called “0h-annealed film”) consists of four phases, *i.e.*, β -Sn, NiSn₃, Ni₃Sn₄ and the Ni current collector. It was reported that NiSn₃ is a metastable intermetallic compound, and that NiSn₃ is obtained by electrodeposition of tin on a nickel layer [13] or co-electrodeposition of tin and nickel [5,6]. Since the peak intensity of Ni₃Sn₄ phase is very weak, the amount of Ni₃Sn₄ phase is small. In the 2h-annealed film, the intensities of β -Sn peaks become weaker and those of Ni₃Sn₄ peaks become stronger. In addition, the preferred orientation of metastable NiSn₃ phase changes to (00 l). In the 10h-annealed film, the metastable

NiSn₃ phase totally disappears while β -Sn and Ni₃Sn₄ phases remain. Such disappearance of metastable NiSn₃ phase was already reported at higher temperatures over 433 K [13]. Finally, after annealing for 25 h, β -Sn phase completely disappears and only Ni₃Sn₄ phase is observed except for the Ni current collector.

6.3.1.2 XPS

Figure 6-2 summarizes XPS depth profiles of Sn–Ni films before charge–discharge tests. For all the films without etching, peaks from Sn 3d_{5/2} orbital are observed at oxidized states of tin (486.5 eV for Sn²⁺, or 486.9 eV for Sn⁴⁺) and no clear difference in their intensities is observed. Since no peaks from Ni 2p_{3/2} are observed, the surfaces of Sn–Ni films are likely to be covered with SnO_x layer. After etching for 2 s, their Sn 3d_{5/2} peaks shift to the Sn⁰ position, indicating the removal of the oxide layer. Sn–Ni films with longer annealing times show stronger peaks of Sn 3d_{5/2}. A clear peak at around 853 eV ascribed to Ni 2p_{3/2} is observed for the 10h-annealed film, suggesting the presence of nickel at near surface while there are no obvious peaks in the 0h- and 2h-annealed films. For the 25h-annealed film, a peak of higher intensity from Ni 2p_{3/2} is observed. In short, a stronger Ni 2p_{3/2} peak and a weaker Sn 3d_{5/2} peak are observed for Sn–Ni films with longer annealing time. Moreover, with further etching (10–120 s), the Ni 2p_{3/2} peak intensities of all the films become stronger and their Sn 3d_{5/2} peak intensities become weaker. Therefore, it is found that the formation of Ni–Sn alloys proceeds from the Sn/Ni interface towards the top surface of β -Sn layer.

6.3.1.3 Cross-sectional FE-SEM

To investigate the morphologies of formed Ni–Sn alloys, the cross-sectional SEM observation was conducted. As shown in **Figure 6-3a**, in the 0h-annealed film, electrodeposited β -Sn (white region) is confirmed on the nickel substrate (black region). However, taking a closer look at the

enlarged view of the β -Sn layer (**Figure 6-3b**), non-uniform morphologies are observed. According to the previous report on the growth of Ni–Sn alloys [13], a thin layer (ca. 100 nm thickness) adjacent to the nickel substrate and a needle-like structure penetrating β -Sn layer correspond to Ni_3Sn_4 phase and metastable NiSn_3 phase, respectively. In the 2h-annealed film (**Figure 6-3c**), the area of the Ni–Sn alloy layer clearly increases and the needle-like morphology disappears, which is consistent with the XRD result (See **Figure 6-1**). Most of β -Sn region has transformed into Ni_3Sn_4 phase in the 10h-annealed film (**Figure 6-3d**), and has completely disappeared in the 25h-annealed film (**Figure 6-3e**).

6.3.2 Charge–discharge behaviors of Sn–Ni films

Figure 6-4a shows the initial charge–discharge curves of Sn–Ni films. For all films except the 25h-annealed film, several plateaus are observed for both charge and discharge processes below 0.6 V. As shown in the previous chapters, these plateaus are assigned to the sodiation/desodiation behavior of β -Sn. Initial discharge (desodiation) capacities are 605, 305, 121, and 2 mAh (g-Sn)^{−1} for the 0h-, 2h-, 10h-, and 25h-annealed films, respectively, *i.e.*, lower initial capacities are obtained for Sn–Ni films with longer annealing time. Combined with the XRD results (**Figure 6-1**), these results suggest that Ni_3Sn_4 phase formed by annealing possesses extremely low activity with sodium. This is different from the case of lithium-ion battery [5,6], in which Ni_3Sn_4 is reported to exhibit high initial capacities (500–600 mAh g^{−1}).

Cycleability of Sn–Ni films are summarized in **Figure 6-4b**. Although the discharge capacity of the 0h-annealed film decreases from 605 to 226 mAh (g-Sn)^{−1} in the initial 10 cycles, it gradually increases again to 343 mAh (g-Sn)^{−1} after 100 cycles. A similar phenomenon was also observed in the previous studies of tin-based negative electrodes for lithium-ion batteries [5,14] and sodium secondary batteries (See **Chapter 5**). The capacity fade in early cycles is explained by the pulverization of the active material in the same manner as the previous chapters.

Concerning the following capacity recovery, the mechanism is discussed later in detail based on the results of XRD and FE-SEM analyses after charge–discharge tests.

In contrast to the 0h-annealed film, the capacities of the 2h- and 10h-annealed films rapidly decrease to 36 and 24 mAh (g-Sn)⁻¹, respectively, within the initial 10 cycles. These results are different from the case of Sn–Cu films (See **Chapter 5**), in which the 4h-annealed Sn–Cu film exhibited the most stable and reversible capacity of ca. 100–120 mAh (g-Sn)⁻¹. These results indicate that Ni₃Sn₄ layers in the 2h- and 10h-annealed films do not act as buffers for the strain generated by the large volume change of Na–Sn alloys during cycling. For the 25h-annealed film, very small capacities lower than 5 mAh (g-Sn)⁻¹ are observed for 100 cycles, which indicates Ni₃Sn₄ phase is almost inactive with sodium, as mentioned above.

6.3.3 Characterization of Sn–Ni films after charge–discharge tests

6.3.3.1 XRD

Figure 6-5 compares the XRD patterns of Sn–Ni films before and after charge–discharge tests. For the 0h-annealed film (**Figures 6-5a** and **6-5b**), the diffraction peak of β -Sn 211 ($2\theta = 45.0^\circ$) is strong before the charge–discharge test, indicating its preferred orientation. This diffraction pattern changed into the reported powder pattern after the test. Moreover, the peaks derived from NiSn₃ phase totally disappear, and those from Ni₃Sn₄ phase become strong after the test. Here, it is likely that metastable NiSn₃ phase also reacts with sodium and transforms into Ni₃Sn₄ and Na–Sn alloy phases according to the following equation:



For the 2h-annealed film (**Figures 6-5c** and **6-5d**), the preferred orientation of β -Sn phase disappears and the diffraction peaks of NiSn₃ phase vanish as in the case of the 0h-annealed film. The peak intensities of Ni₃Sn₄ are almost unchanged, indicating that Ni₃Sn₄ phase is inactive with sodium. For the 10h-annealed film (**Figures 6-5e** and **6-5f**), similar changes with the 2h-annealed

film is observed after the test. For the 25h-annealed film (**Figures 6-5g** and **6-5h**) entirely constituted of inactive Ni_3Sn_4 phase, no change is observed after the test.

6.3.3.2 Surface FE-SEM

Figure 6-6 summarizes the selected surface FE-SEM images of Sn–Ni films before and after charge–discharge tests. As shown in **Figures 6-6a**, **6-6c**, **6-6e**, and **6-6g**, all films are flat before charge–discharge tests. For the 0h-annealed film, the surface has changed somewhat rough after 100 cycles of charge–discharge (**Figure 6-6b**). The surfaces of the 2h- and 10h-annealed films exhibits much rougher morphologies (**Figures 6-6d** and **6-6f**), suggesting that the active material pulverizes to be electrically isolated. No noticeable change is observed on the surface of the 25h-annealed film (**Figure 6-6h**), corresponding to its extremely low reversible capacities. These results are consistent with the cycleability of the Sn–Ni films.

6.3.3.3 Cross-sectional FE-SEM

To further investigate the morphologies of Sn–Ni films, cross-sectional SEM observation was conducted as shown in **Figure 6-7**. **Figures 6-7a** and **6-7b** show the cross-sectional SEM images of the 0h-annealed film after the charge–discharge test. Compared to the morphology before the test (See **Figures 6-3a** and **6-3b**), the Ni_3Sn_4 thin layer (white layer) adjacent to nickel substrate keeps its morphology and is almost unreacted after the test. Moreover, the needle-like morphology of NiSn_3 phase disappears, and white small particles (ca. 100 nm in diameter) are uniformly dispersed above the Ni_3Sn_4 layer. In contrast, as described in **Figures 6-7c** and **6-7d**, a roughened surface and large pores are observed in the 2h-annealed film, which corresponds to the surface SEM observation (See also **Figure 6-6**). Many cracks are also observed in the thicker Ni_3Sn_4 layer (ca. 500 nm in thickness). It has been already reported that the Ni_3Sn_4 layer exhibits lower flexibility and fracture toughness than Cu–Sn alloys (Cu_6Sn_5 and Cu_3Sn), and easily

collapses even as thin as 0.7 μm [15,16]. For the 10h-annealed film (**Figure 6-7e**), similar fracture of the Ni_3Sn_4 region is observed, which also corresponds to its lower reversible capacity. As shown in **Figure 6-7f**, no remarkable change is confirmed for the 25h-annealed film because Ni_3Sn_4 has little sodium activity (See also **Figures 6-4**).

6.3.4 Mechanism of cycle characteristics for Sn–Ni films

6.3.4.1 0h-annealed film

As described in **Subsection 6.3.2**, the 0h-annealed film shows the capacity decline within initial 10 cycles of charge–discharge. After that, the capacity has gradually recovered. Concerning the capacity recovery after 10 cycles, three effects are likely to be involved.

Firstly, the Ni_3Sn_4 thin layer retains its morphology and electrical contact between the active material layer and the Ni current collector even after 100 cycles. Generally, it is important for a tin film electrode to keep the coherent interface between active and inactive regions, because its degradation usually occurs due to the delamination of the former from the latter [11,12].

The second effect is the increase of the effective surface area of the active material. As shown in **Figure 6-3b**, the average thicknesses of the inactive Ni_3Sn_4 and active $\beta\text{-Sn}$ layers (containing needle-like NiSn_3) of the 0h-annealed film are approximately 100 nm and 1 μm , respectively. In addition, NiSn_3 phase in the $\beta\text{-Sn}$ layer is electrochemically active with sodium, as mentioned in **Subsection 6.3.3.1**. Therefore, more than 90% of tin in this film reacts with sodium. However, the observed initial discharge capacity of $605 \text{ mAh (g-Sn)}^{-1}$ is as low as 71% of the theoretical capacity for $\beta\text{-Sn}$ ($847 \text{ mAh (g-Sn)}^{-1}$). Thus, at this point, it is reasonable to consider that some of $\beta\text{-Sn}$ regions such as the inner part of $\beta\text{-Sn}$ grains and/or particles remain unreacted. After several cycles, their particle sizes decrease and microcracks are generated in the Sn–Ni film. Then, the effective surface area increases and sodium ions in the electrolyte can infiltrate the remaining unreacted $\beta\text{-Sn}$. In this way, these regions begin to contribute to the observed capacities after the

initial 10 cycles of charge–discharge.

The third effect is the recovery of the electrical contact of the electrically-isolated β -Sn particles during the initial cycles. As shown in **Figure 6-7b**, small particles are homogeneously distributed on the Ni_3Sn_4 layer of the 0h-annealed film. It is reasonable to consider that some of these particles are Ni_3Sn_4 formed by the electrochemical reaction of the needle-like NiSn_3 (See also **Subsection 6.3.3.1**). Owing to these dispersed Ni_3Sn_4 particles, a part of β -Sn region keeps its electrical contact with Ni current collector, and the fatal degradation of the Sn–Ni film is prevented. Furthermore, since annealing temperature (463 K) and the melting point of tin (505 K) are relatively close to the operation temperature (363 K), the diffusion of tin is fast enough for isolated β -Sn particles to be electrically reconnected to the other β -Sn particles and/or Ni_3Sn_4 particles even at 363 K. Thus, those electrically recovered tin particles gradually contribute to the capacity after the 10 cycles of charge–discharge.

6.3.4.2 2h-, 10h-, 25h-annealed films

For the 2h-annealed film, the discharge capacity has drastically decreased during the initial 10 cycles of charge–discharge. After that, in contrast to the 0h-annealed film, the recovery of the capacity is not observed. The following reasons are considered for this poor cycleability. Firstly, the pulverization of β -Sn occurs significantly because almost no dispersed small Ni_3Sn_4 particles exist in the β -Sn layer. Secondly, as shown in **Figure 6-7d**, the collapsed Ni_3Sn_4 layer loses its electrical contact, and then the active material above this layer also becomes electrically isolated. Similar mechanism is applicable to the 10h-annealed film. For 25h-annealed film, as discussed above, very low capacity is observed during the 100 cycles of charge–discharge because Ni_3Sn_4 major phase is almost inactive with sodium.

6.4 Conclusions

Sn–Ni films were prepared by annealing tin-coated nickel foils at 463 K for 0–25 h. Their charge–discharge behaviors were investigated in an intermediate temperature ionic liquid Na[FSA]–K[FSA] at 363 K. The major findings in this chapter are summarized as follows:

1. From the results of XRD and cross-sectional FE-SEM analyses, it turned out that the 0h-annealed film was composed of β -Sn, needle-like NiSn_3 , and laminar Ni_3Sn_4 . For the 2h- and 10h-annealed films, a thicker Ni_3Sn_4 layer was formed due to the progress of alloying. For the 25h-annealed film, β -Sn totally transformed into Ni_3Sn_4 .
2. As a result of charge–discharge tests, the 0h-annealed film exhibited the best cycleability and retained its reversible capacity of $343 \text{ mAh (g-Sn)}^{-1}$ even after 100 cycles. Although the 2h- and 10h-annealed films showed its initial capacities of 305 and $121 \text{ mAh (g-Sn)}^{-1}$, respectively, their capacities decreased down to lower than $50 \text{ mAh (g-Sn)}^{-1}$ after 10 cycles. The 25h-annealed film showed very small capacity less than $5 \text{ mAh (g-Sn)}^{-1}$, indicating that Ni_3Sn_4 was almost inactive with sodium.
3. XRD and FE-SEM analyses revealed the mechanism of cycleability for Sn–Ni films. In 0h-annealed film, the needle-like NiSn_3 electrochemically decomposed into Ni_3Sn_4 fine particles, which were dispersed in the β -Sn layer and formed a proper matrix for large volume change of Na–Sn alloys, which led to its better capacity retention. In contrast, for the 2h-annealed film, the Ni_3Sn_4 layer collapsed and became electrically isolated during cycling, which brought about its poor cycleability.

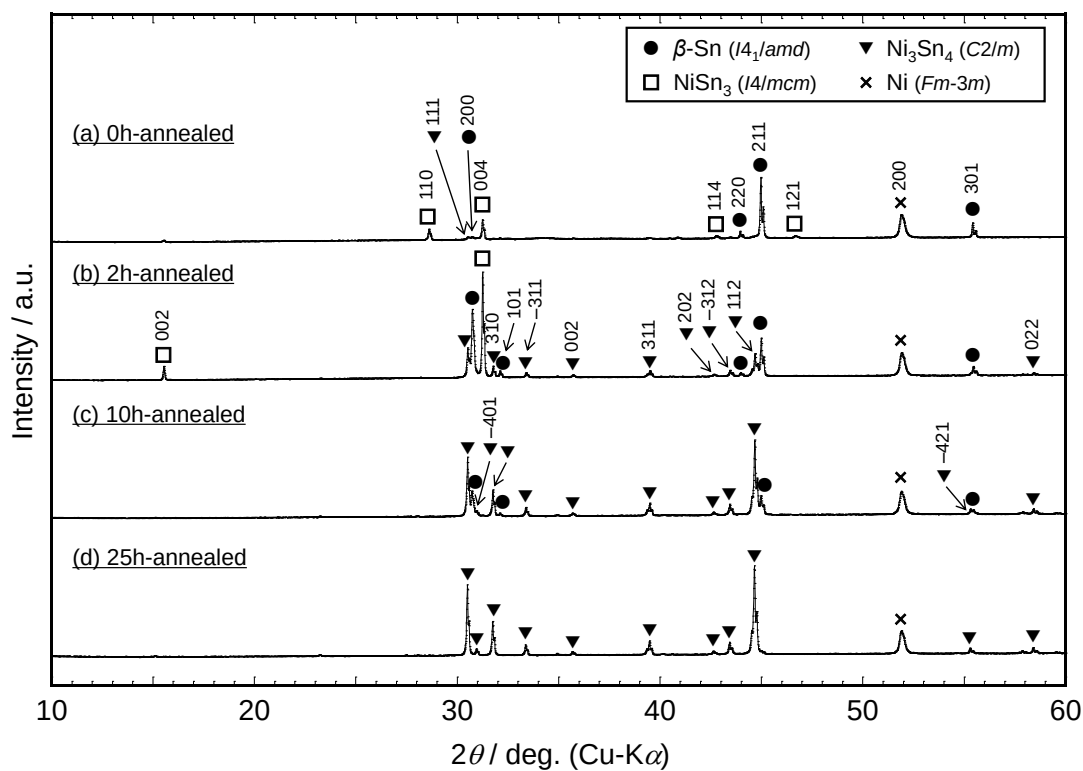


Figure 6-1 XRD patterns of annealed Sn–Ni films. Annealing temperature: 463 K. Annealing time: 0–25 h.

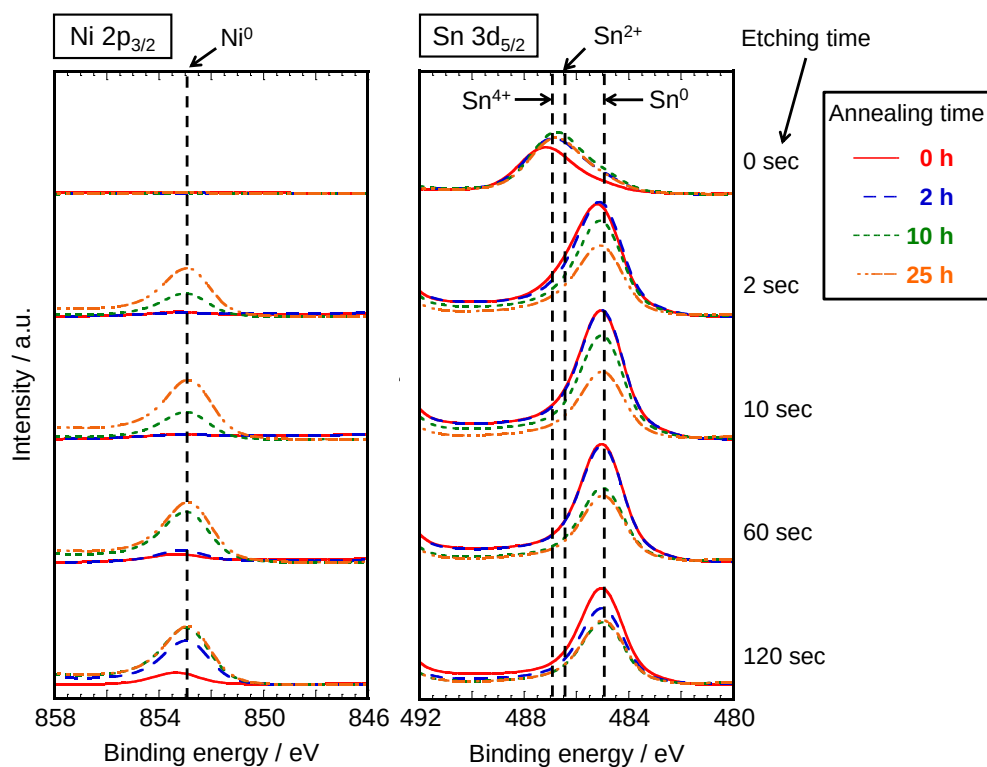


Figure 6-2 XPS depth profiles of annealed Sn–Ni films. Annealing time: 0–25 h.

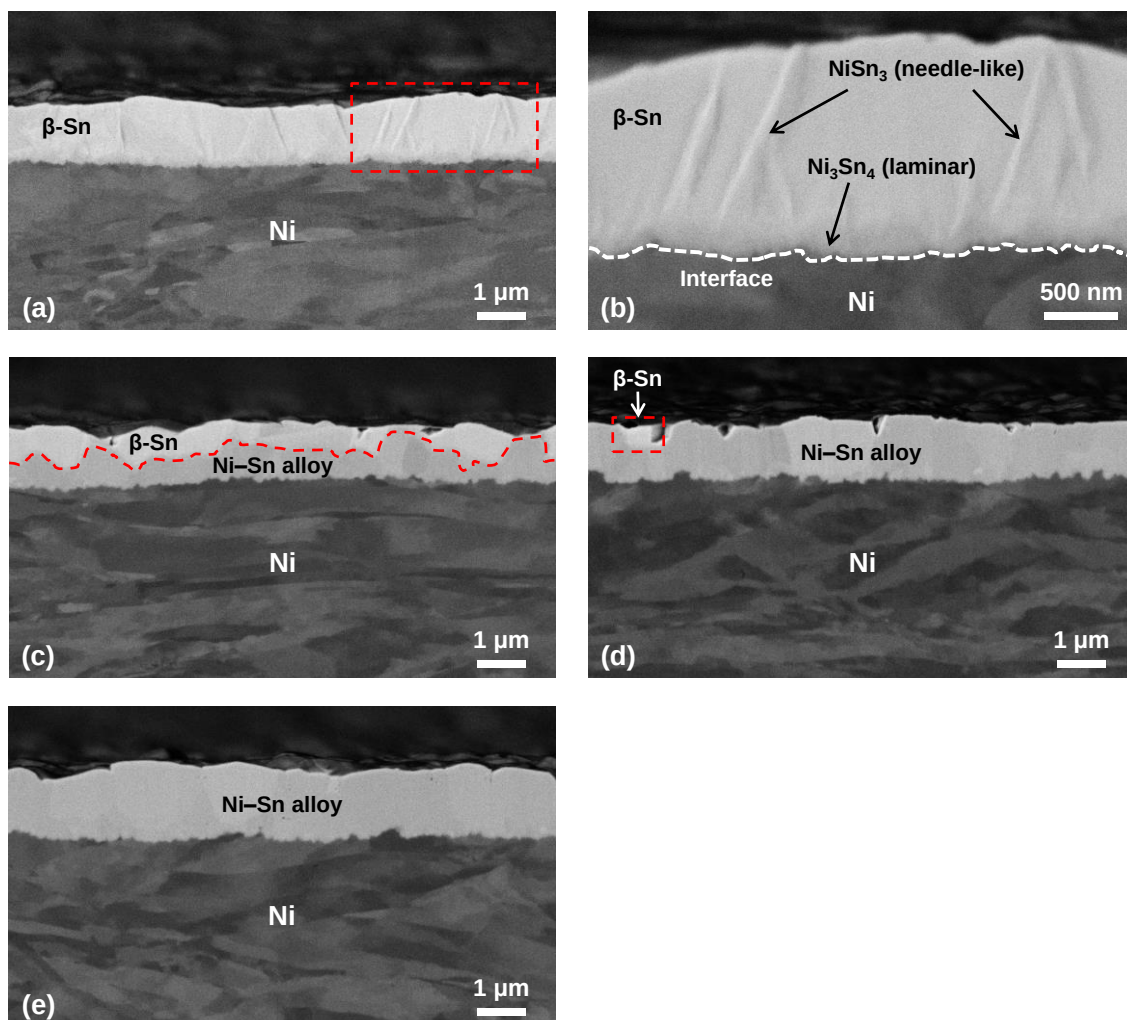


Figure 6-3 Selected cross-sectional FE-SEM images of annealed Sn–Ni films. (a) and (b) 0h-annealed film at different magnifications, (c) 2h-annealed film, (d) 10h-annealed film, and (e) 25h-annealed film. (b) shows the enlarged view of the red rectangular area of (a).

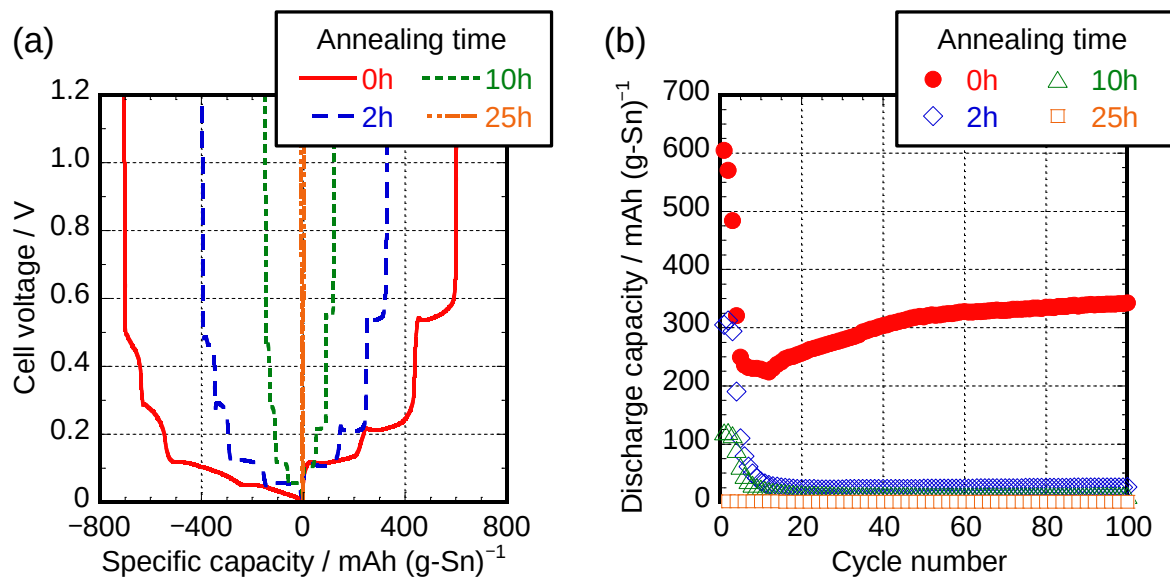


Figure 6-4 (a) Initial charge–discharge curves of annealed Sn–Ni films at a current density of 84.7 mA (g-Sn)⁻¹. (b) Cycle characteristics of these Sn–Ni films for 100 cycles.

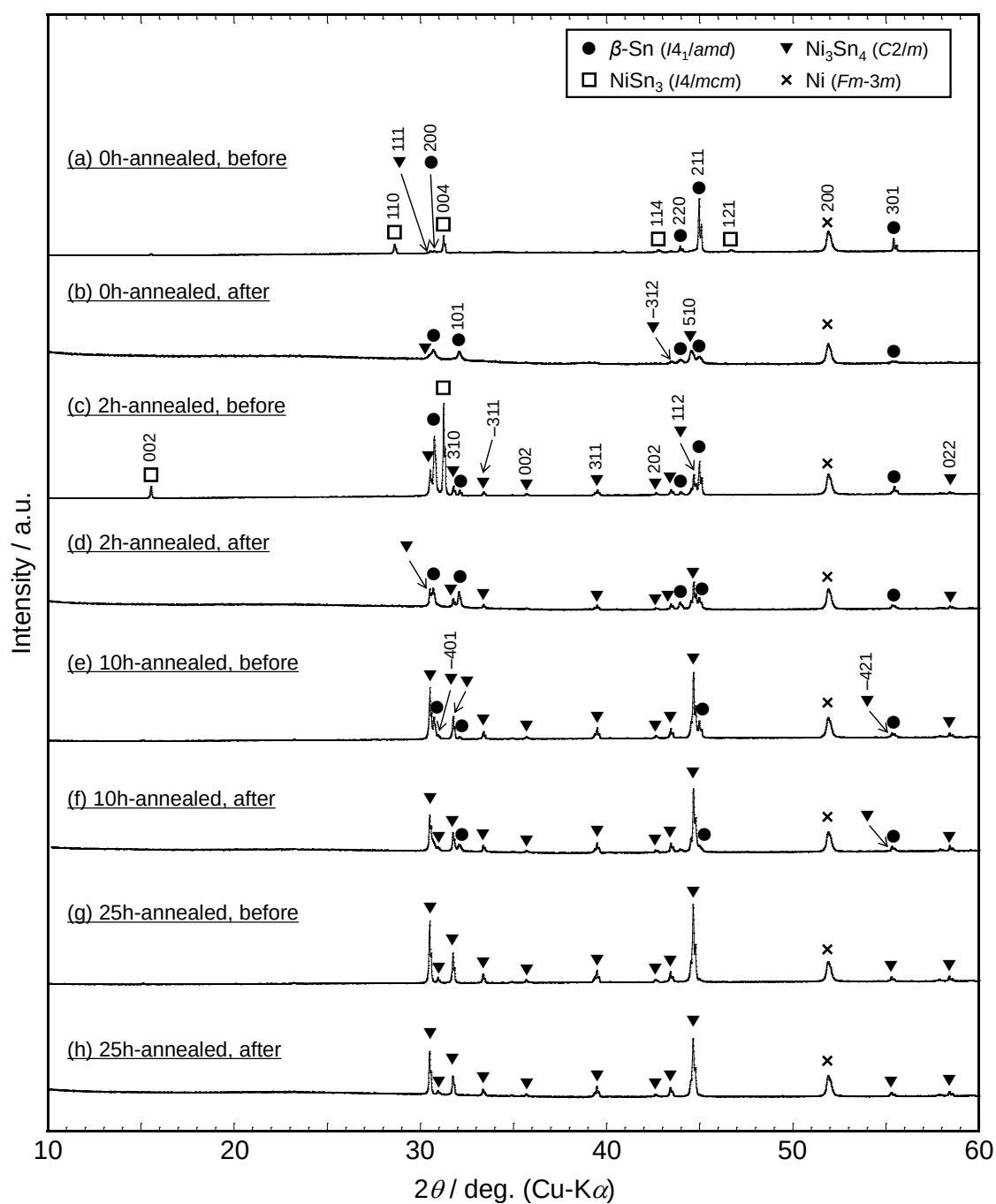


Figure 6-5 Comparison of the XRD patterns of Sn–Ni films before and after charge–discharge tests. (a) 0h-annealed, before, (b) 0h-annealed, after, (c) 2h-annealed, before, (d) 2h-annealed, after, (e) 10h-annealed film, before, (f) 10h-annealed film, after, (g) 25h-annealed film, before, (h) 25h-annealed film, after.

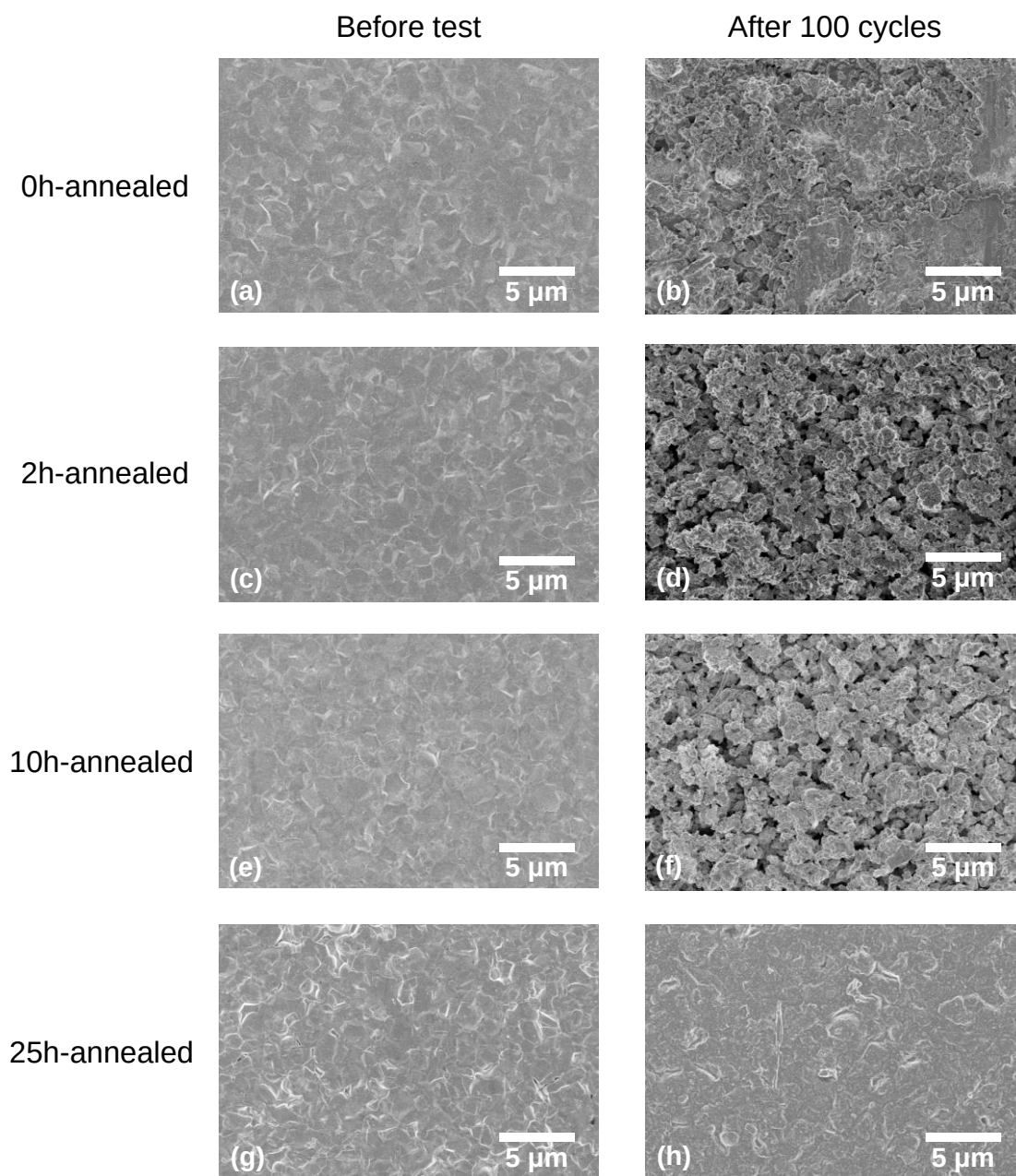


Figure 6-6 Representative surface SEM images of Sn–Ni films before and after charge–discharge tests. (a) 0h-annealed, before, (b) 0h-annealed, after, (c) 2h-annealed, before, (d) 2h-annealed, after, (e) 10h-annealed film, before, (f) 10h-annealed film, after, (g) 25h-annealed film, before, (h) 25h-annealed film, after.

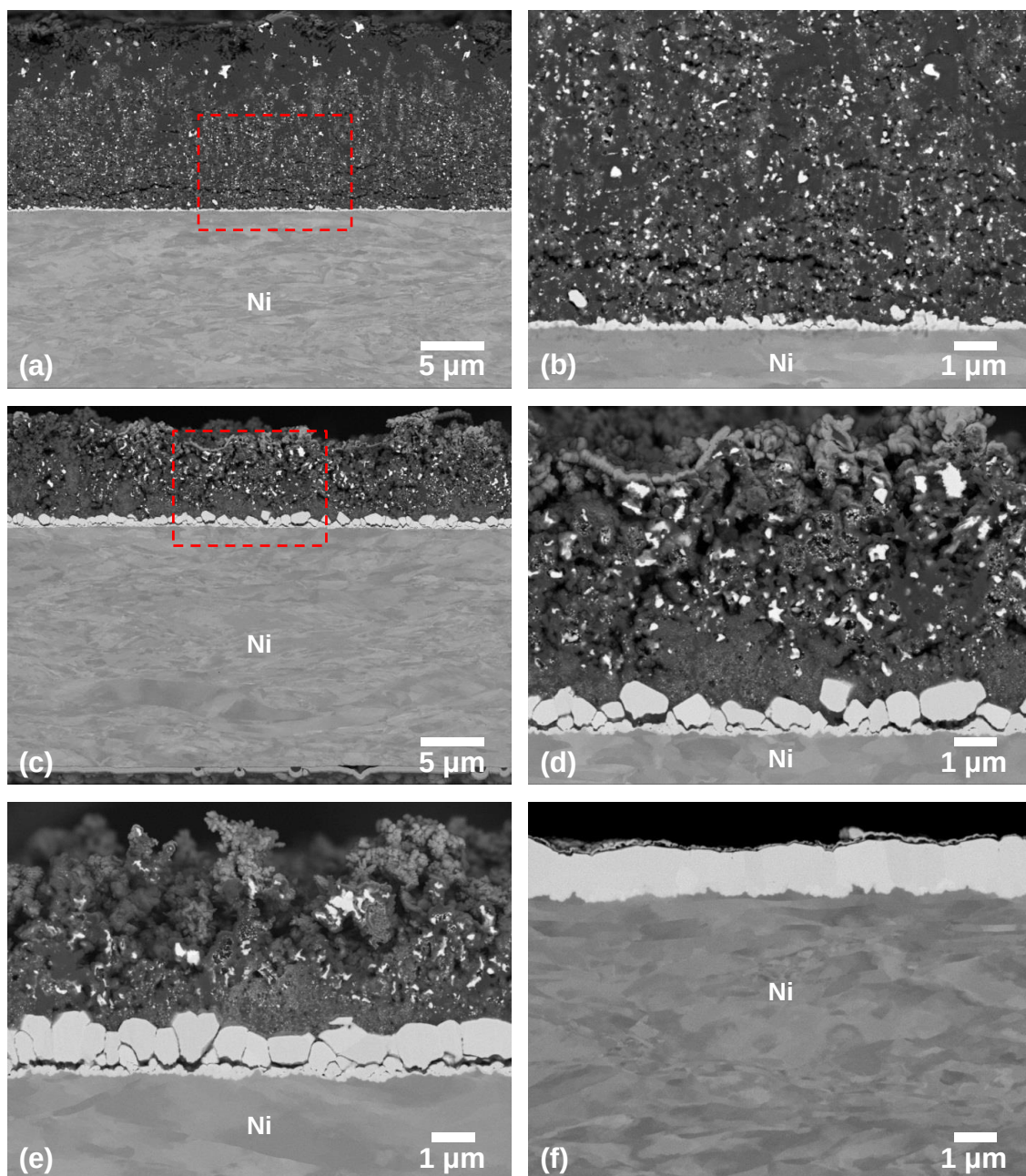


Figure 6-7 Representative cross-sectional SEM images of Sn–Ni films after charge–discharge tests. (a) and (b) 0h-annealed film at different magnifications, (c) and (d) 2h-annealed film at different magnifications, (e) 10h-annealed film, (f) 25h-annealed film. (b) and (d) show the enlarged views of the red rectangular areas of (a) and (c), respectively.

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Chapter 7

Charge–discharge behavior of Sn–Fe film

7.1 Introduction

In the previous chapter, charge–discharge behaviors of Sn–Ni films were investigated, and an interesting phenomenon was discovered. That is, the 0h-annealed Sn–Ni film exhibited a higher reversible capacity of $343 \text{ mAh (g-Sn)}^{-1}$ after 100 cycles, and though other Sn–Ni films showed poor cycleability and low capacities, which was opposite from the case of Sn–Cu films. These results suggest that the formation of M–Sn alloys by annealing does not necessarily play a role to prevent active materials from being electrically isolated. In addition, Ni_3Sn_4 phase is almost inactive with sodium, which is different from the case of lithium-ion batteries.

It is necessary to understand the electrochemical behavior of other Sn–M systems to explore new negative electrode materials for sodium secondary batteries with high charge and discharge performances. There are several reports on the Sn–Fe system for lithium-ion battery [1–6], and it has been found that metastable $\text{Fe}_{1-x}\text{Sn}_5$ phase and stable FeSn_2 phase react with lithium and show relatively high initial reversible capacities of approximately 700 and 500 mAh g^{-1} , respectively. In sodium-ion battery, it has recently been reported that $\text{Fe}_{1-x}\text{Sn}_5$ nanoparticles exhibit an initial reversible capacity of ca. 600 mAh g^{-1} [7]. However, to the best of our knowledge, there is no information on the reactivity of FeSn_2 phase with sodium.

The aim of this chapter is to evaluate cycle performances of Sn–Fe films which were prepared by annealing tin-coated iron foils, as negative electrodes for sodium secondary battery utilizing $\text{Na}[\text{FSA}]\text{--K}[\text{FSA}]$ ionic liquid as an electrolyte at 363 K. Several kinds of Sn–Fe films were prepared by the electrodeposition of tin on iron substrates and the subsequent annealing processes

at 533 K for 0–25 h. Moreover, an FeSn₂ film was prepared by removal of a SnO layer of the 25h-annealed Sn–Fe film, and its charge–discharge behavior mechanism was investigated.

7.2 Experimental

A glove box (Miwa Manufacturing Co., Ltd., DBO-1KH-HNBR2) or a glove box (Miwa Manufacturing Co., Ltd., 1ADB-3-O) connected with a gas purification system (Miwa Manufacturing Co., Ltd., MS3-P60S-N) under dry argon atmosphere was used to handle ionic liquids and assemble all of the electrochemical cells used for the experiments in this chapter. The dew points of the glove box were kept below 197 K. Na[FSA] and K[FSA] used for the experiments in this chapter were dried under vacuum at 353 K for 48 h prior to use. Tin-coated iron foils were prepared by electrodeposition of tin on iron foils. The loading mass of tin was determined to be 0.76(7) mg cm⁻² (corresponding to 1.05(9) μm thickness of tin) via inductively coupled plasma atomic emission spectroscopy (ICP-AES; Thermo Fisher Scientific, Inc., iCAP6300). Before electrochemical measurements, these Sn–Fe films were dried under vacuum at 363 K for 48 h, and some of them were annealed at 533 K under vacuum. Rotary vane pumps were used for drying and annealing processes, and achieved vacuum levels were ca. 1 Pa and 200 Pa, respectively. Annealing time was set at 2, 4, 10, or 25 h.

All electrochemical measurements in this chapter were performed under 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 thickness per sheet), used as a separator, were vacuum-impregnated with the electrolyte prior to the tests. The working electrode and the counter electrode were a Sn–Fe film and Na metal (Sigma-Aldrich, Inc., 99.85%), respectively. Charge–discharge rates were set at a current density of 84.7 mA (g-Sn)⁻¹ that corresponds to C/10 rate. Cut-off voltages were 0.005 and 1.200 V, and

the operating temperature was 363 K for all the tests in this chapter.

To characterize Sn–Fe films before and after charge–discharge tests, X-ray diffraction (XRD) analysis was applied to identify phases of the films using an X-ray diffractometer (Rigaku Co., SmartLab, Cu-K α radiation ($\lambda = 0.15418$ nm)) equipped with a one-dimensional high-speed detector (Rigaku Co., D/teX Ultra 250) with a nickel filter. All XRD patterns are normalized based on the peak intensity from Fe 211 reflection ($2\theta = 82.4^\circ$). The elemental compositions and chemical states of Sn–Fe films were investigated by X-ray photoelectron spectroscopy (XPS; JEOL, JPS-9010) combined with argon-ion etching. The surfaces and cross-sections were observed by a field emission scanning electron microscope (FE-SEM; Hitachi, SU-8020, or JEOL, JSM-7600F) with an energy dispersive X-ray spectrometer (EDX; Horiba, X-max, or Oxford Instruments, X-max^N80). Before the cross-sectional SEM observation, a cross-section polisher (CP; JEOL, IB090-20) was used to cut the Sn–Fe films. Prior to analysis of the samples after charge–discharge tests, the Na[FSA]–K[FSA] salts was removed using dehydrated and deoxidized tetrahydrofuran (Wako Pure Chemical Industries, Ltd., water content < 10 ppm, oxygen content < 1 ppm), and the samples were transferred to the XRD and FE-SEM apparatuses without air exposure by transfer vessels.

7.3 Results and discussion

7.3.1 Characterization of Sn–Fe films before charge–discharge tests

7.3.1.1 XRD

Figure 7-1 shows XRD patterns of the annealed Sn–Fe films. For the Sn–Fe film without annealing (hereinafter, called “0h-annealed film”), β -Sn and Fe current collector are detected, and the diffraction peak of β -Sn 200 ($2\theta = 30.7^\circ$) is strong (**Figure 7-1a**). In addition, no peaks derived from Fe–Sn alloys (FeSn₂ or FeSn) are observed, indicating that Fe–Sn alloys were not

formed during the drying process at 363 K for 48 h. The result is different from the cases of Sn–Cu and Sn–Ni films, in which Cu_6Sn_5 and small amounts of NiSn_3 were confirmed after the drying process (See **Chapters 5 and 6**). After annealing at 533 K for 2 h (**Figure 7-1b**), several peaks of FeSn_2 are confirmed and peak intensities of $\beta\text{-Sn}$ significantly decrease, which is consistent with the previous report that the formation rate constant of FeSn_2 phase drastically increases at around the melting point of tin (505 K) [8]. Moreover, a peak at $2\theta = 37.2^\circ$ is assigned to SnO 002 reflection, indicating that residual oxygen is not negligible for the oxidation of $\beta\text{-Sn}$ at 533 K in a vacuum level achieved by a rotary vane pump. Peak intensities of FeSn_2 and SnO increase with the annealing time. In the 25h-annealed film (**Figure 7-1e**), the peaks of pure metallic tin completely disappear, and the peaks of FeSn_2 and SnO are observed.

7.3.1.2 Cross-sectional FE-SEM

Representative cross-sectional SEM images of the annealed Sn–Fe films are shown in **Figure 7-2**. In the 0h-annealed film (**Figure 7-2a**), a $\beta\text{-Sn}$ layer of 1 μm thickness is observed on the Fe current collector. In contrast, inhomogeneous growth of FeSn_2 phase and the rougher Sn/Fe interface are confirmed in the 2h-annealed film, indicating that the formation of FeSn_2 proceeds from the Sn/Fe interface toward the surface of the tin film. The FeSn_2 area increases in the 4h-annealed film, and the $\beta\text{-Sn}$ area almost disappears in the 10h- and 25h-annealed films. Instead, a SnO layer of ca. 100 nm thickness is observed on the top surface of the 25h-annealed film (**Figure 7-2e**).

7.3.2 Charge–discharge characteristics of Sn–Fe films

Figures 7-3a and 7-3b show the initial charge–discharge curves for all the Sn–Fe films, and the enlarged curves for the 10h- and 25h-annealed films, respectively. Several plateaus corresponding to the alloying/dealloying of tin with sodium are clearly observed for the 0h-, 2h-,

4h-, and 10h-annealed films. The obtained initial discharge (dealloying) capacities are 730, 443, 173, and 52 mAh (g-Sn)⁻¹ for the 0h-, 2h-, 4h, and 10h-annealed films, respectively. Smaller discharge capacities are observed for Sn-Fe films with longer annealing times, because the amount of active β -Sn decreases with the length of the annealing time. Although the peaks of β -Sn have completely disappeared in the XRD pattern (**Figure 7-1e**), the 25h-annealed film shows an initial discharge capacity of 46 mAh (g-Sn)⁻¹. This would be explained by the fact that the 25h-annealed film possesses a larger amount of SnO. As shown in **Figure 7-3b**, two plateaus are observed at 0.45 V and below 0.05 V for the 25h-annealed film, and they closely resemble those for SnO negative electrodes for sodium-ion battery [9]. The discussion on this matter will appear again in the **Subsection 7.3.3.1**.

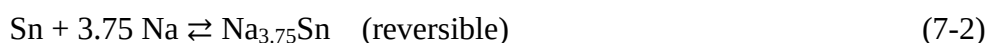
Cycleability of Sn-Fe films is compared in **Figures 7-3c** and **7-3d**. For the 0h-annealed film, although the high discharge capacities over 700 mAh (g-Sn)⁻¹ are observed in the 1st and 2nd cycles, the capacity rapidly decreases down to below 30 mAh (g-Sn)⁻¹ within initial 10 cycles, which is a typical capacity fade for tin negative electrodes, as shown in **Chapter 3**. Although the 2h-annealed film shows the capacity decline from 443 to 122 mAh (g-Sn)⁻¹ within initial 10 cycles, its capacity gradually recovers after 50 cycles and reaches 191 mAh (g-Sn)⁻¹ at 100th cycle. Such capacity recovery was also observed for Sn-Cu and Sn-Ni films, as shown in **Chapters 5** and **6**. For the 4h-annealed film, its capacity decreases from 173 to 76 mAh (g-Sn)⁻¹ within initial 10 cycles, and is maintained at around 80 mAh (g-Sn)⁻¹ after 100 cycles. The 10h- and 25h-annealed films exhibit stable cycle characteristics and retain their reversible capacities of 41 and 25 mAh (g-Sn)⁻¹, respectively, after 100 cycles.

7.3.3 Analysis of Sn-Fe films after charge-discharge tests

7.3.3.1 XRD

Figure 7-4 compares the XRD patterns of Sn-Fe films before and after charge-discharge

tests. For the 0h-annealed film, the $h00$ preferred orientation of β -Sn changes into the reported powder pattern, indicating that β -Sn electrochemically reacts with sodium as in the same case with Sn–Cu and Sn–Ni systems (See also **Chapters 5 and 6**). A similar tendency for β -Sn is observed in other Sn–Fe films after charge–discharge tests except for the 25h-annealed film. Since SnO peaks have disappeared after charge–discharge tests for the annealed Sn–Fe films, SnO reacts with sodium based on the following manner [9].



No detection of β -Sn peaks for the 25h-annealed film is explained by the smaller amount of initial SnO and the low crystallinity of electrochemically formed β -Sn. Peak intensities of FeSn_2 phase have decreased and its orientation has slightly changed, suggesting that FeSn_2 is active with sodium.

7.3.3.2 Surface FE-SEM

Surface SEM images of Sn–Fe films are shown in the **Figure 7-5**. All films possess smooth surfaces before charge–discharge tests. However, large cracks are seen on the surface of the 0h-annealed film after the test. As a result of EDX mapping, Fe substrate is clearly observed in the cracks. This large morphological change is originated from the large expansion/contraction of β -Sn, which leads to the rapid degradation of the negative electrode (**Figure 7-3c**). Although there are no large cracks in the 2h-annealed film, large pores are observed. These pores become smaller in the Sn–Fe films with longer annealing times, resulting in smoother surface morphologies. This is consistent with smaller reversible capacities having smaller volume changes.

7.3.3.3 Cross-sectional FE-SEM

Figure 7-6 depicts cross-sectional SEM images of the Sn–Fe films after charge–discharge tests. For the 0h-annealed film (**Figure 7-6a**), compared to the film before test (see also **Figure 7-2a**), the thickness of the active material layer has increased more than tenfold. Moreover, the formation of large pores and rougher top surface are confirmed. These morphological changes are consistent with surface SEM observation (**Figure 7-5b**) and the poor cycleability (**Figure 7-3c**). In the 2h-annealed film, relatively large particles (white color in the image) with a diameter of several micrometers are distributed in the vicinity of Sn/Fe interface. These particles are considered as FeSn_2 according to the EDX analysis. Moreover, it is worth noting that some FeSn_2 particles are refined into smaller ones, suggesting that FeSn_2 particles partly react with sodium. Concerning the 4h- and 10h-annealed films, similar morphological changes are confirmed. For the 25h-annealed film, some cracks appear in the FeSn_2 layer due to the strain from the reaction of SnO or FeSn_2 .

7.3.4 Charge–discharge mechanism of FeSn_2 phase

7.3.4.1 Preparation of an FeSn_2 film without a SnO layer

To prepare an FeSn_2 film without a SnO layer, the SnO layer of the 25h-annealed film is removed by argon-ion etching attached to the XPS apparatus. **Figure 7-7a** describes XPS depth profiles of the 25h-annealed film. Before argon-ion etching, peaks from Sn $3d_{5/2}$ and Sn $3d_{3/2}$ are observed at the oxidized states (486.5 eV for Sn $3d_{5/2}$ and 495 eV for Sn $3d_{3/2}$). No peaks from Fe $2p_{3/2}$ and Fe $2p_{1/2}$ are detected, suggesting that the surface of the film is covered with SnO layer. After etching for 20 s, the peak intensities corresponding to tin oxides decrease and new peaks appear at around 485 and 493 eV, which are assigned to the metallic state of tin. Simultaneously, peaks from Fe $2p_{3/2}$ and Fe $2p_{1/2}$ are also confirmed to be in the metallic state (707 eV for Fe $2p_{3/2}$ and 720 eV for Fe $2p_{1/2}$). After etching for 40 s, peak intensities of tin in the metallic states

become is enhanced relative to those of tin oxides. In addition, peak intensities ascribed to Fe 2p_{3/2} and Fe 2p_{1/2} increase simultaneously.

Figure 7-7b shows XRD patterns before and after argon-ion etching. The diffraction peak of SnO 002 ($2\theta = 37.2^\circ$) has almost disappeared after etching, indicating that most of the SnO layer has been removed. In addition, the peak intensities of FeSn₂ phase have slightly decreased to ca. 90% of those before etching. Hereinafter, the 25h-annealed film treated with 40sec-etching is called “FeSn₂ film”.

7.3.4.2 Charge–discharge mechanism of an FeSn₂ film without a SnO layer

Figure 7-8a compares the initial charge–discharge curves of the 25h-annealed film and the FeSn₂ film. As mentioned before, for the 25h-annealed film, the plateau corresponding to the reduction of SnO into β -Sn is observed at around 0.45 V in the 1st charge process. However, the capacity of such plateau is negligible in the initial charge curve of FeSn₂ film, which is consistent with the absence of SnO confirmed by XRD (**Figure 7-7b**). Moreover, a long plateau of approximately 300 mAh (g-Sn)^{−1} is confirmed below 0.05 V. According to the previous studies of Fe–Sn alloy negative electrodes for lithium-ion battery [1,2], the following mechanism has been proposed for the 1st charge (lithiation) process:



It is reasonable to consider a similar reaction for the 1st charge (sodiation) process of FeSn₂ phase, that is,



In the 1st discharge (desodiation) process, three distinct plateaus are observed at around 0.11, 0.22, and 0.54 V, which is the typical desodiation behavior of Na–Sn alloys (See also **Chapter 3**). Thus, the assumed whole reaction of the 1st discharge process is:



As shown in **Figure 7-8b**, after the 2nd cycle, several plateaus are observed below 0.6 V in both charge and discharge curves, which closely resembles the alloying/dealloying reaction of tin with sodium.



Figure 7-9a compares the XRD patterns of FeSn₂ film before and after the charge–discharge test. After the test, the peak intensities of FeSn₂ 002 and 211 ($2\theta = 33.7^\circ$ and 35.1°) have decreased to below 25% of initial intensities, suggesting that the large amounts of FeSn₂ phase have reacted with sodium. Moreover, as shown in the enlarged view of the XRD patterns (**Figure 7-9b**), the diffraction peaks of β -Sn 200 and 101 ($2\theta = 30.6^\circ$ and 32.0°) are newly confirmed, indicating that this β -Sn phase is formed by the electrochemical reaction of FeSn₂ (**Equations 7-4–7-6**).

Figure 7-10 shows the cross-sectional SEM images of the FeSn₂ films before and after the charge–discharge test. The thickness of the active material layer has increased from 1 to 5 μm during the test, indicative of the reaction between FeSn₂ and Na. White particles dispersed in the active material layer are considered to be FeSn₂ that remains unreacted.

7.3.4.3 Explanation of the lower capacities for Sn–Fe films with a SnO layer

Cycle characteristics of the 25h-annealed film and FeSn₂ film are compared in **Figure 7-8c**. Initial discharge capacities are 46 and 268 mAh (g-Sn)^{−1} for the 25h-annealed film and the FeSn₂ film, respectively. This difference is explained as follows. Since the 25h-annealed film possesses relatively thick a SnO layer (100 nm thickness, See **Figure 7-2e**), the inactive byproducts such as Na₂O are produced on the electrode surface during the reduction of SnO into Sn at 0.45 V in the 1st charge process (**Equation 7-1**). In fact, as described in **Figure 7-11**, the FeSn₂ layer of the 25h-annealed film is covered with a thick Na₂O layer after the charge–discharge test. Thus, sodium diffusion into the inner part of the electrode is blocked by the Na₂O layer, and most of the

FeSn₂ layer remains unreacted and does not contribute to the charge–discharge capacity. In contrast, since the FeSn₂ film possesses very small amount of SnO, little Sn and Na₂O are produced at 0.45 V and sodium can directly diffuse into FeSn₂ layer. As a result, the larger amount of FeSn₂ reacts with sodium in the 1st charge process below 0.05 V, which leads to the larger initial discharge capacity. After 2nd cycle, although the 25h-annealed film shows small discharge capacities below 50 mAh (g-Sn)^{−1}, the FeSn₂ film retains its capacities over 100 mAh (g-Sn)^{−1} for 25 cycles.

7.4 Conclusions

Various kinds of Sn–Fe films are prepared by annealing tin-coated iron foils at 533 K for 0–25 h. Their charge–discharge behaviors as negative electrode materials for sodium secondary batteries are investigated using Na[FSA]–K[FSA] ionic liquid at 363 K. The major findings in this chapter are summarized as follows:

1. As a result of XRD and cross-sectional FE-SEM analyses, β -Sn and Fe substrate were detected in the 0h-annealed film and the growth of FeSn₂ phase was confirmed in all the annealed films. Especially, for the 25h-annealed film, β -Sn region almost disappeared and a SnO layer of ca. 100 nm thickness was observed.
2. In the charge–discharge tests, Sn–Fe films with longer annealing times showed the smaller initial capacities due to the lower sodium activity of FeSn₂ phase compared to β -Sn. Although the capacities of the 0h-annealed film rapidly decreased from 730 to 30 mAh (g-Sn)^{−1} within initial 10 cycles, the 2h- and 4h-annealed films exhibited high capacities of 191 and 82 mAh (g-Sn)^{−1}, and better capacity retention ratios of 43 and 47% even after 100 cycles.
3. A thick SnO layer on the 25h-annealed film was removed by an argon-ion etching to prepare an FeSn₂ film. In the charge–discharge tests of the FeSn₂ film, the 1st discharge capacity was

268 mAh (g-Sn)⁻¹. Combined with XRD and FE-SEM analyses, FeSn₂ phase was indicated to be active with sodium and changed into Na–Sn alloys and Fe.

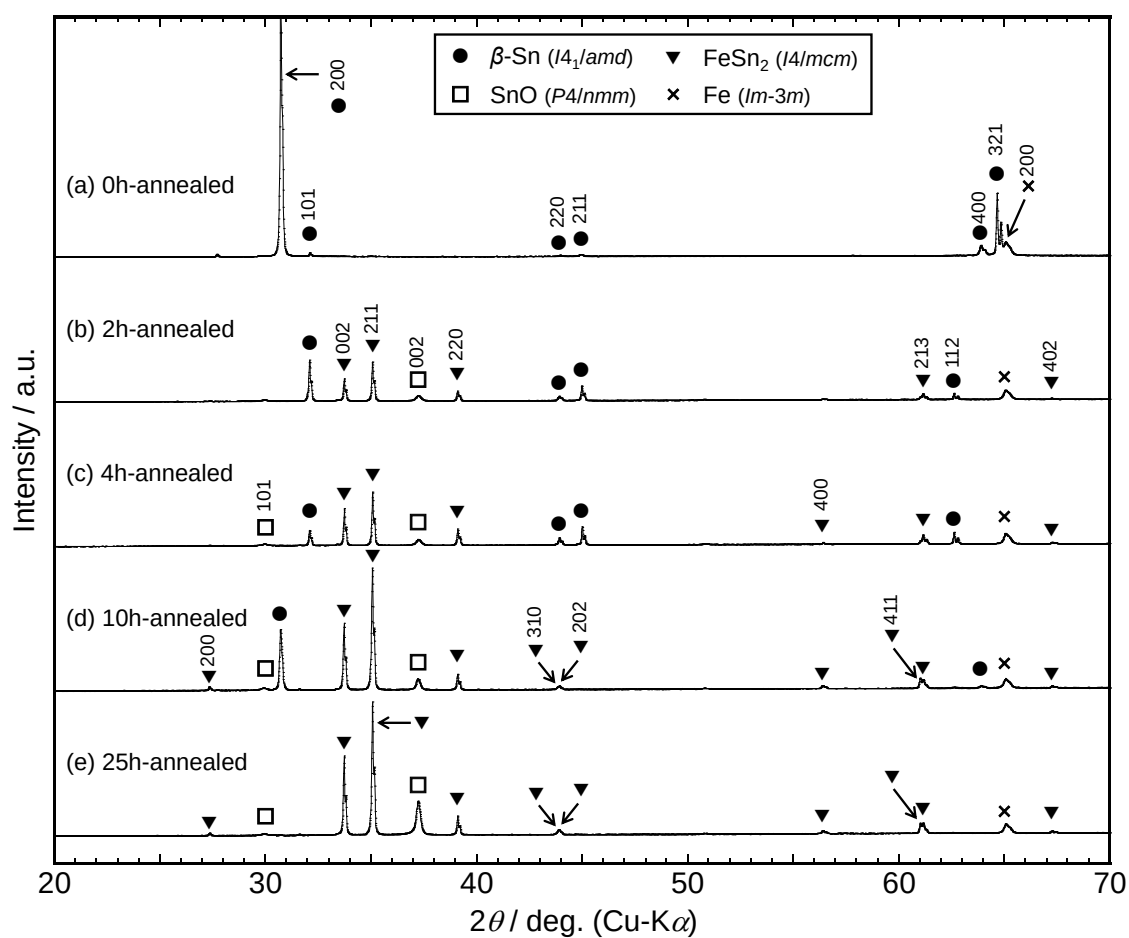


Figure 7-1 XRD patterns of annealed Sn-Fe films. Annealing temperature: 533 K. Annealing time: 0–25 h.

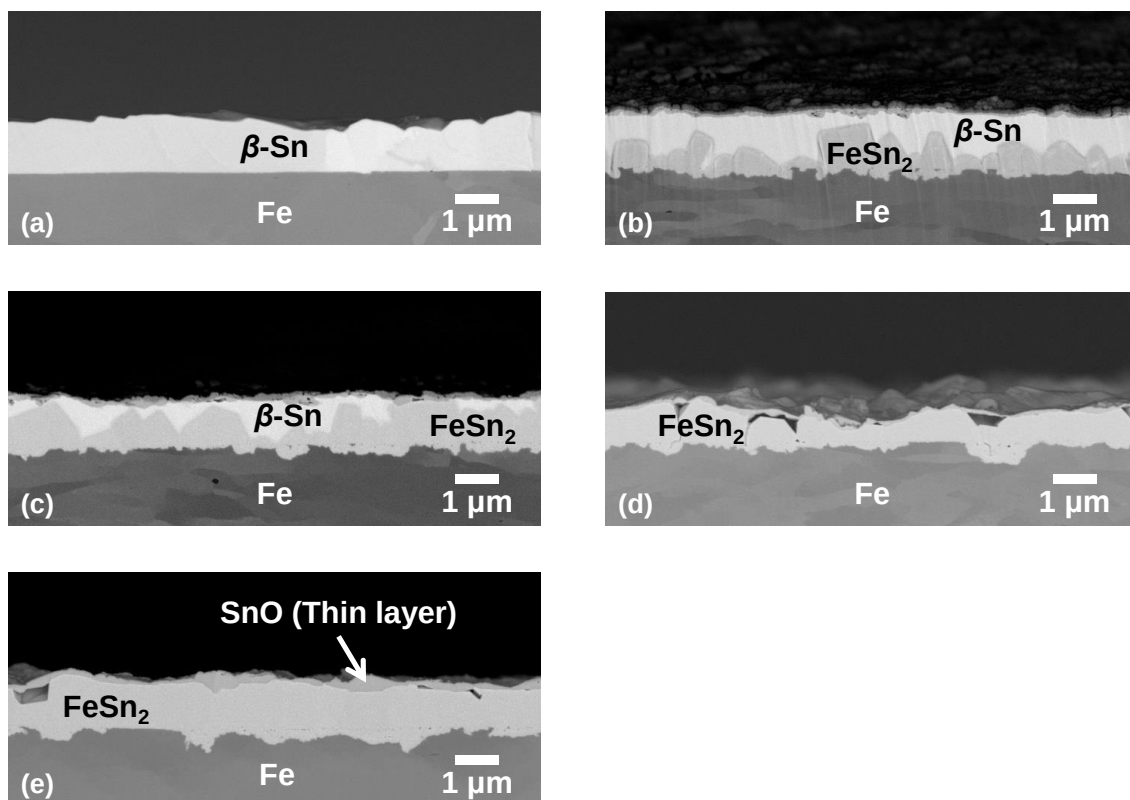


Figure 7-2 Selected cross-sectional FE-SEM images of annealed Sn–Fe films. (a) 0h-annealed film, (b) 2h-annealed film, (c) 4h-annealed film, (d) 10h-annealed film, and (e) 25h-annealed film.

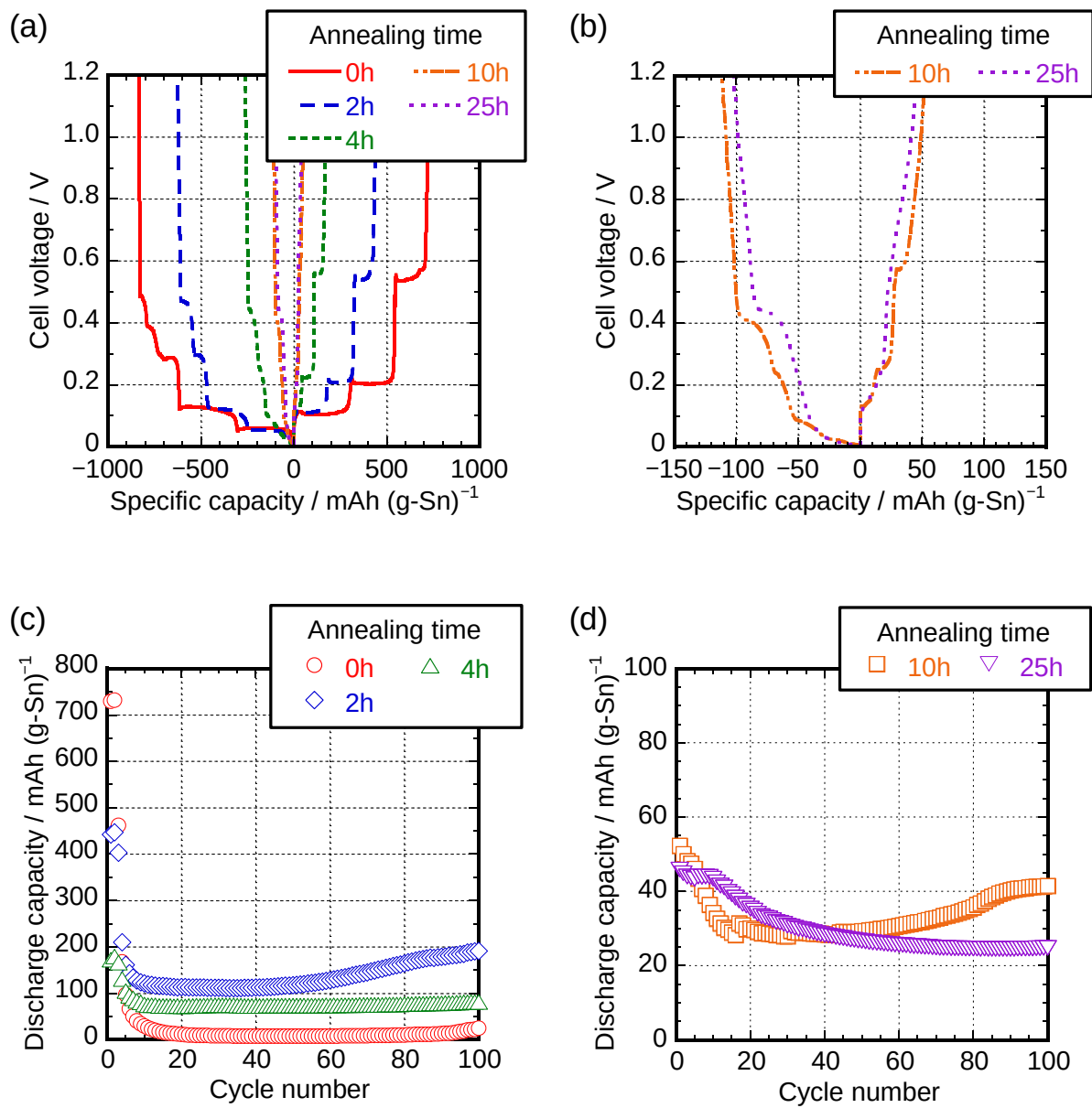


Figure 7-3 (a) and (b) Initial charge-discharge curves of annealed Sn-Fe films at a current density of $84.7 \text{ mA (g-Sn)}^{-1}$. (c) and (d) Cycle characteristics of these Sn-Fe films for 100 cycles.

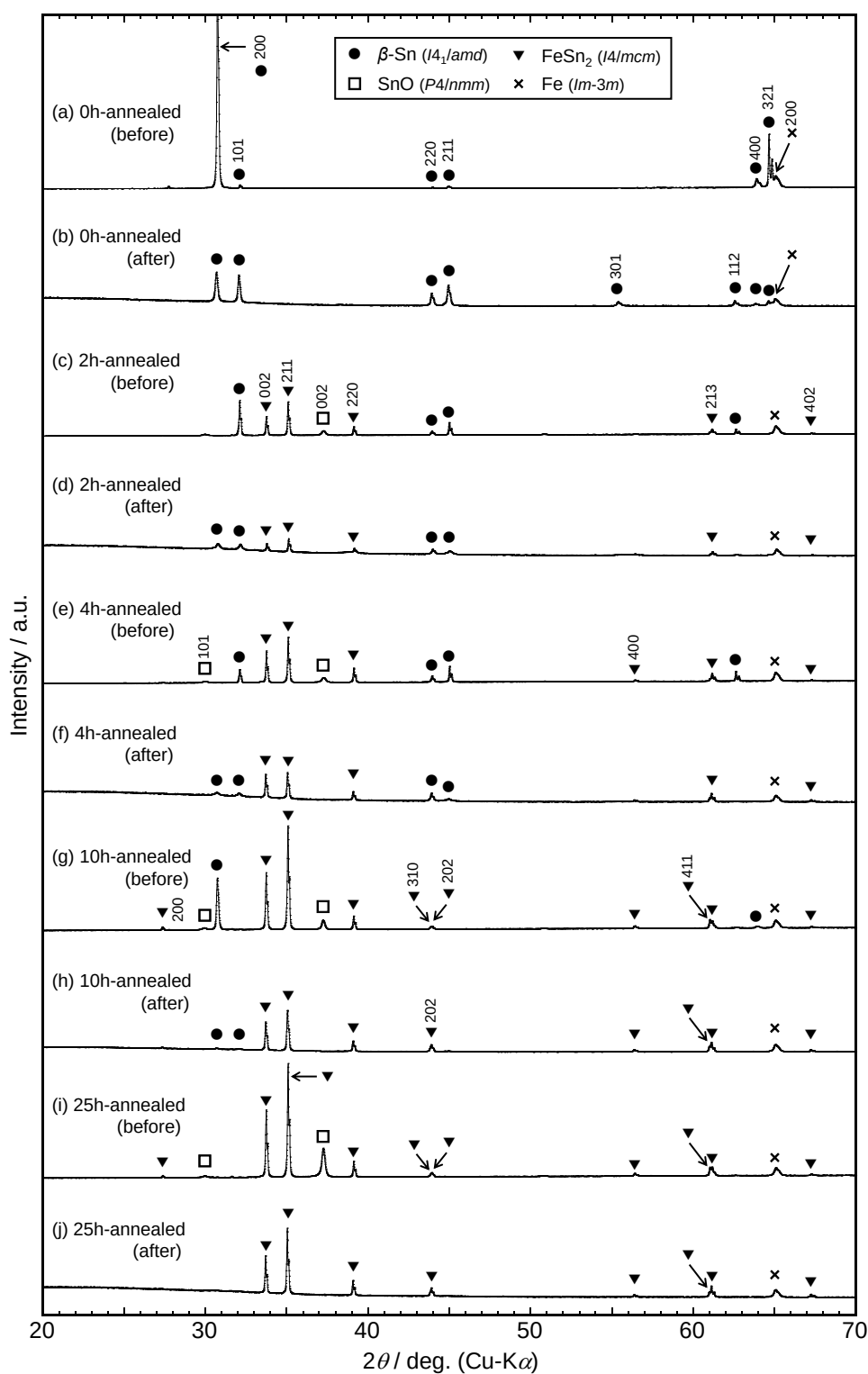


Figure 7-4 Comparison of the XRD patterns of Sn-Fe films before and after charge-discharge tests. (a) 0h-annealed, before, (b) 0h-annealed, after, (c) 2h-annealed, before, (d) 2h-annealed, after, (e) 4h-annealed, before, (f) 4h-annealed, after, (g) 10h-annealed film, before, (h) 10h-annealed film, after, (i) 25h-annealed film, before, (j) 25h-annealed film, after.

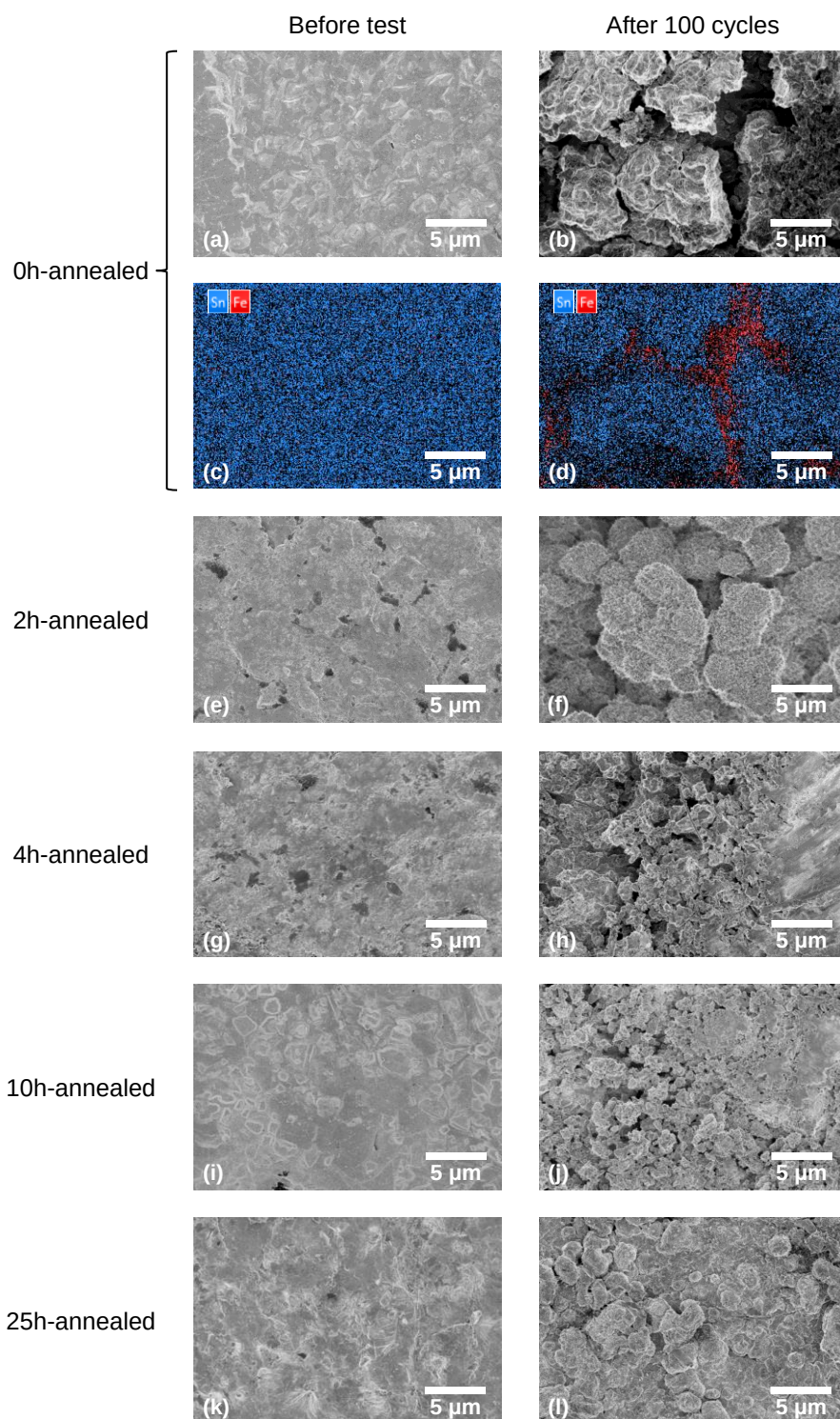


Figure 7-5 Representative surface SEM and EDX mapping images of Sn–Fe films before and after charge–discharge tests. (a) and (c) 0h-annealed, before, (b) and (d) 0h-annealed, after, (e) 2h-annealed, before, (f) 2h-annealed, after, (g) 4h-annealed, before, (h) 4h-annealed, after, (i) 10h-annealed film, before, (j) 10h-annealed film, after, (k) 25h-annealed film, before, (l) 25h-annealed film, after.

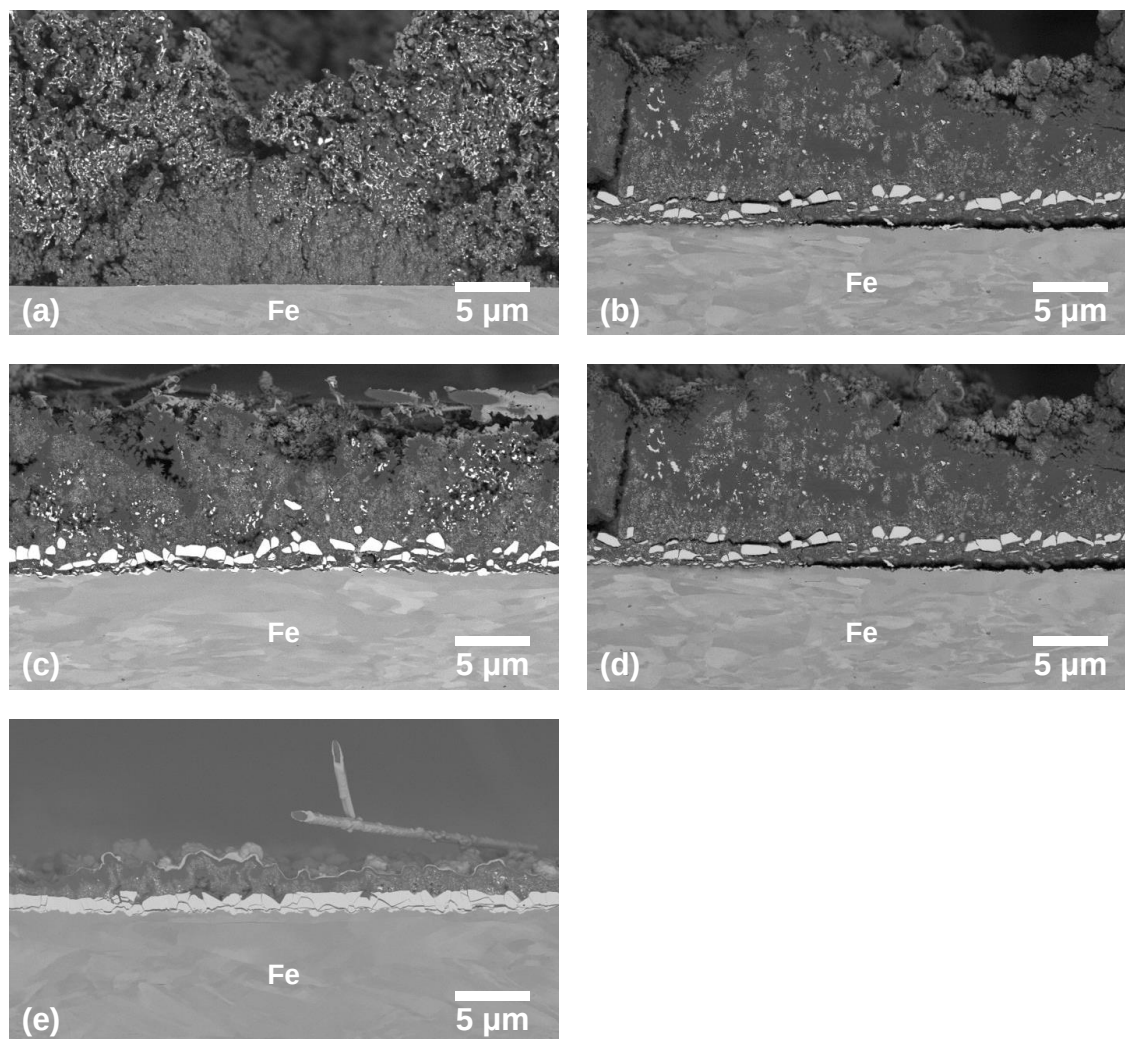


Figure 7-6 Selected cross-sectional SEM images of Sn-Fe films after charge-discharge tests. (a) 0h-annealed film, (b) 2h-annealed film, (c) 4h-annealed film, (d) 10h-annealed film, (e) 25h-annealed film.

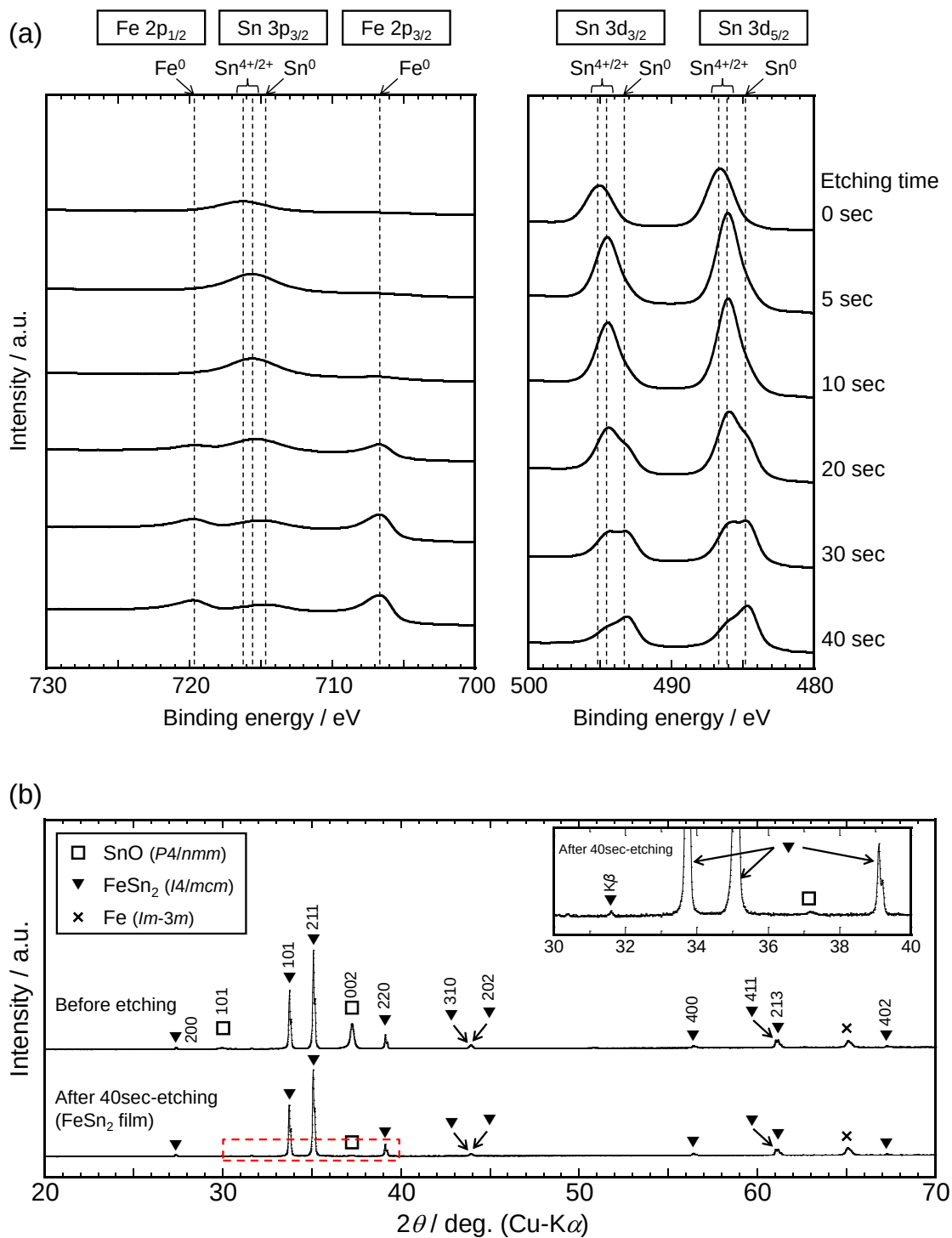


Figure 7-7 (a) XPS depth profiles of the 25h-annealed Sn-Fe film and (b) comparison of the XRD patterns of the 25h-annealed Sn-Fe film before and after 40sec-etching. Inset shows the enlarged views of the red rectangular region.

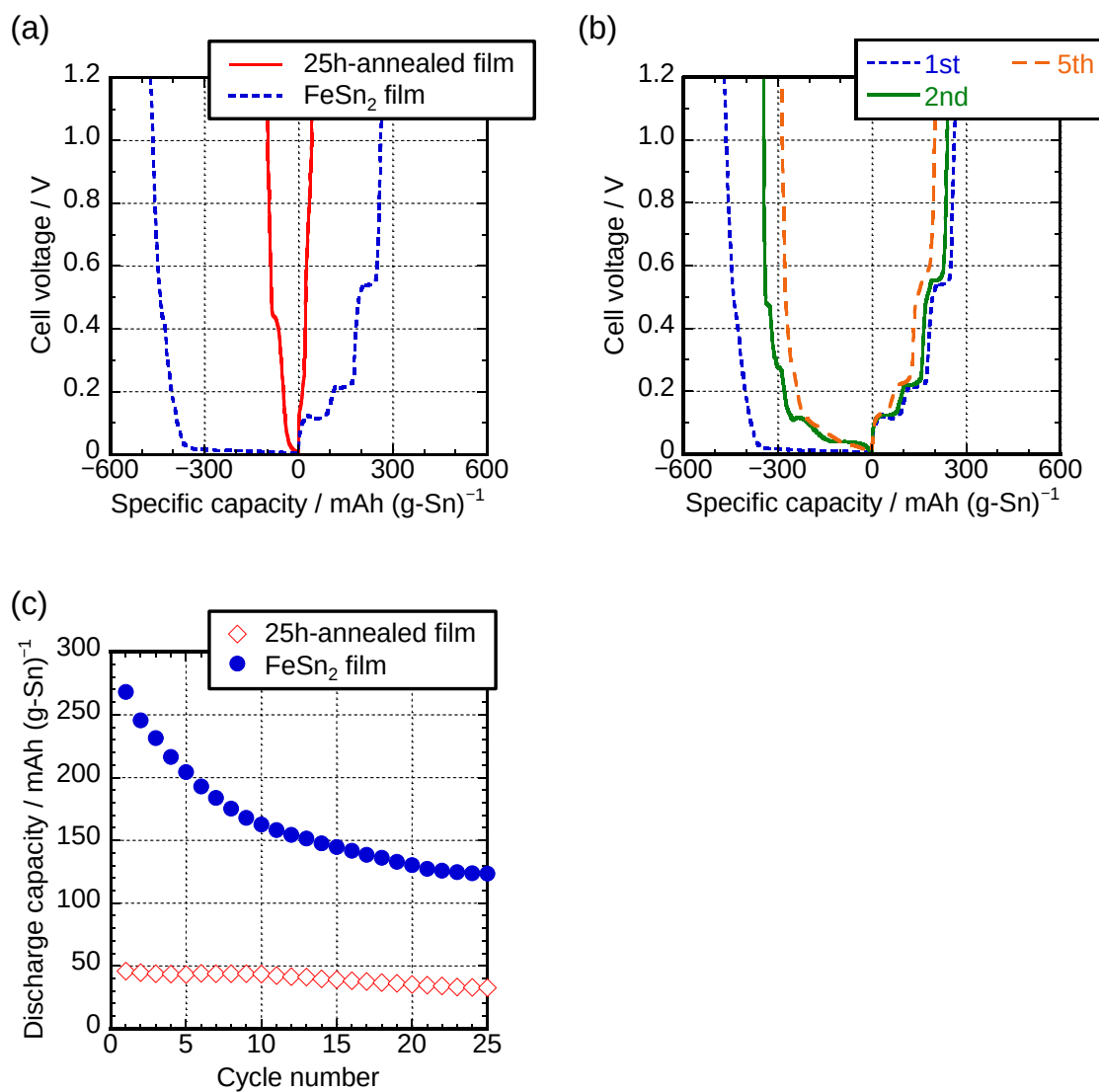


Figure 7-8 (a) Initial charge–discharge curves of the 25h-annealed film and the FeSn₂ film. Current density: 84.7 mA (g-Sn)⁻¹. Cut-off voltages: 0.005–1.200 V. (b) Charge–discharge curves of the 25h-annealed film and the FeSn₂ film. Cycle number: 1st, 2nd, and 5th. (c) Cycle characteristics of these Sn–Fe films for 25 cycles.

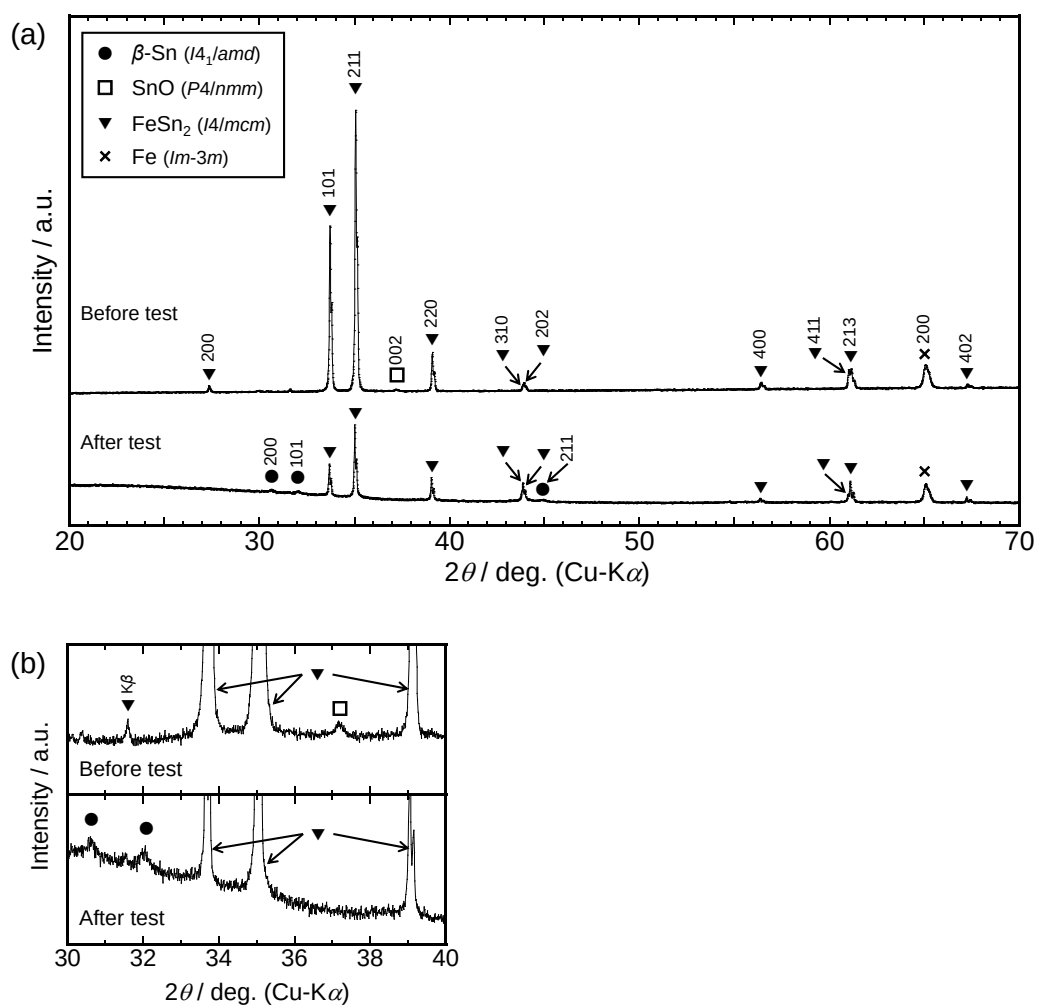


Figure 7-9 (a) XRD patterns of the FeSn₂ film before and after charge–discharge test. (b) Enlarged views of the XRD patterns of and the FeSn₂ film before and after charge–discharge tests.

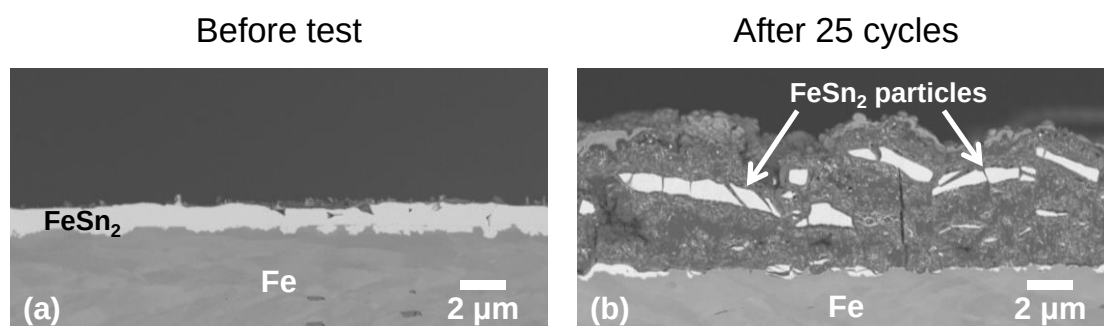


Figure 7-10 Representative cross-sectional FE-SEM images of the FeSn_2 film (a) before and (b) after the charge–discharge test.

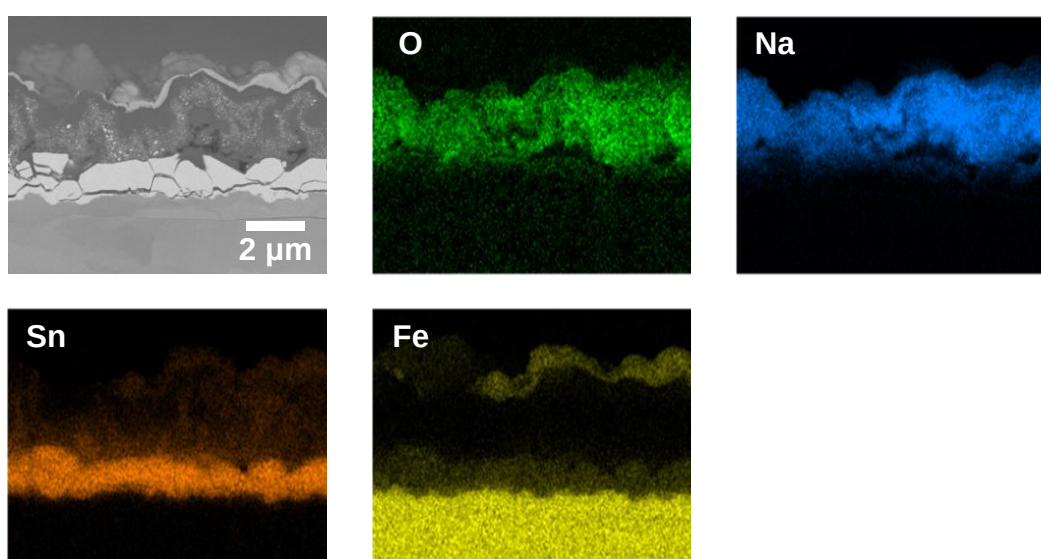


Figure 7-11 A selected cross-sectional FE-SEM image and EDX mapping for the 25h-annealed film after the charge–discharge test.

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Chapter 8

General conclusions

To overcome energy and environmental issues, it is necessary to establish a new energy supply system utilizing renewable energy resources and large-scaled electrical energy storage (EES) devices. Although lithium-ion battery is one of the candidates as EES devices, limited and unevenly distributed resources of lithium and cobalt may lead to the steep rise in price of the lithium-ion battery in the future. Thus, the development of new batteries that utilize more ubiquitous and abundant resources is urgently required. Sodium secondary battery is receiving much attention owing to the abundant resources of sodium in the crust and sea water.

Hagiwara *et al.* have developed a new class of electrolytes for sodium secondary batteries. For example, Na[FSA]–K[FSA] inorganic ionic liquid has high safety of nonflammability and negligible volatility, a wide electrochemical window, and thermal stability. However, in the previous studies, the highly-reactive sodium metal was used as the negative electrode. Thus, in the present study, with an aim to develop a new safer negative electrode material, the author investigated the electrochemical behavior of Na–Sn alloys and the charge–discharge behaviors of various tin-based negative electrode materials in Na[FSA]–K[FSA] eutectic melt ($x(\text{Na[FSA]}) = 0.56$) at 363 K. The results are summarized as follows:

In Chapter 3, the electrochemical formation of Na–Sn alloys was evaluated utilizing tin-coated aluminum foils (Sn–Al films) by cyclic voltammetry and galvanostatic charge–discharge tests. The obtained cyclic voltammogram suggested reversible alloying/dealloying of tin with sodium. In the charge–discharge tests within the cut-off voltages

of 0.005 and 1.200 V, three potential plateaus were observed during both the charging and discharging processes. They were tentatively assigned to the coexisting states of α -NaSn/ β -Sn (plateaus (a) and (a')), $\text{Na}_9\text{Sn}_4/\alpha$ -NaSn (plateaus (b) and (b')), and $\text{Na}_{15}\text{Sn}_4/\text{Na}_9\text{Sn}_4$ (plateaus (c) and (c')). Then, cycleability of each plateau was investigated, in which plateaus (c) and (c') gave the best capacity retention after 30 cycles. This is consistent with the hypothesis that the degradation of the tin negative electrode occurs by volume change, and that a smaller volume change gives better cycleability. Even after the degradation of a tin electrode, the recovery of discharge capacities was observed when sodium metal was deposited on the alloy electrode during the charging process. This is explained by “self-repairing” effect that the pulverized Sn and/or Na–Sn alloys reconnect electrically with each other due to the high diffusivity of deposited sodium metal at the operation temperature (363 K) close to the melting point of sodium (371 K).

In Chapter 4, thermodynamic studies were conducted on Na–Sn alloys at 363 K. The equilibrium potentials of Na–Sn alloys were investigated by galvanostatic intermittent titration technique (GITT). On the basis of this result, Na–Sn alloy samples were prepared by galvanostatic and potentiostatic electrolyses for *ex situ* XRD. Three Na–Sn alloy phases ($\text{Na}_{15}\text{Sn}_4$, trigonal $\text{Na}_{5-y}\text{Sn}_2$, and α -NaSn) were detected by XRD, and the Na composition of trigonal $\text{Na}_{5-y}\text{Sn}_2$ was tentatively assigned as Na_9Sn_4 ($y = 0.5$) from the quantity of electrical charge. Finally, thermodynamic calculations determined ΔG_f^0 value of α -NaSn to be $-23.9 \text{ kJ (mol-atom)}^{-1}$ at 363 K, which is in agreement with previously reported data.

In Chapter 5, Sn–Cu films were prepared by annealing tin-coated copper foils at 463 K for 0–45 h, and their charge–discharge behaviors were evaluated at 363 K. The Cu–Sn alloy formation progressed with the annealing time, and the β -Sn region almost disappeared after annealing for 10 h. In the charge–discharge tests, the Sn–Cu films with longer annealing times exhibited smaller initial capacities because Cu–Sn alloys were less active with sodium. On the other hand, the 4h-annealed film exhibited the stable reversible capacities of ca. 100–120 mAh

(g-Sn)⁻¹ for 1000 cycles. According to the results of XRD and FE-SEM analyses, less-active Cu-Sn alloys contributed to the formation of an appropriate domain structure, and acted as a buffer for the large volume change of tin.

In Chapter 6, Sn-Ni films were prepared by annealing tin-coated nickel foils at 463 K for 0–45 h, and their charge–discharge characteristics were investigated at 363 K. The 0h-annealed film consists of β -Sn, needle-like NiSn₃, and laminar Ni₃Sn₄. The 2h- and 10h-annealed films possessed a thicker Ni₃Sn₄ layer, and the 25h-annealed film was composed of only Ni₃Sn₄. In the charge–discharge tests, the 0h-annealed film exhibited the best capacity retention and maintained its reversible capacity of 343 mAh (g-Sn)⁻¹ after 100 cycles. In contrast, other films showed poor cycleability and capacities of lower than 50 mAh (g-Sn)⁻¹ after 10 cycles. XRD and FE-SEM analyses revealed that, in the 0h-annealed film, the needle-like NiSn₃ phase electrochemically separated into Na-Sn alloys and Ni₃Sn₄, and that the dispersed Ni₃Sn₄ fine particles contributed to the formation of a proper matrix for the large volume change. In the cases of the 2h- and 10h-annealed films, a thick Ni₃Sn₄ layer collapsed and became electrically isolated during the cycling. In addition, Ni₃Sn₄ was found to be almost inactive with sodium.

In Chapter 7, Sn-Fe films were prepared by annealing tin-coated iron foils at 533 K for 0–25 h, and their electrochemical behaviors of tin-coated iron foils were evaluated at 363 K. The growth of FeSn₂ was observed in the annealed films, and at the same time, the formation of SnO was confirmed. In the charge–discharge tests, the 0h-annealed film showed the rapid capacity decline from 730 to 30 mAh (g-Sn)⁻¹ within initial 10 cycles due to the absence of FeSn₂ phase. In contrast, the 2h- and 4h-annealed films showed better capacity retention ratios over 40%, and retained the discharge capacities of 191 and 82 mAh (g-Sn)⁻¹, respectively, after 100 cycles. The results of XRD and SEM analyses indicated that FeSn₂ particles in the active material layer acted as a buffer for the large volume change of β -Sn. However, the poor adhesion of the FeSn₂/Fe interface was also confirmed, suggesting that FeSn₂ phase reacted with sodium. Thus, an FeSn₂

film was prepared to investigate its charge–discharge behavior. The FeSn_2 film showed an initial discharge capacity of $268 \text{ mAh (g-Sn)}^{-1}$, leading to the conclusion that FeSn_2 phase electrochemically separated into Na–Sn alloys and Fe, *i.e.*, FeSn_2 phase possesses reactivity with sodium.

In the present study, to develop a new negative electrode materials for sodium secondary batteries using $\text{Na[FSA]}-\text{K[FSA]}$ inorganic ionic liquid, the electrochemical behaviors of tin and various tin-based materials were evaluated. Firstly, the mechanism of electrochemical formation of Na–Sn alloys was investigated, and their thermodynamic data were obtained. Then, to realize better cycleability of tin negative electrodes, the charge–discharge tests of the Sn–M systems ($\text{M} = \text{Cu, Ni, and Fe}$) were conducted and the role of M–Sn alloys were elucidated. On the basis of these fundamental data and knowledge, the performance of tin-based negative electrodes is well expected to be improved in the future.

Appendix

A.1 Thermodynamic calculation method

A.1.1 Activity of Na in Na–Sn alloys

Using equilibrium potentials, E (V vs. Na^+/Na), of Na–Sn alloys, as designated in **Table 4-3**, the activities of Na in Na–Sn alloys are calculated by **Equations A-1** and **A-2** [1].

$$-FE = \Delta \bar{G}_{\text{Na}} \equiv RT \ln a_{\text{Na}} \quad (\text{A-1})$$

$$\therefore a_{\text{Na}} = \exp \left[-FE/RT \right] \quad (\text{A-2})$$

A.1.2 Activity of Sn in Na–Sn alloys

Gibbs–Duhem equation is represented as **Equation A-3** [1],

$$x_{\text{Na}} d\bar{G}_{\text{Na}} + x_{\text{Sn}} d\bar{G}_{\text{Sn}} = 0 \quad (\text{A-3})$$

Then, transformation of **Equation A-3** leads to **Equations A-4** and **A-5**,

$$x_{\text{Na}} d(\ln a_{\text{Na}}) + x_{\text{Sn}} d(\ln a_{\text{Sn}}) = 0 \quad (\because \bar{G}_i = G_i^0 + RT \ln a_i) \quad (\text{A-4})$$

$$\ln a_{\text{Sn}} (\text{at } x_{\text{Sn}}) = \int_{x_{\text{Sn}}=1}^{x_{\text{Sn}}} d(\ln a_{\text{Sn}}) = - \int_{x_{\text{Sn}}=1}^{x_{\text{Sn}}} \frac{x_{\text{Na}}}{x_{\text{Sn}}} d(\ln a_{\text{Na}}) \quad (\text{A-5})$$

Thus, the activity of Sn is obtained according to **Equation A-5**. **Figure A-1** shows the $x_{\text{Na}}/x_{\text{Sn}} - \ln a_{\text{Na}}$ plots using the data of the present study (See **Table 4-3**).

In case of $x_{\text{Sn}} \rightarrow 1$, however, $\ln a_{\text{Na}}$ sometimes approaches minus infinity. Then, it is impossible to obtain the accurate integral value using **Equation A-5**. For example, using the values reported by Rivier *et al.* [2], the $x_{\text{Na}}/x_{\text{Sn}} - \ln a_{\text{Na}}$ plot at 623 K is obtained as shown in **Figure A-2**. Such a case appears when the alloy system has a solid-solution or a liquidus composition range at a certain temperature. To obtain the accurate integral value, Darken's

method [3] is employed. Firstly, transformation of **Equation A-4** leads to **Equation A-6**,

$$\begin{aligned}
 x_{\text{Na}} d(\ln x_{\text{Na}}) + x_{\text{Na}} d(\ln \gamma_{\text{Na}}) + x_{\text{Sn}} d(\ln x_{\text{Sn}}) + x_{\text{Sn}} d(\ln \gamma_{\text{Sn}}) &= 0 \\
 x_{\text{Na}} \frac{dx_{\text{Na}}}{x_{\text{Na}}} + x_{\text{Na}} d(\ln \gamma_{\text{Na}}) + (1 - x_{\text{Na}}) \frac{-dx_{\text{Na}}}{1 - x_{\text{Na}}} + x_{\text{Sn}} d(\ln \gamma_{\text{Sn}}) &= 0 \\
 x_{\text{Na}} d(\ln \gamma_{\text{Na}}) + x_{\text{Sn}} d(\ln \gamma_{\text{Sn}}) &= 0
 \end{aligned} \tag{A-6}$$

When α -function is defined as **Equation A-7**, **Equation A-8** is obtained.

$$\alpha_{\text{Na}} \equiv \frac{\ln \gamma_{\text{Na}}}{(1 - x_{\text{Na}})^2} \tag{A-7}$$

$$\therefore \ln \gamma_{\text{Na}} = \alpha_{\text{Na}} (1 - x_{\text{Na}})^2$$

$$\therefore d(\ln \gamma_{\text{Na}}) = (1 - x_{\text{Na}})^2 d\alpha_{\text{Na}} - 2(1 - x_{\text{Na}})\alpha_{\text{Na}} dx_{\text{Na}} \tag{A-8}$$

By substituting **Equation A-8** into **Equation A-6**,

$$\begin{aligned}
 d(\ln \gamma_{\text{Sn}}) &= -\frac{x_{\text{Na}}}{x_{\text{Sn}}} d(\ln \gamma_{\text{Na}}) \\
 &= -\frac{x_{\text{Na}}}{x_{\text{Sn}}} \left[(1 - x_{\text{Na}})^2 d\alpha_{\text{Na}} - 2(1 - x_{\text{Na}})\alpha_{\text{Na}} dx_{\text{Na}} \right] \\
 &= -x_{\text{Na}} x_{\text{Sn}} d\alpha_{\text{Na}} - 2x_{\text{Na}} \alpha_{\text{Na}} dx_{\text{Sn}}
 \end{aligned}$$

By integrating of the equation above,

$$\begin{aligned}
 \ln \gamma_{\text{Sn}} (\text{at } x_{\text{Sn}}) &= \int_{x_{\text{Sn}}=1}^{x_{\text{Sn}}} d(\ln \gamma_{\text{Sn}}) \\
 &= - \int_{x_{\text{Sn}}=1}^{x_{\text{Sn}}} x_{\text{Na}} x_{\text{Sn}} d\alpha_{\text{Na}} - 2 \int_{x_{\text{Sn}}=1}^{x_{\text{Sn}}} x_{\text{Na}} \alpha_{\text{Na}} dx_{\text{Sn}} \\
 &= - \left\{ \int_{x_{\text{Sn}}=1}^{x_{\text{Sn}}} d(x_{\text{Na}} x_{\text{Sn}} \alpha_{\text{Na}}) - \int_{x_{\text{Sn}}=1}^{x_{\text{Sn}}} \alpha_{\text{Na}} d(x_{\text{Na}} x_{\text{Sn}}) \right\} - 2 \int_{x_{\text{Sn}}=1}^{x_{\text{Sn}}} x_{\text{Na}} \alpha_{\text{Na}} dx_{\text{Sn}}
 \end{aligned}$$

$$\begin{aligned} \ln \gamma_{\text{Sn}}(\text{at } x_{\text{Sn}}) = & -(x_{\text{Na}} x_{\text{Sn}} \alpha_{\text{Na}} - 0) + \int_{x_{\text{Sn}}=1}^{x_{\text{Sn}}} \alpha_{\text{Na}} x_{\text{Na}} dx_{\text{Sn}} \\ & + \int_{x_{\text{Sn}}=1}^{x_{\text{Sn}}} \alpha_{\text{Na}} x_{\text{Sn}} dx_{\text{Na}} - 2 \int_{x_{\text{Sn}}=1}^{x_{\text{Sn}}} x_{\text{Na}} \alpha_{\text{Na}} dx_{\text{Sn}} \end{aligned}$$

Therefore, the activity coefficient of Sn is represented by a simple form in **Equation A-9**,

$$\ln \gamma_{\text{Sn}}(\text{at } x_{\text{Sn}}) = -x_{\text{Na}} x_{\text{Sn}} \alpha_{\text{Na}} - \int_{x_{\text{Sn}}=1}^{x_{\text{Sn}}} \alpha_{\text{Na}} dx_{\text{Sn}} \quad (\text{A-9})$$

Figure A-3 shows the $\alpha_{\text{Na}} - x_{\text{Sn}}$ plots at 623 K using the values reported by Rivier *et al.* [2].

Even at $x_{\text{Sn}} \rightarrow 1$, $\alpha_{\text{Na}} - x_{\text{Sn}}$ converges to a finite value, and the accurate value of the integral (Second term of the right side of **Equation A-9**) can be calculated. Then, activity of Sn is obtained as follows:

$$a_{\text{Sn}}(\text{at } x_{\text{Sn}}) = \exp \left[-x_{\text{Na}} x_{\text{Sn}} \alpha_{\text{Na}} - \int_{x_{\text{Sn}}=1}^{x_{\text{Sn}}} \alpha_{\text{Na}} dx_{\text{Sn}} \right] \times x_{\text{Sn}} \quad (\text{A-10})$$

A.1.3 Standard Gibbs free energy of formation for Na–Sn alloys

Standard Gibbs free energy of formation for Na–Sn alloys can be calculated using the activities of Sn and Na in the alloy, as follows:

$$\begin{aligned} \Delta \bar{G}_{\text{Na}} &= RT \ln a_{\text{Na}}, \Delta \bar{G}_{\text{Sn}} = RT \ln a_{\text{Sn}} \\ \Delta G_{\text{f}(\text{alloy})}^0 &= G_{\text{alloy}}^0 - x_{\text{Na}} G_{\text{Na}}^0 - x_{\text{Sn}} G_{\text{Sn}}^0 \\ &= \left(x_{\text{Na}} \bar{G}_{\text{Na}} + x_{\text{Sn}} \bar{G}_{\text{Sn}} \right) - x_{\text{Na}} G_{\text{Na}}^0 - x_{\text{Sn}} G_{\text{Sn}}^0 \\ \therefore \Delta G_{\text{f}(\text{alloy})}^0 &= x_{\text{Na}} \Delta \bar{G}_{\text{Na}} + x_{\text{Sn}} \Delta \bar{G}_{\text{Sn}} \end{aligned} \quad (\text{A-11})$$

Supposed that $\Delta H_{\text{f}(\text{alloy})}^0$ and $\Delta S_{\text{f}(\text{alloy})}^0$ are constant with temperature, $\Delta G_{\text{f}(\text{alloy})}^0 - T$ curve is

obtained as a straight line.

$$\Delta G_{f(\text{alloy})}^0 = \Delta H_{f(\text{alloy})}^0 - T\Delta S_{f(\text{alloy})}^0 \propto T$$

At the melting point of Sn or Na, the change in Gibbs free energy is zero; however, changes of fusion enthalpy and entropy should be taken into consideration. For instance, at the melting point of Sn, the deviation of standard enthalpy of formation for Na–Sn alloys is obtained.

$$\begin{aligned} \delta(\Delta H_{f(\text{alloy})}^0) &= \delta(H_{\text{alloy}}^0 - x_{\text{Na}}H_{\text{Na}}^0 - x_{\text{Sn}}H_{\text{Sn}}^0) \\ &= -x_{\text{Sn}}\delta H_{\text{Sn}}^0 \quad (\because \delta H_{\text{alloy}}^0 = 0, \delta H_{\text{Na}}^0 = 0) \\ \delta(\Delta H_{f(\text{alloy})}^0) &= -x_{\text{Sn}}(H_{\text{Sn(liquid)}}^0 - H_{\text{Sn(solid)}}^0) = -x_{\text{Sn}}\delta H_{\text{Sn(fusion)}}^0 \end{aligned} \quad (\text{A-12})$$

Similarly, the deviation of entropy of formation for Na–Sn alloys is

$$\delta(\Delta S_{f(\text{alloy})}^0) = -x_{\text{Sn}}(S_{\text{Sn(liquid)}}^0 - S_{\text{Sn(solid)}}^0) = -x_{\text{Sn}}\delta S_{\text{Sn(fusion)}}^0 \quad (\text{A-13})$$

Then, at the melting points of Sn and Na, the slope of the curve corresponding to $-\Delta S_{f(\text{alloy})}^0$ changes. Using **Equations A-12** and **A-13**, standard Gibbs free energy of formation for Na–Sn alloys at different temperatures is calculated. The calculated result is shown in **Figure A-4** (same as **Figure 4-7**).

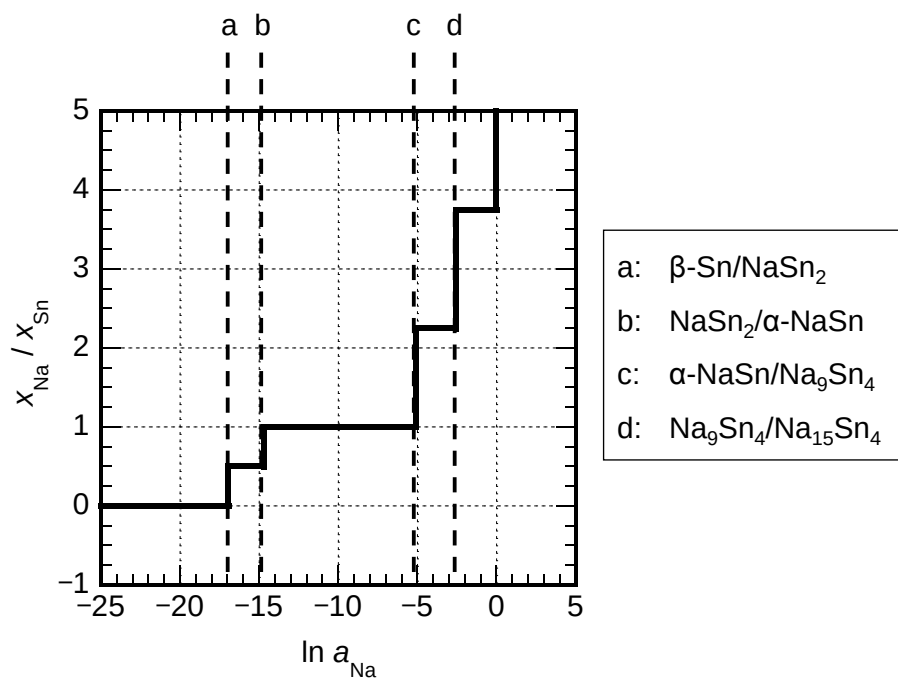


Figure A-1 The $x_{\text{Na}}/x_{\text{Sn}} - \ln a_{\text{Na}}$ plots at 363 K using the data obtained in the present study.

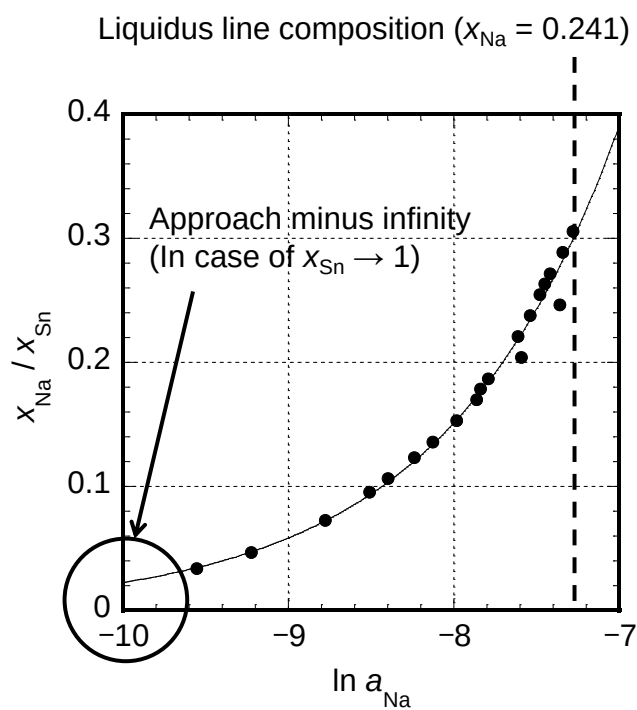


Figure A-2 The $x_{\text{Na}}/x_{\text{Sn}} - \ln a_{\text{Na}}$ plots at 623 K using the values reported by Rivier *et al.* [2].

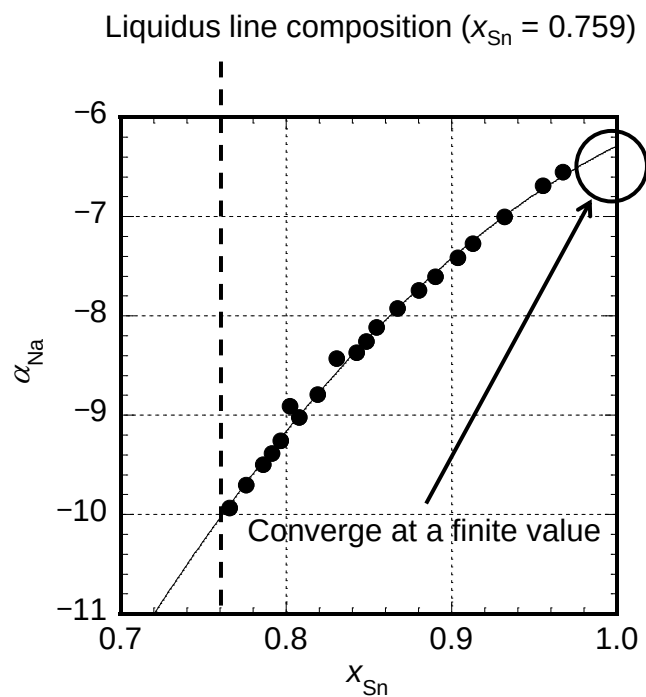


Figure A-3 The $\alpha_{\text{Na}} - x_{\text{Sn}}$ plots at 623 K using the values reported by Rivier *et al.* [2].

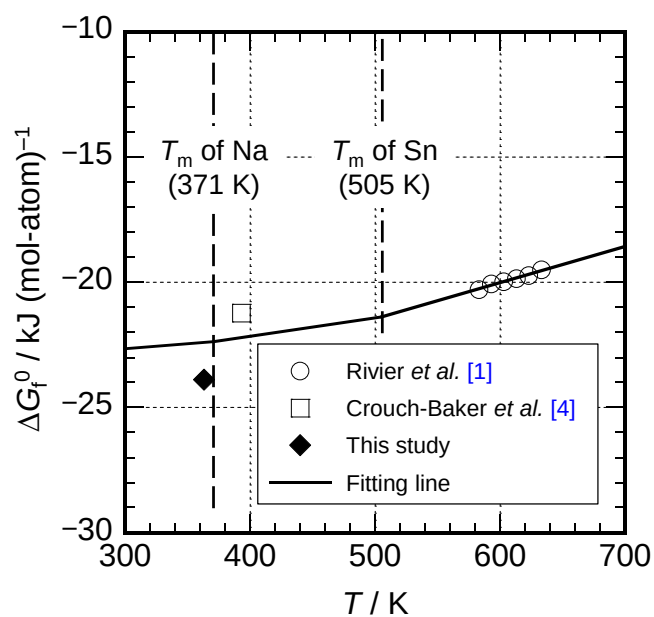


Figure A-4 Comparison of standard Gibbs free energies of formation for α -NaSn calculated from previous studies [2,4] and this study. The solid fitting curve is drawn based on the data reported by Rivier *et al.* [2] and thermodynamic data for Sn and Na [5] (same as **Figure 4-7**).

Nomenclature

$\Delta \bar{G}_i$	relative partial molar Gibbs free energy of component i ($i = \text{Na, Sn}$)
F	Faraday constant (96485 C mol^{-1})
E	potential (V vs. Na^+/Na)
R	gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)
T	temperature (K)
a_i	activity of component i ($i = \text{Na, Sn}$)
γ_i	activity coefficient of component i ($i = \text{Na, Sn}$)
x_i	mole fraction of component i ($i = \text{Na, Sn}$)
$\bar{G}_i$	molar Gibbs free energy of component i ($i = \text{Na, Sn}$)
G_i^0	standard molar Gibbs free energy of component i ($i = \text{Na, Sn}$)
H_i^0	standard molar enthalpy of component i ($i = \text{Na, Sn}$)
S_i^0	standard molar entropy of component i ($i = \text{Na, Sn}$)
$\Delta G_{\text{f(ally)}}^0$	standard Gibbs free energy of formation
$\Delta H_{\text{f(ally)}}^0$	standard enthalpy of formation
$\Delta S_{\text{f(ally)}}^0$	standard entropy free energy of formation

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A.2 Interpretation of Na_{5-y}Sn₂ phase formation

A.2.1 Identification of Na_{5-y}Sn₂ phase

As mentioned in **Chapter 4**, a new X-ray diffraction pattern of a Na–Sn alloy was recently reported by other groups [6–8]. Although Baggetto *et al.* [7] assigned this pattern as trigonal Na₅Sn₂ phase by Rietveld refinement, they later revised the Na composition from Na₅Sn₂ to Na₇Sn₃ [8]. However, the composition of Na₇Sn₃ implies the presence of Na defects in the Na₅Sn₂ structure, which makes difficult to determine the accurate Na composition by the Rietveld refinement and remains as a controversial issue. Thus, in the present study, Rietveld refinement was conducted upon the hypothesis that the composition of this phase is Na₅Sn₂ ($y = 0$).

The result of the refinement for sample 3 is shown in **Figure A-5**. The obtained XRD pattern in the present study is consistent with the previous reports, and crystallizes in the trigonal system and the space group of $R\bar{3}m$, with $a = b = 5.4240(18)$ Å, $c = 22.363(5)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $V = 569.8(4)$ Å³, and $Z = 3$. Unit cell parameters are presented in **Table A-1**.

A.2.2 Thermodynamic data based on Na₅Sn₂ phase formation

The standard Gibbs free energies of formation (ΔG_f^0) of Na–Sn alloys at 363 K were calculated based on the Na₅Sn₂ formation (**Table A-2**). As described in **Table A-3**, the obtained values were -17.0 , -23.9 , -20.3 , and -17.0 kJ (mol-atom)⁻¹ for NaSn₂, α -NaSn, Na₅Sn₂, and Na₁₅Sn₄, respectively. When compared with the case of Na₉Sn₄ formation, NaSn₂ and α -NaSn phases possess the same values because the calculation of activities of tin and sodium starts from the Na poorer phases, as documented in **Appendix A.1**. Although the ΔG_f^0 value of Na₅Sn₂ phase is slightly different from that of Na₉Sn₄ phase, they are close each other within the difference of -0.3 kJ (mol-atom)⁻¹. Concerning Na₁₅Sn₄ phase, no significant difference of the ΔG_f^0 value is observed in both cases.

Table A-1 Atomic coordinates, site occupancies and isotropic atomic displacement parameters of the sample No.3 obtained by Rietveld refinement.

Atom	Wyckoff	x	y	z	Occupancy	B ($\text{\AA}^2$)
Na(1)	3b	0	0	0.5	1	3.00
Na(2)	6c	0	0	0.3543(12)	1	3.00
Na(3)	6c	0	0	0.1996(12)	1	3.00
Sn(1)	6c	0	0	0.0668(4)	1	0.30

* The values of B for Na and Sn sites were fixed at 3.00 and 0.30, respectively.

** $R_{wp} = 7.29\%$, $R_p = 5.61\%$

Table A-2 Equilibrium potentials for Na–Sn alloys in Na[FSA]–K[FSA] at 363 K.

Formation reaction	Potential / V vs. Na^+/Na
$2 \beta\text{-Sn} + \text{Na}^+ + \text{e}^- \rightleftharpoons \text{NaSn}_2$	0.53
$\text{NaSn}_2 + \text{Na}^+ + \text{e}^- \rightleftharpoons 2 \alpha\text{-NaSn}$	0.46
$2 \alpha\text{-NaSn} + 3 \text{Na}^+ + 3 \text{e}^- \rightleftharpoons \text{Na}_5\text{Sn}_2$	0.16
$2 \text{Na}_5\text{Sn}_2 + 5 \text{Na}^+ + 5 \text{e}^- \rightleftharpoons \text{Na}_{15}\text{Sn}_4$	0.08

Table A-3 Comparison of standard Gibbs free energies of formation (ΔG_f^0) for Na–Sn alloys at 363 K, in the cases of Na_5Sn_2 and Na_9Sn_4 phase formation.

Phase	Standard Gibbs free energies of formation (ΔG_f^0) / kJ (mol-atom) $^{-1}$	
	The case of Na_5Sn_2 ($y = 0$)	The case of Na_9Sn_4 ($y = 0.5$)
NaSn_2	–17.0	–17.0
$\alpha\text{-NaSn}$	–23.9	–23.9
$\text{Na}_{5-y}\text{Sn}_2$	–20.6	–20.3
$\text{Na}_{15}\text{Sn}_4$	–16.6	–17.0

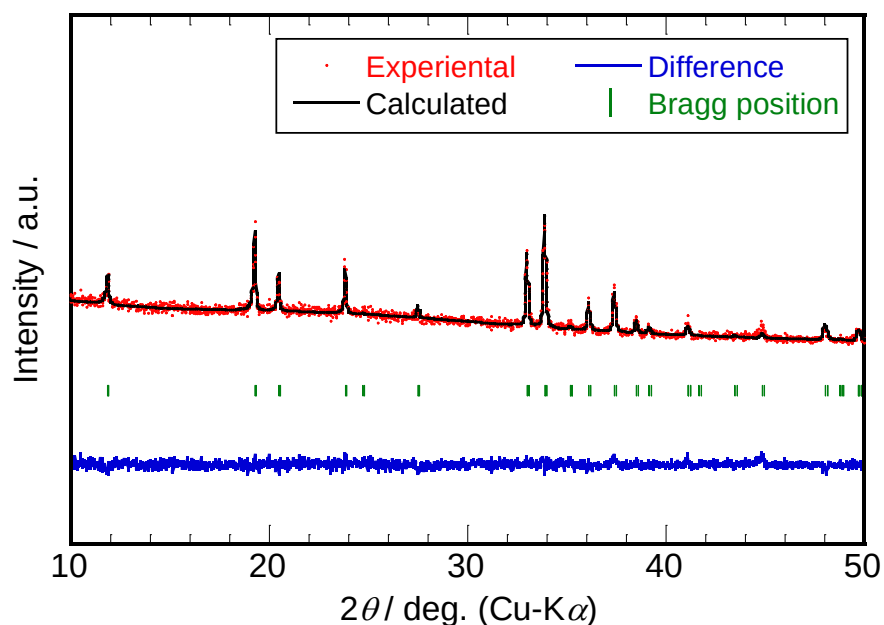


Figure A-5 An XRD pattern of the sample No.3 (Potential: 0.122 V vs. Na^+/Na), with Rietveld refinement of Na_5Sn_2 ($R_{\text{wp}} = 7.29\%$, $R_p = 5.61\%$), with the experiment data (red dots), calculated pattern (black line), Bragg positions (green bars), and difference curve (blue line).

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Chapter 3

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Journal of Power Sources, **217** (2012) 479–484.

“Charge–discharge behavior of tin negative electrode for a sodium secondary battery using intermediate temperature ionic liquid sodium bis(fluorosulfonyl)amide–potassium bis(fluorosulfonyl)amide”

Chapter 4

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Chapter 5

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Koji Nitta, Shinji Inazawa

Electrochimica Acta, **135** (2014) 60–67.

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

Chapter 6

Takayuki Yamamoto, Toshiyuki Nohira, Rika Hagiwara, Atsushi Fukunaga, Shoichiro Sakai,
Koji Nitta

Submitted to *Electrochimica Acta*.

“Charge–discharge behavior of Sn–Ni alloy film electrodes in an intermediate temperature ionic liquid for the electrolyte of a sodium secondary battery”

Chapter 7

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“Electrochemical behavior of Sn–Fe alloy film negative electrodes for a sodium secondary battery using inorganic ionic liquid Na[FSA]–K[FSA]”

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