Optimizing Micrometer-Sized Sn Powder Composite Electrodes for Sodium-Ion Batteries

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ABSTRACT

A nanometer-sized Sn (nano-Sn) powder composite electrode with polyacrylate binder delivers a discharge capacity of 600 mAh g⁻¹ with a good capacity retention for 100 cycles in non-aqueous Na cells, however, a micrometer-sized Sn (micro-Sn) composite electrode exhibits an insufficient cycle performance under the same condition. Although surface analysis of cycled electrodes reveals no apparent difference in solid electrolyte interphase layer formed on the nano- and micro-Sn electrodes, we found that in the case of nano-Sn electrodes the moderately porous composite layers and thin binder coating on Sn particles are responsible for a favorable cycle performance. On the other hand, the dense and less-porous micro-Sn electrode having a relatively thicker coating of binder on micro-Sn particles deteriorates the reversibility of sodium alloying reaction. Therefore, we optimize the electrode preparation process to introduce the suitable porosity and properly thin binder coating in the micro-Sn composite electrodes. The optimization enables the micro-Sn electrode to demonstrate high reversible sodiation capacity of 676–470 mAh g⁻¹ with much improved capacity retention over 100 cycles.

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Keywords : Sn Electrode, Alloy, Na-ion Batteries

1. Introduction

The research activity in development of higher capacity materials for Na-ion battery is rapidly growing in the 2010s, and the energy density of Na-ion battery has been incrementally improved by newly developing sodium insertion materials, binders, electrolytes, electrolyte additives etc. over the past decade based upon the finding and knowledge of Li-ion chemistry since the 1980s.1 Regarding negative electrodes of Na-ion battery, our group studied the mechanism of sodium storage into hard carbon and succeeded in demonstrating high capacity of 350–420 mAh g⁻¹.1,3 Moreover, p-block elements are known to show higher reversible capacities exceeding that of hard carbon; Sn and P electrochemically transform into Na₃.75Sn and Na₃P delivering 847 and 2,600 mAh g⁻¹, respectively.5,6 Though large theoretical capacities can be expected in these materials, they are limited to use as sodium poly(γ-glutamate), and sodium polyacrylate (PANa) which are effective for Sn–Na system as well as Si–Li and P–Na systems.11–14 These binders efficiently suppress the electric isolation of active materials in the composite electrode and act as pre-formed solid electrolyte interphase (SEI). As a result, the decomposition of the electrolyte is suppressed, leading to improvement of electrochemical performances.

As reported by Nam et al., sodium alloying property of electrodeposited Sn electrodes depends on grain sizes of the Sn film, that is, micrometer-sized Sn deposited electrode showed an abrupt capacity degradation after 5 cycles due to the detachment of Sn grains from the Cu substrate, and nanometer-sized Sn grains are advantageous for long-term cycle.15 They described that improved adhesion between an electrodeposited Sn film and the current collector is of importance to achieve a good electrode performance. We reported that a nanometer-sized Sn (hereafter denoted as nano-Sn) powder composite electrode delivered approximately 700 mAh g⁻¹ reversible capacity over 100 cycles by adding graphite and a functional binder, PANa, with the voltage range between 0.00 and 0.65 V vs. Na to avoid oxidative SEI dissolution occurring at 0.68 V vs. Na.16 However, the application of nano-Sn particles to rechargeable batteries is not a realistic solution, because nanosized powder is expensive, much lower tap-density, and dust toxicity, resulting in the difficulty of a practical battery application. Therefore, larger size particles, such as micrometer-sized Sn (micro-Sn) electrodes, are greatly preferable to nano-Sn electrodes. In this article, we elucidate the difference in sodium alloying properties of the nano- and micro-Sn electrodes by using PANa binder to understand the mechanism of capacity decay. On the basis of the understanding, we succeed in preparing the
2.1 Preparation of electrodes and test cells

Two types of reagent-grade Sn powder (Sigma-Aldrich Inc.) were used as the active material without any pretreatment: nano-Sn powder of less than 150 nm in diameter and micro-Sn powder less than 10 µm particles (average particle size: 1–2 µm), with surface areas of 5.6 and 1.1 m² g⁻¹, respectively. Four kinds of conductive carbon materials were used to meet each specific purpose: 3-, 15-, and 30-µm flaky graphites (SNO-3, SNO-15, and SNO-30, respectively, SEC Carbon, Ltd.) and acetylene black (AB). PANa (molecular weight is 2,000,000–6,000,000, Kishida Chemical Co., Ltd.) was used as a binder in this study. The Sn composite electrodes basically consist of a mixture of Sn powder:carbon:PANa = 80:10:10 in weight, except for the study of the dependence on binder content as described below for the electrode optimization.

For the electrode preparation, Sn powder, carbon, and PANa were thoroughly mixed with a dispersant of 10 vol% methanol aqueous solution to prepare a uniform slurry. Each prepared slurry was pasted onto an Al foil uniformly with a doctor blade and dried at 40, 80 or 150°C under atmospheric pressure overnight followed by drying in a vacuum oven for 1 day at the same temperature as the atmospheric pressure drying. The electrode dried at 40°C under atmospheric pressure was dried at 80°C in a vacuum oven. The composite electrodes were punched into discs of 10 mm in diameter, and the loading mass of Sn was around 1.6 mg cm⁻².

R2032-type coin cells were assembled with the Sn composite disc and sodium metal as working and counter electrodes, respectively, which are separated with a glass fiber filter (GB-100R, ADVANTEC) and a microporous polyolefin membrane (Toray Co., Ltd.). The electrolyte solution used is 1.0 mol dm⁻³ NaPF₆ in ethylene carbonate (EC) and diethyl carbonate (DEC) (49:49 vol%, battery grade, Kishida Chemical Co., Ltd.) and 2 vol% fluoroethylene carbonate (FEC) as an electrolyte additive. The cells were assembled in an Ar-filled glove box with the dew point below −95°C.

2.2 Charge-discharge cycle test

The assembled coin cells were tested at 25°C with a battery tester (TOSCAT-3100, Toyo System Co., Ltd.). As the 1st cycle, the Sn 2.2 Charge-discharge cycle test composite electrodes were punched into discs of 10 mm in diameter, atmospheric pressure was dried at 80°C in a vacuum oven. The cell was cycled with a constant current mode. From the 2nd cycle, charge after reaching 0.03 V, the voltage was maintained until the total reduction time including the plateau at 0.56 V only. The second one is Coulombic efficiency of the 1st cycle: 72 and 86% for the nano- and micro-Sn electrodes, respectively, though no significant difference in efficiency is observed after the 2nd cycle. The third one is the charge profile. Figure 2(a) compares the 1st cycle charge curves of the nano- and micro-Sn electrodes, in which four voltage-plateaus located at 0.38, 0.18, 0.07, and 0.03 V appear for the nano-Sn electrode and are referred to Plateau 1, 2, 3, and 4, respectively, as seen in the figure. On the other hand, Plateau 1 does not appear in the micro-Sn electrode, though Plateaus 2, 3, and 4 are observed clearly without apparent polarization. Accordingly, the third difference is found in the 1st cycle charge curves: apparent Plateau 1 only for the nano-Sn electrode. Figure 2(b) compares the discharge curves at the 2nd cycle since the efficiency becomes similar between the nano- and micro-Sn electrodes from the second cycle. In Fig. 2(b), 3 plateaus at 0.18, 0.28 and 0.56 V are found, which are referred to Plateaus 4, 3, and 2, respectively. It was reported that Plateaus 4, 3, and 2 are reverse reactions of Plateaus 4, 3, and 2, respectively. 

The trend of voltage variation during desodiation of the two electrodes is almost the same, indicating no significant difference in the phase evolution during desodiation between the two electrodes. Additionally, we found a larger initial charge capacity of 830 mAh g⁻¹ for the micro-Sn than that of nano-Sn one, 615 mAh g⁻¹, and the initial discharge capacity was larger for the micro-Sn. The difference in the initial charge capacity originates from lower current flow during the constant voltage application (see Supporting Information, Fig. S1). The smaller discharge capacity of nano-Sn electrode is probably due to the larger portion of tin oxides, SnO and SnO₂, as native oxide in as-received nano-Sn.
The electrochemical reaction of Plateau 1 is not fully understood in previous reports.\textsuperscript{15–17} We previously reported that oligomer/polymer on the nano-Sn electrode surface, which was believed to be a part of SEI layer, was anodically oxidized and dissolved at 0.68 V. Indeed, when the desodiation voltage is expanded beyond 0.68 V, Plateau 1 appeared in the following charge curves.\textsuperscript{13} Therefore, we supposed that Plateau 1 corresponds to the reaction to form SEI, and the SEI layer on Sn-Na alloy should not suffer from the oxidative dissolution in this study since the upper cutoff voltage is limited up to 0.65 V. As shown in Fig. 2(a), some plateaus corresponding to the Sn alloying reactions are observed at lower voltage for the both electrodes. One of the possible reasons for the disappearance of Plateau 1 for the micro-Sn is the smaller surface area of micro-Sn particles. Actually, the small surface area of much larger micro-Sn particles than nano-Sn results in the formation of thicker PANa binder coating on the surface of Sn particles, leading to higher electrode resistance and large overvoltage.\textsuperscript{18} As a result, the electrode resistance of the micro-Sn electrode becomes higher than that of the nano-Sn electrode.

To confirm whether the thickness of binder coating on micro-Sn particles affects the 1st charge voltage profile, the composite electrodes were prepared with different ratios of micro-Sn powder:3-\textmu m graphite:PANa = 8:1:1 (w/w), where $x = 5, 10,$ and $20,$ by simply changing the amount of PANa binder. In the 1st charge curves, apparent Plateau 1 was not observed in all electrodes (Fig. S2(a)). However, a small shoulder becomes visible just below the potential of Plateau 1 in the initial charge curve for the electrode containing the least amount of PANa binder, $x = 5.$ The voltage drop until the appearance of the 1st voltage-plateau became larger as the binder content increased, meaning the resistance increased as the binder content increased. This reasonably agrees with our previous data for Si-polyacrylate electrodes.\textsuperscript{18} Therefore, we concluded that
active material particles, which cause severe capacity degradation. Discharge, leading to cracks of electrodes and pulverization of electrodes undergo large volume change during charge and from the current collector of Al foil. It is known that alloy type composite layer severely cracked and was detached by irradiating hard X-rays. Figure 4 shows C 1s and Sn 3d5/2 HAXPES spectra of the nano- and micro-Sn electrodes of pristine and after the initial cycle. From the C 1s spectra of Fig. 4(a), peak intensities of $-\text{CH}_2 > \text{CH}$–COONa at 285.9 eV and $-\text{CH}_2 > \text{CO}$–COONa at 289.6 eV of the micro-Sn electrode are higher than those of the nano-Sn electrode. These peaks are attributable to PANa binder, suggesting that the micro-Sn electrode surface is covered with relatively thicker PANa binder. Figure 4(b) shows the Sn 3d5/2 spectra of the pristine electrodes. Sn metal and tin oxide peaks are observed in Fig. 4(b), while Fig. 4(d) shows no signals in both electrodes after the cycle, suggesting that the electrode surfaces are thoroughly covered with deposited products of the electrolyte decomposition. In the C 1s spectra of Fig. 4(c), electrolyte decomposition products such as alkoxide, carbonate, and so on are confirmed on the both electrodes, which agrees with our previous data. The HAXPES results show that there is no remarkable difference of chemical species between both electrode surfaces, suggesting micro-Sn electrode surface is covered with SEI consisting of the same chemicals. However, the thickness in surface layer of PANa coating and electrolyte decomposition products is different. As for the thickness of electrolyte decomposition products, those peak intensities of the micro-Sn electrode are lower than those of the nano-Sn electrode. It is suggested that the thicker PANa binder coating on micro-Sn particles suppresses the irreversible electrolyte decompositions. This is also consistent with the relatively higher Coulombic efficiency of the micro-Sn electrode at the 1st cycle, as mentioned in Fig. 1(c).

TOF-SIMS is a mass spectrometry that detects the mass signals from the flight time of fragments emitted as secondary ions by irradiating high-energy Au+ cluster pulse beam of 30 keV on the sample surface. Since the penetration depth of the beam is about 1 nm, information of the outermost sample can be collected from the detected mass signals. Figure 5 shows TOF-SIMS spectra of negative ion mode of the micro-Sn electrode. Figure 5(a) indicates peaks of oligomer/polymer from $m/z$ 189 with $m/z$ 106 interval in the micro-Sn electrode after 1 cycle. This is consistent with the result of the nano-Sn electrode reported previously, so it is considered that the outermost passivation layer on micro- and nano-Sn electrodes after 1 cycle are almost the same. We confirmed that this oligomer/polymer was not formed by merely soaking in the electrolyte solution but was formed by the electrochemical reaction.

Plateau 1 is shifted to the lower voltage due to the polarization caused by the smaller net surface area of Sn and thicker binder coating which are pronounced for the micro-Sn electrode compared with the nano-Sn one.

Although the sodiation curve of the electrode of micro-Sn:graphite:PANa = 80:10:5 somewhat resembles that of the nano-Sn electrode due to the reduced polarization, the cycle performance was not improved compared with those of the electrodes containing larger amount of PANa (see Fig. S2(b)), which is because of the lower adhesion strength by reduction of binder content. Besides, since the difference in electrode performance of the micro-Sn composite with different binder contents, $x = 10$ and 20, was not remarkable, the electrode degradation mechanism was further investigated for micro-Sn electrodes containing 10% binder dried at 80°C hereafter.

Figures 3(a) and 3(b) show SEM images of electrode surfaces of the pristine nano- and micro-Sn electrodes, respectively. Both electrodes similarly possess smooth and uniform surfaces. Cross-sectional SEM images of the pristine nano- and micro-Sn electrodes are shown in Figs. 3(c) and 3(d), respectively. The electron microscopic images confirm the existence of bright and round-shaped particles of Sn and dark flakes of graphite. The composite layer of the nano-Sn electrode is porous and thicker, while that of the micro-Sn electrode is dense and thinner and includes a small number of voids. The difference in thickness of the composite layers, 9.6 and 7.1 μm for the nano- and micro-Sn electrodes, respectively, in Table 1, results from the difference in porosity.

A cross-sectional SEM image of a tested micro-Sn electrode after 20 cycles whose capacity degraded to 400 mAh g$^{-1}$ is shown in Fig. 3(e). The composite layer severely cracked and was detached from the current collector of Al foil. It is known that alloy type electrodes undergo large volume change during charge and discharge, leading to cracks of electrodes and pulverization of active material particles, which cause severe capacity degradation. Specifically, sodiation of Sn to form Na$_2$Sn results in a large volume change of about 4.2 times. The actual internal stress of the micro-Sn composite layer is noticeable compared with that of the nano-Sn electrode due to the difference in the porosity of the composite layer as confirmed by Figs. 3(c) and 3(d). That is, the pores properly distributed in the entire composite layer should absorb the volume change and mitigate the internal stress of the electrode, leading to suppression of the detachment.

Based on the above discussion, further analyses of the electrodes are carried out to understand the effect of binder and porosity on the difference between the electrochemical properties of the nano- and micro-Sn electrodes. The surfaces of the micro- and nano-Sn electrode were examined by using HAXPES and TOF-SIMS.

HAXPES enables to study the surface chemistry of electrode by detecting photoelectron generated from approximately 10-nm depth by irradiating hard X-rays. Figure 4 shows C 1s and Sn 3d5/2 HAXPES spectra of the nano- and micro-Sn electrodes of pristine and after the initial cycle. From the C 1s spectra of Fig. 4(a), peak intensities of $-\text{CH}_2 > \text{CH}$–COONa at 285.9 eV and $-\text{CH}_2 > \text{CH}$–COONa at 289.6 eV of the micro-Sn electrode are higher than those of the nano-Sn electrode. These peaks are attributable to PANa binder, suggesting that the micro-Sn electrode surface is covered with relatively thicker PANa binder. Figure 4(b) shows the Sn 3d5/2 spectra of the pristine electrodes. Sn metal and tin oxide peaks are observed in Fig. 4(b), while Fig. 4(d) shows no signals in both electrodes after the cycle, suggesting that the electrode surfaces are thoroughly covered with deposited products of the electrolyte decomposition. In the C 1s spectra of Fig. 4(c), electrolyte decomposition products such as alkoxide, carbonate, and so on are confirmed on both the electrodes, which agrees with our previous data. The HAXPES results show that there is no remarkable difference of chemical species between both electrode surfaces, suggesting micro-Sn electrode surface is covered with SEI consisting of the same chemicals. However, the thickness in surface layer of PANa coating and electrolyte decomposition products is different. As for the thickness of electrolyte decomposition products, those peak intensities of the micro-Sn electrode are lower than those of the nano-Sn electrode. It is suggested that the thicker PANa binder coating on micro-Sn particles suppresses the irreversible electrolyte decompositions. This is also consistent with the relatively higher Coulombic efficiency of the micro-Sn electrode at the 1st cycle, as mentioned in Fig. 1(c).

Table 1. SAICAS results of thickness, peeling strengths of composite layer from Al current collector, and mechanical strengths to cutting force inside the composite layer.

| Composite layer thickness /μm | Peeling strength /kN m$^{-1}$ | Mechanical strength /kN m$^{-1}$ |
|-------------------------------|-----------------------------|-------------------------------|
| nano-Sn                       | 9.6                         | 0.11                          | 0.11                          |
| micro-Sn                      | 7.1                         | 0.27                          | 0.28                          |

Figure 3. SEM images of (a–d) pristine and (e) cycled electrodes: surface morphology of (a) nano- and (b) micro-Sn electrodes, cross-sectional images of (c) nano- and (d) micro-Sn electrodes, and (e) surface and magnified cross-sectional images of the micro-Sn electrode after 20 cycles processed by focused ion beam etching.

Figure 5. TOF-SIMS spectra of negative ion mode of the micro-Sn electrode. Figure 5(a) indicates peaks of oligomer/polymer from $m/z$ 189 with $m/z$ 106 interval in the micro-Sn electrode after 1 cycle. This is consistent with the result of the nano-Sn electrode reported previously, so it is considered that the outermost passivation layer on micro- and nano-Sn electrodes after 1 cycle are almost the same.
Figure 5(b) also proves the existence of the same oligomer/polymer in the degraded micro-Sn electrode after 20 cycles, showing that the degraded micro-Sn electrode is still passivated with the surface layer containing the oligomer/polymer. Since the upper cutoff voltage was set at 0.65 V, the SEI dissolution did not occur and the active material was maintained to be covered with SEI.13 From Figs. 4 and 5, any notable difference in SEI was hardly found on the nano- and micro-Sn electrodes in spite of the thicker PANa coverage leading to the polarization and disappearance of Plateau 1 for the micro-Sn electrode. Furthermore, as is described in Fig. 3(e), the original round shape of micro-Sn particles drastically changed after 20 cycles, evidencing the fracture and aggregation of micro-Sn during cycles.20 However, the resembled SEI layer remained even on the degraded electrode from the surface analyses, suggesting uniform coverage with the SEI containing the oligomer/polymer components. Namely, we do not find any significant difference in SEI between the nano- and micro-Sn electrodes, and we further analyzed the morphological and mechanical property of the composite layer.

SAICAS is employed for elucidating the adhesion strength of both the inner composite layer and the interface between the composite layer and Al foil with a small cutting edge.21 The peeling strength P (N m⁻¹) is given by

$$P = \frac{F_H}{w}$$

where $F_H$ is the horizontal force to peel the electrode composite layer and $w$ (m) is a blade width of the cutting edge.21 During SAICAS test, the pristine nano- and micro-Sn electrodes were immersed in DEC solvent to imitate the actual condition of the electrode in battery. Table 1 shows the results obtained from SAICAS measurements. In case of the nano-Sn electrode, the values of peeling and mechanical strengths are 0.11 and 0.11 kN m⁻¹, while those of the micro-Sn electrode are 0.27 and 0.28 kN m⁻¹, respectively, proving that the micro-Sn electrode shows approximately threefold mechanical strength compared with the nano-Sn electrode. Despite the higher mechanical strengths, the micro-Sn composite layer was separated off from Al foil by cycling as shown in Fig. 3(e). The dense composite layer of micro-Sn should accumulate pronounced internal stress caused by the volume change, leading to the detachment of the composite layer. In contrast, the nano-Sn electrode with porous composite layer can...
deliver the high capacity for 100 cycles because the porous structure absorbs the internal stress of the composite layer. Therefore, it is considered that the cycle performance will be improved if the porous composite layer is also formed in the micro-Sn electrode.

3.2 Dependence of micro-Sn electrode performance on electrode preparation condition

From the above results, we prepared a composite electrode by mixing the nano- and micro-Sn powders in order to improve the rapid capacity degradation of the Sn electrode by introducing the proper pores. The prepared micro/nano-Sn electrode consists of micro-Sn powder:nano-Sn powder:3-μm graphite:PANa = 7:1:1:1 to prove the idea mentioned above. Figure 6(a) shows a cross-sectional SEM image of the pristine micro/nano-Sn electrode, which is more porous than that of the micro-Sn electrode shown in Fig. 3(d). Obviously, Fig. 6(b) shows a superior cycle performance for the micro/nano-Sn electrode delivering more than 500 mAh g\(^{-1}\) for 100 cycles, and the capacity retention becomes comparable to that of the nano-Sn electrode. We prove that adding a small portion of nano-Sn powder into the micro-Sn composite is highly effective in improving the electrode reversibility, because the proper porosity was introduced in the composite by controlling of the binder coating thickness on Sn particles utilizing the large surface area of small particles. Taking the above results including Fig. 6 into consideration, we tried introducing the porosity into micro-Sn composite layer and thinner binder coating on micro-Sn particles by adjusting the drying temperature after slurry coating and by adding different conductive carbon powders having different particle sizes.\(^{22}\)

According to previous reports, the binder distribution and electrode porosity are affected by varying drying temperatures,\(^{23}\) and suitable choice of conductive carbon is effective for controlling porosity and inducing formation of conductive network in the composite layer.\(^{24}\)

First, the effect of drying temperature after the slurry consisting of micro-Sn powder:3-μm graphite:PANa = 8:1:1 pasted onto a current collector was examined with reference to 80°C used as a standard one. Figures 7(a)–(c) show cross-sectional SEM images of pristine electrodes dried at each temperature. Clearly, the composite layer becomes porous as the drying temperature elevates. The estimated porosities calculated from the thickness of the composite layer of the SEM images were approximately 10% for the electrodes dried at 40 and 80°C, and 20% for that dried at 150°C. One of possible reasons why the high drying temperature causes high porosity may be related to evolution of water vapor bubbles in the slurry pasted on Al foil during drying at higher temperatures beyond boiling point of water. Another reason is that the higher temperature accelerates the drying speed and induces a drastic increase of the slurry viscosity bringing the self-formed porous structure as observed in the slurries with partially neutralized polyacrylate binder.\(^{22}\) In Fig. 7(d), the electrode dried at 150°C exhibits the better cycle performance than those dried at 40 and 80°C, whereas the capacity decreases after 30 cycles. Since the porosity of the nano-Sn electrode...
The composite electrode, leading to the di- 

di-cycles (see Fig. S3). We think that the di-

crease in mechanical strength after 10 cycles was observed for the electrode containing only AB, 

ratios of 3-µm graphite:AB than graphite, AB powder absorbs the binder in the composite; 

for the electrode with only AB. As the surface area of AB is larger 

Figs. 8(b) and 8(c), Plateau 1 appears in the 1st charge curve for the 

performance was examined by using the electrodes consisting 

conductive materials on porosity of the composite layer and cycle 

mechanical strength of the composite layer and electric conduction 

results suggest that the 

graphite show good capacity retention even after 30 cycles. These 

pared by using three di-

ference of graphite on the 

ake graphite works effectively to maintain 

mechanical strength of the composite layer and electric conduction 

path in the entire composite layer. From Figs. 8(d) and 8(e), the 

electrode containing both AB and flake graphite exhibits the most stable cycle performance among them. 

We further examined the effect of size of graphite on the 

electrode performance. The composite electrodes of micro-Sn:15-µm graph-

ite:AB:PANa = 8:5.5:10 dried at 150°C. Figure 9(a) shows a charge and discharge curves of the optimized micro-Sn electrode. Compared to the micro-Sn electrode performance in Fig. 1(b), highly reversible and relatively stable charge and discharge were achieved for the optimized micro-Sn electrode. Figure 9(b) shows a cross-sectional SEM image of the pristine micro-Sn electrode prepared under the optimal condition. It exhibits a porous composite layer like the nano-Sn electrode shown in Fig. 3(c). The moderately porous composite layer can be obtained simply by modulating the surface area of electrode materials and drying temperature. Figure 9(c) compares the capacity retention of the micro-Sn electrodes before and after the optimization. The optimized electrode delivers the high capacity of 676 mAh g⁻¹ and satisfactory capacity retention over 100 cycles. Figure 9(d) shows that Coulombic efficiency of the optimized micro-Sn electrode at the 1st cycle is lower than that of the micro-Sn electrode due to the irreversible capacity of larger portion of AB, though the same efficiency was obtained for the two electrodes from the 2nd cycle. We successfully improved the electrode performance of the micrometer-sized Sn based upon understanding and analyzing the mechanism of capacity decay by carefully comparing the electrode behavior of nano- and micro-Sn powders. We believe that the battery performance will be further enhanced by comprehensive approach on electrolyte solvent, electrolyte salt, electrolyte additive, and binder.

4. Conclusion

We attempted to find out the reasons why the cycle performance of the nano-Sn electrode is better than that of the micro-Sn electrode. As the result, we proved that the cycle performance of Sn–Na reaction is affected to the porosity of composite layer. The porosity of the composite layer is varied by using different carbon additives and Sn powders and different drying temperature of the slurry. The properly porous composite layer is formed by drying at 150°C when PANa and graphite are used as binder and conductive additive,

![Figure 8. Charge and discharge curves of the composite electrodes consisting of micro-Sn:3-µm graphite:AB:PANa = (a) 8:1:0:1, (b) 8:0:5:0.5:1, and (c) 8:0:1:1. (d) Cycle performance and (e) Coulombic efficiency of the composite electrodes containing different carbons.](image-url)
respectively. In addition, we found the optimal particle size of graphite for the Sn electrode, and AB addition as conductive additive influences the thickness of the binder coating and mechanical durability of the composite. Optimal thickness of binder coating is important for balancing the passivation and mechanical strength of the composite electrode. By optimization of the electrode preparation condition, we successfully enhanced the micro-Sn electrode performance for the application of Na-ion batteries. These findings and optimization methodology in this study will be able to improve composite electrode performance of Li, Na, and K alloying electrodes delivering higher capacity for next-generation batteries.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.18-00069.

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