Improved electrochemical performance of tin-sulfide anodes for sodium-ion batteries†

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Due to their highly reversible capacity, tin-sulfide-based materials have gained attention as potential anodes for sodium-ion and lithium-ion batteries. Nevertheless, the performance of tin sulfide anodes is much lower than that of tin oxide anodes. The aim of the present investigation is to improve the electrochemical performances of SnS anodes for sodium-ion batteries using conventional organic electrolytes. Three different carbon composite anodes, SnS/reduce graphene oxide (SnS/G), SnS/reduce graphene oxide/hard carbon (SnS/G + C), and SnS/hard carbon (SnS/C), were prepared by hot water bath synthesis followed by mechanical milling. The mechanism of the conversion and alloying reaction was investigated by TEM. The feasibility of SnS anodes was confirmed in a full cell configuration using Na3V2(PO4)2F3 as the cathode.

Introduction

Following their commercialization in 1991, Li-ion batteries (LIBs) have been widely adopted for portable electronic devices and electric vehicles. Quickly this technology has become ubiquitous in societies’ daily life. Although initially LIBs have been used in portable electronic devices, their use has extended to large-scale applications such as battery-assisted bicycles and electric vehicles. The advantages of LIBs over nickel-hydride and lead-acid batteries are high cell voltage and high energy density. In addition, due to their high charge/discharge efficiency and long cycle life, LIBs have recently been considered as a temporary energy storage system for unstable renewable energy sources. However, the limited lithium resources and high cost are drawbacks for large-scale applications. For this reason, Na-ion batteries (SIBs) have recently gained attention as a potential alternative to LIBs because of their lower cost and similar electrochemical behavior to LIBs. Nevertheless, potential electrode candidates for SIBs are limited by the large ionic radius of Na. Some carbonaceous anodes have been investigated for SIBs using a similar analogy to LIBs. Some hard carbon anodes have exhibited low irreversible capacity, low polarization, and good cycling performance. However, thus far, the maximum rechargeable capacity of a hard carbon anode for sodium-ion batteries has been less than ca. 320 mA h g⁻¹. On the other hand, several transition metal oxides have been reported as possible cathode candidates for SIBs. Recently, several Na alloy anodes, such as tin (Sn), antimony (Sb), phosphorus (P), and antimony (Sb), have been proposed to improve the rechargeable capacity. Among these, Sn is a very promising anode material candidate for SIB anodes due to its high theoretical capacity (Na13Sn4: 854 mA h g⁻¹), good chemical stability, and low toxicity. However, the operating voltage is extremely close to the Na plating/stripping potential. Moreover, the large volume change and particle agglomeration during the charge and discharge cause capacity degradation of the metallic Sn. To reduce the volume change and prevent the particle agglomeration of Sn, several compounds and nanostructures have been proposed. Recently, tin oxides (SnO and SnO2) were investigated as anode active materials for SIBs. In the initial cycle, the tin oxides were reduced by Na, generating Sn and Na2O, the latter which forms during the conversion reaction can prevent the agglomeration of Sn particles and reduce the volume expansion of Sn. In our previous work, we compared the electrochemical performance of SnO and SnO2 and found that the bulk conductivity of the anode active material plays an important role in the electrochemical performance. Based on our previous results, tin sulfide should be a more promising anode material than tin oxide. Tin sulfide undergoes a similar first cycle conversion reaction (SnS + 2Na⁺ + 2e⁻ → Sn + Na2S). Nevertheless, the reported tin sulfide anode performance is significantly lower than that of tin oxide anode. L. Wu has reported that a Sn–SnS–C nanocomposite anode delivered 90% capacity retention for over 150 cycles against sodium. X. Xie, T. B. Qu and Y. Liu have integrated SnS2 and reduced graphene
oxide (SnS$_2$@graphene), resulting in excellent reversible capacity with more than 630 mA h g$^{-1}$.23–25 T. Zhou tried thermal treatment to transform SnS$_2$@graphene into SnS@graphene and demonstrated that SnS@graphene had an improved anode performance, delivering 940 mA h g$^{-1}$ at 30 mA g$^{-1}$. After 250 cycles SnS@graphene showed 492 and 308 mA h g$^{-1}$ at the current densities of 810 and 7290 mA g$^{-1}$, respectively.26 Herein, we aimed to synthesize new SnS anode composites using various carbon-based materials such as graphene oxide (GO) to improve the cycling performance and rate capability of SIBs. Moreover, the reasons for the capacity degradation in SnS anodes are discussed.

**Experimental**

**Synthesis of bare SnS and SnS/C**

SnS was prepared by using a hot water bath. 0.75 g SnCl$_2$·H$_2$O (Sigma-Aldrich; 98% purity) was dissolved in 50 ml 0.25 M citric acid (Wako Pure Chemical Industries, Ltd.), which was used as an antioxidant to prevent the oxidation of Sn ions from Sn$^{2+}$ to Sn$^{4+}$. Approximately 20% aqueous ammonia solution was added dropwise to adjust the solution pH to 5. Then 0.25 g thiioacetamide (CH$_3$CSNH$_2$, Wako Pure Chemical Industries, Ltd.) was added as a sulfur source (molar ratio of Sn : S = 1 : 1), and then the solution was stirred and heated at 80 °C. After immersion in a hot water bath, the sample was washed with distilled water and ethanol (EtOH) several times to remove contaminants and dried at 80 °C overnight. Finally, the sample was treated at 450 °C for 3 hours in an inert environment to obtain bare SnS. The composite of SnS and hard carbon (SnS/C) was prepared by mechanical milling. The SnS prepared in the hot water bath was mixed with hard carbon (Carbotron P(J); Kureha Corp.) by mechanical milling at 400 rpm for 1 hour. The nominal weight ratio of SnS to hard carbon was 8 : 2.

**Synthesis of SnS/G and SnS/G + C**

First, GO was prepared by Hummers’ method with modifications.27 0.15 g GO sheets were separated one by one in 100 ml distilled water (1.5 mg ml$^{-1}$) by sonication. After sonication, the separated GO sheets were dissolved in 7.2 g citric acid (0.75 M). Then, 0.75 g SnCl$_2$·H$_2$O with some ammonia hydroxide were added to adjust the solution pH to 5. Because the Sn$^{2+}$ ions would be oxidized by GO$^{28}$ and citric acid could not totally prevent the oxidation of Sn$^{2+}$ ions, the Sn : S molar ratio was adjusted to 1 : 1.4 (0.375 g thiioacetamide). After the hot water bath (80 °C for 12 h), samples were treated at 650 °C for 3 hours under Ar gas to remove the SnS$_2$ and obtain SnS/G. SnS/G + C was prepared in a similar manner to SnS/C, using mechanical milling at 400 rpm for 1 h. The nominal weight ratio of SnS/G to hard carbon was 9 : 1.

Samples were analyzed by X-ray diffraction with a 15 kW high-brilliance Cu-K$_{x}$ rotating anode (XRD; Rigaku TTRIII). The particle size and particle morphology were observed using a field emission scanning electron microscope (FESEM; JEOL JSM-6340F/-5310) and a transmission electron microscope (TEM; JEOL JEM 2100F). The carbon content in the SnS/G composite was measured by thermogravimetry (TG; Rigaku Thermo Plus TG8210).

**Electrochemical measurements in a half cell**

Electrodes were prepared by mixing appropriate amounts of the active material/acetyleone black (AB) mixture with a 2 wt% DI water–absolute alcohol mixture (4 : 1 by weight ratio) of carboxymethyl cellulose (CMC) (MW = 700 000; Sigma-Aldrich). The ingredients were added to a polypropylene vial containing 3 g of zirconia balls (3 mmφ). The vials were then placed in a rocking mill (Seiwa Giken Co., Ltd.) and mixed for 60 min at 50 Hz to form a slurry. Then the slurry was coated onto a 20 μm Cu foil current collector by using the doctor blade technique and dried under vacuum at 80 °C overnight. Electrochemical tests were carried out in two-electrode 2032 coin cells (Hohsen Corp.). Sodium metal foil was used as a counter electrode. Both the working electrode and counter electrode were punched to 15 mmφ. The loading mass of the active material in the electrode was 2.0 (±0.05) mg for a half cell. 1 M NaPF$_6$ dissolved in ethylene carbonate (EC) and propylene carbonate (PC) 1 : 1 by volume (Tomiyama Pure Chemical Industries, Ltd.) was used as an electrolyte. The separator was a GF/A glass fiber filter paper (Whatman). Cycle life and rate performance testing experiments were performed at different current densities in the voltage range of 2.0 V–0.1 V. Cyclic voltammetry (CV) was conducted on a VersaSTAT 3 (Princeton Applied Research) at a scan rate of 0.05 mV s$^{-1}$.

**Electrochemical measurements in a full cell**

A full cell test was carried out in a two-electrode 2032 coin cell. Na$_3$V$_2$(PO$_4$)$_2$F$_3$ mixed with AB and polytetrafluoroethylene (PTFE) was used as the cathode (70 : 25 : 5 in weight). SnO and SnS/G + C were used as anodes and were prepared using the same procedures as for the half-cell. SnO was prepared by the hydrothermal method as previously reported.27 Both the cathode and anode were punched to 10 mmφ. The loading amount of the active material in the electrode was 1.0 (±0.05) mg for the full cell. The separator was a GF/A glass fiber filter paper (Whatman) and the electrolyte was 1 M NaPF$_6$ dissolved in ethylene carbonate (EC) and diethylene carbonate (DEC) 1 : 1 by volume (Tomiyama Pure Chemical Industries, Ltd.). The voltage ranges of the full cells were between 3.7 V and 1.2 V (Na$_3$V$_2$(PO$_4$)$_2$F$_3$/SnO) and 3.6 V–1.1 V (Na$_3$V$_2$(PO$_4$)$_2$F$_3$/SnS/G + C), respectively. The current density of the full cells was tested at a current density of 0.2 mA cm$^{-2}$ (257 mA g$^{-1}$).

**Results and discussion**

**Material characteristics of SnS**

Fig. 1 shows the XRD patterns of bare SnS and SnS/G before and after thermal treatment. In Fig. 1(b), the peaks located at 2θ = 14.9° and 28.6° could be indexed to SnS$_2$ (ICCD 023-0677), suggesting that some of the Sn$^{2+}$ ions were oxidized to Sn$^{4+}$ during the hot water bath. This phenomenon was also reported by M. Zhang.28 After thermal treatment, all of the high crystallinity peaks in Fig. 1(c) could be indexed to SnS.
The XPS measurement results are shown in Fig. 2. In Fig. 2(a), the XPS spectrum showed the GO peaks at 284.1 eV, 285.9 eV, 287.9 eV, and 289.5 eV, which corresponded to the C–C bond, C–O bond, C≡O bond and O–C═O bond, respectively. In the C1s XPS spectrum of SnS/G, the C–C bonds were more intense than the covalent bonds of carbon and oxygen (Fig. 2(b)), suggesting that most of the oxygen functional groups were removed by the hot water bath and thermal treatment. The Sn 3d5/2 peak of SnS/G was located at 486.7 eV corresponding to SnS (Fig. 2(c)), suggesting that the SnS₂ impurities decomposed to SnS after the thermal treatment, which agreed with the XRD results.

The morphologies of SnS and SnS/G before and after thermal treatment are shown in Fig. 3. The SnS particles have a layered structure with random particle size, and the SnS layer thickness of about 200 nm (Fig. 3(a)). Before thermal treatment, the SnS/G material formed a beehive-like porous structure (Fig. 3(b)). After thermal treatment (Fig. 3(c)), the SnS/G lost its original shape and the SnS particles were covered by a graphene nanosheet.

To confirm the morphology of the SnS particles in the SnS/G, the SnS/G powder was dispersed in ethanol, and then sonication was applied to separate the SnS particles from the graphene nanosheet. The SnS showed a plate-like structure forming sheet-like SnS (Fig. 3(e)). The TG data in Fig. 3(f) show that the weight ratio of SnS : reduced graphene oxide (RGO) is 85 : 15. The TG profile was measured to 700 °C at a heating rate of 10 °C min⁻¹ in air. The carbon content of the different carbon composite samples is shown in Table 1.

**Table 1** SnS : carbon ratio in the different carbon compositied samples

<table>
<thead>
<tr>
<th>Anode</th>
<th>SnS</th>
<th>Carbon</th>
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<tbody>
<tr>
<td>SnS/G</td>
<td>85%</td>
<td>15% (RGO)</td>
</tr>
<tr>
<td>SnS/G + C</td>
<td>76.5%</td>
<td>13.5% (RGO), 10% (hard carbon)</td>
</tr>
<tr>
<td>SnS/C</td>
<td>80%</td>
<td>20% (hard carbon)</td>
</tr>
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**Electrochemical measurements in a half cell**

The electrochemical behavior of SnS against Na was characterized by cyclic voltammetry (Fig. 4(a)). The strong peak at 0.7 V, which was only observed in the initial cathodic curve, was attributed to the formation of a solid electrolyte interphase (SEI) layer. From the third cycle the CV curve became stable, suggesting that the SEI layer became stable. The oxidation/
reduction pairs at 0.1/0.02 V, 0.13/0.23 V, and 0.61/0.63 V were attributed to alloying and dealloying reactions between Sn and Na. The reduction peak at 1.15 V was caused by the conversion reaction between SnS and Na. The oxidation peak at 1.34 V and the broad peak at about 1.73 V were attributed to the reconversion reaction between Sn and Na2S.

Fig. 4(b) shows the charge/discharge profiles of the first two cycles for the bare SnS, SnS/G, SnS/G + C, and SnS/C anodes at a current density of 50 mA g\(^{-1}\). The reversible capacities of the first cycle were 621, 638, 598 and 511 mA h g\(^{-1}\) with coulombic efficiencies of 66.2%, 80.4%, 78.2%, and 71.3%, respectively.

Fig. 4(c) compares the cycling performance of the SnS, SnS/G, SnS/G + C, and SnS/C anodes. Compared to the bare SnS sample, all carbon composite samples showed lower polarization, better capacity retention, and higher coulombic efficiency. The SnS/G + C sample especially showed the best performance among the carbon composite anode electrodes.

Fig. 4(d) shows the rate capability of the SnS/G + C and SnS/C anodes. Both showed good rate capability even at high charge/discharge rates. The SnS/C anode delivered 506, 474, 424 and 320 mA h g\(^{-1}\) at a rate of 50, 100, 200, and 500 mA g\(^{-1}\), respectively. In contrast, the SnS/G + C anode delivered 590 mA h g\(^{-1}\) at 50 mA g\(^{-1}\) and showed 458 mA h g\(^{-1}\) even at 500 mA g\(^{-1}\). The higher rate capability of SnS/G + C seems to be due to the high conductivity of the RGO.

Though SnS/G + C showed good cycle and rate performance as a potential anode material for Na-ion batteries, pairing with a cathode material to make a full cell introduces new challenges. Our previously reported Na\(_3\)V\(_2\)(PO\(_4\))\(_2\)F\(_3\) (NVPF) active material was used as the cathode\(^{22}\) and was paired with SnS/G + C to test the electrochemical performance of a full cell. To further examine the relationship between the electrochemical performance and conductivity of the anode active material, our previously reported SnO (cite) was also paired with the NVPF cathode. Considering the irreversible capacity in the first cycle of SnO and SnS/G + C, the NVPF//SnO cell and NVPF//SnS/G + C cell were prepared under cathode-rich conditions (NVPF : SnO = 7 : 1; NVPF : SnS/G + C = 8 : 1 in weight). The electrochemical properties of NVPF are shown in Fig. S1.†

**Electrochemical measurements in a full cell**

The charge/discharge profiles in the selected cycle and cycling performance of the full cells are shown in Fig. 5. Both the NVPF//SnO cell and NVPF//SnS/G + C cell showed good performance, with capacity retentions of 154.4% and 86.3% in 50 cycles. The initial charge/discharge capacities of the NVPF//SnO cell and NVPF//SnS/G + C cell were 322/95 mA h g\(^{-1}\) and 504/319 mA h g\(^{-1}\), with the coulombic efficiencies of 29.5% and 63.4%, respectively. As expected, the SnS/G + C anode outperformed the SnO anode in the full cell configuration.
The capacity fading mechanism of the SnS anodes was further studied by TEM. SnS anodes in their fully discharged and charged states were examined. Fig. 6 shows the TEM image of the fully sodiated SnS/G + C electrode. The first cycle conversion reaction transforms the plate-like pristine SnS to particles with an irregular shape (Fig. 6(a)). The nanoparticles that were distributed throughout the amorphous matrix correspond to the Sn or Na$_{x}$Sn nanoparticles generated from SnS after the conversion reaction (Fig. 6(b)). This result is very similar to the converted SnO$_2$ studied in our previously reported work. The fully disodiated SnS/G + C is shown in Fig. 6(c) and (d). After the full charge, the primary particles disintegrated into nanoparticles around 5 nm. Although SnS in the SnS/G + C completely lost its shape, it still shows evenly dispersed particles without any Sn particle aggregation. This is consistent with the high coulombic efficiencies of SnS/G and SnS/G + C shown in Fig. 4(b). The scheme of the morphological changes is shown in Fig. S2.

Fig. 7(a) and (c) compare the voltage profile and cycling performance of SnS/C at different cutoff voltages. In Fig. 7(c), cutting of the voltage at 1.5 V for SnS/C demonstrates good stability to the tenth cycle. However, after the tenth cycle the capacity gradually decays. In contrast, the sample charged to 2 V was stable and still maintained the electrode integrity over 30 cycles (Fig. S3(c) and (d)). Here the fiber-like structure corresponds to the glass fiber separator. These data could be explained by the incomplete reconversion reaction if reducing the cut-off voltage (reducing the conversion reaction driving force) and the incomplete reconversion reaction could cause the cracking of the Na$_2$S buffer layer during the cycles.

Fig. 5 (a) Voltage profile and (b) cyclabilities of NVPF//SnO and NVPF//SnS/G + C cells.

Fig. 6 TEM images: (a) and (b) SnS/G + C electrode after full charge (sodiated); (c) and (d) SnS/G + C electrode after full discharge (disodiated).

Fig. 7 Voltage profile in the selected cycles, cyclabilities and coulombic efficiencies of (a), (b) SnS/C at different cutoff voltages (c), and (d) SnS/G and SnS/G + C.
Fig. 7(b) and (d) show the charge/discharge profile for selected cycles. As demonstrated, SnS/G + C have a very stable charge/discharge curve for each cycle. The SnS/G + C also showed a stable electrode structure even after 30 cycles (Fig. S3(g) and (h)). During the discharge and charge process, the Na ions were reversibly reacted with SnS to form Na$_x$Sn and Na$_x$S:

$$\text{SnS} + 2\text{Na}^+ + 2e^- \rightleftharpoons \text{Sn} + \text{Na}_2\text{S}$$  \hspace{1cm} (1)

$$\text{Sn} + \text{Na}_x\text{S} + x\text{Na}^+ + xe^- \rightleftharpoons \text{Na}_x\text{Sn} + \text{Na}_2\text{S}$$  \hspace{1cm} (2)

A large volume change occurs during the alloy reaction. The SnS/G + C in particular show a high conversion reversibility, shown in Fig. 7(c). The capacity degradation of the SnS/G might be attributed to the large volume change due to the cracking and substrate lift off from the current collector. However, mixing hard carbon through ball milling can separate the SnS/G into the matrix of hard carbon. This can further reduce the volume expansion and eliminate the stress during the charge/discharge process. Through this reasoning the improved cycle performance of SnS/G + C and SnS/C samples can be explained.

To sum up the results shown in Fig. 7 and S3,† the capacity degradation in the bare SnS could be attributed to the following factors; (1) large volume change during the charge/discharge process; and (2) the incomplete conversion reaction due to the cracking of the Na$_x$S buffer layer. Reconversion reactions must overcome the lattice energy and the poor conductivity of the Na compounds (such as Na$_x$S and Na$_x$O) in order to reverse the transformation reaction. As shown in Fig. 4(b), SnS/G, SnS/G + C and SnS/C showed lower polarization than the bare SnS, suggesting that the conductivity improved after the carbon composition. The distributions of Sn nanoparticles may also play an important role in the reversibility of the conversion reaction. The Sn nanoparticles are highly distributed in Fig. 6(b), suggesting that there was a close contact area between Sn and Na$_x$S. This was beneficial for improving the conversion activity of the reverse transformation reaction and can also explain the lower electrochemical performance of the NVPF//SnO. Moreover, NVPF//SnO has a lower content and conductivity, worse distribution, and higher Na$_x$O lattice energy (the lattice energy of Na$_x$O was 2481 kJ mol$^{-1}$, versus 2203 kJ mol$^{-1}$ for Na$_x$S).

Conclusions

In this study hard carbon and RGO were used to improve the cycling performance of SnS anodes. Three different carbon composite samples, SnS/G, SnS/G + C, and SnS/C, were prepared by means of a hot water bath and mechanical milling. All of the materials showed lower polarization and better cycling performance than the bare SnS. Among these carbon compositon samples, SnS/G + C exhibited the best cycle performance and rate capability. Based on the TEM image of SnS/G + C after the full charge/discharge states, the cycling performance of SnS/C in different voltage ranges, and the comparison of the charge/discharge voltage profiles of SnS/G and SnS/G + C at selected cycles, we conclude that the capacity degradation of the bare SnS is attributed to the large volume change. Moreover, the incomplete reversibility of the conversion is due to the cracking of the Na$_x$S buffer layer. In the full cell test, NVPF//SnS/G + C showed better electrochemical performance than the NVPF//SnO cells. As expected, these results suggest that the conductivity plays an important role in the electrochemical performance of Naion batteries.

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Notes and references