Mechanochemical Synthesis of Na-Sb Alloy Negative Electrodes and Their Application to All-solid-state Sodium Batteries

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ABSTRACT

Na-Sb alloy was synthesized as an advanced negative electrode material for all-solid-state sodium batteries by a mechanochemical process. An all-solid-state symmetric cell using a composite of an Na-Sb alloy and Na3PS4 solid electrolyte operated reversibly with a high reversible capacity of 370 mAh g−1 at room temperature under a current density of 0.064 mA cm−2. The cell also operated at 60°C under the same current density with low polarization compared to room temperature operation. The sodiation process from NaSb to Na 3Sb was examined by ex situ X-ray diffraction (XRD) measurements. An all-solid-state half-cell using a TiS2 composite electrode and a Na3Sb composite electrode showed a high reversible capacity of 200 mAh g−1 at room temperature under a constant current density of 0.064 mA cm−2. Na-Sb alloys are a suitable negative electrode material for all-solid-state sodium batteries.

Keywords : Sodium-antimony Alloy, Negative Electrode, All-solid-state Sodium Batteries, Mechanochemical Synthesis

1. Introduction

Recently, the demand for batteries for large-scale energy storage has been rapidly increasing. All-solid-state batteries using inorganic solid electrolytes are expected to effectively improve safety. Safer all-solid-state sodium batteries are promising next-generation secondary batteries due to their high energy density and low cost. Although metallic sodium has the lowest electrode potential in sodium batteries, there is a risk of short circuiting because of sodium dendrite growth.1 In addition, the solid electrolytes used for all-solid-state sodium cells have an issue in terms of chemical stability at low voltages. It is reported that Na2S is generated by reactions between Na3PS4 and metallic sodium, forming a resistive layer.2

In lithium-ion batteries, graphite is used as a negative electrode material instead of metallic lithium. However, at present, the utilization of graphite negative electrodes for sodium batteries has been unsuccessful, as has the use of metallic sodium electrodes. Although many researchers have found suitable negative electrode materials for sodium batteries,1–6 negative electrode materials for all-solid-state sodium batteries have not been widely studied. Alloy negative electrodes are promising due to their high gravimetric capacities. It has been reported that Sn and Sb have reversible capacities of 500 and 580 mAh g−1, respectively.7,9 Although alloy negative electrodes show high capacities, these materials are hardly used because they tend to decrease the specific capacity and cycle performance of the battery due to their large volume changes during the sodiation and desodiation reactions.

In our group, a Na-Sn alloy with the composition of Na15Sn4 has been used as a negative electrode material in all-solid-state sodium batteries.10 This alloy was synthesized by a mechanochemical process.11 The cell using Na15Sn4 sometimes operates unstably because Na15Sn4 has a low electrode potential and partially precipitates metallic sodium during cycles, causing unfavorable side reactions. Therefore, we focused on the Sn negative electrode with an easy-to-use electrode potential (0.5–1.0 V vs. Na),8 leading to suppression of the side reactions. Although the Sn negative electrode showed a high capacity corresponding to reaction with 3 molar equivalents of sodium during the 1st discharging process, achieving a fully reversible reaction with Sn during the charging process is challenging.3,12 In addition, a large volume expansion of approximately 250% occurs in the reaction from Sb to Na3Sb. However, the volume change decreases to approximately 150% in the reaction between NaSb and Na3Sb, which is a mixture of NaSb and Na3Sb at a molar ratio of 1:1, which is also synthesized to expand the choices of positive electrode materials.

2. Experimental

2.1 Preparation of Na-Sb alloy

Sn (Sigma-Aldrich, 99.99%) was pulverized using an agate mortar. Metallic sodium (Sigma-Aldrich, 99%) was cut out finely. The mixtures of stoichiometric ratios of Na and Sb with Ketjen black (KB) were ball-milled using a stainless-steel ball-mill pot (45 mL in volume) and 10 stainless-steel balls (10 mm in diameter) with a planetary ball-mill apparatus (Fritsch, Pulverisette 7) under an Ar atmosphere. KB with the 1/9 of the weight of sodium was added as a conduction additive agent. The total weight of Na and Sb was 1 g at composition ratios of NaSb, Na2Sb, and Na3Sb. A milling time of 60 min at 370 rpm was sufficient to complete the reaction of Sb and Na. The prepared samples were stored in an Ar-filled glovebox.

2.2 Fabrication of all-solid-state cells

All-solid-state symmetric cells using an electrode composed only of Na-Sb alloy with KB and a composite electrode of Na-Sb alloy with KB and Na3PS4 glass-ceramic13 were fabricated. The composite of Na3Sb and Na3PS4 at a volume ratio of 1:1 was prepared by mixing in an agate mortar. When calculating the volume...
ratio, the density of Na₃PS₄ of 2.00 g cm⁻³ and the theoretical density of NaSb (4.03 g cm⁻³) and NaSb (2.67 g cm⁻³) were used.¹⁴,¹⁵ Na₃PS₄ was also used as a separator layer for all the cells. Trilayer pellets (10 mm in diameter) consisting of two Na-Sb alloy electrode layers (10 mg) and a Na₃PS₄ separator layer (80 mg) were prepared by uniaxial pressing under 360 MPa for 5 minutes with stainless-steel rods as a current collector. A schematic diagram of the all-solid-state cell is shown in Fig. S1 (Supporting Information). Charge-discharge tests at room temperature were conducted using a charge-discharge measurement device (VMP3, Bio-Logic Co.) in an Ar-filled glovebox. The cell packed in an airtight container filled with Ar gas was placed in an oil bath outside the glovebox. The charge-discharge tests were done at 60 °C using a measurement device (BTS-2004, Nagano Co.). Both cells were measured with constant current densities of 0.064 mA cm⁻². Assuming two-electron process, the current density of 0.064 mA cm⁻² corresponds to about C/40 rate. During the charge-discharge tests, a capacity was limited based on the quantity of electricity corresponding to the terminal composition from NaSb to Na₃Sb.

The ionic conductivity of the composite electrode was measured by the DC polarization method. The measurement cell (Na₂Sb/Na₃PS₄/composite electrode/Na₂Sb/Na₃PS₄) consisted of Na₂Sb layers (25 mg), Na₃PS₄ layers (80 mg) and a composite electrode layer (80 mg). The cell was prepared by uniaxial pressing under 360 MPa for 5 minutes with stainless-steel rods as a current collector. Na₃PS₄ was used as a solid electrolyte and sodium ion conduction layer. Na₂Sb was used as a sodium source. The ionic conductivity of the composite electrode was calculated from the resistance obtained by subtracting each resistance separately. The resistance of the cell composed of Na₂Sb and Na₃PS₄ was measured by the DC polarization method. The bulk resistance of Na₃PS₄ was measured by the AC impedance method in the frequency range of 0.01 Hz to 1 MHz. The measurement was conducted at room temperature using a potentiosstat (Cell Test, Solartron Analytical Co.) in an Ar-filled glovebox.

An all-solid-state half-cell (Na₃Sb/Na₂Sb/TiS₂) was fabricated. The positive and negative compositions were prepared by mixing one of the active materials and the Na₃PS₄ solid electrolyte in an agate mortar. The composite positive electrode consisted of TiS₂ and Na₂Sb, with a weight ratio of 6:4. The composite negative electrode consisted of NaSb and Na₃PS₄ combined with a volume ratio of 1:1. The cell consisted of a TiS₂ positive electrode layer (10 mg), Na₂Sb layer (80 mg), and NaSb negative electrode layer (50 mg). The cell was prepared by uniaxial pressing under 360 MPa for 5 minutes with stainless-steel rods as a current collector. The electrochemical performance of the cell was examined under constant current densities of 0.064–0.64 mA cm⁻² at room temperature using a charge-discharge measurement device (VMP3, Bio-Logic Co.).

2.3 Characterization

X-ray diffraction (XRD) patterns of the samples were collected using an X-ray diffractometer (SmartLab, Rigaku Co.) equipped with a one-dimensional X-ray detector using CuKr radiation (λ = 1.54056 × 10⁻⁸ m). A cross-section of the electrode layer was prepared using Ar ion milling system (IM4000, Hitachi High-Technologies Co.) and observed using field-emission scanning electron microscope (FE-SEM, SU8200, Hitachi High-Technologies Co.).

Differential thermal analysis (DTA) was conducted by using a measuring apparatus (Thermo Plus EVO2, Rigaku Co.). These measurements were performed using Al₂O₃ as a reference and under the condition of flowing dry N₂ at a flow rate of 100 mL min⁻¹ with a temperature range from room temperature to 500 °C with a ramp rate of 5 °C min⁻¹. The heating treatment was conducted in an Al pan sealed in an Ar-filled glovebox.

Figure 1. XRD patterns of samples with compositions of NaSb, Na₃Sb, and NaSb prepared by a mechanochemical process.

3. Results and Discussion

XRD patterns of NaₓSb (x = 1, 2, and 3) samples with KB are shown in Fig. 1. The sample with x = 2 is obtained from the mixture of NaSb and NaSb. The peaks of NaSb and NaSb are consistent with the data of JCPDS cards #01-074-0801 and #03-065-3523, respectively.¹⁴,¹⁵ No impurity phases are observed. For comparison, the XRD pattern of the sample synthesized without KB is shown in Fig. S2. The peaks attributable to Sb still remain and the Na-Sb alloy is not obtained in the sample without KB, suggesting that the reaction between Na and Sb is sufficient. It is assumed that Na agglutinates at the initial stage of the ball milling and Sb adheres around agglomerated Na. Therefore, KB plays a role not only as a conduction additive agent but also as a dispersing agent.

An all-solid-state symmetric cell using a composite of Na₂Sb and Na₃PS₄ was fabricated. Charge-discharge tests were performed at room temperature under a constant current density of 0.064 mA cm⁻². Charge-discharge curves of the cell are shown in Fig. 2(a). A cross-sectional SEM image of the electrode layer before charge-discharge test is also shown in Fig. 2(b). The dark-gray and light-gray area denote Na₂Sb and Na₃PS₄, respectively. The theoretical capacity of Na₂Sb with one electron reaction (Na₂Sb → NaSb) is 160 mAh g⁻¹, while that with two electron reactions occurring (Na₂Sb → NaSb) is 320 mAh g⁻¹. The cell showed a 1st discharge capacity of 160 mAh g⁻¹ and reversible capacities of 320 mAh g⁻¹ in the subsequent cycle. A large polarization of 0.384 V estimated from the voltage of x = 2 is observed. This value is greater than that of the 0.3 V previously reported for the cell using an organic liquid electrolyte.⁹,¹³ In this case, the additional polarization is attributable to the lack of sodium ion conduction. The DC polarization measurement is carried out at several voltages to investigate the effective ionic conductivity of the composite of Na₂Sb and Na₃PS₄. Moreover, the measurements are performed until the current is stabilized because a gradual current drop is observed. A Nyquist plot of Na₃PS₄ is shown in Fig. S3. The ionic conductivity of Na₃PS₄ is 1.7 × 10⁻⁴ S cm⁻¹. The effective ionic conductivity of the composite of Na₂Sb and Na₃PS₄ is 3.4 × 10⁻⁵ S cm⁻¹. This value is 5 times larger than the ionic conductivity of Na₂Sb alone (7.1 × 10⁻⁴ S cm⁻¹), suggesting that mixing with Na₃PS₄ is effective in improving the ionic conductivity of the electrode layer. The ionic conductivities of NaSb and NaSb were 1.4 × 10⁻⁵ S cm⁻¹ and 2.5 × 10⁻⁵ S cm⁻¹, respectively. When an all-solid-state symmetric cell with Na₂Sb alone as both electrode layers is fabricated, the cell showed a 1st discharge capacity of 14 mAh (g of Na₂Sb)⁻¹, which is approximately 10% of the theoretical capacity. The charge-discharge profile is shown in Fig. S4. Low utilization is assumed to be caused by poor sodium ion conduction in the Na₂Sb electrode layer.
An all-solid-state cell using Na3Sb and NaSb was fabricated. A composite of Na3PS4 and one of the Na-Sb alloys were used as the electrode layers. Charge-discharge curves of the cell are shown in Fig. 3(a). The cell shows a theoretical capacity of 370 mAh (g of NaSb)\(^{1}\) and operates reversibly at room temperature with a constant current density of 0.064 mA cm\(^{-2}\). Charge-discharge curves are similar to the curves of the Na2Sb symmetric cell. In the initial discharge process, 2 molar equivalents of sodium are inserted into the NaSb electrode to produce Na3Sb. Actually, sodium insertion is confirmed by ex situ XRD measurements of the NaSb electrode during the discharging process. The measurements were conducted at three points: before discharging, after half-discharging, and after full-discharging. The ex situ XRD patterns are shown in Fig. 3(b). Although the peaks attributable to NaSb are observed before the discharging process, they are not observed after the full-discharging. The peaks of Na3Sb and an unknown peak at 2\(\theta\) = 23.4° are observed. After the half-discharging process (\(x = 2\)), only the peaks of NaSb and Na3PS4 are observed in the XRD pattern. It is contrary to expectations that two peaks of NaSb and Na3Sb will be observed. This suggests that an amorphous Na\(_x\)Sb was formed as an intermediate phase between NaSb and Na3Sb phase; the formation of two amorphous phases was observed for the cells using organic liquid electrolytes.\(^{12}\) An all-solid-state half-cell using TiS\(_2\) was fabricated to investigate whether Na-Sb alloys can be used as a sodium source. TiS\(_2\) is a typical active material reported to be used in all-solid-state sodium batteries.\(^{16,17}\) Charge-discharge curves of the cell are shown in Fig. 4(a). The cell show a high reversible capacity of 200 mAh (g of TiS\(_2\))\(^{-1}\) at room temperature under a constant current density of 0.064 mA cm\(^{-2}\) for 20 cycles. It is noted that the weight of the negative electrode sufficiently exceeds that of the positive electrode, so the capacity of the cell is calculated based on the mass of TiS\(_2\). Cycle performance and coulombic efficiency of the cell are shown in Fig. 4(b). The cell retains a reversible capacity of 190 mAh g\(^{-1}\) at the 100th cycle. Therefore, the capacity retention calculated from the 1st discharge capacity and the 100th discharge capacity is 95\%. Average coulombic efficiency was almost 100\% during the 100 cycles. The rate performance of the cell is shown in Fig. 4(c). The reversible capacity decreases slightly from 200 mAh g\(^{-1}\) to 190 mAh g\(^{-1}\) when the current density is increased from 0.064 mA cm\(^{-2}\) to 0.13 mA cm\(^{-2}\). Moreover, the reversible capacity further decreases to 70 mAh g\(^{-1}\) upon increasing the current density to 0.64 mA cm\(^{-2}\). The coulombic efficiency is almost 100\% at current densities of 0.064 mA cm\(^{-2}\), 0.13 mA cm\(^{-2}\), and 0.64 mA cm\(^{-2}\).

In general, the ionic conductivity of the composite electrode is improved by increasing the operating temperature. The thermal stability of the composite including Na3Sb and Na3PS4 was investigated by XRD measurements. XRD patterns of the Na3Sb-Na3PS4 composites before and after heating at 100°C are shown in Fig. 5. The Na3Sb-Na3PS4 composite is thermally stable because there are no changes in the XRD patterns after heating. The result of differential thermal analysis (DTA) is shown in Fig. S5.
exothermic or endothermic changes are observed. These results mean that the Na2Sb-Na3PS4 composite is thermally stable up to 100°C.

An all-solid-state cell using Na3Sb and NaSb was operated at 60°C under a constant current density of 0.064 mA cm\(^{-2}\). The composites of Na3PS4 and Na-Sb alloy are used as electrode layers. Charge-discharge curves of the cell are shown in Fig.6. The cell show a theoretical capacity of 370 mAh (g of NaSb)\(^{-1}\) and operates reversibly. Charge-discharge curves are similar for operation at room temperature (Fig. 3). Moreover, a decrease in polarization is observed as the temperature is changed from room temperature to 60°C. The polarization of 0.304 V is equivalent to that found in previous reports on cells using an organic liquid electrolyte.8,12 The polarization is suppressed by accelerating the migration of sodium ions by increasing the operating temperature.

4. Conclusions

The Na-Sb alloys were mechanochemically prepared with Ketjen black as both conduction additive and dispersion agents. An all-solid-state symmetric cell using the Na2Sb-Na3PS4 composite showed the reversible capacity of 320 mAh g\(^{-1}\) and operated reversibly between NaSb and Na3Sb. The ionic conductivity of the Na2Sb composite electrode was measured by the DC polarization method and it showed an ionic conductivity of 3.4 \(\times\) 10\(^{-5}\) Scm\(^{-1}\). The Na3Sb alloy was also evaluated in the all-solid-state half-cell using TiS2 and the cell showed good cycle performance. An operation test at 60°C was attempted to promote ionic conduction in the electrode layer. XRD measurements showed that the composites of NaSb and Na3PS4 were thermally stable up to 100°C. An all-solid-state cell using NaSb and NaSb operated reversibly at 60°C with a low polarization. We believe that Na-Sb alloys are suitable negative electrode materials in all-solid-state sodium batteries.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.19-00014.

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