Preparation of sodium-ion-conductive Na$_{3-x}$SbS$_4$$_x$Cl$_x$ solid electrolytes

Fumika TSUJI$^1$, So YUBUCHI$^1$, Atsushi SAKUDA$^1$, Masahiro TATSUMISAGO$^1$ and Akitoshi HAYASHI$^{1,2,†}$

$^1$Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1–1 Naka, Sakai, Sakai 599–8531, Japan
$^2$Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, Kyoto University, Sakyo, Kyoto 606–8501, Japan

Solid electrolytes have become important materials for improving the performance of next-generation all-solid-state sodium rechargeable batteries. Therefore, sodium vacancy doping for Na$_3$SbS$_4$ electrolytes was performed by partially substituting Cl for S. Na$_{3-x}$SbS$_4$$_x$Cl$_x$ electrolytes were prepared using a mechanochemical process and consecutive heat treatment. The structures, ionic conductivities, and air safety of the prepared Na$_{3-x}$SbS$_4$$_x$Cl$_x$ electrolytes were evaluated via X-ray diffraction and impedance, air stability, and electrochemical tests. The Na$_{2.9375}$Sb$_{3.9375}$Cl$_{0.0625}$ electrolyte showed a higher room-temperature ionic conductivity of 2.9 × 10$^{-3}$ S cm$^{-1}$ than that of the Na$_3$SbS$_4$ electrolyte. An all-solid-state Na$_{15}$Sn$_4$SbS$_{12}$ cell showed a reversible capacity of approximately 100 mA h g$^{-1}$ at room temperature. Thus, the Na$_{2.9375}$Sb$_{3.9375}$Cl$_{0.0625}$ solid electrolyte has the potential for application as a solid electrolyte in all-solid-state batteries.

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Key-words : All-solid-state battery, Sodium ionic conductivity, Solid electrolyte, Air stability, Mechanochemical technique

1. Introduction

All-solid-state sodium rechargeable batteries are highly safe next-generation batteries with low costs because of the abundance of sodium sources. Solid electrolytes with higher sodium conductivities and improved stabilities are key materials to improve the performance of all-solid-state batteries. Recently, some sodium sulfides and selenides, for example Na$_3$PSe$_4$ and Na$_{10}$SnP$_2$S$_{12}$, have been found to have high ionic conductivities of over 0.1 mS cm$^{-1}$. In particular, Na$_{11}$Sn$_2$S$_{12}$ has a high ionic conductivity exceeding 1 mS cm$^{-1}$ at room temperature, which was prepared using a mechanochemical technical and consecutive heat treatment. An all-solid-state cell with a Na$_3$PS$_4$ solid electrolyte was successfully operated as a rechargeable battery at room temperature.

Alivovalent cation doping is a common strategy to improve the ionic conductivities of crystalline electrolytes. Earlier, we developed the solid electrolyte 94Na$_3$PS$_4$.6Na$_x$SiS$_4$ (mol %) with an Na-excess composition that showed a ionic conductivity of 7.4 × 10$^{-4}$ S cm$^{-1}$, higher than that of the Na$_3$PS$_4$ solid electrolyte. Sodium vacancy doping is effective for increasing conductivity; Chu et al. have reported the synthesis of Cl-doped tetragonal Na$_3$PS$_4$ (t-Na$_{3-x}$PS$_4$.Cl$_x$, x = 0.0625) electrolytes with a room-temperature conductivity exceeding 1 mS cm$^{-1}$. Yu et al. have also reported that Na$_3$PS$_4$ materials with Na vacancies have high Na-ion mobilities through molecular dynamics simulations. Therefore, Na$_{3-x}$PS$_4$.Cl$_x$ materials where Na vacancies are introduced by partially substituting the halogen (X) with sulfur can possess higher Na-ion conductivities.

However, when exposed to an ambient environment, these electrolytes release H$_2$S gas, and thus their ionic conductivity decreases. In recent years, tetragonal and cubic Na$_3$SbS$_4$ solid electrolytes showing high ionic conductivities (exceeding 1 mS cm$^{-1}$) at room temperature and high chemical stabilities have been reported. In addition, Na$_{11}$Sn$_2$S$_{12}$ maintains its phase after exposure to dry air for 36 h. Air stability is determined based on the hard and soft acid and base (HSAB) theory, where a hard acid reacts preferentially with a hard base and a soft acid reacts preferentially with a soft base. Based on the HSAB theory, the Sb$_2$S$_3$ group is stable against H$_2$O molecules in an ambient atmosphere because of the strong Sb–S bonding, which is a soft acid–soft base combination.

In this study, anion-substituted Na$_{3-x}$SbS$_4$.Cl$_x$ (x = 0, 0.03, 0.0625, 0.09, and 0.125) solid electrolytes were first synthesized using a mechanochemical technique and consecutive heat treatment. The electrolyte composition was selected based on the reported composition Na$_{2.9375}$PS$_4$.9375Cl$_{0.0625}$, where Na vacancies were introduced into Na$_3$PS$_4$. The structure of Na$_{3-x}$SbS$_4$.Cl$_x$ was investigated using X-ray diffraction (XRD) and Raman spectroscopy, and the ionic conductivities were evaluated by AC impedance. The air and electrochemical stabilities of...
a Na$_{2.9375}$Sb$_{3.9375}$Cl$_{0.0625}$ solid electrolyte were also evaluated.

2. Experimental

Stoichiometric mixtures of Na$_2$S (>99.1%; Nagao), Sb$_2$S$_3$ (>99.95%; Aldrich Chemical), S (>99.98%; Aldrich Chemical), and NaCl (>99.999%; Aldrich Chemical) having the composition Na$_{3-x}$Sb$_x$S$_4-x$Cl$_x$ (x = 0, 0.03, 0.0625, 0.09, and 0.125) were processed mechanochemically using a planetary ball mill (Pulverisette 7; Fritsch) with a zirconia pot (225 mL in volume) and 2500 zirconia balls (4 mm in diameter). The total mass of the starting materials was 2.0 g in each pot. The rotation speed and milling duration were 210 rpm and 50 h, respectively. The milled powder was heated at 170 or 290 °C in an electric furnace for 1 h. The heating temperatures were selected based on the crystallization or phase transition temperatures determined via differential thermal analysis (DTA).

All the processes were performed in a dry Ar atmosphere.

XRD measurements of the prepared materials were performed using Cu Kα radiation with a diffractometer (SmartLab; Rigaku). Diffraction data were collected in steps of 0.01° in the 2θ range of 10.0–60.0°. All the powder patterns were refined using the Rietveld method in the software package RIETAN-FP. DTA was performed using a thermal analyzer (Thermo Plus TG8110; Rigaku) at a heating rate of 10 °C min$^{-1}$. The ionic conductivities of the Na$_{3-x}$Sb$_x$S$_4-x$Cl$_x$ (x = 0 and 0.0625) samples were determined via AC impedance measurements using an impedance analyzer (Solartron, 1260) in the frequency range from 8 MHz to 0.1 Hz. The measurements were carried out using compressed powder pellets (10 mm in diameter and thickness of approximately 1 mm). The pellets were prepared by cold or hot pressing at 360 MPa. Gold thin films (10 mm in diameter and ca. 120 nm in thickness) as ion-blocking electrodes were deposited on both faces of the pellets with a quick coater (Quick coater SC-701; Sanyu Electron). The measurement was performed in the heating step and the samples were left at each temperature for 1.5 to 2 h until the temperature became stable.

The densities of the powder-compressed pellets ($d_1$) were calculated from the weight and volume of the pellets, and those of the powders ($d_2$) were measured using a gas pycnometer (Accupyc II 1340; Shimadzu). The microstructures of the cross-sections of the pellets were observed via scanning electron microscopy (SEM) (JSM-6610A; JEOL).

An all-solid-state cell was constructed as follows: the prepared Na$_{2.9375}$Sb$_{3.9375}$Cl$_{0.0625}$ powder (80 mg) was used as the solid electrolyte. A composite (10 mg) of TiS$_2$ (Kojundo Kagaku, 99 %, 40 wt %) and the electrolyte (60 wt %) was used as the positive electrode. A mixture (25 mg) of Na$_{15}$Sn$_4$ and acetylene black (Denka Black) was used as the negative electrode. An all-solid-state cell was charged and discharged under a constant current density of 0.013 mA cm$^{-2}$ at 25 °C in the voltage range from 1.17 to 2.40 V under an Ar atmosphere using a charge–discharge measurement device (Nagano, BTS-2004).

3. Results and discussion

Figure 1 shows the XRD patterns of the (a) Na$_3$SbS$_4$ and (b) Na$_{2.9375}$Sb$_{3.9375}$Cl$_{0.0625}$ milled and heat-treated (HT) samples. The heating temperature was 170 or 290 °C. These temperatures were decided from the DTA curves of the milled samples shown in Figures S1 and S2. Some exothermic peaks attributable to crystallization are observed. The samples were heated at temperatures above the corresponding peaks, where the heating temperatures are indicated by arrows in the figures. The milled sample...
shows XRD patterns attributable to cubic Na$_2$SbS$_4$, indicating that crystalline Na$_2$SbS$_3$Sb$_{1.9375}$Cl$_{0.0625}$ was directly synthesized via the mechanochemical process. An impurity phase, i.e., NaSbS$_2$, was also detected in the HT sample. The Raman spectra of the milled and HT Na$_2$SbS$_3$Sb$_{1.9375}$Cl$_{0.0625}$ powders are shown in Figure S3. All the samples show spectra similar to that of the Na$_3$SbS$_4$ crystal. In addition, the HT samples show a broad peak at 310 cm$^{-1}$ attributable to the NaSbS$_2$ impurity phase. The XRD patterns for other compositions are shown in Figure S4. Na$_3$SbS$_4$ crystals were mainly formed in all compositions with added chlorine. Since the XRD peaks of the electrolytes were quite broad even after heat-treatment at 170 °C, it is difficult to discuss the peak shift as a function of chlorine content in this study.

**Figure 2** shows the Rietveld refinement results of the XRD patterns of the Na$_2$Sb$_{3.9375}$SbS$_{3.9375}$Cl$_{0.0625}$ powder heated at 170 °C. Solid red and black lines denote the observed and calculated XRD patterns, respectively, while the green and purple ticks mark the positions of the reflections allowed by the space groups t-Na$_3$SbS$_4$ (P4$_2$1/c$^\text{17}$) and NaSbS$_2$ (JSPDS: 071-0499, Fm3m$^{23}$) respectively.

![Rietveld refinement of the XRD pattern of Na$_2$Sb$_{3.9375}$SbS$_{3.9375}$Cl$_{0.0625}$ heated at 170 °C.](image)

**Table 1.** Rietveld refinement results of XRD pattern of Na$_2$Sb$_{3.9375}$SbS$_{3.9375}$Cl$_{0.0625}$ heated at 170 °C

| Phase 1 | Na$_2$Sb$_{3.9375}$SbS$_{3.9375}$Cl$_{0.0625}$ (X: S = 3.9375, Cl = 0.0625) |
|---------|--------------------------------------------------------------------------------|
| Crystal system | Tetragonal |
| Space group | P-42$_c$(c (No. 114)) |
| Lattice parameters, volume, Z | a = 7.176(28) Å, c = 7.183(28) Å, V = 369.9 Å$^3$, Z = 2 |

**Table 1.** Rietveld refinement results of XRD pattern of Na$_2$Sb$_{3.9375}$SbS$_{3.9375}$Cl$_{0.0625}$ heated at 170 °C

| Atom | x | y | z | Site | Occupancy | $B_{eq}$ |
|------|---|---|---|-----|-----------|---------|
| Sb  | 0 | 0 | 0 | 2a | 1 | 0.4 |
| X   | 0.199(1) | 0.199(1) | 0.1623(5) | 8e | 1 | 1.4 |
| Na1 | 0 | 0.5 | 0.0763(5) | 4d | 0.9792 | 2.6 |
| Na2 | 0 | 0 | 0.5 | 2b | 0.9792 | 2.5 |

R$_p$ = 1.760, R$_wp$ = 2.230, S = 1.7755.

Because the refinement based on no-vacancy model resulted in a higher $S$ value (1.8033) than that of vacancy model (1.7755), the latter model with Na vacancy is suitable for this study. The cell volume of the Na$_2$Sb$_{3.9375}$SbS$_{3.9375}$Cl$_{0.0625}$ sample heated at 170 °C, 369.9837 Å$^3$, is smaller than that of the reported Na$_2$SbS$_4$ solid electrolyte, 371.52 Å$^3$, indicating that the slight difference between the ionic radii of S$^2-$ (1.84 Å) and Cl$^-$ (1.81 Å) $^{23}$ Although the HT Na$_2$Sb$_{3.9375}$SbS$_{3.9375}$Cl$_{0.0625}$ sample had a tetragonal structure, its lattice parameters (a = 7.176 Å and c = 7.183 Å) were somewhat different from the reported tetragonal parameters (a = 7.145 Å, c = 7.277 Å$^{17}$) and rather similar to those of a cubic structure. Therefore, we treat this phase as a pseudo-cubic phase in this study.

To evaluate the ionic conductivities and activation energies of these samples, two types of pellets were prepared. One type, denoted “cold press (CP),” was prepared by heating the milled powder sample and then cold-pressing at 360 MPa. The other type, denoted “hot press (HP),” was prepared by hot-pressing the milled powder sample at 170 °C under 360 MPa.

The temperature dependence of the ionic conductivity of the Na$_2$Sb$_{3.9375}$SbS$_{3.9375}$Cl$_{0.0625}$ (HP) electrolyte is shown in **Figure 3(a)**. The inset shows the Nyquist plot at $-25$ °C. A semicircle in the higher-frequency region and spike in the lower-frequency region were observed, indicating behavior typical of an ionic conductor. Because the bulk and grain boundary components were difficult to separate, the total conductivity was determined from the total resistance ($R$), as shown in the inset of **Figure 3(a)**. The temperature dependence of the ionic conductivities obeyed the Arrhenius equation, and thus the activation energies for conduction were calculated from the slope of the conductivities. The room-temperature ionic conductivity and activation energy of Na$_2$Sb$_{3.9375}$SbS$_{3.9375}$Cl$_{0.0625}$ (HP) were $2.9 \times 10^{-3}$ S cm$^{-1}$ and 23 kJ mol$^{-1}$, respectively.
The room-temperature ionic conductivities and activation energies of milled and HT Na$_{3-x}$SbS$_4$-$x$Cl$_x$ ($x = 0, 0.03, 0.0625, 0.09, 0.125$) with different heat-treatment temperatures are summarized in Fig. 3(b) and Table 2. The Na$_{2.9375}$SbS$_{3.9375}$Cl$_{0.0625}$ sample showed a higher ionic conductivity than the other samples. The room-temperature ionic conductivity and activation energy of HT Na$_{2.9375}$SbS$_{3.9375}$Cl$_{0.0625}$ (CP) were $1.4 \times 10^{-3}$ S cm$^{-1}$ and 24 kJ mol$^{-1}$, respectively. This conductivity is higher than that reported for tetragonal Na$_3$SbS$_4$.17) The ionic conductivity of the impurity NaSbS$_2$ phase was measured and its conductivity of $1.3 \times 10^{-3}$ S cm$^{-1}$ is much lower than those of Na$_{3-x}$SbS$_{4-x}$Cl$_x$. Thus, the partial substitution of Cl$^-$ for S$^2$- and introducing Na vacancies are effective for increasing the ionic conductivity of these HT materials. In all the compositions, the samples heated at 170 $^\circ$C showed higher ionic conductivities and lower activation energies than the milled samples. In contrast, the ionic conductivities of Na$_{3-x}$SbS$_{4-x}$Cl$_x$ ($x = 0, 0.03, 0.09, 0.125$) samples decreased after HT at 290 $^\circ$C. One possible reason for this conductivity decrease is a change in the crystal structure. The pseudo-cubic phase appeared upon heating the Na$_{2.9375}$SbS$_{3.9375}$Cl$_{0.0625}$ sample at 170 $^\circ$C, whereas the phase heated at 290 $^\circ$C had lattice parameters ($a = 7.195$ Å, $c = 7.219$ Å) close to those reported for the tetragonal phase.17) In the case of Na$_3$PS$_4$, the ionic conductivity of

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**Table 2.** Room-temperature ionic conductivities ($\sigma_{25}$), activation energies ($E_a$), densities of pellets ($d_1$) and powders ($d_2$), and relative densities ($d_1/d_2$) of Na$_{3-x}$SbS$_{4-x}$Cl$_x$ ($x = 0, 0.03, 0.0625, 0.09, 0.125$) solid electrolytes. CP and HP indicate cold-pressed and hot-pressed samples, respectively.

| $x$    | Condition       | $\sigma_{25}$/S cm$^{-1}$ | $E_a$/kJ mol$^{-1}$ | $d_1$/g cm$^{-3}$ | $d_2$/g cm$^{-3}$ | $d_1/d_2$/%  |
|--------|-----------------|---------------------------|---------------------|-------------------|-------------------|--------------|
| 0      | CP Milled       | $1.6 \times 10^{-4}$     | 30                  | 2.199             | 2.707             | 81.2         |
|        | CP HT at 170 $^\circ$C | $5.7 \times 10^{-4}$    | 25                  | 2.141             | 2.805             | 76.3         |
|        | HP HT at 170 $^\circ$C | $1.6 \times 10^{-3}$    | 24                  | 2.536             | 2.805             | 90.4         |
|        | CP HT at 290 $^\circ$C | $2.4 \times 10^{-4}$    | 27                  | 2.097             | 2.858             | 73.4         |
| 0.03   | CP Milled       | $3.6 \times 10^{-4}$     | 28                  | 2.173             | 2.751             | 79.0         |
|        | CP HT at 170 $^\circ$C | $7.9 \times 10^{-4}$    | 21                  | 2.207             | 2.797             | 78.9         |
|        | CP HT at 290 $^\circ$C | $3.3 \times 10^{-4}$    | 24                  | 2.189             | 2.844             | 77.0         |
| 0.0625 | CP Milled       | $1.8 \times 10^{-4}$     | 24                  | 2.197             | 2.711             | 81.1         |
|        | CP HT at 170 $^\circ$C | $1.4 \times 10^{-3}$    | 24                  | 2.216             | 2.818             | 78.6         |
|        | HP HT at 170 $^\circ$C | $2.9 \times 10^{-3}$    | 23                  | 2.618             | 2.818             | 92.9         |
|        | CP HT at 290 $^\circ$C | $5.0 \times 10^{-3}$    | 25                  | 2.080             | 2.859             | 72.7         |
| 0.09   | CP Milled       | $1.3 \times 10^{-4}$     | 30                  | 2.199             | 2.725             | 80.7         |
|        | CP HT at 170 $^\circ$C | $9.5 \times 10^{-4}$    | 24                  | 2.122             | 2.790             | 76.1         |
|        | CP HT at 290 $^\circ$C | $3.3 \times 10^{-4}$    | 25                  | 2.179             | 2.852             | 76.4         |
| 0.125  | CP Milled       | $1.1 \times 10^{-4}$     | 40                  | 2.291             | 2.715             | 84.4         |
|        | CP HT at 170 $^\circ$C | $2.7 \times 10^{-4}$    | 25                  | 2.209             | 2.792             | 79.1         |
|        | CP HT at 290 $^\circ$C | $3.5 \times 10^{-4}$    | 24                  | 2.110             | 2.873             | 73.5         |

$d_1$: calculated from the volume measured by the dimensions of the pellet. $d_2$: calculated from the volume measured by gas pycnometer.
the cubic phase is higher than that of the tetragonal phase.\textsuperscript{9)} Detailed structural analyses of the HT Na\textsubscript{3−x}SbS\textsubscript{4−x}Cl\textsubscript{x} samples will be needed to determine the reasons for this conductivity difference.

**Figure 4** shows SEM images of the fractured cross-sections of the milled and HT Na\textsubscript{2.9375}SbS\textsubscript{3.9375}Cl\textsubscript{0.0625} pellets. The samples examined were (a) milled (CP), (b) heated at 170 °C (CP), (c) heated at 170 °C (HP), and (d) heated at 290 °C (CP). Voids and pores are clearly observed in the SEM images of the CP samples [Figs. 4(a) and 4(b) and 4(d)]. In contrast, the SEM image of the HP sample shows that it is dense [Fig. 4(c)]. Table 2 lists the densities of the powder-compressed pellets (d\textsubscript{1}), powders (d\textsubscript{2}), and relative densities (d\textsubscript{1}/d\textsubscript{2}) of the milled and HT Na\textsubscript{3−x}SbS\textsubscript{4−x}Cl\textsubscript{x} (x = 0, 0.03, 0.0625, 0.09, and 0.125) samples. The relative density of the Na\textsubscript{2.9375}SbS\textsubscript{3.9375}Cl\textsubscript{0.0625} sample heated at 170 °C (CP) is 78.6 %. However, the HP sample of the same composition has a relative density of 92.9 %. This densification is the main reason for the higher conductivity of the HP sample compared with that of the CP sample. The CP samples heated at 170 °C showed lower relative densities than those of the milled samples for all the compositions because of the increase in crystallinity of Na\textsubscript{3−x}SbS\textsubscript{4−x}Cl\textsubscript{x} in the HT samples. Regardless of the lower relative density of the HT samples, they showed higher conductivities than the milled samples. This is because the crystal growth of Na\textsubscript{3−x}SbS\textsubscript{4−x}Cl\textsubscript{x} is highly effective in increasing the conductivity of the samples.

**Figure 5** shows the amounts of H\textsubscript{2}S gas generated from the Na\textsubscript{3}PS\textsubscript{4} and the Na\textsubscript{2.9375}SbS\textsubscript{3.9375}Cl\textsubscript{0.0625} powder after exposure to air at room temperature. The relative humidity of the air was 25 % for Na\textsubscript{3}PS\textsubscript{4} and 70 % for Na\textsubscript{2.9375}SbS\textsubscript{3.9375}Cl\textsubscript{0.0625}. The relative humidity of the air was 25 % for Na\textsubscript{3}PS\textsubscript{4} and 70 % for Na\textsubscript{2.9375}SbS\textsubscript{3.9375}Cl\textsubscript{0.0625}. The surface area and relative humidity for the Na\textsubscript{2.9375}SbS\textsubscript{3.9375}Cl\textsubscript{0.0625} sample heated at 170 °C were higher than those of the Na\textsubscript{3}PS\textsubscript{4} sample. Despite the harsher experimental conditions, the Na\textsubscript{2.9375}SbS\textsubscript{3.9375}Cl\textsubscript{0.0625} sample generated a considerably lower amount of H\textsubscript{2}S than the Na\textsubscript{3}PS\textsubscript{4} sample. Therefore, the heated Na\textsubscript{2.9375}SbS\textsubscript{3.9375}Cl\textsubscript{0.0625} electrolyte not only exhibits a high ionic conductivity but is also highly safe during atmospheric exposure.

XRD patterns of the Na\textsubscript{2.9375}SbS\textsubscript{3.9375}Cl\textsubscript{0.0625} sample before and after air exposure and after heating the air-exposed sample at 170 °C for 1 h are shown in **Fig. 6**. After
The Na$_{2.9375}$SbS$_{3.9375}$Cl$_{0.0625}$ electrolyte powder heated at 170 °C was used as the electrolyte in an all-solid-state cell. Figure 7 shows the initial five charge-discharge curves of the all-solid-state Na$_{15}$Sn$_4$/Na$_{2.9375}$SbS$_{3.9375}$Cl$_{0.0625}$/TiS$_2$ cell. The cell was operated as a sodium secondary battery at room temperature and showed an initial charge capacity of 120 mA h g$^{-1}$. The irreversible capacity at the initial cycle was observed. The origin of the irreversible capacity has not been clarified yet, but it is based on the difficulty of full extraction (full-charge) of Na-ions from the discharged NaTiS$_2$ positive electrode.\(^{25}\)

Another possible reason is related with contact loss due to the volume change of the active material, leading to blocking ion-conduction paths. A capacity of approximately 100 mA h g$^{-1}$ was retained from the second to the fifth cycle, suggesting that Na$_{2.9375}$SbS$_{3.9375}$Cl$_{0.0625}$ is effective as a solid electrolyte for all-solid-state cells.

4. Conclusions

Na$_{x}$Sn$_{1-x}$Sb$_4$Cl$_x$ ($x = 0$, 0.03, 0.0625, 0.09, and 0.125) electrolytes were prepared using a mechanochemical process, which was followed by heat treatment at 170 °C. The room-temperature ionic conductivity and activation energy of the Na$_{2.9375}$SbS$_{3.9375}$Cl$_{0.0625}$ electrolyte were 2.9 × 10$^{-3}$ S cm$^{-1}$ and 23 kJ mol$^{-1}$, respectively. This ionic conductivity is higher than that of Na$_3$SbS$_4$, suggesting that partially substituting Cl with S and introducing Na vacancies effectively improved the Na-ion conductivity of Na$_3$SbS$_4$. An all-solid-state Na$_{15}$Sn$_4$/TiS$_2$ cell with the Na$_{2.9375}$SbS$_{3.9375}$Cl$_{0.0625}$ electrolyte exhibited a reversible capacity of approximately 100 mA h g$^{-1}$ during five charge-discharge cycles at room temperature. The solid electrolyte not only exhibited a high ionic conductivity but was also safe in terms of H$_2$S gas generation during atmospheric exposure. Therefore, the prepared Na$_{2.9375}$SbS$_{3.9375}$Cl$_{0.0625}$ electrolyte is a promising candidate for practical application as a solid electrolyte in all-solid-state sodium batteries.

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References

1) K. B. Hueso, M. Armand and T. Rojo, *Energy Environ. Sci.*, 6, 734–749 (2013).
2) M. Tatsumisago and A. Hayashi, *Funct. Mater. Lett.*, 1, 31–36 (2008).
3) A. Sakuda, A. Hayashi and M. Tatsumisago, *Chem. Mater.*, 22, 949–956 (2010).
4) A. Hayashi, A. Sakuda and M. Tatsumisago, *Front. Energy Res.*, 4, 1–25 (2016).
5) S.-H. Bo, Y. Wang, J. C. Kim, W. D. Richards and G. Ceder, *Chem. Mater.*, 28, 252–258 (2016).
6) L. Zhang, K. Yang, J. Mi, L. Lu, L. Zhao, L. Wang, Y. Li and H. Zeng, *Adv. Energy Mater.*, 5, 1501294 (2015).
7) W. D. Richards, T. Tsujimura, L. J. Miara, Y. Wang, J. C. Kim, S. P. Ong, I. Uechi, N. Suzuki and G. Ceder,
8) M. Duchardt, U. Ruschewitz, S. Adams, S. Dehnen and B. Roling, *Angew. Chem. Int. Edit.*, 57, 1351–1355 (2018).

9) Z. Zhang, E. Ramos, F. Lalère, A. Assoud, K. Kaup, P. Hartman and L. F. Nazar, *Energy Environ. Sci.*, 11, 87–93 (2018).

10) A. Hayashi, K. Noi, N. Tanibata, M. Nagao and M. Tatsumisago, *J. Power Sources*, 258, 420–423 (2014).

11) A. Hayashi, K. Noi, A. Sakuda and M. Tatsumisago, *Nat. Commun.*, 3, 856 (2012).

12) N. Tanibata, M. Deguchi, A. Hayashi and M. Tatsumisago, *Chem. Mater.*, 29, 5232–5238 (2017).

13) N. Tanibata, K. Noi, A. Hayashi, N. Kitamura, Y. Idemoto and M. Tatsumisago, *ChemElectroChem*, 1, 1130–1132 (2014).

14) N. Tanibata, K. Noi, A. Hayashi and M. Tatsumisago, *RSC Adv.*, 4, 17120–17123 (2014).

15) I.-H. Chu, C. S. Kompella, H. Nguyen, Z. Zhu, S. Hy, Z. Deng, Y. S. Meng and S. P. Ong, *Sci. Rep.*, 6, 33733 (2016).

16) C. Yu, S. Ganapathy, N. J. J. de Klerk, E. R. H. van Eck and M. Wagemaker, *J. Mater. Chem. A*, 4, 15095–15105 (2016).

17) A. Banerjee, K. H. Park, J. W. Heo, Y. J. Nam, C. K. Moon, S. M. Oh, S. T. Hong and Y. S. Jung, *Angew. Chem. Int. Edit.*, 55, 9634–9638 (2016).

18) H. Wang, Y. Chen, Z. D. Hood, G. Sahu, A. S. Pandian, J. K. Keum, K. An and C. Liang, *Angew. Chem. Int. Edit.*, 55, 8551–8555 (2016).

19) L. Zhang, D. Zhang, K. Yang, X. Yan, L. Wang, J. Mi, B. Xu and Y. Li, *Adv. Sci.*, 3, 1600089 (2016).

20) D. Zhang, X. Cao, D. Xu, N. Wang, C. Yu, W. Hu, X. Yan, J. Mi, B. Wen, L. Wang and L. Zhang, *Electrochim. Acta*, 259, 100–109 (2018).

21) E. P. Ramos, Z. Zhang, A. Assoud, K. Kaup, F. Lalère and L. F. Nazar, *Chem. Mater.*, 30, 7413–7417 (2018).

22) F. Izumi and K. Momma, *Solid State Phenom.*, 130, 15–20 (2007).

23) A. Hayashi, K. Noi, N. Tanibata, M. Nagao and M. Tatsumisago, *J. Power Sources*, 258, 420–423 (2014).

24) J. Olivier-Fourcade, E. Philippot and M. Maurin, *Z. Anorg. Allg. Chem.*, 446, 159–168 (1978).

25) R. D. Shannon, *Acta Crystallogr. A*, 32, 751–767 (1976).

26) Z. Jinghuan, N. Raftery and D. Field, *Powder Diffr.*, 8, 61–64 (1993).

27) E. Lee, S. Sahgong, C. S. Johnson and Y. Kim, *Electrochim. Acta*, 143, 272–277 (2014).