Mechanochemically Prepared Highly Conductive $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4\text{-NaI}$ Composite Electrolytes for All-Solid-State Sodium Battery

Takuma TAKAYANAGI,^a Akira NASU,^a Fumika TSUJI,^a Atsushi SAKUDA,^{a,§}
 Masahiro TATSUMISAGO,^{a,§§} and Akitoshi HAYASHI^{a,b,*§}

^a Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University,
 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

^b Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, Sakyo, Kyoto 606-8501, Japan

* Corresponding author: hayashi@chem.osakafu-u.ac.jp

ABSTRACT

Solid electrolytes with high ionic conductivity, high formability, and high electrochemical properties are required to improve the performance of all-solid-state sodium batteries. In this study, we focus on a combination of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ and NaI for preparing composite electrolytes $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4\cdot x\text{NaI}$, and investigate their crystal structures, microstructures, and electrochemical properties. NaI is uniformly dispersed in the composites without forming a solid solution with $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$. $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4\cdot 0.5\text{NaI}$ shows a high ionic conductivity of $3.6 \times 10^{-2} \text{ S cm}^{-1}$ after sintering at 275 °C for only 1.5 h. The charge-discharge characteristics of all-solid-state cells using the $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4\cdot x\text{NaI}$ composite are also improved.

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1. Introduction

All-solid-state batteries are expected to be the next-generation energy storage devices owing to their safety and high energy densities. All-solid-state batteries use inorganic solid electrolytes instead of organic liquid electrolytes.^{1,2} Therefore, all-solid-state batteries can be used to improve safety by reducing the risk of leakage and ignition.

Among all-solid-state batteries, all-solid-state sodium batteries have attracted considerable attention.^{3–6} Sodium is an inexpensive resource because of its abundance in the earth's crust.^{7–9} Moreover, sodium-ion-conducting solid electrolytes exhibit higher ionic conductivities than lithium-ion-conducting ones owing to a lower charge density of sodium than lithium ions based on their respective ionic radii.

Solid electrolytes are essential for the practical application of all-solid-state sodium batteries. A typical sodium-ion-conducting solid electrolyte is β'' -alumina ($\text{Na}_2\text{O} \cdot x\text{Al}_2\text{O}_3$).¹⁰ This electrolyte is used for sodium-sulfur batteries (NAS batteries). The NAS batteries are operated at high temperatures (300–350 °C) to maintain the active materials i.e. sodium and sulfur, in a molten state, and to increase the ionic conductivity of β'' -alumina.¹¹ To ensure battery safety, a room-temperature operation is desirable. Therefore, it is necessary to develop solid electrolytes that exhibit high ionic conductivities, even at room temperature. Oxide-based crystalline electrolytes like β'' -alumina must be sintered at high temperatures to reduce the grain boundary resistance and increase the ionic conductivity. In contrast, sulfide solid electrolytes exhibit high ionic conductivities at room temperature and can be easily densified by cold pressing.^{12,13} This is due to the fact that the electrostatic interaction between S^{2-} ions and sodium ions is lower than that of O^{2-} ions and sodium ions because the polarizability of S^{2-} ions are greater than that of O^{2-} ions.

One of the typical sodium-ion-conducting sulfide solid electrolytes, viz. Na_3PS_4 , prepared by a mechanochemical process and subsequent heat treatment,¹⁴ exhibited an ionic conductivity of $2.0 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C.¹⁴ An all-solid-state Na-Sn/ Na_3PS_4 /TiS₂ cell operated as a secondary battery at 25 °C.¹⁴ However, the capacity of this all-solid-state cell is approximately 90 mAh g⁻¹, and solid electrolytes with higher ionic conductivities are required to achieve higher capacity.

In 2016, a Na_3SbS_4 solid electrolyte was reported, which exhibited a high ionic conductivity of over $10^{-3} \text{ S cm}^{-1}$ at 25 °C.¹⁵ Na_3SbS_4 was prepared by using various methods, such as solid-phase, liquid-phase, and mechanochemical methods.^{15–17} In general, most sulfide-based solid electrolytes generate toxic H₂S gas upon hydrolysis when exposed to the atmosphere. However, Na_3SbS_4 forms a hydrate ($\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$), and thus, the generation of H₂S gas is substantially reduced.^{16,17} Therefore, Na_3SbS_4 is considered an excellent solid electrolyte in terms of both ionic conductivity and safety. To further improve the properties of Na_3SbS_4 , the effect of the addition of NaI was investigated.^{18,19} The $0.9\text{Na}_3\text{SbS}_4 \cdot 0.1\text{NaI}$ composite electrolyte exhibited a higher ionic conductivity than Na_3SbS_4 . The iodide anions have a larger ionic radius and higher polarizability than sulfide anions; therefore, the iodide anion has weaker electrostatic interaction with sodium cation than sulfide anions. In addition, the performance of the all-solid-state cell using the $0.9\text{Na}_3\text{SbS}_4 \cdot 0.1\text{NaI}$ electrolyte was found to be improved over that using Na_3SbS_4 .^{18,19}

We reported the preparation of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ electrolyte, in which Sb in Na_3SbS_4 is partly substituted by W. $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ was sintered at 275 °C for 12 h and exhibited a higher conductivity of $3.2 \times 10^{-2} \text{ S cm}^{-1}$ at 25 °C.²⁰ Two other research groups have also reported W-substituted solid electrolytes derived from Na_3SbS_4 .^{21,22} Fuchs et al. used the solid-phase method to prepare $\text{Na}_{2.9}\text{Sb}_{0.9}\text{W}_{0.1}\text{S}_4$ by heating at 550 °C for 20 h. They reported that $\text{Na}_{2.9}\text{Sb}_{0.9}\text{W}_{0.1}\text{S}_4$ exhibits an ionic conductivity of $4.1 \times 10^{-2} \text{ S cm}^{-1}$ at 25 °C.²¹ Feng et al. fabricated $\text{Na}_{2.895}\text{Sb}_{0.7}\text{W}_{0.3}\text{S}_4$ via a mechanochemical process, followed by heat treatment at 500 °C for

[§]ECSJ Active Member

^{§§}ECSJ Fellow

A. Hayashi orcid.org/0000-0001-9503-5561

12 h. They reported an ionic conductivity of $2.4 \times 10^{-2} \text{ S cm}^{-1}$ at 25 °C using $\text{Na}_{2.895}\text{Sb}_{0.7}\text{W}_{0.3}\text{S}_4$.²² Thus, W-substituted Na_3SbS_4 solid electrolytes show a very high ionic conductivity exceeding $10^{-2} \text{ S cm}^{-1}$; however, their preparation requires a long heat treatment time.

In this study, a composite electrolyte consisting of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ and NaI are prepared by a mechanochemical process to improve the properties of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$. Here, we show that sintering with NaI shortens the heat treatment period and increases the ionic conductivity of the composite electrolytes, which improves the electrochemical performance of all-solid-state sodium batteries. The crystal structures, microstructures, ionic conductivities, and electrochemical properties of the $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot x\text{NaI}$ ($x = 0, 0.10, 0.20, 0.50$, and 0.75 , in a molar ratio) composites are evaluated.

2. Experimental Section

2.1 Preparation of materials

Stoichiometric amounts of Na_2S (>99.1 %; Nagao), Sb_2S_3 (>99.8 %; Nihon Seiko), S (>99.98 %; Kojundo Chemical Lab.), and WS_2 (>99 %; Aldrich) were mixed for the composition $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$. The mixture of starting materials was processed mechanochemically at ambient temperature using a planetary ball mill (Pulverisette 7; Fritsch) with zirconia pots (45 mL in volume) and zirconia balls (4 mm in diameter, 50 g). The total mass of the starting materials was 0.6 g in each pot. The rotation speed and milling duration were kept at 510 rpm and 30 h, respectively. In the next step, the composite was prepared by mechanochemical treatment of the prepared $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ and NaI (>99.999 %; Aldrich) under milder milling conditions. The rotation speed and milling duration were kept at 250 rpm and 30 min, respectively. The milled samples were cold-pressed at 360 MPa to make pellets. Then, the pellets were heat-treated at 275 °C for 1.5 h. This heat treatment condition is a typical one for obtaining $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ electrolyte.²⁰ Powder samples were obtained by grinding heat-treated pellets. All the processes were performed in dry Ar atmosphere.

2.2 Material characterization

X-ray diffraction (XRD) analyses of the prepared samples were performed on an X-ray diffractometer (SmartLab; Rigaku) using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The diffraction data were collected in the 2θ range of 10.0° – 60.0° in steps of 0.02° at a scan rate of $10^\circ \text{ min}^{-1}$.

Raman spectroscopy was performed using a Raman spectrophotometer (RAMANtouch; Nanophoton). The prepared samples were placed in an airtight vessel filled with dry Ar gas, and Raman scattering signals from the samples were collected through a transparent quartz plate mounted on the upper side of the vessel. The laser beam was focused onto the sample using a $50\times$ objective (NA = 0.70, Nikon) with an excitation wavelength of 532 nm.

The densities of the powder-compressed pellets (d_1) were calculated from the weight and volume of the pellets, while those of the powders (d_2) were measured using a gas pycnometer (AccuPyc II 1340; Shimadzu). Scanning electron microscopy (SEM) (SU8220; Hitachi High Technologies) equipped with an energy-dispersive X-ray spectroscopy system (EDS) (EMAX Evolution; Horiba Ltd.). The samples were transferred to an airtight container filled with Ar gas.

2.3 Electrochemical characterization

The ionic conductivities were obtained via AC impedance measurements using an impedance analyzer (1260, Solartron) over a frequency range from 10 MHz to 0.1 Hz with an applied AC

voltage of 10 mV. The measurements were performed in a temperature range from -30 to 10°C . The diameter and thickness of the pellets were approximately 4 mm and 2 mm, respectively. Gold thin films (4 mm in diameter) were deposited as ion-blocking electrodes on both faces of the heat-treated pellets using a quick coater (Quick Coater SC-701; Sanyu Electron).

The electrochemical properties of the samples were investigated by cyclic voltammetry measurements using an electrochemical workstation (VMP3, Bio-Logic Co.). A stainless-steel disk attached to one side of the prepared pellets was used as the working electrode, and Na metal (>99 %; Aldrich) was attached to the other side of the pellet as the counter electrode and reference electrode. Cyclic voltammograms were obtained with a scan rate of 0.05 mV s^{-1} between -0.5 V and OCV (vs. Na metal) at 25°C .

2.4 Construction of all-solid-state cell

A mixture (10 mg) of TiS_2 (40 wt%) and the prepared $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot x\text{NaI}$ composite (60 wt%) was used as the positive electrode layer. On the other hand, mixture (30 mg) of $\text{Na}_{15}\text{Sn}_4$ and acetylene black (Denka Black) was used as the negative electrode layer. A composite electrolyte powder of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot x\text{NaI}$ (80 mg) was used as the separator layer. An all-solid-state cell was fabricated by placing the three-layered powder in a polycarbonate cylinder of 10 mm diameter and applying uniaxial pressure at 360 MPa for 5 min with two stainless steel rods used as current collectors. The all-solid-state cell was charged and discharged under a constant current density of 0.038 mA cm^{-2} at 25°C in the voltage range of 1.2–2.4 V under an Ar atmosphere using a charge-discharge measurement device (VMP3, Bio-Logic Co.).

3. Results and Discussion

Figures 1a and 1b show the XRD patterns and Raman spectra of the $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot x\text{NaI}$ ($x = 0, 0.10, 0.20, 0.50$, and 0.75 , in a molar ratio) samples, respectively. In the XRD patterns, the diffraction peaks of both NaI and $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ were observed. Moreover, no peak shift was observed on the high-angle side of the XRD patterns. These results indicate that NaI and $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ form composites without forming a solid solution. In the Raman spectra, three peaks were observed at 340 – 400 cm^{-1} for all the samples, attributed to the different vibrational

Figure 1. (a) XRD patterns and (b) Raman spectra of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot x\text{NaI}$ composites.

Figure 2. Cross-sectional SEM images of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot x\text{NaI}$. Secondary electron images of (a) $x = 0$ and (b) $x = 0.5$, backscattered electron images of (c) $x = 0$ and (d) $x = 0.5$, secondary electron images with high magnification of (e) $x = 0$, and (f) $x = 0.5$.

modes of the SbS_4^{3-} units of Na_3SbS_4 .²³ Peaks at 460–480 cm^{-1} were also observed for all the samples, attributed to the different vibrational modes of WS_4^{2-} units.²⁴ The presence of these peaks indicates that SbS_4^{3-} and WS_4^{2-} units were formed in all the samples.

Figure 2 shows cross-sectional SEM images of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot x\text{NaI}$ pellets sintered at 275 °C for 1.5 h. Figure 2a shows a large number of voids in $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$. However, the number of voids is found to be decreased in $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot 0.5\text{NaI}$ (Fig. 2b). These images show that NaI filled the voids and improved the relative density of the pellets. The backscattered electron image of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ (Fig. 2c) did not show any contrast; however, the contrast was observed in $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot 0.5\text{NaI}$ (Fig. 2d). The white areas in Fig. 2d represent NaI, showing that NaI is uniformly dispersed in the composite. The EDS mappings given in the Supporting Information (Fig. S1) also suggest that NaI is uniformly dispersed. In the high-magnification secondary electron image of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ (Fig. 2e), the shape of the particles and the appearance of grain boundaries were clearly visible. However, individual particles and grain boundaries were not observed in

Table 1. Relative density, room temperature conductivities, activation energy, and NaI volume ratio of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot x\text{NaI}$ composites.

Sample	Relative density (%)	$\sigma_{25^\circ\text{C}}$ (S cm^{-1})	E_a (kJ mol^{-1})	NaI volume ratio (%)
$\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$	82.5	2.5×10^{-3}	16	0
$\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot 0.10\text{NaI}$	83.1	2.2×10^{-2}	15	3.5
$\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot 0.20\text{NaI}$	90.3	2.3×10^{-2}	19	6.8
$\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot 0.50\text{NaI}$	88.4	3.6×10^{-2}	15	15.4
$\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot 0.75\text{NaI}$	84.9	5.5×10^{-3}	13	21.4

Figure 3. Temperature dependence of the conductivities for $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot x\text{NaI}$ composites.

$\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot 0.5\text{NaI}$ (Fig. 2f). Therefore, the $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ particles adhere to each other and reduce the grain boundaries after sintering with NaI. Furthermore, the interfaces between NaI and $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ become closer. Sintering with NaI may facilitate sodium diffusion among $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ particles, where ductile NaI particles adhered in advance via mechanochemistry.

Figure 3 shows the temperature dependence of the ionic conductivity calculated from the AC impedance measurements. Figure S2 shows the Nyquist plots for $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot 0.5\text{NaI}$ and the conductivity was calculated from total resistance R_{total} at each plot. The temperature dependence of the ionic conductivity is expressed by the Arrhenius equation ($\sigma = \sigma_0 \exp(-E_a/RT)$), where σ_0 and E_a are the pre-exponential factor and activation energy for ionic conduction, respectively. The relative densities, ionic conductivities at 25 °C ($\sigma_{25^\circ\text{C}}$), activation energies, and NaI volume ratios of the composites are listed in Table 1. The ionic conductivities at 25 °C ($\sigma_{25^\circ\text{C}}$) were calculated by extrapolating the Arrhenius plots. The relative densities (d_1/d_2) were calculated by measuring the pellet density (d_1) and powder density (d_2). The detailed calculations are provided in the Supporting Information (Table S1). The relative density of the pellets increased to approximately 90 % after mixing and sintering with NaI. This result is in good agreement with the SEM observations (Fig. 2). The ionic conductivity increased for $x \leq 0.50$, and was found to be higher than $10^{-2} \text{ S cm}^{-1}$ for $0.10 \leq x \leq 0.50$. The W-substituted solid electrolytes for Na_3SbS_4 showed ionic conductivities above $10^{-2} \text{ S cm}^{-1}$ only after heat treatment for more than 12 h.^{20–22} In contrast, the NaI-mixed composites showed an ionic conductivity of more than $10^{-2} \text{ S cm}^{-1}$ after only 1.5 h of sintering at 275 °C. We have not found any correlation between the activation energy and the amount of NaI added to the composites. The maximum ionic conductivity

Figure 4. (a) The magnified figures in XRD patterns of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot x\text{NaI}$ composites and (b) Raman spectra of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot 0.5\text{NaI}$ composite milled and heated samples.

was obtained at a NaI volume ratio of approximately 15 %, which indicates that the NaI domains do not percolate in the composite electrolyte (Fig. 2f), and does not contribute to ionic conduction.

Herein, we discuss the reasons behind the increase in ionic conductivity after the addition of NaI. Figure 4a shows the magnified XRD patterns of milled and heated $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot x\text{NaI}$ ($x = 0$ and 0.50) samples. It can be seen that the broad peaks of the milled sample became sharper after heat treatment. It is also observed that $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot 0.5\text{NaI}$ has a smaller full width at half maximum (FWHM) of the diffraction peaks as compared to that of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$. Therefore, $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot 0.5\text{NaI}$ has a higher crystallinity than $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$. The FWHM of the added NaI also decreased with heat treatment. In the Raman spectra of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot 0.5\text{NaI}$ (Fig. 4b), a peak was observed around $400\text{--}420\text{ cm}^{-1}$ in the milled sample, which did not appear in the heated sample. Crystalline WS_2 (one of the starting materials) shows Raman peaks at 420 cm^{-1} and 350 cm^{-1} , which are attributed to the A_{1g} and E_{2g} vibrational modes, respectively.²⁵ We believe a portion of WS_2 remained in the milled samples. In addition, the intensity of the peak attributed to WS_4^{2-} units around $460\text{--}480\text{ cm}^{-1}$ was found to be increased after heat treatment, which indicates the formation of additional WS_4^{2-} units in $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$. Therefore, the heat treatment after the addition of NaI facilitated the chemical reaction to form $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ solid solution with higher crystallinity, which contributed to the increase in ionic conductivity. Moreover, NaI domains with polarizable iodide ions were uniformly dispersed in the composites and affected sodium-ion conduction, as reported in the literature.¹⁸ The previously reported $\text{Na}_3\text{SbS}_4 \cdot \text{NaI}$ composites^{18,19} were prepared by a liquid-phase process in which Na_3SbS_4 and NaI were dissolved in methanol, stirred, and then dried. The mixing and heat-treatment processes are quite different from the $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot \text{NaI}$ composite in this study. The comparison of these composites is difficult to discuss at the present stage.

Figures 5a and 5b show the CV curves of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ and $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot 0.5\text{NaI}$, respectively. Cyclic voltammetry was performed with a sweep to the reduction side of the OCV. The reduction current was observed from approximately 1.1 V for both samples. This reduction current may be attributed to the reduction of tungsten and antimony in the solid electrolytes, but no detailed structural analysis has been performed to identify the decomposed compounds. This reduction current is attributed to the decom-

Figure 5. Cyclic voltammograms of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot x\text{NaI}$ composites. (a) $x = 0$ and (b) $x = 0.5$.

position reaction of the solid electrolytes. $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ showed a higher reduction current than $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot 0.5\text{NaI}$ in the voltage range of $1.1\text{--}0.5\text{ V}$ suggesting that NaI addition may mitigate decomposition of the electrolyte. This decomposition was irreversible because the corresponding oxidation current was not observed in the cyclic voltammograms. In both samples, the reduction current increased from approximately 0.3 V. These reduction currents are primarily related to the Na plating. However, oxidation current related to Na stripping was not observed. After the first cycle, the reduction current of the Na plating was not observed. The decomposition reaction of the solid electrolytes at the reduction current in the first cycle may form a resistive layer between the Na metal and solid electrolytes, leading to the suppression of further Na stripping/plating behavior.

Figures 6a and 6b show the charge-discharge curves of the all-solid-state Na-Sn/TiS₂ cell using $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ and $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot 0.5\text{NaI}$, respectively. Capacity degradation was observed for $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ in each cycle. The cell was firstly discharged, and the decomposition reaction of the solid electrolyte at the Na-Sn negative electrode proceeded simultaneously with the insertion of Na into the TiS₂ positive electrode. In contrast, for $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot 0.5\text{NaI}$, irreversible capacity was observed in the first and second cycles, and better cycling characteristics were observed in the second and fifth cycles probably due to the improved electrochemical properties of the solid electrolyte with NaI. Figures S3a and S3b show the Nyquist plots of the all-solid-state cell constructed with $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ and $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot 0.5\text{NaI}$, respectively. The increase in the total resistance of the cell was found to be suppressed for $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot 0.5\text{NaI}$ because the electrolyte decomposition was reduced by the addition of NaI. Therefore, NaI addition to the electrolytes suppressed the decomposition of the electrolytes, resulting in good cycle characteristics.

4. Conclusions

$\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot x\text{NaI}$ composite electrolytes were prepared

Figure 6. Charge-discharge curves of the all-solid-state cells constructed with Na-Sn/ $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot x\text{NaI}/\text{TiS}_2\text{-Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot x\text{NaI}$. (a) $x = 0$ and (b) $x = 0.5$.

by a mechanochemical process. NaI was uniformly dispersed in the composites without forming a solid solution with $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$. The addition of NaI leads to an increase in relative density and ionic conductivity. The improved crystallinity of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$, which was achieved by the complete reaction of the starting material WS_2 at 275°C for 1.5 h, resulted in a high conductivity exceeding $10^{-2} \text{ S cm}^{-1}$ at 25°C . The addition of NaI to $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ mitigated the decomposition of the $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ electrolyte in the low voltage region. Therefore, the all-solid-state cell using $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4 \cdot 0.5\text{NaI}$ showed a better performance than that using $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$.

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CRediT Authorship Contribution Statement

Takuma Takayanagi: Formal analysis (Lead), Investigation (Lead), Resources (Lead),

Writing – original draft (Lead)

Akira Nasu: Formal analysis (Equal), Investigation (Equal)

Fumika Tsuji: Investigation (Equal), Resources (Supporting)

Atsushi Sakuda: Supervision (Supporting), Validation (Lead), Writing – review & editing (Lead)

Masahiro Tatsumisago: Writing – review & editing (Equal)

Akitoshi Hayashi: Conceptualization (Lead), Funding acquisition (Lead), Supervision (Lead), Writing – review & editing (Lead)

Data Availability Statement

The data that support the findings of this study are openly available under the terms of the designated Creative Commons License in J-STAGE Data listed in D1 of References.

Conflict of Interest

The authors declare no conflict of interest in the manuscript.

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