Aqueous-Solution Synthesis of Na$_3$SbS$_4$ Solid Electrolytes for All-Solid-State Na-ion Batteries

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Table of Contents

1. Experimental Section

2. Supporting Figures
1. Experimental Section

**Preparation of Materials:** The homogeneous aqueous solutions were prepared by dissolving a total of 500 mg of Na$_2$S (Sigma Aldrich), Sb$_2$S$_3$ (99.5%, Sigma Aldrich), and elemental sulfur (99.5%, Alfa Aesar) powders with a mole ratio of 6 : 1 : 2 in 3 mL of deionized water (Scheme 1a). For the preparation via the Route-1, 10 mL of acetone was added to the solution, resulting in the precipitation of solids. After the solid powders were collected by filtration, they were rinsed with ethanol, after which they were dried under vacuum at room temperature (NSbSH1). They were then heat-treated at 200 °C under vacuum (NSbS1). For the preparation via the Route-2, the solution was placed under vacuum at room temperature, resulting in the production of solid powders (NSbSH2). The final product (NSbS2) was obtained by subsequently rinsing with ethanol and heat-treatment, in the same way as the Route-1. The Na$_3$SbS$_4$-coated FeS$_2$ powders were prepared by adding FeS$_2$ (99.9%, Alfa Aesar) powders to the aqueous Na$_3$SbS$_4$ solution, followed by the procedures via either Route-1 or Route-2 (Scheme 1b). The weight fraction of Na$_3$SbS$_4$ for the Na$_3$SbS$_4$-coated FeS$_2$ samples via the Route-2 and the Route-1 was 13 and 17%, respectively, as determined by the ICP-OES measurements. The Na$_3$PS$_4$ powders were prepared by the mechanochemical milling of a stoichiometric mixture of Na$_2$S and P$_2$S$_5$ (99%, Sigma Aldrich) for 1.5 h, followed by heat-treatment at 270 °C for 1 h in a sealed glass ampoule.

**Materials characterization:** For the measurement of H$_2$S generated during the aqueous-solution synthesis of Na$_3$SbS$_4$, after total 500 mg of Na$_2$S, Sb$_2$S$_3$, and elemental S were put into a deionized water (3 mL), the as-prepared solution was kept in a closed container (2.5 L) in which an air was circulated by a small electric fan at 23.5 °C. After 10 h, acetone was added to the aqueous solution for precipitation. The amount of H$_2$S was also measured during washing the as-obtained Na$_2$S/Na$_3$SbS$_4$·xH$_2$O samples using EtOH. The amount of H$_2$S was measured using H$_2$S sensor (SP2297, SENKO). XRD cells containing hermetically sealed SE samples with a beryllium window were mounted on a D8-Bruker Advance diffractometer equipped with Cu K$_{α}$ radiation (1.54056 Å), and were subjected to measurements at 40 kV and 40 mA using a continuous scanning mode at 0.025° s$^{-1}$. The weight fraction of the SE coating layer for the Na$_3$SbS$_4$-coated FeS$_2$ powders was determined by ICP-OES using the
700-ES (Varian Corp.). The FESEM images were obtained using the S-4800 (Hitachi Corp.). The Raman spectra were measured using a Raman spectrometer (Alpha300R, WITec) with a 532 nm He–Ne laser. The HRTEM images and the EDXS elemental maps or line profiles for the FIB-cross-sectioned Na$_3$SbS$_4$-coated FeS$_2$ were obtained using a JEOL-JEM2100F (JEOL) by using 30 keV Ga$^+$ ion beam (FEI, Helios NanoLab 450). The HRTEM images were obtained with 200 kV of acceleration voltage. The TGA profile was obtained from 30 to 400 °C at 10 °C min$^{-1}$ under N$_2$ using a SDT Q600 (TA Instrument Corp.).

**Electrochemical characterization:** After the Na$_3$SbS$_4$ pellets were prepared by cold-pressing at 370 MPa, the ionic conductivity was measured by an AC impedance method using an Iviumstat (IVIUM Technologies Corp.) with symmetric Na-ion blocking Ti/SE/Ti cells under a pressure of 75 MPa. All-solid-state Na-ion cells were fabricated as follows: Na$_3$Sn prepared by mixing of Na metal (Sigma Aldrich) with Sn metal powders (Sigma Aldrich) served as the counter electrode, exhibiting an operating voltage of ~0 V (vs. Na/Na$^+$). A Na$_3$SbS$_4$/Na$_3$PS$_4$ bilayer pellet (100 and 20 mg, respectively) prepared by cold-pressing under 370 MPa was used as the SE layer. 5 mg of the Na$_3$SbS$_4$-coated FeS$_2$ powders were spread on the Na$_3$SbS$_4$ side of SE bilayer, followed by pressing at 370 MPa. Then, 50 mg of the as-prepared Na$_3$Sn was attached on the other side (Na$_3$PS$_4$) of SE bilayer by pressing at 370 MPa. The Na$_3$SbS$_4$/Na$_3$PS$_4$ bilayer was used to achieve better interfacial stability at the negative electrode (Na$_3$Sn)$^{5,24}$ All the procedures were performed in a polyaryletheretherketone (PEEK) mould (diameter = 13 mm) with two Ti metal rods as current collectors. All processes for fabricating the all-solid-state cells were performed in an Ar-filled dry box. Galvanostatic charge-discharge measurements were performed under a pressure of 75 MPa at 30 °C.
2. Supporting Figures

Fig. S1 TGA profile under N$_2$ for the NSbSH1 sample prepared during the aqueous-solution synthesis of Na$_3$SbS$_4$. 
**Fig. S2** $\text{H}_2\text{S}$ amount as a function of time during the aqueous-solution synthesis of $\text{Na}_3\text{SbS}_4$ a) for the Route-1 before filtration and b) for the process of washing with EtOH.
Fig. S3 a) XRD patterns and b) Arrhenius plots of Na-ion conductivities for the aqueous-solution synthesized Na$_3$SbS$_4$ heat-treated at different temperatures.
Fig. S4 XRD patterns of Na$_{3.75}$Sn$_{0.75}$Sb$_{0.25}$S$_4$ prepared by conventional solid-state synthesis at 450 °C and by aqueous solution synthesis using precursors of Na$_2$S, SnS$_2$, Sb$_2$S$_3$, and elemental sulfur with two different heat-treatment temperatures of 200 °C and 550 °C. The Bragg positions for Na$_{3.75}$Sn$_{0.75}$Sb$_{0.25}$S$_4$, Na$_4$SnS$_4$ (JCPDS no. 65-1668), and Na$_3$SbS$_4$ are shown in blue, green, and red, respectively.
**Fig. S5** HRTEM image of the FIB-cross-sectioned Na$_3$SbS$_4$-coated FeS$_2$ and its corresponding FFT patterns, revealing the FeS$_2$ and Na$_3$SbS$_4$ crystallites.
**Fig. S6** Scanning TEM image of the FIB-cross-sectioned Na$_3$SbS$_4$-coated FeS$_2$ and its corresponding EDXS elemental line profiles for Sb, Fe, S, and O.
**Fig. S7** First two-cycle discharge-charge voltage profiles at 50 μA cm$^{-2}$ for FeS$_2$/Na-Sn ASNBs employing Na$_3$SbS$_4$-coated FeS$_2$ prepared by the aqueous-solution process (*via* the Route-1).