Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

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[Electronic Supplementary Information (ESI)]

Aqueous-Solution Synthesis of Na₃SbS₄ Solid Electrolytes for All-Solid-State Na-ion Batteries

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1. Experimental Section

Preparation of Materials: The homogeneous aqueous solutions were prepared by dissolving a total of 500 mg of Na₂S (Sigma Aldrich), Sb₂S₃ (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 Na₃SbS₄-coated FeS₂ powders were prepared by adding FeS₂ (99.9%, Alfa Aesar) powders to the aqueous Na₃SbS₄ for the Na₃SbS₄-coated FeS₂ samples *via* the Route-2 and the Route-1 was 13 and 17%, respectively, as determined by the ICP-OES measurements. The Na₃PS₄ powders were prepared by the mechanochemical milling of a stoichiometric mixture of Na₂S and P₂S₅ (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_2S generated during the aqueous-solution synthesis of Na_3SbS_{4} , after total 500 mg of Na_2S , Sb_2S_3 , and elemental S were put into a deionized water (3 mL), the asprepared 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_2S was also measured during washing the as-obtained $Na_2S/Na_3SbS_4 \cdot xH_2O$ samples using EtOH. The amount of H_2S was measured using H_2S 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_3SbS_4 -coated FeS₂ powders was determined by ICP-OES using the

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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 Na₃SbS₄-coated FeS₂ were obtained using a JEM-2100F (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 N₂ using a SDT Q600 (TA Instrument Corp.).

Electrochemical characterization: After the Na₃SbS₄ 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: Na₃Sn 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 Na₃SbS₄/Na₃PS₄ bilayer pellet (100 and 20 mg, respectively) prepared by cold-pressing under 370 MPa was used as the SE layer. 5 mg of the Na₃SbS₄-coated FeS₂ powders were spread on the Na₃SbS₄ side of SE bilayer, followed by pressing at 370 MPa. Then, 50 mg of the as-prepared Na₃Sn was attached on the other side (Na₃PS₄) of SE bilayer by pressing at 370 MPa. The Na₃SbS₄/Na₃PS₄ bilayer was used to achieve better interfacial stability at the negative electrode (Na₃Sn).^{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.

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2. Supporting Figures



Fig. S1 TGA profile under N_2 for the NSbSH1 sample prepared during the aqueous-solution synthesis of Na_3SbS_4 .



Fig. S2 H_2S amount as a function of time during the aqueous-solution synthesis of Na_3SbS_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_3SbS_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_2S , SnS_2 , Sb_2S_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_4SnS_4 (JCPDS no. 65-1668), and $Na_3SbS_4^5$ are shown in blue, green, and red, respectively.



Fig. S5 HRTEM image of the FIB-cross-sectioned Na_3SbS_4 -coated FeS_2 and its corresponding FFT patterns, revealing the FeS_2 and Na_3SbS_4 crystallites.



Fig. S6 Scanning TEM image of the FIB-cross-sectioned Na₃SbS₄-coated FeS₂ and its corresponding EDXS elemental line profiles for Sb, Fe, S, and O.



Fig. S7 First two-cycle discharge-charge voltage profiles at 50 μ A cm⁻² for FeS₂/Na-Sn ASNBs employing Na₃SbS₄-coated FeS₂ prepared by the aqueous-solution process (*via* the Route-1).