[Supporting Information]

Solution-Derived Glass-Ceramic NaI·Na₃SbS₄ Superionic Conductors for All-Solid-State Na-Ion Batteries

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Supporting Experimental Methods

For the measurement of H$_2$S generated from Na$_3$PS$_4$ and 0.1NaI-0.9Na$_3$SbS$_4$, the SE powders were kept in a sealed container (2.6 L) with a water (2 mL) in an open vial. A small electric fan circulated an air in the container and the relative humidity was 60-80%. The amount of H$_2$S was measured using an H$_2$S sensor (SP2297, SENKO). The XPS data were collected with a monochromatic Al K$_\alpha$ source (1486.6 eV) at 72 W, 12 kV, and 6 mA using an X-ray photoelectron spectrometer (ThermoFisher).
Fig. S1 Nyquist plots at 30 °C for the solution-derived 0.1NaI·0.9Na$_3$SbS$_4$ prepared at 150 °C.

Fig. S2 XRD patterns for the solution-derived $x$NaI·$(1-x)$Na$_3$SbS$_4$ prepared at a) 200 °C and b) 300 °C.
**Fig. S3** H$_2$S amount as a function of time for Na$_3$PS$_4$ and 0.1Na$_3$-0.9Na$_3$SbS$_4$ exposed in air.

**Fig. S4** First two-cycle cyclic voltammetry curves for Ti/0.1NaI-0.9Na$_3$SbS$_4$/Na$_3$PS$_4$/Na$_3$Sn cells in the negative potential range (0.0-3.0 V (vs. Na/Na$^+$)) and in the positive potential range (2.5-5.0 V (vs. Na/Na$^+$)) at 30 °C. The solid and dashed lines are at first and second cycles, respectively. The scan rate was 20 mV s$^{-1}$. 30 mg of 0.1NaI-0.9Na$_3$SbS$_4$, 100 mg of Na$_3$PS$_4$, and 60 mg of Na$_3$Sn were used for the cells.
**Fig. S5** HRTEM image of the solution-derived 0.1NaI·0.9Na₃SbS₄ prepared at 150 °C and its corresponding FFT pattern. The spots in the FFT pattern correspond to Na₃SbS₄.¹⁰
**Fig. S6** a) XRD patterns of Na₃SbS₄ and Na₃₋ₓSbS₄₋ₓIx (x = 0.10, nominal composition) prepared by the solid-state reaction at 550 °C. The DFT-calculated XRD pattern of Na₃₋ₓSbS₄₋ₓIx (x = 0.112) is compared. Photographs of b) Na₃SbS₄ and c) Na₃₋ₓSbS₄₋ₓIx (x = 0.1) powders.
Fig. S7 XPS spectra of a) Na 1s, b) Sb 3d, c) S 2p, and d) I 3d for the solution-derived $x\text{NaI} \cdot (1 - x)\text{Na}_3\text{SbS}_4$ prepared at 200 °C. The spectrum of $\text{Na}_3\text{SbS}_4$ prepared by solid-state synthesis at 550 °C is compared.
Fig. S8 Activation energies of the Na$^+$ conductivities for solution-derived $x$NaI-$\left(1-x\right)$Na$_3$SbS$_4$ prepared at 150, 200, or 300 °C.
Fig. S9 Rate capability results at 30 °C for FeS$_2$/\((\text{Na}_3\text{SbS}_4/\text{Na}_3\text{PS}_4)/\text{Na}_3\text{Sn}\) all-solid-state cell using 0.1NaI-0.9Na$_3$SbS$_4$-coated FeS$_2$. a) Discharge capacities and b) charge-discharge voltage profiles varied by the current density. The amount of coated 0.1NaI-0.9Na$_3$SbS$_4$ was 20 wt%.

Fig. S10 Nyquist plots at 30 °C for Na$_3$Sn/Na$_3$PS$_4$/Na$_3$Sn cells as a function of storage time.