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[Supporting Information]

Solution-Derived Glass-Ceramic NaI·Na_3SbS_4 Superionic Conductors for All-Solid-State Na-Ion Batteries

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Supporting Experimental Methods

For the measurement of H_2S generated from Na_3PS_4 and $0.1NaI{\cdot}0.9Na_3SbS_4$, 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_2S was measured using an H_2S sensor (SP2297, SENKO). The XPS data were collected with a monochromatic Al K_α source (1486.6 eV) at 72 W, 12 kV, and 6 mA using an X-ray photoelectron spectrometer (ThermoFisher).

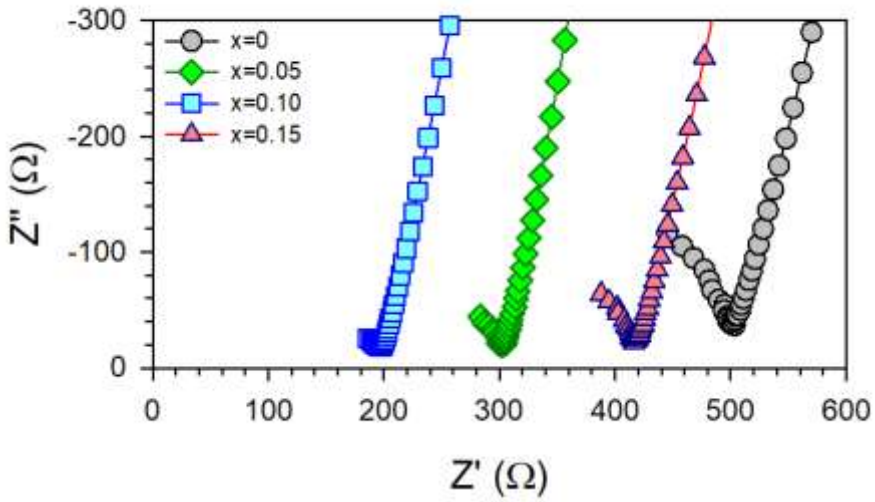

Fig. S1 Nyquist plots at 30 °C for the solution-derived 0.1NaI·0.9Na_3SbS_4 prepared at 150 °C.

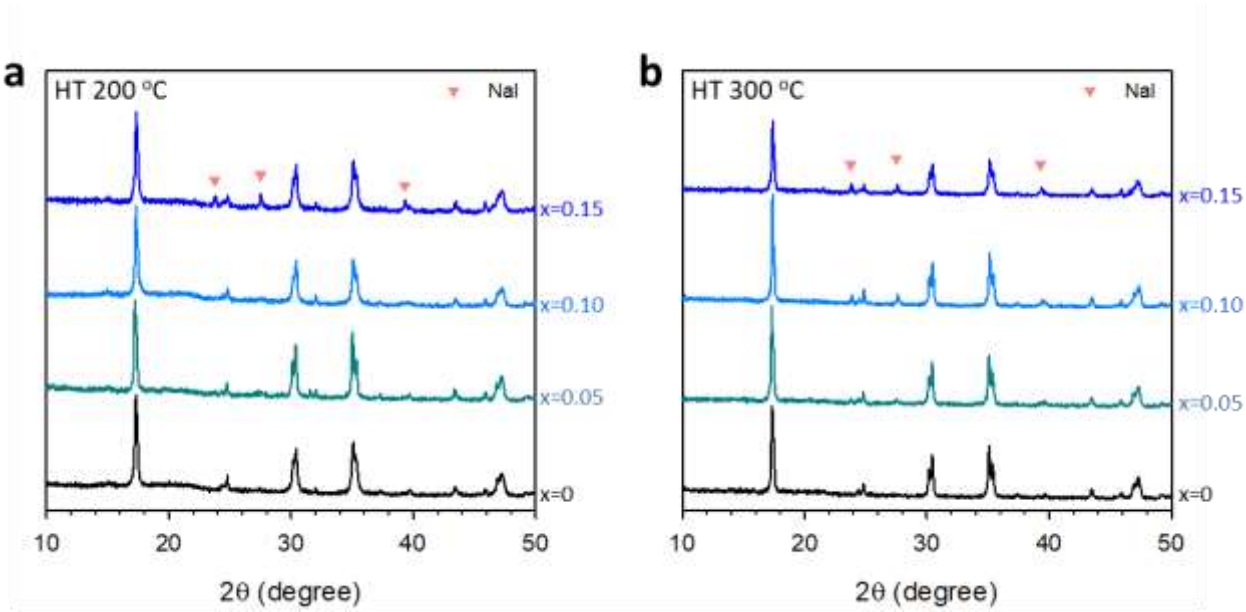

Fig. S2 XRD patterns for the solution-derived *x*NaI·(1 − *x*)Na_3SbS_4 prepared at a) 200 °C and b) 300 °C.

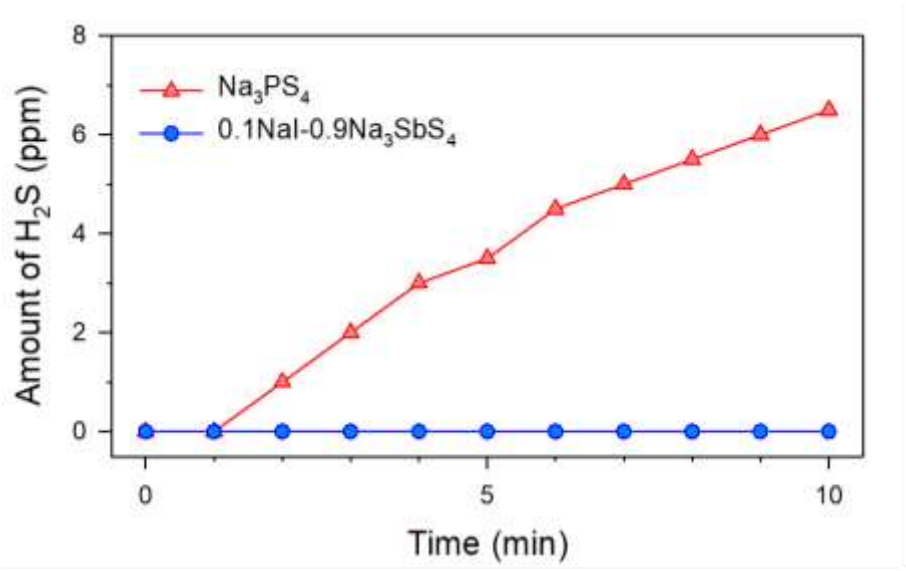

Fig. S3 H_2S amount as a function of time for Na_3PS_4 and 0.1Na·0.9Na_3SbS_4 exposed in air.

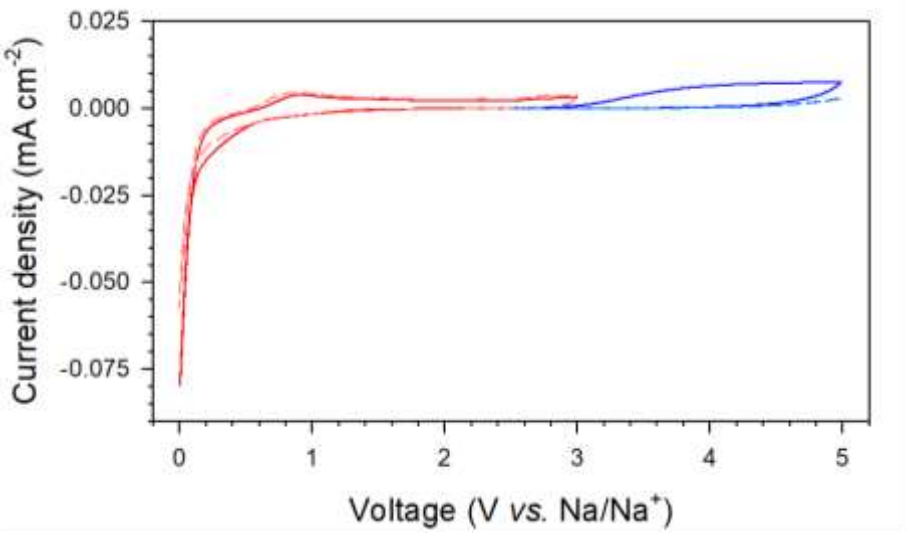

Fig. S4 First two-cycle cyclic voltammetry curves for Ti/0.1NaI·0.9Na_3SbS_4/Na_3PS_4/Na_3Sn cells in the negative potential range (0.0-3.0 V (vs. Na/Na^+)) and in the positive potential range (2.5-5.0 V (vs. Na/Na^+)) at 30 °C. The solid and dashed lines are at first and second cycles, respectively. The scan rate was 20 mV s^{-1}. 30 mg of 0.1NaI·0.9Na_3SbS_4, 100 mg of Na_3PS_4, and 60 mg of Na_3Sn were used for the cells.

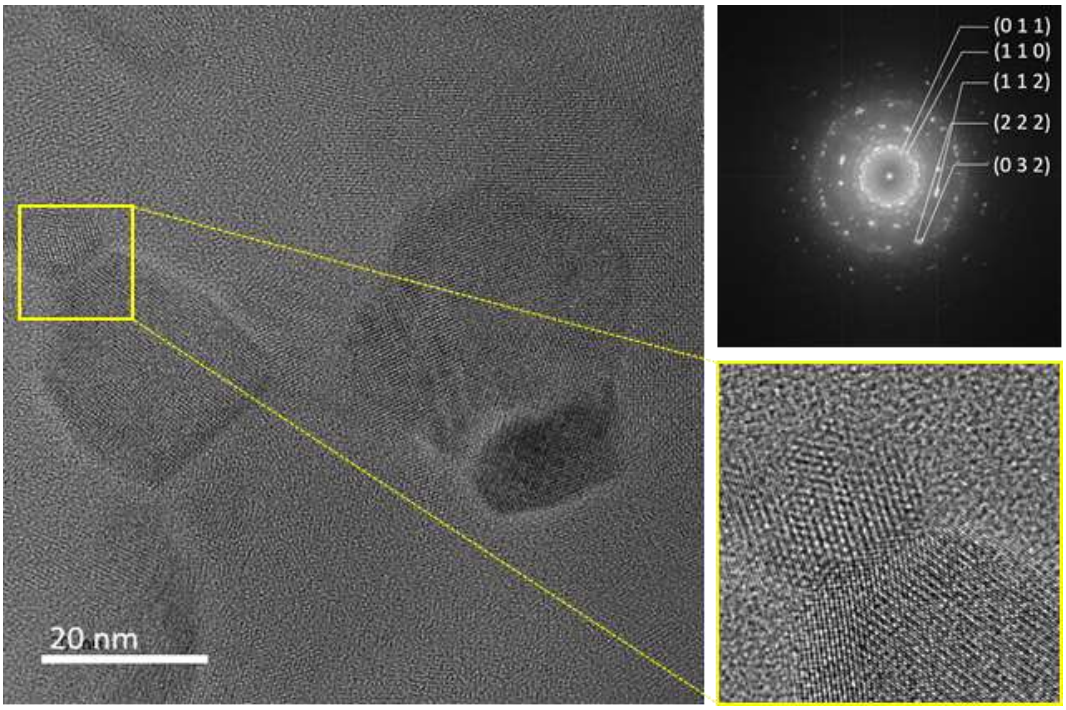

Fig. S5 HRTEM image of the solution-derived 0.1NaI·0.9Na_3SbS_4 prepared at 150 °C and its corresponding FFT pattern. The spots in the FFT pattern correspond to Na_3SbS_4.[10]

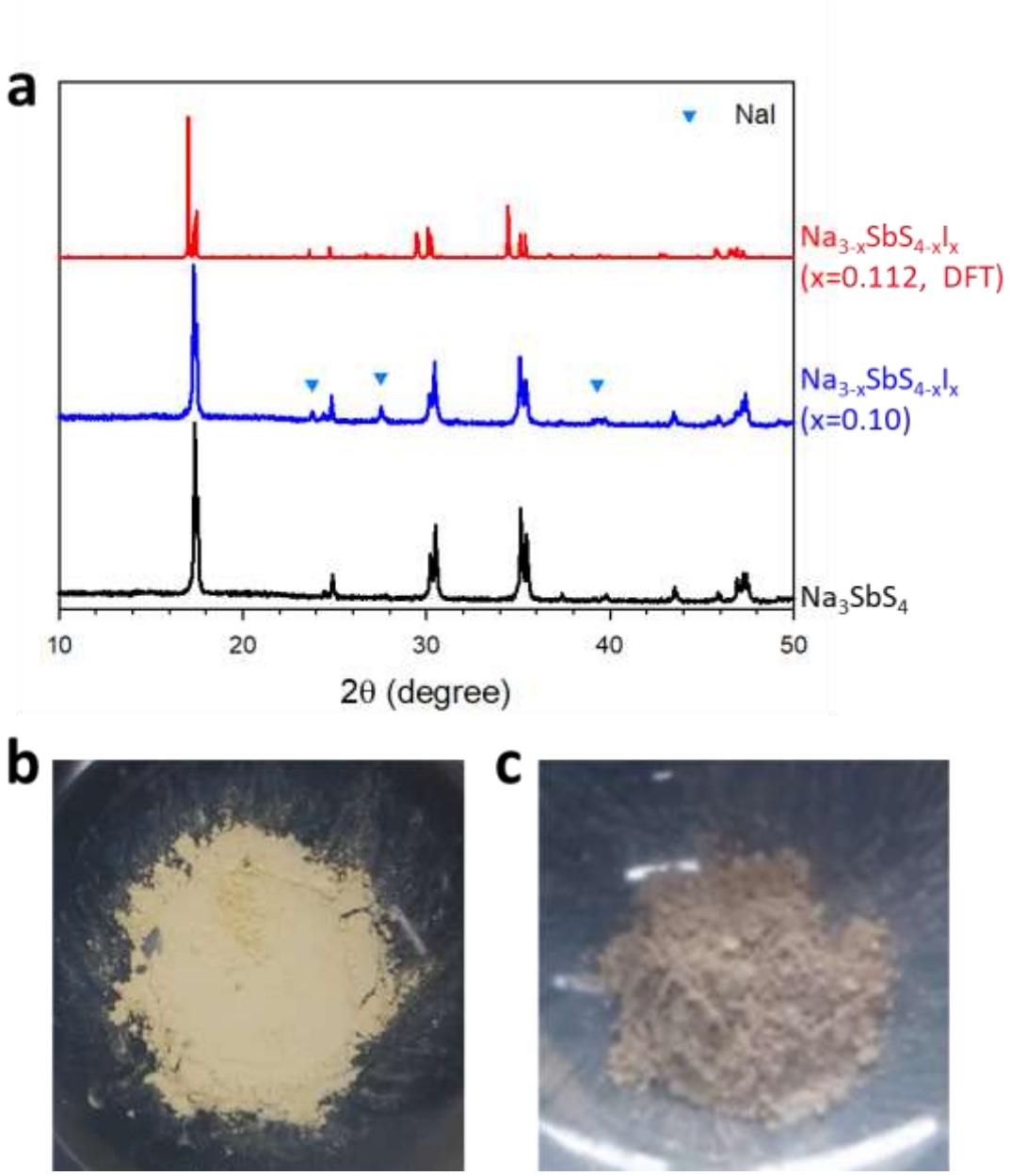

Fig. S6 a) XRD patterns of Na_3SbS_4 and $Na_{3-x}SbS_{4-x}I_x$ (x = 0.10, nominal composition) prepared by the solid-state reaction at 550 °C. The DFT-calculated XRD pattern of $Na_{3-x}SbS_{4-x}I_x$ (x = 0.112) is compared. Photographs of b) Na_3SbS_4 and c) $Na_{3-x}SbS_{4-x}I_x$ (x = 0.1) powders.

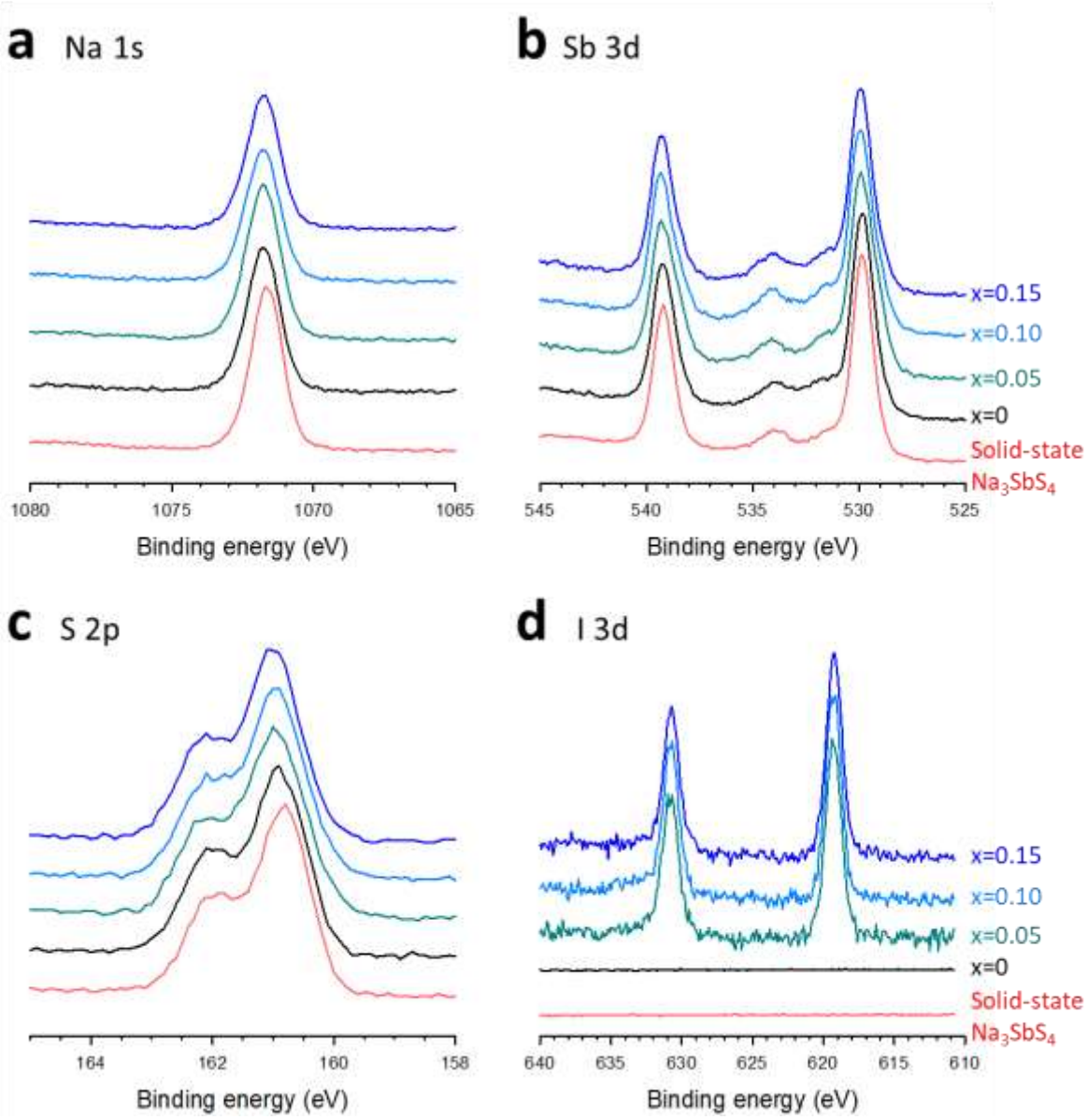

Fig. S7 XPS spectra of a) Na 1s, b) Sb 3d, c) S 2p, and d) I 3d for the solution-derived *x*NaI·(1 − *x*)Na_3SbS_4 prepared at 200 °C. The spectrum of Na_3SbS_4 prepared by solid-state synthesis at 550 °C is compared.

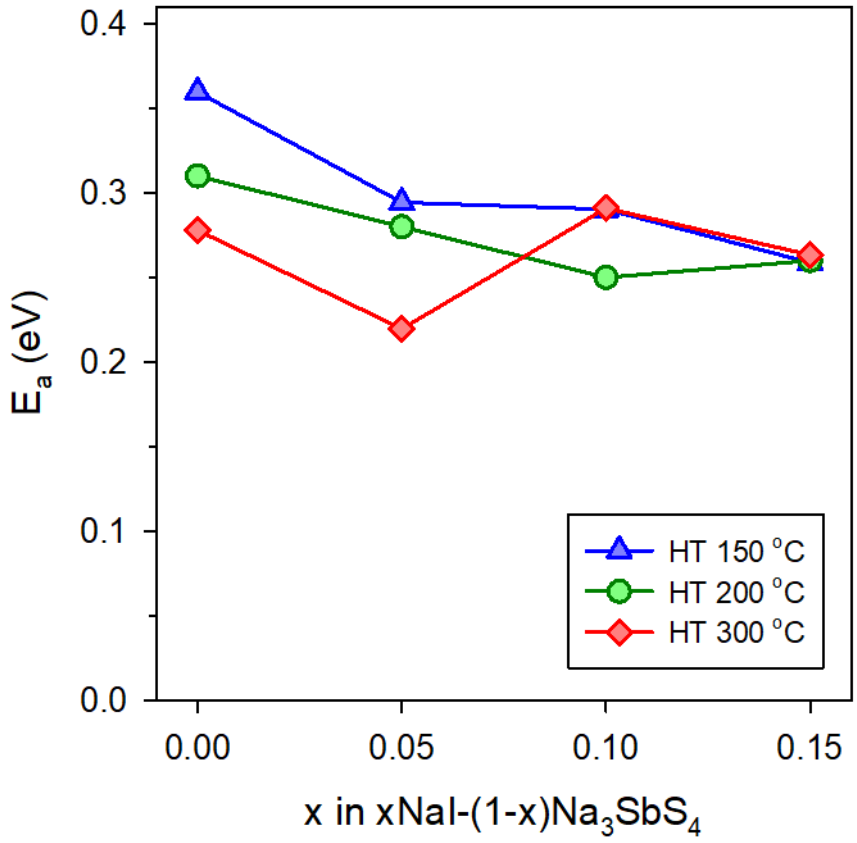

Fig. S8 Activation energies of the Na^+ conductivities for solution-derived *x*NaI·(1 − *x*)Na_3SbS_4 prepared at 150, 200, or 300 °C.

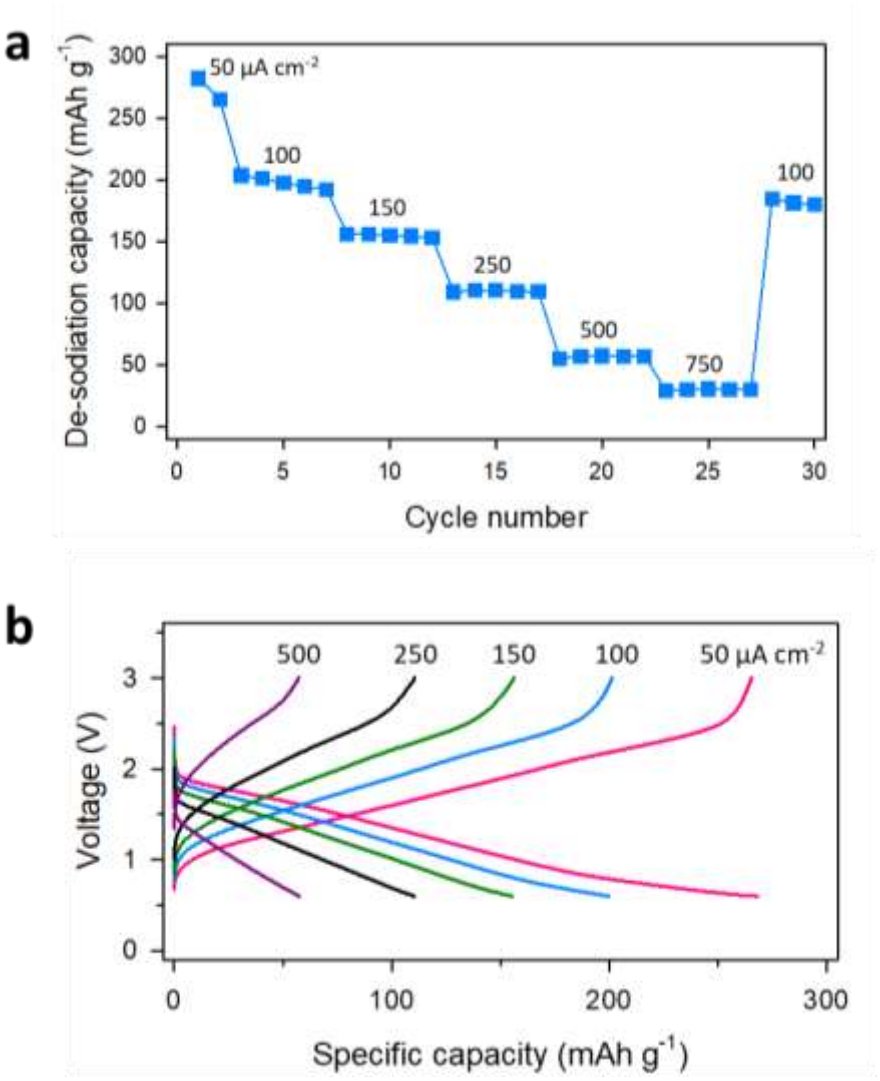

Fig. S9 Rate capability results at 30 °C for FeS_2/(Na_3SbS_4/Na_3PS_4)/Na_3Sn all-solid-state cell using 0.1NaI·0.9Na_3SbS_4-coated FeS_2. a) Discharge capacities and b) charge-discharge voltage profiles varied by the current density. The amount of coated 0.1NaI·0.9Na_3SbS_4 was 20 wt%.

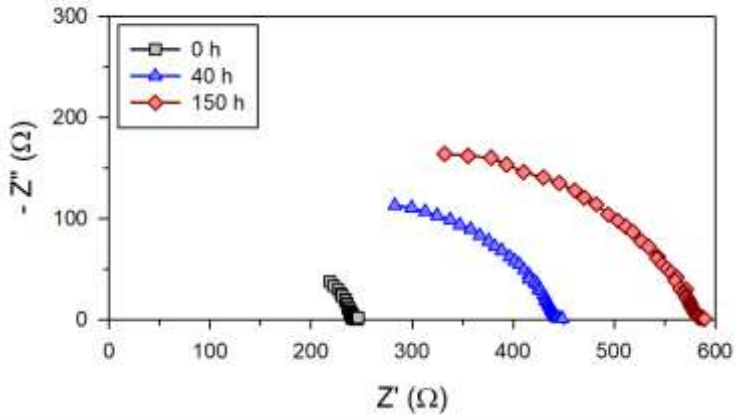

Fig. S10 Nyquist plots at 30 °C for Na_3Sn/Na_3PS_4/Na_3Sn cells as a function of storage time.