## Supporting Information

## **Evaluating Electrolyte–Anode Interface Stability in Sodium All-Solid-State Batteries**

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Figure S1. Linear sweep voltammograms for NYZC, NPS, and NBH.



**Figure S2.** XRD patterns for mixtures of Sn with a) NYZC, b) NPS, and c) NBH after heating at 80 °C for 10 h.



Figure S3. FIB-SEM with EDS mapping of Sn | SSE |  $Na_9Sn_4$  cells.



Figure S4. Symmetric cell evaluation using NYZC and NPS electrolytes.



**Figure S5.** FIB-SEM anode cross-section and EDS elemental mapping for (a) Sn | NPS | NYZC | NaCrO<sub>2</sub> and (b) Sn | NBH | NYZC | NaCrO<sub>2</sub> cells after cycling. (c) Electrochemical cycling data for both cells.



**Figure S6.** EIS measurements of (a) NYZC, (b) NPS, and (c) NBH showing Na<sup>+</sup> conductivities of 0.0627, 0.185, and 1.8 mS/cm respectively. DC Polarization measurements of (d) NYZC, (e) NPS, and (f) NBH showing e<sup>-</sup> conductivities of 26, 10, and 76 nS/cm respectively.



Figure S7. XRD refinement results of (a) NaCrO<sub>2</sub> and (b) Na<sub>9</sub>Sn<sub>4</sub>.