Self-Sacrifice of Sulfide Electrolytes Facilitating Stable Solid-State Sodium-Sulfur Batteries

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Supplementary Fig. 1: Ionic conductivity of prepared Na₃SbS₄ (NAS) and Na₃PS₄ (NPS).



Supplementary Fig. 2: XRD patterns of S@C-NAS/NPS cathode composite at the pristine state and post the first charge.



Supplementary Fig. 3: SEM surficial images at two scales (5 and 20 μ m) of a) pristine S@C-NAS, b) charged S@C-NAS, c) pristine S@C-NPS, and d) charged S@C-NPS.



Supplementary Fig. 4: a) galvanostatic charge-discharge (GCD) curves of S@C-NAS and NAS-C cathode in areal capacity. **b)** GCD curves of NAS-C cathodes with different cut-off voltage ranges. **c)** Cycling performance of NAS-C cathode within 0.7-2.6 V.

To avoid the oxidation of the central cation of the SbS_4^{3-} tetrahedron, a discharge cut-off voltage of 0.7 V was set to cease the complete reduction of NAS. The NAS-C cathodes with different cut-off voltages were measured (0.01-4.2 V, 0.7-2.6 V), as shown in Fig. S4b. Upon discharging to near 0 V, the NAS-C cathode unleashed an areal capacity of 1.9 mAh cm⁻². The long plateau starting at around 0.6 V indicates the conversion of the Sb valence structure. However, the lack of reversibility in the second cycle reveals the importance of ion transport. In contrast, by setting the cut-off voltage at 0.7 V, the reduction of NAS was limited to the sulfur part. As shown in Fig. S4c, the cell operating within 0.7-2.6 V exhibits a stable performance for over 250 cycles.



Supplementary Fig. 5: CV of S@C-NAS cathode at a) room temperature, and b) 60 °C.



Supplementary Fig. 6: **a)** Enlarged Raman spectra at 240-340 cm⁻¹, and **b)** full Raman spectra at 0-800 cm⁻¹.



Supplementary Fig. 7: S K-edge XANES spectra of NAS-C cathode during cell operation.



Supplementary Fig. 8: Phase-uncorrected Sb K-edge EXAFS in R-space of NAS with FEFF calculated model.



Supplementary Fig. 9: GCD voltage profiles for the corresponding cell configuration, a) NAS-NPS as electrolyte bilayer, b) NAS as sole electrolyte layer, and c) NPS as sole electrolyte layer.



Supplementary Fig. 10: SEM images of pressed NAS solid electrolyte pellet at the scale of **a**) 2 μ m, and **b**) 20 μ m.



Supplementary Fig. 11: XRD patterns of the self-formed interlayer with Na-Sn references.



Supplementary Fig. 12: Cross-sectional SEM images of the SE-anode interface attached to anode for NAS at **a**) discharged, **b**) charged; and NPS at **c**) discharged, **d**) charged.



Supplementary Fig. 13: EDS on the cross-sectional SEM images of the in-situ formed NASanode interlayer, **a**) interested area, and elemental mappings for **b**) Na, **c**) Sn, **d**) Sb, and **e**) S.



Supplementary Fig. 14: Galvanostatic cycling profiles of NAS symmetric cell at 0.51 mA cm⁻²-0.51 mAh cm⁻².



Supplementary Fig 15: Modeling of SE-anode interface with a surface defect. a) voltage distribution around the surface defect. b) Na-ion current density distribution along the top surface.



Supplementary Fig. 16: Cycling performance of NPS-aided S@C cathode at 0.41 mA cm⁻² (0.5C).



Supplementary Fig. 17: a) GCD curves for S@C-NAS cathodes with various S content, operating at 0.05C.

Two S@C-NAS cathodes with different S@C contents (S@C: NAS=3:7 or 4:6) were measured within the same solid-state battery configuration (S@C-NAS|NAS|NaSn). The total cathode loading remained the same at 3.2 mg, but the testing C-rate was set to 0.05C (0.061, 0.082 mA cm⁻² for 3:7, 4:6, respectively).



Supplementary Fig. 18: Optical image of the customized XCT cell, mounted on the holder during XCT tests.

Voltage (V vs. Na ₁₅ Sn ₄ /Na ⁺)	Decompositions Reaction	E _{rxt} (eV/atom)
0.1-0.63	$Na_3SbS_4 + 8 Na \rightarrow Na_3Sb + 4 Na_2S$	[-1.713, -0.891]
0.64-0.93	$Na_3SbS_4 + 6 Na \rightarrow NaSb + 4 Na_2S$	[-0.862, -0.514]
0.94-1.27	$Na_3SbS_4 + 5 Na \rightarrow Sb + 4 Na_2S$	[-0.502, -0.172]
1.28-1.63	$Na_3SbS_4 + 2 Na \rightarrow Na_3SbS_3 + Na_2S$	[-0.168, -0.028]
1.64-1.66	$Na_3SbS_4 + Na \rightarrow Na_3SbS_3 + NaS$	[-0.024, -0.02]
1.67-1.74	$Na_3SbS_4 + 0.5 Na \rightarrow Na_3SbS_3 + 0.5 NaS_2$	[-0.019, -0.012]
1.75-1.91	$Na_3SbS_4 \rightarrow Na + NaSbS_2 + NaS_2$	[-0.011, -0.043]
1.92-2.28	$Na_3SbS_4 \rightarrow 1.2 Na + NaSbS_2 + 0.4 Na_2S_5$	[-0.045, -0.131]
2.29-3.08	$Na_3SbS_4 \rightarrow 2 Na + 0.5 Sb_2S_3 + 0.5 Na_2S_5$	[-0.135, -0.451]
>3.08	$Na_3SbS_4 \rightarrow 3 Na + 0.5 Sb_2S_3 + 2.5 S$	-0.457

Supplementary Table 1: Summarized table for redox of Na₃SbS₄.

Voltage (V vs. Na ₁₅ Sn ₄ /Na+)	Decompositions Reaction	E_rxt (eV/atom)
0.1-0.38	$Na_3PS_4 + 8 Na \rightarrow Na_3P + 4 Na_2S$	[-1.4, -0.995]
0.38-0.73	$Na_3PS_4 + 6 Na \rightarrow NaP + 4 Na_2S$	[-0.968, -0.547]
0.74-1.08	$Na_3PS_4 + 5.273 Na \rightarrow 0.091Na_3P_{11} + 4 Na_2S$	[-0.536, -0.167]
1.09-1.23	Na ₃ PS ₄ + 5.143 Na -> 0.143 NaP ₇ + 4 Na ₂ S	[-0.168, -0.023]
1.24-1.33	$Na_3PS_4 + Na \rightarrow Na_2PS_3 + Na_2S$	[-0.018, -0.0]
1.34-2.21		
2.22-2.30	Na ₃ PS ₄ -> 0.6 Na + Na ₂ PS ₃ + 0.2 Na ₂ S ₅	[-0.001, -0.01]
2.31-3.08	$Na_3PS_4 \rightarrow 2.8 Na + 0.5 P_2S_7 + 0.1 Na_2S_5$	[-0.013, -0.445]
>3.08	Na ₃ PS ₄ -> 3 Na + 0.5 P ₂ S ₇ + 0.5 S	-0.457

Supplementary Table S2: Summarized table for redox of Na₃PS₄.

The anodic and cathodic (electro)chemical stability of Na₃SbS₄ and Na₃PS₄ were evaluated by simulating conditions at the low (reduction, high mNa) and high (oxidation, low mNa) voltage regimes of a typical battery cycling process. The evaluation is assumed to be closely linked to Na insertion/de-insertion into/from the solid electrolyte structure. The above tables summarize the competing phases that would likely form during electrochemical cycling.