

## Supplementary Information

### Surface modification and interfacial engineering of Na<sub>3</sub>SbS<sub>4</sub> solid electrolytes by polymethylsiloxane-based polymer for high-performance all-solid-state sodium-ion batteries

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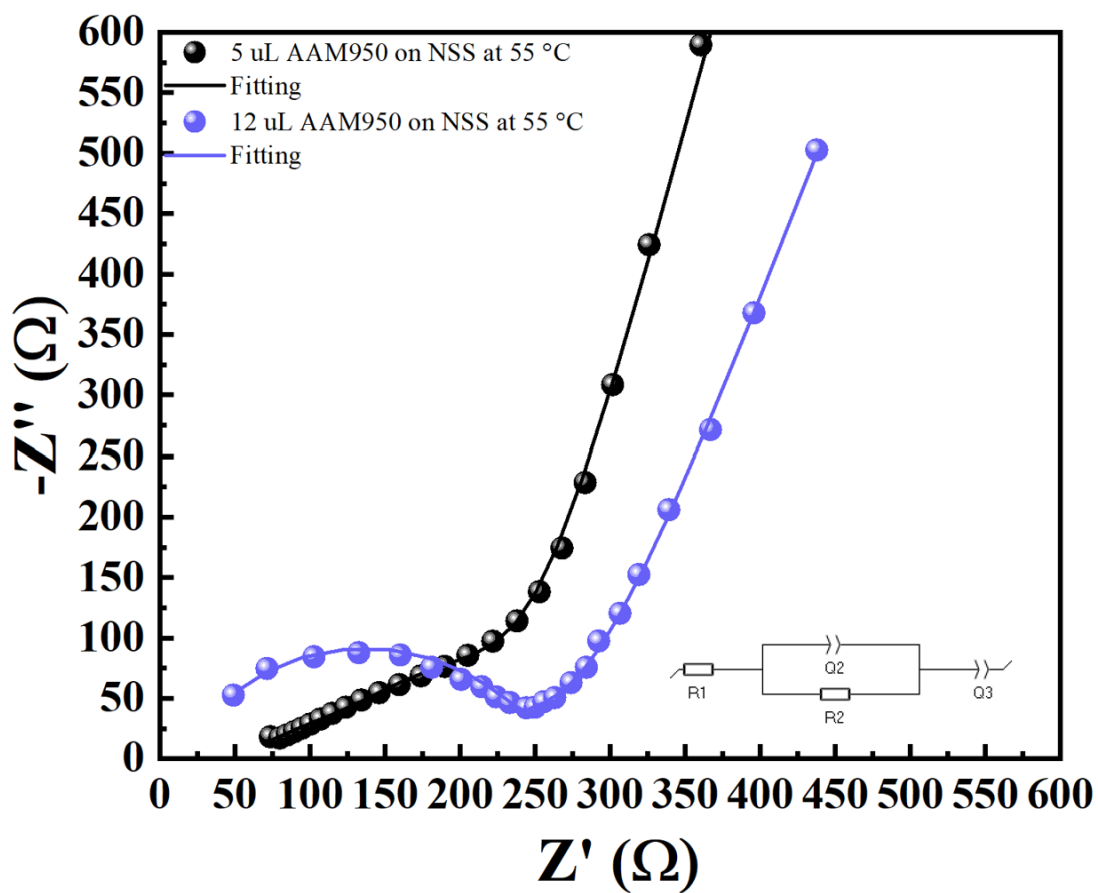
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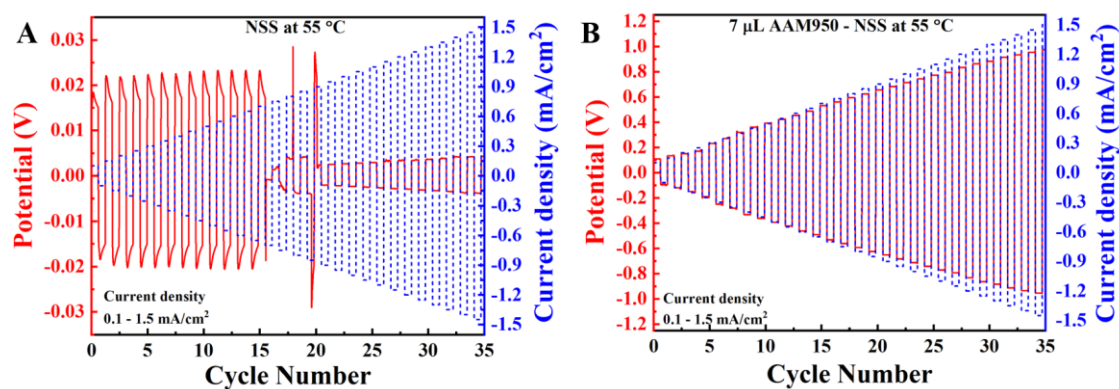
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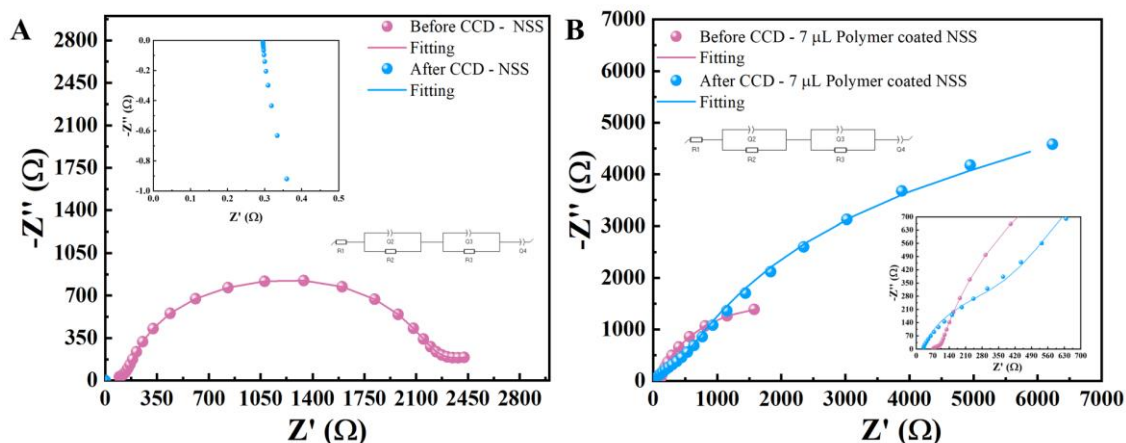
**Figure S1.** Nyquist plot of NSS pellets coated with 5 and 12  $\mu\text{L}$  AAM950–NaTFSI at 55  $^{\circ}\text{C}$  (Inset: Equivalent circuit).

**Table S1.** Total resistance and ionic conductivity values of NSS pellets coated with 5 and 12  $\mu\text{L}$  AAM950–NaTFSI at 55  $^{\circ}\text{C}$ .

Sample (NSS-AAM950)	$R_{\text{tot}}=(R_1+R_2)$ ( $\Omega$ )	L ( $\mu\text{m}$ )	Ionic conductivity ( $\times 10^{-3} \text{ S cm}^{-1}$ )
5 $\mu\text{L}$ at 55 $^{\circ}\text{C}$	223.34	390	0.222
12 $\mu\text{L}$ at 55 $^{\circ}\text{C}$	235.75	486	0.262



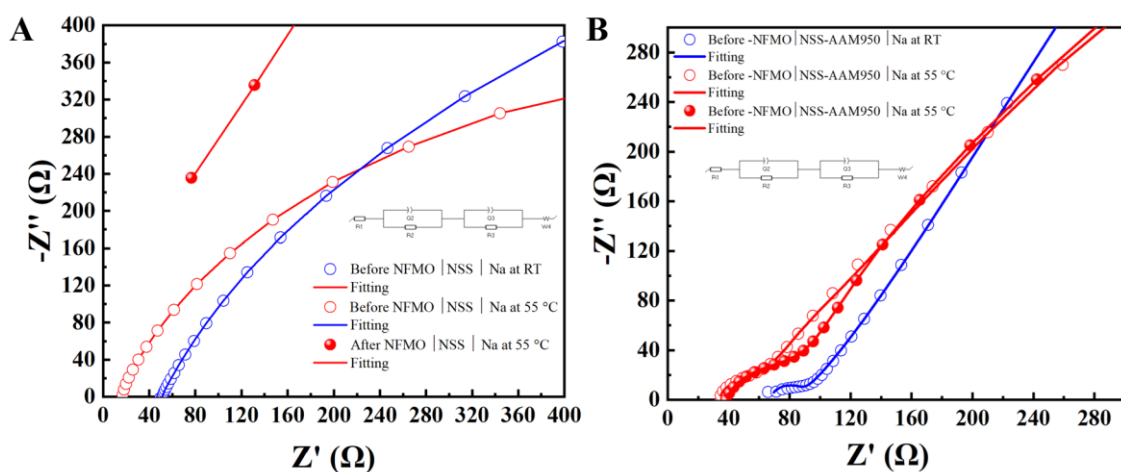
**Figure S2.** Critical current density (CCD) tests at 55 °C: (A) Na|NSS|Na and (B) Na|AAM950–NSS|Na with a 7  $\mu$ L polymer coating.



**Figure S3.** Nyquist plots measured at room temperature before and after CCD testing at 55 °C: (A) Na|NSS|Na and (B) Na|AAM950–NSS|Na with a 7  $\mu$ L polymer coating (Inset: Equivalent circuit).

**Table S2.** Resistance values obtained from EIS measurements performed at room temperature before and after CCD testing at 55 °C.

Samples	$R_1(\Omega)$	$R_2(\Omega)$	$R_3(\Omega)$
Before CCD - NSS	56.39	2130	79.55
Before CCD - 7 $\mu$ L	71.33	43.1	1485
After CCD - 7 $\mu$ L	29.0	357	6452



**Figure S4.** High-frequency Nyquist plots of NFMO|SE|Na cells before and after cycling at 55 °C: (A) NFMO|NSS|Na and (B) NFMO|AAM950–NSS|Na with a 7  $\mu$ L polymer coating (Inset: Equivalent circuit).



**Figure S5.** Cross-sectional SEM image of the NSS electrolyte after 50 cycles in a disassembled NFMO|NSS|Na cell at 55 °C.