

Engineered Grain Boundary Enables the Room Temperature Solid-State Sodium Metal Batteries

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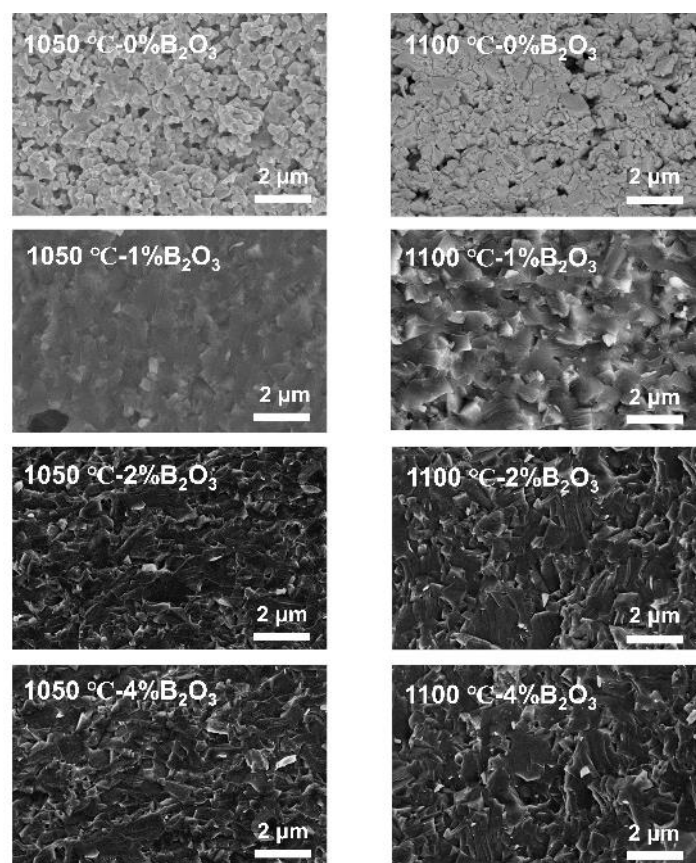


Figure S1. Sectional SEM images of the NZSP- x B₂O₃-1050 °C and NZSP - x B₂O₃-1100 °C ceramics.

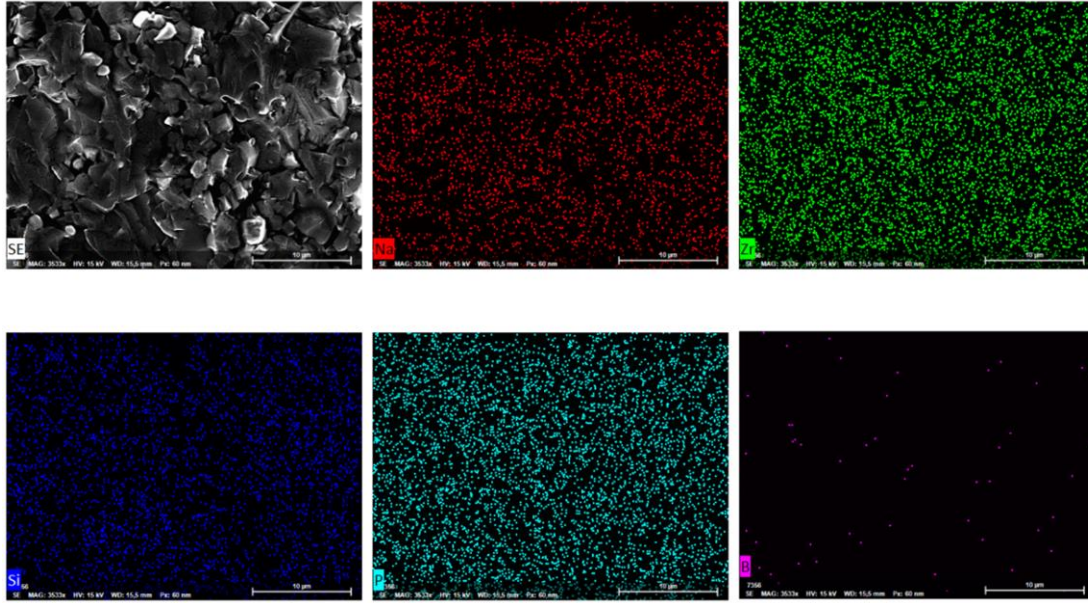


Figure S2. EDS mapping results with an enlarged scale for NZSP-2%B₂O₃-1150 °C ceramic.

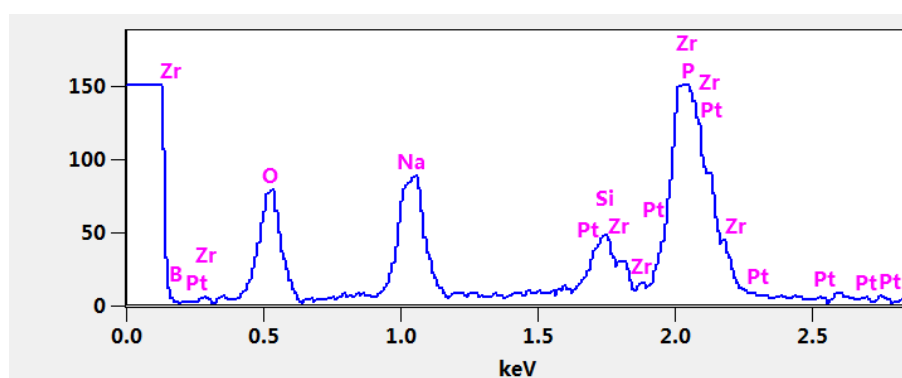


Figure S3. Energy spectrum element analysis of grain boundaries for NZSP-2%B₂O₃-1150 °C ceramic.

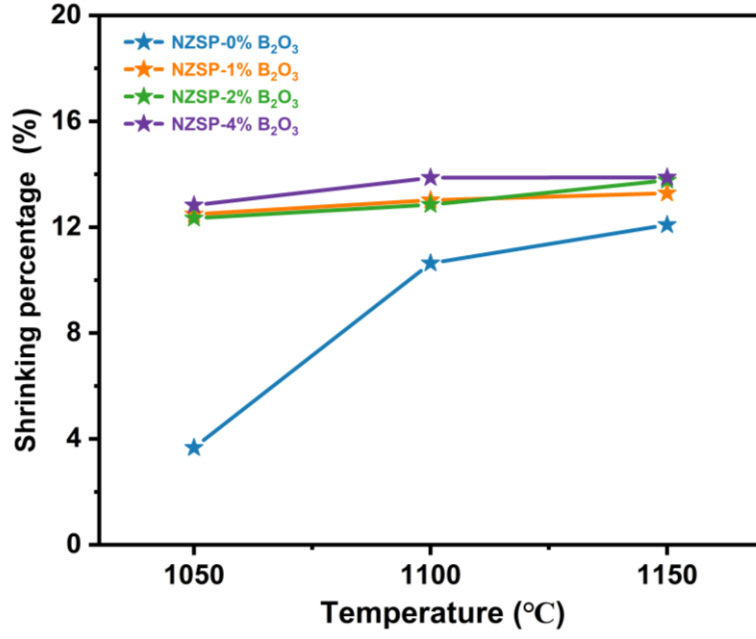


Figure S4. Shrinkage variation of the NZSP- x B₂O₃ ceramics pellets sintered at different temperatures.

The shrinking percentage (φ) of samples can be described by $\varphi = \frac{D_0 - D_1}{D_0} \times 100\%$, wherein D_0 is the diameter of green pellets and D_1 is the diameter of the as-sintered samples.

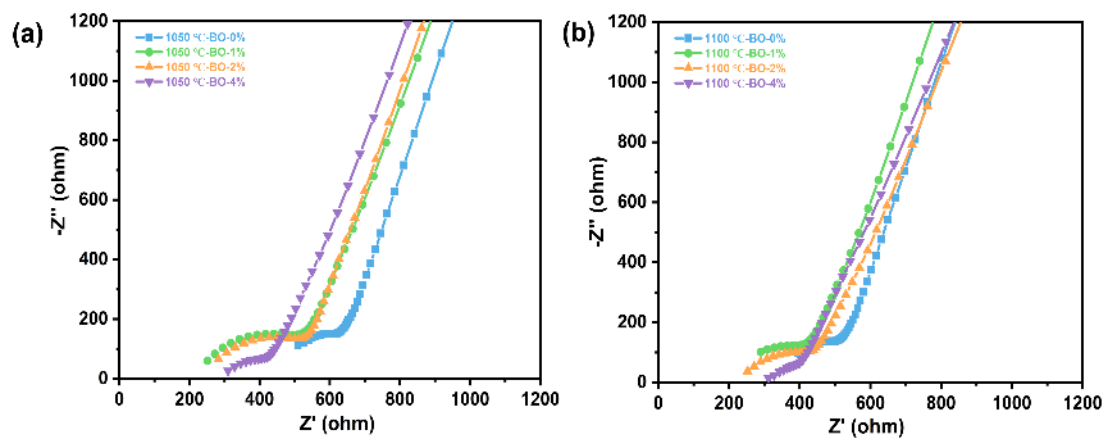


Figure S5. Nyquist plots of the room temperature EIS of (a) NZSP- x B₂O₃-1050 °C and (b) NZSP- x B₂O₃-1100 °C ceramic pellets.

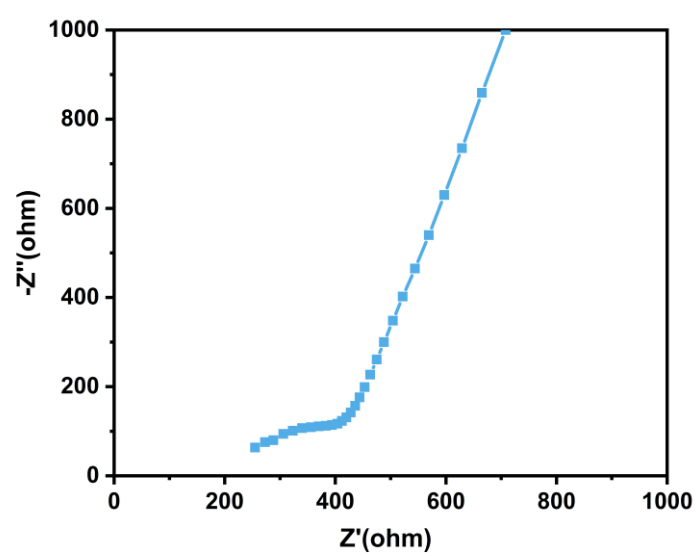


Figure S6. Nyquist plots of NZSP-1250 °C.

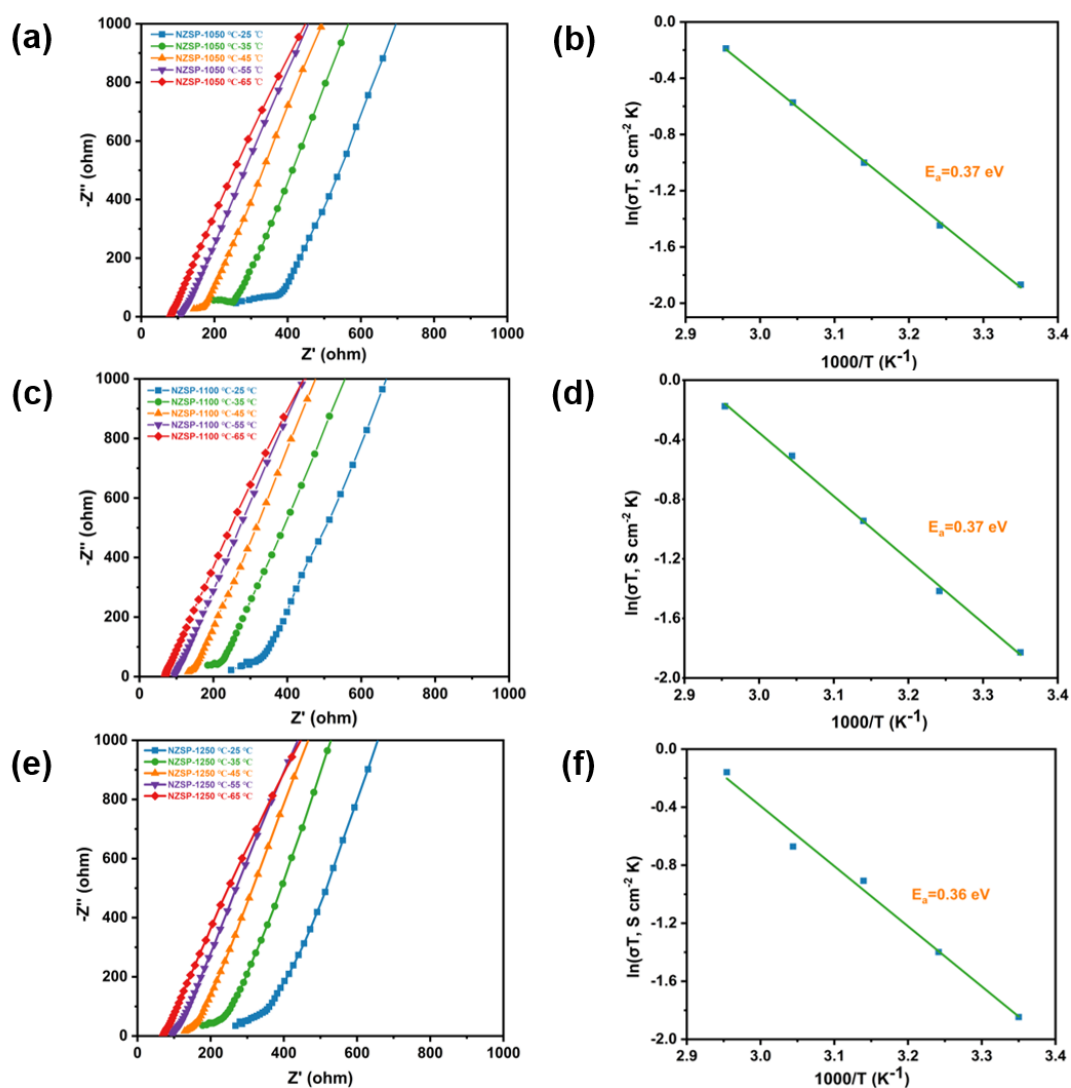


Figure S7. The temperature-dependent Nyquist plots of (a) NZSP-4%B₂O₃-1050 °C, (c) NZSP-4%B₂O₃-1100 °C, and (e) NZSP-1250 °C. The Arrhenius temperature-dependent total conductivity plots of (b) NZSP-4%B₂O₃-1050 °C, (d) NZSP-4%B₂O₃-1100 °C, and (f) NZSP-1250 °C.

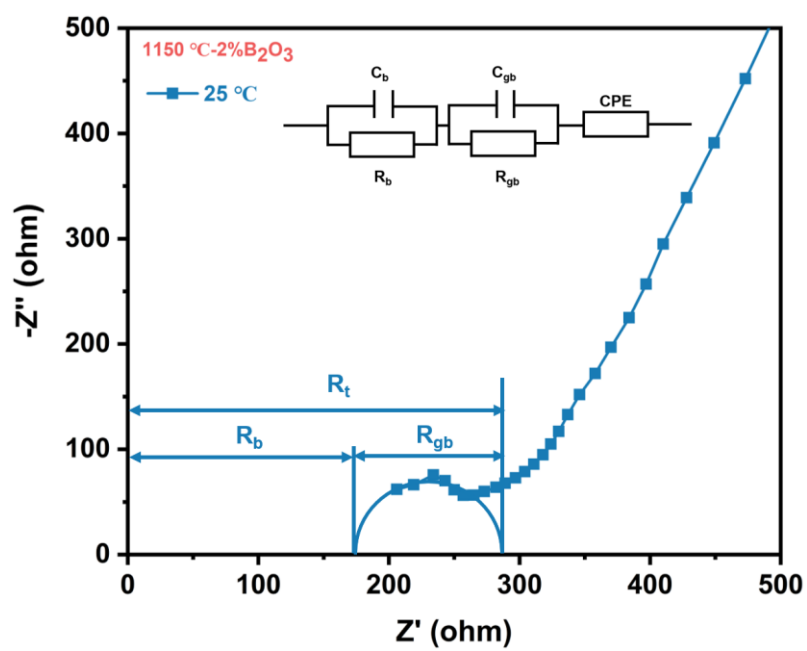


Figure S8. Nyquist plot of NZSP-2%B₂O₃-1150 °C at room temperature, simulation results based on the equivalent circuit, and illustration of analysis of R_b and R_{gb} .

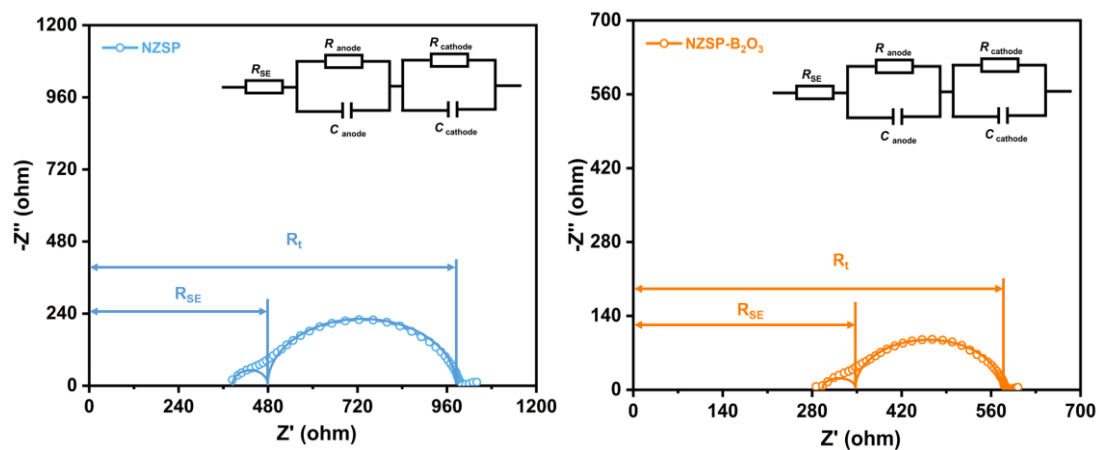


Figure S9. Room temperature Nyquist plots of symmetric sodium metal batteries based on NZSP-1250 °C and NZSP-2%B₂O₃-1150 °C ceramic electrolytes. The insets are the equivalent circuit and illustration of analysis of R_{SE} and R_t .

Table S1. Cell Parameters and volume of NZSP- x B₂O₃

Composition	Space group	a (Å)	b (Å)	c (Å)	Volum e (Å ³)	$S=R_{wp}/R_e$
NZSP-1250 °C	C2/c (96.8 wt.%)	15.5443	9.0152	9.1834	1080.51	1.20
NZSP-1%B ₂ O ₃ - 1150 °C	C2/c (98.1 wt.%)	15.6672	9.0556	9.2166	1085.99	1.38
NZSP-2%B ₂ O ₃ - 1150 °C	C2/c (97.7 wt.%)	15.6673	9.0591	9.2156	1085.19	1.47
NZSP-4%B ₂ O ₃ - 1150 °C	C2/c (96.4 wt.%)	15.6714	9.0564	9.2187	1085.88	1.25

These results of Rietveld refinement were obtained according to the constructed model structure.