Supporting Information

Dual Thermal-Stimulated Self-Adhesive Mix-Phase Interface to Enable Ultra-Long Cycle Life of Solid-State Sodium Metal Batteries

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Experimental section

Preparation of solid electrolyte: $Na_3Zr_2Si_2PO_{12}$ (NZSP) solid electrolyte was synthesized by the conventional solid phase sintering method. The stoichiometric ratio of Na_2CO_3 (99.8%, Aladdin), ZrO_2 (99.99%, Aladdin), SiO_2 (analytically pure, Aladdin), and $NH_4H_2PO_{12}$ (99%, Aladdin) raw materials were ball-milled at 400 rpm for 5 h and then calcinated at 1100 ℃ in the air for 12 h to obtain the precursor. The ball-milling process was carried out using Φ10 mm and Φ7 mm ZrO_2 beads mixed during the ball-milling process, and 15 wt.% excess of Na_2CO_3 and $NH_4H_2PO_{12}$ were added to compensate for the damage of Na and P elements at high temperature. The obtained precursors were ball-milled again at 400 rpm for 10 h and pressed into Φ10 mm pellet at 480 MPa, and then sintered at 1150 ℃ under the air atmosphere for 12 h with a temperature increase rate of 5 ℃ min^{-1}. Finally, the sintered NZSP electrolyte sheets were polished with 200-1200 grit sandpaper.

Preparation of SnF_2 interface layer: 300 mg of SnF_2 (99%, Aladdin) powder was added to a bottle contained with 10 mL isopropanol, sonicated for 5 h, and then magnetically stirred at 500 rpm for 10 h to obtain a homogeneous solvent dispersion. Then 10 uL of the above dispersion was spin-coated onto the surface of NZSP at 1000 rpm, which operation can be done several times to obtain different thicknesses (denoted as SnF_2@NZSP).

Dual thermal stimulation: The SnF_2@NZSP pellet was placed onto a heating plate. A simple physical thermal stimulation (220 °C) allowed the rigid SnF_2 particles to melt and self-adhere to the surface of the ceramic electrolyte within 5 min. Then, a 200 µm thick sodium sheet was pressed onto the SnF_2 modified NZSP in an argon-filled glove box, and a secondary thermal stimulation (110 ℃) was used to rapidly (30 s) in situ chemically activate the SnF_2 interfacial layer to obtain a homogeneous and mixed-phase (Na_xSn, NaF).

Characterization of materials: The phase of the materials was characterized by XRD (Bruker AXS D2 Advance with Cu-Kα radiation, λ=1.54178Å) and X-ray photoelectron spectroscopy (AXIS-ULTRA DLD-600W). The microstructure of the materials was characterized by field-emission scanning electron microscopy (FESEM) (Quanta 650 FEG).

Electrochemical testing: To measure the ionic conductivity of NZSP solid-state electrolyte, 50 nm thick Au was sputtered at both sides of the NZSP pellet as blocking electrodes. The electrochemical impedance spectroscopy (EIS) test was conducted via Solartron Electrochemical Interface SI 1260 and SI 1287 at frequencies ranging from 1 MHz to 0.1 Hz with an AC amplitude of 10 mV. The in-situ chemical sodiation process was carried out from the heating plate at 110 ℃, and the sodiated DTS-SnF_2@NZSP was directly assembled into a 2032-type button cell. Charge/discharge tests were performed on the assembled symmetric cells using the Landian (Wuhan CT2001A) test system, the deposition/stripping time interval of the symmetric cells was 0.5 h.

Assemble of the full cells: The active material (NVP), Super P, and polyvinylidene fluoride (PVDF) were mixed at a mass ratio of 8:1:1, and then the mixed slurry was poured onto an aluminum foil and vacuum-dried in an oven at 80 °C overnight. The surface loading of the active material was about 1.2 mg cm^{-2}. 5 µL of liquid electrolyte (EC/DMC(1:1) + 5% FEC in 1 M $NaPF_6$) was used to wet the positive electrode-solid electrolyte interface. The cells were tested for charge/discharge at room temperature in the voltage range of 2.0-3.8 V vs. Na/Na^+.

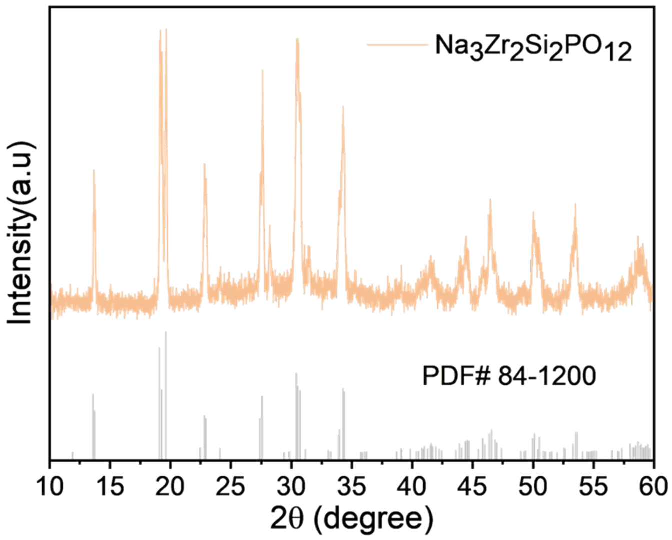


Figure S1 XRD pattern of NZSP pellet.

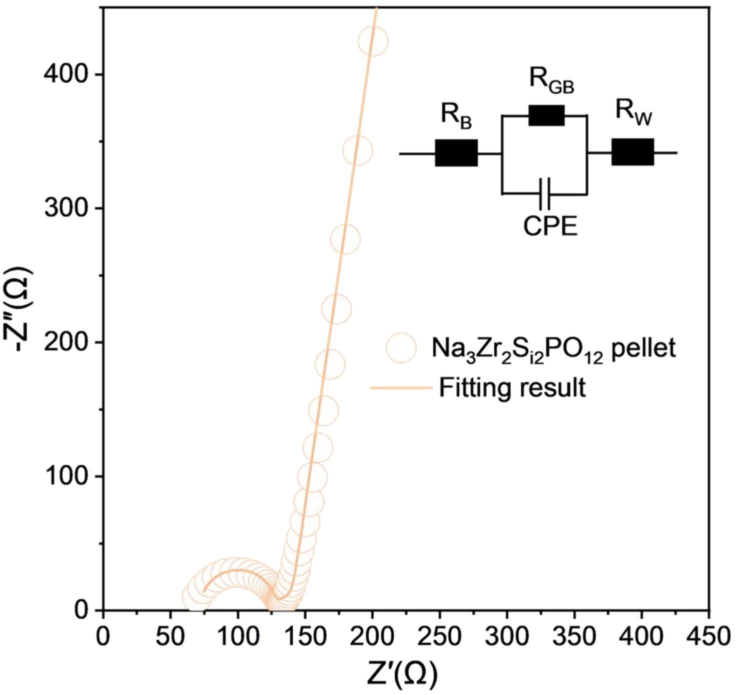


Figure S2 Nyquist plot of Au/NZSP/Au cell measured at room temperature and the resulting ionic conductivity of 7.76×10^{-4} S cm^{-1}.

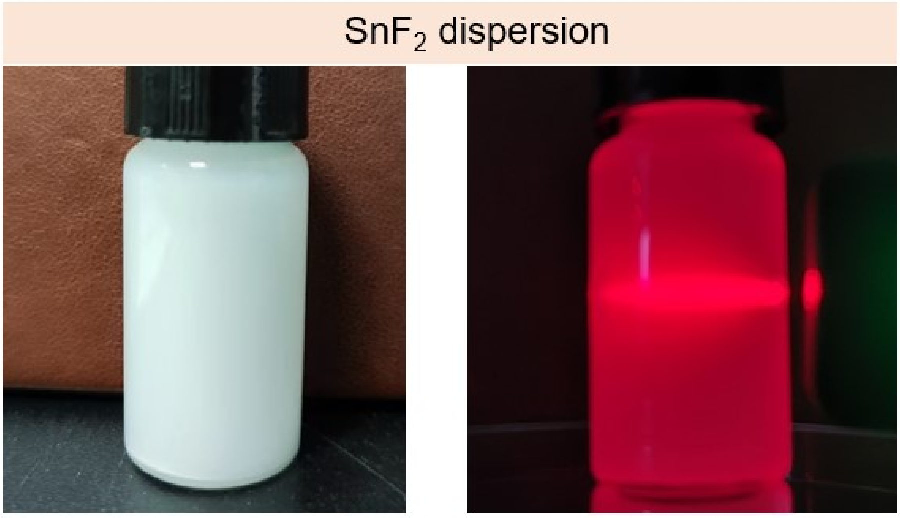


Figure S3 Digital photos of SnF$_2$ dispersions.

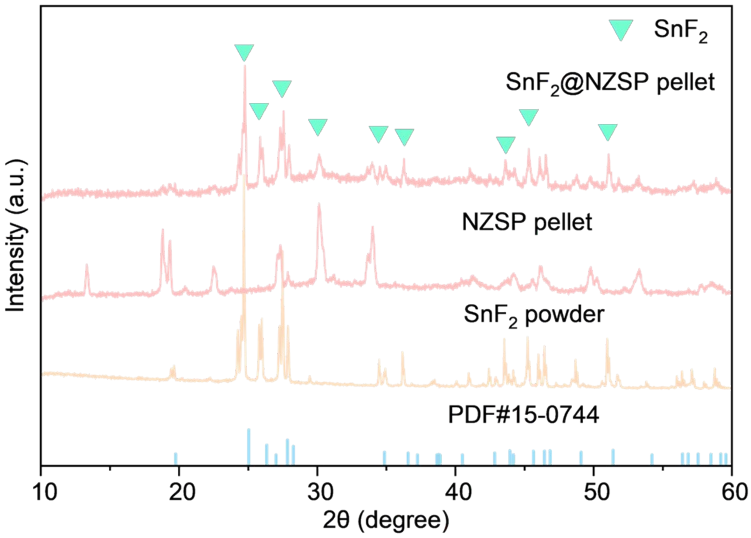


Figure S4 XRD patterns of SnF_2 powder, bare NZSP pellet, and SnF_2@NZSP pellet.

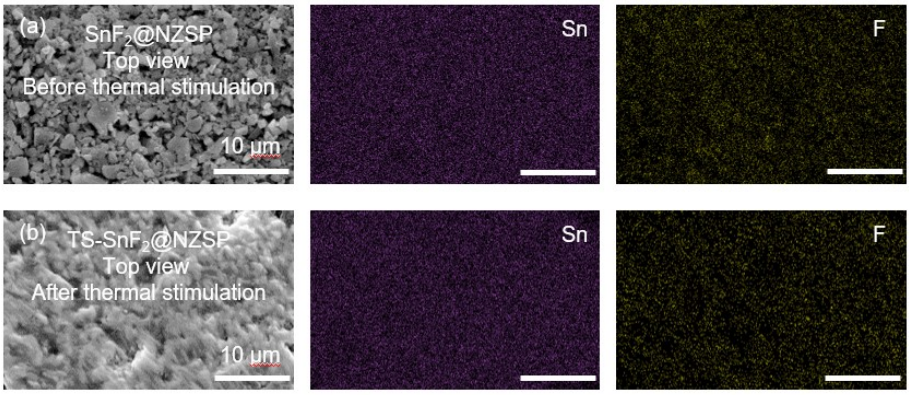


Figure S5 The surface SEM images and the corresponding EDS mapping of Sn and F elements of pristine SnF_2@NZSP (a) and TS-SnF_2@NZSP (b).

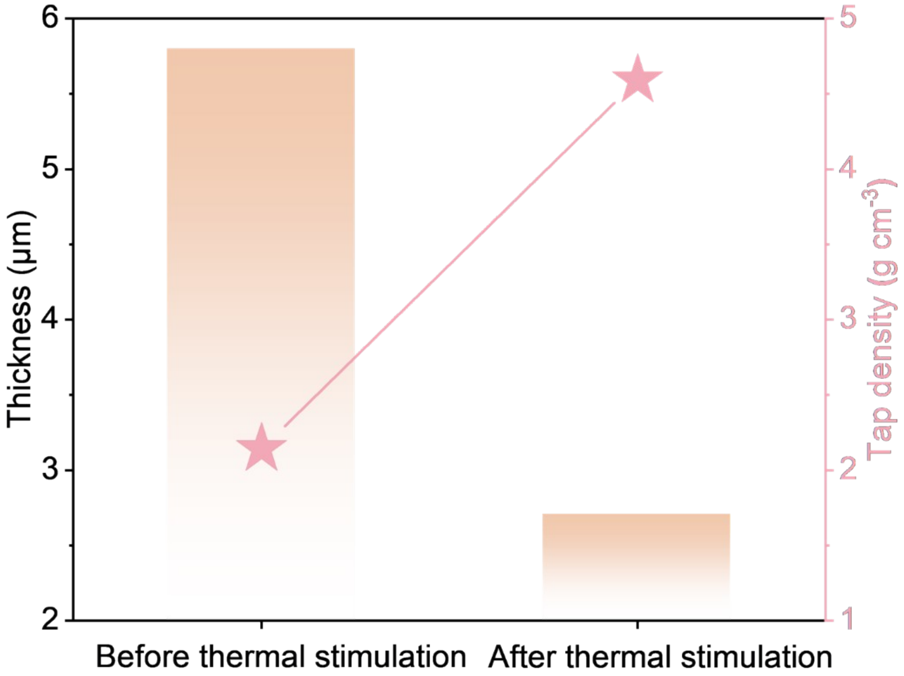


Figure S6. Thickness and compaction density of the melting self-adhesive layer before (SnF_2) and after thermal stimulation (TS-SnF_2).

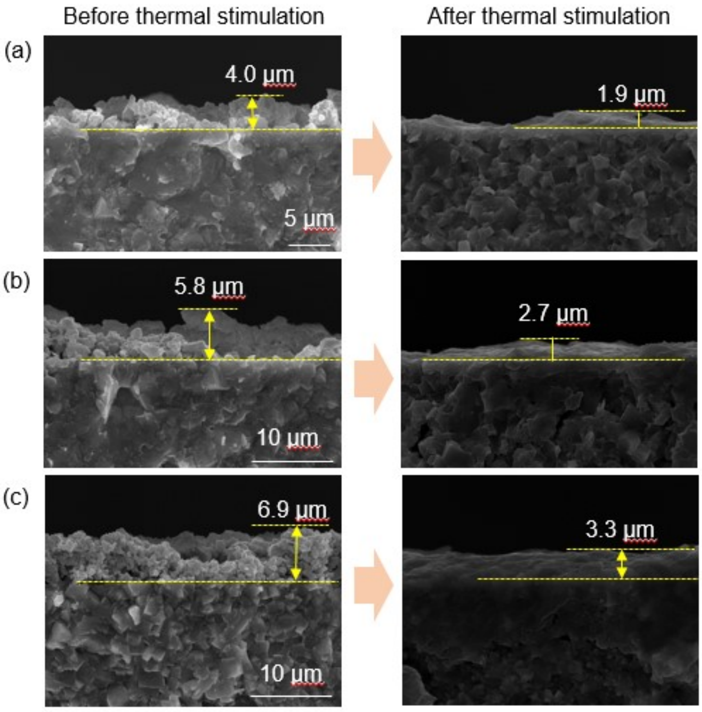


Fig. S7 SEM images of the thickness evolution of SnF_2 interfacial layer before and after thermal stimulation.

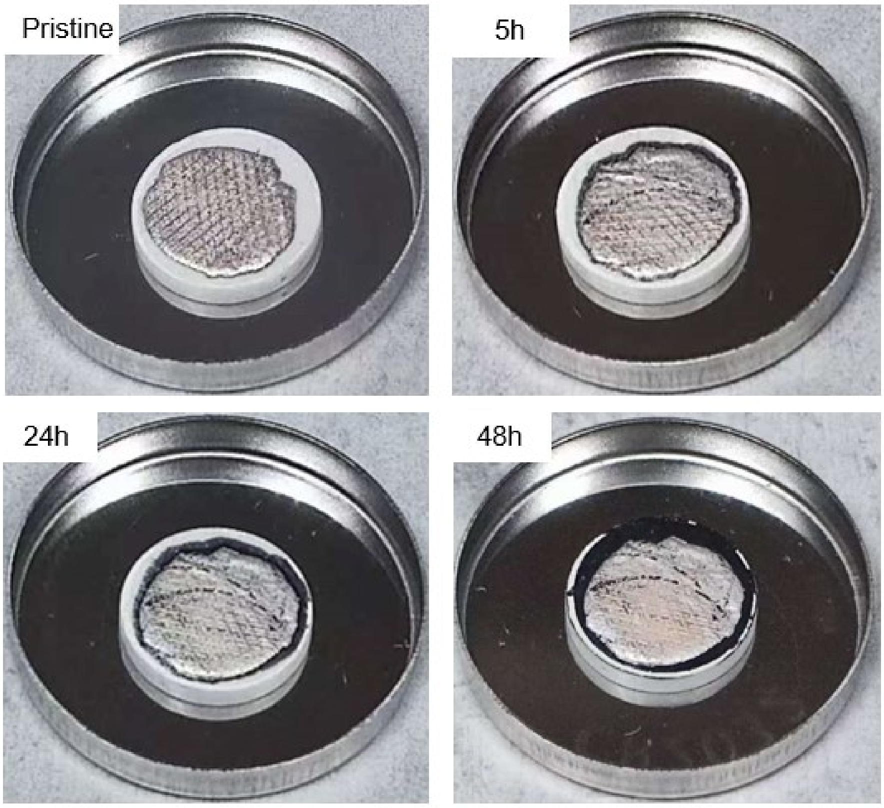


Figure S8 Without thermally stimulated activation, the optical photographs of Na/TS-SnF_2@NZSP upon standing for 5 h, 24 h and 48h, respectively.

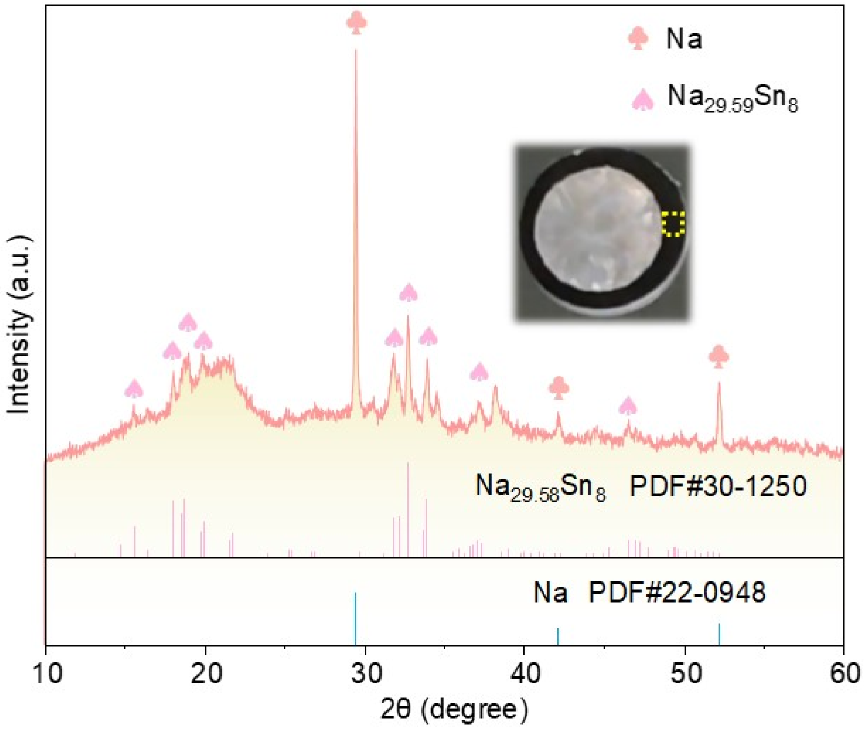
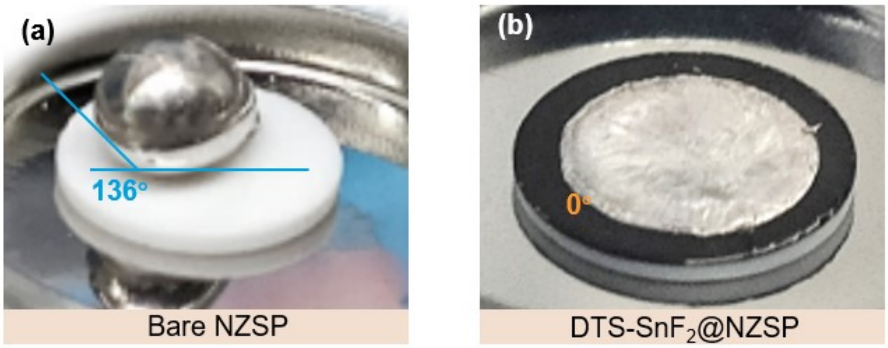


Figure S9 XRD spectrum pattern of DTS-SnF_2@NZSP pellet after sodiation, with the inset showing the region tested.



Bare NZSP

DTS-SnF_2@NZSP

Figure S10 Contact-angle measurements of molten Na on (a) bare NZSP and (b) DTS-SnF_2@NZSP at 110 °C.

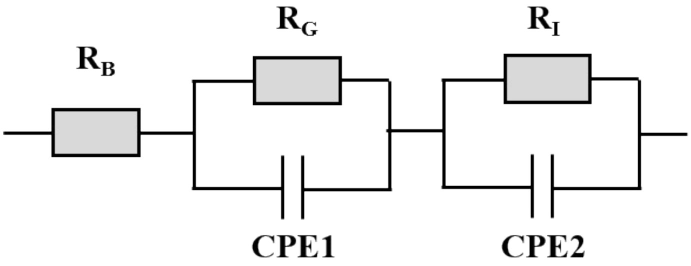


Figure S11 Equivalent circuit of Na|bare NZSP|Na cell, Na|SnF_2@NZSP|Na and Na|DTS-SnF_2@NZSP|Na.

Table S1 The fitting result of Na|bare NZSP|Na cell, Na|SnF_2@NZSP|Na cells and Na|DTS-SnF_2@NZSP|Na.

Type	**R_G**	**CPE1**	**τ1**	**R_I**	**CPE2**	**τ2**
bare NZSP	266.04	1.1705×10^{-7}	0.741	21087.46	5.7225×10^{-8}	0.901
SnF_2@NZSP	285.91	2.4595×10^{-8}	0.850	1295.25	1.4848×10^{-7}	0.8887
DTS-SnF_2@NZSP	120.91	6.5367×10^{-8}	0.812	21.42	1.4011×10^{-8}	0.706

Note: the units of R, CPE and τ are Ω cm_2, F cm^{-2} and μs, respectively.

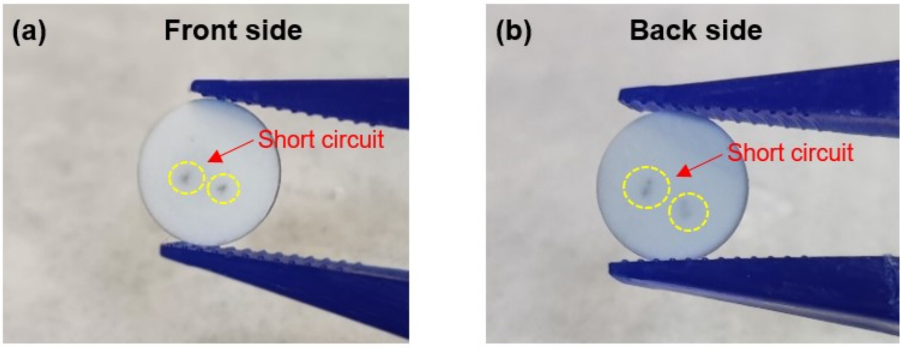


Figure S12 The digital images of bare NZSP pellet after short circuit.

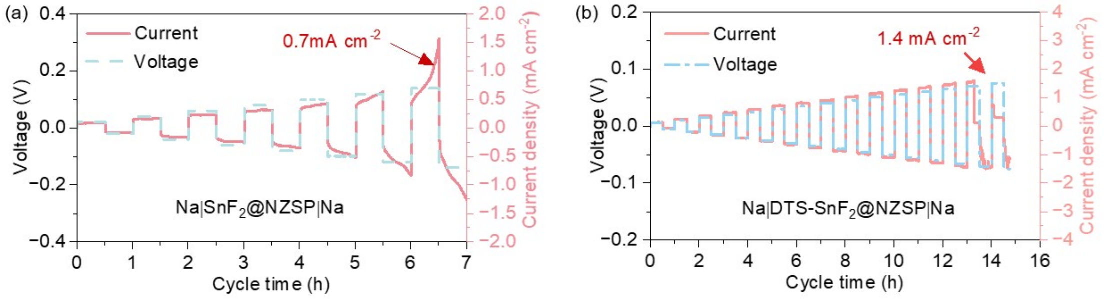


Figure S13 Critical Current Density Testing (CCD) of Na|SnF$_2$@NZSP|Na and Na|DTS-SnF$_2$@NZSP|Na Symmetric Cells.

Table S2 Comparison of the cycling life of our prepared dual thermal-stimulated self-adhesive mix-phase interface (DTS-SnF_2) and previously reported interfacial materials on solid-state sodium symmetric batteries.

Samples	Electrolytes	Current density	Cycling life	Reference
DTS-SnF_2	**$Na_3Zr_2Si_2PO_{12}$**	**0.1 mA cm^{-2}**	**17000 h**	**This work**
ZnO	$Na_3Zr_2Si_2PO_{12}$	0.1 mA cm^{-2}	5000 h	Advanced Materials, 2024, 36, 2309298.
SbF_3	$Na_3Zr_2Si_2PO_{12}$	0.1 mA cm^{-2}	8000 h	Energy Storage Materials, 2024, 72: 103755.
MgF_2	$Na_3Zr_2Si_2PO_{12}$	0.1 mA cm^{-2}	3000 h	eScience, 2024, 100274.
α-FeOF	$Na_3Zr_2Si_2PO_{12}$	1 mA cm^{-2}	1000 h	Advanced Functional Materials, 2024, 34, 2301670.
Au	$Na_3Zr_2Si_2PO_{12}$	0.3 mA cm^{-2}	1000 h	Carbon Energy, 2023, 5, e299.
$BaTiO_3$	$Na_3Zr_2Si_2PO_{12}$	0.1 mA cm^{-2}	1000 h	Small, 2022, 18, 2200716.
TiO_2	$Na_3Zr_2Si_2PO_{12}$	0.1 mA cm^{-2}	750 h	Advanced Energy Materials, 2022, 12, 2103607.
SnO_2	$Na_{3.4}Zr_2Si_{2.4}P_{0.6}O_{12}$	0.1 mA cm^{-2}	6000 h	Advanced Energy Materials, 2022, 12, 2102579.
CuO	$Na_3Zr_2Si_2PO_{12}$	0.3 mA cm^{-2}	5000 h	Small, 2022, 18, 2204487.
SnS_2	$Na_3Zr_2Si_2PO_{12}$	0.1 mA cm^{-2}	800 h	Journal of Materials Chemistry A, 2021, 9, 16039-16045.
Na-Sn alloy	$Na_3Zr_2Si_2PO_{12}$	0.5 mA cm^{-2}	500 h	Advanced Energy Materials, 2021, 11, 2101228.
p-PAN	$Na_3Zr_2Si_2PO_{12}$	0.1 mA cm^{-2}	500 h	Advanced Energy Materials, 2021, 11, 2003469.
UW-Na	$Na_3Zr_2Si_2PO_{12}$	0.2 mA cm^{-2}	400 h	Nature Communications, 2021, 12, 7109.
AlF_3	Na3Zr2Si2PO12	0.15 mA cm^{-2}	300 h	Energy Storage Materials, 2020, 30, 170-178

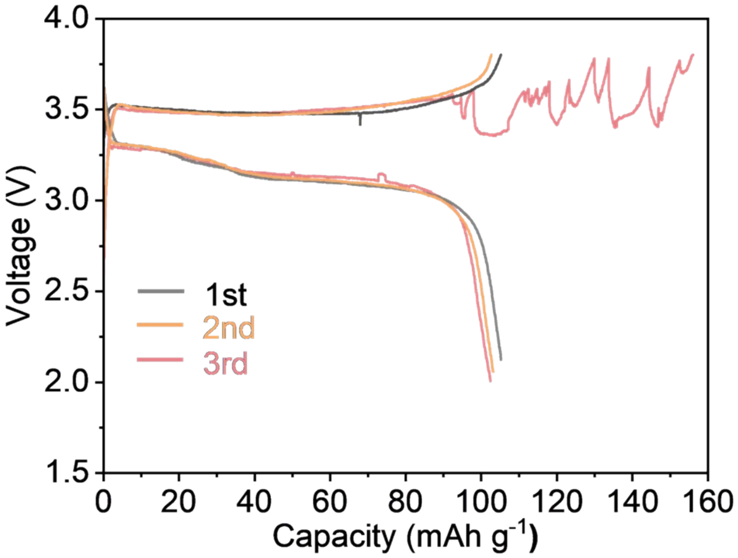


Figure S14 Typical charge/discharge voltage profiles of the assembled NVP|bare NZSP|Na cell at room temperature.

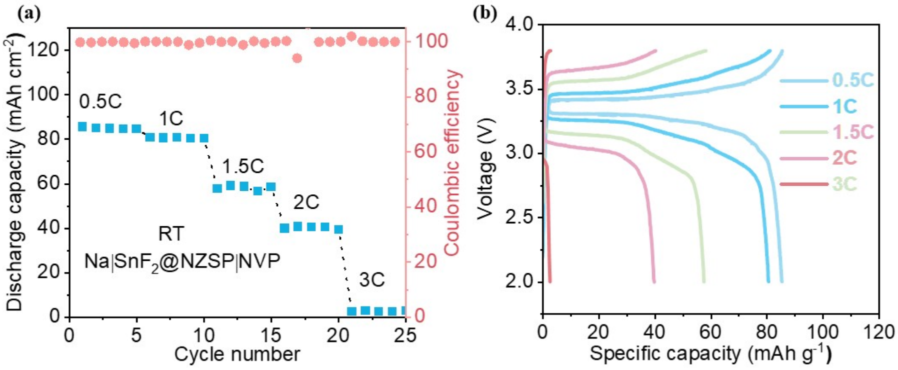


Figure S15. (a) The rate performance of assembled NVP|SnF$_2$@NZSP|Na cell at various current densities at RT. (b) Typical charge/discharge curves at various current densities.