

Supporting information

Enhanced ionic conductivity of $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ solid electrolyte with Na_2SiO_3 by liquid phase sintering for Na^+ solid-state batteries

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EXPERIMENTAL METHOD

Synthesis of the solid electrolyte

Chemicals

All chemical reagents were purchased and used as received without any other purification unless otherwise stated. Zirconium dioxide (ZrO_2 , 99%) was bought from Shanghai Macklin Biochemical Co., Ltd. Silicon dioxide (SiO_2 , AR) was purchased from Xilong Science Co., Ltd. Sodium carbonate anhydrous (Na_2CO_3 , 99%+) was supplied by Tianjin Fengchuan chemical reagent Technology Co., Ltd. Ammonium Dihydrogen Phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$, 99%+) was bought from GEBERAL-REAGENT. Sodium metasilicate (Na_2SiO_3 , 98%+) was purchased from Adamas-beta.

Preparation of NZSP precursor powders

The $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (NZSP) powders were prepared by solid state sintering process. Firstly, the Na_2CO_3 , ZrO_2 , SiO_2 and $\text{NH}_4\text{H}_2\text{PO}_4$ were mixed in the zirconia jars in the molar ratio of 1.5:2:2:1. Secondly, all powders were ball milled in the ethanol with zirconia balls for 12h, rotary speed of 400rpm. These mixtures were dried at 80 °C in a vacuum oven for overnight. Finally, the powders were calcined at 1000 °C for 12h with a heating rate of 5 °C/min to form precursors.

Preparation of ceramics with Na_2SiO_3 additives

The prepared NZSP powders with different amounts of Na₂SiO₃ additives (0, 1, 3, 5 and 7 wt %) were twice ball milled at 400 rpm for 12 h. The milled powder was pressed for disk-shaped pellets (16 mm in diameter and 1.2 mm in thickness) at around 150 MPa for 5 min with a certain amount of 5 wt % polyvinyl alcohol (binder). The green pellets were held at 800 °C for 4 h to remove glue, and then sintered at 1100 °C for 12 h with a heating rate of 5 °C/min in a muffle furnace. A thin green pellet of the same composition was also placed under the actual pellets as a buffer to prevent any crack formation of the actual pellets during the sintering process.

Material characterizations

X-ray diffraction (XRD) was carried out by Rigaku SmartLab SE operated at 40 kV and 50 mA equipped with Cu-K α radiation with $\lambda=1.5406$ Å in the 2θ range of 10-90° and a step size of 0.01°. The thermostability of NZSP-NSO-0 and NZSP-NSO-5 were measured by thermogravimetric- differential thermal analysis (TG-DTA) carried out on a Netzch STA449F3 analyzer under air atmosphere at a heating rate of 10 °C/min from room temperature to 800 °C. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo K-Alpha+. Scanning electron microscope (SEM) images and energy dispersive spectrum (EDS) mapping were acquired on a AMRAY 1000B.

Electrochemical measurements

To measure sodium ion conductivity, the silver paste was applied to both side of the sample as the Na blocking electrode. The EIS was measured on electrochemical

workstation (CHI760E) in the frequency range of 1 MHz to 1 Hz with 5 mV signal. Grain boundary, grain and total resistance were determined by fitting Nyquist plots using the Z-View software (Scribner, Inc.). The temperature dependence conductivity was measured at several specific temperatures ranging from 303 to 353 K. Before being tested for each temperature, the samples were placed at the corresponding temperature for 1 h. The CA polarization test (with an applied voltage of 10 mV) was performed on Ag || NZSP || Ag cell to measure the electronic conductivity. Linear sweep voltammetry (LSV) experiments were performed on the Na || NZSP || SS cell at a scanning rate of 1 mV s⁻¹ in the range of 2-5 V to evaluate the electrochemical stability window of the solid electrolyte. Galvanostatic cycling for symmetrical Na || NZSP-NSO-5 || Na cell was evaluated at a current density of 0.1 mA cm⁻² and a capacity of 0.1 mA h cm⁻² on NEWARE battery testing system at 30 °C.

Solid-state sodium batteries assembly and testing

To prepare the cathode, the carbon coated sodium vanadium phosphate (Na₃V₂(PO₄)₃/C), carbon black, and poly(vinylidene fluoride) (PVDF) binder were mixed at the weight ratio of 8:1:1 with moderate amount of N-methyl-2-pyrrolidone (NMP). After being stirred for 5 h, the slurry was cast on aluminum foil and then dried at 80 °C overnight in vacuum. The loading of Na₃V₂(PO₄)₃ in the electrodes was 1.0 mg cm⁻².

The all-solid-state Na || NZSP-NSO-5 || Na₃V₂(PO₄)₃ cells were fabricated and tested with a coin-cell configuration. The NZSP-NSO-5 solid electrolyte was

sandwiched in between pure sodium foil and the $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathode. In the meantime, 6 μL liquid electrolyte of 1.0 M NaClO_4 in PC with 5.0% FEC was added to two sides of the solid electrolyte to improve the contact of interface. Next, the CR2025 cell was sealed at 12.5 MPa in a glove box filled with argon.

The rate of discharge ability and cycling performance of the Na || NZSP-NSO-5 || $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cells were tested with a NEWARE battery testing system. The measurements were performed using the range of 2.0–4.0 V.

Density functional theory (DFT) calculations

The first-principles^{1,2} were employed to perform all Spin-polarization density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE)³ formulation. To describe the ionic cores, the projected augmented wave (PAW) potentials^{4,5} were chosen and valence electrons were taken into account using a plane wave basis set with a kinetic energy cutoff of 520 eV. Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10^{-5} eV. A geometry optimization was considered convergent when the energy change was smaller than 0.02 eV \AA^{-1} . The Brillouin zone integration was performed using $2 \times 2 \times 1$ Monkhorst-Pack k-point sampling for a structure. ClimbingImage-Nudged Elastic Band had been employed to calculate the migration barrier.

References

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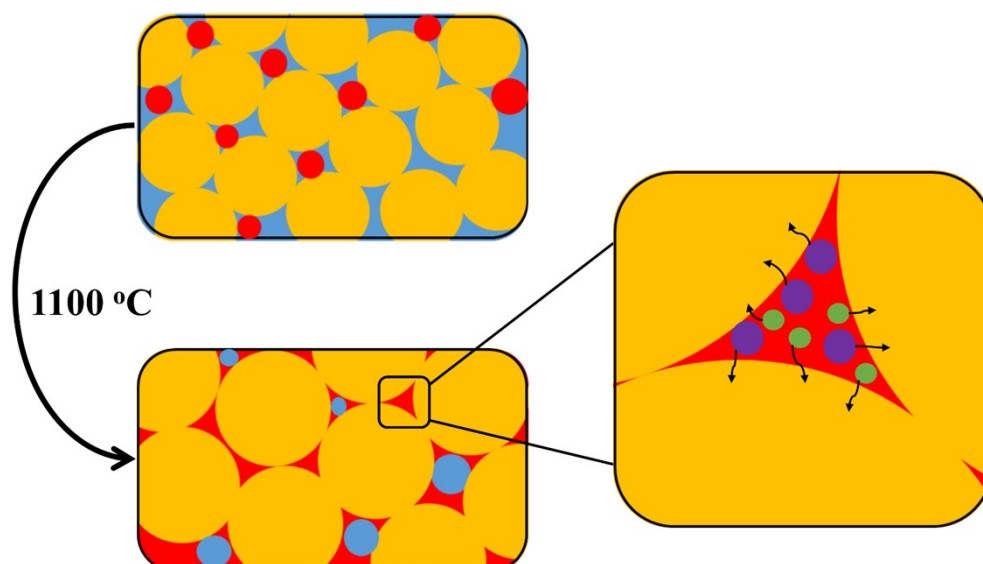


Figure S1. Schematic of the liquid phase sintering process.

The yellow ball represents $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$, the red part represents Na_2SiO_3 , the blue part represents pores, and the green and purple balls represent Si and Na atoms respectively.

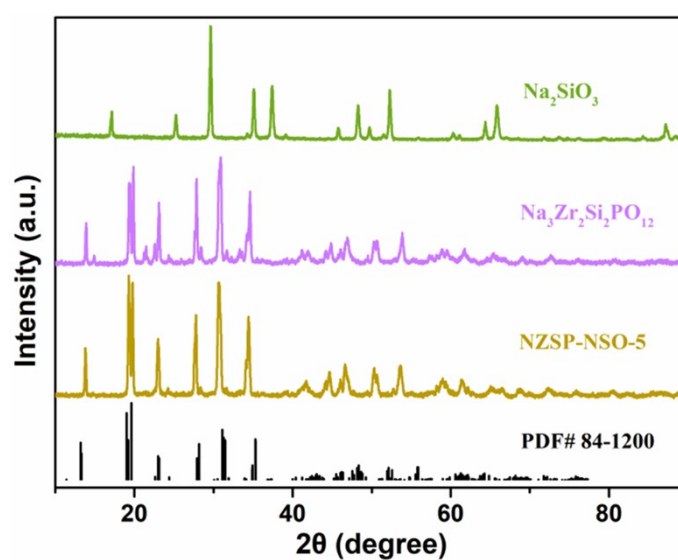


Figure S2. XRD patterns of Na_2SiO_3 , $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ and NZSP-NSO-5.

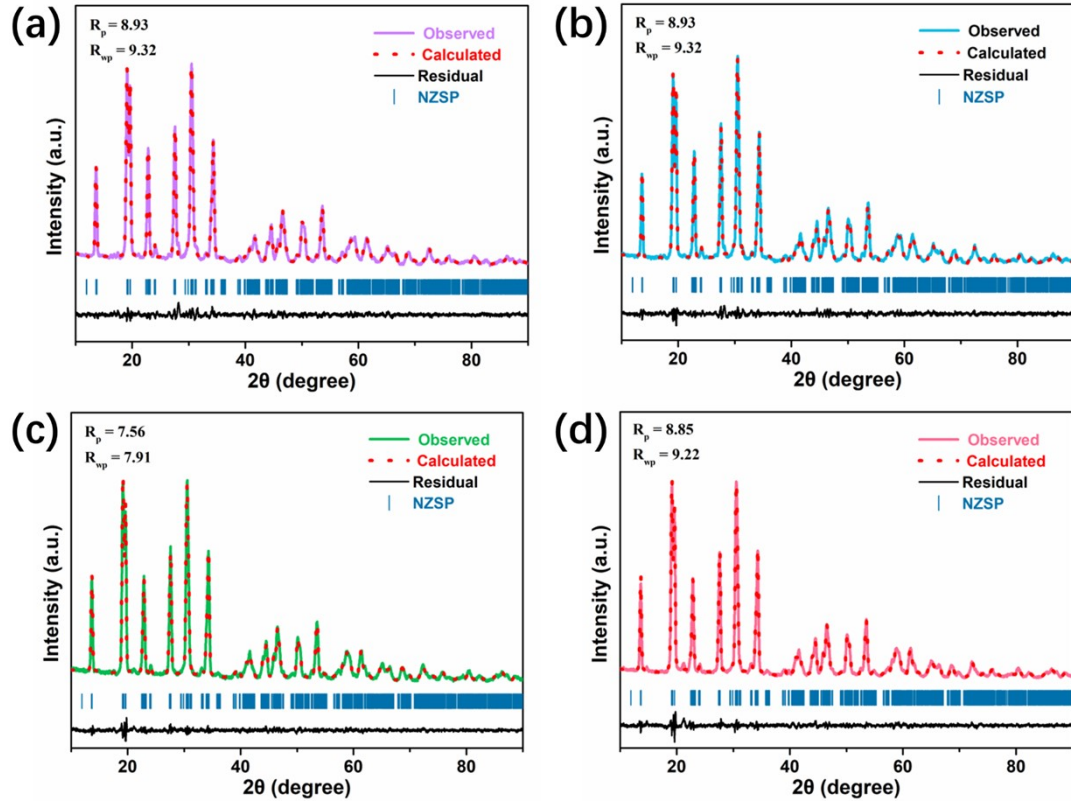


Figure S3. Structural refinement of NZSP-NSO-0 (a), NZSP-NSO-1 (b), NZSP-NSO-3 (c) and NZSP-NSO-7 (d).

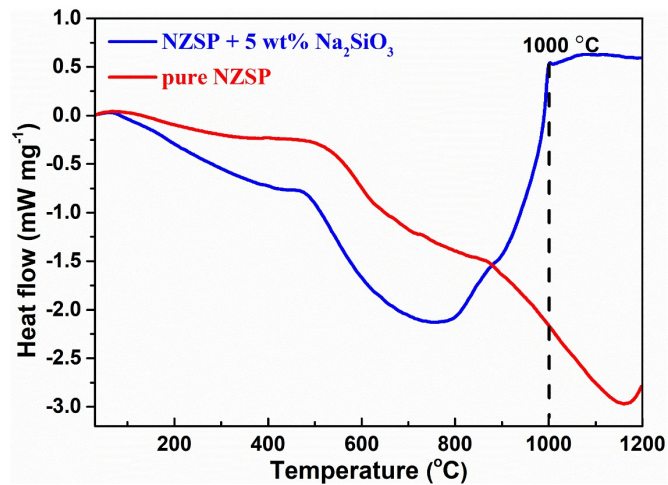


Figure S4. DSC curves of NZSP + 5 wt% Na_2SiO_3 and pure NZSP powders.

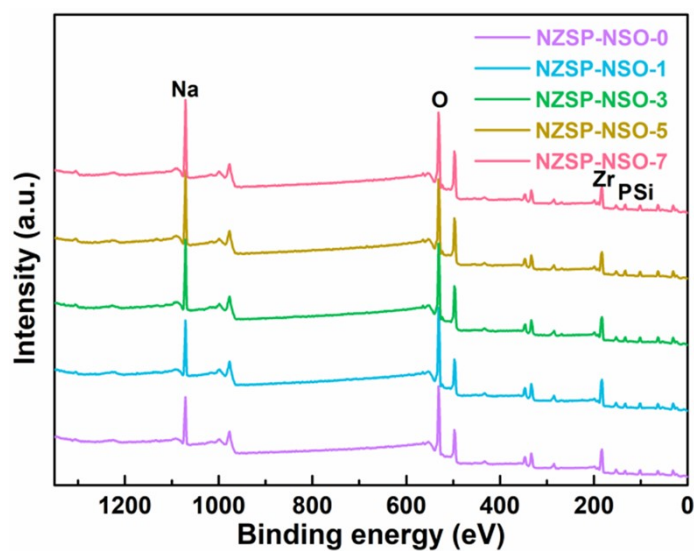


Figure S5. Survey XPS spectra of NZSP-NSO-0, NZSP-NSO-1, NZSP-NSO-3, NZSP-NSO-5 and NZSP-NSO-7.

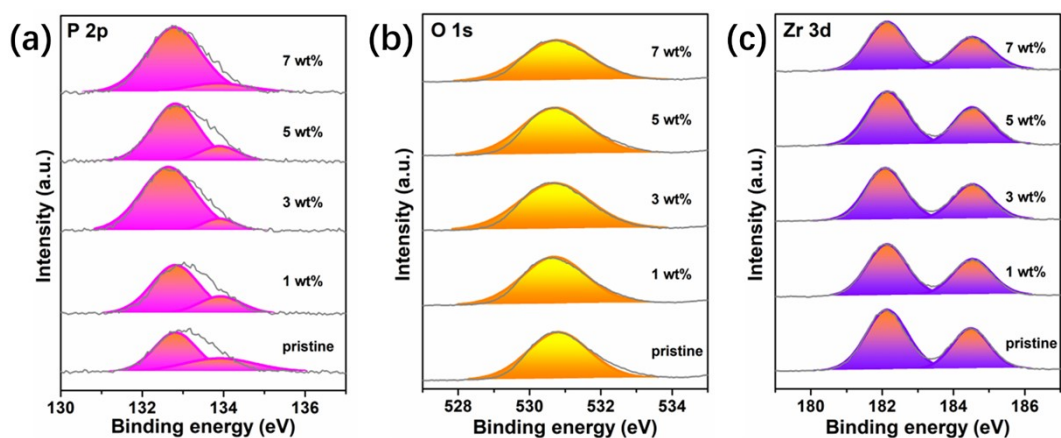


Figure S6. (a), (b) and (c) are P 2p, O 1s and Zr 3d XPS spectra of NZSP-NSO-0, NZSP-NSO-1, NZSP-NSO-3, NZSP-NSO-5 and NZSP-NSO-7, respectively.

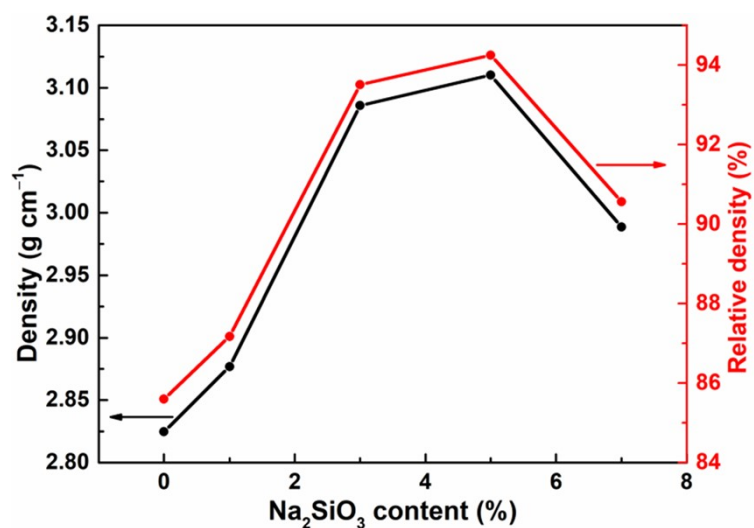


Figure S7. Densities and relative densities of NZSP pellets with different amounts of Na₂SiO₃.

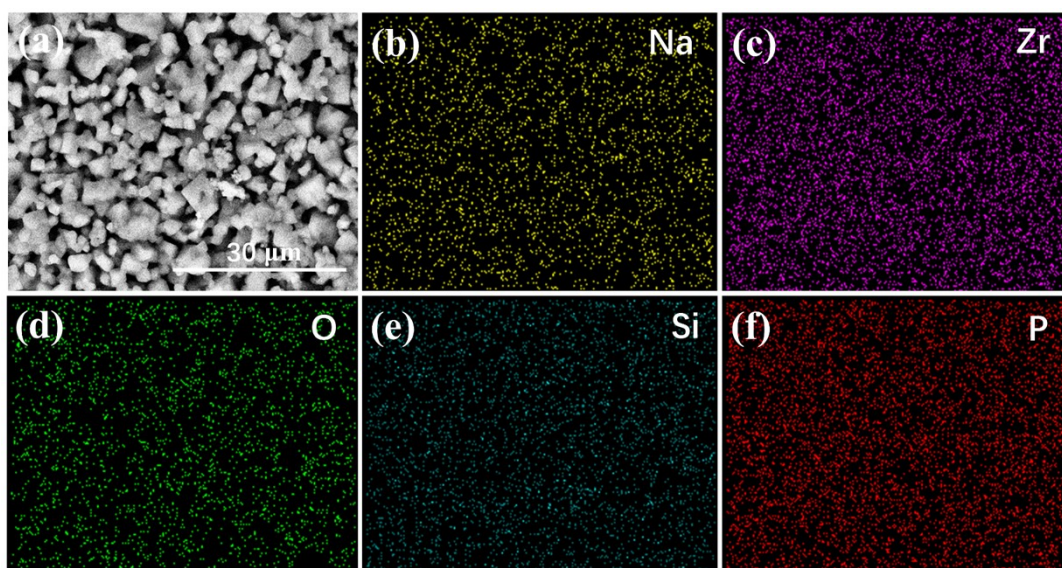


Figure S8. SEM image (a) and EDS mappings of NZSP-NSO-0 sample of different elements: (b) Na, (c) Zr, (d) O, (e) Si and (f) P.

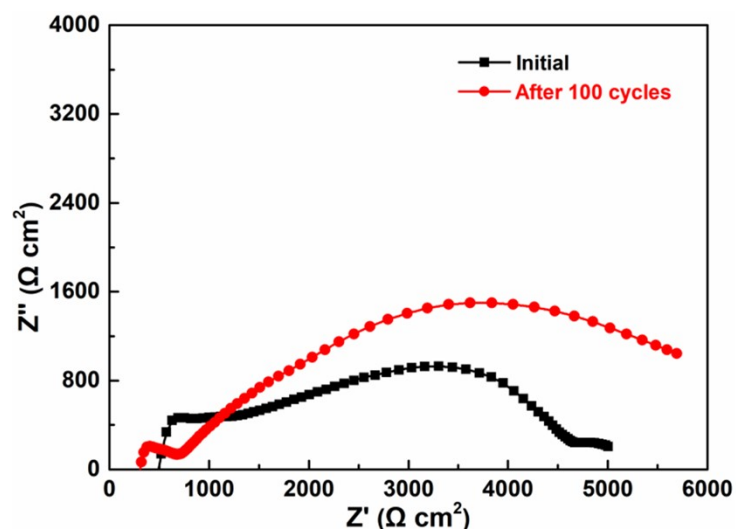


Figure S9. Impedance curves in the initial state and after 100 cycles at room temperature of Na || NZSP-NSO-5 || Na₃V₂(PO₄)₃ battery.

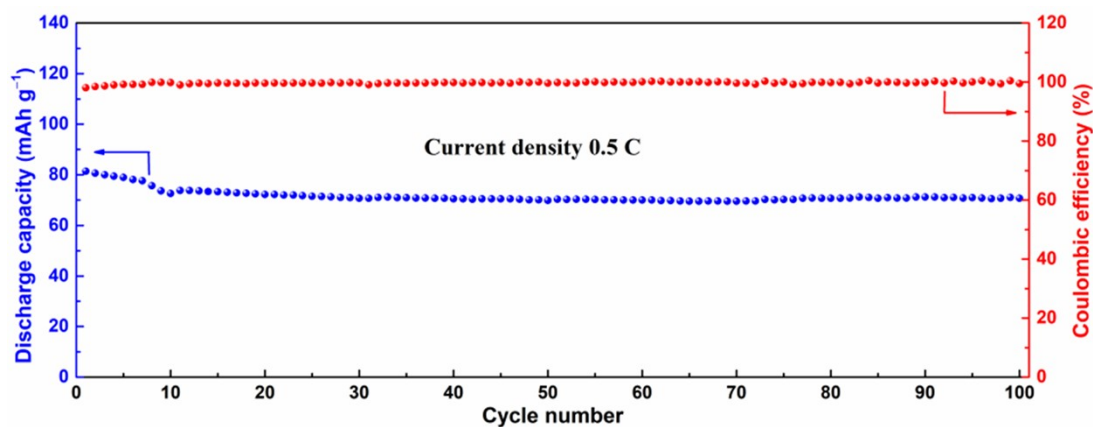


Figure S10. Cycling performance of Na || NZSP-NSO-5 || Na₃V₂(PO₄)₃ battery under a current of 0.5 C at 30 °C.

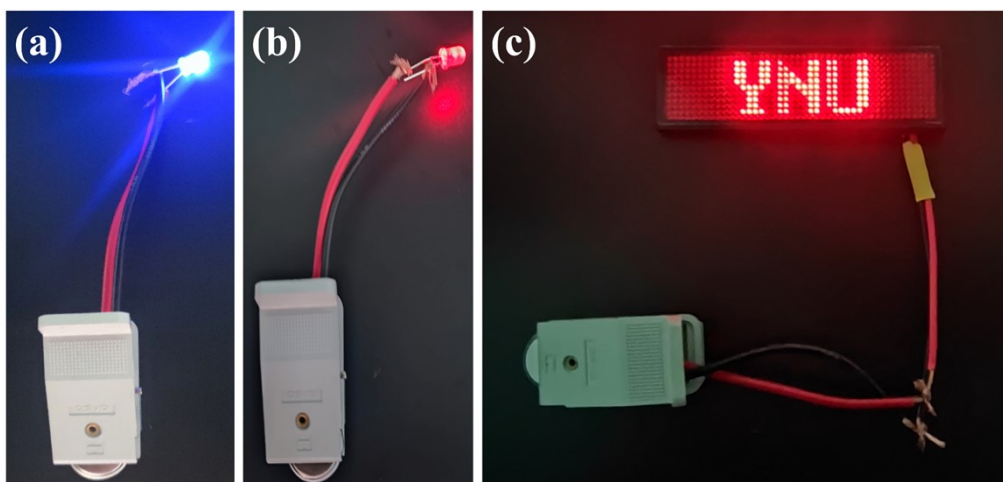


Figure S11. The lighted LEDs driven by SSE.

The voltage of blue light and red light lit by the battery is 2.4 V and 2.0 V respectively, and the voltage of LED light band is 3.07 V.

Table S1. The comparison of ionic conductivity between NZSP-NSO and other NZSP electrolytes.

Synthesis Method	Relative Density (%)	Ionic conductivity (mS cm^{-1})	Reference
Liquid phase sintering	94	1.28	This work
Solid state reaction	91	0.90	1
Sol-gel method	-	1.67	2
Liquid phase sintering	86	0.11	3
Spark plasma sintering	95	0.93	4
Cold sintering process	92	0.25	5
Aqueous cold sintering processes	82	0.53	6

References

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