

Supplementary Information File for:

A Flexible, Ceramic-Rich Solid Electrolyte for Room-Temperature Sodium-Sulfur Battery

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Experimental Methods

Synthesis of $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (NZSP) powder: NZSP powder is prepared from citrate sol-gel method described elsewhere in the literature ¹. 0.02 mol of Zirconyl chloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 98% Sigma Aldrich) is dissolved in 50 ml of millipore water. 0.0075 mol of citric acid ($\text{C}_6\text{H}_8\text{O}_7$, Merck, 99%) and 0.03 mol of ammonia solution is added to get zirconyl citrate. 0.01 mol of tri-sodium citrate dihydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, Merck, 99%) is dissolved separately in 100 ml of Millipore water and is mixed with the zirconyl citrate. The sodium and zirconyl citrate solution is stirred vigorously and 0.02 mol of tetrachlorosilane (SiCl_4 , TCI, stored in glove box) and 0.01 mol of phosphoric acid (H_3PO_4 , ACS reagent) are added. The pH of the citrate sol is adjusted to 6 by adding NH_4OH and the sol is heated for 24 hours at 80°C . Water gets evaporated from the sol and the dried gel is calcinated at 900°C for 10 hours to get NZSP powder.

Preparation of liquid electrolyte: Tetraethylene glycol dimethyl ether (TEGDME, >99%, Sigma Aldrich) and sodium perchlorate (NaClO_4 , > 98% Sigma Aldrich) are used as solvent and salt respectively for the electrolyte. TEGDME is dried on molecular sieves for at least 72 hours and NaClO_4 is dried in vacuum for 24 hours before use. 0.01 mol of NaClO_4 is dissolved in 10 mL of TEGDME to get the electrolyte. The electrolyte is prepared and stored inside the glove box.

Physical Characterization: X-ray diffraction (XRD) measurements were carried with Rigaku Smartlab X-ray diffractometer with $\text{Cu } \alpha$ ($\lambda = 1.5418$) source. XRD patterns were recorded with a step size of $0.02^\circ 2\theta$ and a scan rate of $2.5^\circ \text{min}^{-1}$. Scanning electron microscope (SEM) images and elemental mapping were carried out with Quanta 200 (FEG) with EDAX attachment. Thermogravimetric analysis is carried out in SDTQ600 TGA analyzer by TA instruments with a temperature range of room temperature to 1000°C at $10^\circ\text{C min}^{-1}$ rate, in air atmosphere (150 mL min^{-1}). Tensile measurements were carried out in The Instron® 8501 uniaxial tensile machine with a maximum load of 15 kN.

Electrochemical Characterization:

Measurement of Ionic conductivity: Ionic conductivity measurement is carried out in an ion blocking configuration, with PICF-HE sandwiched between two stainless steel spacers in a 2032 coin cell. Electrochemical impedance spectrum was recorded using a Biologic VSP-300 electrochemical work station at room temperature (27 °C), 30 °C, 40 °C and 50 °C in a Neware temperature chamber. The ionic conductivity σ of the cell is calculated using the formula.

$$\sigma = \frac{t}{R A}$$

Where t and A is the thickness and area of the electrolyte respectively and R is the total resistance.

Measurement of Transference number: Transference number T^+ is measured by the method proposed by Bruce, Evans and Vincent². The method involves application of a small constant potential (~ 10 mV) to a non-blocking Na/PICF-HE/Na cell configuration. When a small potential is applied, while Na^+ cation passes across the electrode-electrolyte interface, anions accumulate at the positive electrode, and are depleted at the negative electrode. This concentration gradient across the electrolyte leads to ionic motion constituting an initial current I^0 . Under a constant potential ΔV , the ion current reaches a steady state value I^s . The transference number T^+ is given by:

$$T^+ = \frac{I^s[\Delta V - I^0 R_1^0]}{I^0[\Delta V - I^s R_1^s]}$$

Where R_1^0 and R_1^s are the interfacial resistances before and after applying the potential, measured by fitting the corresponding electrochemical impedance spectra. The initial current I^0 is calculated by $\Delta V/R_t$ where R_t is the total resistance of the cell.

Sodium stripping and plating experiment: Sodium stripping and plating experiment was carried out in a symmetric cell Na/PICF-HE/Na configuration. Cells were subjected to galvanostatic charge-discharge cycles with a current density of 0.1 mA cm^{-2} . 1 hour time interval was maintained for charge and discharge.

Preparation of Catholyte: Hydrated Sodium sulfide $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$ (Ranchem) is vacuum dried at two stages, $90 \text{ }^\circ\text{C}$ for 12 hours and $140 \text{ }^\circ\text{C}$ for 24 hours at a vacuum less than 100 m bar to remove the solvated water from Na_2S as described elsewhere in the literature³. After drying, the vacuum chamber is purged with Argon gas and the Na_2S is transferred immediately inside glove box. Sulfur powder is also dried and transferred inside glove box. 0.008 mol of Na_2S and 0.001 mol of S is added to 6 mL of the electrolyte and the solution is stirred vigorously at 50°C until a dark brown solution of Na_2S_6 catholyte is obtained. The amount of sulfur in the catholyte is 1.5 mol/L.

Fabrication of Room temperature Na/S cells: ~ 20 mg of sodium metal (Sigma Aldrich) is spread on the stainless steel spacer of a coin cell is used as anode. PICF-CC-HE cut in the form of disc of 1.2 cm diameter is used as electrolyte/current collector. 48 mg of conductive carbon (Alpha Aesar) is suspended in a solution of 2 mL electrolyte + 1 mL of catholyte (containing ~48 mg of S) by vigorous stirring. The carbon cloth side of the PICF-CC-HE is soaked with this catholyte+carbon suspension, in order to prepare the solid electrolyte/cathode composite. The sulfur loading is determined to be $0.5\text{-}0.7 \text{ mg/cm}^2$. Finally, a coin cell is fabricated in the sodium metal/PICF-HE-CC/catholyte configuration in a 2032 coin cell for electrochemical testing. For comparison, 2032 coin cells with PICF-HE-CC replaced with a celgard membrane are also fabricated in sodium metal/Celgard soaked with electrolyte/carbon cloth-catholyte configuration.

Galvanostatic charge/discharge (GCPL) and cyclic voltammetry studies were carried out using Biologic BCS-310 battery cycler. GCPL measurements were carried out with a constant current of 0.2 mA cm^{-2} . Cyclic voltammetry was carried out between 1.2 V to 2.4 V vs. Na/Na^+ with a scan rate of 0.1 mV s^{-1} .

X-ray Diffraction pattern of NZSP and polymer in ceramic film PICF:

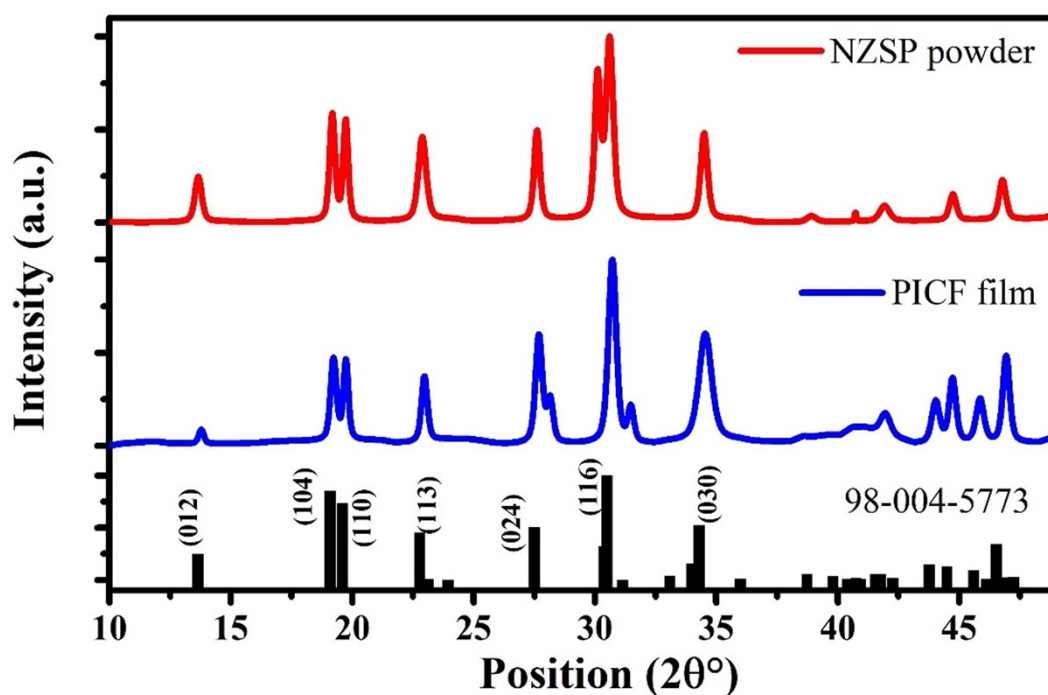


Figure S1. XRD pattern of as prepared NZSP powder and PICF film

Thermo gravimetric Analysis (TGA) of PICF:

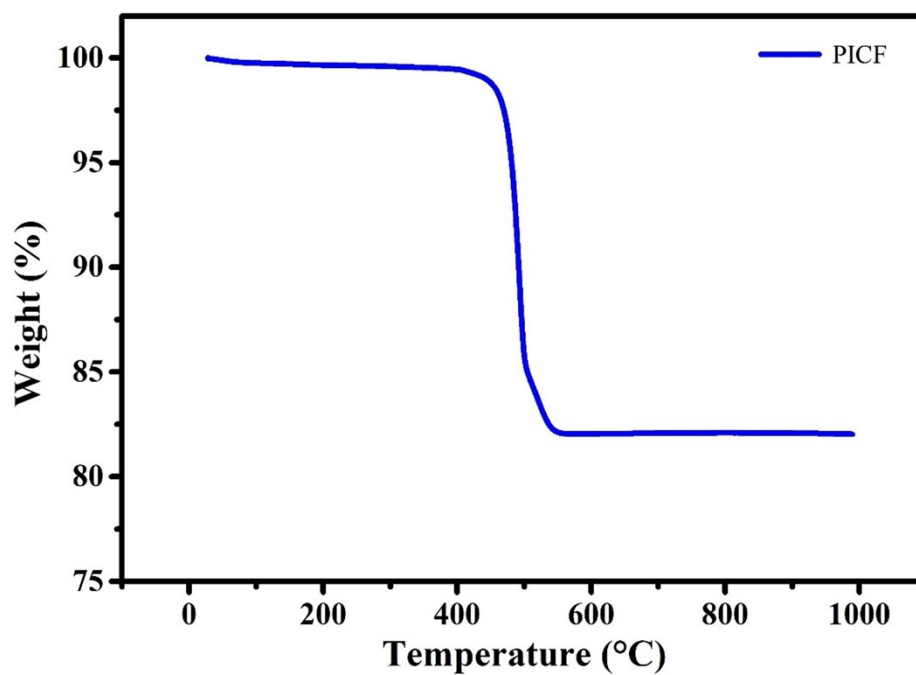


Figure S2. Thermo gravimetric analysis of PICF film

Cross sectional scanning electron microscope image of PICF:

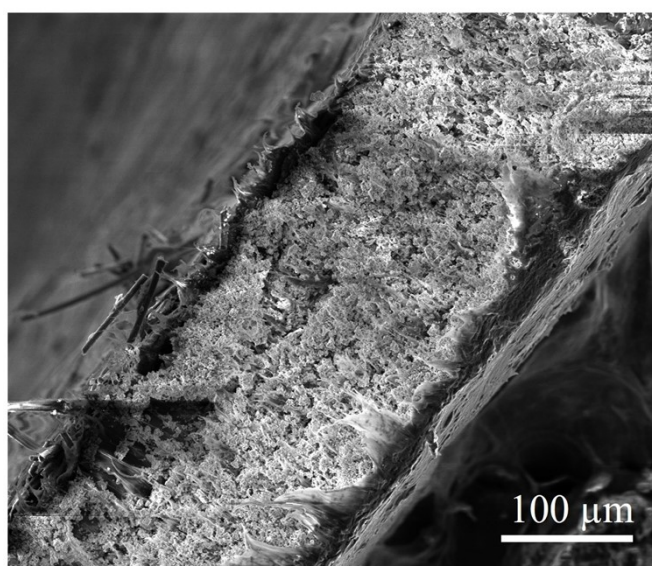
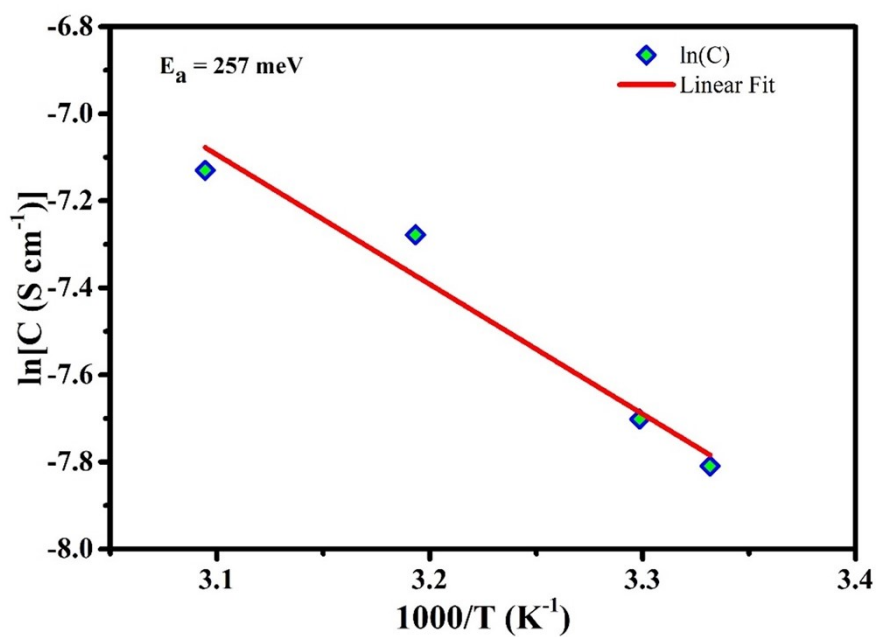
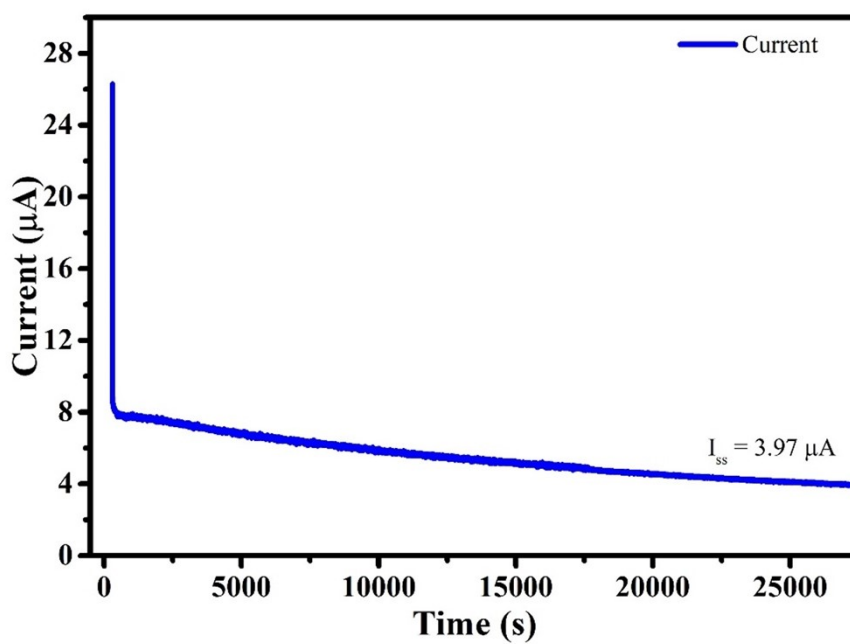


Figure S3. Cross-sectional scanning electron microscope image of PICF shown in Fig. 2 (g) in the main manuscript.



Arrhenius Plot of PICF-HE:

Figure S4. Arrhenius plot of PICF-HE shown in inset of Fig. 3(b) of the main manuscript



DC polarization experiment to determine transference number:

Figure S5. DC polarization current vs time in a Na/PICF-HE/Na cell when a small potential of 10 mV is applied plot to determine steady-state current

RT-Na/S cell with liquid electrolyte- cyclic stability test:

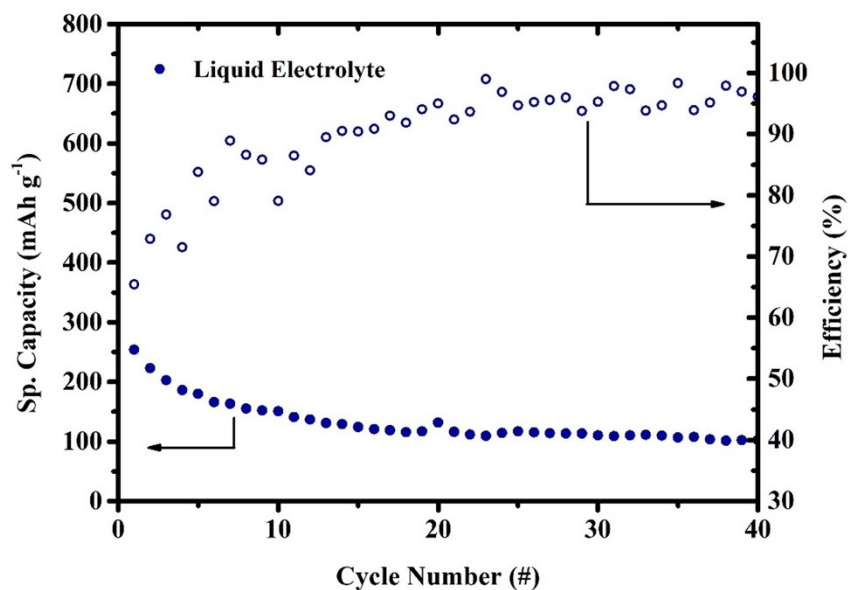
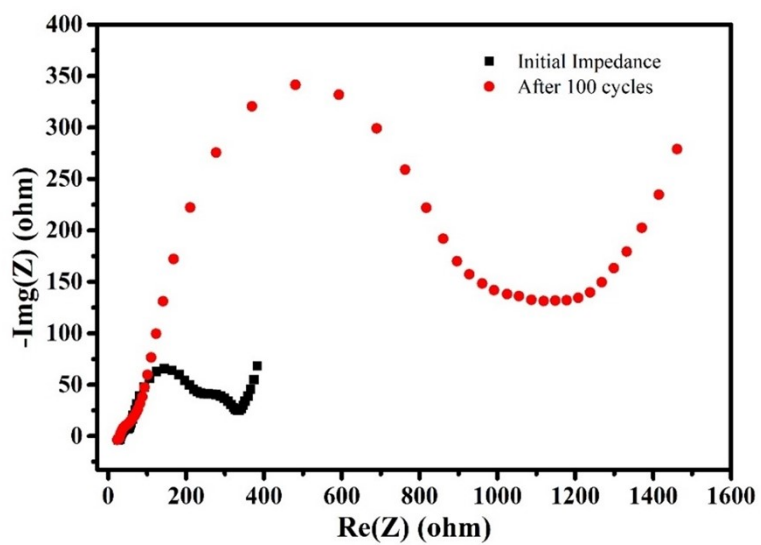


Figure S6. Cyclic stability test at a current of 0.2 mAh cm⁻² of a RT-Na/S cell with liquid electrolyte soaked celgard membrane as separator

RT-Na/S cell with PICF-CC-HE:



Cell impedance before and after 100 cycles:

Figure S7. Na/S cell impedance (with PICF-CC-HE) before and after 100 cycles

Sodium metal anode before and after cycling:



Figure S8. A fresh sodium metal anode spread on a stainless steel spacer (left) and sodium metal anode used in RT-Na/S cell after 100 charge-discharge cycles.

References:

- (1) Choy, J. H.; Han, Y. S.; Kim, Y. H.; Suh, K. S. Physico-Chemical Characterization of Na₃Zr₂Si₂PO₇ Fine Powders Prepared by Sol-Gel Method Using Citrates. *Jpn. J. Appl. Phys.* **1993**, 32 (3 R), 1154–1159. <https://doi.org/10.1143/JJAP.32.1154>.
- (2) Bruce, P. G.; Evans, J.; Vincent, C. A. Conductivity and Transference Number Measurements on Polymer Electrolytes. *Solid State Ionics* **1988**, 28–30 (PART 2), 918–922. [https://doi.org/10.1016/0167-2738\(88\)90304-9](https://doi.org/10.1016/0167-2738(88)90304-9).
- (3) Smith, W. H.; Birnbaum, J.; Wolden, C. A. Production and Purification of Anhydrous Sodium Sulfide. *J. Sulfur Chem.* **2021**, 42 (4), 426–442. <https://doi.org/10.1080/17415993.2021.1907390>.