

Supporting Information for:

Polymer Electrolyte Glue: A Universal Interfacial Modification Strategy for All-Solid-State Li Batteries

Derui Dong,† Bin Zhou,† Yufei Sun, Hui Zhang, Guiming Zhong, Qingyu Dong, Fang Fu, Hao Qian, Zhiyong Lin, Derong Lu, Yanbin Shen, Jihuai Wu, Liwei Chen, and Hongwei Chen**

† These authors contributed equally to this work.

Experimental section

a) Chemicals and materials

4,4'-Dipyridyl (>98%, Sigma-Aldrich Chemical), succinonitrile and lithium bis(trifluoromethanesulfonyl)amide were used as received from Aldrich. Hexakis(bromomethyl)benzene (>98%) was purchased from TCI Chemicals. Solvents (analytical grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. The reagents were used as purchased without purification or treatment.

b) Synthesis of low cross-linking PIN precursor

The PIN precursor was synthesized according to literature with slight modification.^[1] Hexakis(bromomethyl)benzene (635.6 mg, 1 mmol) and 4,4'-Dipyridyl (546 mg, 3 mmol) were added to N-methyl-2-pyrrolidinone (50 mL) solvent. The reactor was

flowed with argon for 20 minutes. The reaction solution was stirred at room temperature for 5 h and then further heated to 80°C for 15 h under argon atmosphere. The resulting compounds was collected by filtration and rinsed with N-methyl-2-pyrrolidinone for no less than three times. The obtained product was then dispersed and stirred in a 15 wt% LiTFSI aqueous solution (100 mL×3) at room temperature for ion exchange. The as-prepared solid product was obtained by filtration and washed with deionized water and ethanol. The final product was dried at 50 °C in vacuum (>24h).

c) P@S glue preparation

SN solution preparation: Molten succinonitrile was mixed with lithium bis(trifluoromethanesulfonyl)amide in different ratios (80 °C). The whole processes were operated in an argon filled glove-box.

P@S glue preparation: SN solution was mixed with PIN precursor in weight ratio of 1:2 and then heated to 80 °C for 12 h. The whole processes were operated in an argon filled glove-box.

d) Characterization

Solid-state NMR spectra were acquired on a Bruker Avance III- 500 at Larmor frequencies of 73.6 for ¹³C. A 2.5 mm Bruker HXY probe was used and the samples were spun at 25 kHz for DP and 10 kHz for CP. The NMR measurements were performed in room temperature (~25 °C). FTIR spectra were collected using a

ThermoScientific Nicolet 6700 spectrometer. TGA measurements were carried out using a NETZSCH STA 449C by heating samples from 30 to 800 °C at a rate of 10 °C/min in N₂. XRD patterns were recorded on a Bruker D8-advance X-ray diffractometer with Cu-K α radiation (λ = 1.5418 Å), using an operation voltage and current of 40 kV and 40 mA, respectively. SEM images were obtained with a FEI Quanta 400 FEG equipped with EDX (Apollo 40 SDD) operated at 10 kV. AFM images were acquired in tapping mode in air using a Digital Instrument Dimension 3100. The contact angle experiment was carried out by adding 10 μ L glue droplet on the electrode or electrolyte films (JC2000D). To characterize the adhesive capability of the P@S glue, the 180° peel-off strength of cured glue toward two symmetrical electrode (or electrolyte) was measured (Autograph AGS-X, SHIMADZU). P@S glue or PEO solution (2 wt% in H₂O) was coated between the two solid and heated at 80 °C for 12h. Peel Strength = $\frac{F}{d}$ (F is release force; d is sample width).

e) Electrode preparation and battery assembly

Electrode preparation: To fabricate the PANS electrode, PANS (prepared according to *J. Mater. Chem. A*, **2015**, 3, 1392), PEO (EO : Li⁺ = 18 : 1) and carbon black were mixed with the weight ratio of 60: 20: 20 in acetonitrile to afford slurry with appropriate viscosity before it is coated on Al foil by doctor blading. After drying, calender process was performed to densify the electrodes. The thickness of cathode is ~25-30 μ m and the cathode material loading is about 4-5 mg/cm².

Symmetric Li cell fabrication: The surfaces of LLZTO pellets were polished by 400 grit size sandpaper before used. The symmetric cells with glue were constructed as follows: first, the glue liquid (3 μ l) was uniformly dripped on both surfaces of LLZTO pellets. The coated pellets were heated at 80 $^{\circ}$ C for 0.5 h. Then, the coated pellets were sandwiched between two pieces of Li metal (polished before used) to assemble the symmetric cells. A pressure (0.08 MPa) was exerted to keep a close contact. The resulted cells were further heated at 80 $^{\circ}$ C for 1 h. Li/bare LLZTO/Li symmetric cells were also fabricated under the same procedure (without glue coating) as a comparison. The whole processes were operated in an argon filled glove-box.

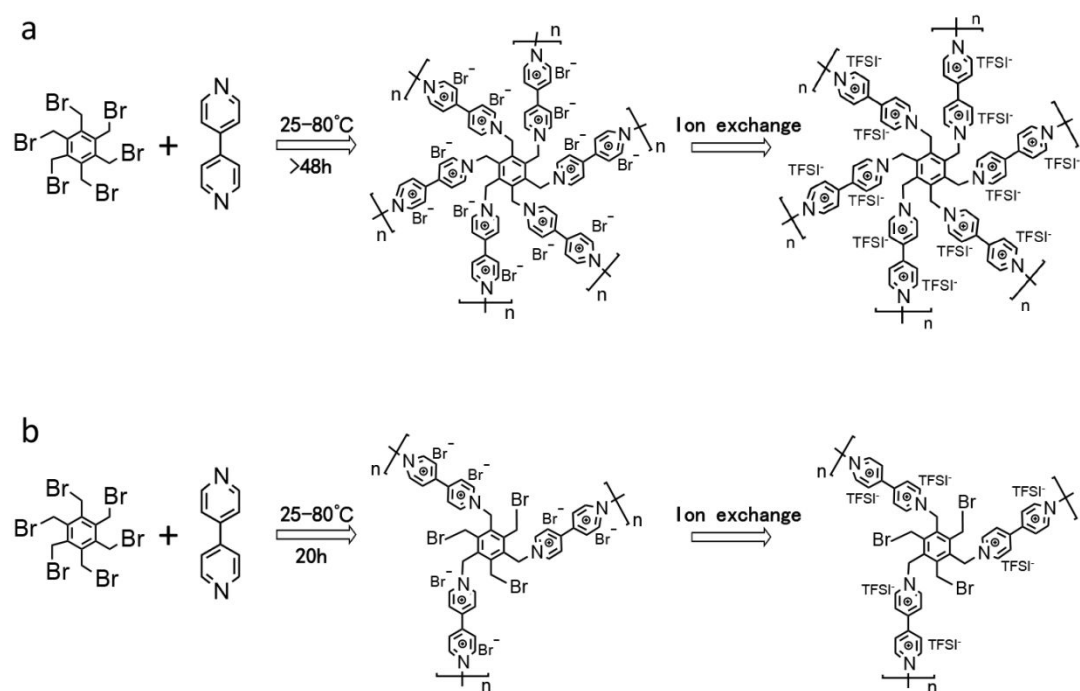
Solid-state Li-S cell fabrication: The surfaces of LLZTO pellets were polished by 400 grit size sandpaper before used. The PANS cells with glue were constructed as follows: first, the glue liquid (5 μ l) was uniformly dripped on both surfaces of LLZTO pellets. The coated pellets were heated at 80 $^{\circ}$ C for 0.5 h. Then, the coated pellets were sandwiched between the as-prepared PANS cathode film and Li metal (polished before used) to assemble the cells. A pressure (0.08 MPa) was exerted to keep a close contact. The resulted cells were further heated at 80 $^{\circ}$ C for 1 h. The control PANS cells were also fabricated under the same procedure except using glue. The whole processes were operated in an argon filled glove-box.

f) Electrochemical test

EIS data was collected using an Autolab PGSTAT 302N system (frequency range

from 0.01 Hz to 1 MHz with AC amplitude of 10 mV). LSV experiment was performed on a working electrode of stainless steel as a counter and reference electrode of lithium metal, with a sweep rate of 0.1 mV s^{-1} between 0 and 5.0 V. The PANS cells were discharged and charged on a battery test system (NEWARE, NEWARE technology Ltd. Shenzhen) from 1.0 to 3.0 V with a current density of 0.05 mA/cm^2 .

Supplemental results and discussion



Scheme S1. Schematic diagram for PIN synthesis. (a) Ideal nucleophilic substitution between hexakis(bromomethyl)benzene and 4,4'-bipyridine. (b) Partial nucleophilic substitution between hexakis(bromomethyl)benzene and 4,4'-bipyridine (precursor synthesis).

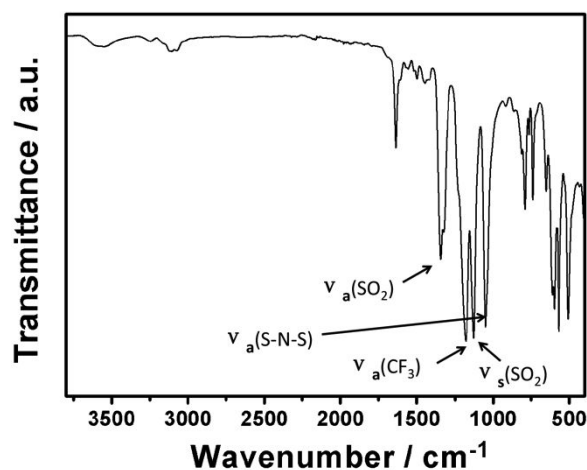


Figure S1. FTIR spectra of low cross-linking PIN precursor after ion exchange. Four peaks appeared (1344 , 1177 , 1128 , and 1050 cm^{-1}) that could be assigned to the vibration sorption of TFSI anions ($\nu_a(\text{SO}_2)$, $\nu_a(\text{CF}_3)$, $\nu_s(\text{SO}_2)$, and $\nu_a(\text{S-N-S})$, respectively).

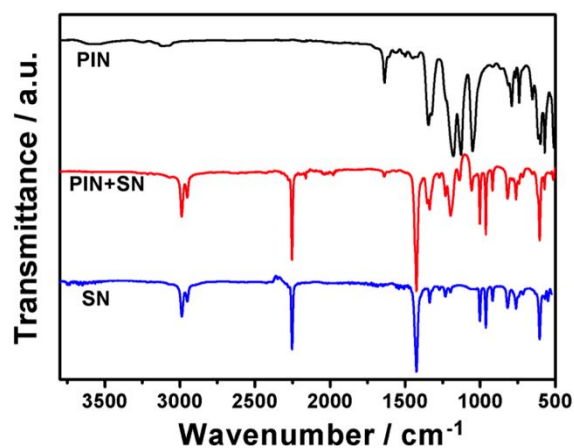


Figure S2. FTIR spectrum of PIN, PIN+SN and SN.

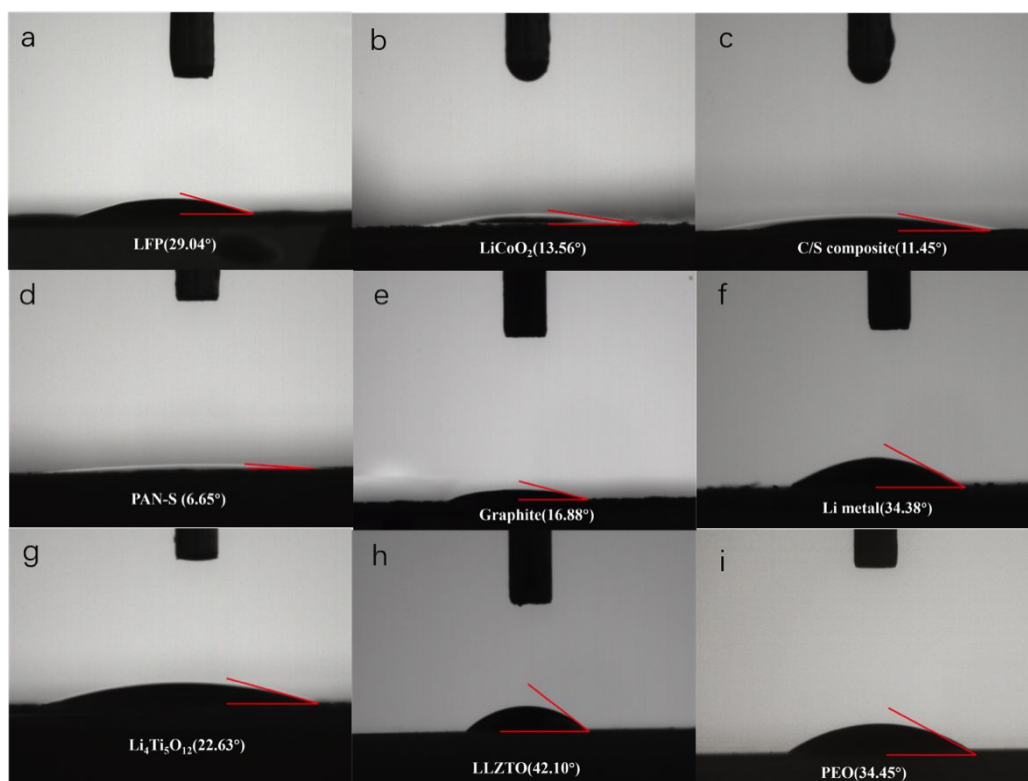


Figure S3. Contact angle measurements of glue on LiFePO₄, LiCoO₂, carbon/sulfur composite (C/S), PAN-S, graphite, Li metal, Li₄Ti₅O₁₂, LLZTO and PEO film.

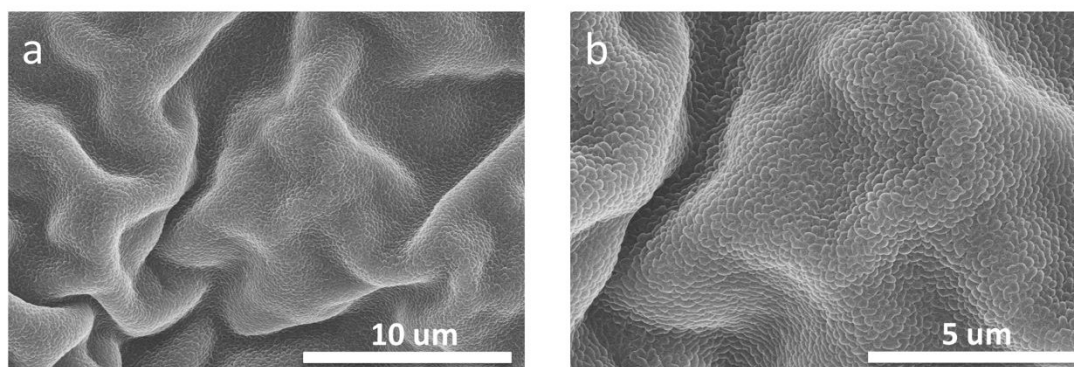


Figure S4. Supplementary SEM images of cured PIN.

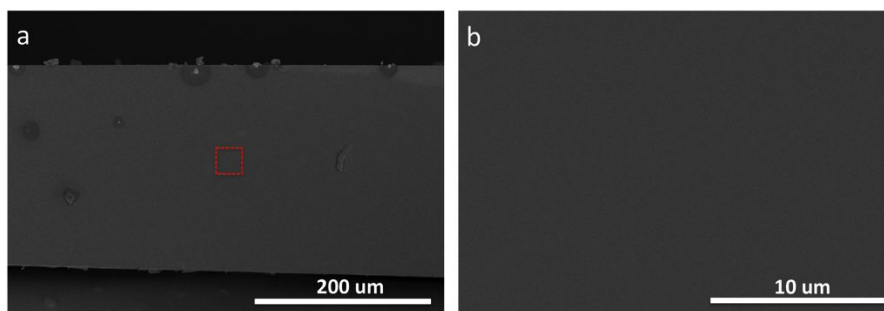


Figure S5. PIN glue was cured on a glass plate at 80 °C for 1h. (a)&(b) SEM images of the cross-section of the cured PIN glue.

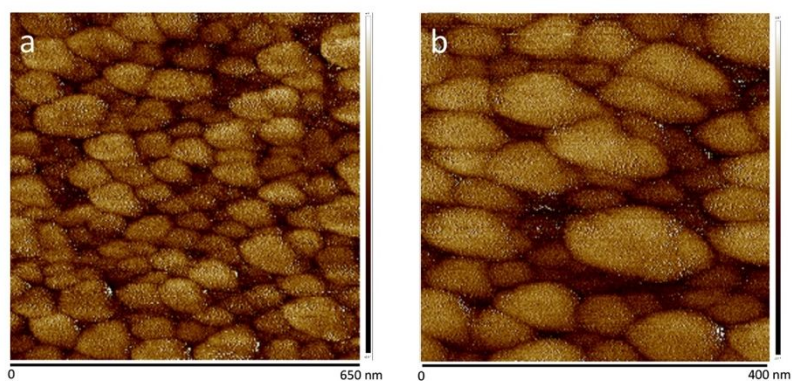


Figure S6. AFM images of cured PIN particles.

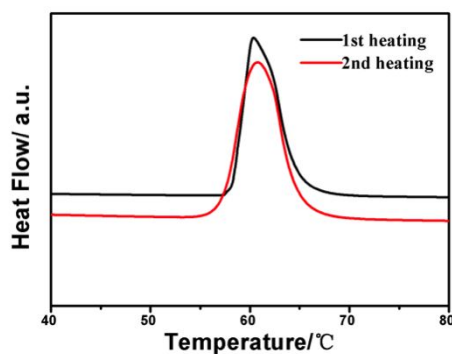


Figure S7. 1st and 2nd DSC heating curves of the pure SN. Heating at 10 °C/min under N₂.

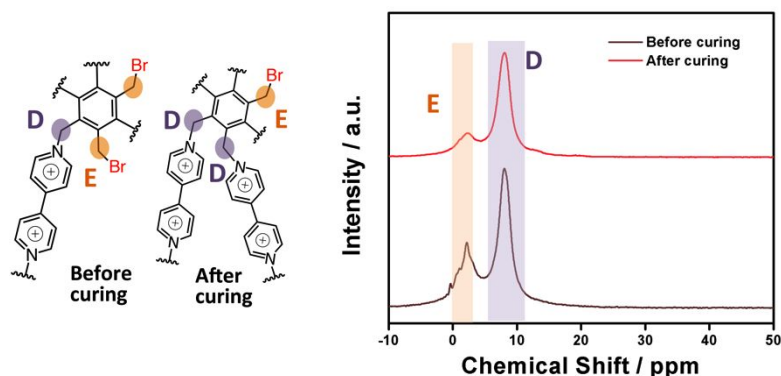


Figure S8. H NMR of the PIN before and after curing process.

H NMR of PIN before and after curing also confirmed the curing reaction as concluded from the ^{13}C NMR results. The peak E at ~ 3 ppm is attributed to hydrogen atom in $-\text{CH}_2\text{-Br}$ and the peak D at ~ 8 ppm is attributed to hydrogen atom in $-\text{CH}_2-$. After the curing stage, the relative intensity of peak E decreased markedly, indicating the proposed nucleophilic substitution of the hexakis(bromomethyl)benzene monomer during the curing. The H NMR results correspond to ^{13}C NMR results very well.

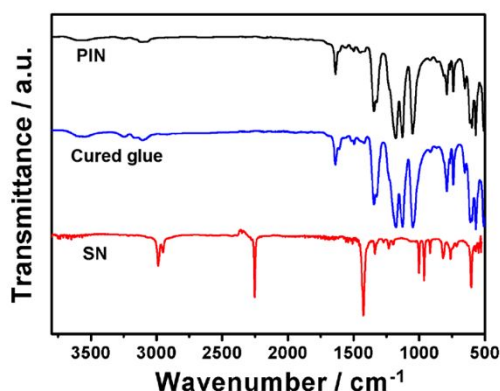


Figure S9. FTIR spectra of PIN, cured glue and SN, respectively. The similar PIN and cured glue spectra suggested that no other reaction occurred except the

subsequent nucleophilic substitution during the curing process.

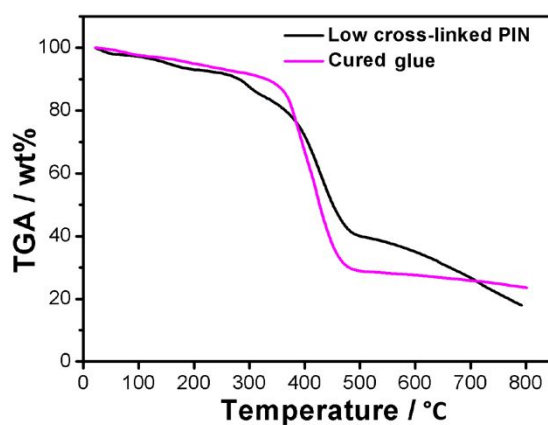


Figure S10. TG analysis of low cross-linked PIN and cured P@S glue. The cured P@S shows relatively stable weight loss curves and the decomposition temperature shifts toward higher temperature.

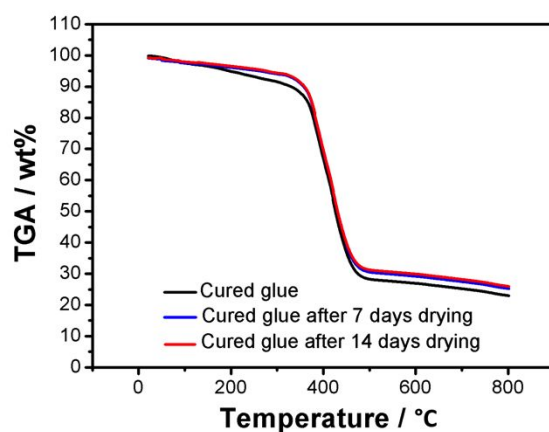


Figure S11. TG analysis of cured glue and control cured glue samples.

The two control cured glue samples were obtained by further drying at 100 °C under vacuum for 7 and 14 days after the established curing process, aiming to remove any possible SN. As shown in Figure S11, the control samples showed almost same weight loss, demonstrating that SN can be totally removed even after

7 days of drying. On the other hand, the original cured glue shows a slight weight loss during 100-350 °C and results in a relatively large weight loss compared with the two control samples, which was attributed to the residual SN (~1.9 wt%).

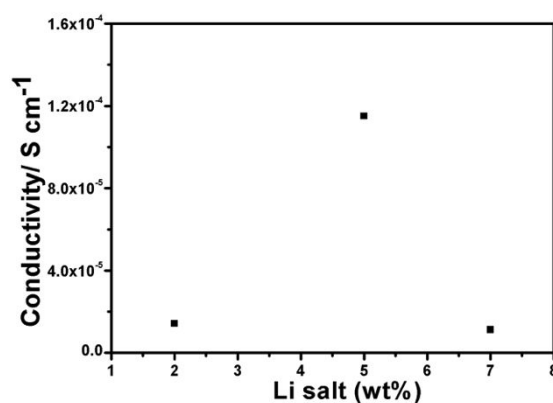


Figure S12. Ionic conductivity of cured P@S glue with increasing Li salt contents.

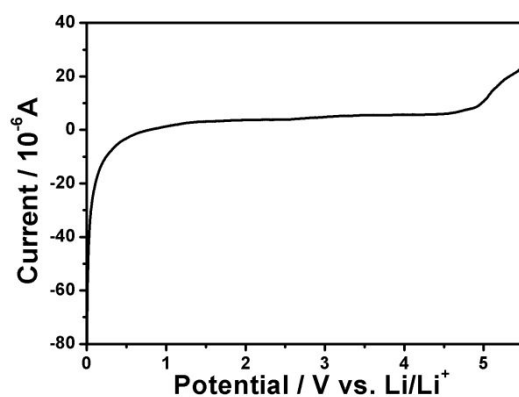


Figure S13. LSV result of cured P@S glue (with a sweep rate of 0.1 mV s⁻¹).

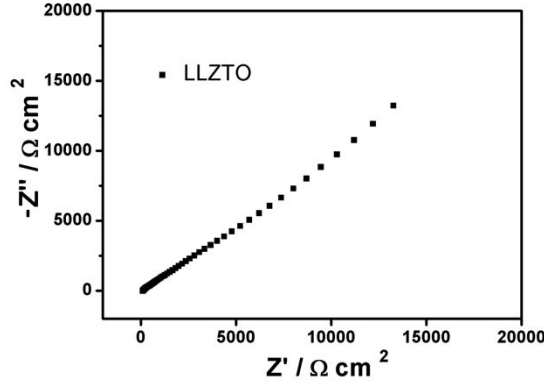


Figure S14. EIS measurement of Au|LLZTO|Au blocking electrode cell. The overall resistance of the LLZTO (bulk and grain boundary) measured using Au electrodes is $101 \, \Omega \, \text{cm}^2$ (RT).

To calculate the interfacial resistance: the first semi-circle of EIS at high frequency was attributed to the overlap of bulk and grain boundary of LLZTO and interface impedances of cells, which was used to analyze the interfacial resistance between the Li metal electrode and the LLZTO electrolyte with/without glue. Interfacial resistance was thus determined for the interface resistance on either side of the symmetric cells by subtracting the electrolyte resistance from the total cell resistance, dividing by two, and then normalizing to the electrode surface area.

As shown in Figure 5b, the first semi-circle of the Li|LLZTO|Li cells with and without glue yield total resistance of 308 and $10328 \, \Omega \, \text{cm}^2$, respectively. By subtracting the resistance of the LLZTO ($101 \, \Omega \, \text{cm}^2$) and dividing by a factor of two, the interfacial resistance of Li|LLZTO|Li cells with and without glue was calculated: 104 and $5114 \, \Omega \, \text{cm}^2$, respectively.^[2]

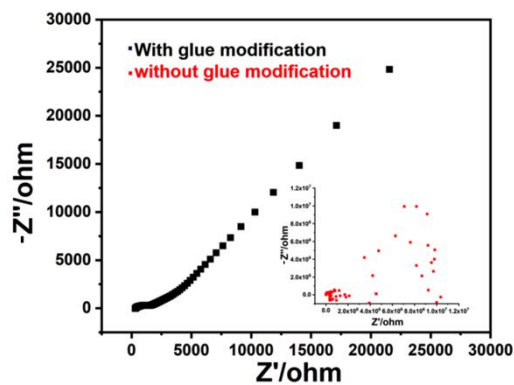


Figure S15. EIS measurements of Li-S cells with/without glue modification. Inset: the disordered EIS curve of the cell without glue modification on cathode-electrolyte interface indicated the poor interfacial contact within the cell.

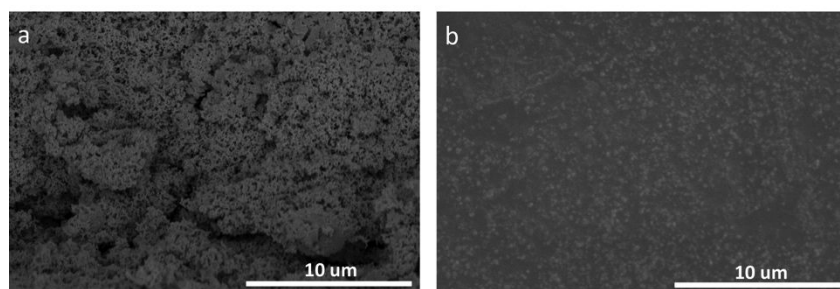


Figure S16. SEM image of the cathode film before glue modification.

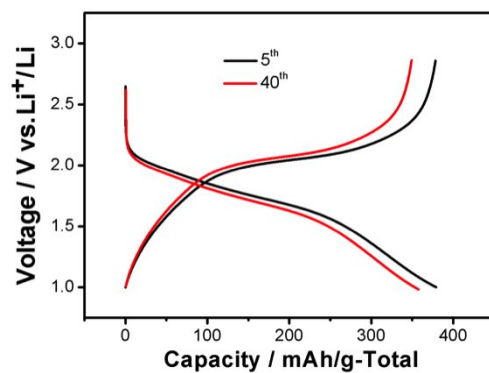


Figure S17. 5th and 40th charge and discharge profiles of the PANS batteries with glue modification.

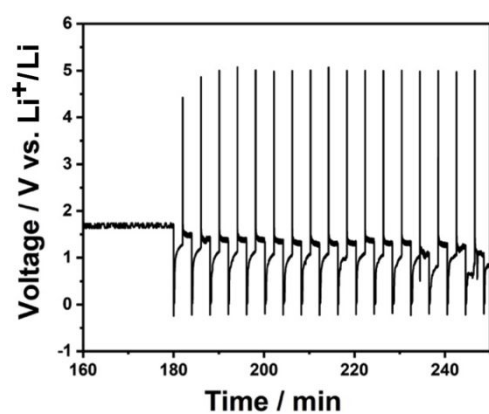


Figure S18. Charge and discharge profiles of solid-state Li-S batteries without glue modification between cathode and electrolyte. They cannot be charge or discharge.

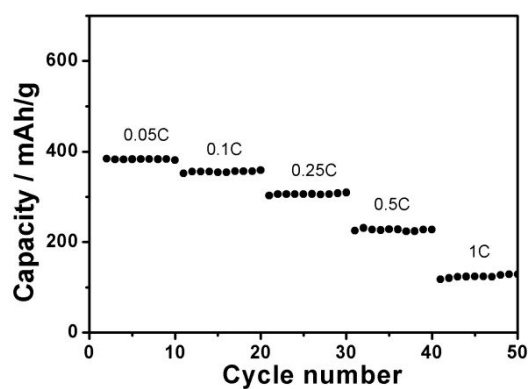


Figure S19. Rate performances of the PANS batteries.

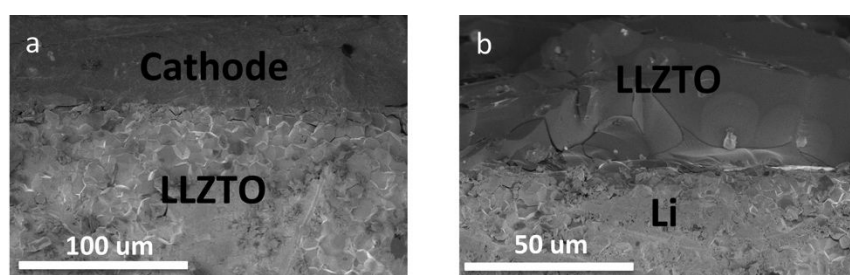


Figure S20. SEM images of the battery cross-section after 10 cycles.

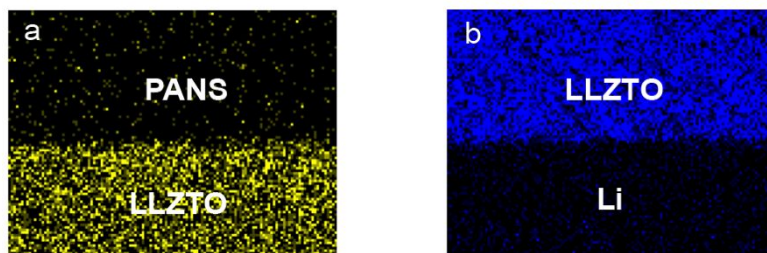


Figure S21. Corresponding EDX (Zr element) mapping images of the cross-section of cathode-electrolyte and Li anode-electrolyte showed in Figure 5e&f.

References

- [1] P. Zhang, M. Li, B. Yang, Y. Fang, X. Jiang, G.M. Veith, X.-G. Sun, S. Dai, *Advanced Materials*, 27 (2015) 8088-8094.
- [2] X. Han, Y. Gong, K. Fu, X. He, G.T. Hitz, J. Dai, A. Pearse, B. Liu, H. Wang, G. Rublo, Y. Mo, V. Thangadurai, E.D. Wachsman, L. Hu, *Nature Materials*, 16 (2017) 572.