

Supporting Information

A novel thioctic acid-functionalized hybrid network for solid-state batteries

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Experimental section

Preparation of TA-hybrid network

List of reagents: Poly(ethylene glycol) diacrylate (PEGDA, $M_n=400, 700, 1000 \text{ g mol}^{-1}$), (\pm)- α -thioctic acid (TA), bis(trifluoromethane) sulfonamide lithium (LiTFSI), were purchased from Aldrich. Poly (vinylidene fluoride-co-hexafluorpropylene) (PVDF-HFP, $M_w \approx 455,000$) was purchased from Sigma-Aldrich. Anhydrous ethanol and acetone were purchased from Sinopharm Chemical Reagent Co. Ltd. The above all the chemicals were used directly as purchased without further purification treatment.

Synthesis of TA-hybrid network: The mixture of 1.0 g PEGDA and 0.2g TA were added in anhydrous acetone and vigorously stirred until completely dissolved. The weight ratio of P(VDF-HFP) to the total weight of PEGDA and TA is 1:2. In the meanwhile, LiTFSI was added and with the molar ratio of PEGDA and to LiTFSI was 10:1. Then the mixtures were stirred by magnetic agitation and heated at 75 °C for 2 h. The resultant viscous/yellow solution was evenly casted on a ziplock bag by a doctor blade to form a uniform membrane, and then vacuum-dried at 55 °C for 12 h to remove the acetone residue (Scheme S1). The flexible and adhesive SPE were obtained.

Control group was prepared via the same method as TA-hybrid network, except without TA.

Materials Characterizations

The morphology of SPE membranes were examined via a JEOL JSM-7100F scanning electron microscope with an accelerating voltage of 20 kV. Fourier transform infrared spectrometer (FT-IR) (Thermo Nicolet Corporation; 7800-350/cm 0.01/cm/6700) was used to analyze the samples. The X-ray photoelectron spectroscopy (XPS) analysis was tested by ESCALAB 250 Xi spectrometer. The Raman spectra were recorded by using

Raman spectrometer (Horiba Lab RAM HR Evolution) with a 532 nm excitation wavelength. XRD patterns were recorded using a D8 discover X-ray diffractometer with Cu K α radiation. The thermal stability was executed by thermogravimetric analysis (TGA) using a NETZSCH STA 449F5 instrument over the temperature range between 25 and 600 °C Under air conditions at a heating rate of 10 °C min⁻¹. A tensile testing machine was used to obtain the stress-strain curves of the SPEs with the tensile speed of 0.2 cm min⁻¹.

Electrochemical performance measurements

Ionic Conductivity and activation energy

The stainless steel (SS)/TA-hybrid network/SS cells were assembled to measure ionic conductivities. The electrochemical impedance spectroscopy (EIS) was measured in the temperature range from 20 °C to 80 °C (record every 10 °C) decrease using a Autolab PGSTAT302N in the frequency range from 10⁶Hz to 10²Hz with a perturbation of 10 mV. The SPE was sandwiched between two pieces of stainless-steel blocking electrode with a diameter of 16 mm. and the ionic conductivity(σ)was calculated from the

$$\sigma = \frac{L}{R_b S} \quad (1)$$

Where L is the thickness of the SPE, S is the contact area between the two stainless steel plates, and R(Ω) is the bulk resistance of the SPE.

In our case, as shown in Fig. S6 the thickness is 85 μ m, the area is 2.0096 cm², and the resistance at 30 °C, is 36.2 Ω . From equation (1), the ionic conductivity of the calculated area is 0.11 mS/cm. This matches the values of table S1 in the supporting information.

The activation energy (E_a) was calculated according to the Arrhenius law:

$$\sigma = A \exp(-E_a/RT) \quad (2)$$

Where A is the frequency factor, R is the molar gas constant, T is the measure

absolute temperature of the SPE.

Electrochemical Stability Window

The Electrochemical Stability Window of electrolytes can be measured by building Li/TA-hybrid network/SS cells and conducting linear sweep voltammetry (LSV) measurements range from 0-6 V at 10 mV s⁻¹ via Autolab PGSTAT302N.

Li⁺ Transference Number

Li⁺ Transference Number can be tested using Li/TA-hybrid network/Li symmetric cells at 25 °C via Autolab PGSTAT302N. The cell resistances are determined before and after polarization using EIS and currents measured by the DC method. t_{Li^+} is obtained according to the following Equation (3):

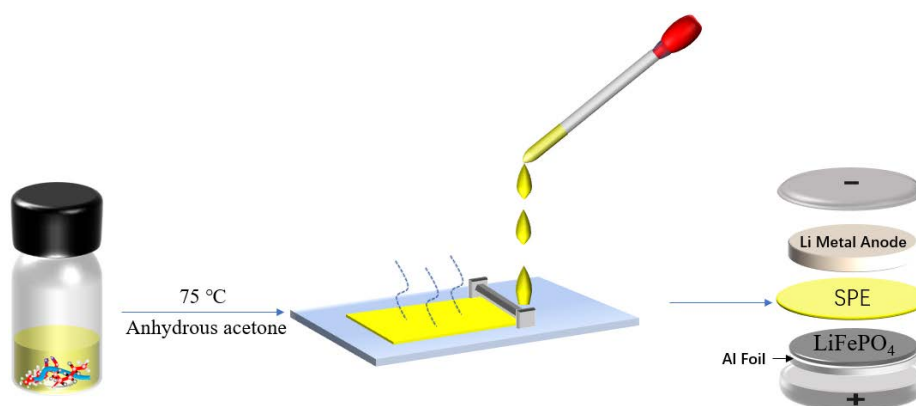
$$t_{Li^+} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} \quad (3)$$

Where I_0 and I_s are the initial and steady-state currents. The R_0 and R_s are the resistances before and after polarization of the cell, respectively. ΔV is the DC potential applied across the cell.

Battery assembly and testing

Li/TA-hybrid network/Li symmetric cells assembled in an argon-filled glovebox were tested by a multichannel battery testing system (Neware CT4008). A certain constant current density was applied to the battery and the current signal was changed every 60 minutes. The rate and cycle performance were performed by using LiFePO₄/SPE/Li coin cell assembled in an argon-filled glovebox. To prepare the cathode, LiFePO₄ powder, Super P and P(VDF-HFP)-LITFSI (molar ratio 10:1) were mixed with a weight ratio of 8:1:1 solvent and the homogenized slurry was pasted on an Al foil, and dried at 75 °C under vacuum for 24 h. The mass loading of LiFePO₄

active material was about 2-3 mg/cm². The solid-state LiFePO₄/SPE/Li cells were assembled with a coin type (CR2016) configuration. The charge–discharge and cycling performances were investigated using a battery testing system (Neware CT4008) at a potential between 2.4 and 4.0 V at 25 °C.



Scheme S1. Schematic preparation procedure of TA-hybrid network.



Fig. S1. Optical image of heating crosslinking process of polymer blends (top) and TA-hybrid network (bottom)

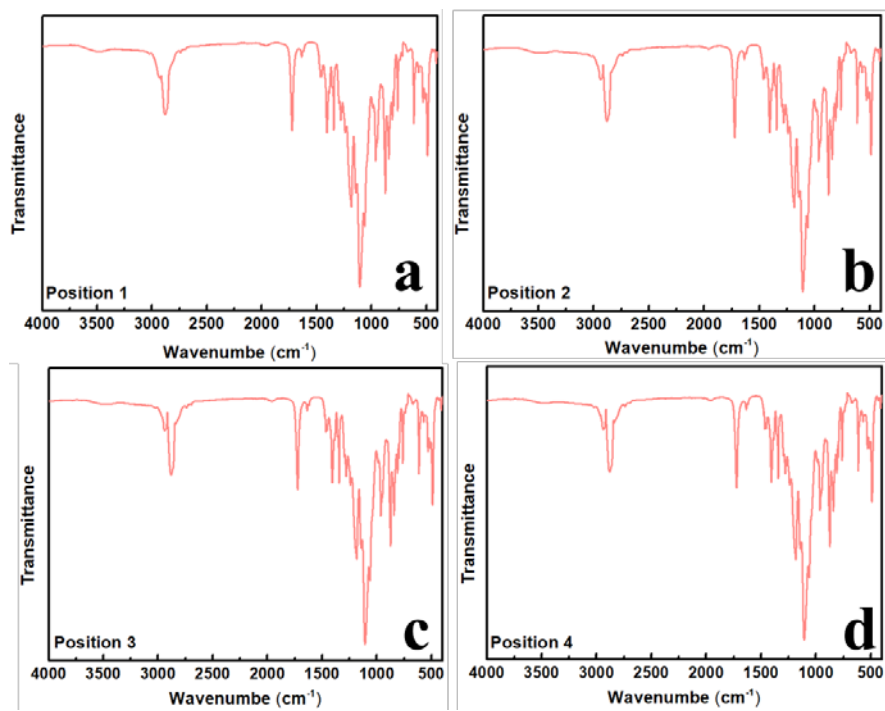


Fig. S2. FT-IR of different positions of the same electrolyte membrane

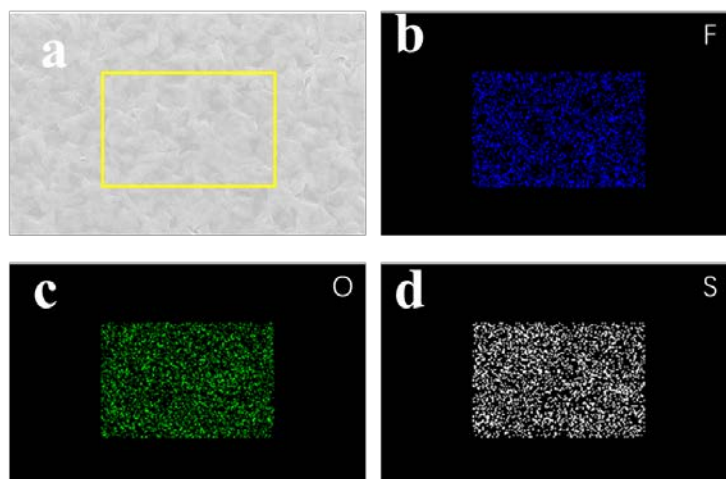


Fig. S3. Top-view SEM image of the TA-hybrid network and EDS mapping images of F, O, and S element.

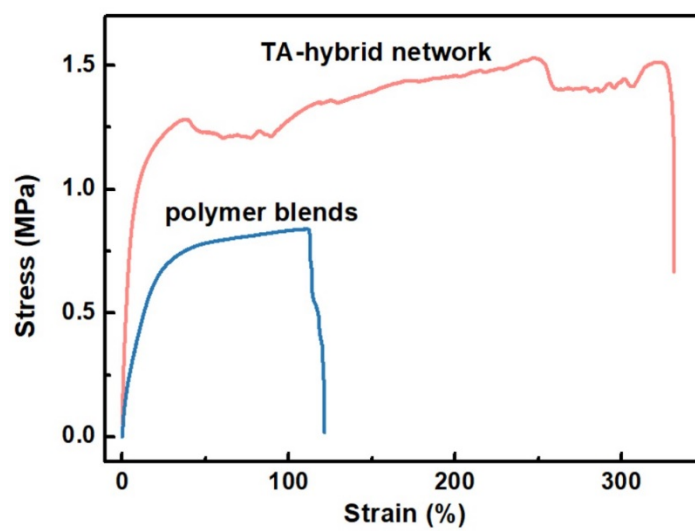


Fig. S4. Stress-strain curves for membranes of TA-hybrid network and polymer blends

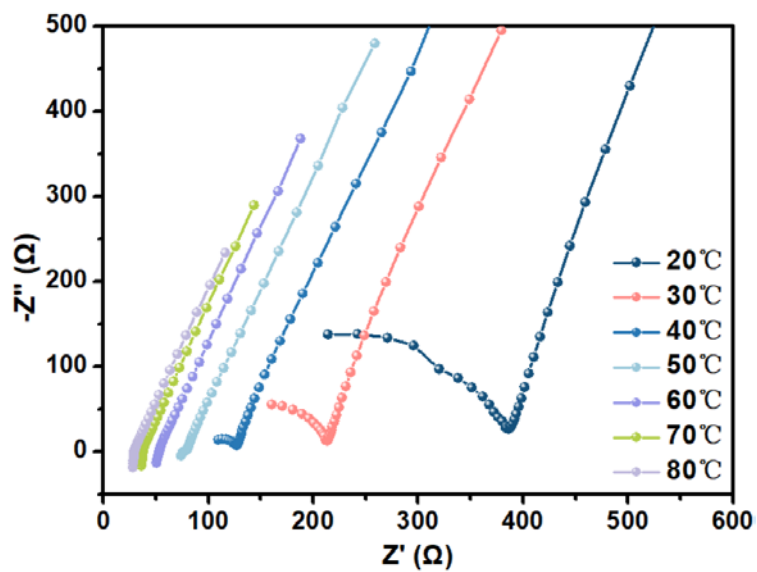


Fig. S5. EIS curves of polymer blends from 20 to 80 °C.

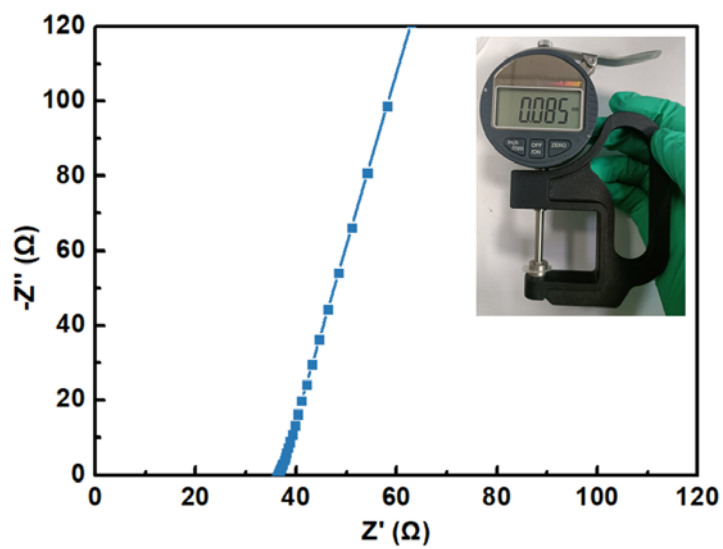


Fig. S6. Electrochemical impedance spectroscopy and thickness measurement of TA-hybrid network.

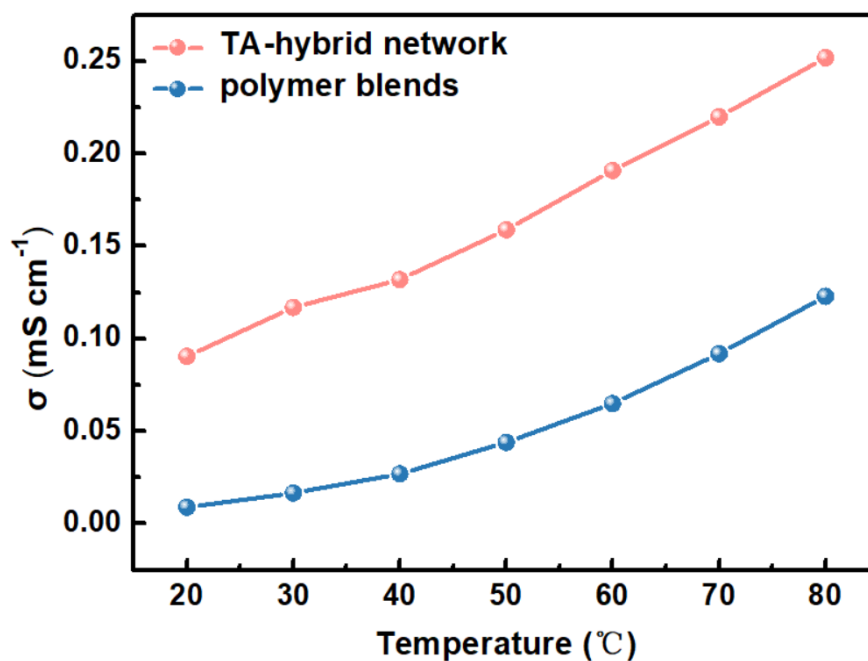


Fig. S7. Ionic conductivity of SPE from 20 to 80 °C

Table S1. Comparison of ionic conductivity (unit: mS/cm) of TA-hybrid network and polymer blends at different temperatures

	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C
polymer blends	0.009	0.017	0.027	0.044	0.065	0.092	0.123
TA-hybrid network	0.091	0.117	0.132	0.159	0.191	0.220	0.252

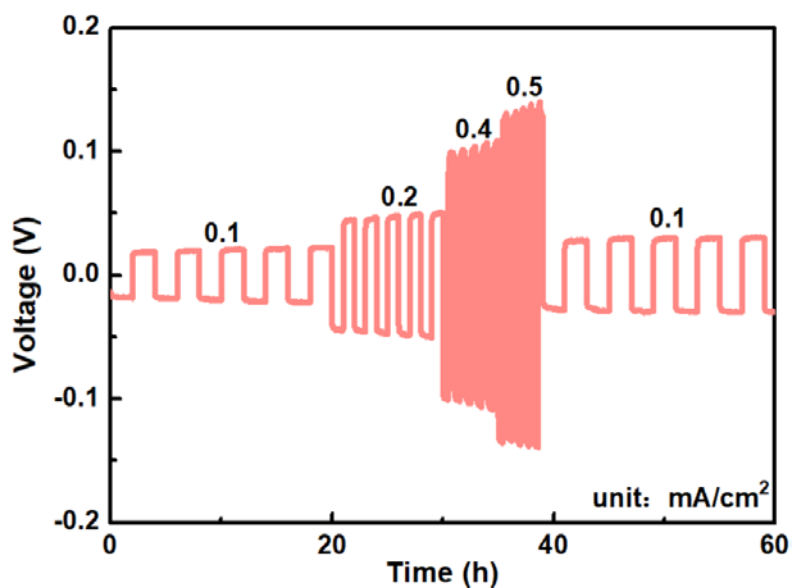


Fig. S8. Li-Li symmetric cells with TA-hybrid network at a current capacity of 0.2 mAh cm^{-2} with different current densities of $0.1, 0.2, 0.4,$ and 0.5 mA cm^{-2} respectively at $25 \text{ }^\circ\text{C}$.

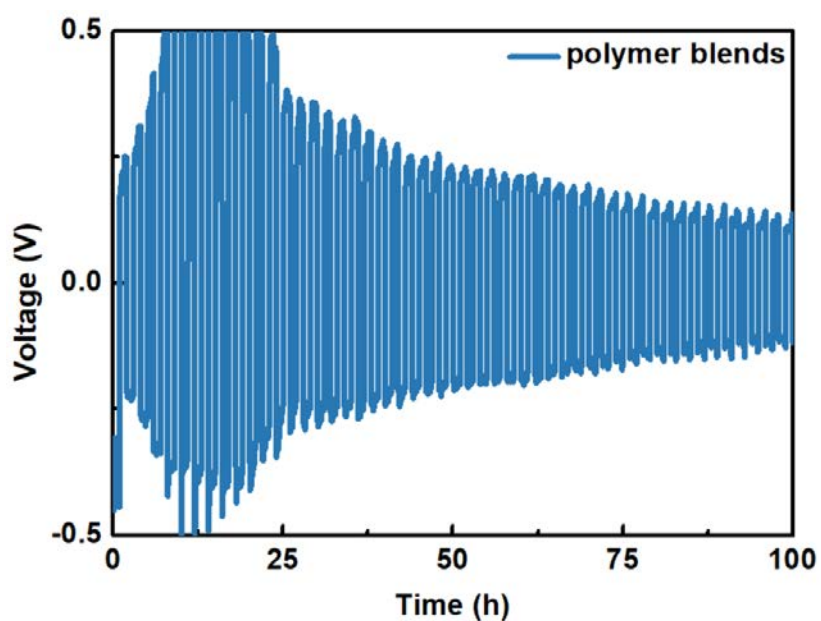


Fig. S9. Li-Li symmetric cells with polymer blends at a current density of 0.1 mA cm^{-2} with a capacity of 0.1 mAh cm^{-2} at $25 \text{ }^\circ\text{C}$.

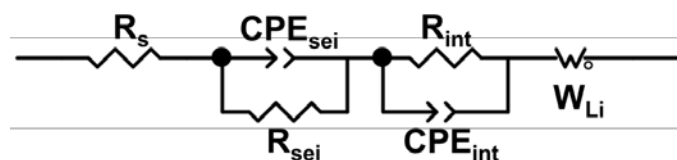


Fig. S10. Equivalent circuit models for Li/TA-hybrid network/Li symmetric cell

Table S2 TA-hybrid network with other solid polymer electrolytes

Electrolytes	Initiators	Temperature	Performance	References
3PEG-SSH	AIBN	60 °C	0.1C, 100 cycle, 97.5 %	Ye. et al [1].
3PEG-CCH			0.1C, 100 cycle, 85.5 %	
shPE	AIBN	60 °C	0.1C, 80 cycle, 91.6 %	Zhou. et al [2].
UV-cured SPEs	DMPA	60 °C	0.1 C,60 cycle, 90 %	Wei. et al [3].
PEO/PEG-3LGP	/	60 °C	0.5C, 150 cycle, 91 %	Pan. et al [4].
LLZTO@PAN	/	60 °C	0.1C, 100 cycle, 89.6%	Chen. et al [5].
eEPE-PE	/	25 °C	0.1C,120 cycle, 93 %	Zeng. et al [6].
LLTO NTs/PAN CSE	/	25 °C	0.5 C, 100 cycles,90 %	Hu. et al [7].
TA-hybrid network	/	25 °C	0.5 C, 150 cycles, 97 %	This Work

Remarks: all the cathode materials used are LFP in the table.

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