

## Supporting Information

### **Ultra-thin Polymer Electrolyte Based on Single-Helical-Structured Agarose for High Performance Solid-State Lithium Batteries**

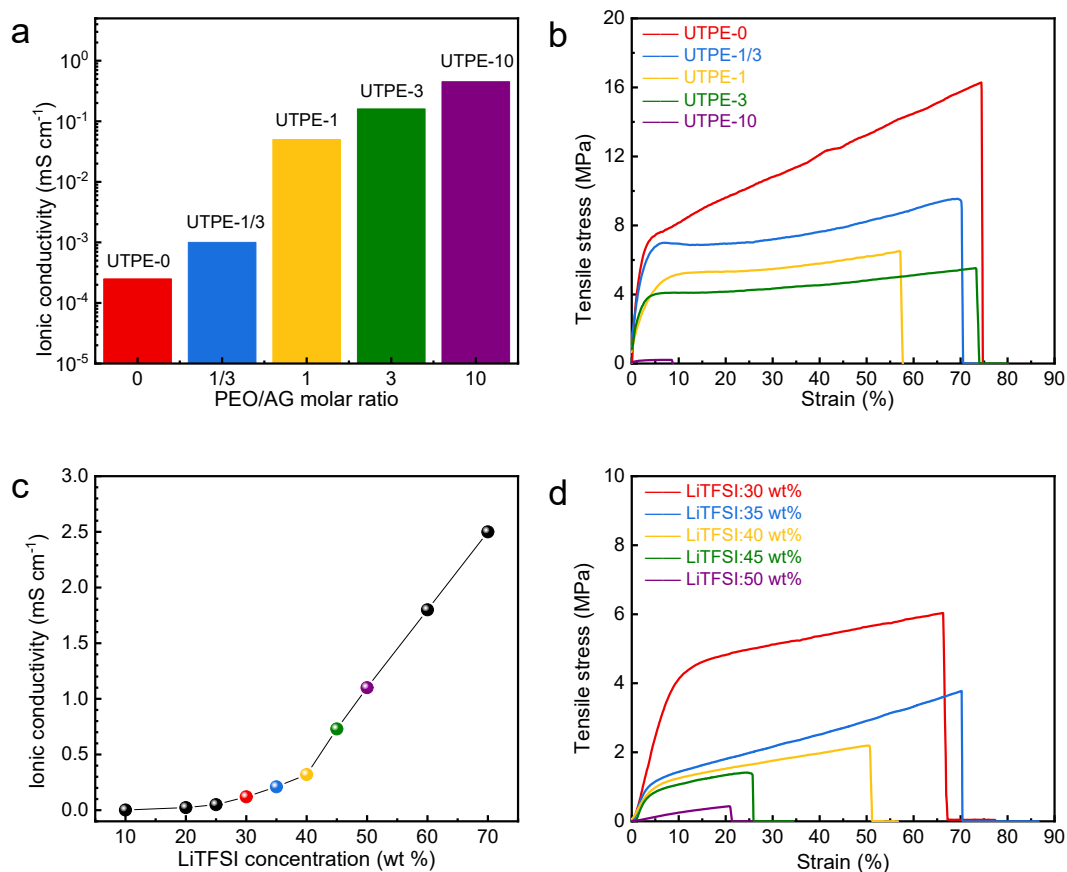
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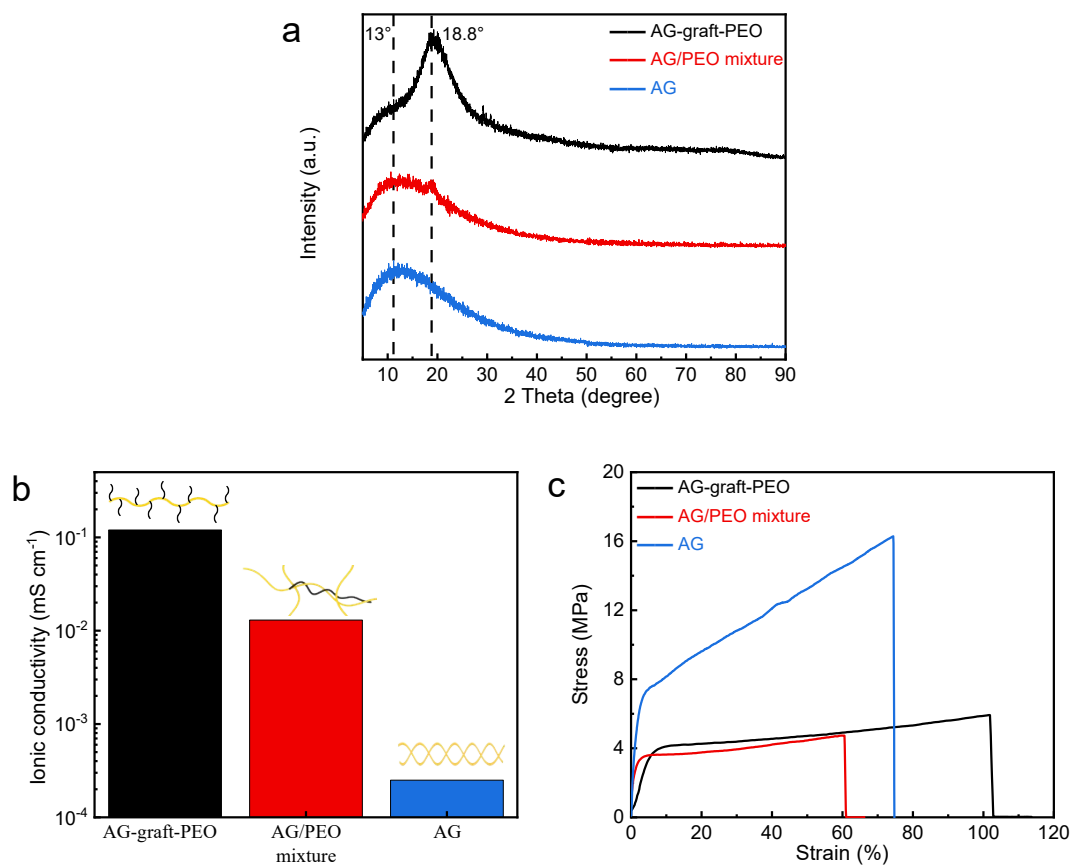
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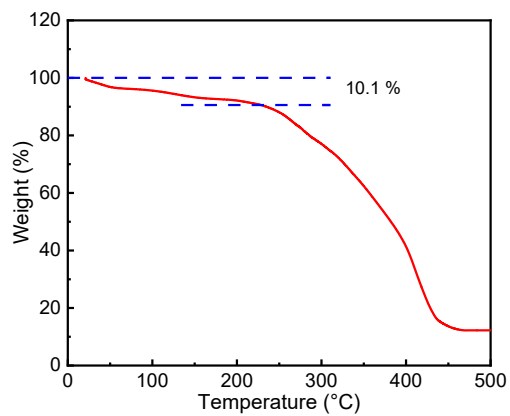
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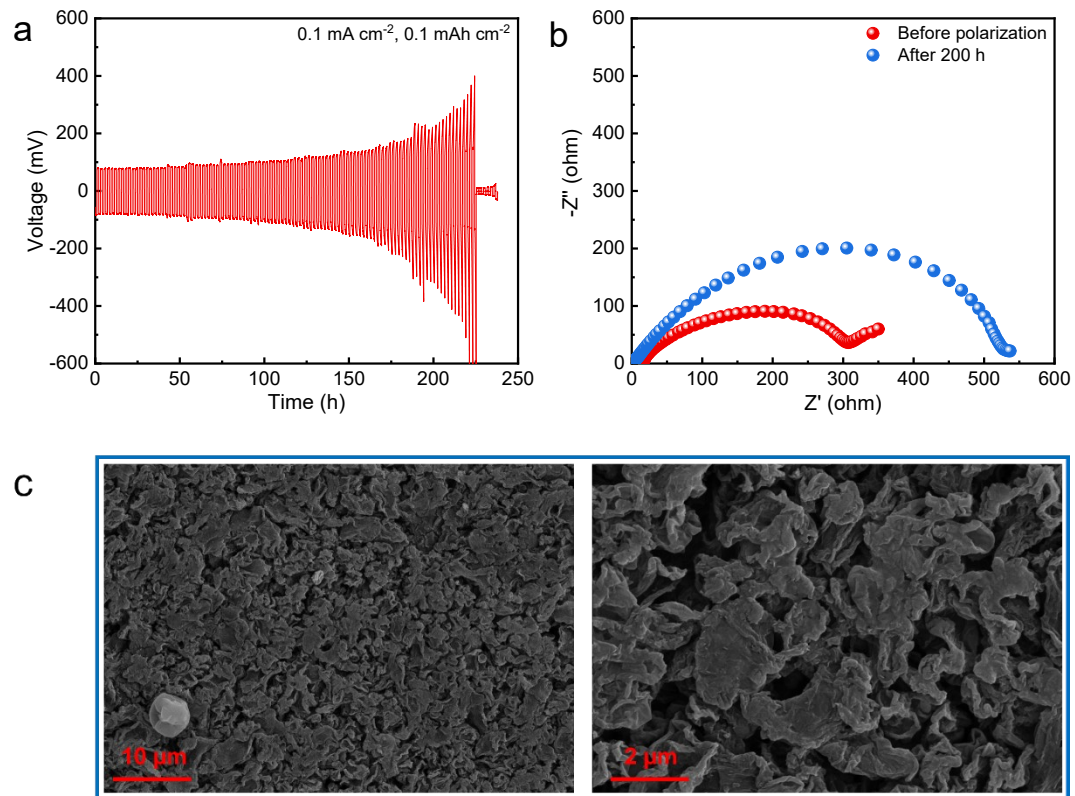
**Fig. S1.** (a) Ionic conductivity of UTPEs with different molar ratio of PEO/AG at room temperature (LiTFSI concentration: 30 wt%); (b) Stress-strain curves of UTPEs with different molar ratio of PEO/AG (LiTFSI concentration: 30 wt%); (c) Ionic conductivity of UTPEs with different concentrations of LiTFSI at room temperature (PEO/AG molar ratio: 3); (d) Stress-strain curves of UTPEs with different concentrations of LiTFSI (PEO/AG molar ratio: 3).



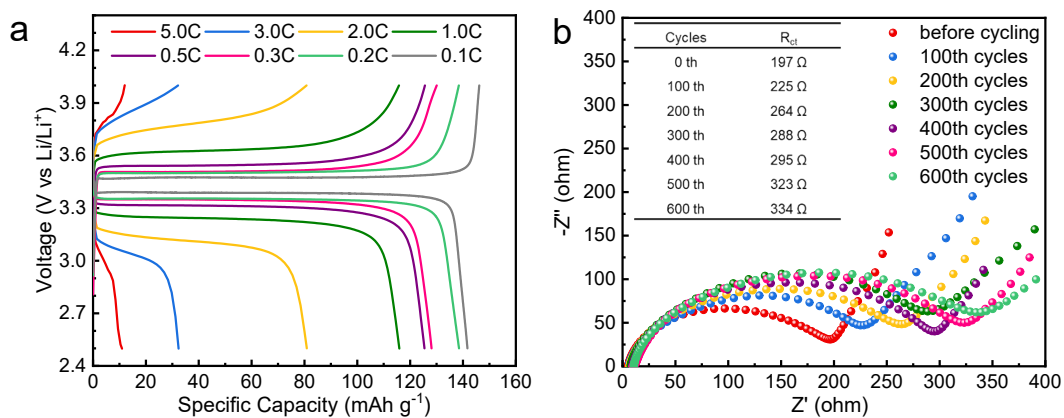
**Fig. S2.** (a) XRD pattern of AG-graft-PEO, AG/PEO-mixture and AG electrolytes; (b) Ionic conductivity of AG-graft-PEO, AG/PEO-mixture and AG electrolytes at room temperature; (c) Stress-strain curves of AG-graft-PEO, AG/PEO-mixture and AG electrolytes.



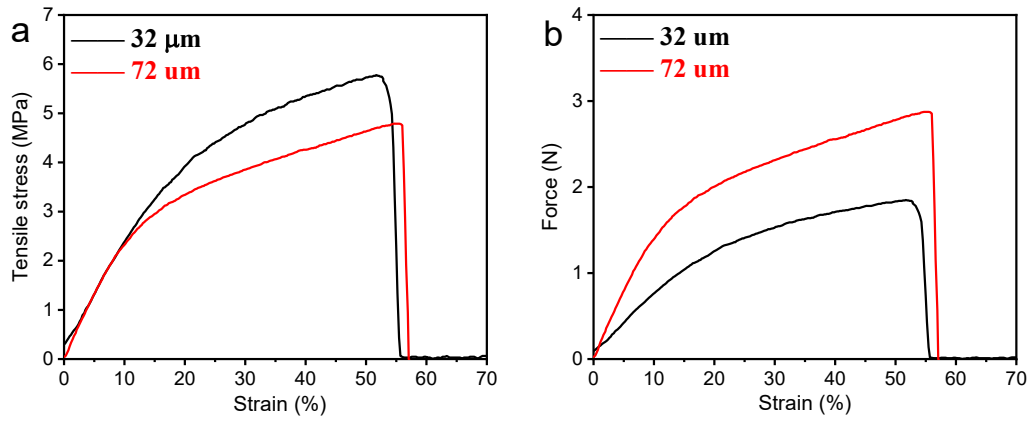
**Fig. S3.** Thermogravimetric curve of UTPE at a rate of  $5\text{ }^{\circ}\text{C min}^{-1}$ .



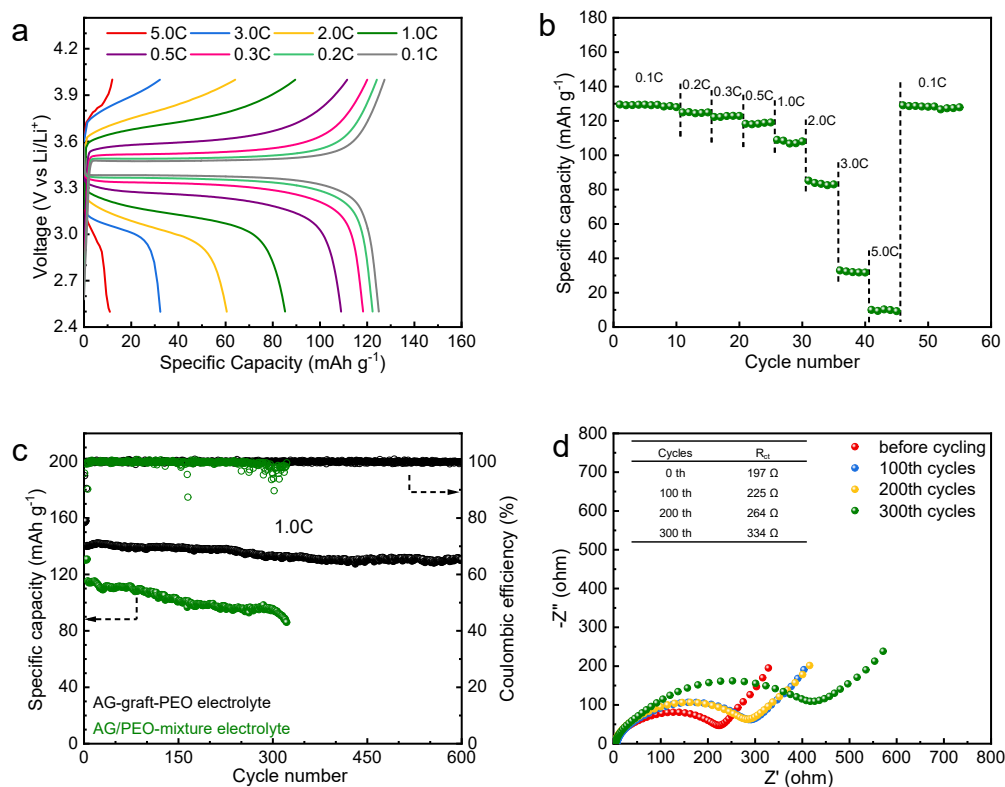
**Fig. S4.** (a) Galvanostatic Li plating/stripping profiles of Li symmetric cell with AG/PEO mixture electrolyte at room temperature ( $0.1 \text{ mAh cm}^{-1}$ ); (b) Alternating current impedance profiles of Li symmetric cell with AG/PEO mixture electrolyte at different cycles; (c) SEM images of the Li anode from Li symmetric cell with AG/PEO mixture electrolyte operating for 240 h at a current density of  $0.1 \text{ mAh cm}^{-1}$ .



**Fig. S5.** (a) Voltage profiles of Li||LFP cell with 72  $\mu\text{m}$ -thick UTPE at different charging/discharging rates at room temperature (2.5-4.0 V); (b) Electrochemical impedance spectra of LFP||Li cell with 72  $\mu\text{m}$ -thick UTPE after different cycles.



**Fig. S6.** (a) Stress-strain curves of 32 μm-thick and 72 μm-thick UTPE (b) Force-strain curves of 32 μm-thick and 72 μm-thick UTPE.

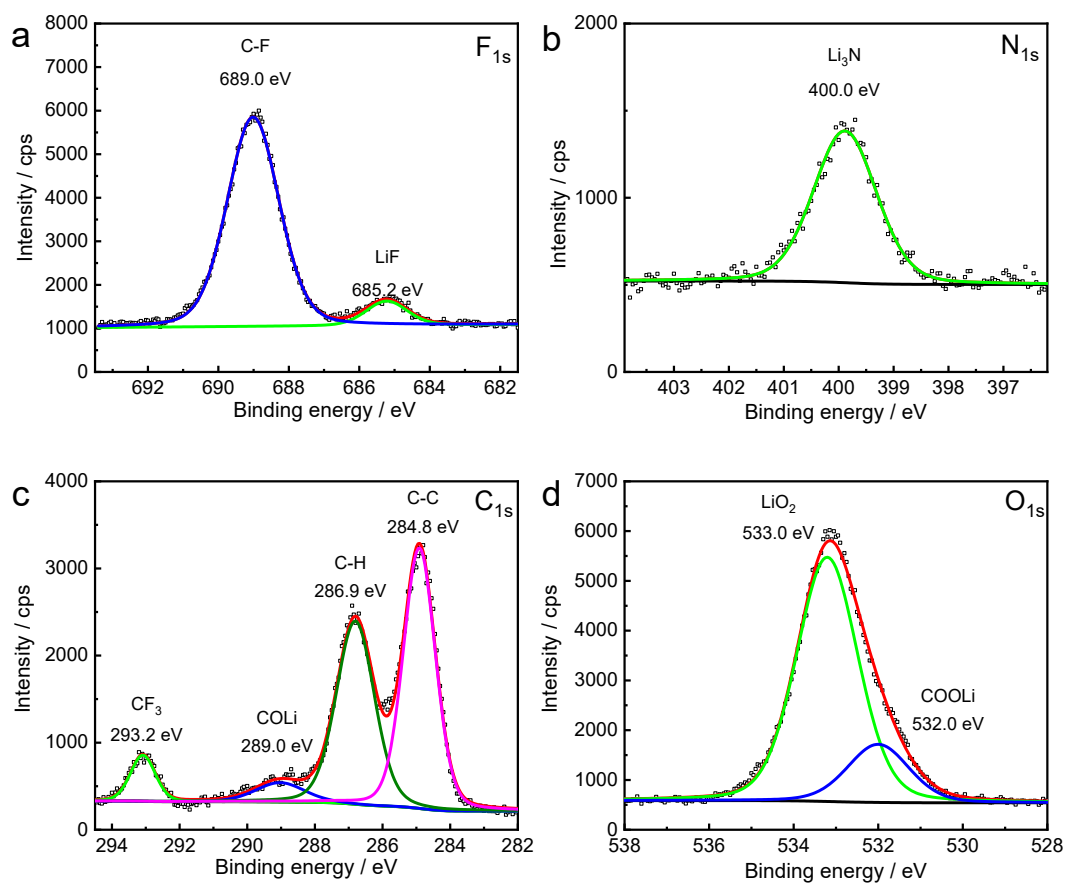


**Fig. S7.** (a) Rate performance of Li||LFP cells with 32  $\mu\text{m}$ -thick AG/PEO/LiTFSI mixture electrolyte at room temperature; (b) Voltage profiles of Li||LFP cell with 32  $\mu\text{m}$ -thick AG/PEO/LiTFSI mixture electrolyte at different charging/discharging rates at room temperature (2.5-4.0 V); (c) Discharge specific capacity and Coulombic efficiency of Li||LFP cells with AG-grafted-PEO and AG/PEO/LiTFSI mixture ultra-thin electrolytes at room temperature (1.0 C); (d) Electrochemical impedance spectra of LFP||Li cell with 32  $\mu\text{m}$ -thick AG/PEO/LiTFSI mixture electrolyte after different cycles.



**Table S1.** The electrochemical performance of Li batteries using different solid electrolytes.

Composition	Thickness ( $\mu\text{m}$ )	RT ionic conductivity ( $\text{S cm}^{-1}$ )	Electrochemical performance in LFP  Li cell at RT	Reference
AG-graft-PEO electrolyte	32	$1.2 \times 10^{-4}$	131 $\text{mA h g}^{-1}$ (1.0 C, 600 cycles)	This work
Crosslinked-PEGDE on cellulose	30	$8.9 \times 10^{-5}$	95 $\text{mA h g}^{-1}$ (0.1 C, 100 cycles)	[1]
PEO electrolyte on PE separator	7.5	$3.7 \times 10^{-5}$	108 $\text{mA h g}^{-1}$ (0.1 C, 50 cycles)	[2]
PEO electrolyte on PI film	8.5	$2.3 \times 10^{-4}$	100 $\text{mA h g}^{-1}$ (0.5 C, 60 cycles)	[3]
LLZTO/PTEE/SN electrolyte	100	$1.2 \times 10^{-4}$	135 $\text{mA h g}^{-1}$ (0.2 C, 200 cycles)	[4]
LPS/PEG-Ti electrolyte	20	$1.6 \times 10^{-4}$	103 $\text{mA h g}^{-1}$ (0.05 C, 8 cycles)	[5]
Crosslinked IL- PVDF electrolyte	32	$8.8 \times 10^{-4}$	129 $\text{mA h g}^{-1}$ (1.0 C, 200 cycles)	[6]



**Fig. S8.** XPS spectra of Li anode in LFP||Li cell with 32  $\mu\text{m}$ -thick UTPE after 600<sup>th</sup> cycles: (a)  $\text{F}_{1s}$ ; (b)  $\text{N}_{1s}$ ; (c)  $\text{C}_{1s}$ ; (d)  $\text{O}_{1s}$

## References

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