ADVANCED MATERIALS

Supporting Information

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Amphipathic Binder Integrating Ultrathin and Highly Ion-Conductive Sulfide Membrane for Cell-Level High-Energy-Density All-Solid-State Batteries

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This PDF file includes:

Figs. S1 to S14
Tables S2 to S5
References (S1 to S23)

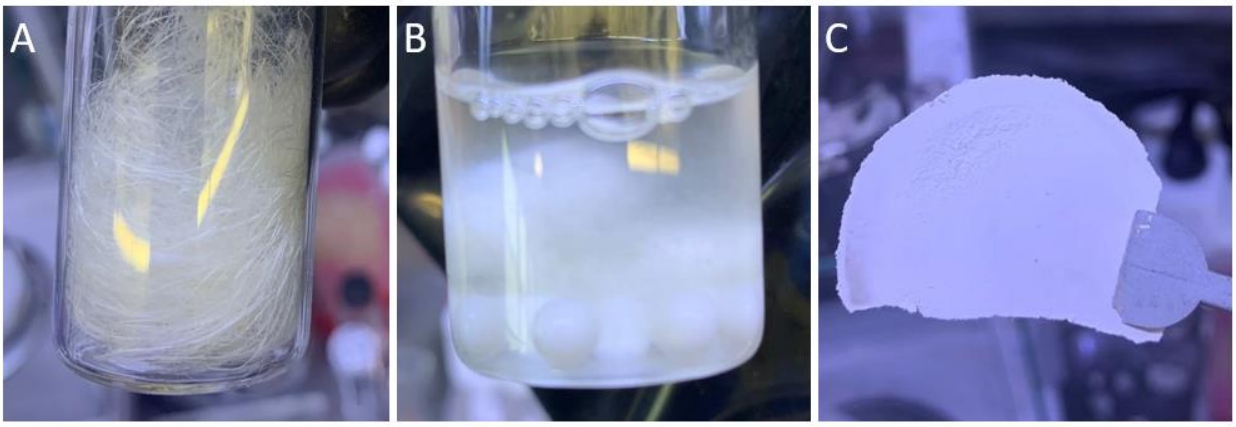

Fig. S1. Membrane fabrication using flax as building blocks. Photos of (a) raw flax, (b) the dispersion of flax in toluene after mechanical stirring, and (c) membranes composing of flax and Li_6PS_5Cl. After the mechanical stirring, the length of flax fiber reduced a lot. Thus, flax can disperse in toluene. However, the obtained membrane broke a little while peeling off the filler paper, suggesting poor mechanical strength.

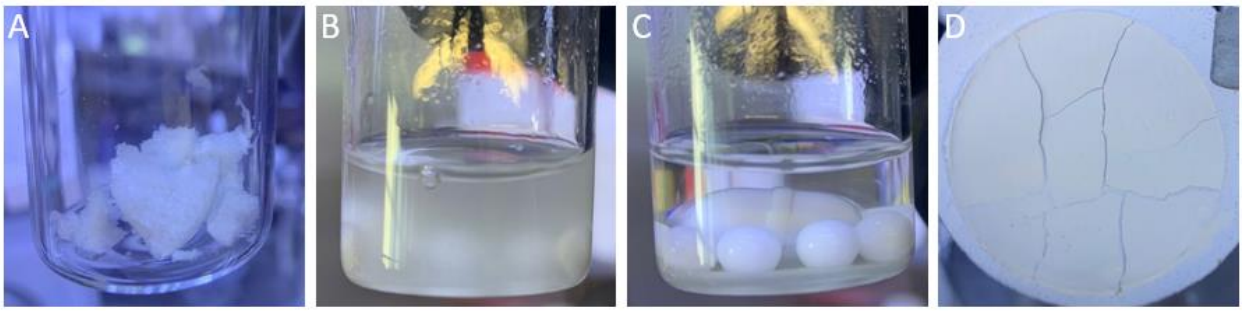

Fig. S2. Membrane fabrication using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) oxidized cellulose nanofiber grafted with Polyethylene glycol (CNF-PEG) as building blocks. Photos of (a) CNF-PEG, (b) the dispersion of CNF-PEG in toluene after mechanical stirring, and (c) the dispersion of CNF-PEG in toluene after standing for 1 min, (d) membranes composing of CNF-PEG and Li_6PS_5Cl. To obtain a uniform dispersion of CNF in toluene, we grafted PEG on the CNF through an as-reported ion-exchange treatment. The CNF-PEG uniformly dispersed in toluene after mechanically stirring for 2 h, but precipitated after standing for 1 min. After filtration, the membrane broke into several pieces, suggesting poor mechanical strength.

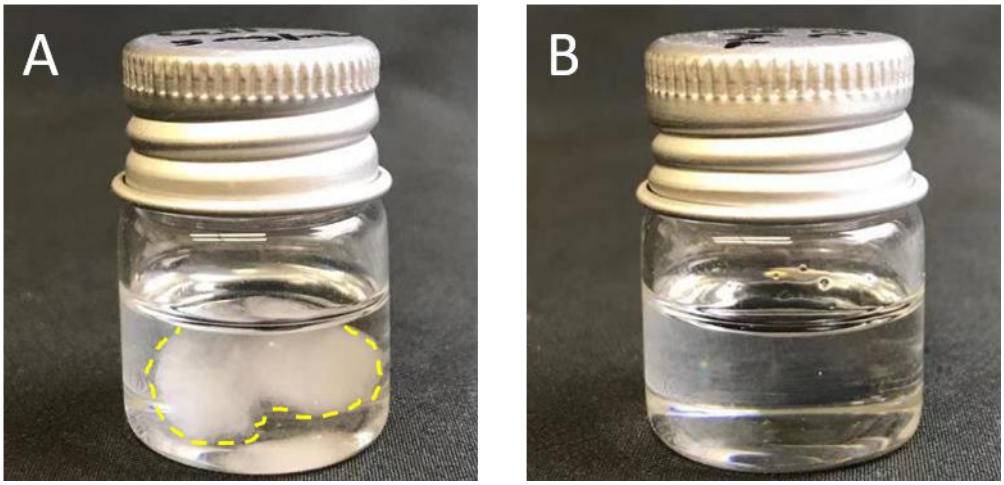

Fig. S3. Photos of the dispersion of (A) cellulose and (B) ethyl cellulose in toluene to compare the solubility.

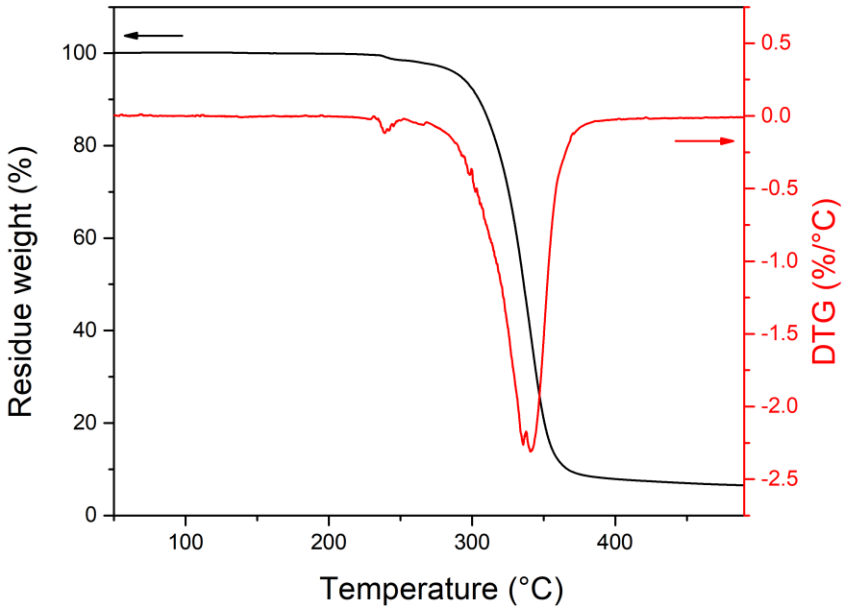

Fig. S4. Thermogravimetric analysis of ethyl cellulose.

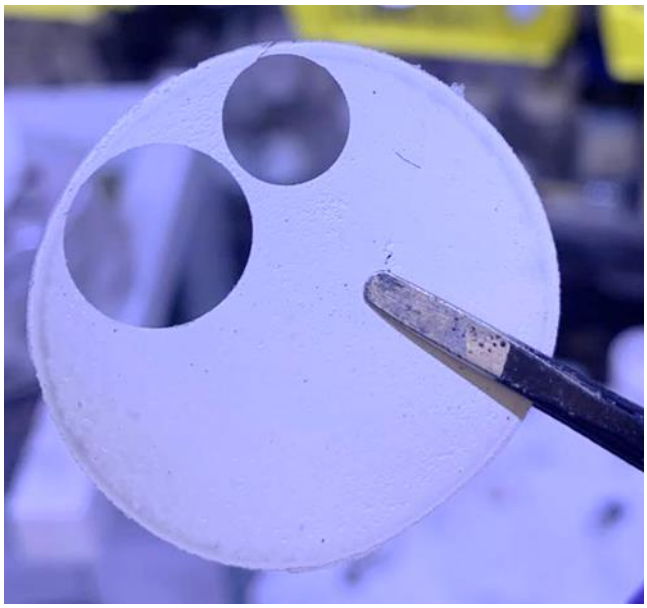

Fig. S5. Photo of SE membrane after punch to show the robustness.

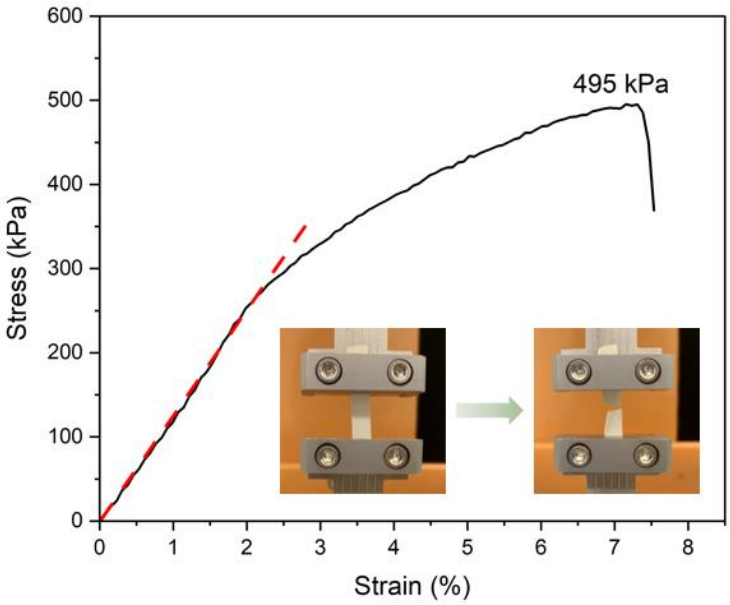

Fig. S6. Tensile stress-strain curve of the thin SE membrane. The inset photos show the sample before and after the tensile test.

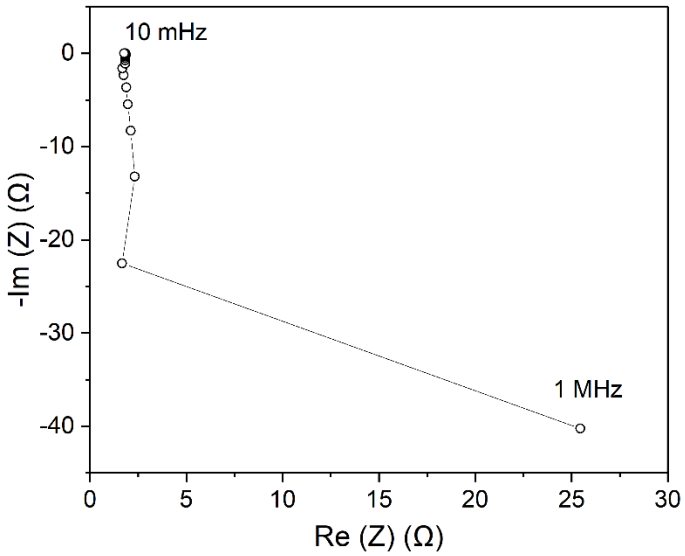

Fig. S7. Nyquist plot of the bare cell to test external resistance.

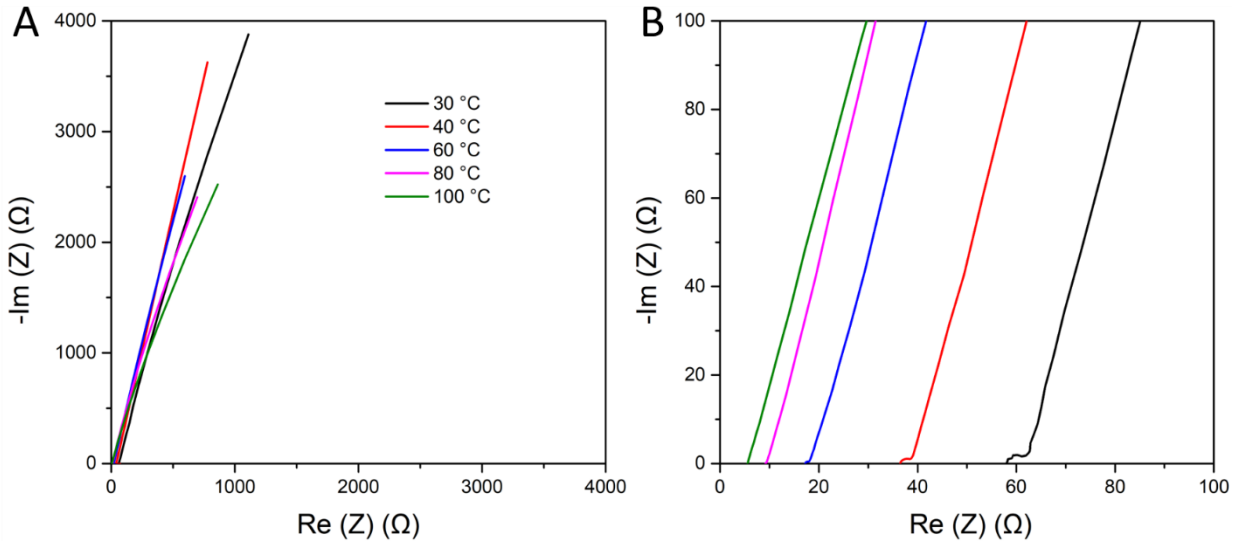

Fig. S8. Nyquist plots of thick SE pellet in (A) overall and (B) high frequencies range in ionic conductivity measurement at various temperature.

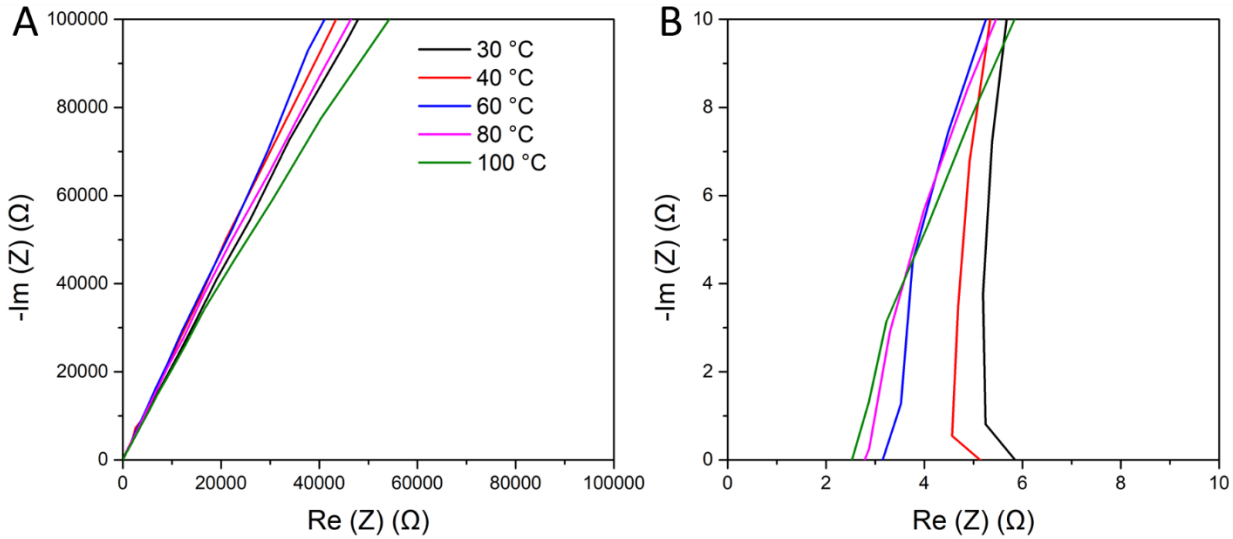

Fig. S9. Nyquist plots of thin SE membrane in (A) overall and (B) high frequencies range in ionic conductivity measurement at various temperatures.

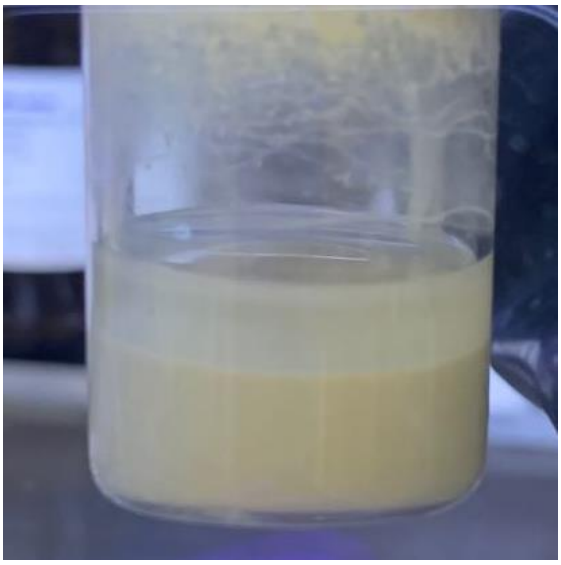

Fig. S10. Photo of the dispersion of Li_6PS_5Cl and regular cellulose in toluene after standing for one min.

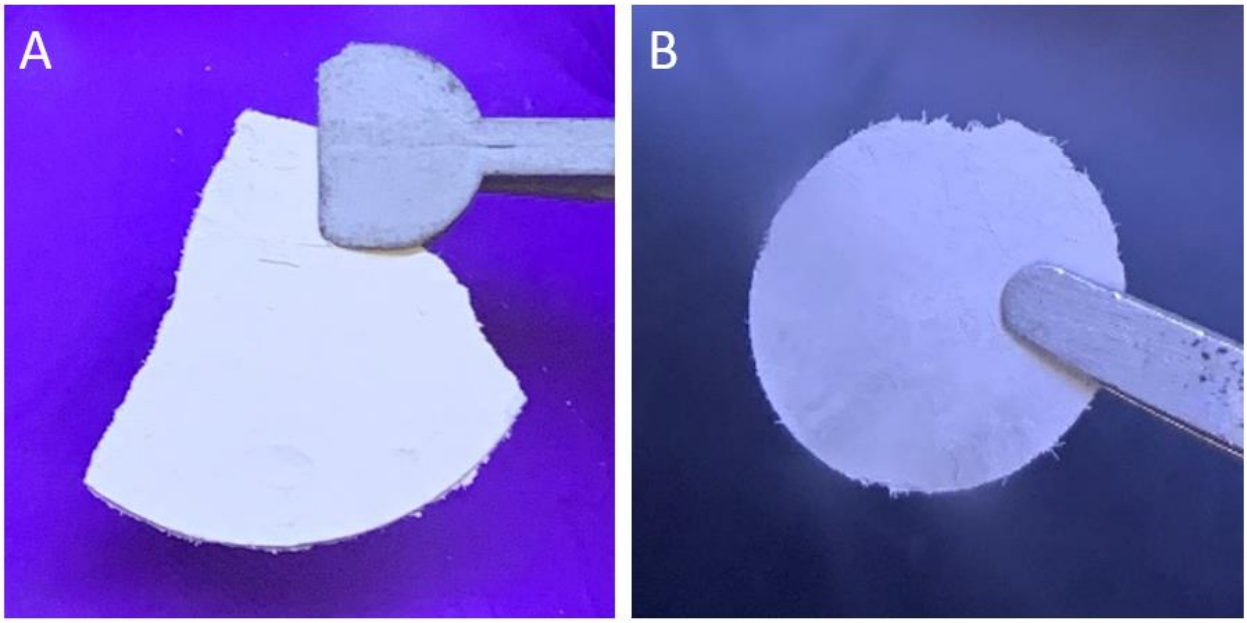

Fig. S11. (A) Photo of the as-prepared SE membrane composed with Li_6PS_5Cl and regular cellulose. (B) Photo of the as-punched membrane after cold press.

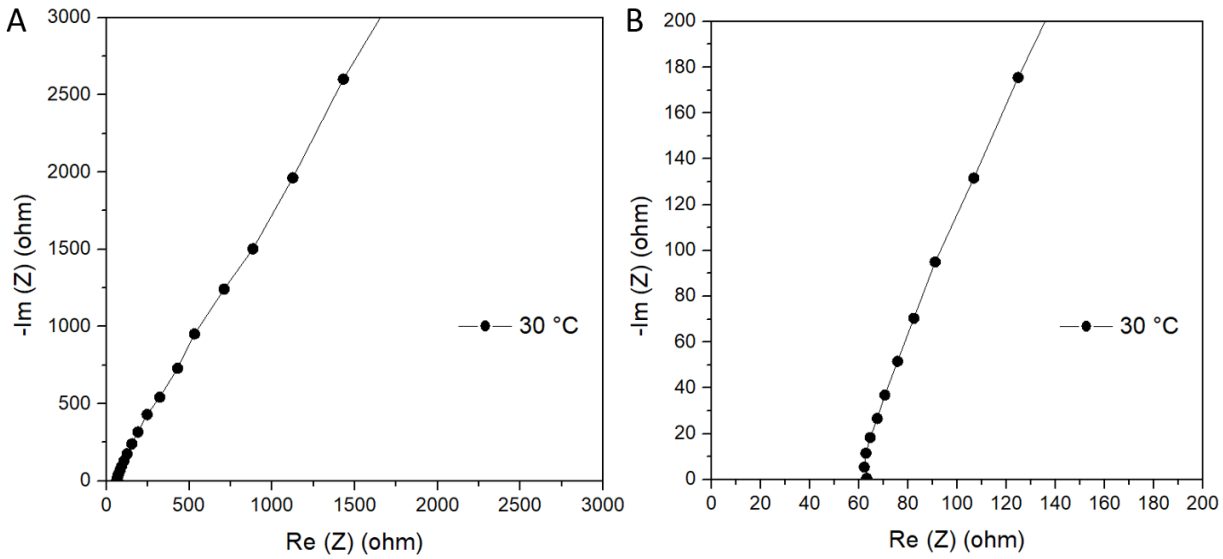

Fig. S12. Nyquist plots of SE membrane composed with 10 wt.% of regular cellulose in (A) overall and (B) high frequencies range in ionic conductivity measurement at 30 ℃.

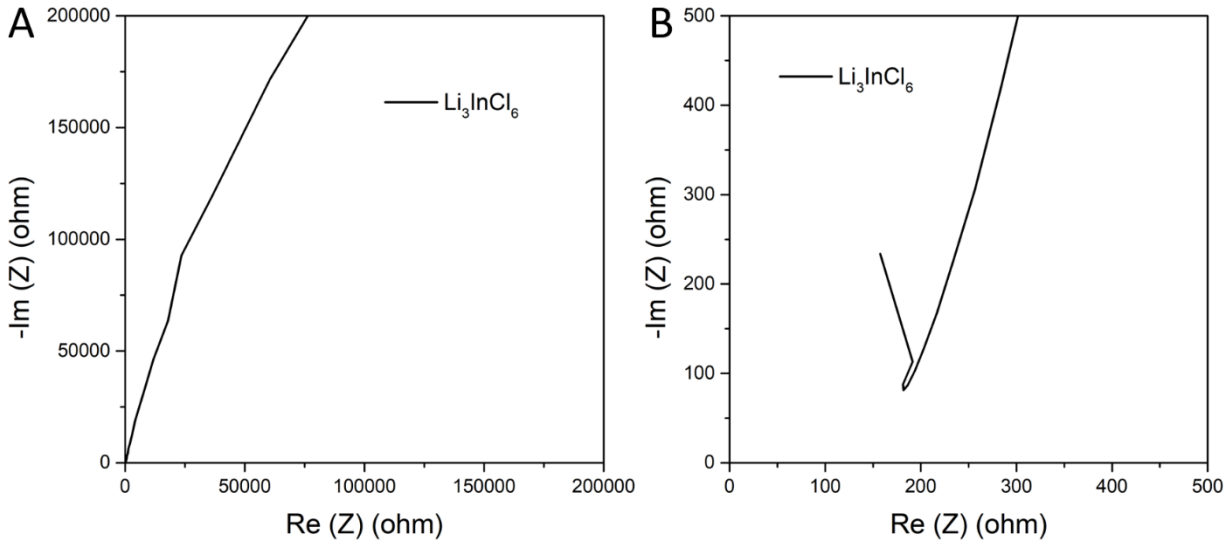

Fig. S13. Nyquist plot of Li_3InCl_6 in ionic conductivity measurement.

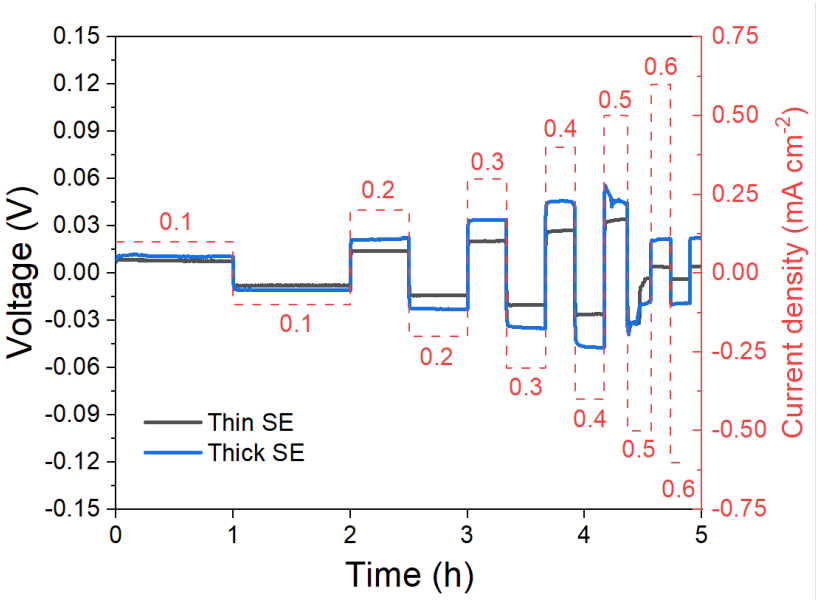

Fig.14. Critical current density investigation of SE with Li metal in a symmetric cell.

Table S2. Ion conduction comparison between thin SE and thick SE at various temperatures.

	Thin SE membrane				Thick SE pellet			
Temperature (℃)	Re (Ω)	Areal resistance (Ω cm^2)	Ion conductance (mS)	Ionic conductivity (mS cm^{-1})	Re (Ω)	Areal resistance (Ω cm^2)	Ion conductance (mS)	Ionic conductivity (S cm^{-1})
30	3.43	4.32	291.55	1.65	60.17	75.81	16.62	1.67
40	2.73	3.44	366.30	2.08	36.57	46.08	27.34	2.75
60	1.67	2.10	598.80	3.40	16.17	20.37	61.84	6.23
80	1.01	1.27	990.10	5.62	7.57	9.54	132.10	13.31
100	0.63	0.79	1587.30	9.01	3.67	4.62	272.48	27.44

Table S3 Performance comparison with other reported thin SE membranes.

* Estimated values.

Ref.	Sulfide	Binder or template	Mass loading (mg cm^{-2})	Layer thickness (μm)	Ionic conductivity (mS cm^{-1})	Ion conductance (mS)	Areal (cm^{-2})	Areal resistance (Ω cm^2)
This work	Li6PS5Cl	Ethyl cellulose	7.9	47	1.65	291	1.27	4.32
[1]	Li_3PS_4	Nonwoven	5.7	70	0.2	37	1.32	35.85
[2]	Li_3PS_4	Nonwoven	5.7	70	0.2	37	1.32	35.85
[3]	Li_3PS_4	Kevlar	17.68	100	0.3	24	0.785	33.33
[4]	$Li_6PS_5Cl_{0.5}Br_{0.5}$	Polyimide	9.5	70	0.2	29	1.03	35.52
[5]	Li3PS4-Polyethylene sulfide	Kevlar	9.95	60	0.02	4.4	**1.32***	**300***
[6]	75Li2S:25P2S5	Poly(propylene carbonate)	13.92	59	0.52	**14.4***	0.785	**54.31***
[7]	Li6PS5Cl	PEO-SiO2	11.46	65	0.283 (40 ℃)	34.2	0.785	22.97
[8]	77.5Li2S-22.5P2S5	Methyl-imine	7.54	63.7	0.092	19.2	1.32665	69.24

Table S4 Energy density comparison.

Ref	Gravimetric energy density (Wh kg^{-1})			Volumetric energy density (Wh L^{-1})		
	E_1 Cathode+SE	E_2 Cathode+SE+Anode	E_3 Calculated	E_1 Cathode+SE	E_2 Cathode+SE+Anode	E_3 Calculated
This work	325.49	175.26	365.62	861.07	669.72	795.30
[9]	21.18	11.20	24.85	37.43	30.83	41.76
[10]	21.37	11.30	25.07	37.76	31.10	42.14
[11]	24.05	12.72	28.22	42.51	35.01	47.43
[12]	20.11	14.62	23.59	35.43	32.55	41.03
[13]	20.98	15.26	24.61	36.97	33.97	42.81
[14]	26.13	15.96	30.36	46.77	40.46	53.06
[15]	26.63	16.26	30.94	47.66	41.23	54.07
[16]	25.25	16.53	29.45	44.76	39.74	51.21
[17]	33.75	17.85	39.59	60.19	49.49	67.12
[18]	30.55	18.32	35.95	54.15	46.63	61.34
[19]	2.86	1.90	3.33	4.89	4.12	5.56
[20]	34.62	21.55	40.62	61.94	53.91	70.52
[21]	38.12	25.24	44.28	68.74	57.44	77.95
[22]	35.58	30.11	41.74	63.40	59.42	70.71
[23]	6.75	3.82	7.81	11.61	9.84	13.09

Energy densities evaluation

The energy densities were calculated, excluding the current collector and packing materials, because these materials can be further optimized. The E_1 was calculated based on the mass/volume of the cathode and SE. The E_2 was calculated based on the mass/volume of the cathode, SE, and anode. Finally, the E_3 was calculated based on the mass/volume of the cathode, SE, and Li metal anode.

E_1

Gravimetric energy density $E_G = \frac{Mass_{CAM} * Specific\ capacity * Voltage}{Mass_{Cathode} + Mass_{SE}}$

Volumetric energy density $E_V = \frac{Mass_{CAM} * Specific\ capacity * Voltage}{Volume_{Cathode} + Volume_{SE}}$

E_2

Gravimetric energy density $E_G = \frac{Mass_{CAM} * Specific\ capacity * Voltage}{Mass_{Cathode} + Mass_{SE} + Mass_{Anode}}$

Volumetric energy density $E_V = \frac{Mass_{CAM} * Specific\ capacity * Voltage}{Volume_{Cathode} + Volume_{SE} + Volume_{Anode}}$

E_3

Gravimetric energy density $E_G = \frac{Mass_{CAM} * Specific\ capacity * Voltage}{Mass_{Cathode} + Mass_{SE} + Mass_{Li\ metal}}$

Volumetric energy density $E_V = \frac{Mass_{CAM} * Specific\ capacity * Voltage}{Volume_{Cathode} + Volume_{SE} + Volume_{Li\ metal}}$

Table S5 Parameters for energy density evaluation.

Ref	SE layer		Cathode			Anode		Area (cm^2)	Capacity (mAh g^{-1})	Voltage (V)	Li metal anode		
	Mass (mg)	Thickness (um)	Mass of cathode (mg)	Ratio of CAM (%)	Thickness (um)	Mass of anode (mg)	Thickness (um)				Mass (mg)	Voltage (V)	Thickness (um)
This work	10.00	50.00	25.00	80.00	55.00	30.00	30.00	1.26	178.00	3.20	2.00	3.80	30.00
[9]	140.00	411.76	25.00	39.00	55.03	146.90	100.00	2.00	112.00	3.20	2.00	3.80	30.00
[10]	140.00	411.76	25.00	39.00	55.03	146.90	100.00	2.00	113.00	3.20	2.00	3.80	30.00
[11]	140.00	411.76	25.00	39.00	55.03	146.90	100.00	2.00	127.20	3.20	2.00	3.80	30.00
[12]	150.00	1124.02	12.70	70.00	52.19	61.00	104.00	0.79	115.00	3.20	2.00	3.80	30.00
[13]	150.00	1124.02	12.70	70.00	52.19	61.00	104.00	0.79	120.00	3.20	2.00	3.80	30.00
[14]	80.00	599.48	10.00	70.00	41.10	57.40	100.00	**0.79***	105.00	3.20	2.00	3.80	30.00
[15]	80.00	599.48	10.00	70.00	41.10	57.40	100.00	0.79	107.00	3.20	2.00	3.80	30.00
[16]	100.00	749.34	10.00	70.00	41.10	**58.00***	**100.00***	0.79	124.00	3.20	2.00	3.80	30.00
[17]	150.00	441.18	15.00	80.00	21.35	146.90	100.00	2.00	145.00	3.20	2.00	3.80	30.00
[18]	200.00	588.24	20.00	70.00	32.26	146.90	100.00	2.00	150.00	3.20	2.00	3.80	30.00
[19]	80.00	599.48	10.00	6.60	71.74	45.90	125.00	0.79	122.00	3.20	2.00	3.80	30.00
[20]	150.00	668.45	15.00	85.00	30.19	100.00	104.00	1.32	140.00	3.20	2.00	3.80	30.00
[21]	80.00	599.48	10.00	80.00	36.26	45.90	125.00	0.79	134.00	3.20	2.00	3.80	30.00
[22]	150.00	441.18	15.00	78.40	21.80	30.00	31.00	2.00	156.00	3.20	2.00	3.80	30.00
[23]	55.00	412.14	20.00	7.00	143.10	57.40	100.00	0.79	113.00	3.20	2.00	3.80	30.00

* Estimated values.

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