

Supplementary Information

Constructing an anion-capturing interface to achieve Li⁺ cross-phase transport in composite solid electrolytes

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Supplementary Notes

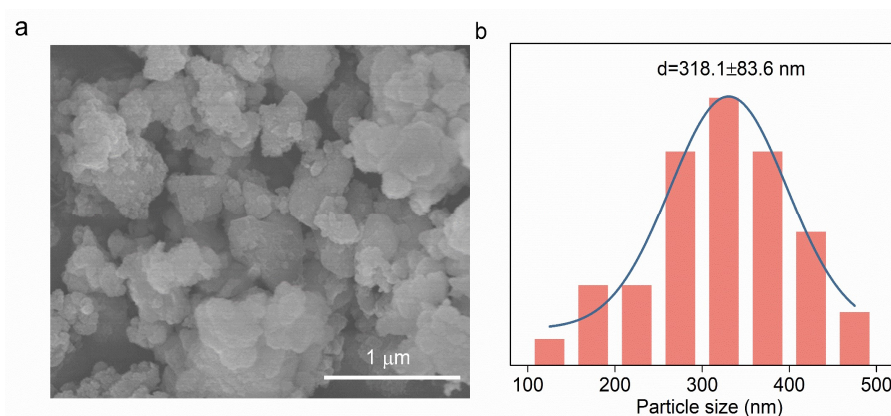
Supplementary Note 1: FeF₃@LLZTO powder composition analysis

LLZTO particle sizes ranging from 100-500 nm and a rough surface (Supplementary Fig. 1). As shown in supplementary Fig. 2, LLZTO would spontaneously form a layer of Li₂CO₃ on its surface when exposed to air and in contact with CO₂ and H₂O. By coating a layer of FeF₃ on the surface of LLZTO with Fe(NO₃)₃·9H₂O and NH₄F to isolate CO₂ and H₂O, thus avoiding the formation of Li₂CO₃. The high-resolution TEM image clearly showed that the surface of LLZTO was coated with FeF₃ layer (2-6 nm), with a lattice stripe spacing of 5.26 Å, corresponding to the (211) crystal plane of LLZTO. The XRD pattern shows that FeF₃ coating did not damage the crystal structure of LLZTO, while Li₂CO₃ corresponding to 2θ=32.4° disappears, indicating that FeF₃ effectively isolated CO₂ and H₂O, preventing the generation of Li₂CO₃. The broad peak at 2θ=22.3° indicated that the synthesized FeF₃ had an amorphous structure. The surface element composition of LLZTO and FeF₃@LLZTO was further analyzed by XPS test. It is evident that two signal peaks related to F and Fe elements were detected in the FeF₃@LLZTO spectrum, while the peak corresponding to C 1s almost disappeared. The peak at 685.3 eV in the F 1s spectrum was related to Fe-F bond in FeF₃. The Fe 2p spectrum showed that the binding energy of Fe 2p_{1/2} and Fe 2p_{3/2} were 724.7 eV and 710.7 eV, respectively. In addition, the peaks of 733.4 eV and 717.7 eV correspond to the satellite peaks of Fe 2p_{1/2} and Fe 2p_{3/2}, proving that the valence state of Fe in FeF₃ was +3.^[1] These results demonstrated that FeF₃ not only successfully coated the surface of LLZTO, but also effectively inhibited the formation of Li₂CO₃.

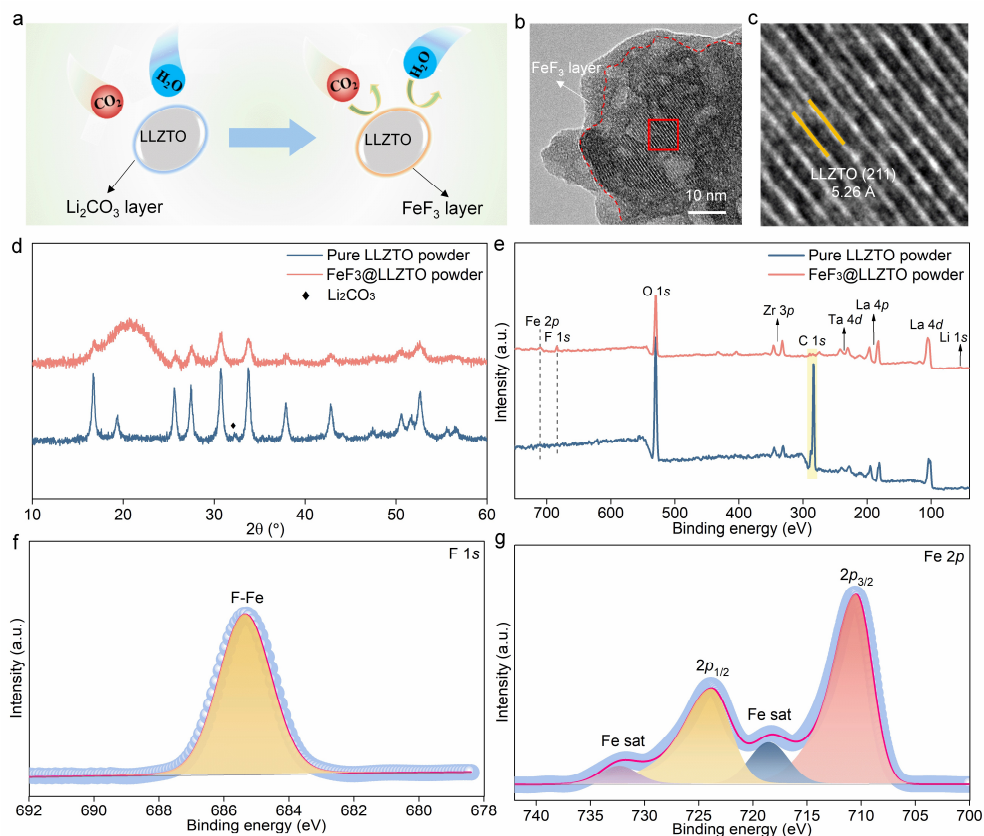
Supplementary Note 2: Against other materials with similar properties

We have prepared $\text{MgF}_2@\text{LLZTO}$ and $\text{AlF}_3@\text{LLZTO}$ through a similar procedure. As shown in Supplementary Fig. 8, FTIR results illustrate that the peak corresponding to the S-N bond of $\text{LiTFSI}@\text{MgF}_2@\text{LLZTO}$ shifts from 771 to 770 cm^{-1} , while the peak blueshift to 766 cm^{-1} is identified in $\text{LiTFSI}@\text{AlF}_3@\text{LLZTO}$. Such result coincides with $\text{LiTFSI}@\text{FeF}_3@\text{LLZTO}$. According to DFT calculations, the binding energy of $\text{MgF}_2/\text{TFSI}^-$ (-4.34 kcal/mol) is weaker than that of $\text{Li}^+/\text{TFSI}^-$ (-10.24 kcal/mol), while the binding energy of $\text{AlF}_3/\text{TFSI}^-$ (-36.16 kcal/mol) or $\text{FeF}_3/\text{TFSI}^-$ (-29.78 kcal/mol) is stronger than that of $\text{Li}^+/\text{TFSI}^-$. This method is universally applicable, yet variations in the results arise from differences in the composition of the metals and their respective binding energies.

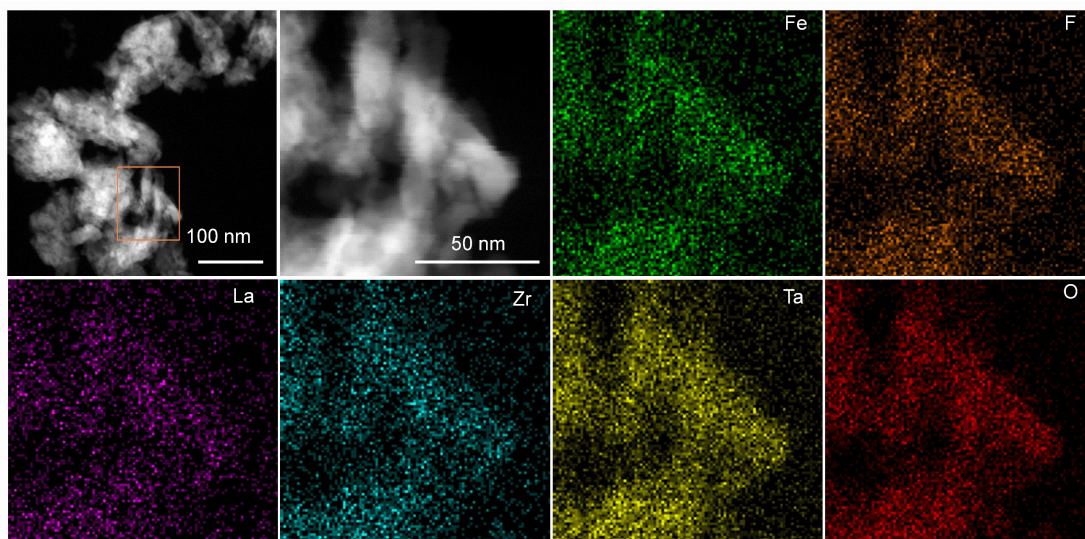
Supplementary Figures



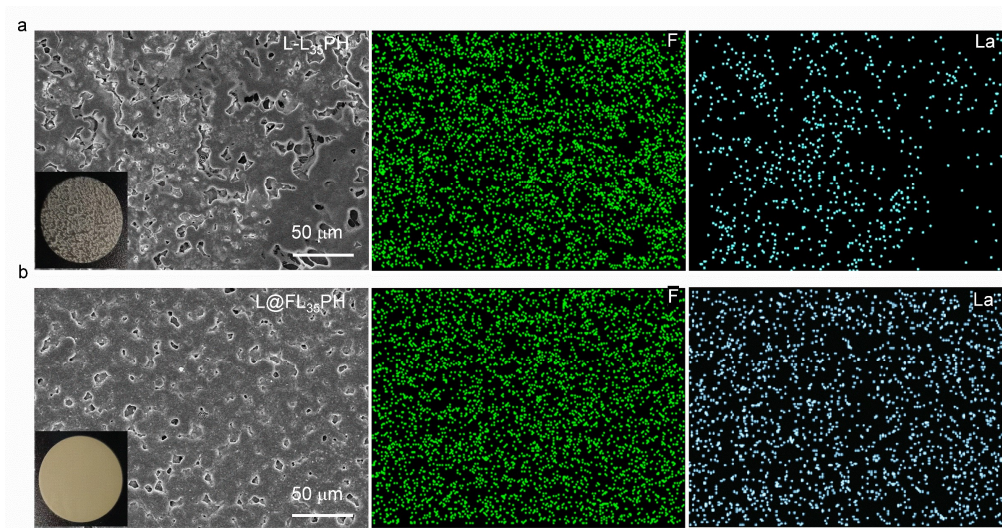
Supplementary Fig. 1 | Surface morphology and particle size of fresh LLZTO (a) SEM image and (b) particle size distribution of LLZTO powder. LLZTO particle show rough surface, and the sizes about 318.1 ± 83.6 nm.



Supplementary Fig. 2 | The phase and chemical composition of FeF₃@LLZTO. (a) Optical photos and schematic diagrams of LLZTO and FeF₃@LLZTO powders, (b) TEM and (c) high-resolution TEM images of FeF₃@LLZTO, (d) XRD and (e) XPS spectra of LLZTO and FeF₃@LLZTO powders, (f) F 1s and (g) Fe 2p spectra of FeF₃@LLZTO powder.

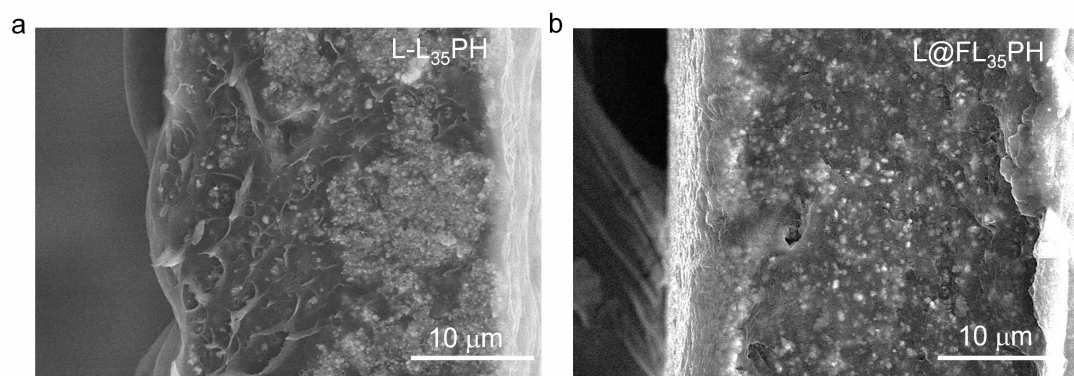


Supplementary Fig. 3 | The element distribution of $\text{FeF}_3\text{@LLZTO}$ particle. EDS images of $\text{FeF}_3\text{@LLZTO}$ powder. The fluorescence distribution of F and Fe elements aligns with the contour of LLZTO particles, with FeF_3 uniformly coating the particle surface.

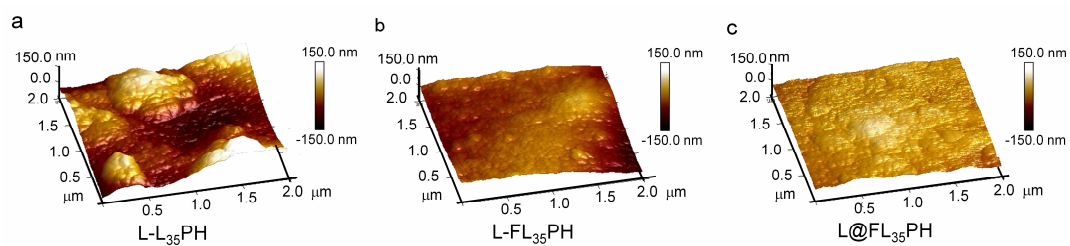


Supplementary Fig. 4 | FeF₃ effect on compatibility with LLZTO and PVDF-HFP.

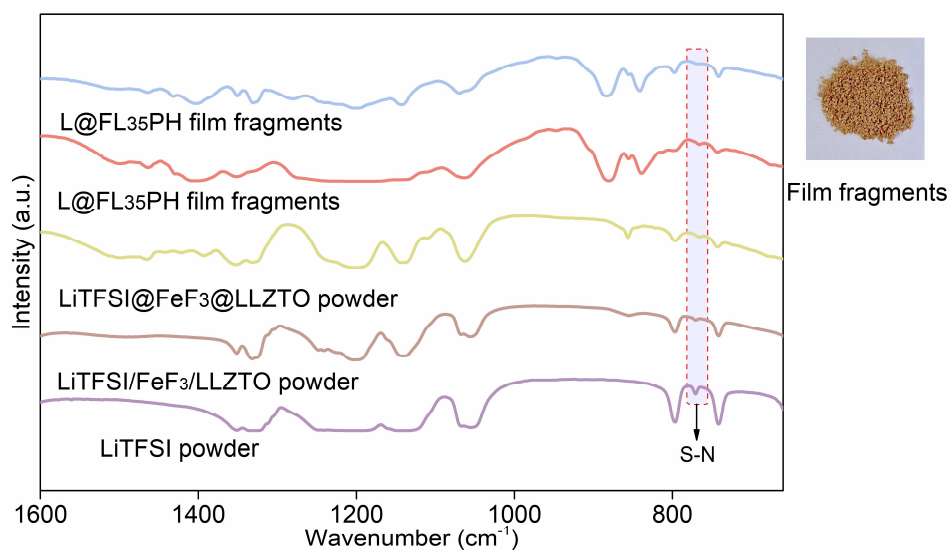
(a-b) SEM image, EDS image and optical photos of L-L₃₅PH and L@FL₃₅PH electrolytes. The presence of FeF₃ layer reduces the surface free energy difference between LLZTO and PVDF-HFP, avoiding spontaneous aggregation of nanoparticles.^[1]



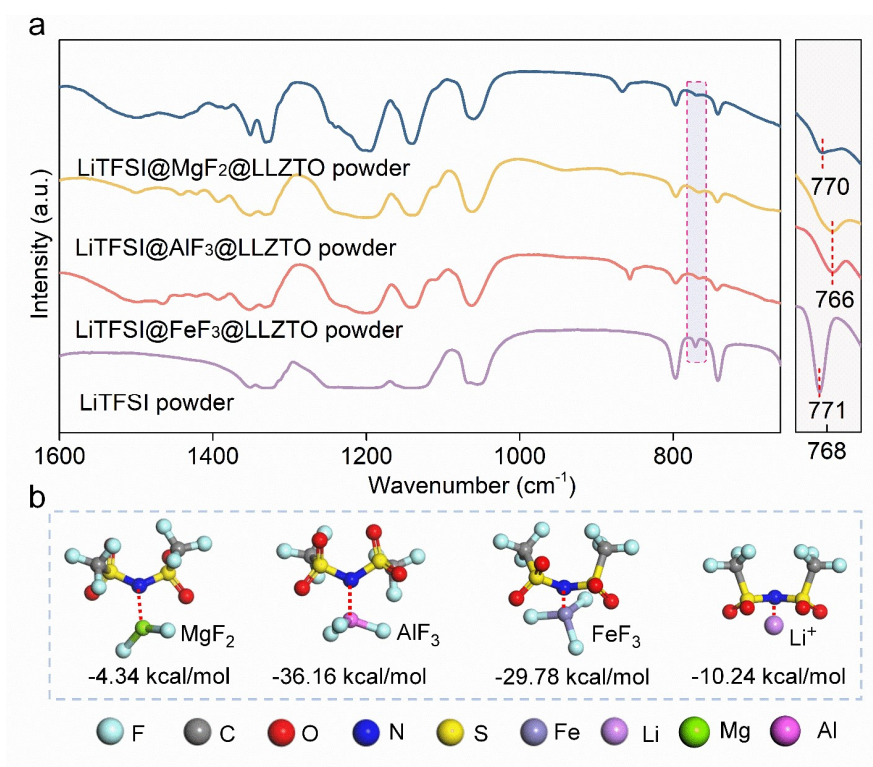
Supplementary Fig. 5 | Distribution of FeF₃@LLZTO in CSEs. (a-b) The cross-sectional morphology of L-L₃₅PH and L@FL₃₅PH electrolytes.



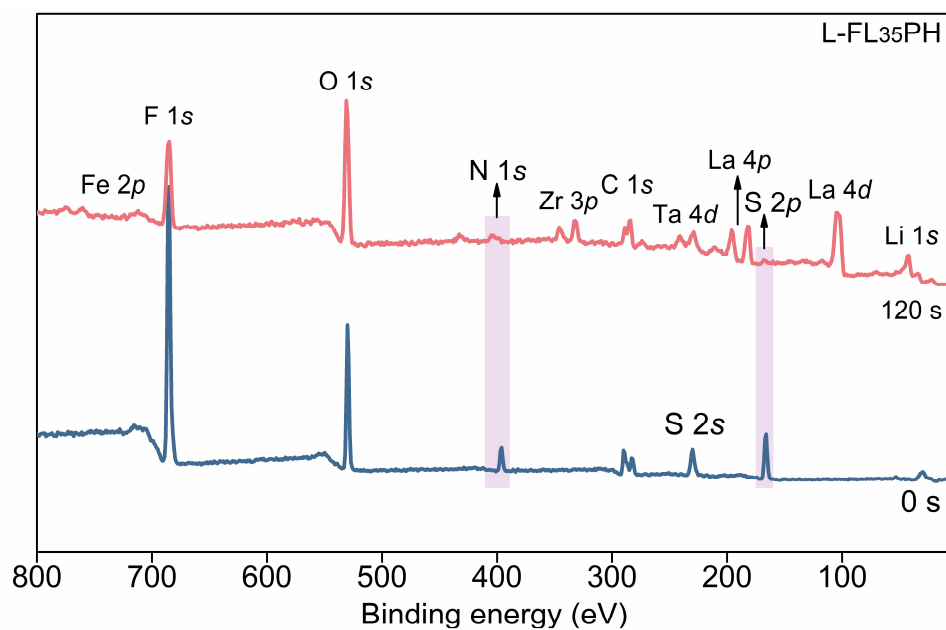
Supplementary Fig. 6 | Surface roughness of various CSEs. (a-c) KPFM image of L-L₃₅PH, L-FL₃₅PH and L@FL₃₅PH electrolytes. The presence of FeF₃ layer reduced the roughness of CSEs.



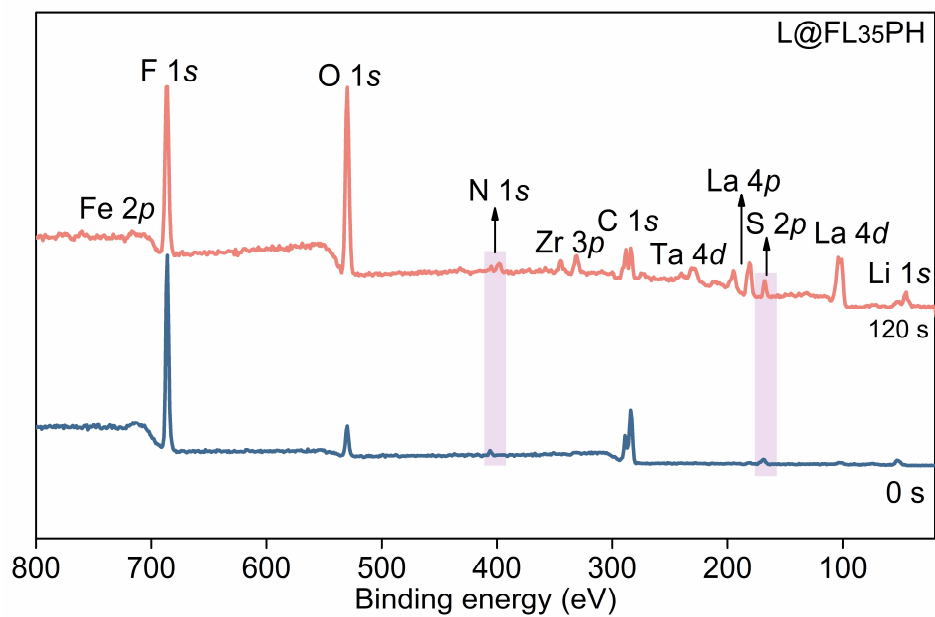
Supplementary Fig. 7 | FeF₃ effect on LiTFSI microstructure. FTIR spectra of L@FL₃₅PH film, L-FL₃₅PH film, LiTFSI@FeF₃@LLZTO powder, LiTFSI/FeF₃/LLZTO powder and LiTFSI powder. The inset figure shows the film being ground into fragments by placing it in liquid nitrogen.



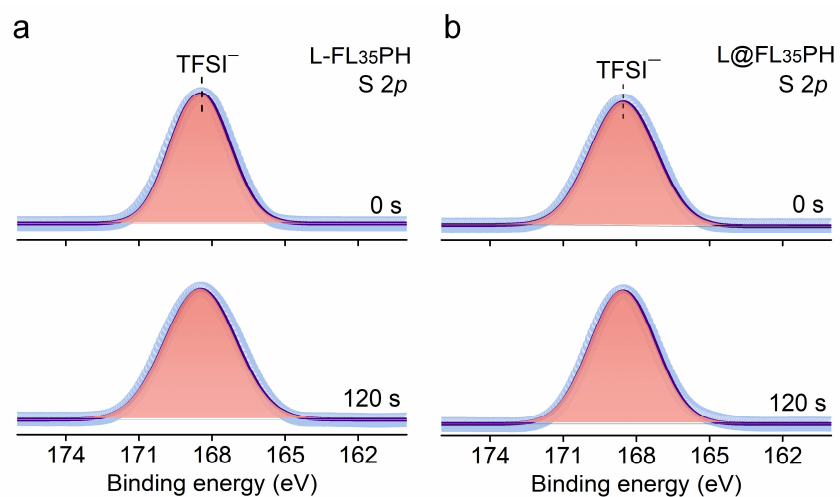
Supplementary Fig. 8 | The chemical shifts between TFSI⁻ and LLZTO coated with various metal fluorides. (a) FTIR spectra of LiTFSI@FeF₃@LLZTO, LiTFSI@AlF₃@LLZTO, LiTFSI@MgF₂@LLZTO and LiTFSI powders (b) interactions between FeF₃, MgF₂, AlF₃ and Li⁺ with TFSI⁻.



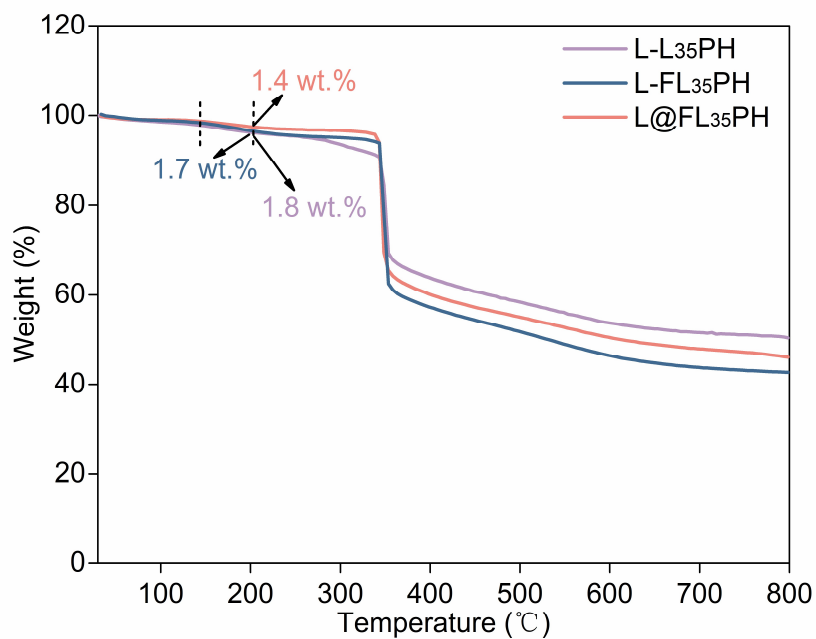
Supplementary Fig. 9 | The elemental composition of L-FL₃₅PH. XPS spectra of L-FL₃₅PH electrolyte after etching 0 s and 120 s. The blue curve represents the XPS spectrum of the L-FL₃₅PH surface, and the red curve represents the XPS spectrum of the L-FL₃₅PH internal.



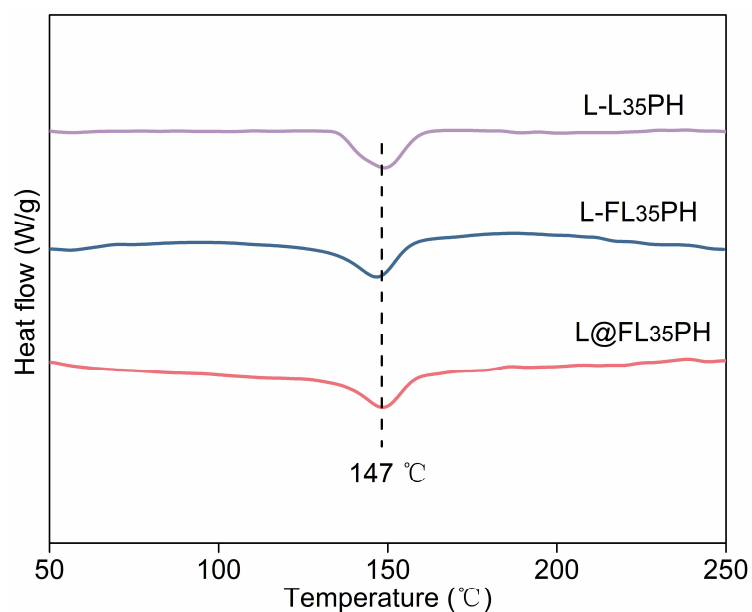
Supplementary Fig. 10 | The elemental composition of L@FL₃₅PH. XPS spectra of L@FL₃₅PH electrolyte after etching 0 s and 120 s. The blue curve is the XPS spectrum of the L@FL₃₅PH surface, and the red curve is the XPS spectrum of the L-FL₃₅PH internal.



Supplementary Fig. 11 | The chemical shifts of S. S 2p spectra of (a) L-FL₃₅PH and (b) L@FL₃₅PH electrolytes after etching 0 s and 120 s.

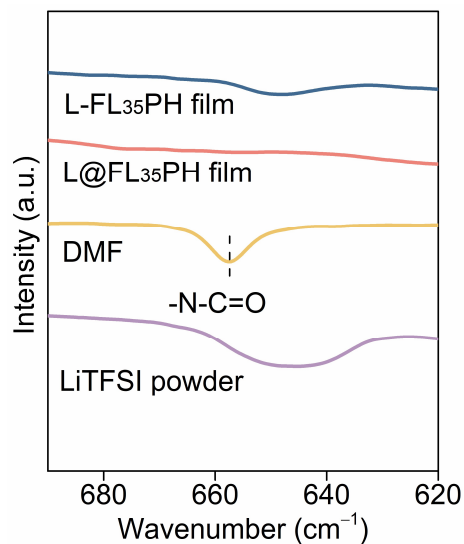


Supplementary Fig. 12 | The thermal stability of CSEs. TGA curves of L-L₃₅PH, L-FL₃₅PH and L@FL₃₅PH electrolytes. The residual DMF solvent of L@FL₃₅PH, L-FL₃₅PH and L-L₃₅PH is 1.4 wt.%, 1.7 wt.% and 1.8 wt.% according to the weight loss of 140–200 °C, respectively.

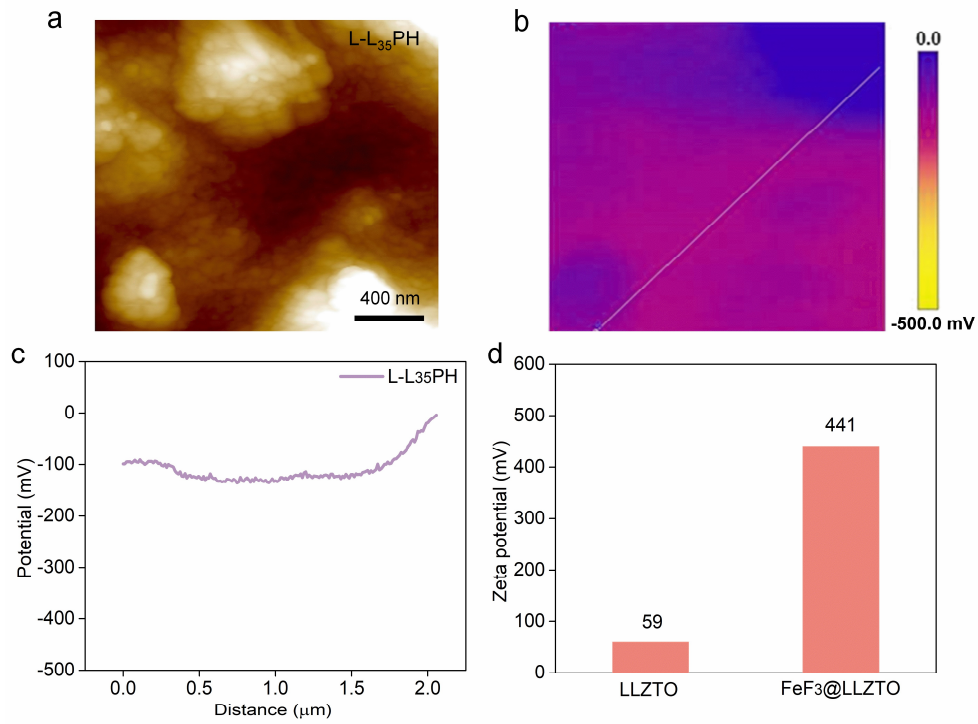


Supplementary Fig. 13 | $\text{FeF}_3@LLZTO$ effect on the melting temperature of CSEs.

The differential scanning calorimetry (DSC) curves of L-L₃₅PH, L-FL₃₅PH and L@FL₃₅PH electrolytes from 50 to 250 °C. The purple curve is the DSC curve of the L-L₃₅PH electrolyte, the blue curve is the DSC curve of the L-FL₃₅PH electrolyte, and the red curve is the DSC curve of the L@FL₃₅PH electrolyte.

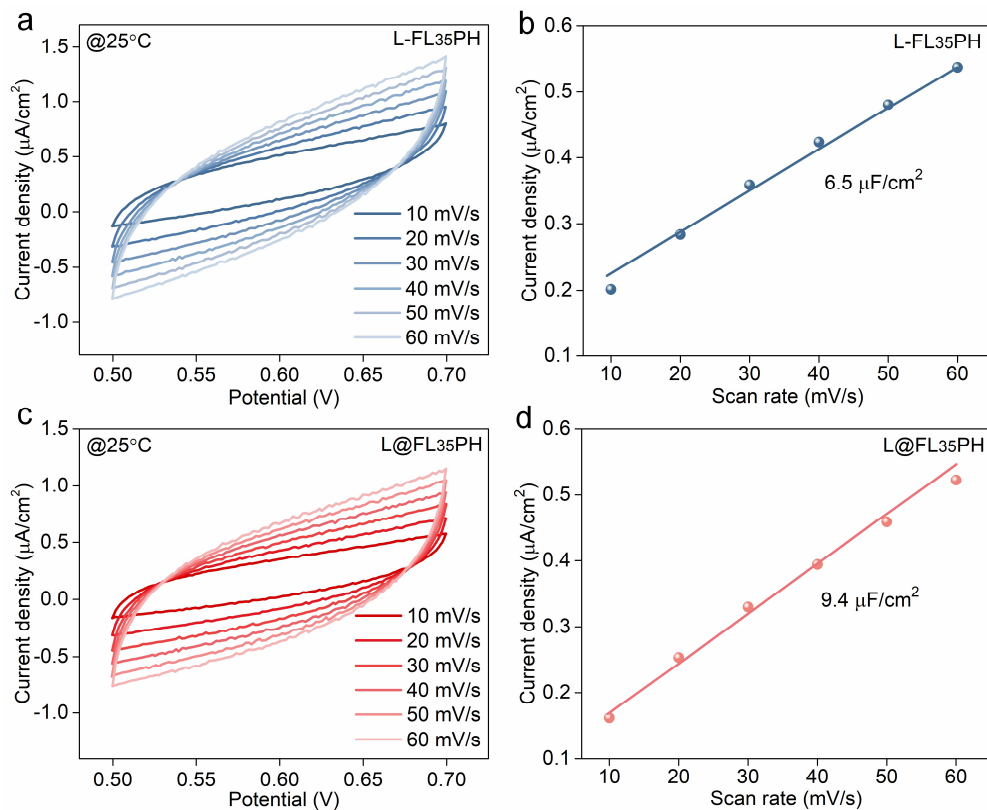


Supplementary Fig. 14 | DMF effect on CSEs microstructure. The FTIR spectra of DMF, LiTFSI powder, L-FL₃₅PH and L@FL₃₅PH. The purple curve corresponding to LiTFSI powder, the orange curve corresponding to DMF, the blue curve is the FTIR spectrum of the L-FL₃₅PH, and the red curve is the FTIR spectrum of the L@FL₃₅PH.

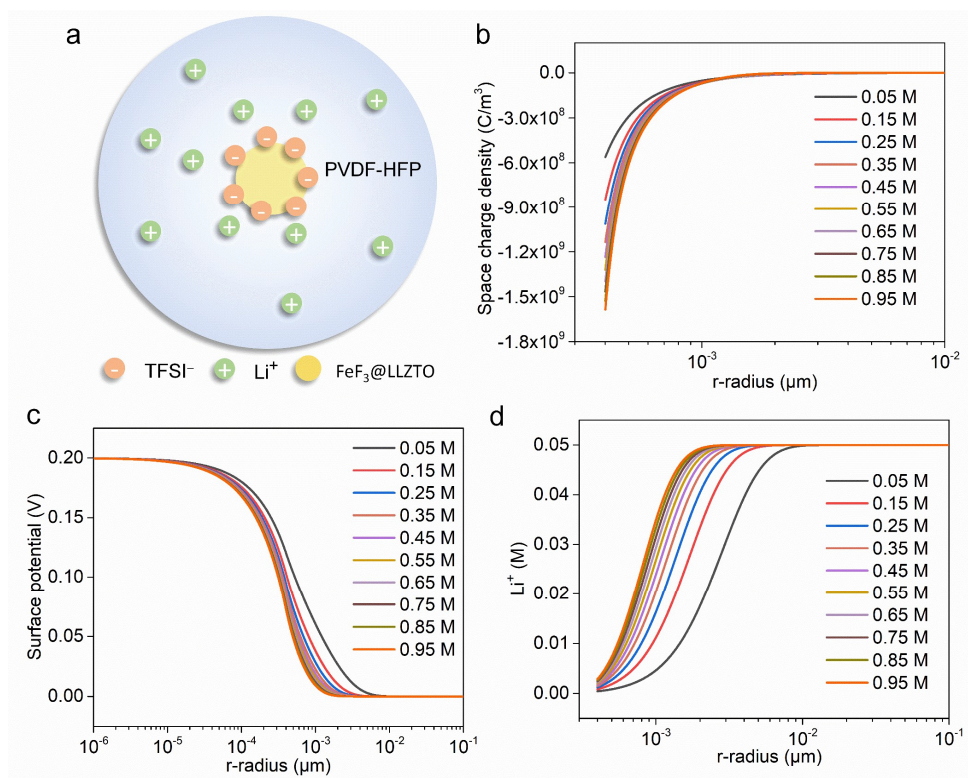


Supplementary Fig. 15 | Surface roughness and interfacial potential distribution.

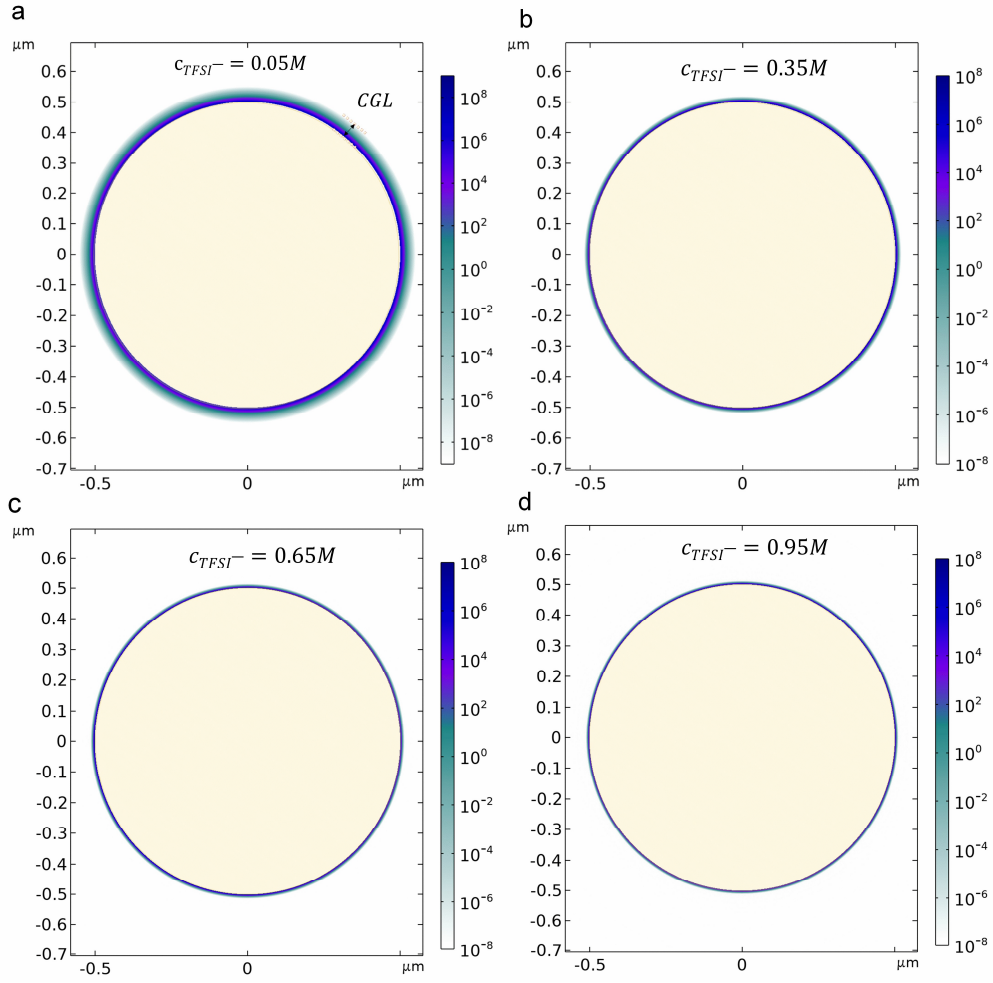
(a) KPFM image and (b-c) interface potential distribution images of L-L₃₅PH electrolyte. (d) The surface Zeta potential of LLZTO and FeF₃@LLZTO particles.



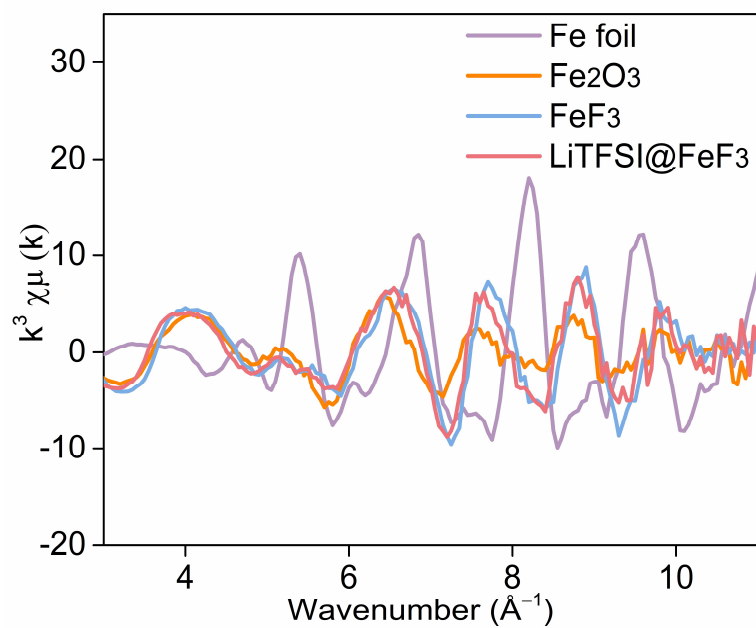
Supplementary Fig. 16 | The double-layer behavior of different CSEs. (a-d) CV curves and electric double layer capacitances of SS|Celgard|L-FL₃₅PH and SS|Celgard|L@FL₃₅PH at 10 mV/s, 20 mV/s, 30 mV/s, 40 mV/s, 50 mV/s and 60 mV/s.



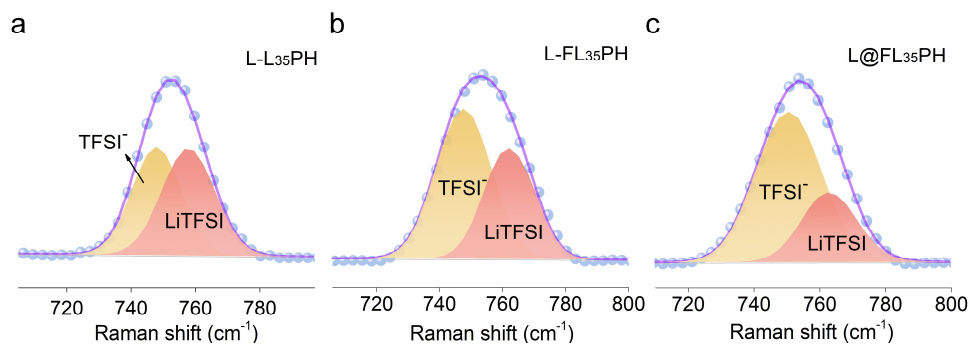
Supplementary Fig. 17 | The steady-state numerical simulations on modelling ionic transport. (a) Establishing TFSI^- in $\text{FeF}_3@LLZTO$ hypothesis model of surface aggregation, (b-d) the change of charge density, surface potential and Li^+ concentration with varying the TFSI^- concentration around $\text{FeF}_3@LLZTO$ in the range of 0.05-0.95 M.



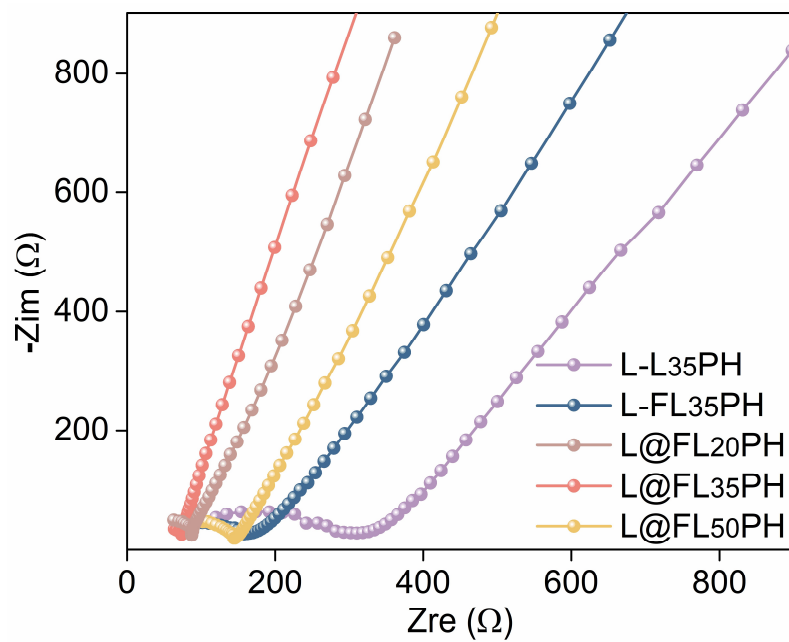
Supplementary Fig. 18 | Evaluated the compressive behavior of the charge gradient layer. (a-d) The relationship between the thickness of CGL and the concentration of TFSI⁻ (c_{TFSI^-} =0.05 M, 0.35 M, 0.65 M and 0.95 M) on the surface of FeF₃@LLZTO.



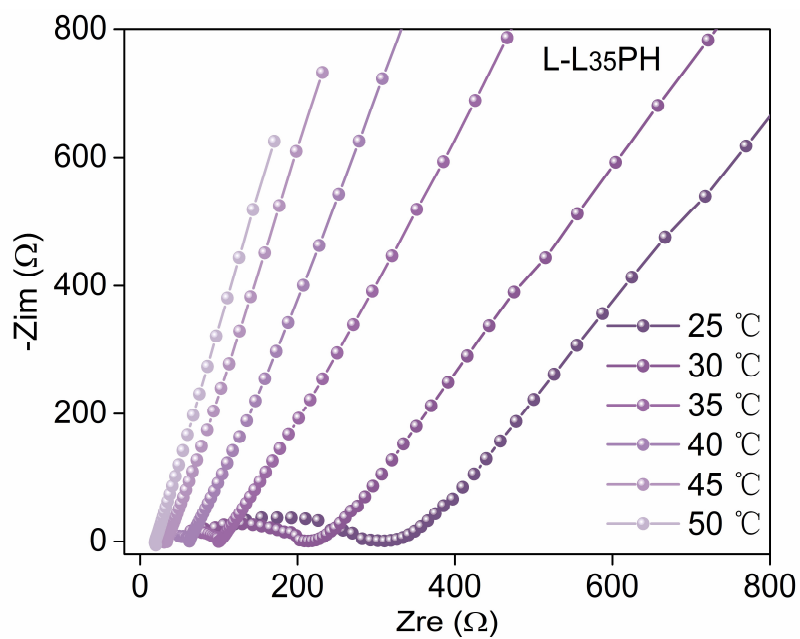
Supplementary Fig. 19 | The coordination environment of Fe sites. Fe R-space EXAFS spectra of Fe foil, Fe₂O₃, FeF₃ and LiTFSI@FeF₃.



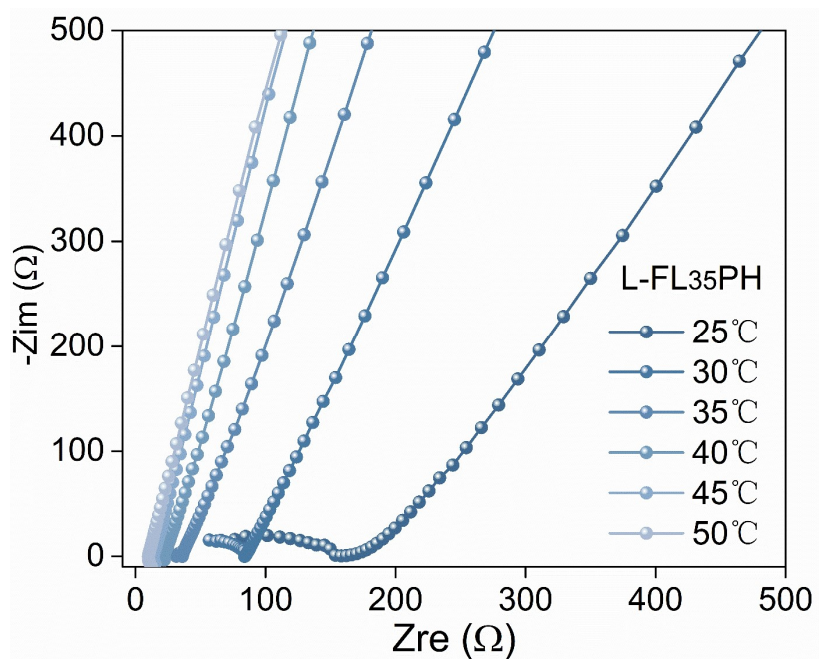
Supplementary Fig. 20 | $\text{FeF}_3\text{@LLZTO}$ effect on LiTFSI dissociation within various electrolytes. Raman spectra of (a) L-L₃₅PH, (b) L-FL₃₅PH and (c) L@FL₃₅PH electrolytes fitted with TFSI⁻ and LiTFSI groups at 710-800 cm⁻¹.



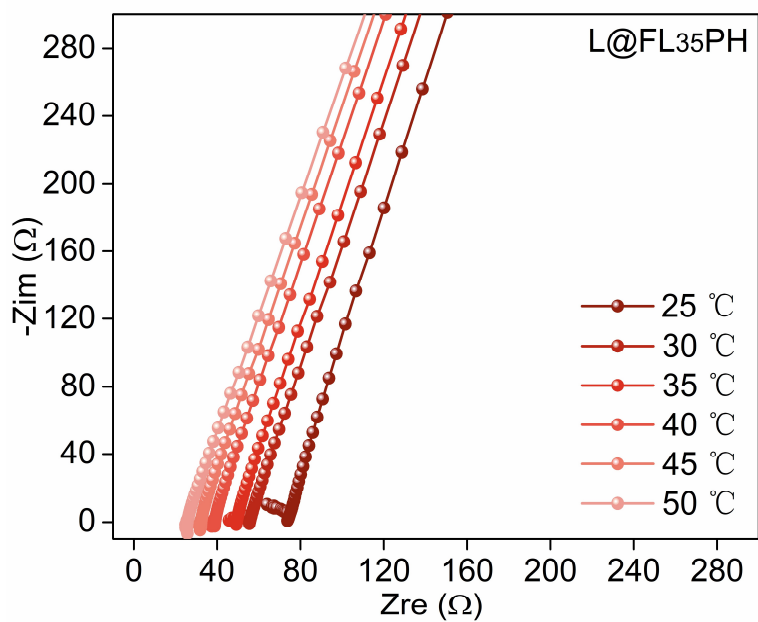
Supplementary Fig. 21 | Effect of TFSI⁻ adsorption concentration on the ionic conductivity of CSEs. Nyquist plots of the SS||SS battery assembled from L-L₃₅PH, L-FL₂₀PH, L@FL₃₅PH, L@FL₅₀PH and L@FL₃₅PH electrolytes at 25°C.



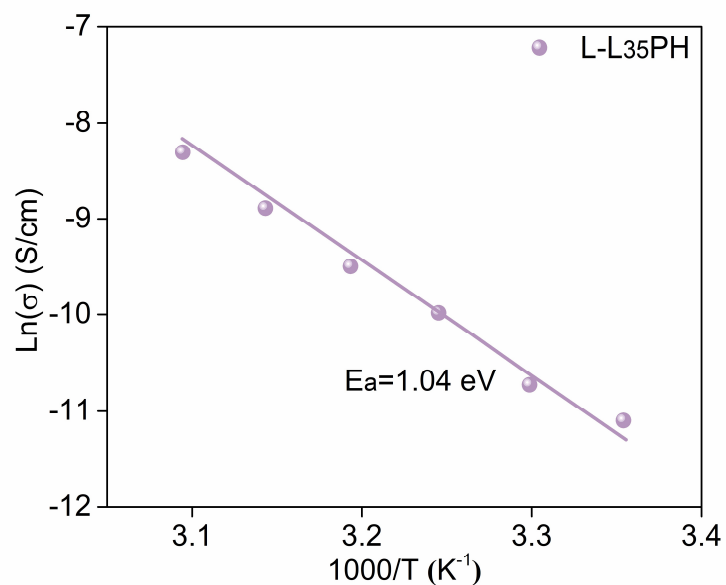
Supplementary Fig. 22 | The ionic conductivity of L-L₃₅PH electrolyte at different temperature. Nyquist plots of SS|L-L₃₅PH|SS battery at 25-50°C. Place the battery in a thermostat and measure the impedance at 5°C intervals between 25°C and 50°C.



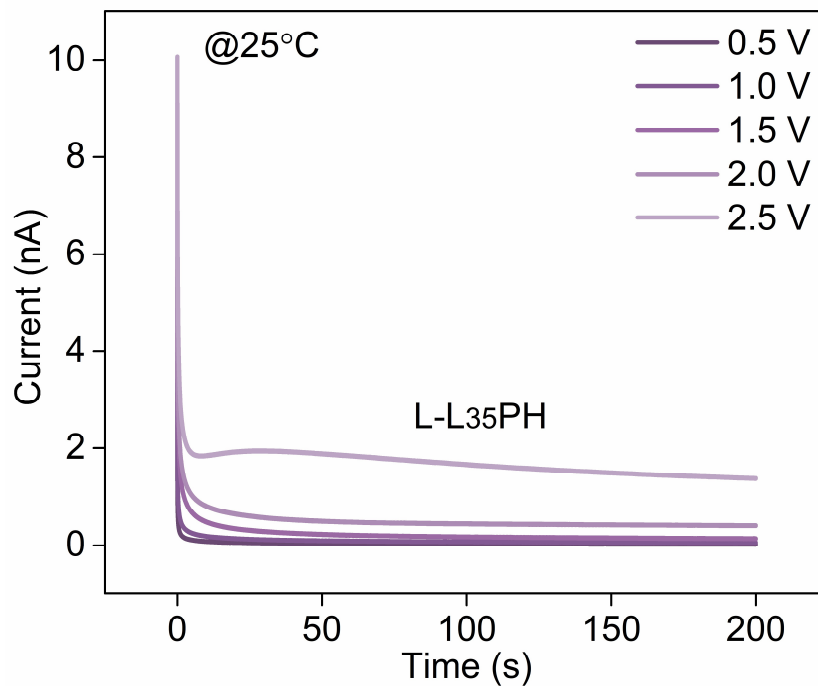
Supplementary Fig. 23 | The ionic conductivity of L-FL₃₅PH electrolyte at different temperature. Nyquist plots of SS|L-FL₃₅PH|SS battery at 25-50°C.



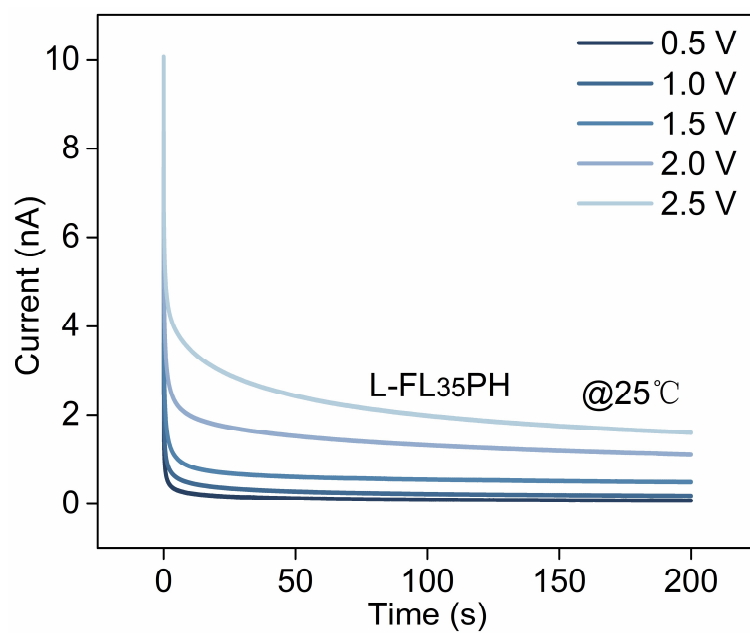
Supplementary Fig. 24 | The ionic conductivity of L@FL₃₅PH electrolyte at different temperature. Nyquist plots of SS|L@FL₃₅PH|SS battery at 25-50°C.



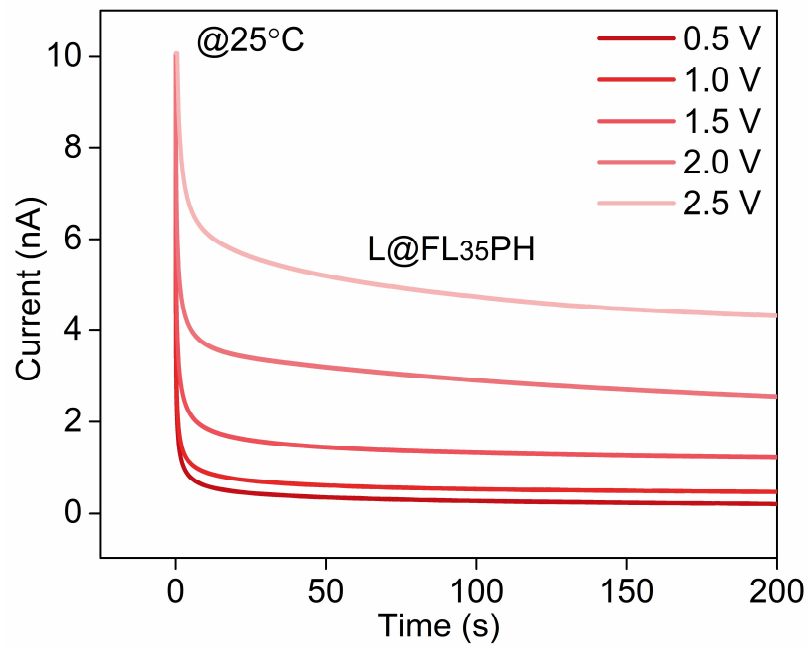
Supplementary Fig. 25 | The calculation of Li⁺ diffusion energy barrier in L-L₃₅PH electrolyte. Arrhenius plot of the ionic conductivities of L-L₃₅PH electrolyte at 25-50°C. Calculated ionic conductivity at different temperatures, plotted against temperature. The slope of the linear fit to these data corresponds to the Li⁺ diffusion energy barrier.



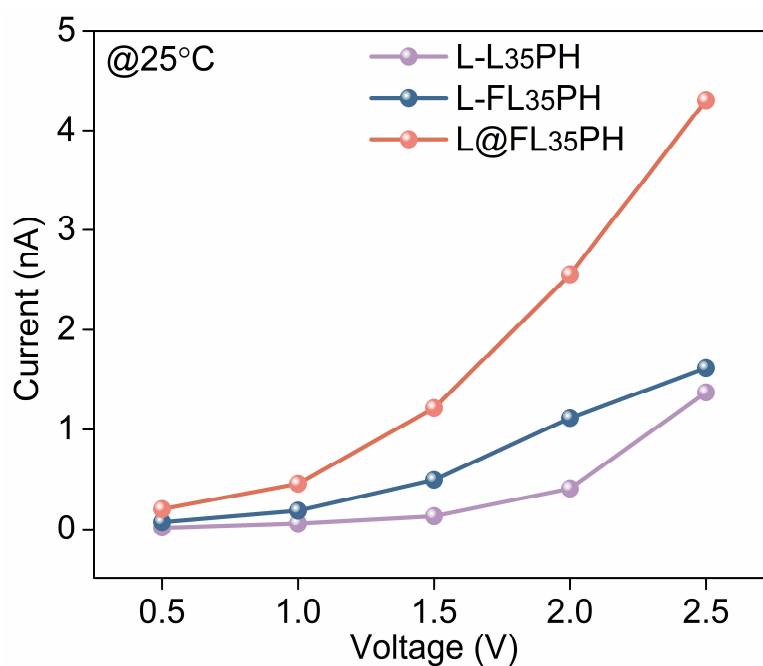
Supplementary Fig. 26 | The average electronic conductivities of L-L₃₅PH electrolyte. The current/time relationship curves of SS|L-L₃₅PH|SS battery under different input voltages. The steady-state current plots for L-L₃₅PH electrolyte at 0.5 V intervals between 0.5 V and 2.5 V using the Hebb-Wagner polarization method.



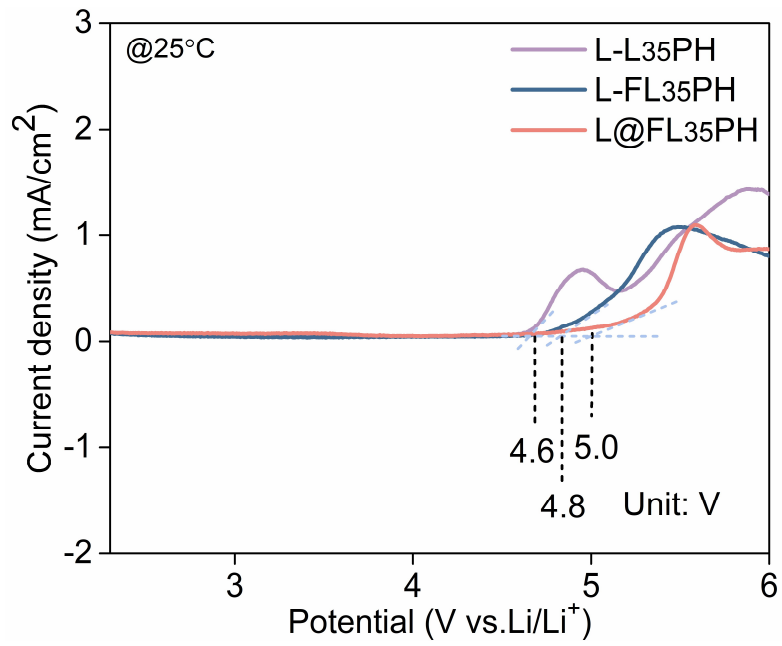
Supplementary Fig. 27 | The average electronic conductivities of L-FL₃₅PH electrolyte. The current/time relationship curves of SS|L-FL₃₅PH|SS battery under input voltages from 0.5 V–2.5 V.



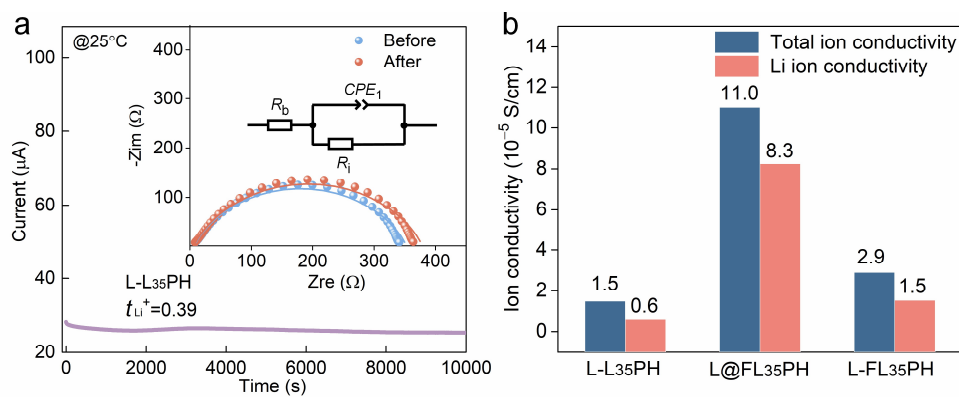
Supplementary Fig. 28 | The average electronic conductivities of L@FL₃₅PH electrolyte. The current/time relationship curves of SS|L@FL₃₅PH|SS battery under input voltages from 0.5 V–2.5 V.



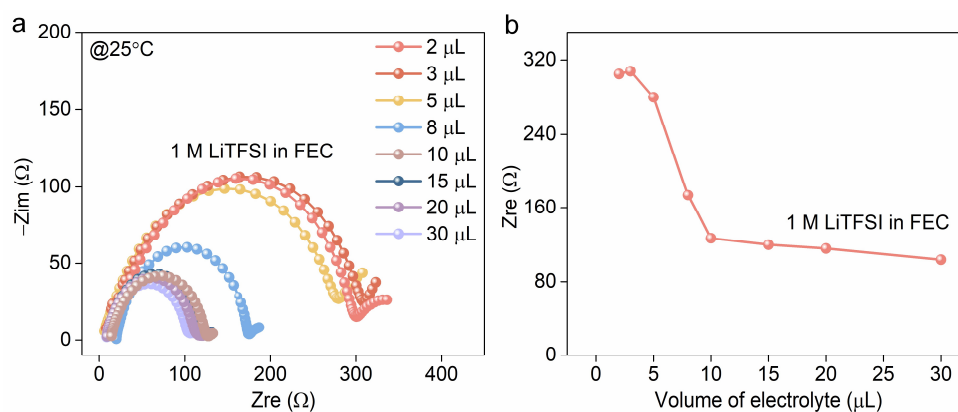
Supplementary Fig. 29 | Variation of steady-state current with voltage. Steady-state current as a function of the applied voltage at 25°C for L-L₃₅PH, L-FL₃₅PH and L@FL₃₅PH electrolytes by the Hebb-Wagner polarization method.



Supplementary Fig. 30 | Evaluating the oxidation voltage window of CSEs. Linear sweep voltammetry plots of L-L₃₅PH, L-FL₃₅PH and L@FL₃₅PH electrolytes.

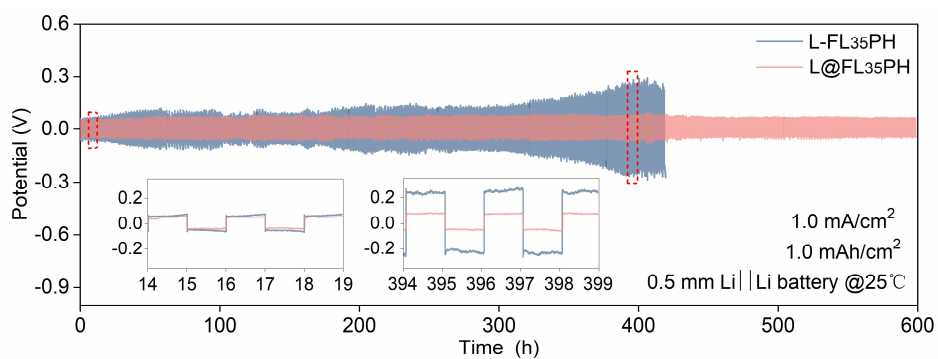


Supplementary Fig. 31 | Effect of different processes on the Li^+ migration number and Li^+ conductivity. (a) Variation of current with time during polarization of a Li|L-L₃₅PH|Li symmetric battery configuration; the inset figure shows the Nyquist plots before and after polarization. (b) Total ion conductivity and Li^+ conductivity of three electrolytes.



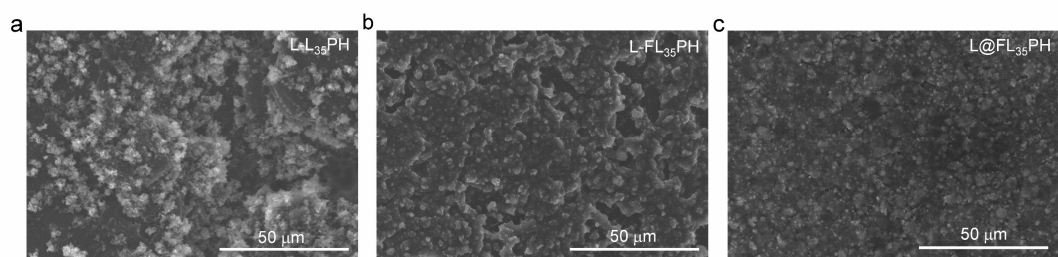
Supplementary Fig. 32 | The wetting-percolation threshold of liquid electrolytes.

(a-b) The impedances changes of the Li|L@FL₃₅PH|Li symmetric batteries with adding various volumes of liquid electrolyte (1 M LiTFSI in FEC solvent). Interfacial wetting effects and bulk-phase ionic percolation between CSEs and electrode were assessed by adding a volume threshold of electrolyte.

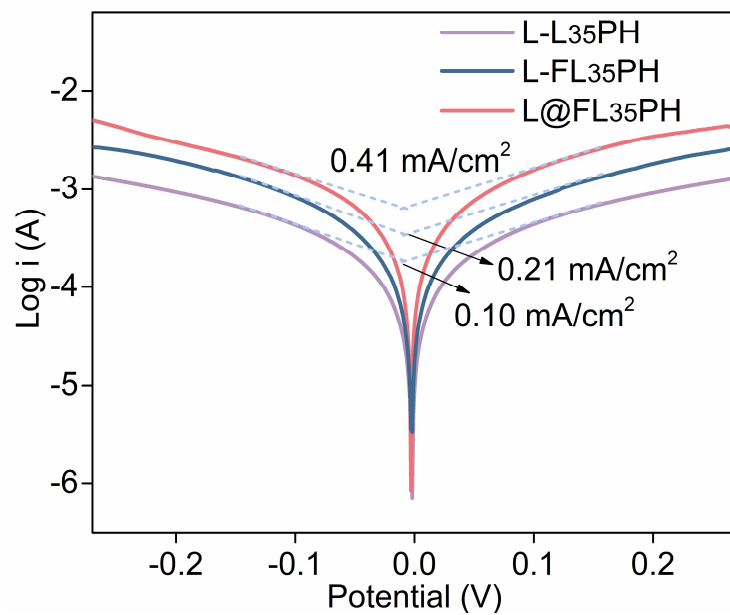


Supplementary Fig. 33 | Evaluation of Li deposition stripping stability of CSEs.

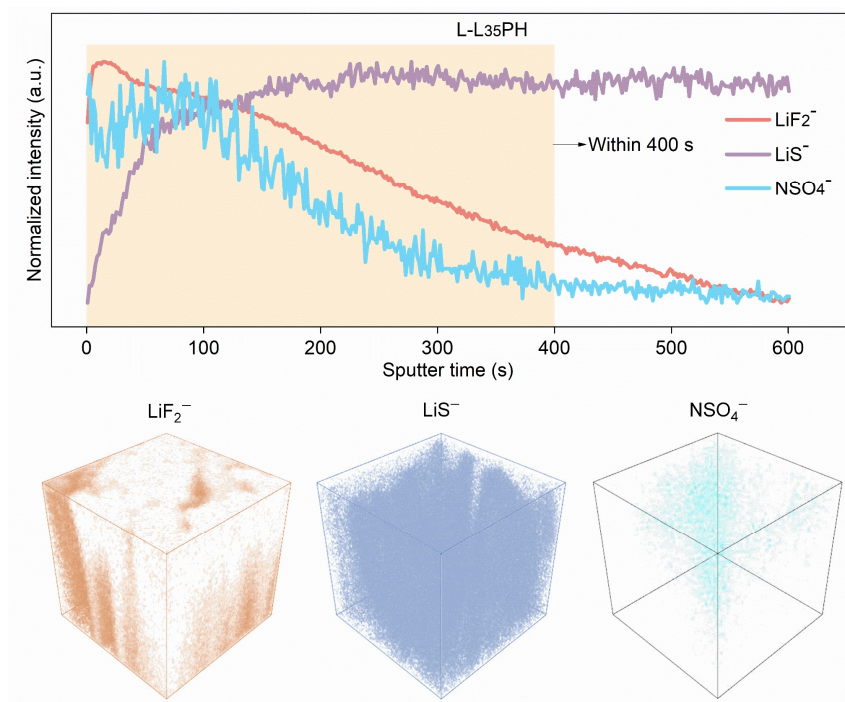
Cycling performances of Li|CSEs|Li symmetric batteries with L-FL₃₅PH and L@FL₃₅PH electrolytes at 1.0 mA/cm² (1.0 mAh/cm²) at 25°C. The insets show the polarization curves in the ranges of 14–19 h and 394–399 h, respectively.



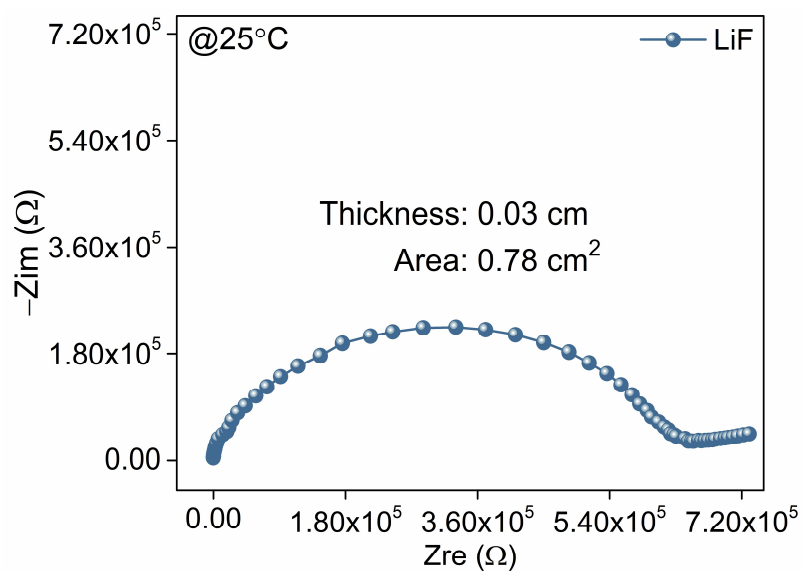
Supplementary Fig. 34 | CSEs effect on dendrite growth. (a-c) Morphology of Li negative electrode surface of Li|CSEs|Li symmetrical batteries with L-FL₃₅PH and L@FL₃₅PH electrolytes after Li plating/stripping 40 h for 0.1 mA/cm² at 25°C.



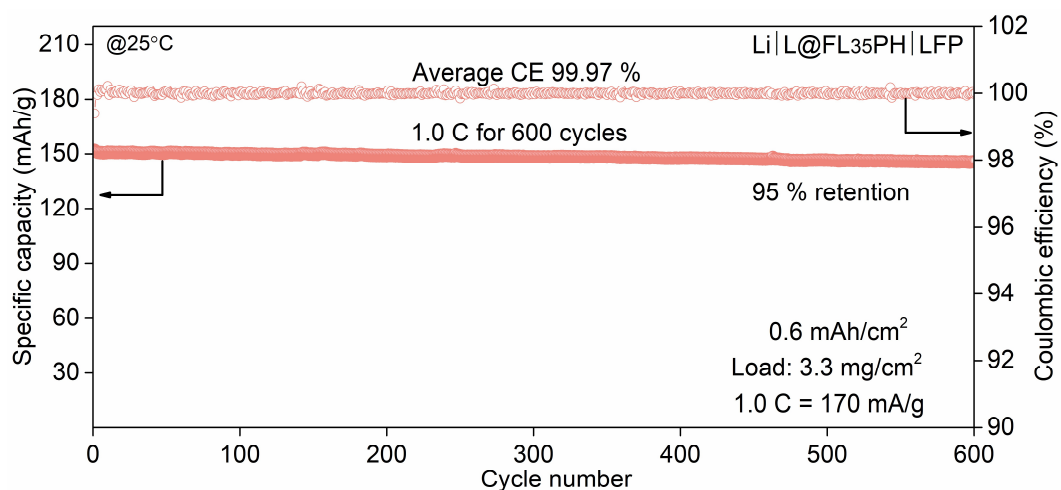
Supplementary Fig. 35 | Evaluation of exchange density between CSEs and Li negative electrode. The Tafel curves of Li|L-L₃₅PH|Li, Li|L-FL₃₅PH|Li and Li|L@FL₃₅PH|Li symmetric batteries at 25°C.



Supplementary Fig. 36 | Ionic composition analysis of SEI layer on the Li negative electrode. ToF-SIMS depth profile (Min-Max normalized), with the 3D view of LiF_2^- , LiS^- and NSO_4^- in L-L₃₅PH electrolyte Li plating/stripping (0.1 mA/cm²) for 40 h at 25°C.

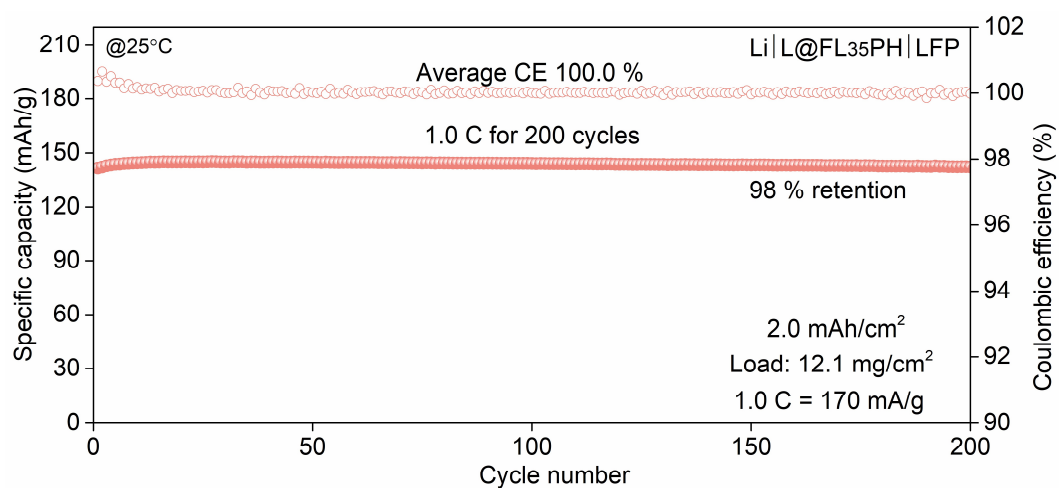


Supplementary Fig. 37 | The ionic conductivity of LiF. The Nyquist plots of SS|LiF|SS battery at 25 °C. The thickness of LiF electrolyte is 0.03 cm and the area of 0.78 cm².

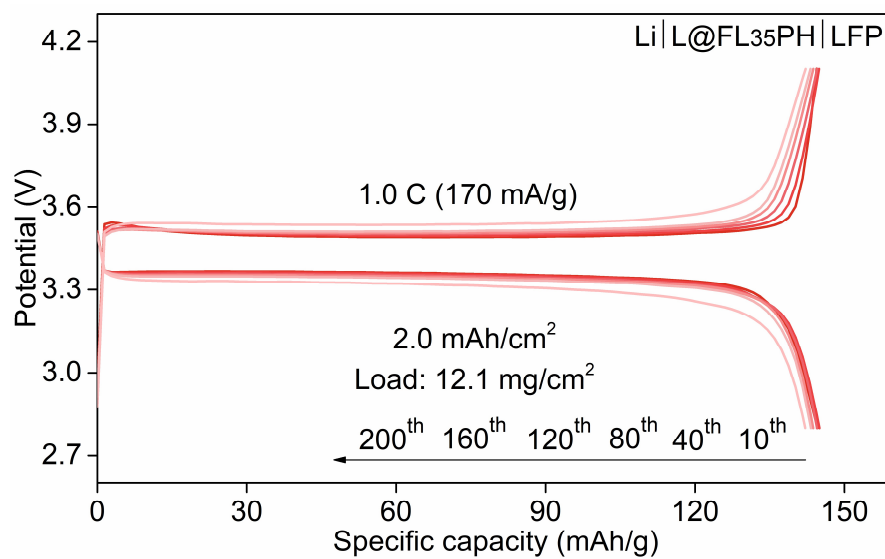


Supplementary Fig. 38 | Electrochemical performance of Li|CSEs|LFP batteries.

Capacity retention performance and average coulombic efficiency of Li|L@FL₃₅PH|LFP batteries at 1.0 C (170 mA/g) with 0.6 mAh/cm². LFP load is 3.3 mg/cm.

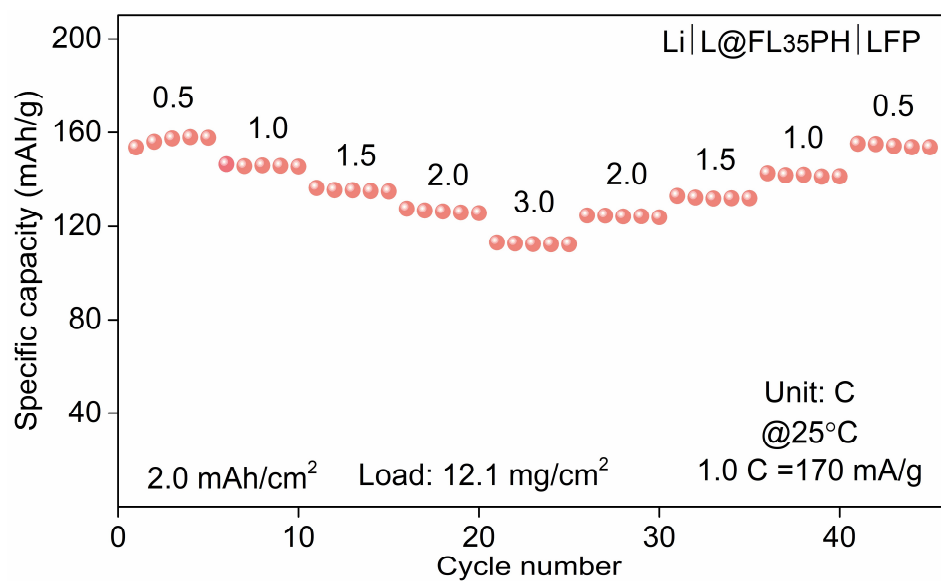


Supplementary Fig. 39 | Electrochemical performance of Li|CSEs|LFP battery with high LFP loading. Capacity retention performance and average coulombic efficiency of Li|L@FL₃₅PH|LFP batteries at 1.0 C (170 mA/g) with 2.0 mAh/cm². LFP load is 12.1 mg/cm.

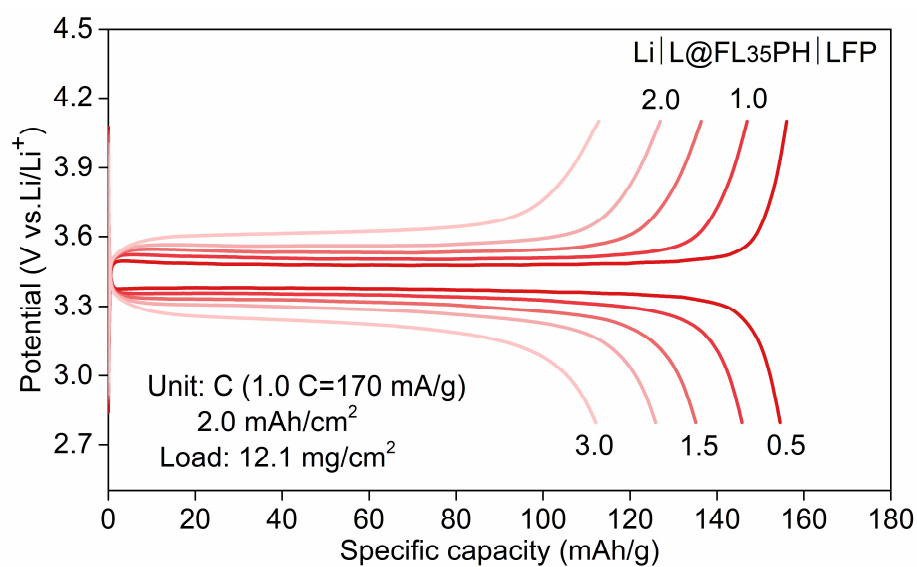


Supplementary Fig. 40 | The charge/discharge profiles of Li|CSEs|LFP battery.

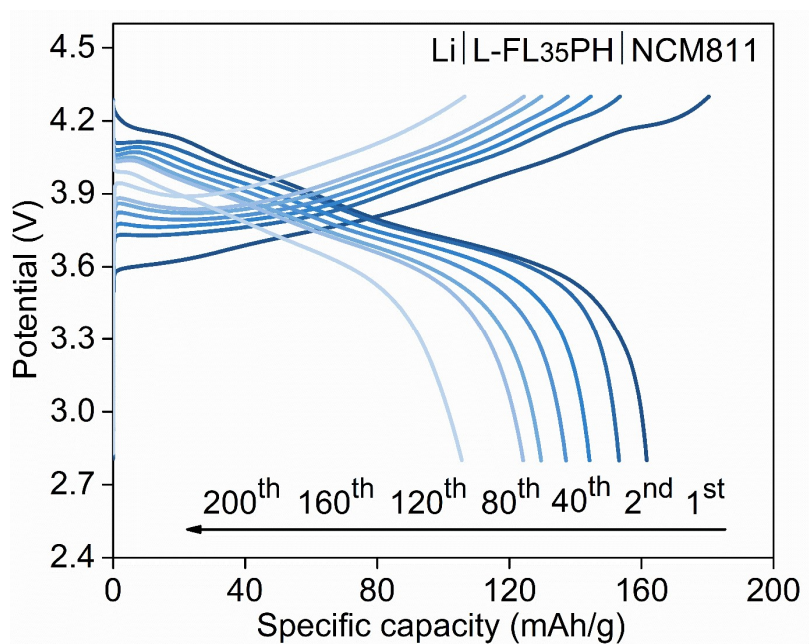
Galvanostatic discharge/charge voltage profiles of Li|L@FL₃₅PH|LFP battery at 1.0 C (170 mA/g) with 2.0 mAh/cm². LFP load is 12.1 mg/cm.



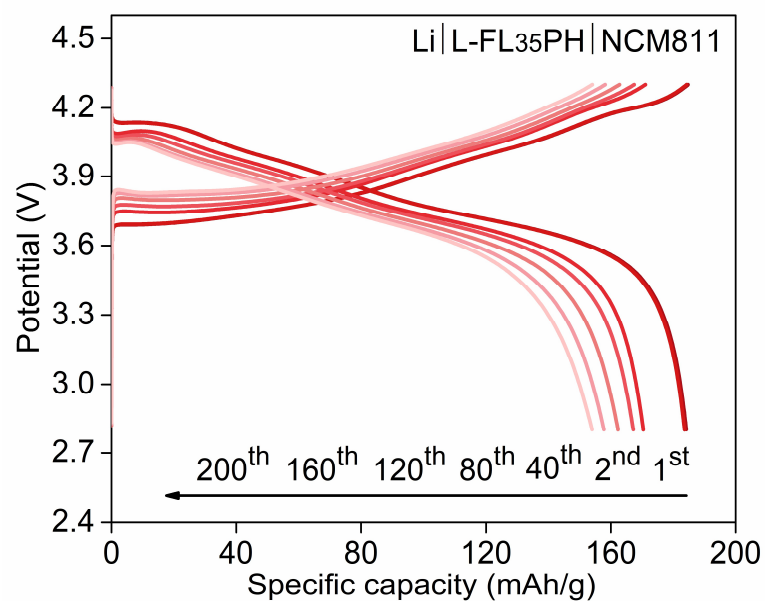
Supplementary Fig. 41 | Rate performance of Li|CSEs|LFP battery with high LFP loading. Rate performances of Li|L@FL₃₅PH|LFP battery at different charging rates (0.5 C, 1.0 C, 1.5 C, 2.0 C and 3.0 C) with 2.0 mAh/cm². LFP load is 12.1 mg/cm.



Supplementary Fig. 42 | Polarization effect of different rates. Galvanostatic discharge voltage profile of Li|L@FL₃₅PH|LFP batteries at different charging rates (0.5 C, 1.0 C, 1.5 C, 2.0 C and 3.0 C) with 2.0 mAh/cm². LFP load is 12.1 mg/cm.



Supplementary Fig. 43 | The charge-discharge curves of Li|L-FL₃₅PH|NCM811 battery. Galvanostatic charge/discharge curves of Li|L-FL₃₅PH|NCM811 battery at different cycle number with 1.0 C (200 mA/g).



Supplementary Fig. 44 | The charge-discharge curves of Li|L@FL₃₅PH|NCM811 battery. Galvanostatic charge/discharge curves of Li|L@FL₃₅PH|NCM811 battery at different cycle number with 1.0 C (200 mA/g).

Supplementary Tables

Supplementary Table 1 | The area ratio of each functional group of L-FL₃₅PH and L@FL₃₅PH electrolytes before and after etching

Samples	Etching time	S _{C-F} /S _{C-C}	S _{C-S} /S _{C-C}	S _{TFSI⁻} /S _{C-N}
		(C 1s)	(C 1s)	(N 1s)
L-FL ₃₅ PH	0 s	0.87	0.41	—
	120 s	0.13	0.61	0.87
L@FL ₃₅ PH	0 s	0.03	0.25	—
	120 s	0.20	0.99	2.78

Supplementary Table 2. Battery resistance (R_b) and interfacial resistance (R_i) of Li||NCM811 based on various CESs before and after cycling in Figs. 6d-4e.

Samples	Battery status	R_b	R_b (Error%)	R_i	R_i (Error%)
Li L-FL ₃₅ PH NCM811	Before cycle	2.7 Ω	1.7	137.5 Ω	1.7
	After 20 th cycle	3.4 Ω	2.0	221.5 Ω	1.9
Li L@FL ₃₅ PH NCM811	Before cycle	2.6 Ω	1.3	83.6 Ω	1.5
	After 20 th cycle	4.0 Ω	1.8	128.9 Ω	2.1

Supplementary Table 3. Battery resistance (R_b) and interfacial resistance (R_i) of Li||Li based on various CESs before and after Li plating/stripping in Fig. 3b and Supplementary Fig. 31a.

Samples	Battery status	R_b	R_b (Error%)	R_i	R_i (Error%)
Li L-L ₃₅ PH Li	Before Polarization	7.3 Ω	3.0	345.4 Ω	0.8
	After Polarization	6.6 Ω	3.7	372.1 Ω	1.0
Li L-FL ₃₅ PH Li	Before Polarization	29.6 Ω	1.2	339.1 Ω	0.5
	After Polarization	31.8 Ω	1.1	374.7 Ω	0.5
Li L@FL ₃₅ PH Li	Before Polarization	9.8 Ω	2.9	306.9 Ω	0.9
	After Polarization	7.1 Ω	3.6	368.3 Ω	0.8

Supplementary Table 4 | Performance comparison with the state-of-the-art CSEs based solid-state Li batteries at 25°C.

Solid-state Li batteries	t_{Li^+}	1 st discharge capacity	Rate	Cutoff voltage
		(mAh/g)		(V)
Li PVBL NCM811 ^[2]	0.57	172.9	1.0 C (200 mA/g)	4.3
Li PPHT LFP ^[3]	0.53	121.9	1.0 C (170 mA/g)	3.8
Li PIA-SPE NCM811 ^[4]	0.36	110.0	0.5 C (100 mA/g)	4.2
Li PEO/CuF ₂ NCM83 ^[5]	0.42	152.0	0.1 C (20 mA/g)	4.1
Li A-ISPE LFP ^[6]	0.67	150.4	0.5 C (85 mA/g)	4.0
Li PVLN-15 NCM811 ^[7]	0.58	150.2	0.5 C (100 mA/g)	4.3
Li PEGDA/o-LLZO NCM811 ^[8]	0.58	144.2	1.0 C (200 mA/g)	4.3

Supplementary References

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