Electronic Supplementary Information

Ammonium fluoride induced barrier-free and oxygen vacancies enhanced LLZO powder for fast interfacial lithium-ion transport in composite solid electrolytes

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Additional Figures

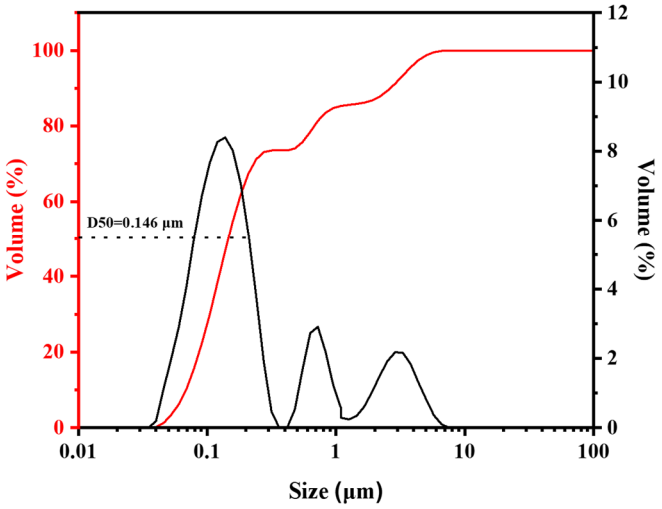

Figure S1. Particle size distribution curve of pristine LLZO powder

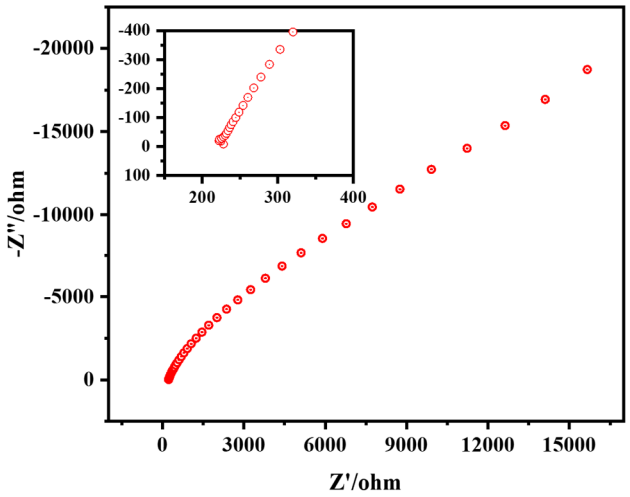

Figure S2. Nyquist plot of $Li_{6.4}Ga_{0.2}La_3Z_2O_{12}$ pellet

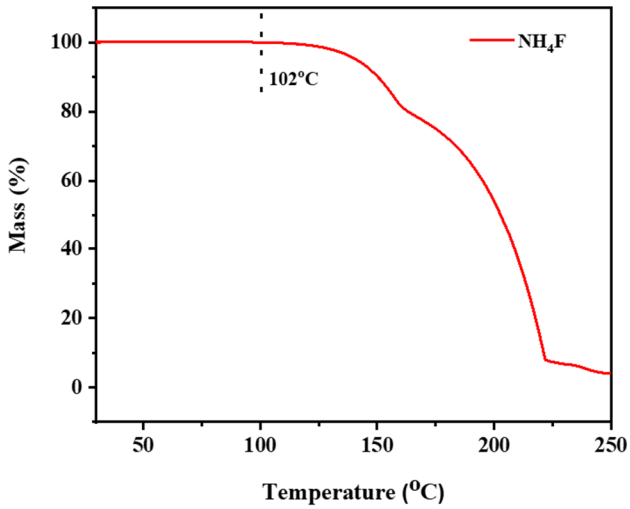

Figure S3. TG curve of NH_4F powder

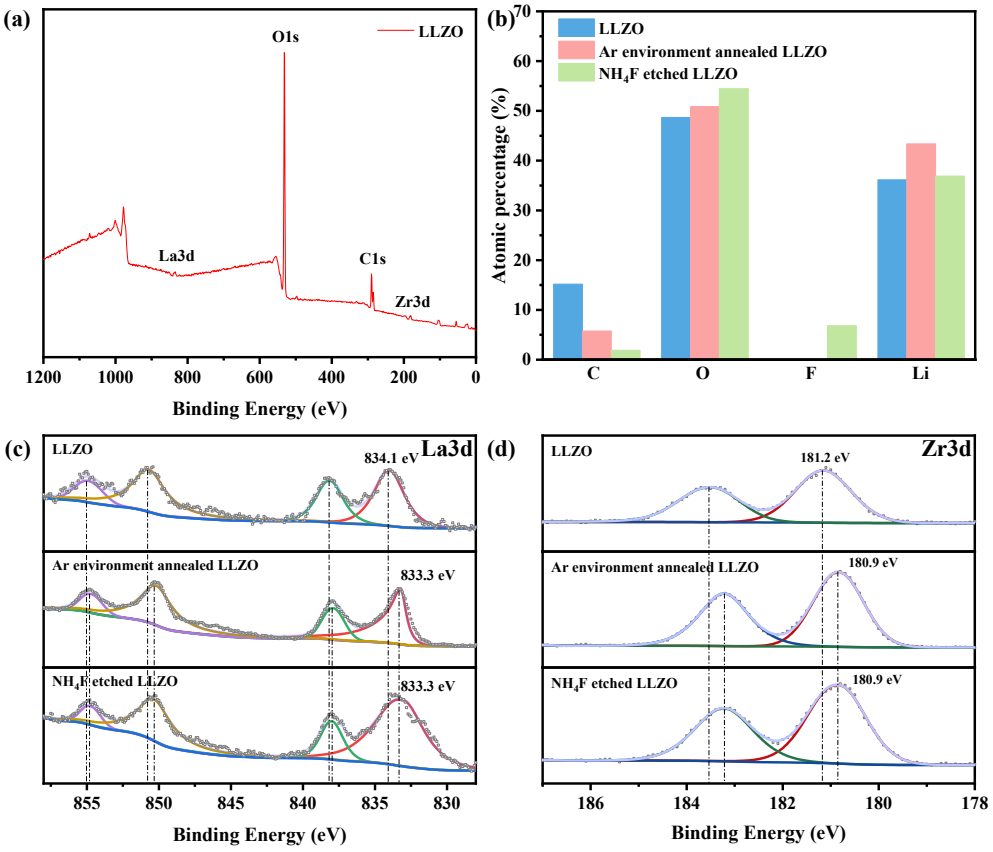

Figure S4. (a) XPS spectra of pristine LLZO powder. Surface elements contents (b); La 3d spectra (c); Zr 3d spectra (d) of LLZO, Ar environment annealed LLZO and NH_4F etched LLZO powder that detected by XPS.

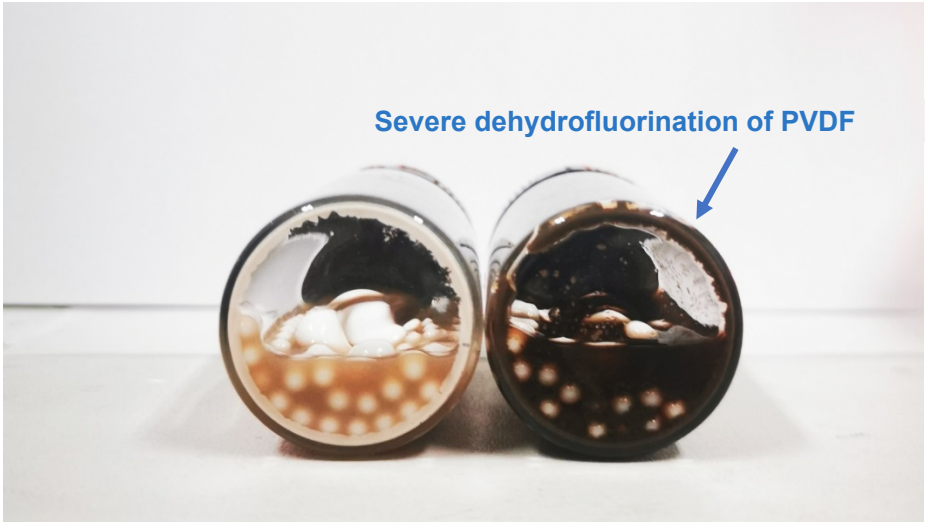

Figure S5. Optical photograph of PVDF-LiTFSI-NH_4F etched LLZO, PVDF-LiTFSI-LLZO.

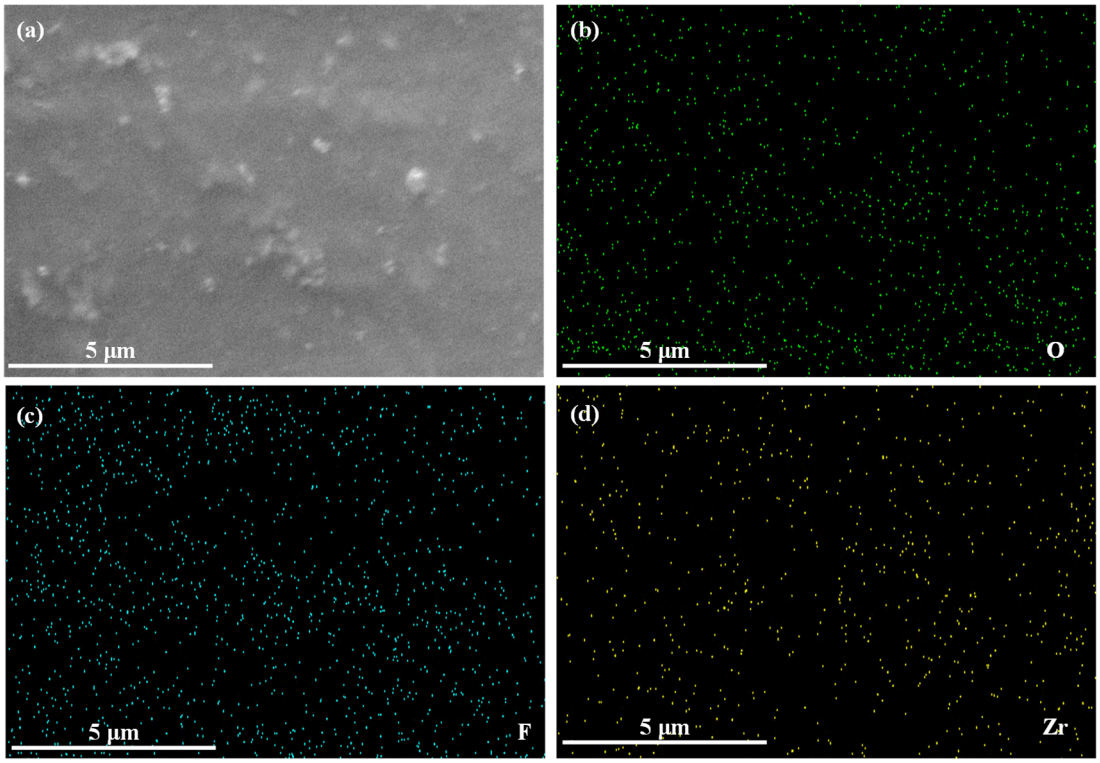

Figure S6. Morphologies of PEO-LiTFSI-LLZO membrane (a) were captured by SEM. The distribution of O, F and Zr respectively on surface of PEO-LiTFSI-LLZO membrane (b)-(d) were detected by EDX mapping.

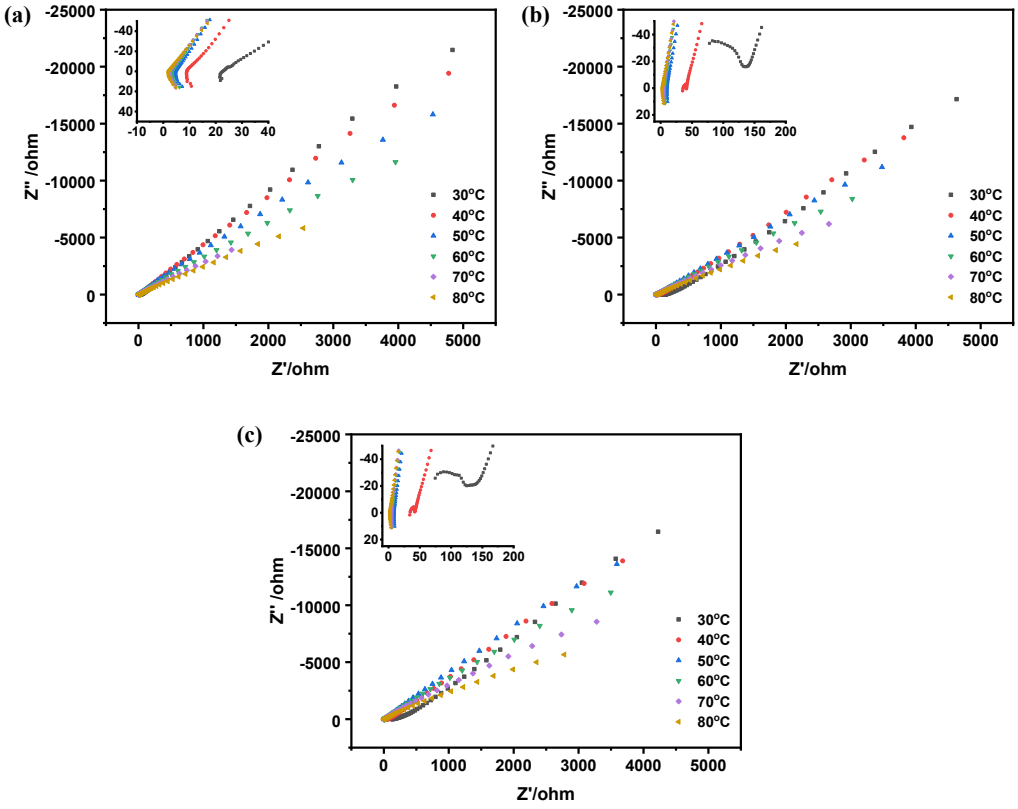

Figure S7. Nyquist plots of PEO-LiTFSI-NH_4F etched LLZO (a); PEO-LiTFSI-LLZO (b); PEO-LiTFSI (c) membranes.

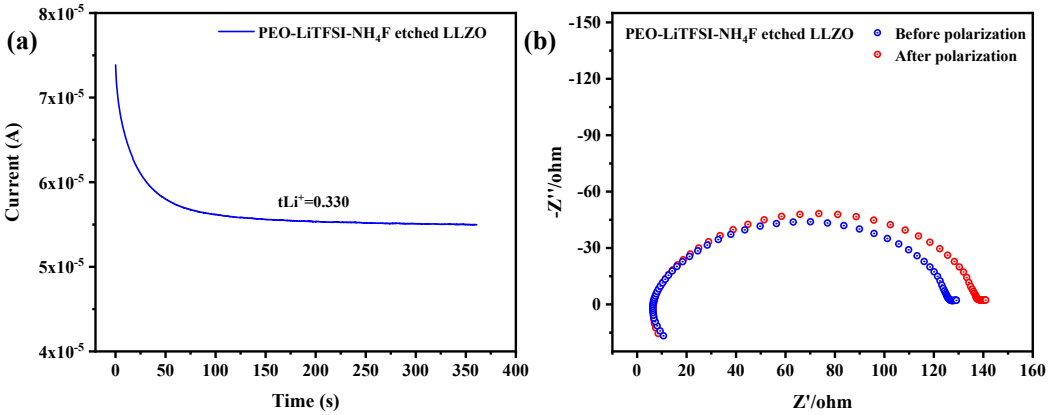

Figure S8. Detailed lithium-ion transference number data of PEO-LiTFSI-NH_4F etched LLZO membrane

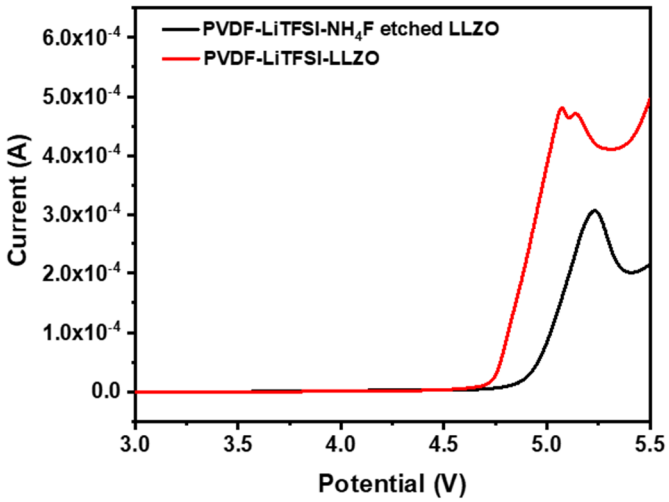

Figure S9. LSV curves of PVDF-LiTFSI-NH_4F etched LLZO and PVDF-LiTFSI-LLZO

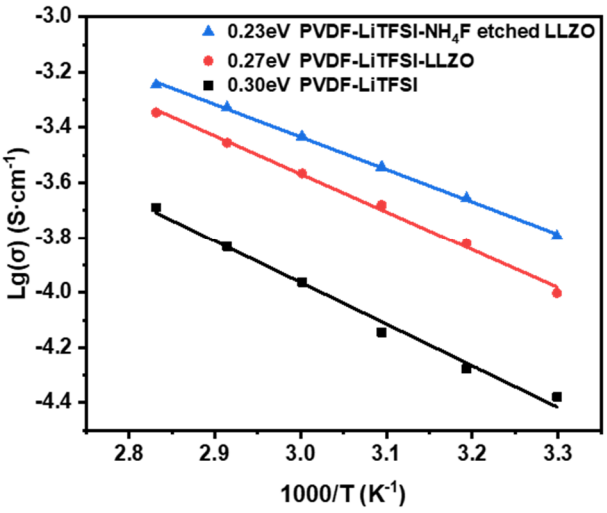

Figure S10. Arrhenius plots of PVDF-LiTFSI-NH_4F etched LLZO, PVDF-LiTFSI-LLZO and PVDF-LiTFSI.

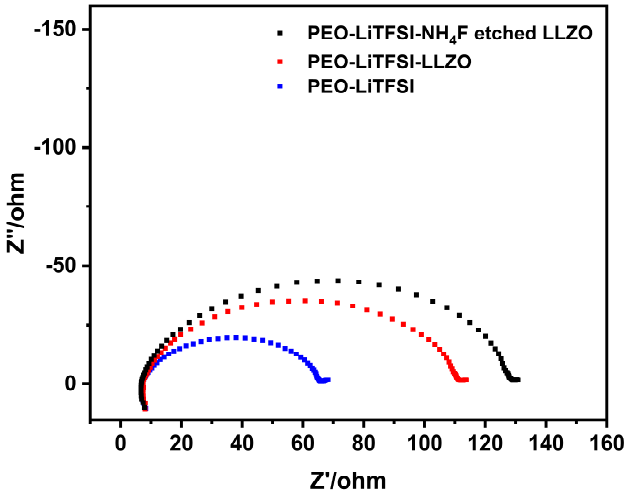

Figure S11. EIS spectra of Li symmetric cells with PEO-LiTFSI, PEO-LiTFSI-LLZO, and PEO-LiTFSI-NH_4F etched LLZO membranes

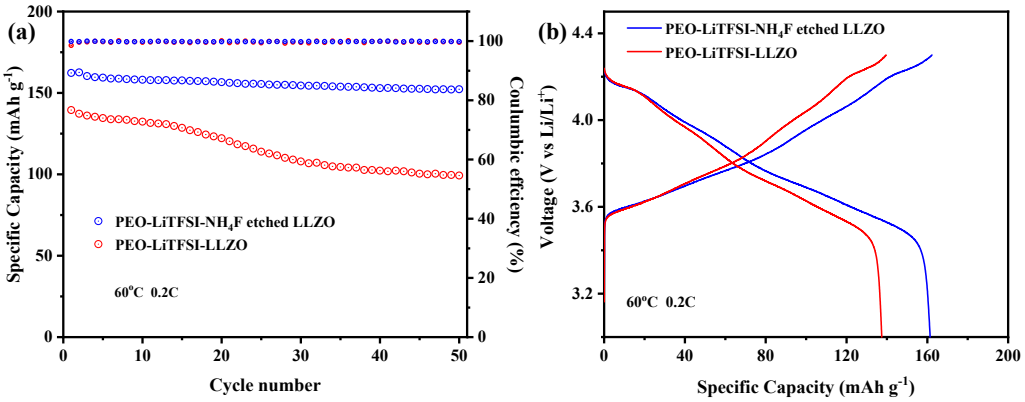

Figure S12. a) Cycling performance of different electrolytes coupled with NCM811 cathode and lithium metal anode at 0.2 C and b) corresponding voltage curves at first cycle.

Additional Table

Table S1. Ionic conductivity of PEO-LiTFSI, PEO-LiTFSI-LLZO and PEO-LiTFSI-NH_4F etched LLZO membranes under different temperatures.

Electrolytes	Ionic conductivity (10^{-4} S cm^{-1}) at different temperature (°C)					
	30	40	50	60	70	80
PEO-LiTFSI-NH_4F etched LLZO	1.93	4.88	9.10	12.8	16.7	21.7
PEO-LiTFSI-LLZO	0.279	0.885	3.69	6.45	8.66	12.2
PEO-LiTFSI	0.335	1.02	5.05	8.50	12.0	18.2

Additional Experiment section

Preparation of PVDF matrix composite solid electrolytes:

LiTFSI (Aladdin, 99.95%), and PVDF (Arkema, Kynar 761) were dried under vacuum at 80 °C for 24 h before use. PVDF solid electrolyte membranes were prepared via solution-casting method. PVDF and LiTFSI were dissolved in N, N-dimethylformamide (DMF) with weight ratio of 2:1 followed by ball-milling at 200 rpm for 3 h. After that, PVDF solid electrolytes solution was cast onto a Teflon mold (4 × 4 cm^2) and then dried at 60°C for 24-36 h to evaporate solvent. PVDF-LLZO and PVDF-NH_4F etched LLZO composite electrolytes were prepared by adding different amounts of inorganic electrolytes into PVDF solid electrolytes solution. Then the suspension was ball-milled at 200 rpm for 12 h to ensure the fine dispersion before casting.