Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Modifying an ultrathin insulating layer to suppress lithium dendrite formation within garnet solid electrolytes

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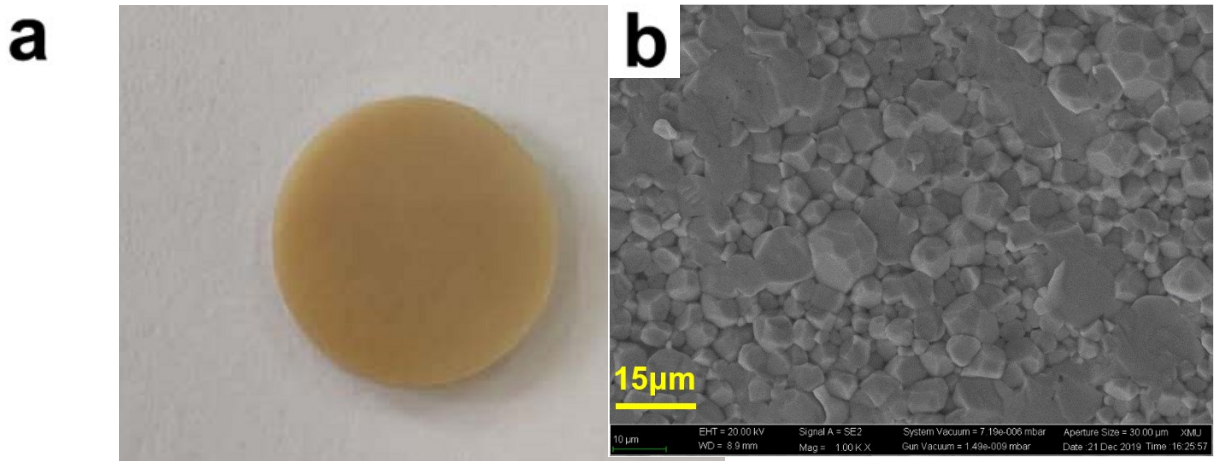

Figure S1. (a) Digital photograph of LLZTO pellet. (b) Cross sectional SEM image of LLZTO pellet.

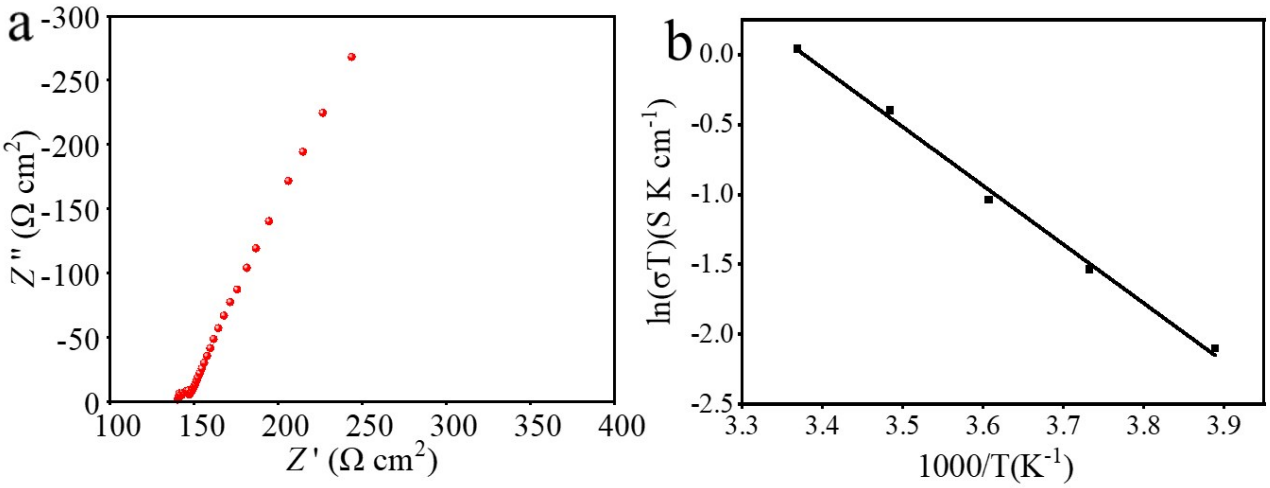

Figure S2. (a) Nyquist plots of LLZTO solid state electrolyte pellet measured at room temperature (surface area = 0.865 cm^2, thickness = 0.8 mm). (b) Arrhenius plot of the ionic conductivity of LLZTO.

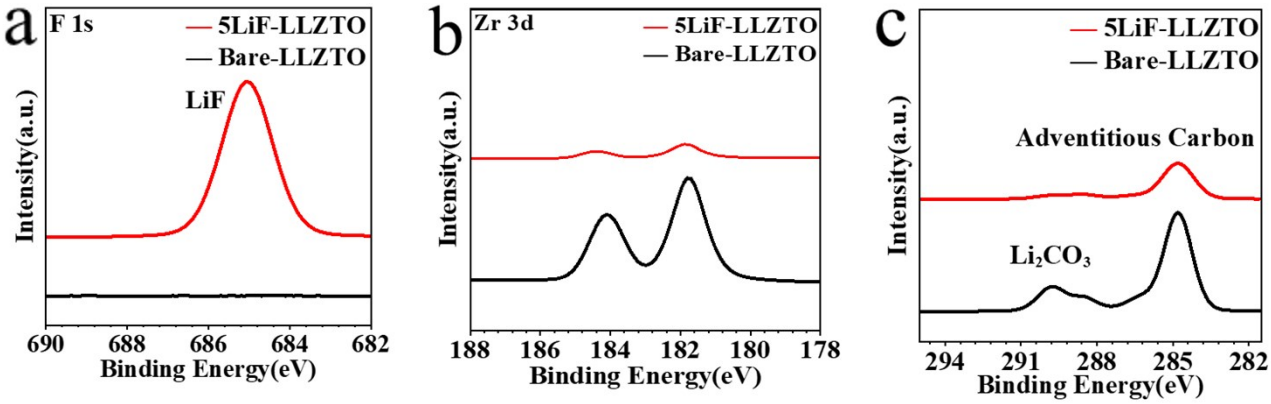

Figure S3. XPS results of pristine LLZTO and 5LF-LLZTO.

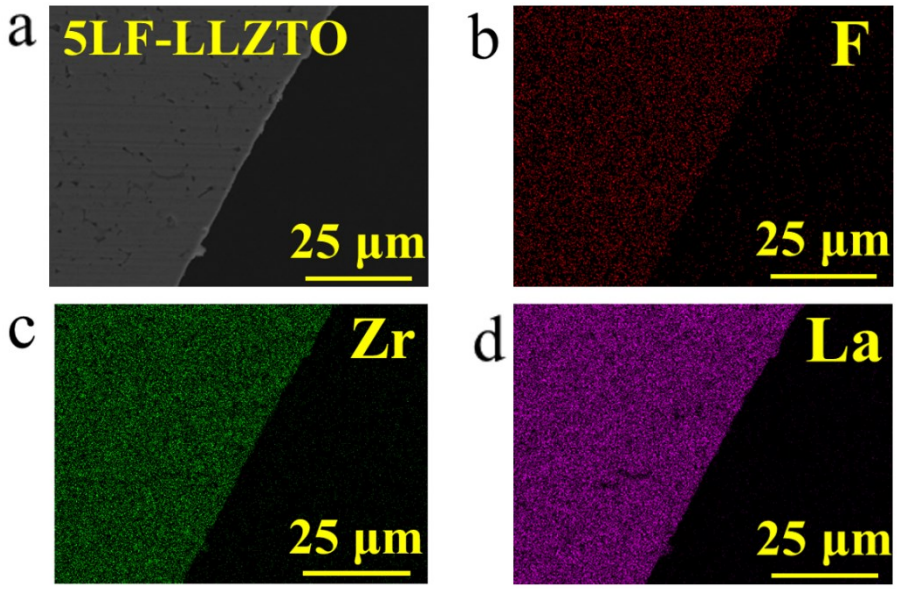

Figure S4. Top-view SEM image of 5LF-LLZTO pellets and corresponding EDS mapping images.

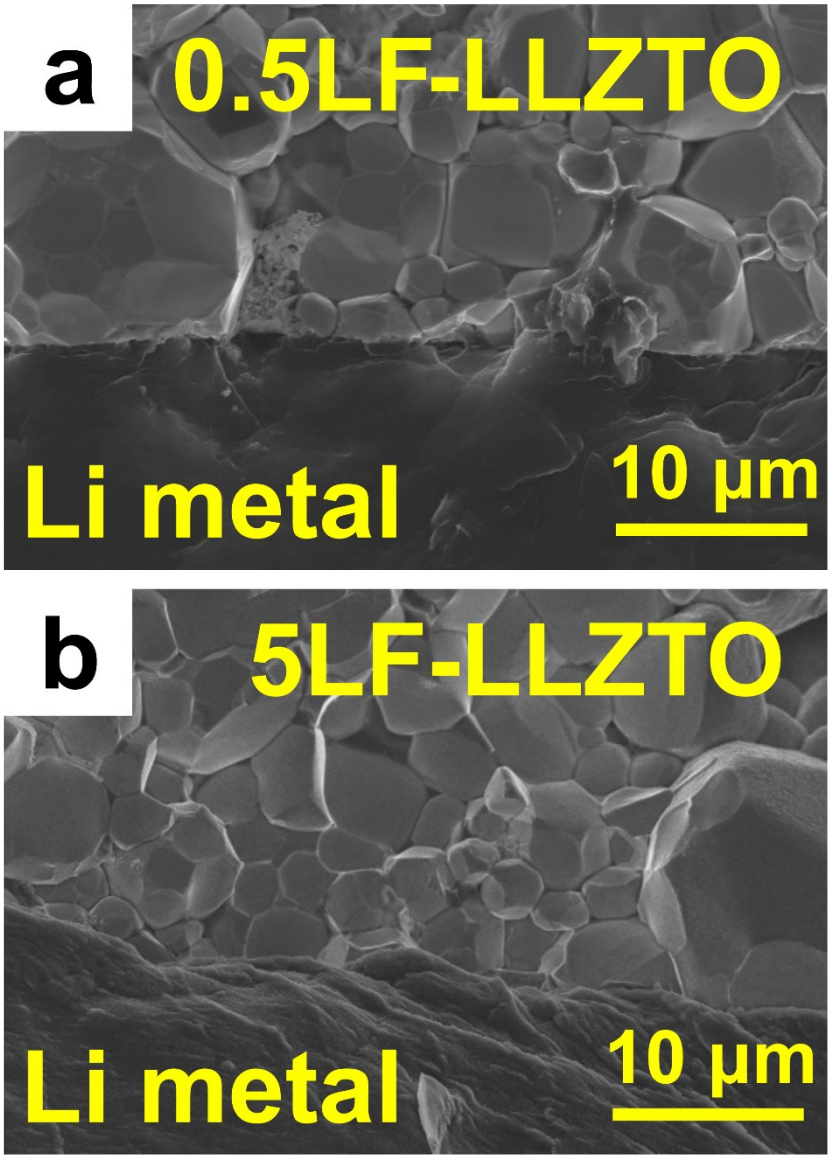

Figure S5. Interface SEM images of the LiF-coated LLZTO electrolytes with metallic Li before Li plating/stripping. (a) 0.5LF|LLZTO and (b) 5LF-LLZTO.

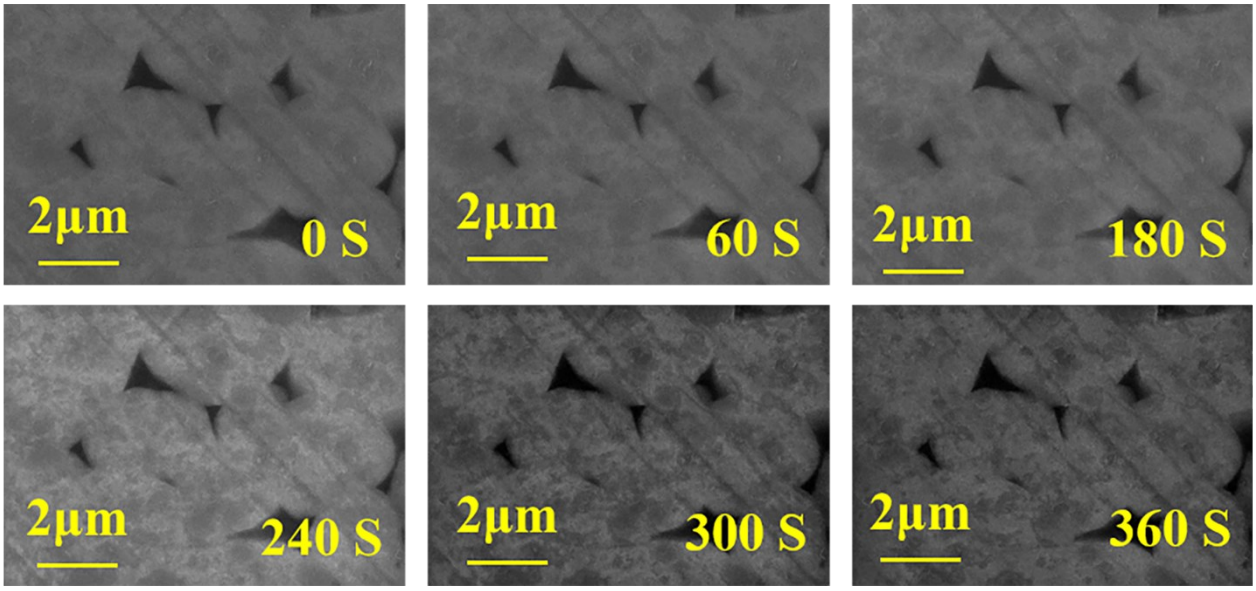

Figure S6. Lithium expulsion behaviors recorded under continuous frame scan at 5LF-LLZTO pellet surface.

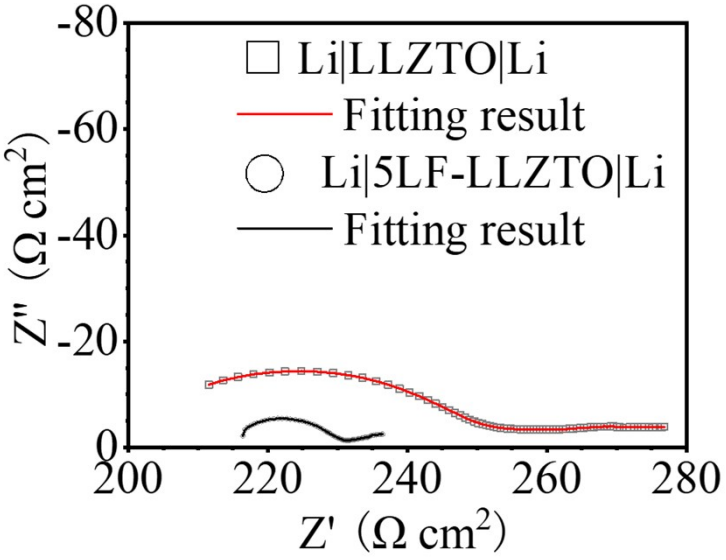

Figure S7. Comparison of EIS profiles of Li|LLZTO|Li and Li|5LF-LLZTO|Li symmetric cells.

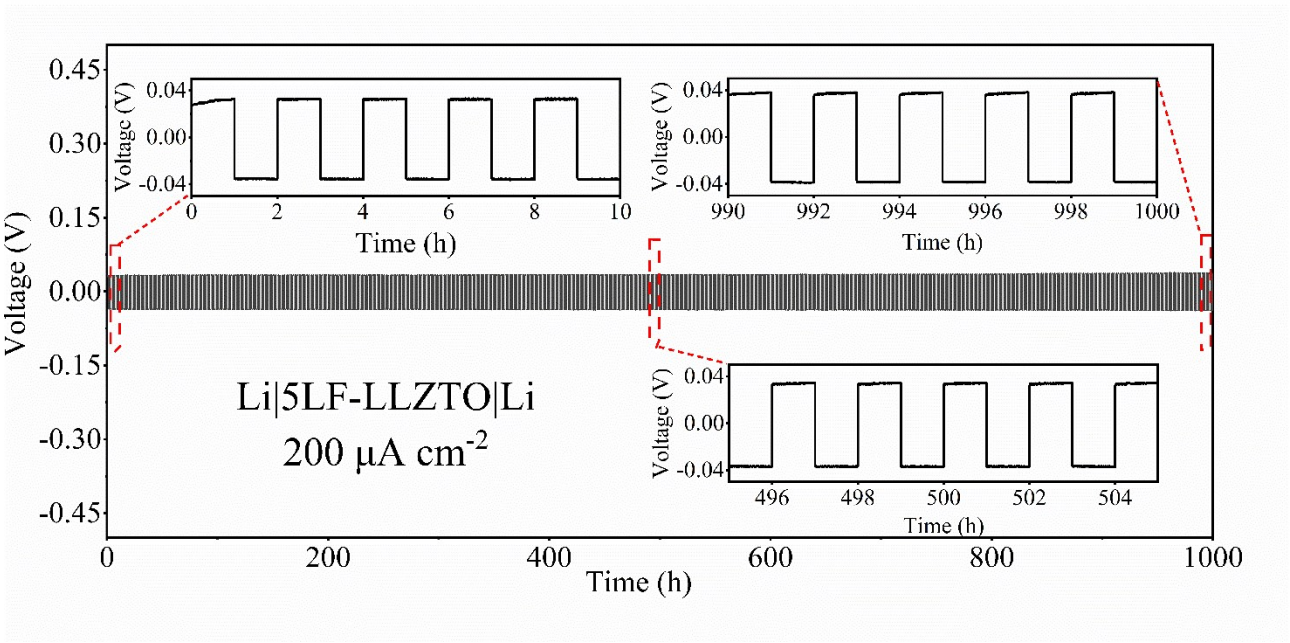

Figure S8. Galvanostatic cycling performance of Li|5LF-LLZTO|Li symmetric cell.

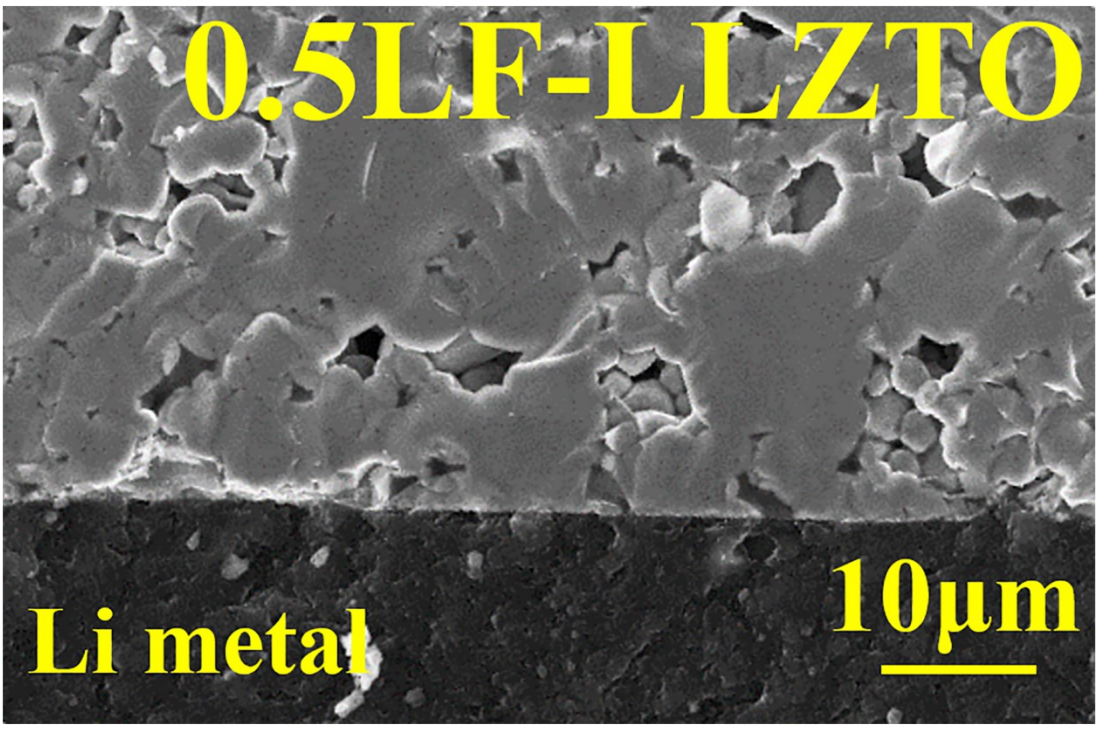

Figure S9. Cross-section SEM image of the Li/0.5LF-LLZTO interface after Li plating/stripping for 1500 h.

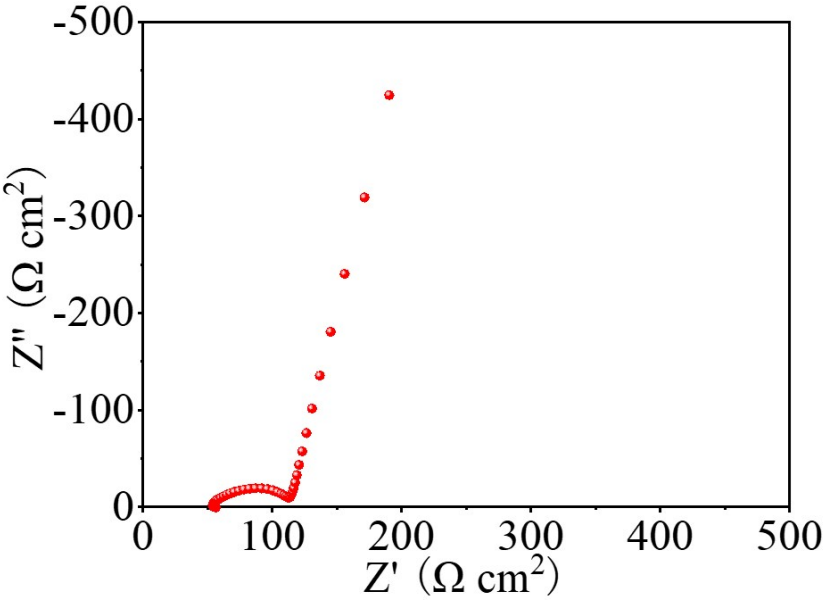

Figure S10. EIS plot of the Li|0.5LF-LLZTO|$LiCoO_2$ hybrid solid-state full cell with toothpaste-like cathode before cycling at 60℃.

Table S1. Comparison of electrochemical performances by different modification on garnet solid state electrolytes.

Surface modification materials	**Methods**	**Interfacial resistance ($\Omega \cdot cm^2$)**	**Cycling performance ($mA \cdot cm^{-2}$/hours)**	**Temperature**	**Ref.**
Carbon	Thermal reduction	45	0.1/450	65℃	1
Al	Ebeam evaporator	75	0.1/40 0.2/41	20℃	2
Graphite	Drawing	105	0.3/1000	RT	3
Ag	Magnetron Sputtering	66	0.1/100 0.2/100	RT	4
Al_2O_3	ALD	1	0.2/90	25℃	5
SnO_2	Magnetron sputtering	25	0.2/650	RT	6
MoS_2	Polishing	14	0.2/40	100℃	7
HCl	Acid treatment	26	0.2/700	30℃	8
Candle soot	Flame vapor deposition	50	0.1/450	60℃	9
Cu_3N	Magnetron sputtering	83.4	0.1/1000	RT	10
LiF	Vacuum evaporation deposition	12.7	0.2/1500 0.4/300	RT	This work

Table S2. Lattice parameters of cubic lithium, LiF, and LLZO obtained from first-principle calculation.

	Li	**LiF**	**LLZO**
Space group	*Fm-3m*	*Fm-3m*	$I4_1/acd$
a(Å)	4.404	4.083	13.069

Table S3. Lattice parameters, interfacial work of adhesion and contact angle of Li/LiF and Li/LLZO interface obtained from first-principle calculation.

Interface	**Li/LiF**	**Li/LLZO**
a(Å)	10.014	13.070
b(Å)	10.014	12.951
W_{ad} **(J m^{-2})**	0.82	0.63
Contact angle (°)	38	68

References

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