Electronic Supplementary Information for

The Role of Solid Electrolyte Interphase Layer in Preventing Li Dendrite Growth in Solid-State Batteries

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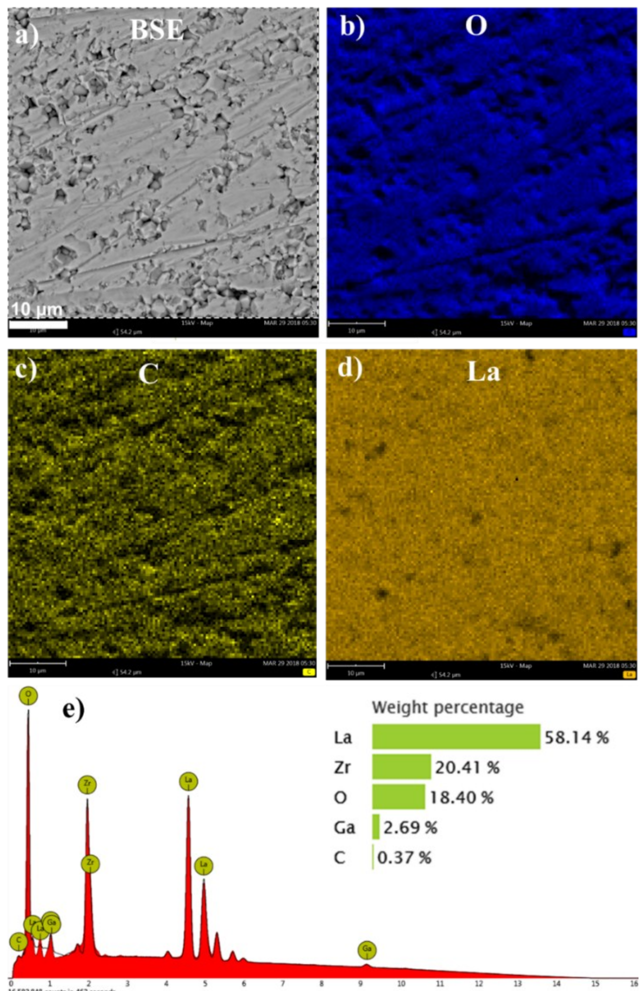

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Fig. S1 Phase and composition of fresh LLZO. a) Back scattered image; b)-d) elemental mapping of O, C, and La; e) EDS spectrum and element weight percentage.

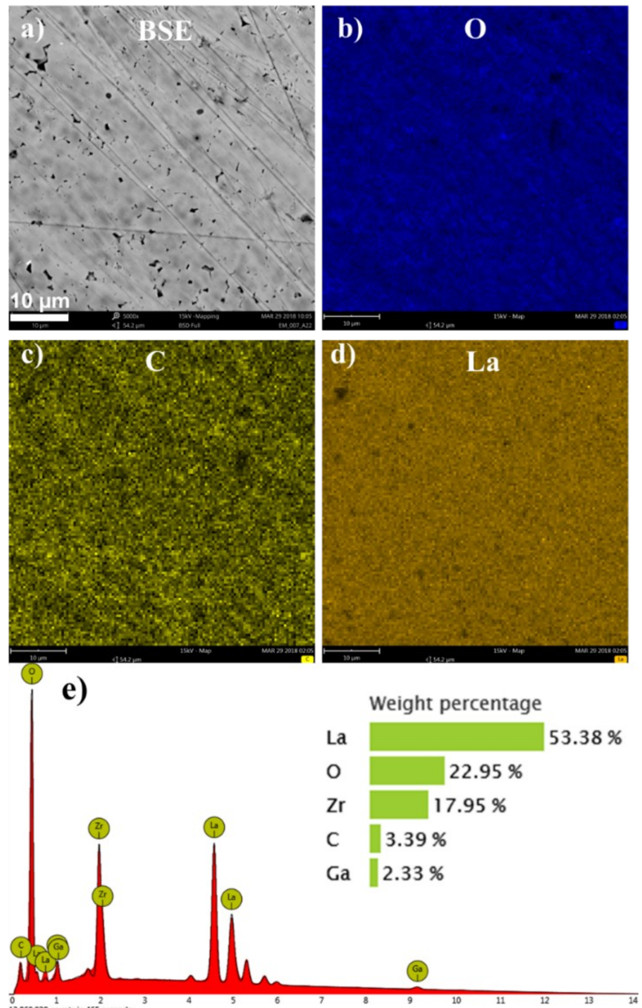


Fig. S2 Phase and composition of LLZO after exposed in lab environment (20 ^{o}C, 40% relative humidity) for 3 days. a) Back scattered image; b)-d) elemental mapping of O, C, and La; e) EDS spectrum and elemental weight percentage.

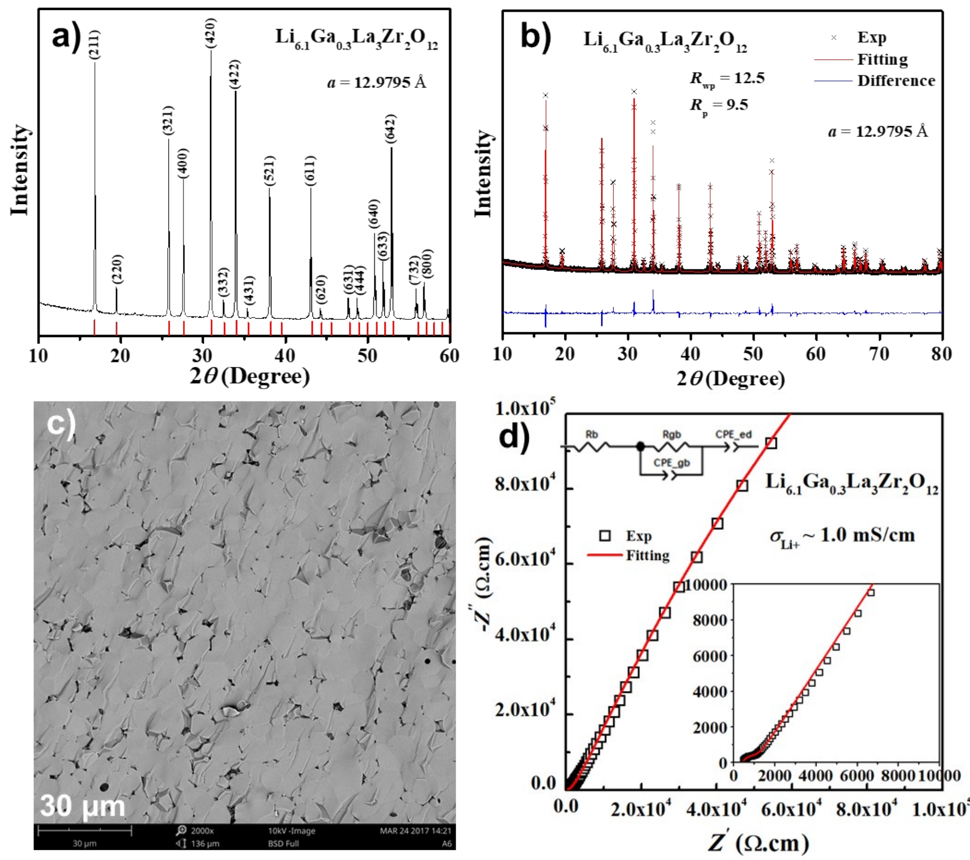


Fig. S3 a) XRD pattern and b) refinement; c) SEM image of fractural surface; d) Electrochemical Impedance Spectroscopy data (Nyquist Plot) of $Li_{6.1}Ga_{0.3}La_3Zr_2O_{12}$. The inset in d) shows the equivalent circuit used for Nyquist plot fitting, which consists of a serial combination of bulk resistance Rb, grain boundary resistance Rgb (paralleled with a constant phase element CPE_gb), and constant phase element CPE_ed representing the ion-blocking effect of Ag electrodes. The ionic conductivity $Li_{6.1}Ga_{0.3}La_3Zr_2O_{12}$ is estimated to be 1.0 mS cm^{-1} according to the σ=L/(Rb*A), where σ is the ionic conductivity of the LLZO, L is the thickness of the LLZO pellet and A is its area.

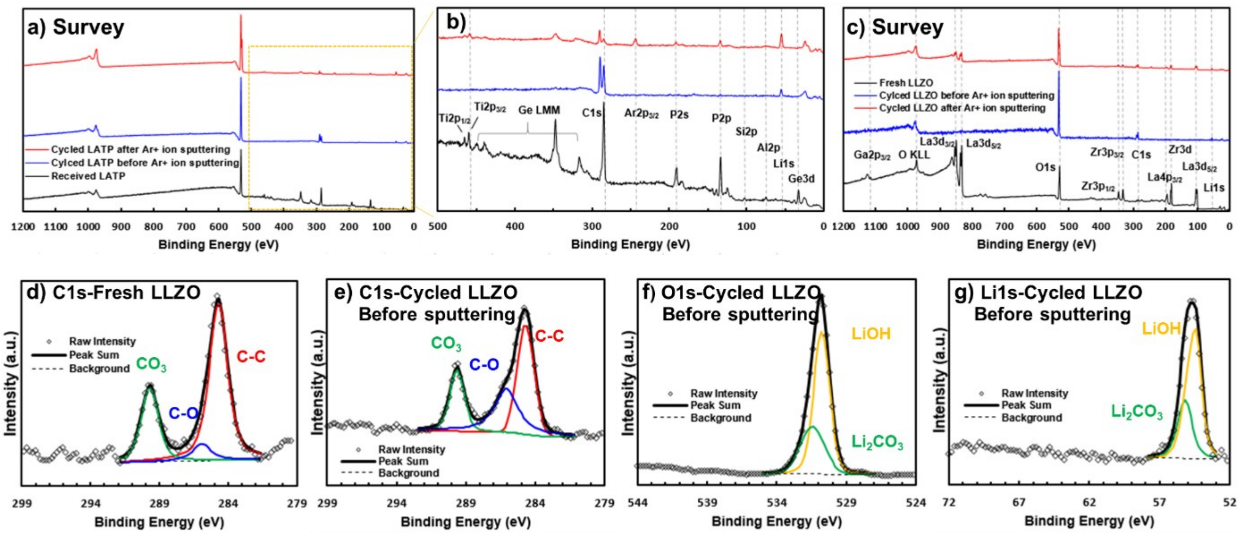


Fig. S4 XPS full survey of both fresh and cycled a) LATP and c) LLZO with or without an Ar^+ ion sputtering. b): enlarged image of (a) with the binding energy ranges from 0 to 500 eV; (d): C1s spectra of fresh LLZO; e-g): C 1s, O 1s, and Li 1s spectra of the cycled LLZO before Ar^+ ion sputtering.

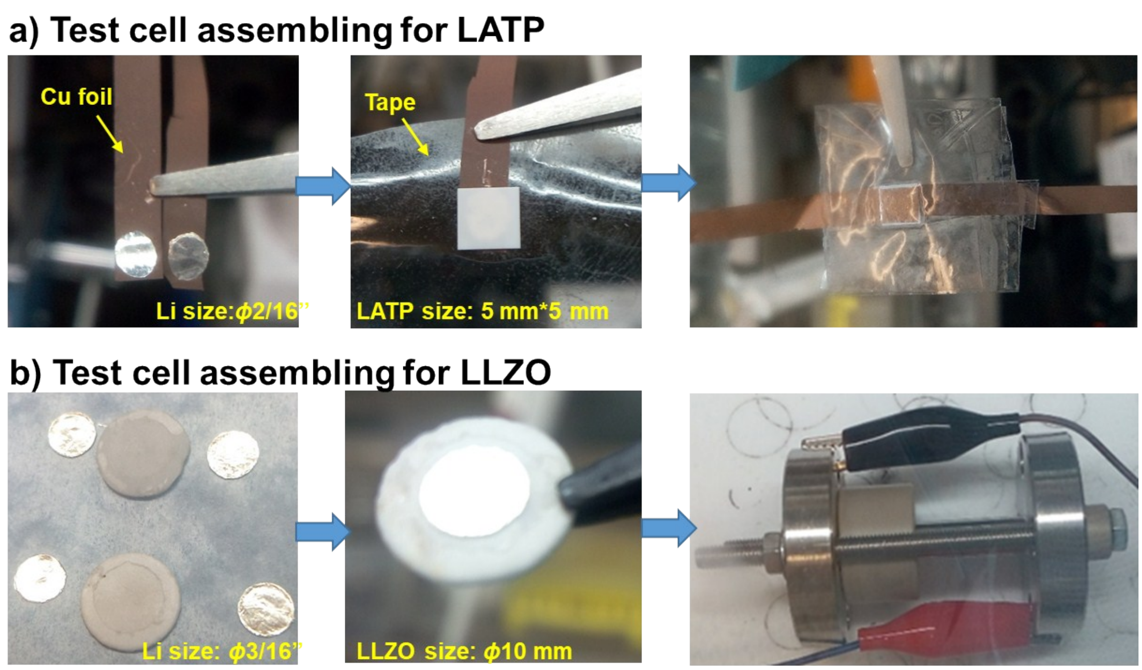


Fig. S5 Structures and assembling processes of a) Li/LATP/Li and b) Li/LLZO/Li symmetric cells.

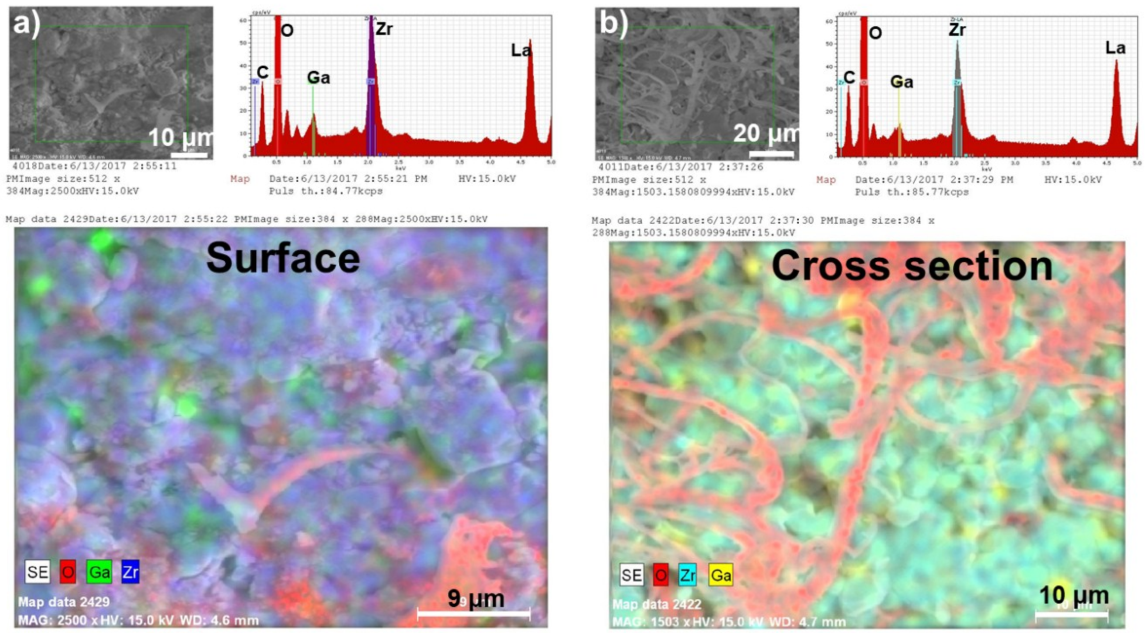


Fig. S6 EDS mapping of cycled LLZO after exposed in the air for 3 days. a) Surface; b) Cross section. O, Ga, and Zr were detected and analyzed.

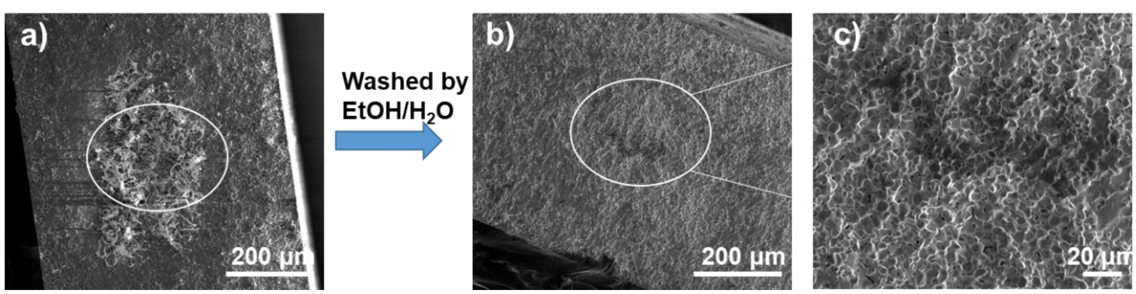
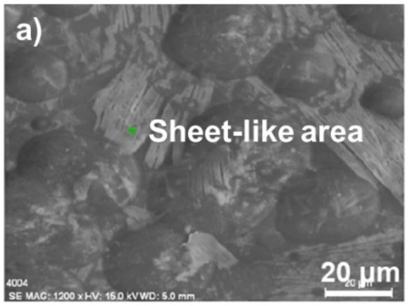
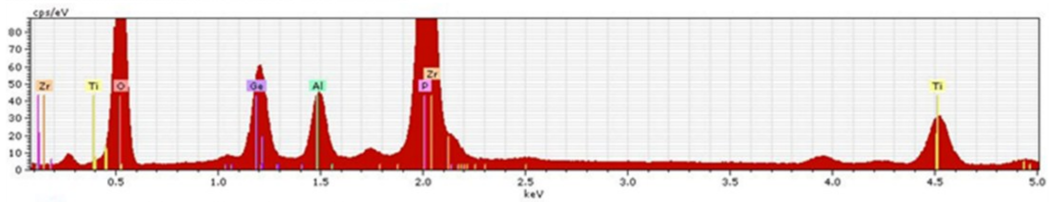
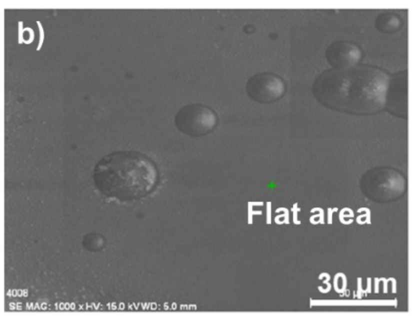


Fig. S7 SEM images of the cycled LLZO after exposed in the air for 3 days (a) (same image in Fig. 3c) and then washed by EtOH/H_2O (b) and its enlarged image (c). The fibers in (a) were completely removed after washed by EtOH/H_2O.

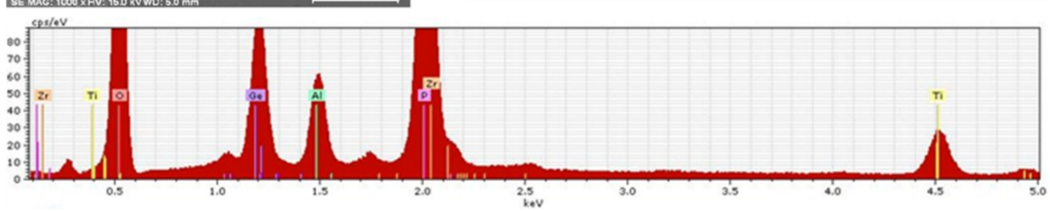


El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [wt.%]
O	8	K-series	29.71	44.24	68.28	3.3
P	15	K-series	13.40	19.95	15.91	0.5
Ti	22	K-series	8.18	12.17	6.28	0.3
Al	13	K-series	2.56	3.81	3.49	0.1
Ge	32	L-series	6.48	9.65	3.28	0.4
Zr	40	L-series	6.83	10.18	2.75	0.3
		Total:	67.16	100.00	100.00	





El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [wt.%]
O	8	K-series	38.73	45.04	69.62	4.4
P	15	K-series	15.04	17.49	13.97	0.6
Ti	22	K-series	8.19	9.52	4.92	0.3
Ge	32	L-series	11.53	13.41	4.57	0.7
Al	13	K-series	3.99	4.64	4.25	0.2
Zr	40	L-series	8.51	9.90	2.68	0.3
		Total:	85.99	100.00	100.00	



c)

Elements	Atomic percentage [at.%]	
	Sheet-like area in Fig. S8a	Flat area in Fig. S8b
O	68.28	69.62
P	15.91	13.97
Ti	6.28	4.92
Al	3.49	4.25
Ge	3.28	4.57

Fig. S8 EDS analysis of the cycled LATP surface after exposed in the air for 3 days. a) Sheet-like area; b) Flat area. O, P, Ti, Al, and Ge were detected and analyzed. c) Comparison of atomic percentages of the sheet-like area in (a) and flat area in (b).

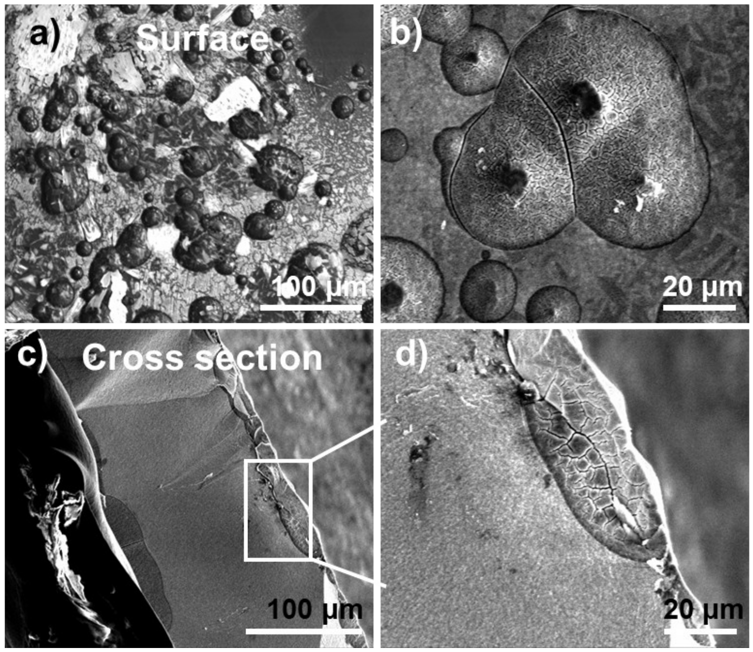


Fig. S9 SEM morphologies of a, b) surface and c, d) cross section of the cycled LATP in a lithium symmetric cell washed by EtOH/H_2O.

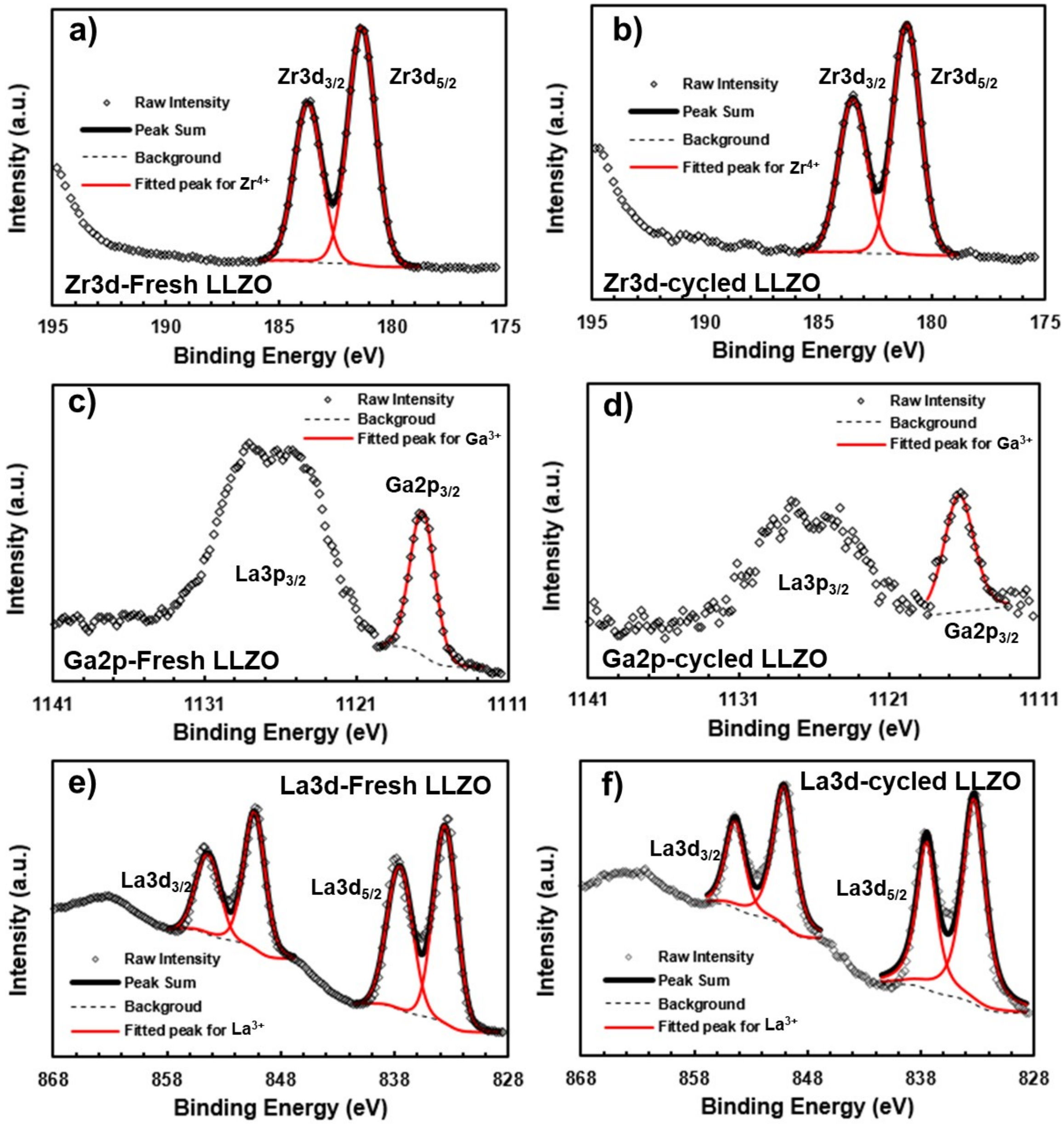


Fig. S10 XPS results of a, b) Zr *3d*, c, d) Ga *2p*, and e, f) La *3d* of LLZO before and after cycled in a Li/LLZO/Li symmetric cell.

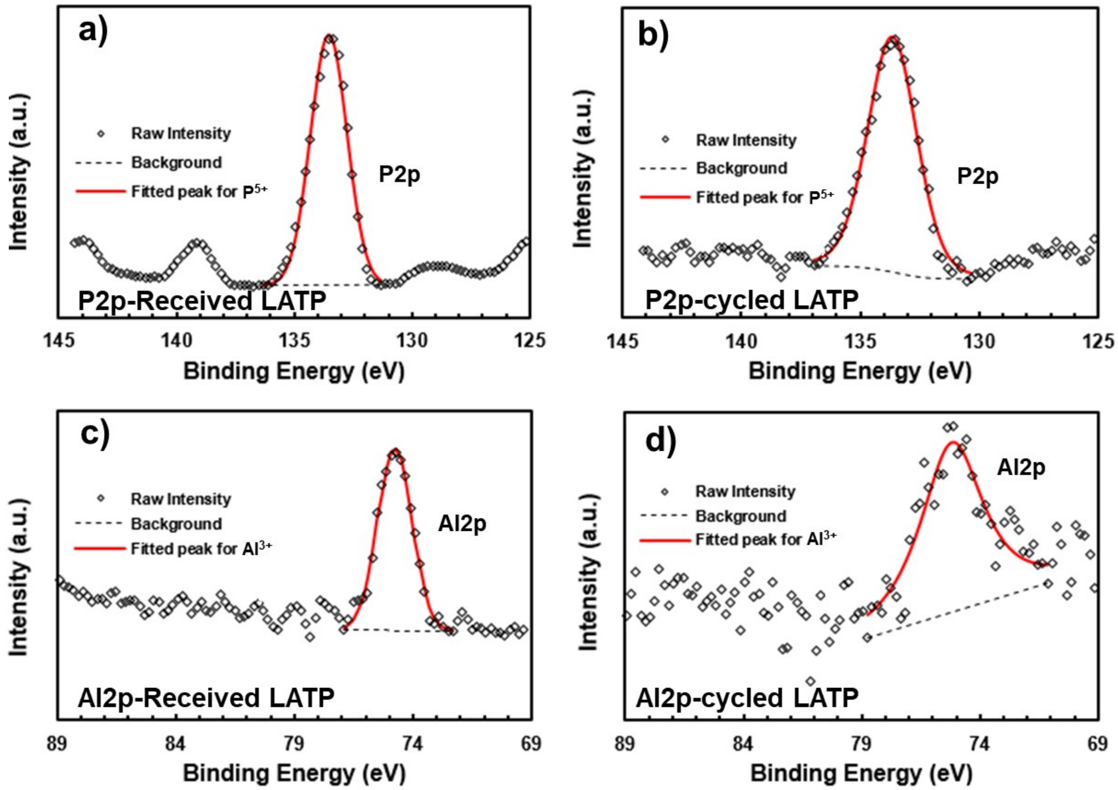


Fig. S11 XPS results of a, b) P *2p* and c, d) Al *2p* of LATP before and after cycled in a Li/LATP/Li symmetric cell.

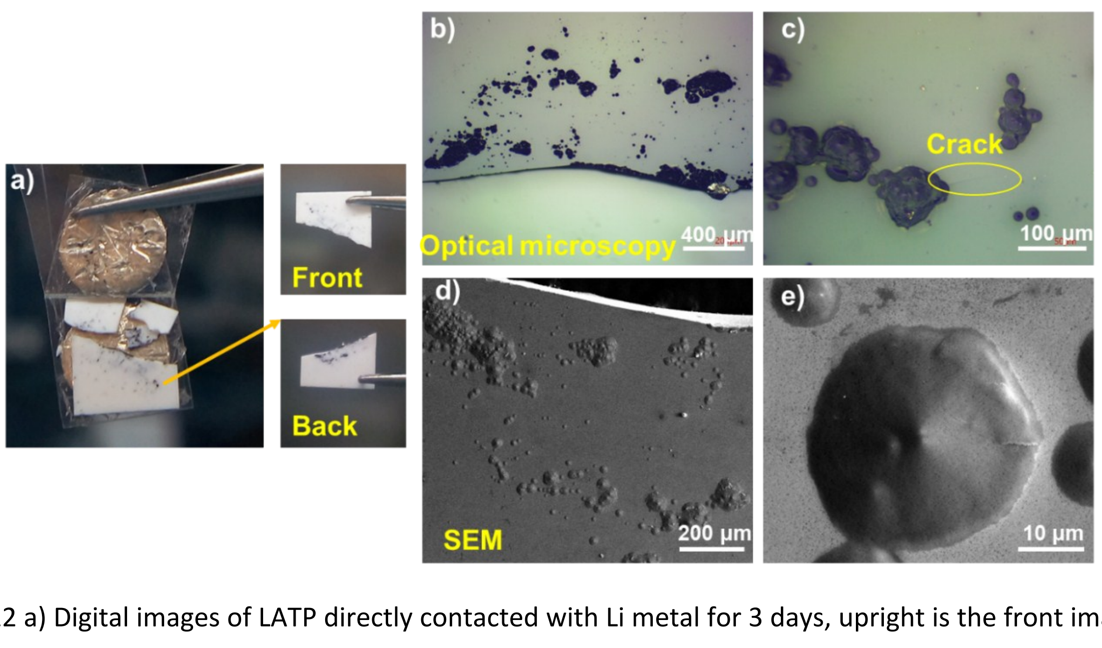


Fig. S12 a) Digital images of LATP directly contacted with Li metal for 3 days, upright is the front image of the broken LATP piece while the downright is the back. b, c): Optical images of the surface of LATP after contacted with Li metal; d, e): SEM images of the surface of LATP after contacted with Li metal.

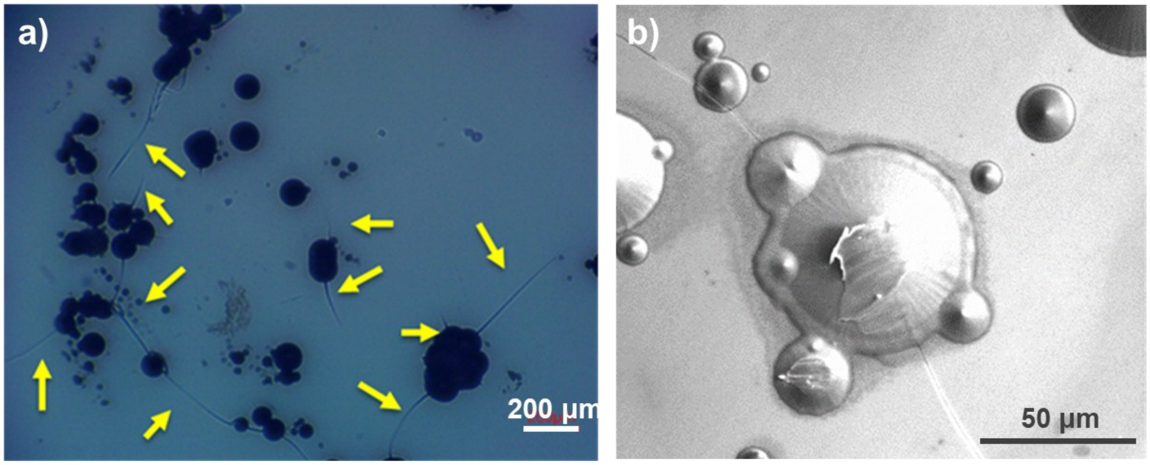


Fig. S13 a) Optical and b) SEM images of cracks on the surface of LATP after cycled in a lithium symmetric cell.

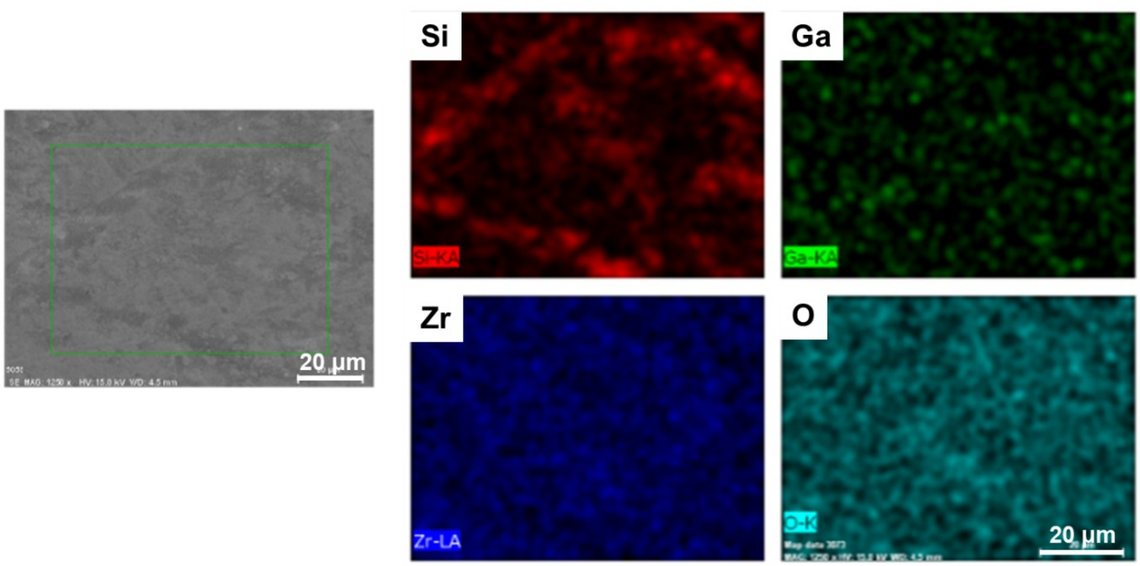


Fig. S14 EDS mapping of nano-Si polished LLZO. EDS mapping of Si, Ga, Zr and O were shown.

Table S1. Summary of XPS fitting results for LATP and LLZO before and after cycled in lithium symmetric cells.

SSEs	State	Element	Spectral Line	Binding Energy (eV)	FWHM (eV)	Area Ratio (%) a)
LATP	Fresh	Ti	$Ti2p_{1/2}$ (Ti^{4+})	465.2	1.98	33.3
			$Ti2p_{3/2}$ (Ti^{4+})	459.4	1.33	66.7
		Ge	Ge3d (Ge^{4+})	32.7	1.53	100
		Al	Al2p (Al^{3+})	74.8	1.71	100
		P	P2p (P^{5+})	133.5	1.83	100
	Cycled	Ti	$Ti2p_{1/2}$ (Ti^{4+})	464.3	2.15	21.1
			$Ti2p_{3/2}$ (Ti^{4+})	458.6	2.12	42.1
			$Ti2p_{1/2}$ (Ti^{3+})	462.6	1.91	12.3
			$Ti2p_{3/2}$ (Ti^{3+})	457.2	1.77	24.5
		Ge	Ge3d (Ge^{4+})	32.9	1.55	91.2
			Ge3d (Ge^{2+})	31.1	1.13	8.8
		Al	Al2p (Al^{3+})	75.2	3.14	100
		P	P2p (P^{5+})	133.6	2.42	100
LLZO	Fresh	Zr	$Zr3d_{3/2}$ (Zr^{4+})	183.7	1.44	39.3
			$Zr3d_{5/2}$ (Zr^{4+})	181.3	1.44	60.7
		Ga	$Ga2p_{3/2}$ (Ga^{3+})	1116.6	1.93	100
		La b)	$La3d_{5/2}$ (La^{3+})	833.5 837.5	2.42 2.65	56.5 43.5
	Cycled	Zr	$Zr3d_{3/2}$ (Zr^{4+})	183.5	1.48	40.6
			$Zr3d_{5/2}$ (Zr^{4+})	181.1	1.43	59.4
		Ga	$Ga2p_{3/2}$ (Ga^{3+})	1116.4	2.34	100
		La	$La3d_{5/2}$ (La^{3+})	833.3 837.5	2.39 2.05	61.5 38.5

a) Area ratio was normalized by the total area of each spectral line related to each element.
b) Doublet peak of $La3d_{5/2}$ by spin-orbit splitting with 4.0 eV of $\boldsymbol{\Delta E}$.

Table S2. Phase equilibria and Gibbs free energies of Li and $Li_{6.25}Ga_{0.25}La_3Zr_2O_{12}$

Phase Equilibria [a)]	ΔG (eV)
Li_5GaO_2, ZrO_2, La_2O_3, Li_2O	2.69
$Li_2Zr_2O_7$, $La_4Ga_2O_9$, La_5GaO_2, La_2O_3, Li_2O	2.38
$Li_2Zr_2O_7$, $La_4Ga_2O_9$, $LaZr_2O_4$, La_2O_3, Li_2O	2.82
$Li_2Zr_2O_7$, $La_4Ga_2O_9$, $LiZrO_2$, La_2O_3, Li_2O	3.22
$Li_2Zr_2O_7$, $La_4Ga_2O_9$, Li_3ZrO_3, La_2O_3, Li_2O	2.76
$La_2Zr_2O_7$, $La_3Ga_5O_{12}$, Li_5GaO_2, La_2O_3, Li_2O	7.90
$La_2Zr_2O_7$, $La_3Ga_5O_{12}$, $LiZrO_2$, La_2O_3, Li_2O	7.74
$La_2Zr_2O_7$, $La_3Ga_5O_{12}$, Li_3ZrO_3, La_2O_3, Li_2O	7.28
$La_2Zr_2O_7$, $La_3Ga_5O_{12}$, $LiZr_2O_4$, La_2O_3, Li_2O	8.34

a) Li and LLZO reactions involved in related phase equilibria above:

1. $4Li_{6.25}Ga_{0.25}La_3Zr_2O_{12} + 4Li \rightarrow Li_5GaO_2 + 8ZrO_2 + 6La_2O_3 + 12Li_2O$

   ΔG = 2.69 eV

2. $12Li_{6.25}Ga_{0.25}La_3Zr_2O_{12} + 4Li \rightarrow 12Li_2Zr_2O_7 + La_4Ga_2O_9 + La_5GaO_2 + 4La_2O_3 + 37Li_2O$

   ΔG = 2.38 eV

3. $8Li_{6.25}Ga_{0.25}La_3Zr_2O_{12} + Li \rightarrow 7Li_2Zr_2O_7 + La_4Ga_2O_9 + LaZr_2O_4 + 3La_2O_3 + 25Li_2O$

   ΔG = 3.35 eV

4. $8Li_{6.25}Ga_{0.25}La_3Zr_2O_{12} + 2Li \rightarrow 7Li_2Zr_2O_7 + La_4Ga_2O_9 + 2LiZrO_2 + 3La_2O_3 + 25Li_2O$

   ΔG = 3.75 eV

5. $8Li_{6.25}Ga_{0.25}La_3Zr_2O_{12} + 2Li \rightarrow 7Li_2Zr_2O_7 + La_4Ga_2O_9 + 2Li_3ZrO_3 + 3La_2O_3 + 23Li_2O$

   ΔG = 3.77 eV

6. $24Li_{6.25}Ga_{0.25}La_3Zr_2O_{12} + 4Li \rightarrow 24La_2Zr_2O_7 + La_3Ga_5O_{12} + Li_5GaO_2 + 10.5La_2O_3 + 74.5Li_2O$

   ΔG = 7.90 eV

7. $20Li_{6.25}Ga_{0.25}La_3Zr_2O_{12} + 2Li \rightarrow 19La_2Zr_2O_7 + La_3Ga_5O_{12} + 2LiZrO_2 + 9.5La_2O_3 + 62.5Li_2O$

   ΔG = 8.27 eV

8. $20Li_{6.25}Ga_{0.25}La_3Zr_2O_{12} + 2Li \rightarrow 19La_2Zr_2O_7 + La_3Ga_5O_{12} + 2Li_3ZrO_3 + 9.5La_2O_3 + 60.5Li_2O$

   ΔG = 8.29 eV

9. $20Li_{6.25}Ga_{0.25}La_3Zr_2O_{12} + Li \rightarrow 19La_2Zr_2O_7 + La_3Ga_5O_{12} + LiZr_2O_4 + 9.5La_2O_3 + 62.5Li_2O$

   ΔG = 8.87 eV

It is worth mentioning that the products Li_3ZrO_3, $LiZrO_2$, and $LiZr_2O_4$ in formulas 3, 4, 5, 7, 8, and 9 can be further decomposed into ZrO_2, ZrO_3, and Li_2ZrO_3, etc., but this will neither change the Gibbs free energies much nor the overall conclusion.