

Supplementary Information

Surface engineering of inorganic solid-state electrolytes via interlayers strategy for developing long-cycling quasi-all-solid-state lithium batteries

Ju-Sik Kim^{1†*}, Gabin Yoon^{1†}, Sewon Kim¹, Shoichi Sugata², Nobuyoshi Yashiro², Shinya Suzuki², Myung-Jin Lee¹, Ryounghee Kim¹, Michael Badding³, Zhen Song³, JaeMyung Chang³, Dongmin Im^{1*}

1 Battery Material Lab., Samsung Advanced Institute of Technology, 130, Samsung-ro, Yeongtong-gu, Suwon-si, Gyeonggi-do, Republic of Korea, 443-803

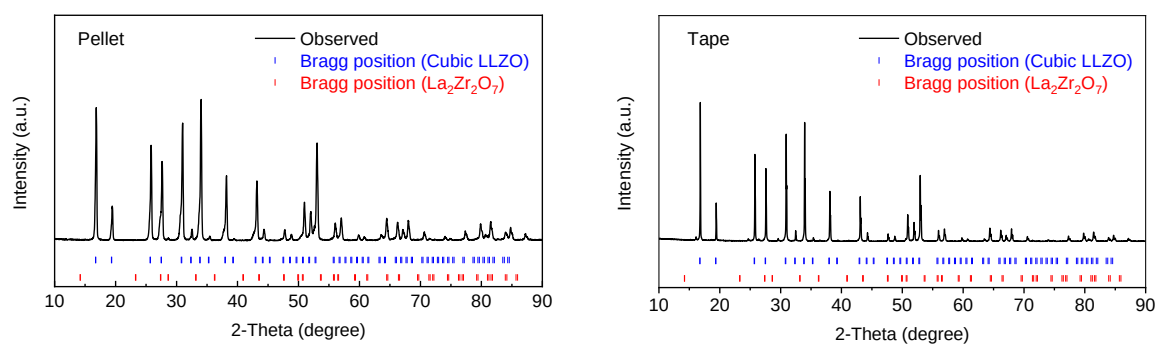
2 Samsung R&D Institute Japan, Samsung Electronics, 2-1-11, Semba Nishi, Minoh, Osaka, Japan

3 Sullivan Park Campus, Corning Incorporated, 21 Lynn Morse Rd, Painted Post, NY 14870, USA

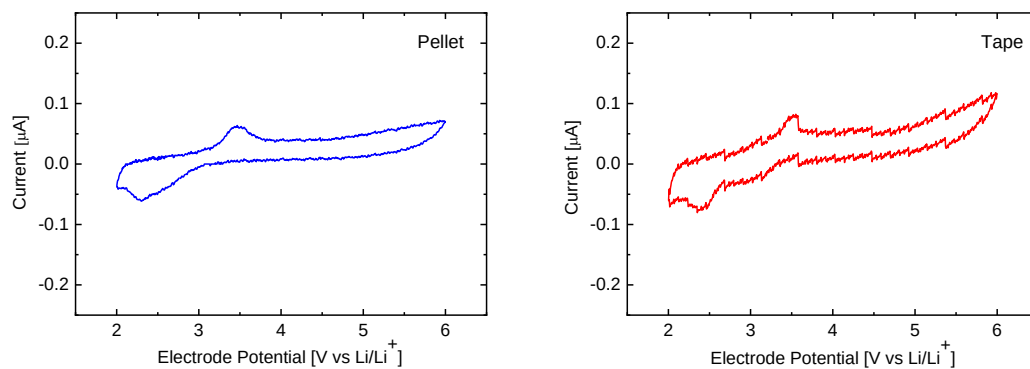
† Ju-Sik Kim and Gabin Yoon contributed equally to this study.

*Ju-Sik Kim: jusik.kim@samsung.com.

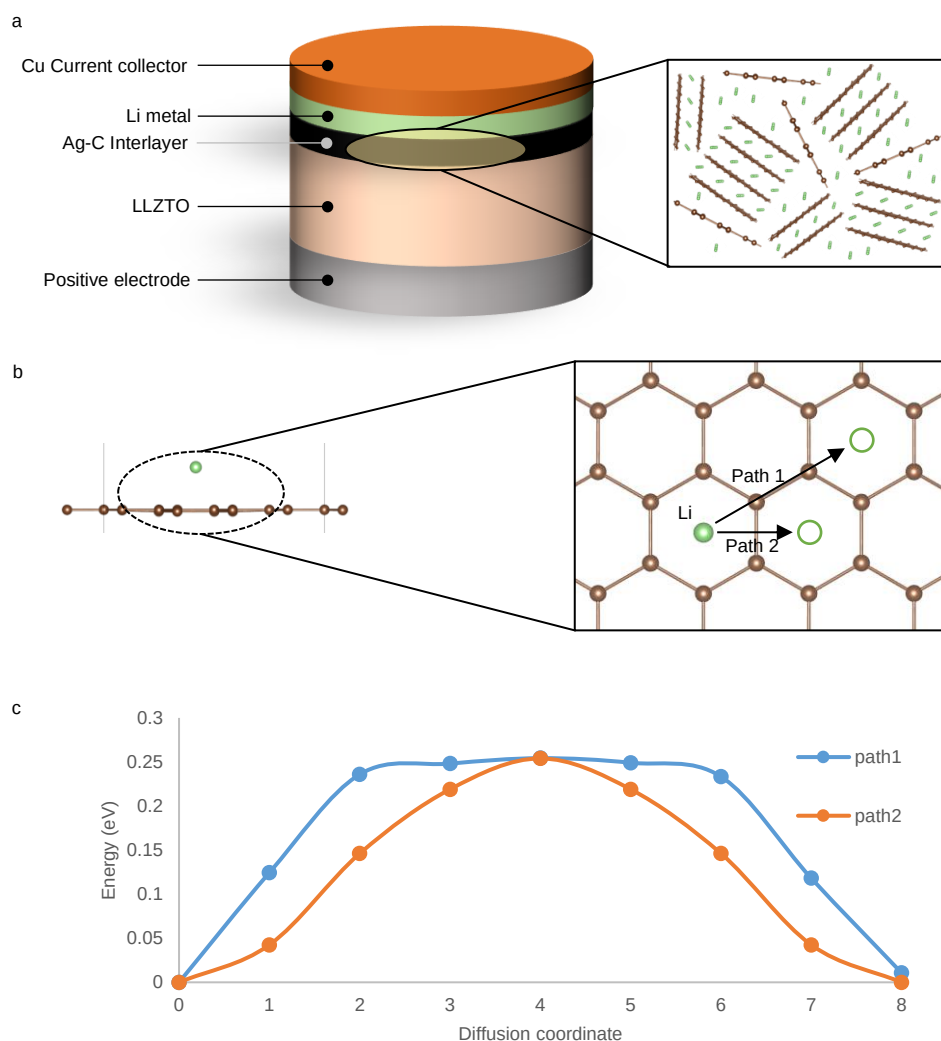
*Dongmin Im: dongmin.im@samsung.com



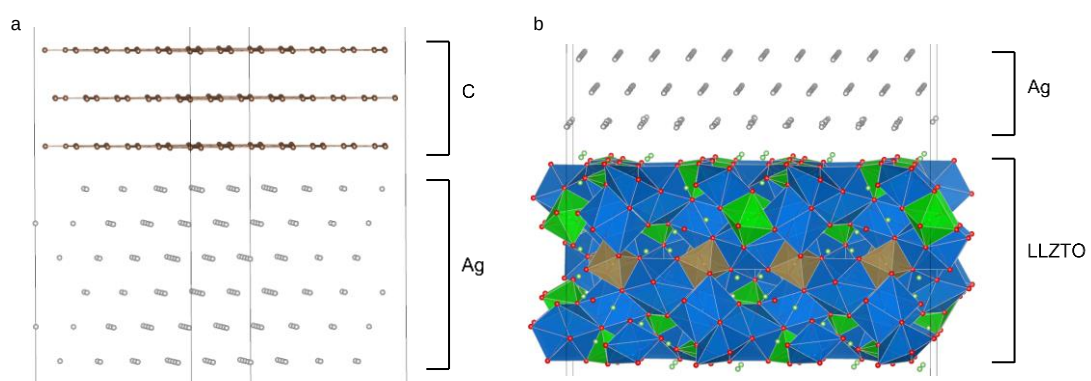
Supplementary Figure 1. **Crystal structure of LLZTO solid electrolytes.** X-ray powder diffraction (XRD) patterns of the pellet and tape LLZTO solid electrolytes.



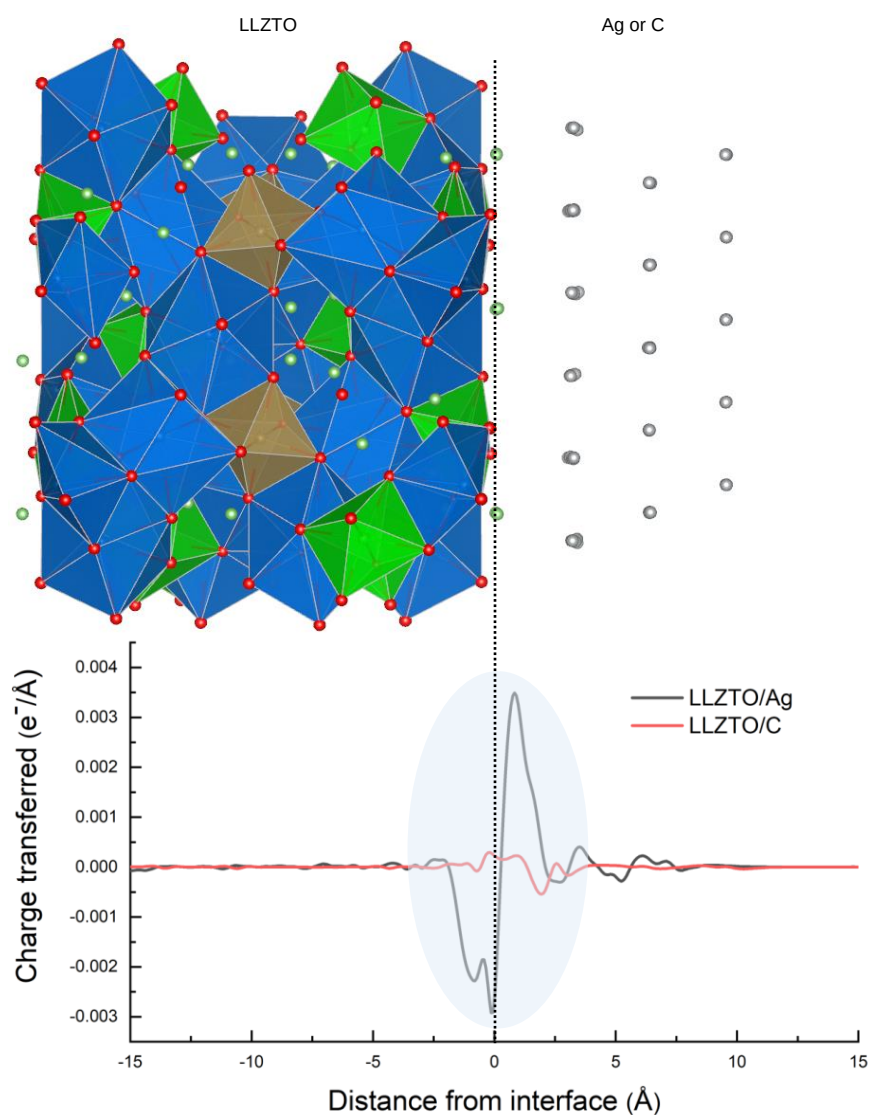
Supplementary Figure 2. **Electrochemical stability of LLZTO solid electrolyte.** Cyclic voltammograms of pellet and tape measured from Au|LLZTO|Li single-layer pouch cells at a scan rate of 0.2 mV s^{-1} at 25°C within the voltage range of 2–6 V vs. Li/Li^+ .



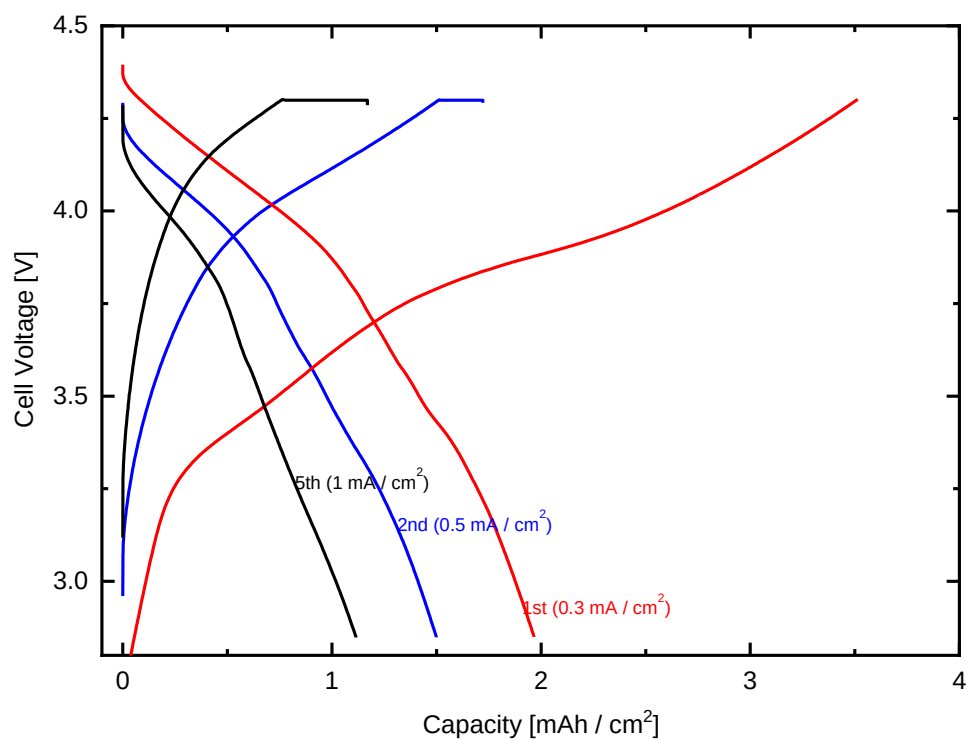
Supplementary Figure 3. **Surface diffusion of Li in the carbon component of Ag-C composite interlayer.** (a) Schematics of cell configuration using LLZTO solid electrolyte and Ag-C interlayer. Enlarged schematic illustrates Li distribution inside Ag-C interlayer. (b) Li diffusion pathways along the surface of carbon component of Ag-C composite interlayer. (c) Energy profiles of Li diffusion along the surface of carbon component of Ag-C composite interlayer.



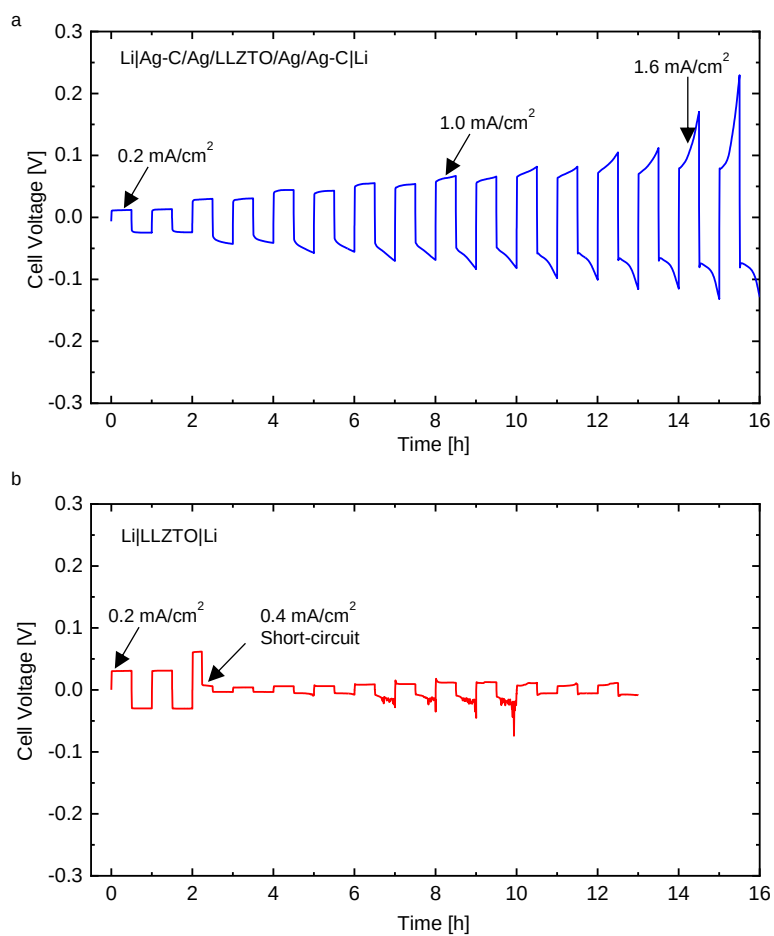
Supplementary Figure 4. **Atomic models of interfaces used for the calculation of adhesion energies.** (a) Ag/C interface model describing Ag/Ag-C interface. (b) Ag/LLZTO interface model.



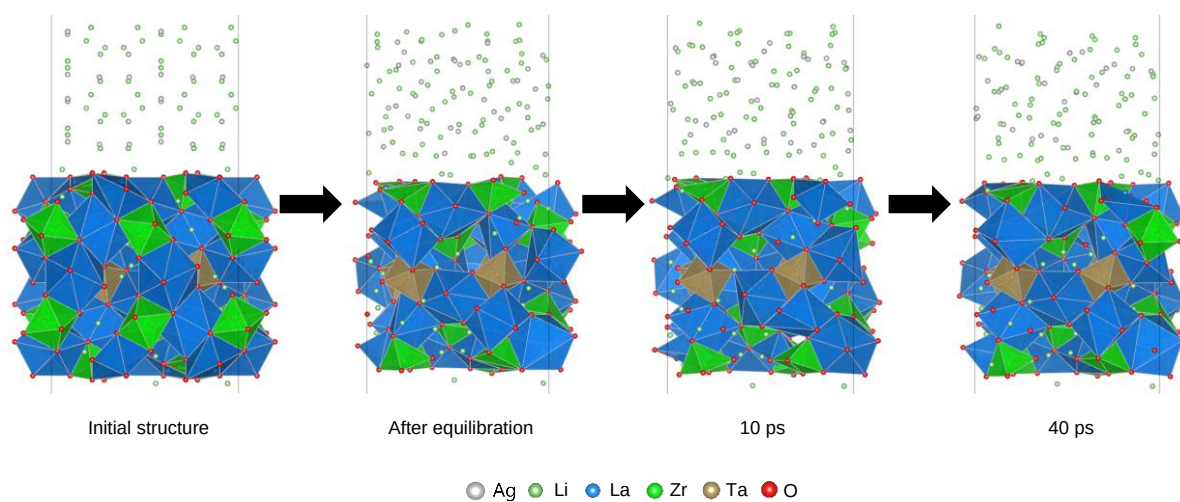
Supplementary Figure 5. **Comparison of plane-averaged differential charge densities at LLZTO/Ag and LLZTO/C interfaces.** It is clearly shown that a larger amount of charge is transferred at LLZTO/Ag interface compared to LLZTO/C interface, which may be responsible for stronger adhesion.



Supplementary Figure 6. **Electrochemical performance of anode-free cell.** Galvanostatic voltage profiles of the Cu|Ag-C/Ag/LLZTO/IL|NCM333 single-layer pouch cell at 25 °C.



Supplementary Figure 7. **Effect of Ag-C/Ag interlayer on dendrite inhibition.** Galvanostatic cycling of the symmetric pouch cells (a) with Ag/Ag-C interlayer and (b) without interlayer with increasing current densities from 0.2 to 1.6 mA/cm² with a step size of 0.2 mA/cm² at 25 °C.



Supplementary Figure 8. **Structure evolution of LLZTO/Li₉Ag₄ interface upon NVT AIMD simulation.** LLZTO/Li₉Ag₄ interface remains intact for at least 40 ps, suggesting that the interface possesses reasonable chemical stability.

Supplementary Table 1. Comparison of conductivities of LLZTO pellet and tape from the symmetric cells (Au | LLZTO | Au) by AC-impedance spectroscopy and Hebb–Wagner polarization method at 25°C. The ionic transference numbers were estimated from the electronic and ionic conductivities:

$$t_{Li^+} = \frac{\sigma_{Li^+}}{\sigma_e + \sigma_{Li^+}}. \text{ For data reliability, five symmetric cells for each electrolyte were evaluated.}$$

Sample	Ionic conductivity [S/cm]	Electronic conductivity [S/cm]	Ionic transference number, t_{Li^+}
LLZTO Pellet	5.1×10^{-4}	1.46×10^{-9}	0.999997
LLZTO Tape	4.4×10^{-4}	2.8×10^{-9}	0.999993

Supplementary Table 2. Calculated adhesion energies of various interfaces. LPSCl stands for argyrodite $\text{Li}_6\text{PS}_5\text{Cl}$.

Interface	LLZTO/C	LLZTO/Li	Cu/C	Cu/Li	Fe/C	Fe/Li	LPSCl/C	LPSCl/Li
Adhesion energy (J/m^2)	-0.330	-0.708	-0.595	-1.485	-0.698	-2.051	-0.167	-0.854

Supplementary Table 3. Sums of interfacial adhesion energies in two different Li plating scenarios. Adhesion energy of the Li/interlayer interface was omitted because it is accounted for in both scenarios. Detailed schematics of the two scenarios are shown in Figure 1. SUS stands for stainless steel, and the unit for all numerical values in the table is J/m².

Cases	Li plating at the electrolyte/interlayer interface (Figure 1a)	Li plating at the collector/interlayer interface (Figure 1b)
	Interfaces:	Interfaces:
	Collector/Interlayer + Li/Electrolyte	Collector/Li + Interlayer/Electrolyte
Electrolyte: LLZTO Current collector: Cu	$(-0.595) + (-0.708) = \mathbf{(-1.303)}$	$(-1.485) + (-0.330) = \mathbf{(-1.815)}$
Electrolyte: LLZTO Current collector: Fe (SUS)	$(-0.698) + (-0.708) = \mathbf{(-1.406)}$	$(-2.051) + (-0.330) = \mathbf{(-2.381)}$
Electrolyte: Li₆PS₅Cl Current collector: Cu	$(-0.595) + (-0.854) = \mathbf{(-1.449)}$	$(-1.485) + (-0.167) = \mathbf{(-1.652)}$

Supplementary Table 4. Fitting parameters determined from complex nonlinear least-squares (CNLS) fitting of the measured impedance spectra in Figure 5b.

Fitting parameters	Anode interlayer			
	Ag-C		Ag/Ag-C	
	Fit values	Error (%)	Fit values	Error (%)
$R_b [\Omega \text{ cm}^2]$	11.5	0.20	10.7	0.29
$R_l [\Omega \text{ cm}^2]$	39.4	1.05	22.8	1.58
$R_2 [\Omega \text{ cm}^2]$	27.0	1.57	9.7	4.37
$R_{ct} = R_l + R_2 [\Omega \text{ cm}^2]$	66.4		32.5	
$\text{CPE}_1\text{-T}$	1.17×10^{-6}	1.89	1.29×10^{-6}	2.42
$\text{CPE}_1\text{-n}$	0.96	0.39	0.97	0.50
$W_R [\Omega \text{ cm}^2]$	58.0	0.97	44.4	0.82
W-T	0.21	1.39	0.17	1.16
W-n	0.41	0.35	0.42	0.27
$\text{CPE}_2\text{-T}$	2.03×10^{-6}	3.69	5.41×10^{-6}	11.77
$\text{CPE}_2\text{-n}$	0.72	0.45	0.70	1.44
chi-square	1.58×10^{-5}		2.32×10^{-5}	

Supplementary Table 5. Parameters considered for estimating energy densities of the full cells at 25 °C.

Cathode	Composition	NCM333
	Areal capacity (mAh/cm ²)	3.2
	Active material (wt%)	96
	Thickness (μm)	50
Non-aqueous liquid electrolyte additive	Composition	2M LiFSI in Pyr13FSI
	Amount relative to cathode (wt%)	~ 7
Solid electrolyte	Initial thickness (μm)	80
	Thickness after acid treatment	74
Anode	Ag/Ag-C interlayer (μm)	6
	Li thickness (μm)	20
Current collector	Al for cathode (μm)	9
	Cu for anode (μm)	5
Total thickness (μm)		164
Cell area (cm²)		30.2
Cell volume including package film (L)		0.540
Discharge V_{ave} (V)		3.8
Energy density (Wh/L)		680

Supplementary Table 6. Summary of LLZO-based batteries reported in the literature. IL, LE, and PCE stand for ionic liquid, liquid electrolyte, and polymer composite electrolyte, respectively. Full cells, which are reversibly cycled around 100 times at room temperature, are presented.

(*) Thickness of electrolytes are not explicitly reported. Since pellets are used in those studies, we assumed a thickness of 1 mm in accordance with the typical thickness of LLZO pellets.

Cell structure	Cathode capacity (mAh/cm ²)	Current density (mA/cm ²)	Electrolyte thickness (μm)	Number of cycles	Reference
Li LLZO/LCBO LCO	0.09	0.006	1000	100	[1]
Li graphite/LALZWO/IL NCM523	0.15	0.1	1000	500	[2]
Li Ge/LLCZNO/Gel LFP	0.09	0.1	1000 (*)	100	[3]
Li LLZNO LCO	0.04	0.004	2000	100	[4]
Li LLZO/PCE LFP	0.43	0.04	900	300	[5]
Li Gel/LLCZNO/Gel LFP	0.04	0.05	450	70	[6]
Li LiF-LiCl/LLZTO/IL LFP	0.79	0.2	1000	100	[7]
Si LLZTO LFP	0.04	0.008	1000	100	[8]
Li LGLZNO/LE LFP	0.3	0.05	650	50	[9]
Li LLZTO-Li ₃ OCi/LE LFP	0.3	0.05	1000	110	[10]
Li graphite/LLZTO/LE LCO	0.18	0.02	130	100	[11]
Li Sb/LALZO/IL V ₂ O ₅	0.45	0.05	1000	80	[12]
Li LLZTO/LE LFP	0.32	0.07	1000 (*)	100	[13]
Li Al/LLCZN/LE LFP	0.13	0.1	300	100	[14]
Li LE/LLSZSO/LE LFP	0.45	0.05	1000 (*)	100	[15]
Li LLZTO/IL LFP	0.25	0.03	1000	150	[16]
Li Ag-C/Ag/LLZTO/IL NCM	2.7	1.6	80	800	This work

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