

Supplementary Information

A porous tellurium interlayer for high-power and long-cycling garnet-based quasi-solid-state lithium-metal batteries

Ju-Sik Kim^{1†*}, Gabin Yoon^{2†}, Yong Su Kim^{2†}, Tae-Hee Kim², Sewon Kim², Jirae Kim², Junhyeong Lee², Ryounghee Kim², Myung-Jin Lee², Nobuyoshi Yashiro³, Shinya Suzuki³, Tetsuya Asano³, Michael Badding⁴, Zhen Song⁴, Sung Heo^{5*}

1 Energy Solution Technical Unit, Samsung Advanced Institute of Technology, 130, Samsung-ro, Yeongtong-gu, Suwon-si, Gyeonggi-do, 16678, Republic of Korea

2 Battery Material Technical Unit, Samsung Advanced Institute of Technology, 130 Samsung-ro, Yeongtong-gu, Suwon-si, Gyeonggi-do, 16678, Republic of Korea

3 Energy Device Solutions Lab., DSRJ, Samsung Electronics, 2-1-11, Semba Nishi, Minoh, Osaka, Japan

4 Sullivan Park Campus, Corning Incorporated, 21 Lynn Morse RD, Painted Post, NY 14870, USA

5 Department of Semiconductor Convergence Engineering, Sungkyunkwan University (SKKU), Suwon, 16419, Republic of Korea

Keywords: Garnet solid electrolytes, Li-metal batteries, negative electrode interlayers, Li-metal/Garnet electrolyte interface

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

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

*Sung Heo: sung1.heo@samsung.com

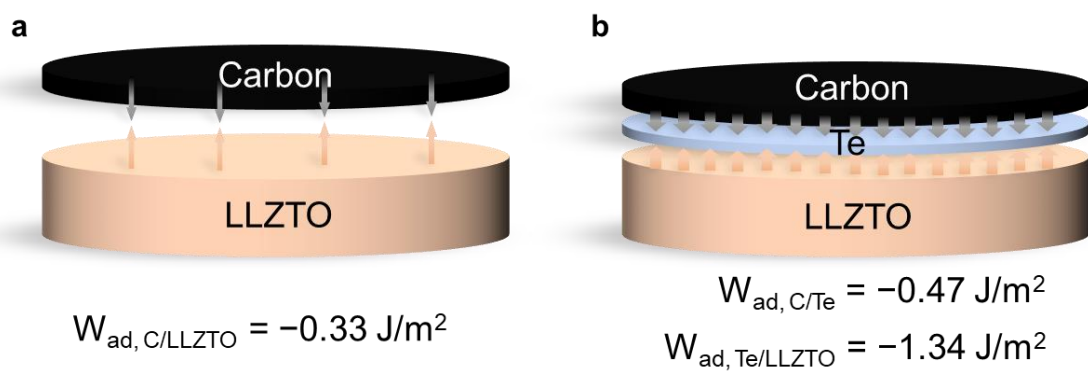


Fig. S1 | **Work of adhesion for different interfaces.** Calculated work of adhesion (W_{ad}) for (a) the carbon/LLZTO interface, and (b) the carbon/Te and Te/LLZTO interfaces.

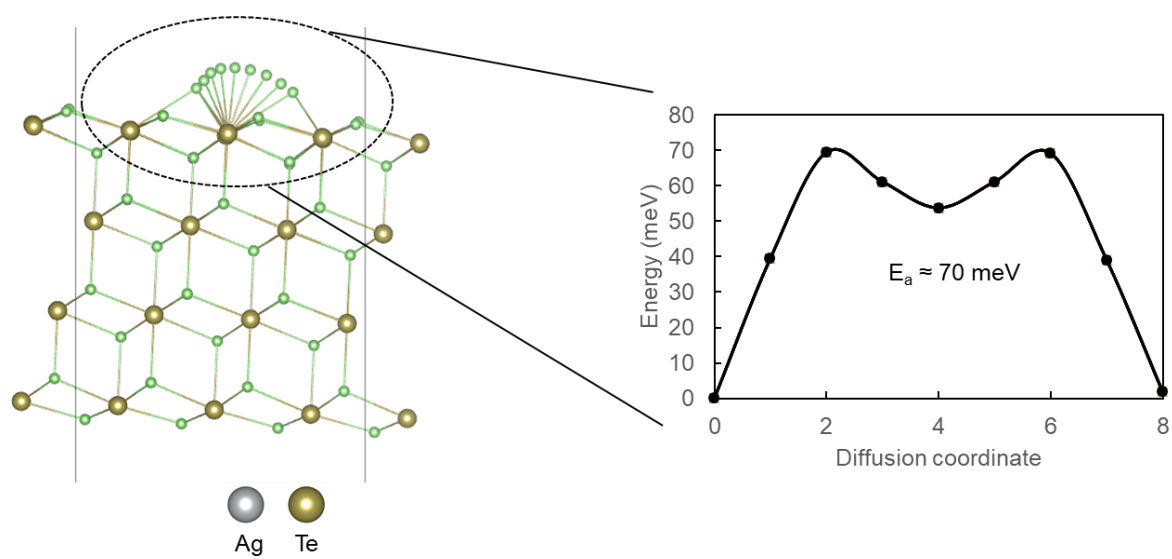


Fig. S2 | **Li migration barrier at the surface of Li_2Te .** Calculated activation barrier of Li diffusion at the Li_2Te surface.

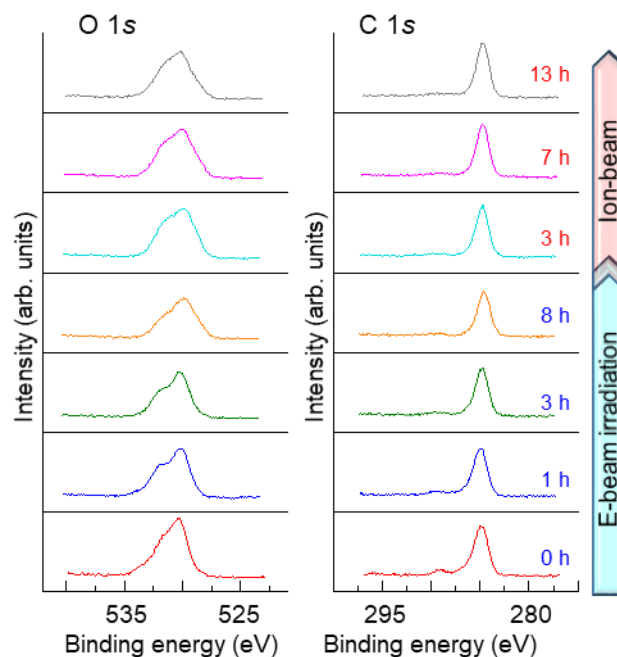


Fig. S3 | **Core level spectra change.** Change in the core level spectra of the LLZTO electrolyte during Li-ion migration.

O 1s spectrum contains contributions from oxygen bound to Te, oxygen in the solid electrolyte, and oxygen associated with surface contaminants such as carbon. However, the binding energies of these species are not sufficiently distinct to allow clear and precise peak separation. Consequently, peak fitting of the O 1s spectrum does not yield accurate results (Fig. S3). For the same reason, accurate deconvolution of the Li 1s spectrum through peak fitting is also challenging. Despite the challenges in peak fitting for O 1s and Li 1s, the spectral separation of Te-metal, Li-Te alloy, and Te oxides (e.g., TeO_2) is relatively well-defined, allowing for a relatively precise analysis of changes in Li plating and stripping near the interface. (Figs. 2(d) and 2(e))

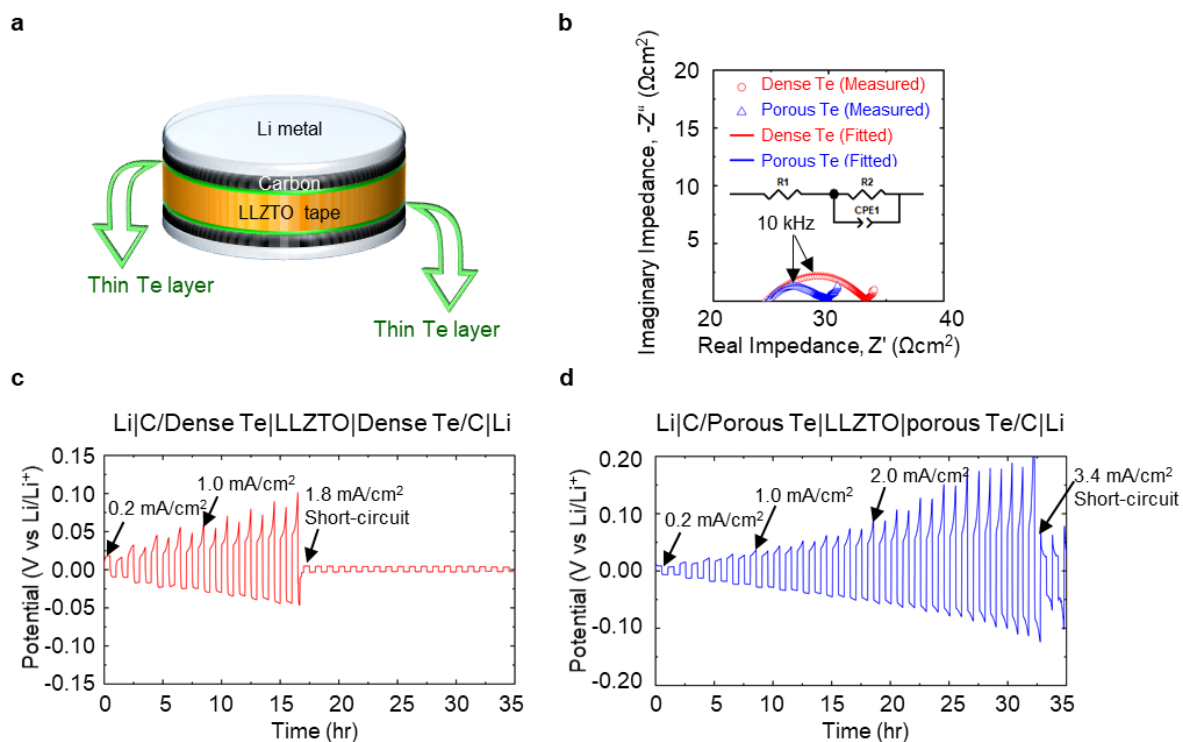


Fig. S4 | **Comparison of dense Te and porous Te layer.** (a) Schematic of the assembled $\text{Li}|\text{C}/\text{Te}|\text{LLZTO}|\text{Te}/\text{C}|\text{Li}$ cell. (b) Nyquist plots of the AC impedance spectra obtained from the cell (inset: equivalent circuit). Galvanostatic cycling tests recorded with an increasing current density using (c) dense Te and (d) porous Te layers.

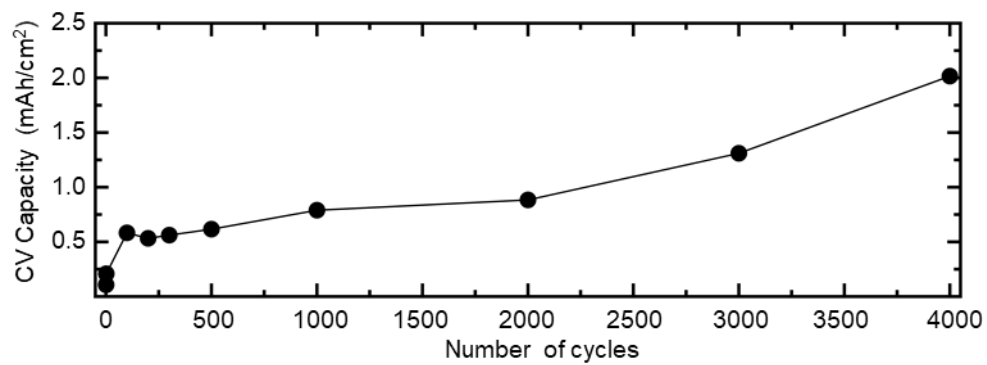


Fig. S5 | **Constant voltage capacity upon cycles.** Constant voltage (CV) capacity of the Li|C/Te|LLZTO|LCO-EMIFSI (2M LiFSI) single cell per cycle.

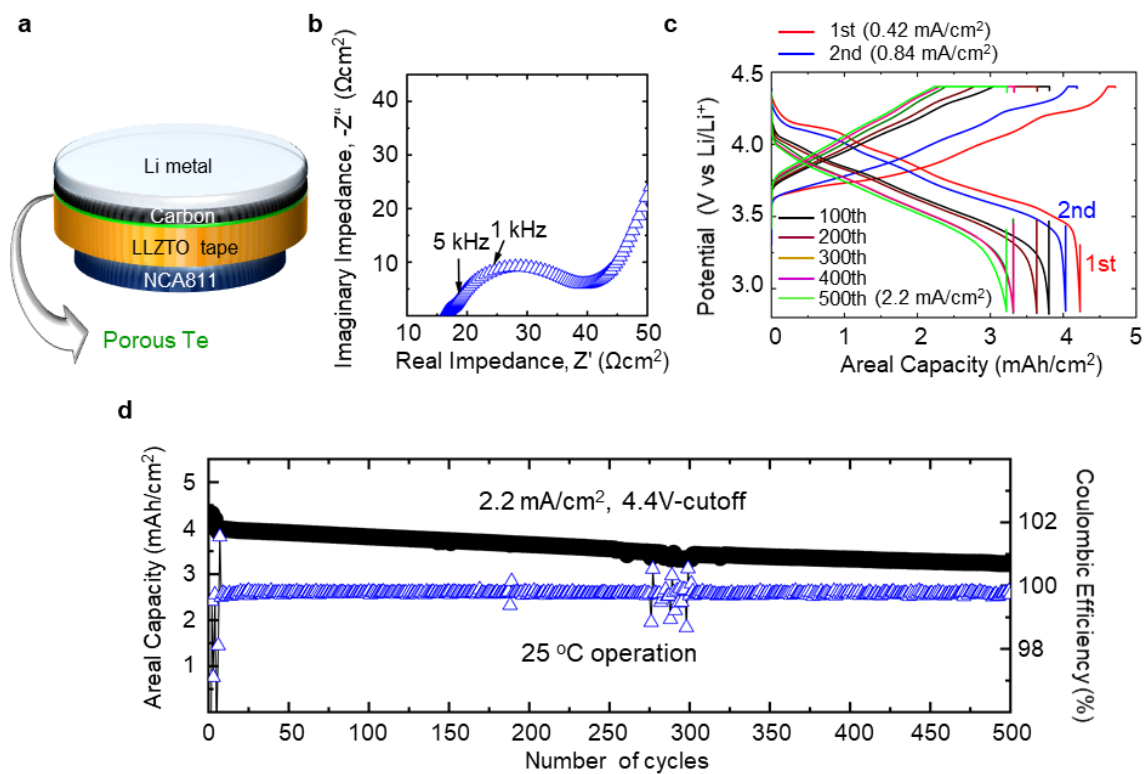


Fig. S6 | **Electrochemical tests employing carbon-only interlayer.** (a) Schematic of the assembled Li|C/Te|LLZTO|NCA811 cell (1 C-rate = 205 mA/g). (b) Nyquist plots of the AC impedance spectra obtained from the cell. (c) Galvanostatic voltage profile of the cell. (d) Cycling performance of the quasi-all-solid-state lithium-metal battery.

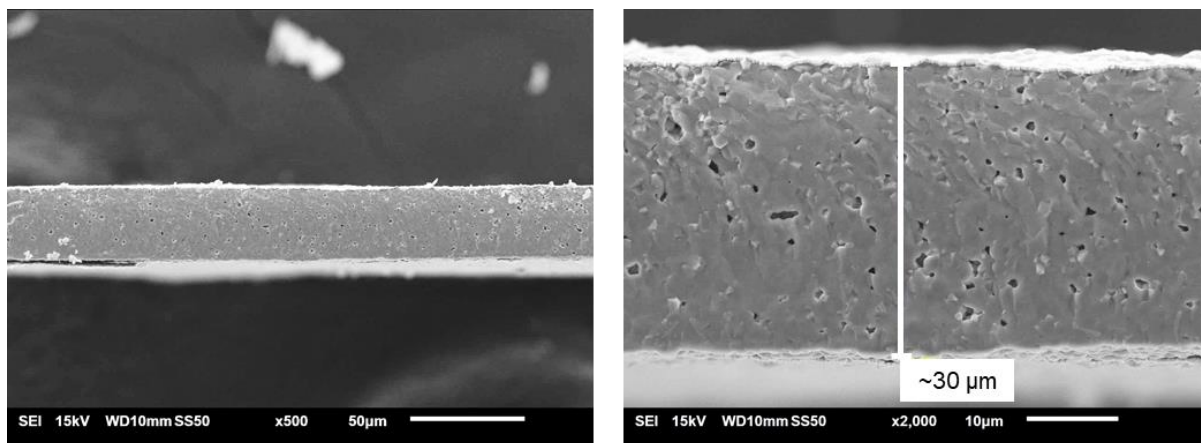


Fig. S7 | **Thickness of thin LLZTO solid electrolyte used.** SEM images of the as-prepared thin LLZTO solid electrolyte (~30 μm).

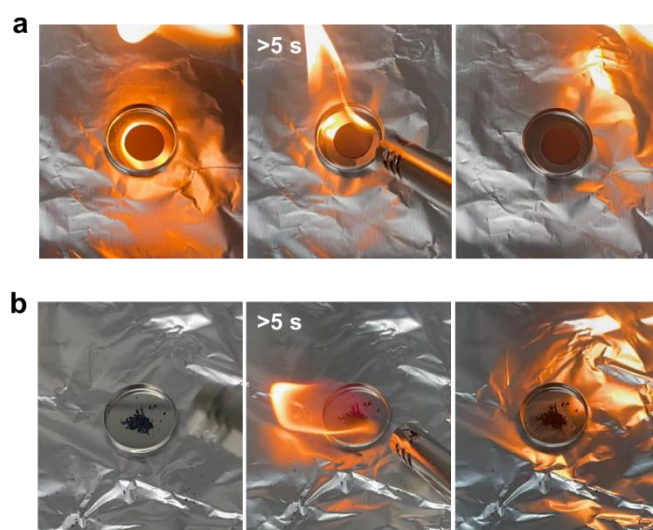


Fig. S8 | **Flammability tests for LCO electrodes.** Flammability tests for (a) the charged LCO electrode and (b) the LCO powder scraped off the charged cells. The positive electrodes contain 2 M LiFSI in EMIFSI as the ionic liquid.

Supplementary Table S1. Fitting parameters determined from complex nonlinear least-squares (CNLS) fitting of the measured impedance spectra in Fig. S4.

Fitting parameters	Negative electrode			
	Dense Te / Ag-C / Li		Porous Te / Ag-C / Li	
	Fit values	Error (%)	Fit values	Error (%)
$R_1 [\Omega \text{ cm}^2]$	24.51	0.44	24.79	0.23
$R_2 [\Omega \text{ cm}^2]$	8.65	0.65	4.98	1.40
$\text{CPE}_1\text{-T}$	9.3×10^{-6}	9.40	3.99×10^{-5}	20.99
$\text{CPE}_1\text{-n}$	0.73	1.29	0.69	0.84
chi-square	7.74×10^{-4}		4.84×10^{-3}	

Supplementary Table S2. Parameters used for estimating energy densities of the full cells.

Positive electrode	Composition	NCM811
	Areal capacity (mAh/cm ²)	4.4
	Thickness (μm)	62
Solid electrolyte	Initial thickness (μm)	140
Negative electrode	Te/AgC interlayer (μm)	6
	Li thickness (μm)	20
	Increased thickness after charging	22
Current collector	Al for positive electrode (μm)	9
	Cu for negative electrode (μm)	9
Total thickness (μm)		246
Cell volume including package film (L)		0.880
Discharge V_{ave} (V)		3.75
Energy density (Wh/L)		519

Supplementary Video 1

To evaluate the safety of the quasi-all-solid-state Li-metal batteries, a nail penetration test was conducted using a single pouch cell of capacity 100 mAh (Supplementary Video 1). After the first formation cycle at 4.5 V (vs. Li^+/Li) at 0.05 C, the cell was charged to SOC 40% (3.92 V) and then placed in a test chamber. A metal nail with a diameter of 3 mm was used to penetrate the cell at a speed of 5 mm/s, and the changes in the cell voltage were recorded during the test. The cell did not experience thermal runaway, emit smoke, ignite, or explode. Although a temporary short circuit occurred during the penetration test, the cell voltage returned to its initial value (3.92 V) after completion of the test.

