

Supporting Information

A surface sulfurization strategy for tuning the lithiophilicity of garnet electrolyte pellets towards advanced solid-state Lithium metal electrolyte

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Methods

Computational methods and models. All calculations were carried out by using the projector augmented wave method in the framework of the density functional theory^[1], as implemented in the Vienna ab-initio Simulation Package (VASP). The generalized gradient approximation (GGA) and Perdew–Burke–Ernzerhof (PBE) exchange functional^[1] was used. Structural relaxation calculations were performed by using the spin-polarized GGA method^[2]. For the interface calculations with large supercells, we just need to use the $1 \times 1 \times 1$ k-mesh. The convergence criterions of energy and force calculations were set to 10^{-5} eV/atom and 0.01 eV \AA^{-1} , respectively. The Li_2CO_3 (001)/Li (001) and Li_2S (001)/Li (001) interface models were constructed by Li_2CO_3 (001) slab, Li_2S (001) slab and Li (001) slab, which are the low-energy surfaces^[3-5]. The coherent interface approximation was applied, in which the soft Li (001) 4×4 surface slabs are less strained to match the Li_2S (001) 2×2 surface slabs. The Li (001) 3×2 surface slab is less strained to match the Li_2CO_3 (001) 1×1 surface slab.

To evaluate the wettability of Li metal on the Li_2CO_3 and Li_2S surfaces, we calculated the interface formation energies of Li_2CO_3 (001)/Li(001) and Li_2S (001)/Li (001) systems, which can be evaluated by the energy difference between an interface system and the bulk energy of the two materials that comprise it, $E_f = (E_{ab} - N_a * E_a - N_b * E_b) / 2S$ ^[6], here, E_{ab} denotes the total energy of the complete system containing the interface, and it depends on how many formula units of materials a and b comprise the interface (N_a and N_b , respectively). E_a and E_b denote the bulk energy per formula unit for materials a and b, respectively, and S refers to the interfacial area, 2 means two interfaces in the interface models.

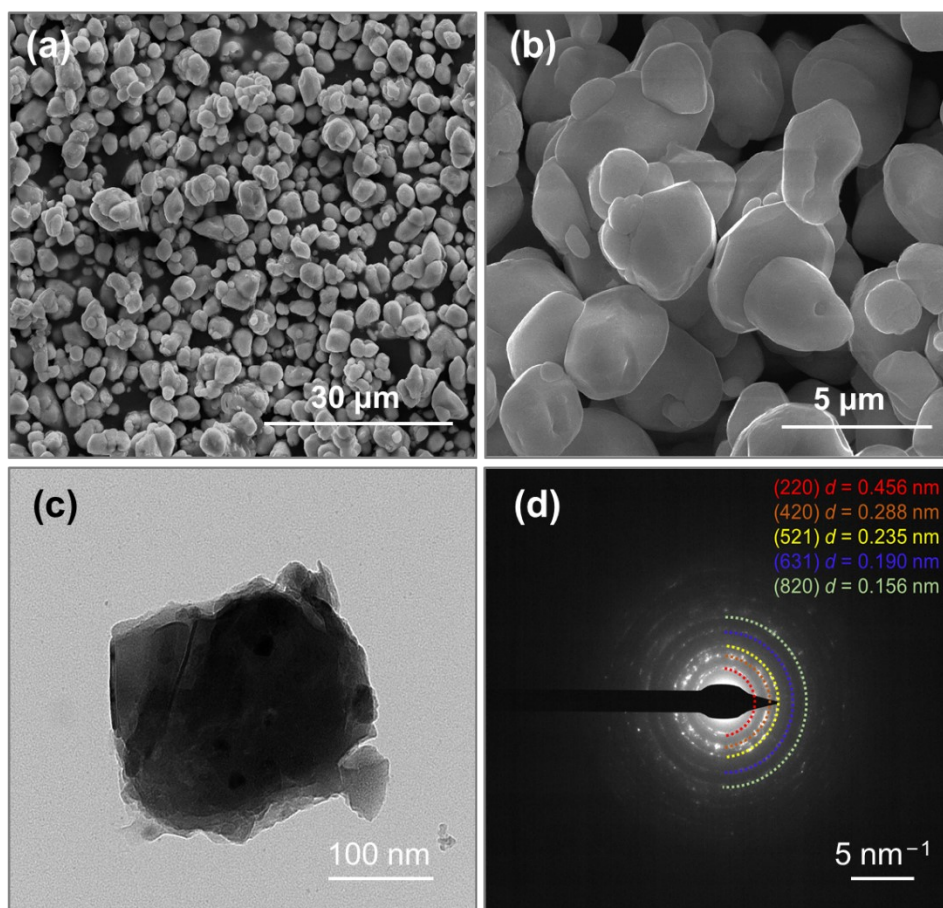


Figure S1 (a), (b) SEM images of LLZT particles at different magnifications, (c), (d) TEM image of LLZT@LS particle and corresponding SAED pattern.

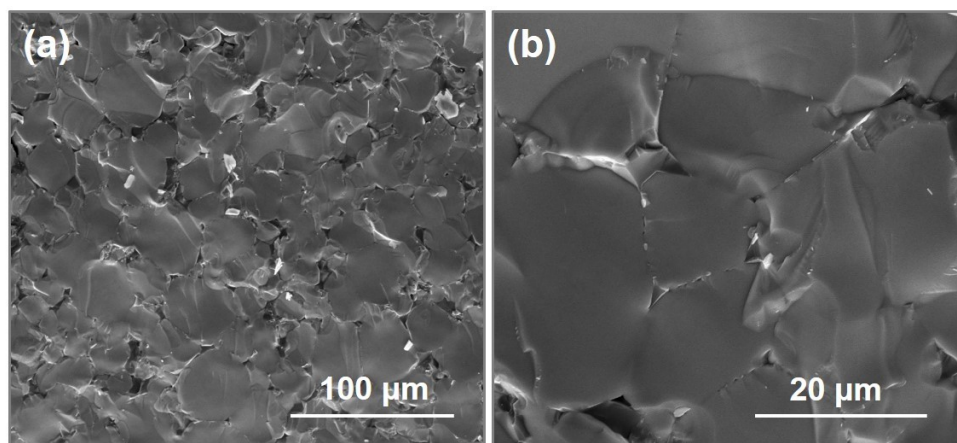


Figure S2 (a), (b) Cross-section SEM images of LLZT pellet at different magnifications.

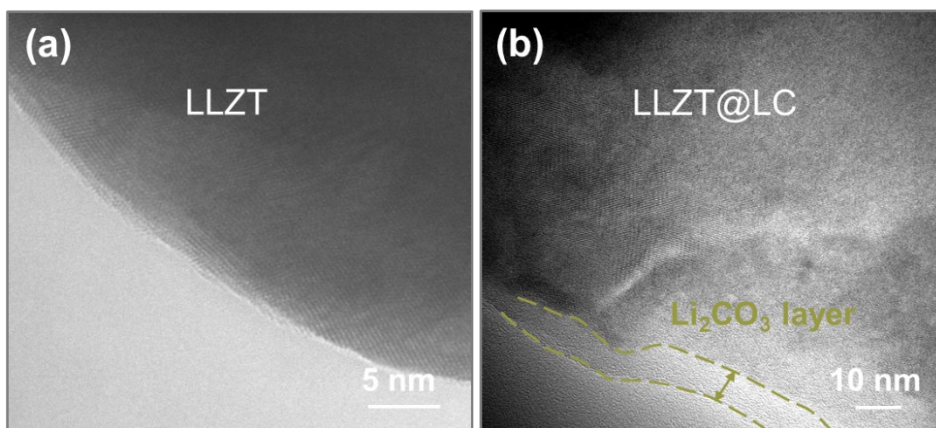


Figure S3 (a), (b) TEM image of LLZT and LLZT@LC particles, respectively.

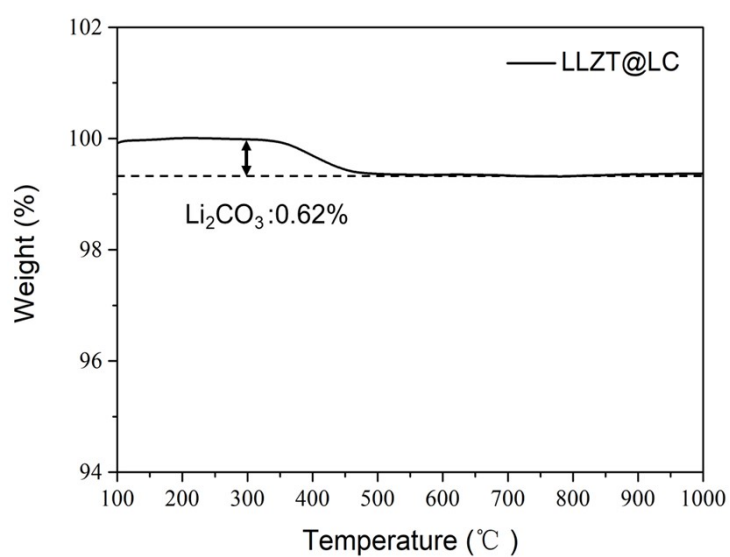


Figure S4 TGA curve of LLZT@LC particles.

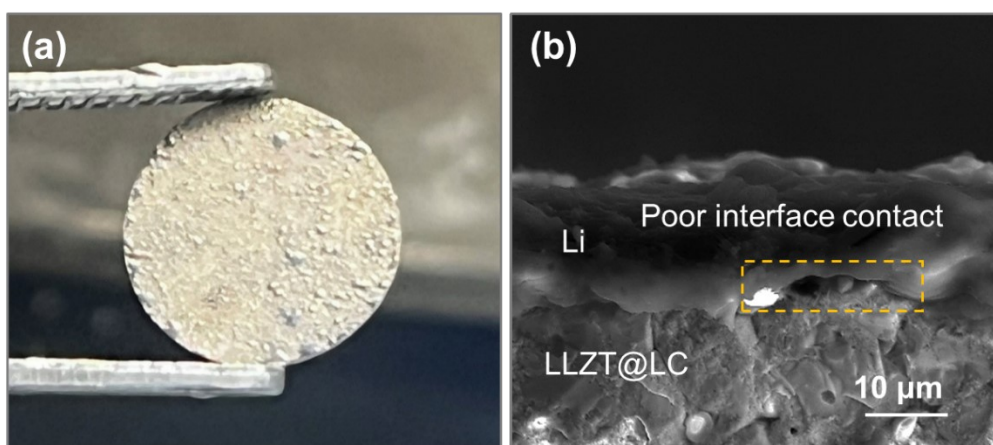


Figure S5 (a) Optical image of molten lithium on LLZT@LC by repeated rubbed, (b) Surface SEM images of LLZT@LC after rub-coating molten Li.

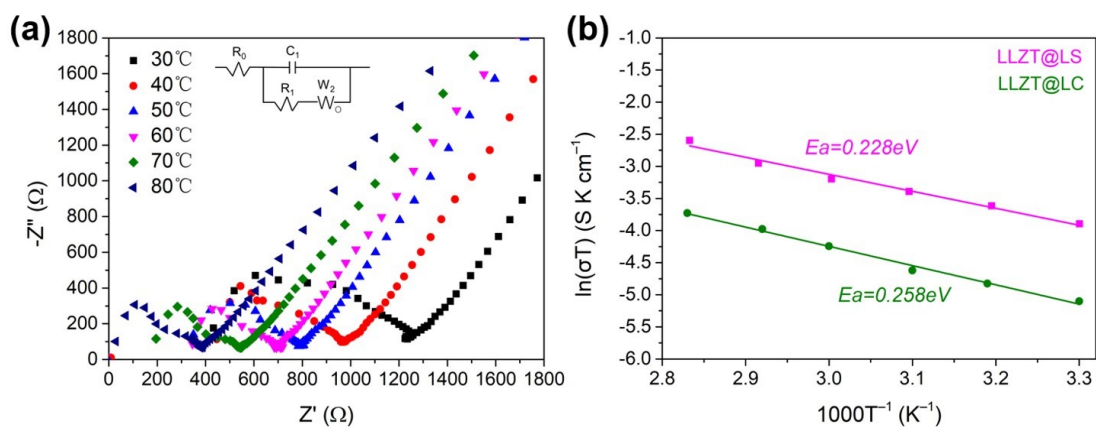


Figure S6 (a) Nyquist plots of the LLZT@LS pellets at temperatures arranged from 30 °C to 80 °C, the inset shows the equivalent circuit, (b) Arrhenius plots of the ionic conducting for the LLZT@LS and LLZT@LC.

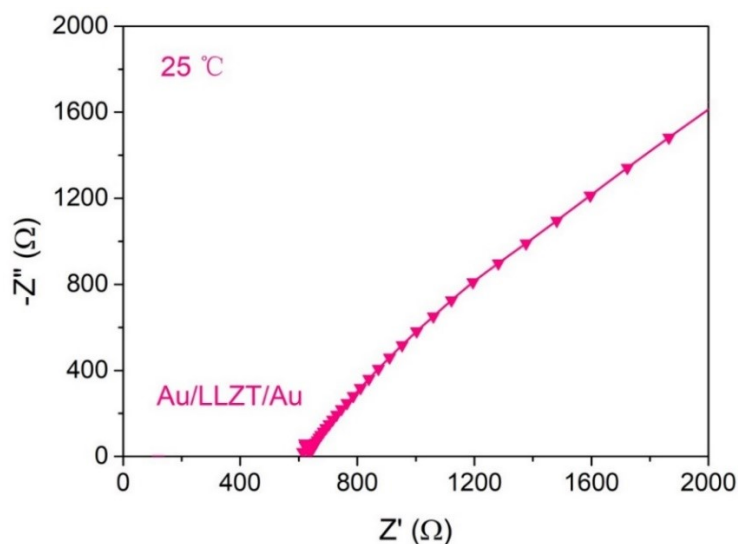


Figure S7 EIS spectrum of the LLZT pellet at 25 °C.

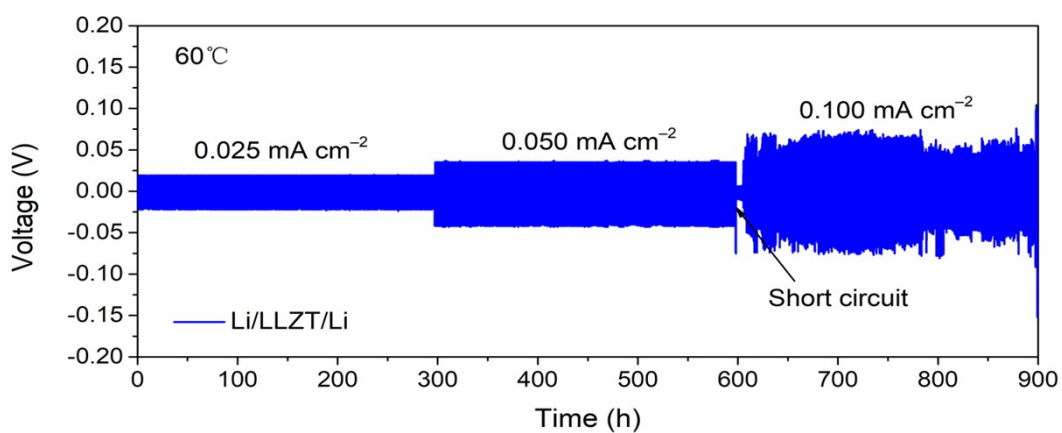


Figure S8 Charge-discharge voltage profiles of Li/LLZT/Li cell at a current density of 0.025, 0.05, and 0.1 mA cm⁻².

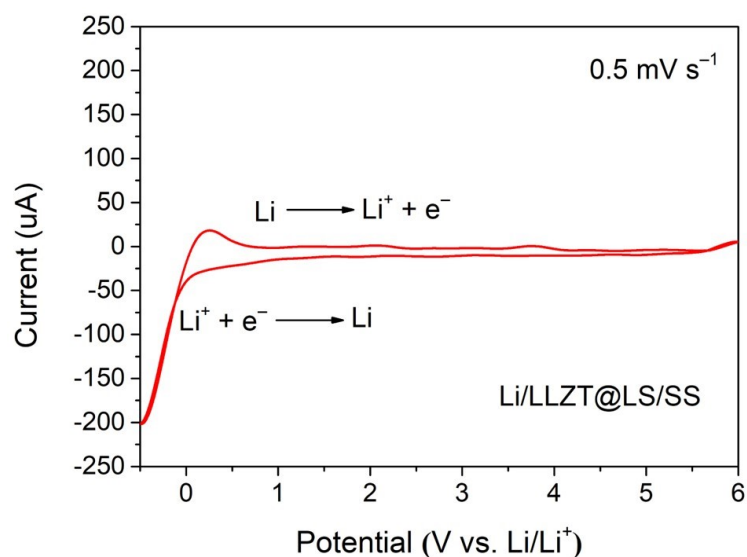


Figure S9 Cyclic voltammogram of the Li/LLZT@LS/SS cell at 0.5 mV s^{-1} and $60 \text{ }^\circ\text{C}$.

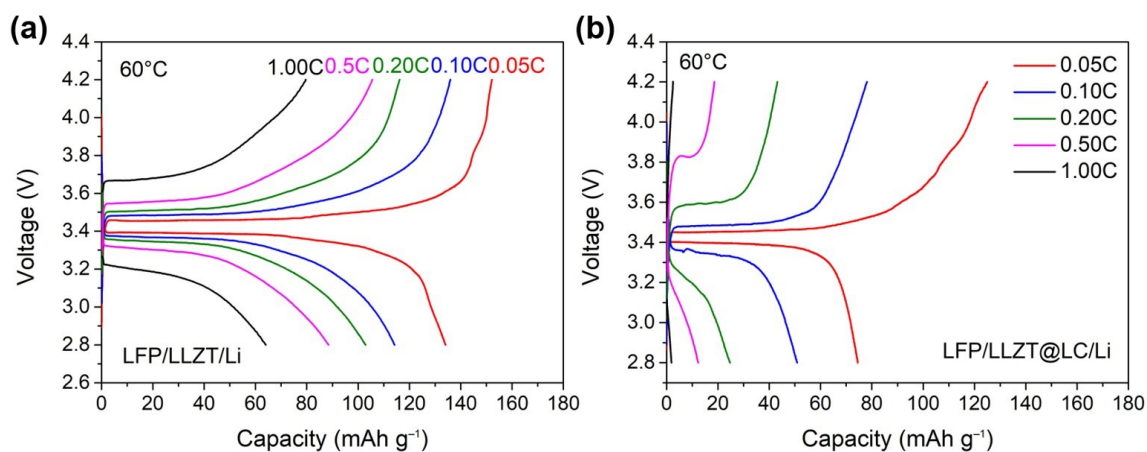


Figure S10 Charge-discharge voltage profiles of (a) LFP/LLZT/Li and (b) LFP/LLZT@LC/Li cell at different rates.

Table S1 Relative density data for cubic LLZT pellets.

LLZT	m_{LLZT}	P_{ethanol}	$m_{\text{submerged}}$	P_{real}	$P_{\text{theoretical}}$	P_{relative}
Group 1	0.598 g	0.789 g cm^{-3}	0.512 g	5.486 g cm^{-3}	5.5 g cm^{-3}	99.7%
Group 2	0.578 g	0.789 g cm^{-3}	0.495 g	5.494 g cm^{-3}	5.5 g cm^{-3}	99.8%

Table S2 The interface formation energies (in J m^{-2}) of Li_2CO_3 (001)/Li (001) and Li_2S (001)/Li (001) systems.

Interface	Li ₂ CO ₃ (001)/Li (001)	Li ₂ S (001)/Li (001)
E _f (in J m ⁻²)	-0.78	-4.54

Supplementary References:

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