Supporting information

Construction of an intimately riveted Li/garnet interface with ultra-low interfacial resistance for solid-state batteries

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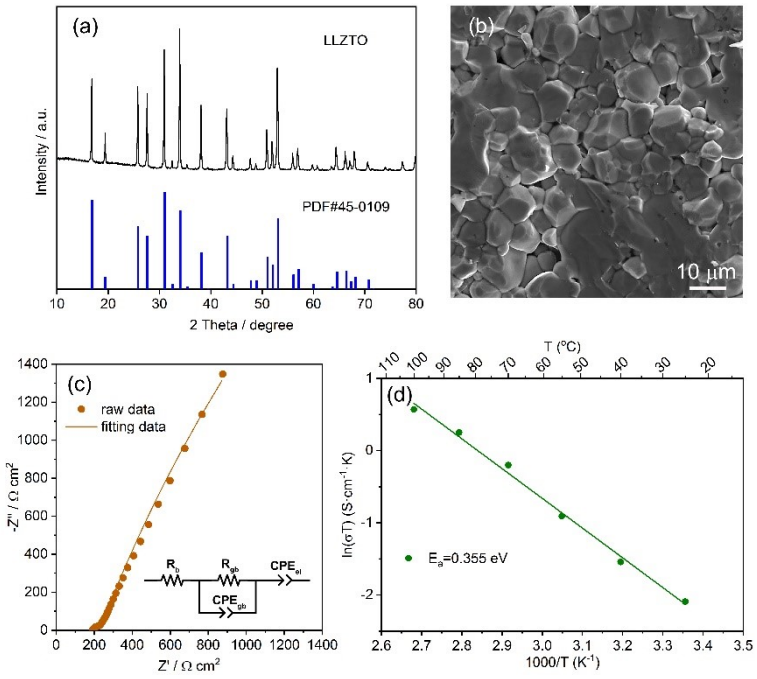

Fig. S1 (a) XRD pattern of the LLZTO electrolyte. (b) SEM image of the cross-section of the sintered LLZTO pellet. (c) EIS data of LLZTO pellet with Ag blocking electrodes recorded at room temperature. (d) The temperature dependence of the ionic conductivity of LLZTO in the 25-100 °C temperature range, with the calculated activation energy value.

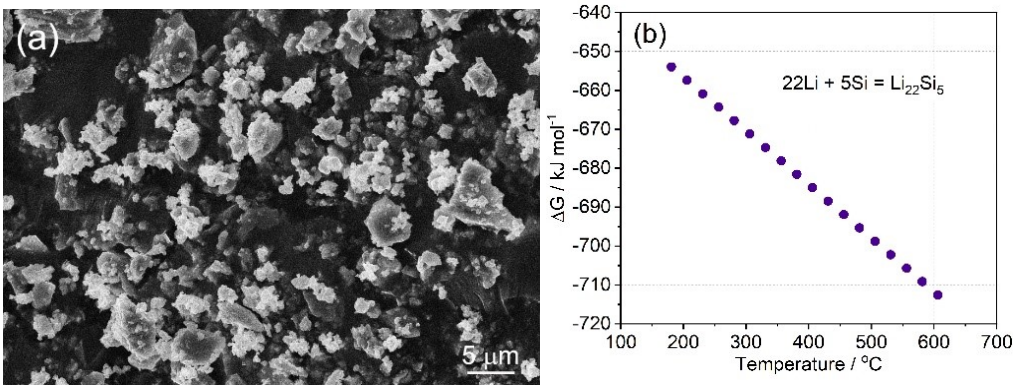

Fig. S2 (a) SEM image of the commercial Si powder. (b) Gibbs free energy change as a function of temperature for the $Li_{22}Si_5$ formation reaction.

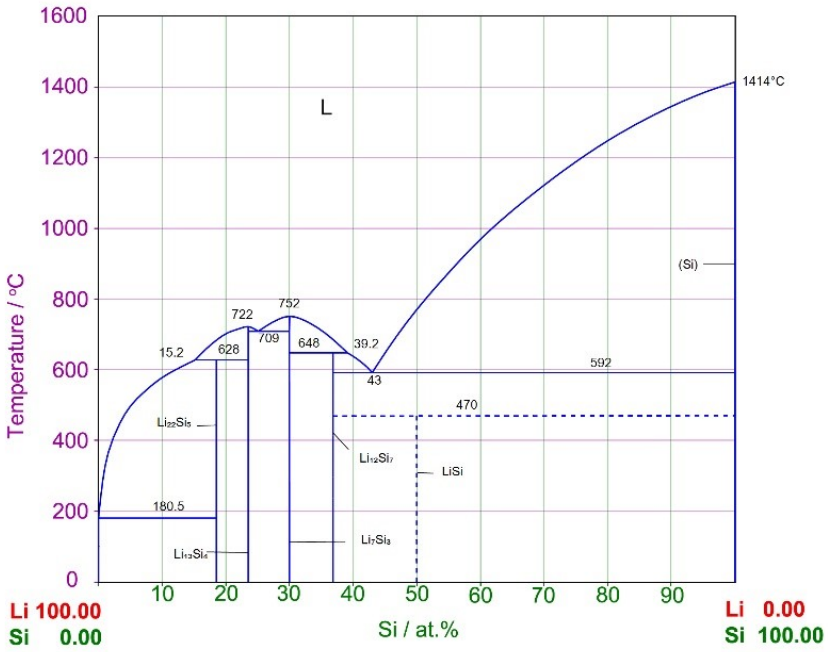

Fig. S3 The binary phase diagram of Li-Si.

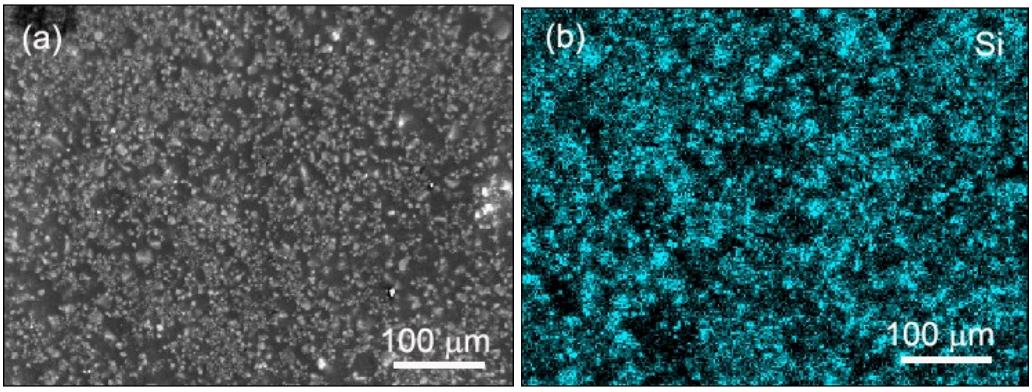

Fig. S4 (a) Surface SEM and (b) corresponding EDS elemental mapping images of the LSi30 composite.

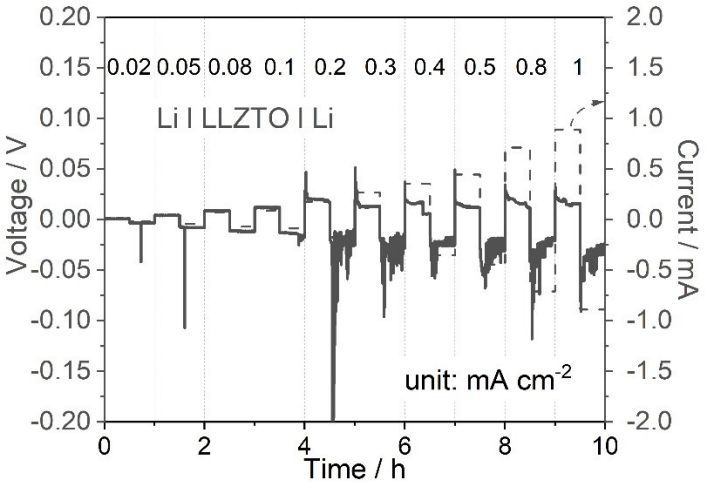

Fig. S5 CCD of the Li|LLZTO|Li symmetric cell.

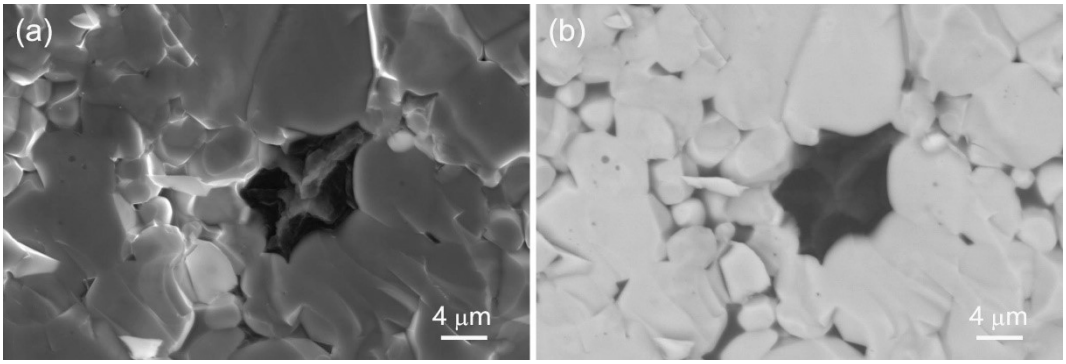

Fig. S6 Cross-sectional (a) SEM and (b) backscattered electron images of the LLZTO electrolyte from the cycled Li|LLZTO|Li symmetric cell.

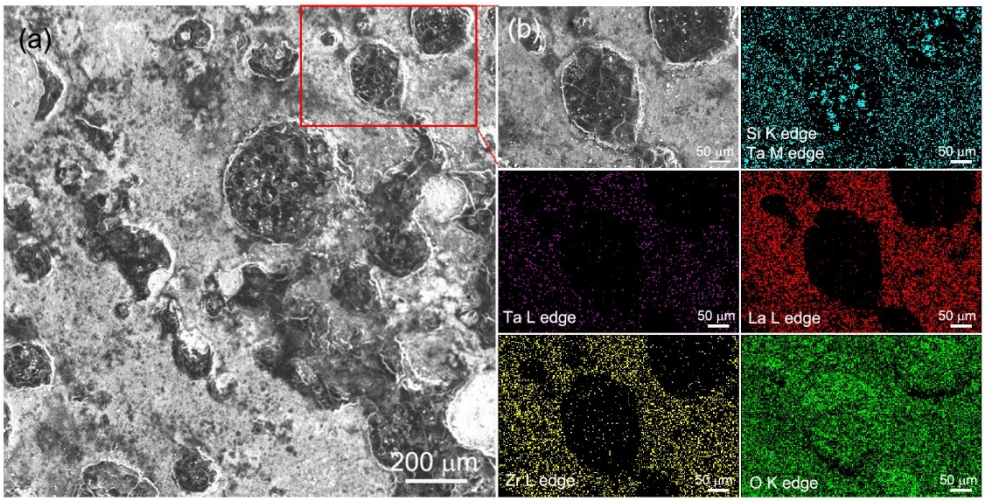

Fig. S7 (a) Surface SEM and (b) corresponding EDS elemental mapping images of the LLZTO electrolyte after long-term cycling in the LSi15|LLZTO|LSi15 symmetric cell.

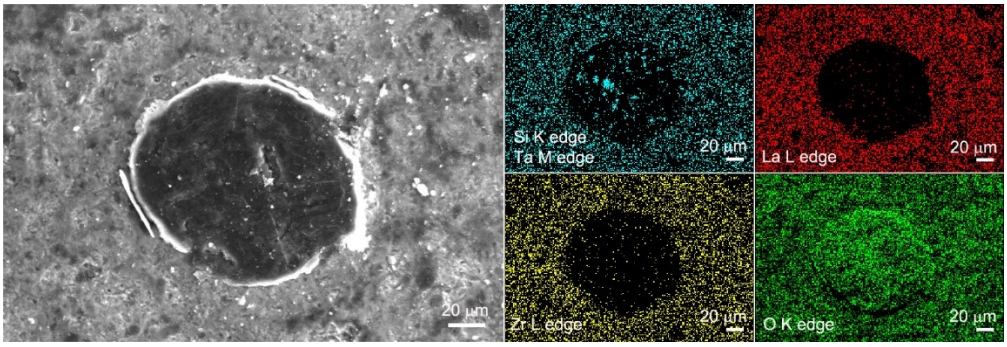

Fig. S8 SEM and corresponding EDS elemental mapping images of dark spot on the LLZTO surface after long-term cycling in the LSi15|LLZTO|LSi15 symmetric cell.

Table S1 The detailed calculation results of mutual reaction energy between LLZO and lithiated silicon.

Reactants	Ratio of LLZO	Mutual reaction energy(eV atom^{-1})	Phase equilibria
LLZO+$Li_{22}Si_5$	100%	0	$Li_7La_3Zr_2O_{12}$
	73.3%	-0.051	Li_2O,Zr_3Si_2,ZrSi,La_2O_3
	66.1%	-0.048	Li_2O,Zr_3Si_2,$Li_2La_2Si_3$,La_2O_3
	46.2%	-0.039	Li_2O,Zr_3Si_2,$Li_2La_2Si_3$,Li
	43.5%	-0.037	Li_2O,ZrSi,$Li_2La_2Si_3$,Li
	0%	-0.017	$Li_{21}Si_5$,Li
LLZO+$Li_{21}Si_5$	100%	0	$Li_7La_3Zr_2O_{12}$
	72.4%	-0.046	Li_2O,Zr_3Si_2,ZrSi,La_2O_3
	63.3%	-0.040	Li_2O,Zr_3Si_2,$Li_2La_2Si_3$,La_2O_3
	46.2%	-0.030	Li_2O,Zr_3Si_2,$Li_2La_2Si_3$,Li
	43.5%	-0.028	Li_2O,ZrSi,$Li_2La_2Si_3$,Li
	0%	0	$Li_{21}Si_5$
LLZO+Li	100%	0	$Li_7La_3Zr_2O_{12}$
	12.5%	-0.006	Li_2O,La_2O_3,Zr_4O
	0%	0	Li