Supporting information

Enabling a compatible Li/garnet interface via a multifunctional additive of sulfur

Jie Wang,†[ab] Saisai Zhang,†[a] Shaokang Song, [a] Jintao Liu, [a] Zhaolin Li [ab] and Hailei Zhao *[ab]

[a] School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

[b] Beijing Municipal Key Lab of Advanced Energy Materials and Technologies, Beijing 100083, China

*Corresponding author: hlzhao@ustb.edu.cn

† These authors contributed equally to this work.

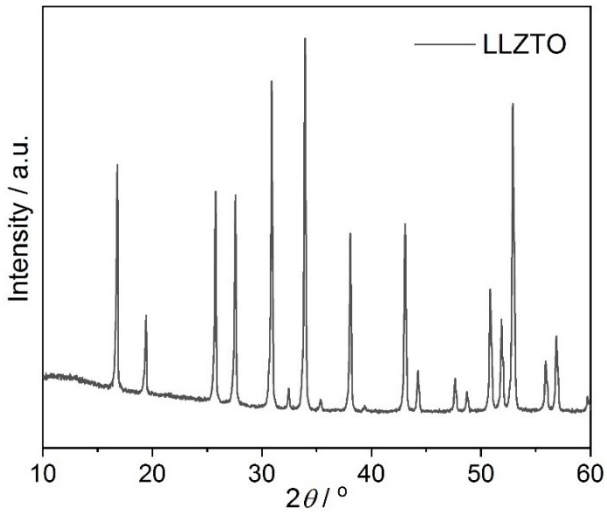

Fig. S1 XRD pattern of the synthesized LLZTO electrolyte.

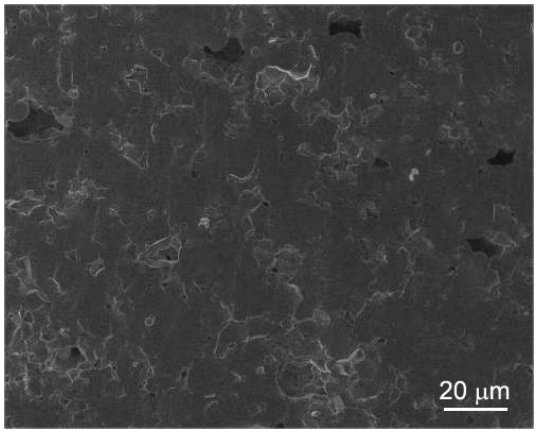

Fig. S2 Cross-section FESEM image of the LLZTO electrolyte.

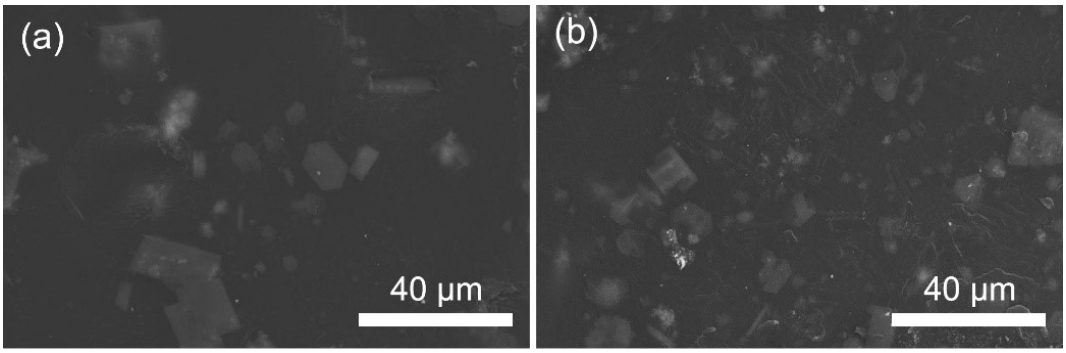

Fig. S3 The surface FESEM images of (a) LS5 and (b) LS20.

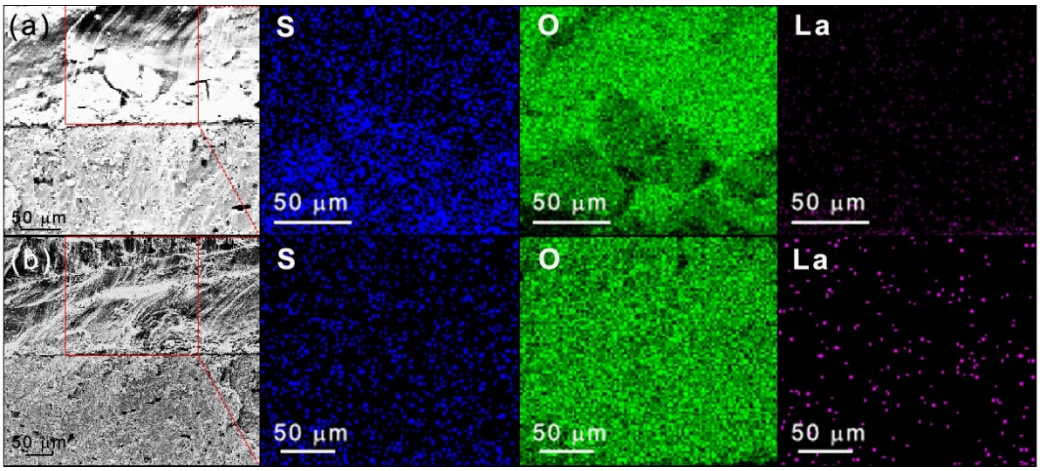

Fig. S4 (a, b) FESEM images of the cross-section of the LS10 electrode and the corresponding EDS mapping analysis on the different marked areas in the LS10|LLZTO|LS10 symmetric cell.

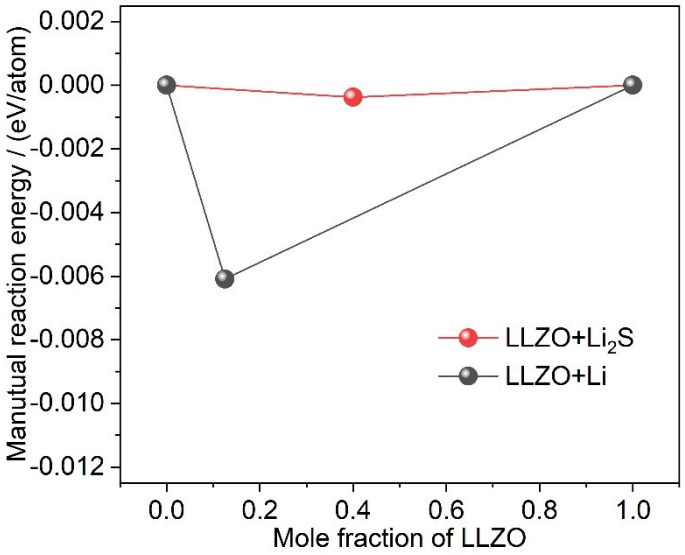

Fig. S5 Calculated mutual reaction energy between Li_2S/pure Li and garnet LLZO electrolyte.

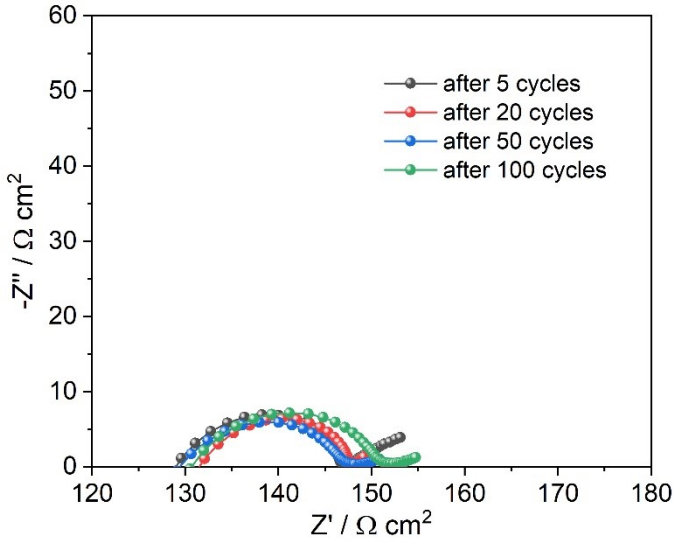

Fig. S6 EIS plots of the LS10|LLZTO|LS10 symmetric cell after different cycles.

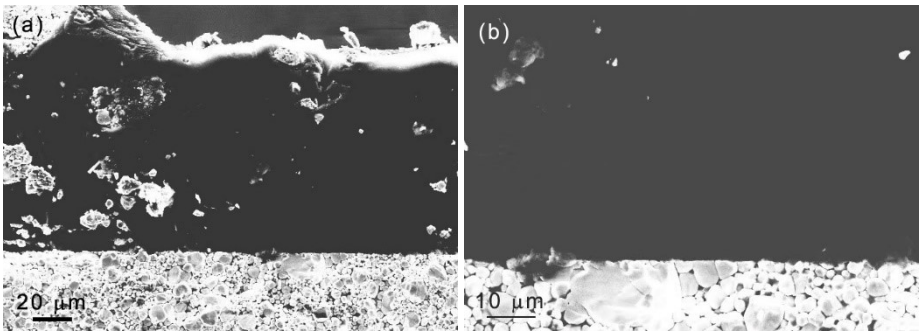

Fig. S7 The cross-sectional FESEM image of the LS10|LLZTO|LS10 symmetric cell after cycling at the current density of 0.2 mA cm^{-2}: (a) low magnification and (b) high magnification.

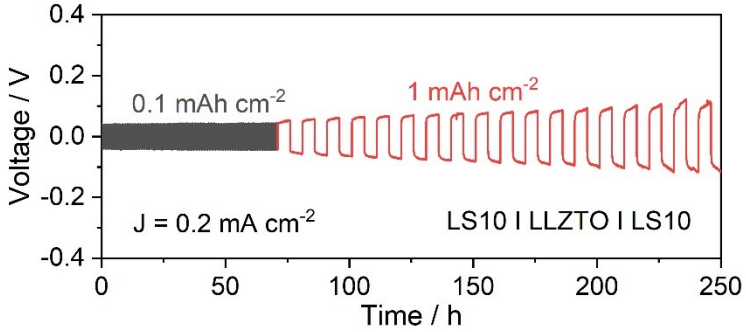

Fig. S8 Cycling performance of the LS10|LLZTO|LS10 symmetric cell at the current density of 0.2 mA cm^{-2} and capacity of 1 mAh cm^{-2}.

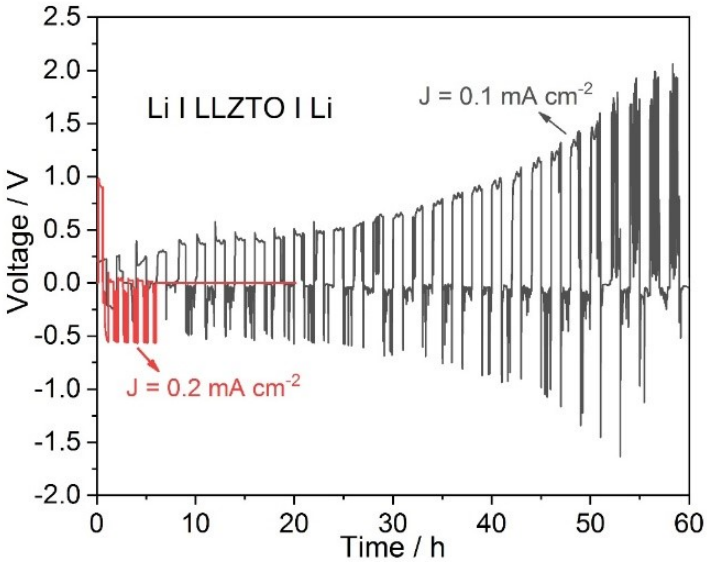

Fig. S9 Galvanostatic Li plating/stripping curves of symmetric Li|LLZTO|Li cells at room temperature.

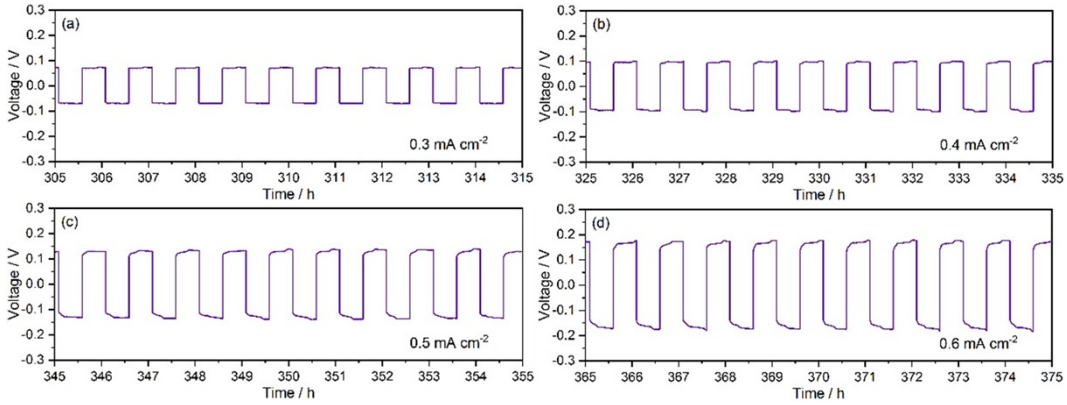

Fig. S10 Enlarged Li plating/stripping curves of symmetric LS10|LLZTO|LS10 cells at different current densities.

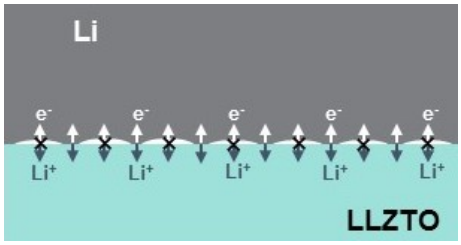

Fig. S11 Schematic illustration of the charge transfer at the interface for the Li|LLZTO|Li symmetric cell.

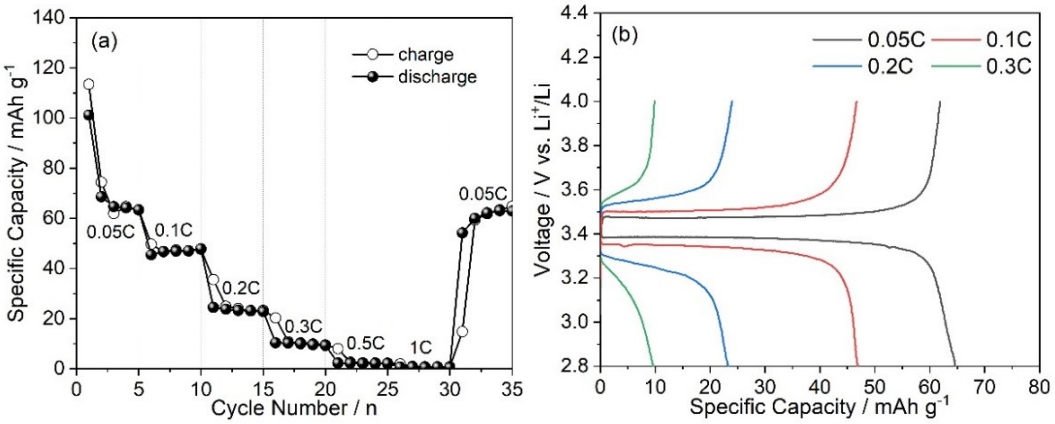

Fig. S12 (a) Stepped rate-capability of the fabricated Li|LLZTO|$LiFePO_4$ cell and (b) the corresponding charge/discharge curves at the different current densities.

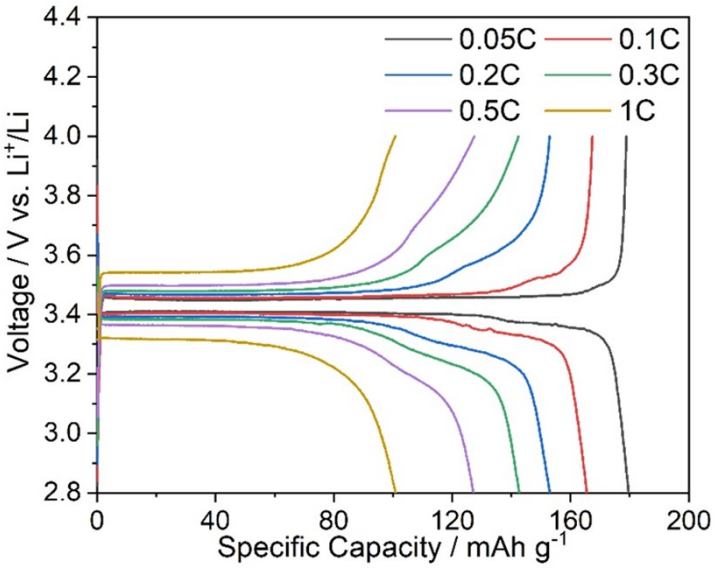

Fig. S13 Discharge/charge curves of the LS10|LLZTO|$LiFePO_4$ cell at the different current densities.

Table S1 The detailed first-principles calculation results

Reactants	Ratio of LLZO	Mutual reaction energy(eV/atom)	Phase equilibria
LLZO+Li_2S	100%	0	$Li_7La_3Zr_2O_{12}$
	40%	-0.00038	La_2SO_2,Li_2O,$Li_6Zr_2O_7$
	0%	0	Li_2S
LLZO+Li	100%	0	$Li_7La_3Zr_2O_{12}$
	12.5%	-0.006	Li_2O,La_2O_3,Zr_4O
	0%	0	Li