Supporting information

Enabling a compatible Li/garnet interface via a multifunctional additive of sulfur
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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 \( \text{Li}_2\text{S} \)/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

<table>
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<tr>
<th>Reactants</th>
<th>Ratio of LLZO</th>
<th>Mutual reaction energy(eV/atom)</th>
<th>Phase equilibria</th>
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<td>LLZO+Li$_2$S</td>
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