Supplemental Information

An *In Vivo* Formed Solid Electrolyte Surface Layer Enables Stable Plating of Li Metal

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Supplemental Figures

Figure S1. Photograph of the Li₂S₆ - LSPS solutions with different Li₂S₆: P₂S₅ ratios in DME solvent, related to Experimental Procedures. The complete reaction of the LSPS is indicated by the formation of transparent solutions. A ratio of Li₂S₆: P₂S₅ lower than 0.25:2 leads to incomplete dissolution of P₂S₅ and a ratio higher than 3:2 leads to a dark brown colored solution indicative of excess lithium polysulfide.

Figure S2. ¹H NMR spectrum of neat DME solvent and the LSPS-1:2 solution, related to Figure 1A, shows that there is no chemical reaction between the solvent and the LSPS complex, but only solvation, which causes the slight shift.
Figure S3. Characterization of the synthesized Li$_3$PS$_4$ powder, the reaction products of Li with LSPS, related to Figure 2. (a) The XRD pattern and (b) EDX spectrum of the synthesized Li$_3$PS$_4$ powder, showing that it is pure phase β-Li$_3$PS$_4$ (ICDD-01-076-0973) and that EDX is accurate in probing the stoichiometric ratios of this sulfide material with a particle size in the micrometer range; (c) XRD pattern of the a-Li$_3$PS$_4$ film on Li, the three sharp reflections are those of the underlying Li metal; (d) The Raman spectrum of lithium powder (SLMP®) reacted with a stoichiometric amount of LSPS, after vacuum drying: the orange band shows where Li$_3$PS$_4$ should lie, indicating that other phases such as Li$_4$P$_2$S$_7$ and Li$_2$P$_2$S$_6$ (380 - 410 cm$^{-1}$) are formed, but not Li$_3$PS$_4$. 
Figure S4. EDS characterization of the Li-LSPS foil, related to Figure 2F. (a) The EDS spectrum of the Li-LSPS showing the presence of P and S, with a P:S ratio of 19.5: 80.5 (very close to 1:4) of LSPS-1:2 solution treated Li foil, Li-LSPS; (b, c) EDS mapping of S and P on the Li-LSPS surface, respectively, showing their uniform distribution. The scale bars in (b,c) are 5 µm.
Figure S5. Supplementary scheme of the ion concentration, electric field and potential distribution at the vicinity of the Li surface in various electrolytes, related to Scheme 1. Schematic showing the ideal profile of cation/anion concentration ($C_c, C_a$), electrostatic potential ($V$), electric field ($E$) as a function of distance to the Li surface within $L/2$ ($L$ = inter-electrode distance) for Li|Li symmetric cells during plating in (a) blank liquid electrolyte, (b) pure single-ion-conducting electrolyte (e.g. Li$_3$PS$_4$) and (c,d) LSPS electrolyte (c) above and (d) below the limiting current $J^*$. Figures (a, c) are replicated from Scheme 1a, b in the main text, for ease of comparison and discussion here.

$C'_c$ and $C'_a$ represent the ion concentration in Li$_3$PS$_4$ (which is estimated to be ~ 30 M and 10 M based on crystallographic data for β-Li$_3$PS$_4$) and are not on the same scale with the $C_0$ in liquid electrolyte in the schematic. $C_0$ and $C'_0$ is the bulk ion concentration in the liquid and Li$_3$PS$_4$, respectively, $V_0$ is the potential at $L/2$ and $E_0$ is the steady-state electric field across the electrolyte, which is equal to $2V_0/L$.

The models applied here are based on revisiting previous reports by Chazalviel et al. and Koch et al. and only some essential equations are listed below for clarity (see Ref.11, 12, 42 and S1). Assumptions made include: (1) ideal planar electrodes without protrusions or non-uniform SEI, (2) the deposition reaction has fast kinetics and is not reaction-limited, (3) the plating capacity is small and does not noticeably move the Li front surface, (4) the plating occurs at a constant current density, $J$, i.e. galvanostatic, (5) the diffusion coefficient is concentration independent. The derivation of $C_c, C_a, V$ and $E$ follows the equations below.

\[
\frac{\partial C_c}{\partial t} = D_c \frac{\partial^2 C_c}{\partial x^2} + \mu_c \frac{\partial}{\partial x} \left( C_c \frac{\partial V}{\partial x} \right)
\]

\[
\frac{\partial C_a}{\partial t} = D_a \frac{\partial^2 C_a}{\partial x^2} + \mu_a \frac{\partial}{\partial x} \left( C_a \frac{\partial V}{\partial x} \right)
\]

where $D$ is the diffusion coefficient, $\mu$ is the mobility and the subscripts $c$ and $a$ refer to the anion and cation. The boundary condition is that at the Li electrode surface, $J_c = J, J_a = 0$, assuming that the current density at $x = 0$ is entirely due to the cations.
**Figure S5a**: In the blank electrolyte and when $t_a >> 0$ and $J > J^*$, $t > \tau$ ($J^*$ and $\tau$ are defined in Equations 2, 3 in the main text), two regions are formed, where a quasi-neutral distribution occurs in region I and anion depletion occurs in region II.

In **region I**, $C_a \approx C_c$, and the ion concentration $C_a$, $V, E$ is given by solving:

$$\frac{dC_a}{dx} = \frac{-J_t a}{FD} = \text{constant}$$

$$E = \frac{dV}{dx} = kT \frac{dC_a}{C_a} \propto \frac{1}{C_a}$$

In **region II**, anions are depleted ($C_a \ll C_c$), therefore a space charge accumulates: $q = F C_c$, and the potential $V, C_c, E$ is given by solving the combination of the two equation below:

$$\frac{d^2V}{dx^2} = -\frac{FC_c}{\varepsilon \varepsilon_0}$$

$$J = -F \mu_c C_c \frac{dV}{dx}$$

$$E = \frac{dV}{dx}$$

where $\varepsilon_0, \varepsilon$ refer to the vacuum permittivity and the relative permittivity of the electrolyte.

**Figure S5b**: Using Li$_3$PS$_4$ as the electrolyte where Li$^+$ is the only charge carrier ($\mu_a, t_a \rightarrow 0$), based on Equations and below, the ionic concentrations and electric filed are constant, and the $J^*$ and $\tau$ are close to infinity.

$$\frac{dC_a}{dx} = -\frac{J_t a}{FD} = 0 \Rightarrow C_a = C_c = C' \text{ and } \frac{dC_a}{dt} = 0$$

$$E = E_0 = \frac{dV}{dx} = \frac{2V_0}{L}$$

$$J^* = \frac{2FC_cD}{t_a L} \rightarrow \infty$$

$$\tau = \pi D \left( \frac{C_0 F}{2J_t a} \right)^2 \rightarrow \infty$$

**Figure S5c**: In the LSPS electrolyte where single-ion-conducting Li$_3$PS$_4$ forms in conjunction with the liquid electrolyte, above $J^*$, the scenario in **Figure S5a and b** combines at the SE|LE interface, where we expect discontinuity in $C_a/c$ and $E$ and continuity in $V$. In this case, at the Li surface, there is no large $E$ thus eliminating the driving force for dendrite growth.

**Figure S5d**: In the LSPS at below $J^*$, ion depletion is absent and it stays quasi-neutral in the liquid electrolyte; therefore, the $V$ and $E$ profiles are similar to **Figure S5b**, while there is discontinuity in $C_a/c$ from $C'$ to $C_0$. 
Figure S6. The potential profiles of working electrodes (Ewe) as resolved in three-electrode symmetric cells (vs. Li metal reference electrode) upon plating/stripping, related to Figure 3D. (a) The comparison of 1st cycle (plating followed by stripping) for the Li electrodes in blank and LSPS – 0.025 M electrolyte; (b,c) the evolution of potential profiles for cells in (b) blank and (c) LSPS – 0.025 M electrolyte for 20 cycles. Current density: 1 mA cm\(^{-2}\); capacity: 1 mA h cm\(^{-2}\).

Figure S7. XPS analysis of the Li surface after plating in the LSPS electrolyte, related to Figure 2A. High-resolution XPS (a) P 2p and (d) S 2p spectra of Li electrodes after the first plating of 2 mAh cm\(^{-2}\) in the 0.025 M- LSPS electrolyte. The spectra show the same P and S environment as that of Li\(_3\)PS\(_4\), Figure 2A,B.
Figure S8. Setup of the transparent Li|Li symmetric cells for \textit{operando} optical microscope studies, related to Figure 4E, F. The Li foil cross-sections are the active front surface for Li plating/stripping (the observation area). (a) is the top view, (b) is the front view, and (c) is the representative picture showing the cell under the microscope.

Figure S9. The voltage evolution of Li|Li symmetric cells using 0.025M $\text{Li}_2\text{S}_6$ electrolyte compared with the blank electrolyte at a current density of 1 mA cm$^{-2}$ with a capacity of 1 mA h cm$^{-2}$.
Figure S10. The evolution of impedance (Nyquist plots) of the Li|Li symmetric cells, related to Figure 5. The cells were in (a) the blank DEM/DOL electrolyte and (b) the 0.025M-LSPS electrolyte over 150 cycles at a current density of 1 mA cm$^{-2}$ with a capacity of 1 mA h cm$^{-2}$. After 150 cycles, the cell using blank electrolyte is globally short-circuited, showing only one point in the Nyquist plot at all frequencies.

Figure S11. The SEM and photographic images of Li electrodes after cycling, related to Figure 2. (a,b) SEM and (c,d) photographic images of Li electrodes after 100 plating/stripping cycles in (a,c) the blank electrolyte and (b,d) the 0.025 M-LSPS electrolyte at a current density of 1 mA cm$^{-2}$ with a capacity of 1 mA h cm$^{-2}$; insets in (a,b) are the respective enlarged SEM images.
Figure S12. Surface characterization of the Li surface after cycling in LSPS electrolytes, related to Figure 2. EDX mapping of (a) P and (b) S for the Li electrode surface after 100 plating/stripping cycles in LSPS-0.025 M electrolyte at a current density of 1 mA cm$^{-2}$ with a capacity of 1 mA h cm$^{-2}$. High-resolution XPS (c) F 1s and (d) C 1s spectra of Li electrodes after 100 cycles in the blank electrolyte and LSPS-0.025 M electrolyte. As quantified from the XPS spectra, the atomic ratio of P and S is ~47% on the upper surface (5-10 nm for XPS detection depth) after 100 cycles. This indicates that there are sulfur-containing LiTFSI decomposition products on the top surface of the Li$_3$PS$_4$ film, as expected.
Figure S13. The voltage evolution of Li|Li symmetric cells using LSPS electrolytes at varied current and capacity, related to Figure 5. The voltage evolution of Li|Li symmetric cells using (a) LSPS-0.0125 M electrolyte at a current density of 1 mA cm\(^{-2}\) with a capacity of 1 mA h cm\(^{-2}\), (b,c) LSPS-0.025 M electrolyte at (b) a current density of 8 mA cm\(^{-2}\) with a capacity of 1 mA h cm\(^{-2}\) and (c) a current density of 4 mA cm\(^{-2}\) with a capacity of 2 mA h cm\(^{-2}\).
Figure S14. Electrochemical performance of the LTO|Li cells using high loading LTO electrodes, related to Figure 5G. (a) The discharge capacity retention and Coulombic efficiency of LTO|Li full cells with ~7.0 mg\textsubscript{LTO} cm\textsuperscript{-2} electrodes on cycling at 1C (capacity: ~ 1 mAh cm\textsuperscript{-2}; current: 1 mA cm\textsuperscript{-2}). (b) The evolution of energy efficiency (as calculated by discharge energy \cdot 100/charge energy), (c) a representative discharge/charge profile at the 60\textsuperscript{th} cycle and (d) the time-evolved cell voltage of the LTO|Li full cells with ~7.0 mg\textsubscript{LTO} cm\textsuperscript{-2} electrodes in corresponding electrolytes.

Supplemental References