## **Electronic Supplementary Information (ESI)**

Mechanistic Understanding of Lithium-anode Protection by Organosulfide-based Solidelectrolyte Interphases and its Implications

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Figure S1. (a) Efficiency of Li-metal stripping and plating in the form of Coulombic efficiency in the baseline electrolyte with LiNO<sub>3</sub> additive and (b) the corresponding SEM micrograph, showing the morphology of Li surface on Ni after 25 cycles of plating and stripping.



Figure S2. Cross sectional SEM micrographs, showing the morphology of Li surface on Ni after 25 cycles of plating and stripping in (a) the baseline electrolyte and (b) the DMPS-containing electrolyte. The deposited Li and the Ni foil substrate have been identified for the reader. The high reactivity of Li-metal with E1 electrolyte leads to coarse and voluminous Li deposits with obvious porosity. In sharp contrast, the SEM of the Li metal cycled in DMPS electrolyte is compact and dense.



Figure S3. S 2p XPS data of the SEI on Li-metal deposited on Ni after 25 cycles in baseline electrolyte and with LiNO<sub>3</sub>-containing electrolyte.



Figure S4. Li 1s XPS data of the SEI on the Li-metal deposited on Ni in different electrolytes.



Figure S5. F 1s XPS data of the SEI on the Li-metal deposited on Ni after 25 cycles in different electrolytes.



**Figure S6.** Visualization of the electric field along the depth and on the surface of a lithium slab with (a) a sulfide SEI and (b) a thiolate SEI.



**Figure S7.** Visualization of the electric field along the depth of the lithium slab with (a) methyl thiolate species and (b) allyl thiolate species indicating a minimal difference in electron distortion capability between them.



Figure S8. F 1s XPS spectra of the SEI on the Li-metal deposited on Ni after 25 cycles with different organopolysulfide additives.



Figure S9. CE of Li||Ni cells with DAPS additive under different areal current densities.



Figure S10. Performance of Li-S coin cells with and without DAPS additive. The high rate cycling highlights the faster degradation of the lithium-metal anode, which leads to lower CE and faster capacity fade in the cells without the DAPS additive.



Figure S11. EIS data of pristine Li||S pouch cells.



Figure S12. EIS data of Li||S pouch cells after 40 cycles.