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## **Supporting Information:**

## Self-smoothing Li-metal Anode Enabled via a Hybrid Interface Film

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Figure S1. <sup>7</sup>Li NMR spectra in Electrolyte (1M LiTFSI in DOL-DME ) or m-Electrolyte (1M LiTFSI in DOL-DME with 0.5 wt% AgNO<sub>3</sub> additive).

The introduction of AgNO<sub>3</sub> into the DOL-DME-LiTFSI solution causes a significant shift of <sup>7</sup>Li NMR spectra, which can be ascribed to the effect  $NO_3^-$  ion that possesses higher electrondonating ability and exhibits a stronger interaction with Li<sup>+</sup> ion than TFSI<sup>-</sup> ion.



Figure S2. Photos of solutions: 0.5 wt% AgNO<sub>3</sub> in DOL-DME (a) and DOL-DME-LiTFSI (b).



**Figure S3.** Digital images of Li-metal sheets pretreated with the solution containing various AgNO<sub>3</sub> concentrations (a); Cyclic stability of the corresponding modified Li anodes in Li symmetrical battery at 2.5 mA cm<sup>-2</sup>, 2.5 mA h cm<sup>-2</sup> (b).



Figure S4. Cross-section view of modified Li anode (a) and its corresponding element mappings (b-d).



Figure S5. FTIR spectra of bare Li and modified Li anodes.



Figure S6. TEM lattice fringe spacing of the hybrid interface film. The lattice fringe spacing of 0.233 nm corresponds to the (111) crystal plane of LiF.



Figure S7. EDX element mappings of the hybrid interface film under TEM.



Figure S8. SEM image of the hybrid texture after reversibility verification.



**Figure S9.** Air stability of bare Li and modified Li anodes: Digital images of bare Li and modified Li anodes before (a) and after (d) exposure to air; SEM images of bare Li and modified Li anodes before (b, e) and after (c, f) exposure to air for 300s.



Figure S10. Contact angles of bare Li (a) and modified Li (b) anodes.



Figure S11. Digital image of modified Cu foil.



Figure S12. SEM image and Ag mapping of modified Li anode with depositing 2 mA h cm<sup>-2</sup> Li .



Figure S13. Voltage-capacity curve and the positions for morphological observation of Li deposition.



Figure S14. Voltage-time curves in symmetric cells at 2.5 mA cm<sup>-2</sup>, 2.5 mAh cm<sup>-2</sup>. The bare Li symmetric cell fails at 375 h.



Figure S15. Voltage-time curves of Li symmetric cells at 10 mA cm<sup>-2</sup>, 2.5 mAh cm<sup>-2</sup>. The bare Li symmetric cell fails at 35 h.



**Figure S16.** Voltage-time curves of Li symmetric cells at 10 mA cm<sup>-2</sup>, 2.5 mAh cm<sup>-2</sup>. The modified Li cell operates stably compared to the failure of the bare Li cell at about 35 h.



**Figure S17.** Voltage-time curves of Li symmetric cells at 10 mA cm<sup>-2</sup>, 10 mAh cm<sup>-2</sup>. The bare Li symmetric cell shows a random voltage oscillation (a) and significant 'saltation point' (b).



Figure S18. Voltage-time curves of Li symmetric cells when they are cycled with gradient currents of 1, 2.5, 5, 10, 15, 20, 15, 10, 5, 2.5 and 1 mA cm<sup>-2</sup>. The plating/stripping capacity is controlled at 2.5 mA h cm<sup>-2</sup>.



Figure S19. Coulombic efficiency of Li-Cu batteries based on bare and modified Li anodes at 1mA cm<sup>-2</sup> and 1 mAh cm<sup>-2</sup>.



Figure S20. SEM images of bare Li (a, b) and modified Li (c, d) anodes after 200 cycles in Li-LFP cells.



Figure S21. CV curves of Li-NCA cells at a scan speed of 0.5 mV s<sup>-1</sup>.



Figure S22. Electrochemical impedance spectra of fresh bare Li-NCA and modfied Li-NCA cells at 25  $^{\circ}$ C (a) and -10  $^{\circ}$ C (b).



**Figure S23.** Electrochemical impedance spectra and the fitted results of the cycled bare Li-NCA and modified Li-NCA cells at 25 °C (a) and -10 °C (b).



Figure S24. SEM images of bare Li (a, b, c) and modified Li (d, e, f) anodes after 500 cycles in Li-NCA cells.