

Supplementary Information

Bilayer electrolyte design toward high-voltage durable solid-state lithium metal batteries

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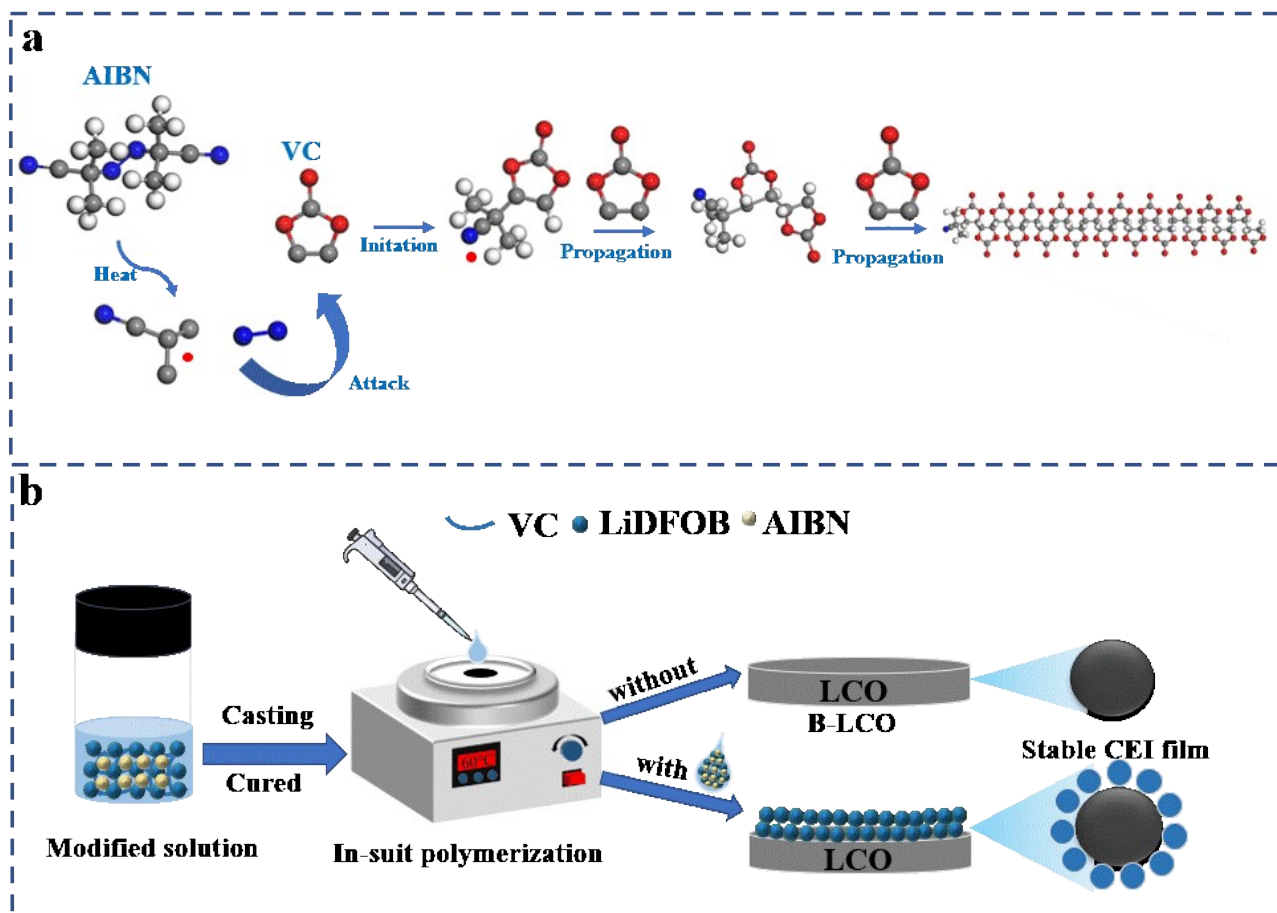


Fig. S1. (a) Mechanism for polymerization of VC. (b) Schematic illustration of preparation process of in-situ CEI coating.

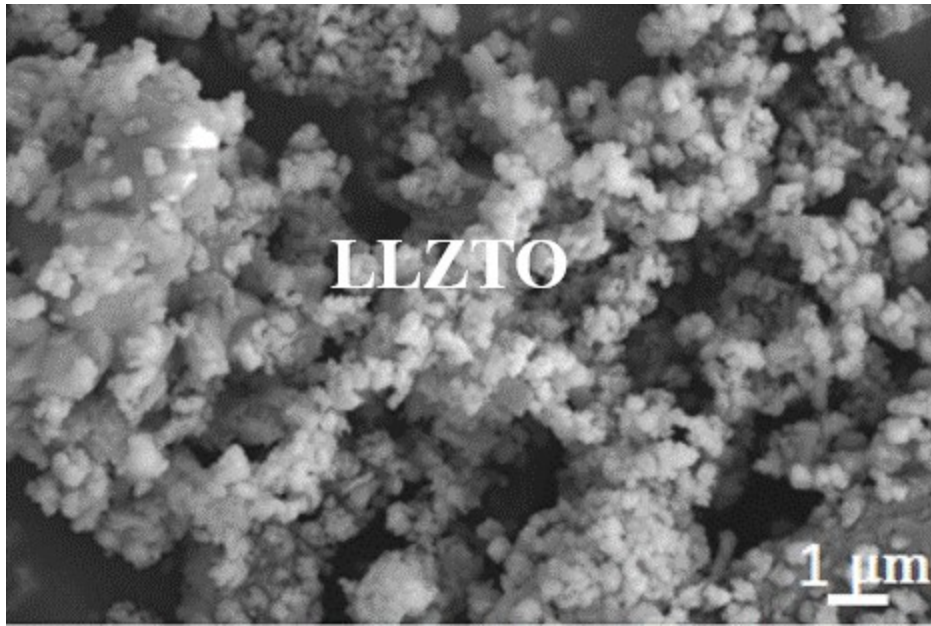


Fig. S2. SEM images of the LLZTO

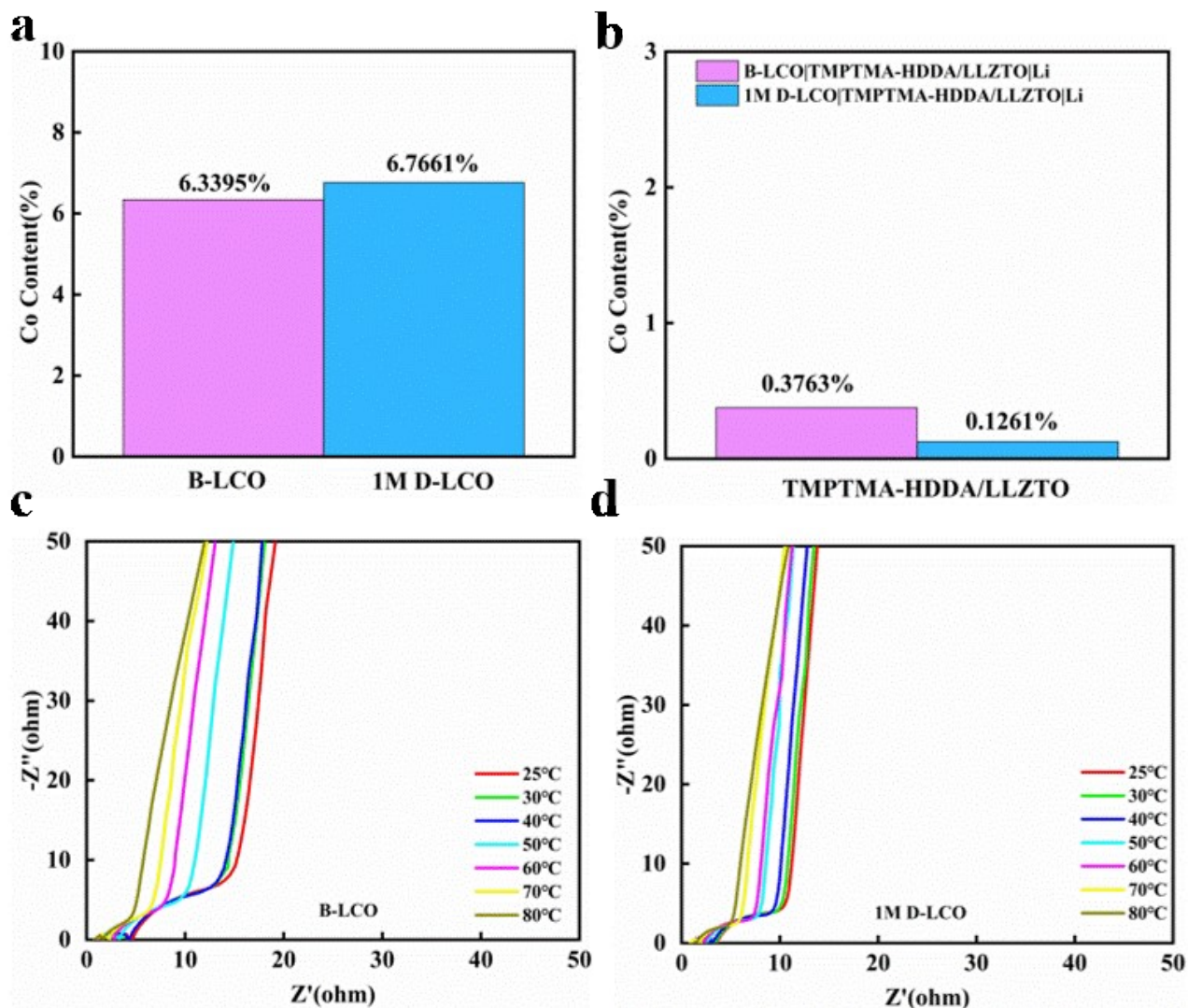


Fig. S3. (a) Comparison of Co content in B-LCO and 1M D-LCO after cycling (b) Comparison of Co content of TMPTMA-HDDA/LLZTO electrolyte in B-LCO|TMPTMA-HDDA/LLZTO|Li and 1M D-LCO|TMPTMA-HDDA/LLZTO|Li cells after cycling. Electrochemical impedance spectroscopy (EIS) of (c) B-LCO and (d) 1M D-LCO at different temperatures.

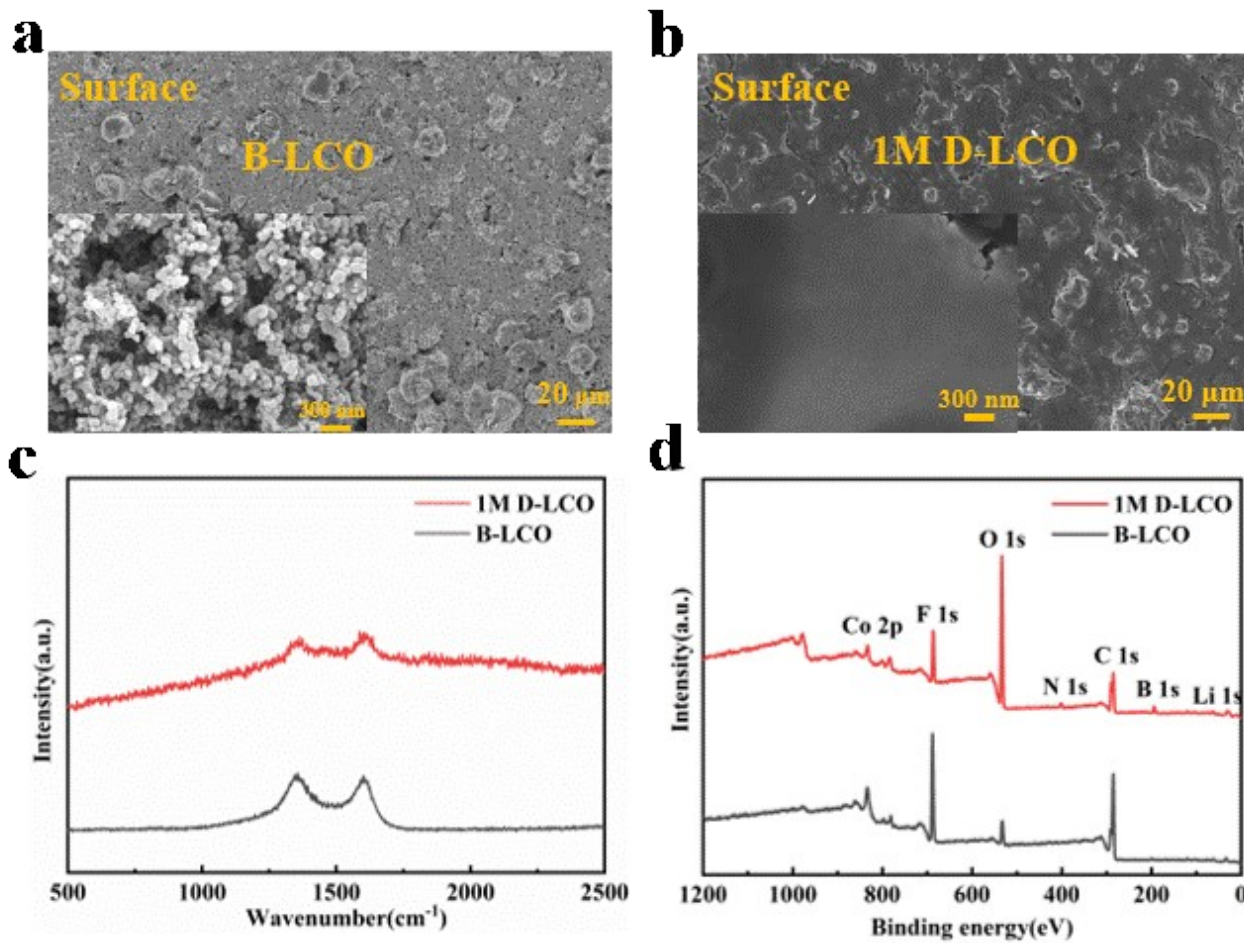


Fig. S4. The morphology SEM images of (a) B-LCO, (b) 1M D-LCO. (c) Raman spectra of B-LCO and 1M D-LCO. (d) XPS analysis of B-LCO and 1M D-LCO.

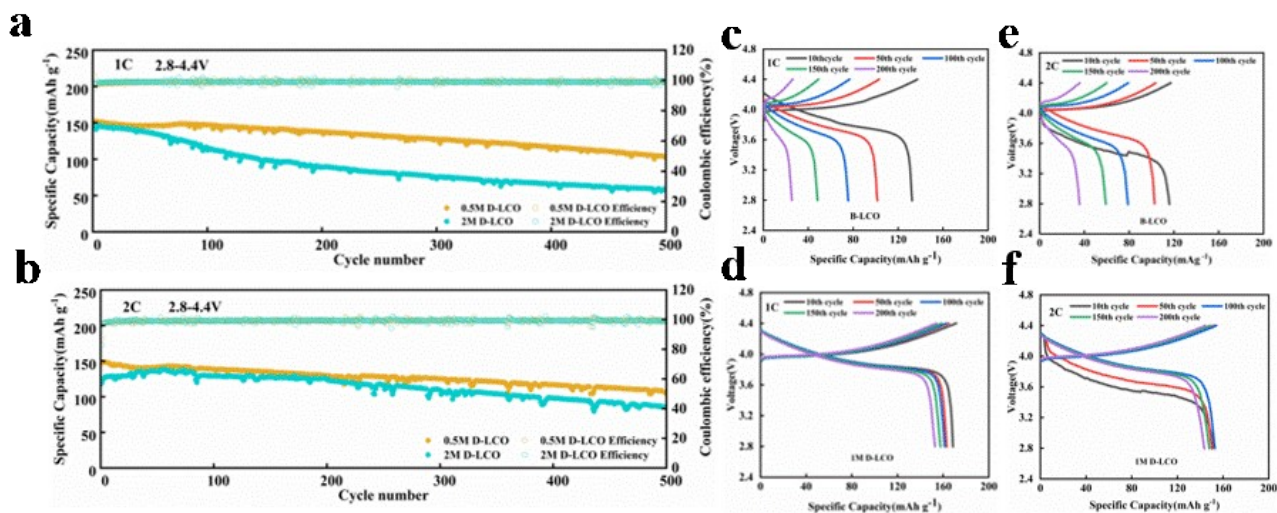


Fig. S5. The discharge capacity and coulombic efficiency of 0.5M D-LCO|TMPTMA-HDDA/LLZTO|Li, 2M D-LCO|TMPTMA-HDDA/LLZTO|Li, cells for 500 cycles at 2.8-4.4 V (a) at 1 C, (b) at 2 C. Charge-discharge curves of (c) B-LCO|TMPTMA-HDDA/LLZTO|Li and (d) 1M D-LCO|TMPTMA-HDDA/LLZTO|Li cells during cycling at 1 C at 2.8-4.4V. Charge-discharge curves of (e) B-LCO|TMPTMA-HDDA/LLZTO|Li and (f) 1M D-LCO|TMPTMA-HDDA/LLZTO|Li cells during cycling at 2 C at 2.8-4.4V.

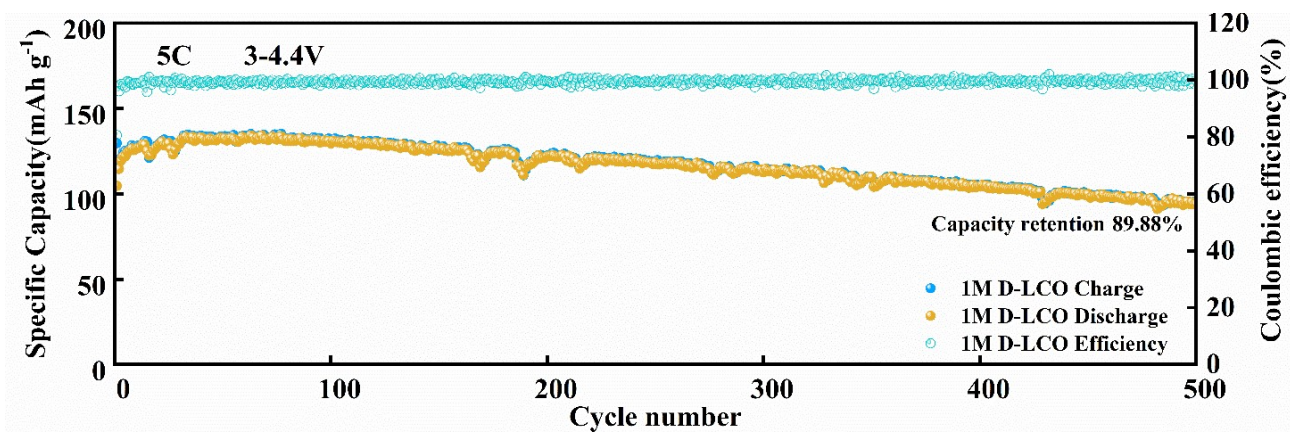


Fig. S6. The discharge capacity and coulombic efficiency of 1M D-LCO|TMPTMA-HDDA/LLZTO|Li cell for 500 cycles at 2.8-4.4 V at 5 C.

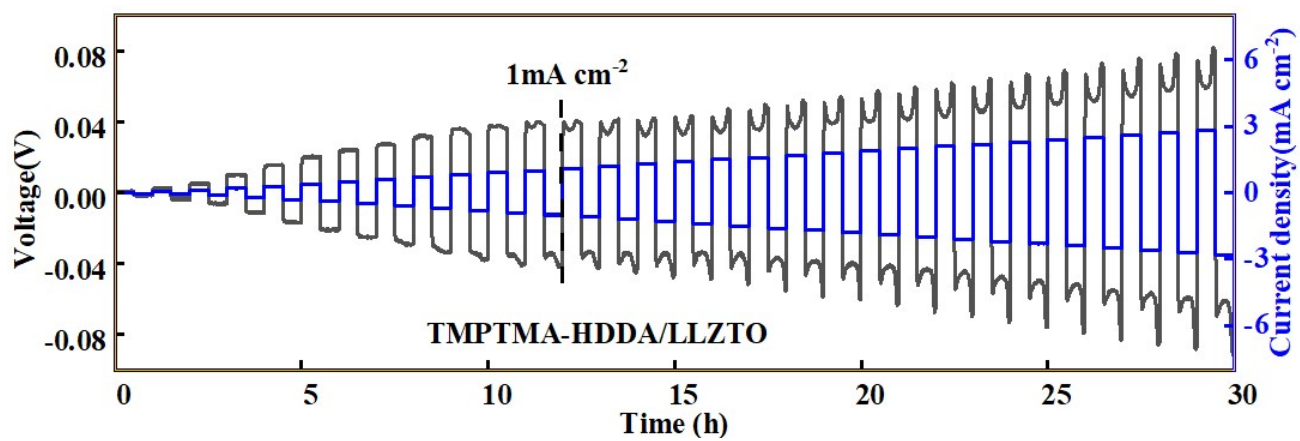


Fig. S7. The critical current density of the TMPTMA-HDDA/LLZTO.

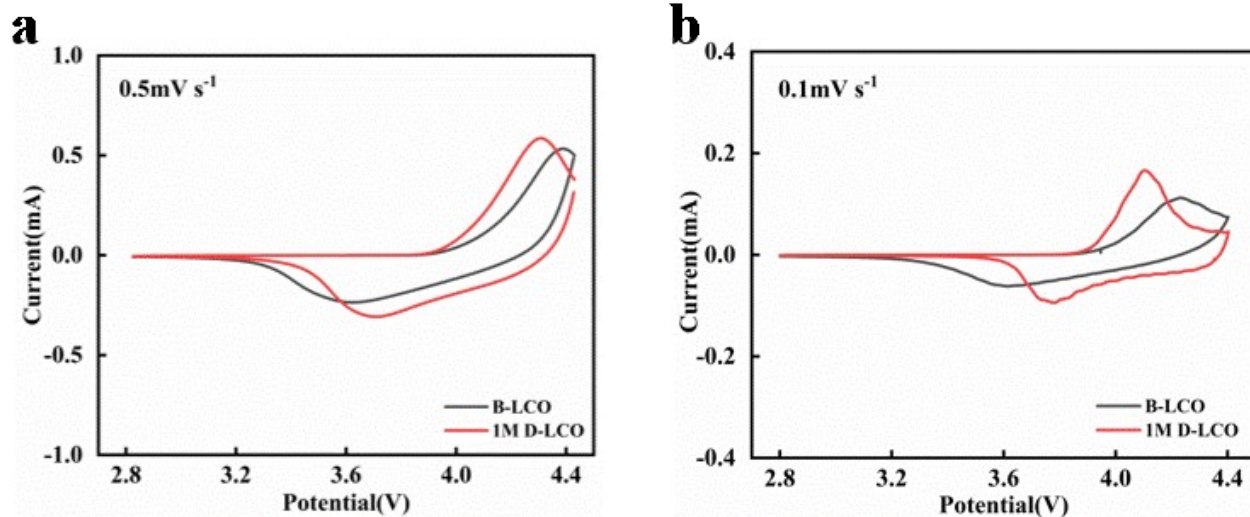


Fig. S8. (a) CV curves of B-LCO and 1M D-LCO at 0.5 mV s⁻¹. (b) CV curves of B-LCO and 1M D-LCO at 0.1 mV s⁻¹ after cycling .

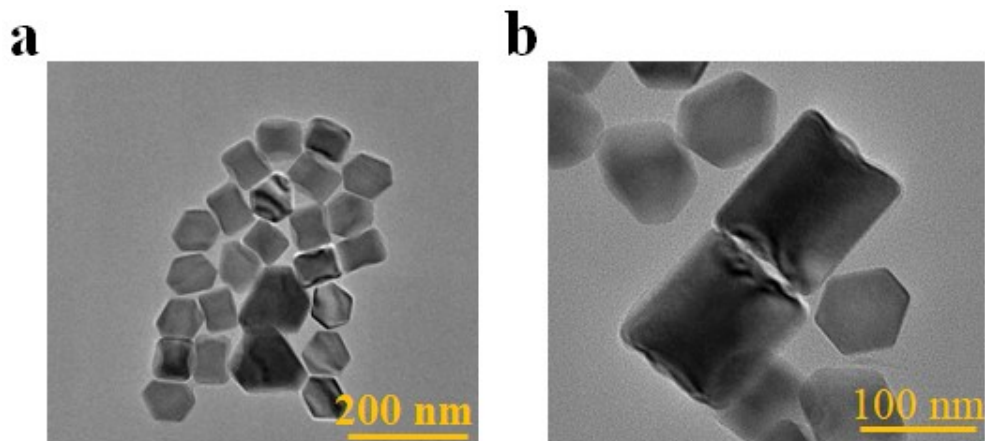


Fig. S9. (a, b) TEM images of 1M D-LCO after cycling.

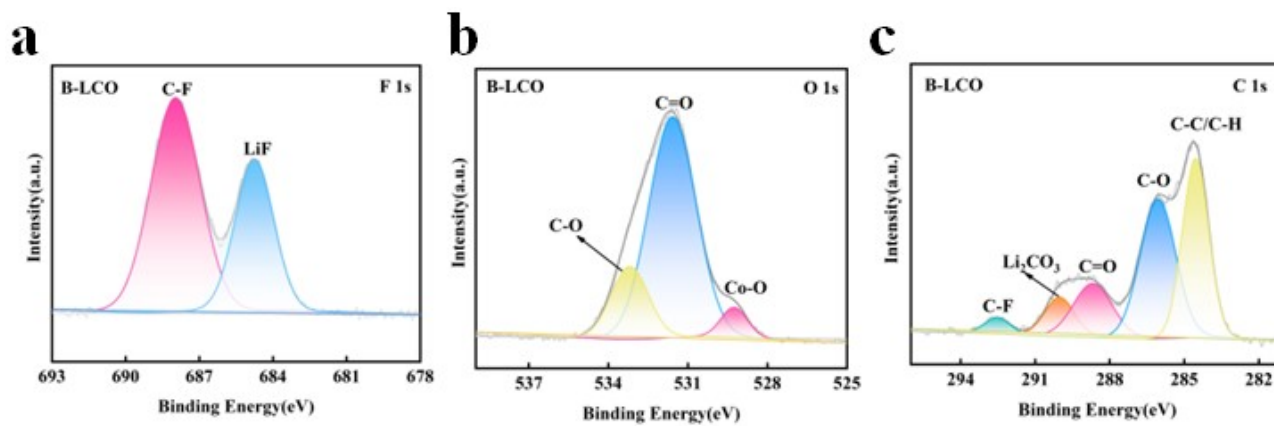


Fig. S10. XPS spectra of the B-LCO after cycling (a) F 1s, (b) O 1s and (c) C 1s.

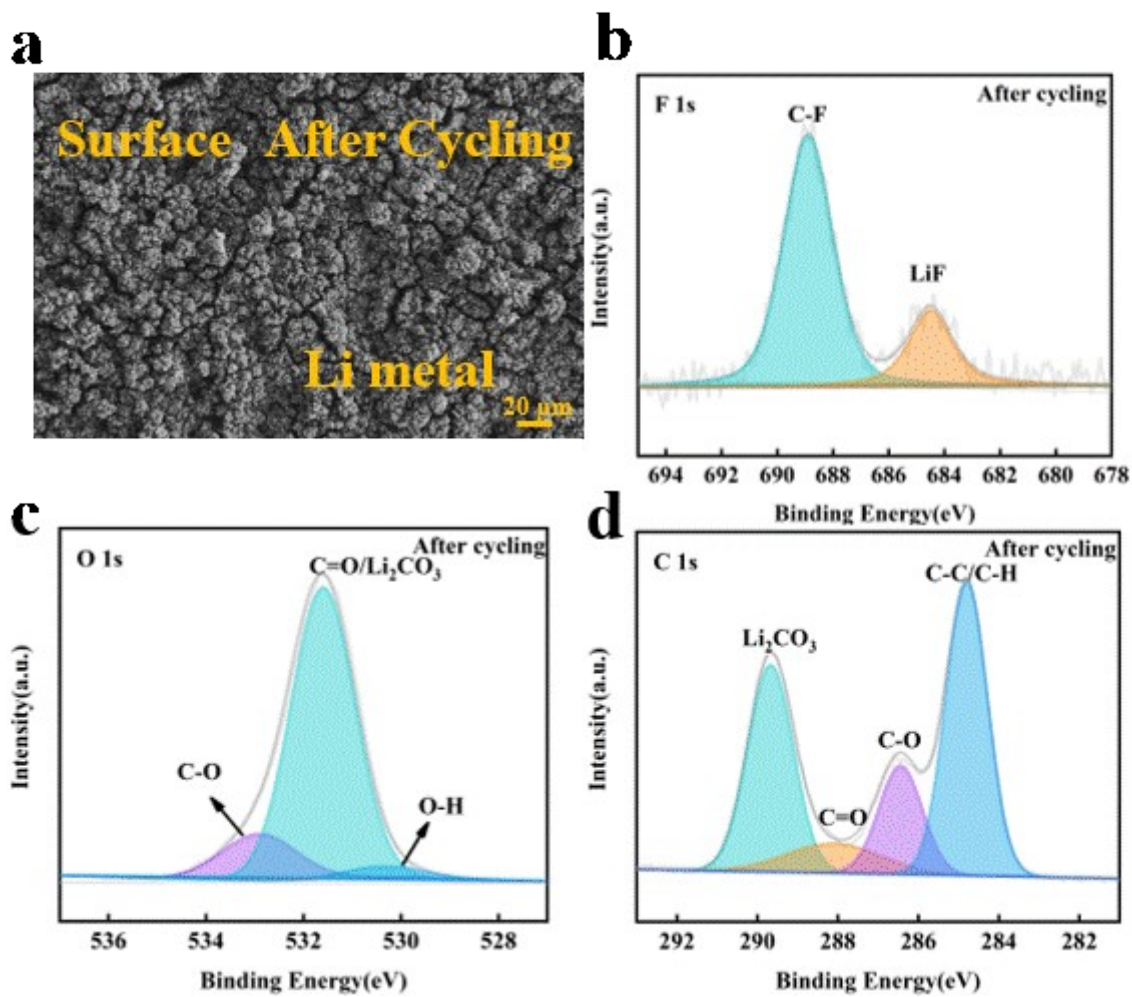


Fig. S11. (a) The surface SEM images, and XPS analysis of (b) F 1s, (c) O 1s, (d) C 1s of Li metal anode after cycling.

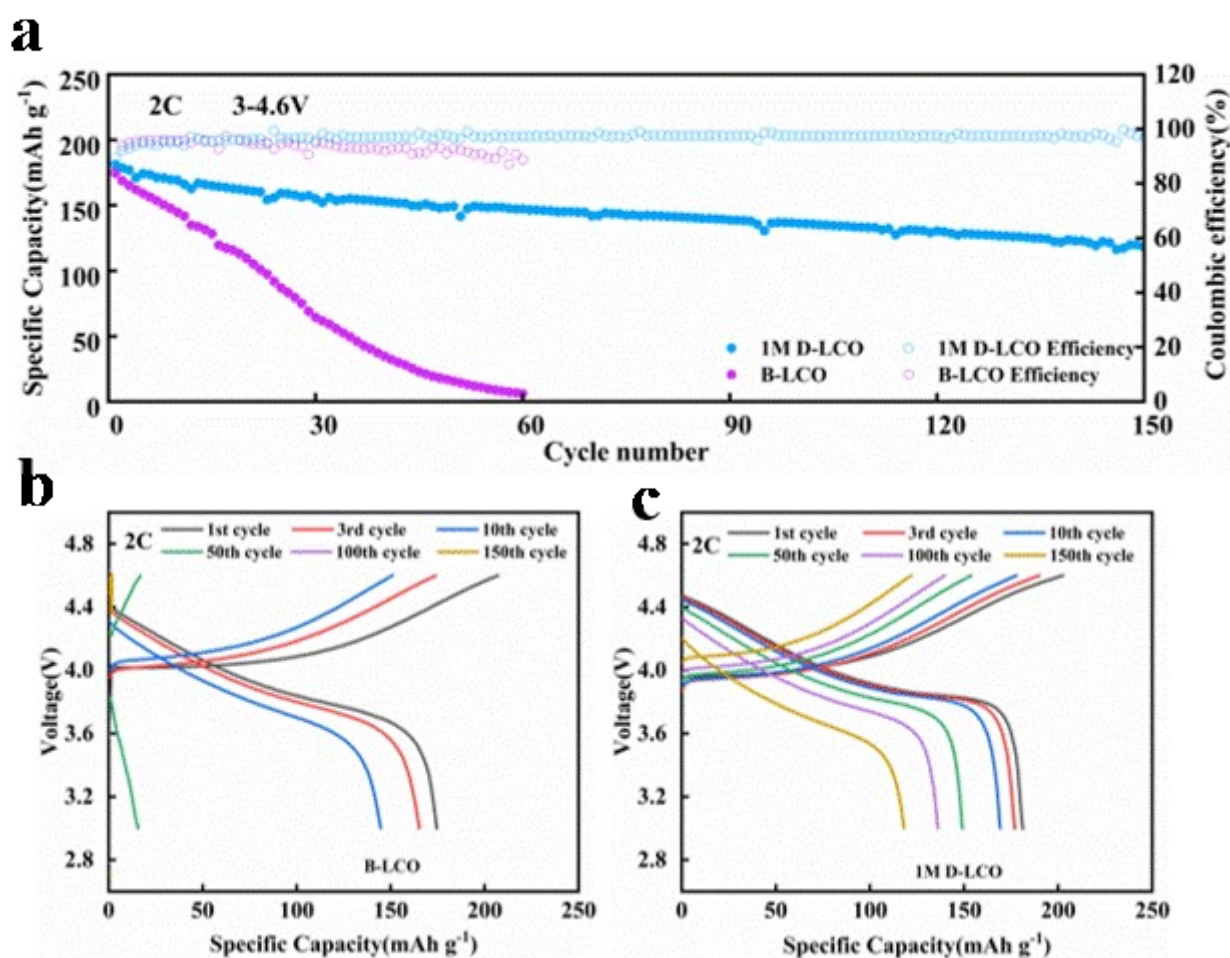


Fig. S12. (a) Cycling performance of the B-LCO|TMPTMA-HDDA/LLZTO|Li, 1M D-LCO|TMPTMA-HDDA/LLZTO|Li, cells for 150 cycles at 2 C in the voltage range of 3.0-4.6 V and the corresponding charge-discharge curves of (b) B-LCO|TMPTMA-HDDA/LLZTO|Li, and (c) 1M D-LCO|TMPTMA-HDDA/LLZTO|Li cells during cycling at 2 C.

Tab. S1 Comparison of electrochemical performance of matched high-voltage LCO cathode cell

Modified Cathode	Volatge (V vs Li/Li ⁺)	Current density	Discharge capacity (mAh g ⁻¹)	Capacity retention	Cell	Reference
PECA-LCO	2.5-4.45	/	172.8	/	PECA-LCO PEO-LiDFOB Li	1
PMA-LiTFSI-LCO	2.5-4.25	0.2 C	119	91.2%/100 th	LCO PEO-LiTFSI/PMA-LiTFSI Li	2
0.5%PAA-LCO	3-4.3	0.05 C	150.2	83.33%/90 th	0.5%PAA-LCO PEO-based SSE Li	3
LCO	2.75-4.3	0.5 C	140	87.2/350 th	LCO CSPE Li	4
PEO/LiDFOB-LCO	3-4.2	0.2 C	125	75%/100 th	D-PEO PEO-LiTFSI Li	5
LaPO ₄ /Al ₂ O ₃ -LCO	3-4.6	1 C	/	87%/200 th	LIBs	6
PVC/LiDFOB-LCO	2.8-4.4	2 C	141.2	83.57%/500th	1M D-LCO TMPTMA-HDDA/LLZTO Li	This work

Reference

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