

Figure S1. Tafel curves of Li||Li batteries in different electrolytes. (a) RCE, (b) LCE, (c) HCE.

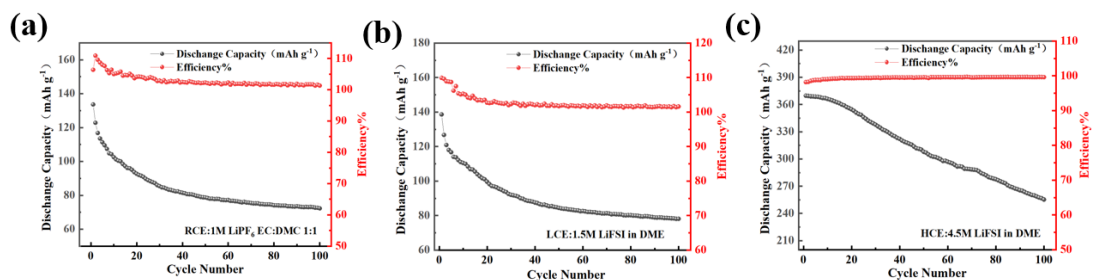


Figure S2. Cycle performance of Li||C batteries in different electrolytes. (a) RCE, (b) LCE, (c) HCE.

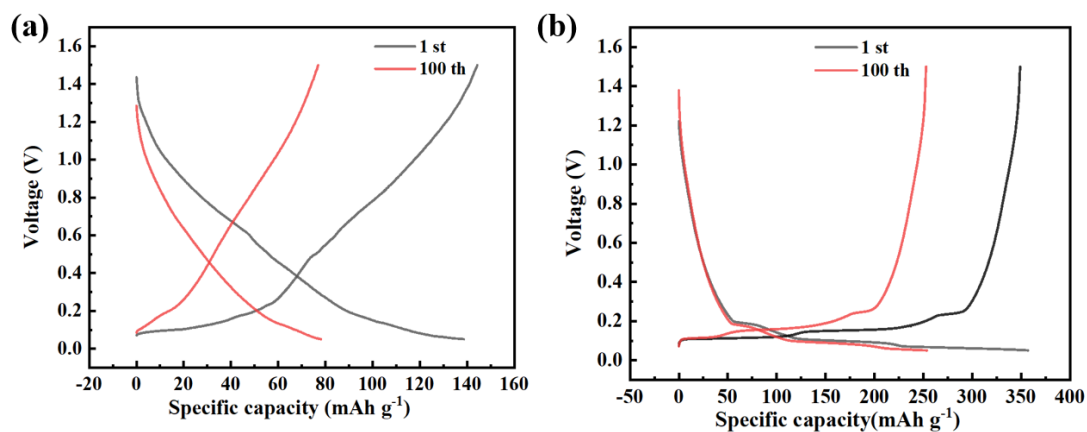


Figure S3. Capacity-voltage curves of Li||C batteries cycled in different electrolytes for the 1st and 100th cycles. (a) LCE, (b) HCE.

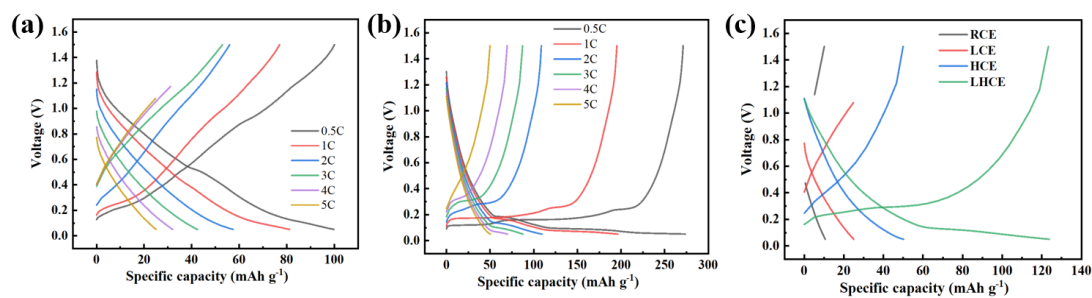


Figure S4. Capacity-voltage curves of Li||C batteries in different electrolytes at different rates. (a) LCE, (b) HCE, (c) Capacity-voltage curves of Li||C batteries in four electrolytes at 5C rate.

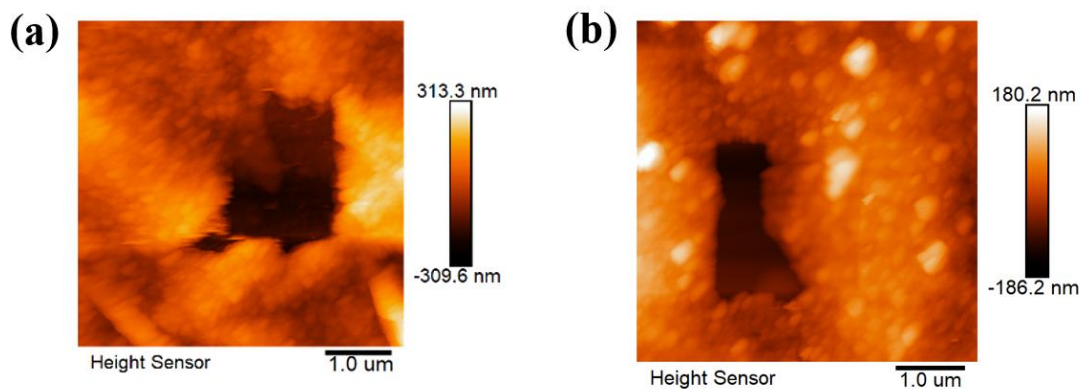


Figure S5. The SEI film appearance was removed by the AFM tip with a force of 5V. (a) RCE, (b) LHCE.

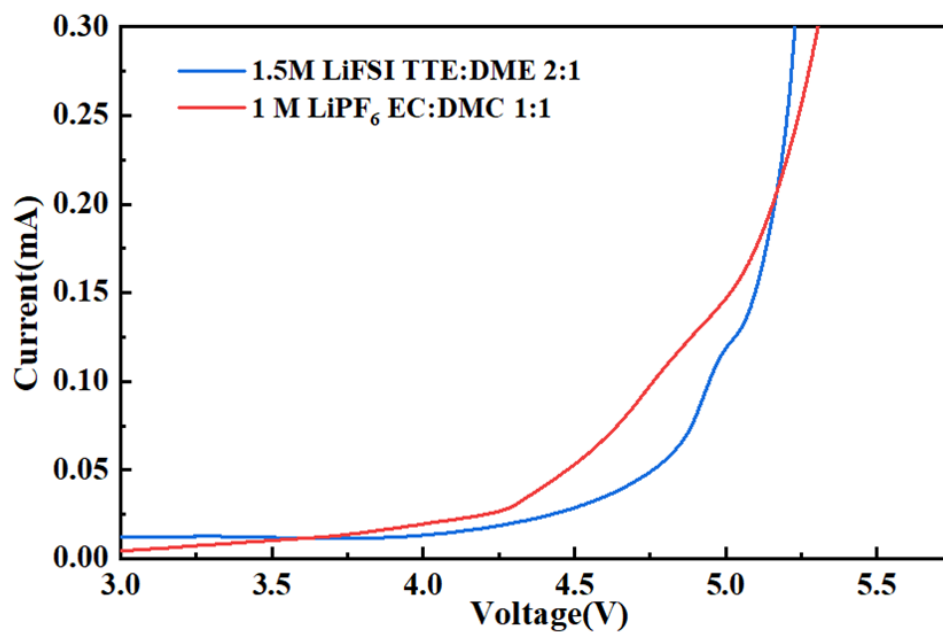


Figure S6. LSV curves of two electrolytes.

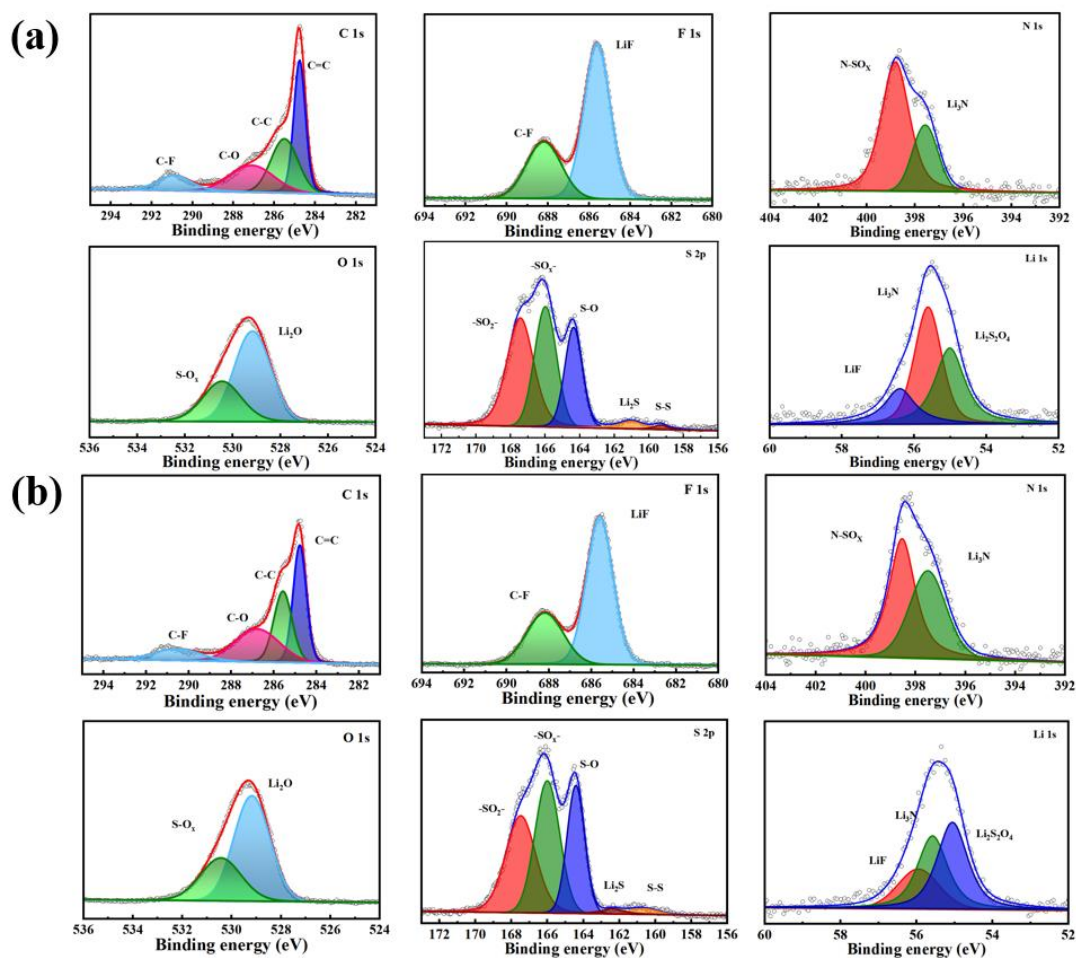


Figure S7. XPS analysis of graphite anode after three cycles in electrolyte. (a) LCE, (b) HCE.

Table S1. Research progress and comparison of LHCE

Year	Li metal battery	Electrolyte	Cycleability	Feature	Ref
2021	Li NCM87	TMP:LiDFOB:D ₂ 2:1:5	135 mAh g ⁻¹ (3 C)	electrochemical potential window : 5.2 V Nonflammable	[41]
2022	LFP Li	1.1 M LiFSI PFPN: DME 2: 1	130.8 mAh g ⁻¹ (5 C)	electrochemical potential window : 4.62 V Nonflammable	[42]
2022	Li-S	LiTFSI:DME:DOL:TME 1:1.5:1.5:6	554.68 mAh g ⁻¹ (0.5 C 400th)	electrochemical potential window : 4.8 V	[43]
2021	Li NCM523	2.3 M LiFSI DME: TTE 4:5	2.4 mAh cm ⁻² (3.2 C)	electrochemical potential window : 4.3 V	[44]
2022	Li NCM523	LiFSI:DME:FB (1:1.2:3.2)	3.1 mAh cm ⁻² (0.33 C)	exchange current density (0.26 mA/cm ²) Nonflammable	[45]
2023	Li NMC811	LiFSI:FEC:DME 1:0.1:1.4 +TTE +LiDFOB	155 mAh g ⁻¹ (0.5 C charge, 1 C discharge)	electrochemical potential window : 4.5 V	[46]
2020	Li C	1.5 M LiFSI BTFE:DME	90 mAh g ⁻¹ (-20°C,0.1C)	electrochemical potential window : 4.3 V	[30]
2020	Li LiCoO ₂	1.2 M LiPF ₆ FEC/DMC/HFE + 0.15 M LiDFOB	168 mAh g ⁻¹ (1 mA cm ⁻² ,300th)	electrochemical potential window : 4.85 V	[47]
2020	Li NCM523	2 M LiFSI-DMC/1,2- dfBen	120 mAh g ⁻¹ (0.5 C, 140th)	1,2-dfBen	[48]
2023	Li C	1.5 M LiFSI TTE:DME 2:1	124 mAh g ⁻¹ (5 C)	electrochemical potential window : 5.1 V	This study