Supplementary Information (SI) for New Journal of Chemistry.

Synergistic effect of fluorinated solvents and LiDFOB on stable cycling of Li metal batteries with limited Li

Calculation of the theoretical thickness of the thin lithium anode

The Li||Cu battery was subjected to constant current discharge at 0.1 mA for 24 hours, assuming no lithium loss during the discharge process. Formulas (1), (2), and (3) describe the calculation process.

$$m_{Li} = \frac{M_{Li} \times Q}{F} = \frac{6.94g/mol \times 8.64C}{96500C/mol} = 0.000621g \quad (1)$$

$$V_{Li} = \frac{m_{Li}}{p_{Li}} = \frac{0.000621g}{0.534g/cm^3} = 0.00116cm^3 \quad (2)$$

$$d_{Li} = \frac{V_{Li}}{A} = \frac{0.00116cm^3}{1.76cm^2} = 6.6\mu m \quad (3)$$

The total charge Q is given by Q = I·t, where I is the current and t is the time. F represents Faraday's constant (96,500 $C \cdot mol^{-1}$), M_{Li} is the molar mass of lithium (6.94 $g \cdot mol^{-1}$), ρ_{Li} is the density of lithium (0.534$g \cdot cm^{-3}$), and A is the surface area of the copper foil (1.76·cm^2). m_{Li} denotes the mass of lithium deposited on the copper foil, V_{Li} is the volume of lithium deposited on the copper foil, and d_{Li} is the thickness of the lithium deposited on the copper foil.

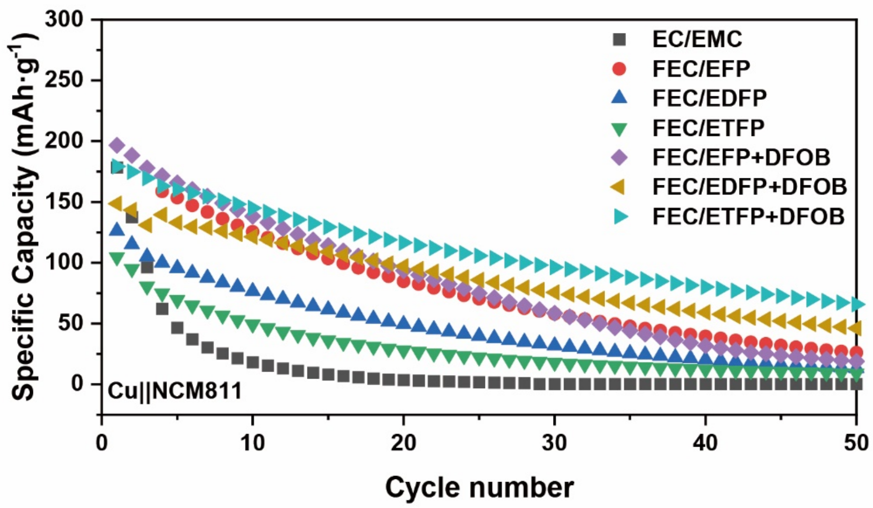

Fig S1 Cycling performance of Cu||NCM811 batteries using ethyl propionate electrolyte systems with varying degrees of fluorination.

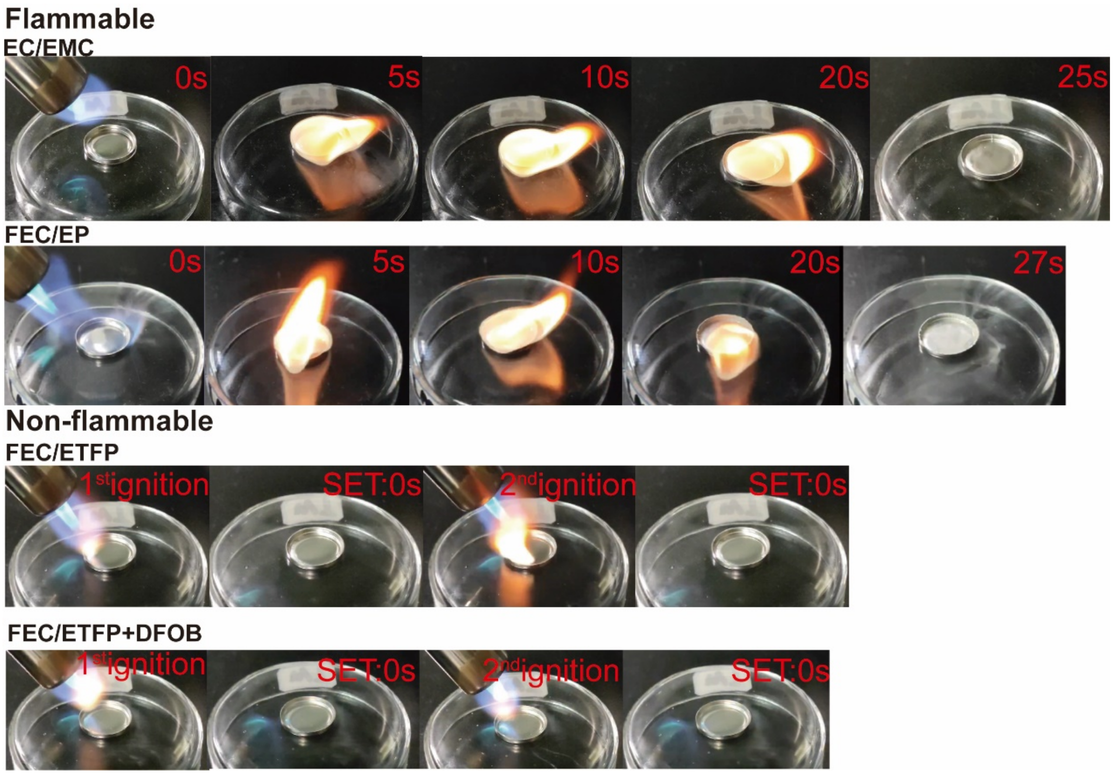

Fig S2 Photographs of the self-extinguishing experiments with different electrolytes.

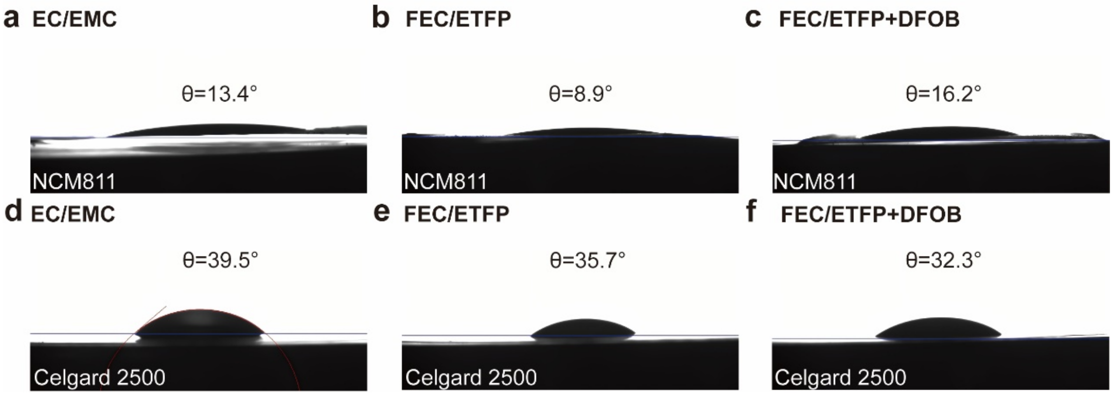

Fig S3 Contact angle measurements of three electrolytes: EC/EMC, FEC/ETFP, and FEC/ETFP+DFB.

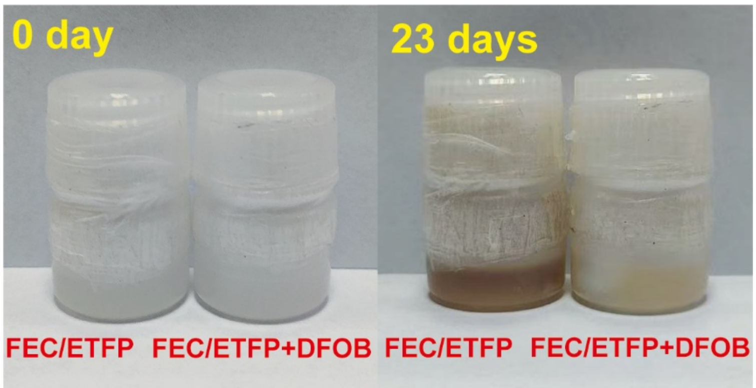

Fig S4 Color changes of FEC/ETFP and FEC/ETFP+DFOB electrolytes after 23 days of storage.

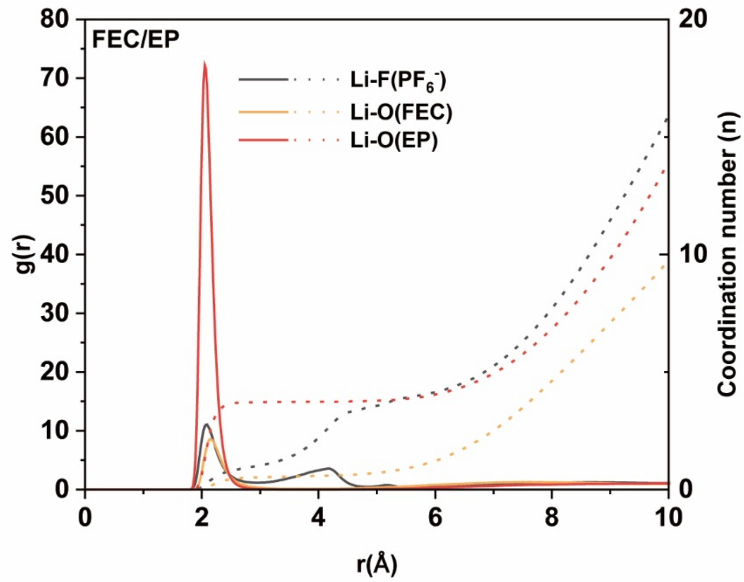

Fig S5 RDF and CN of FEC/EP.

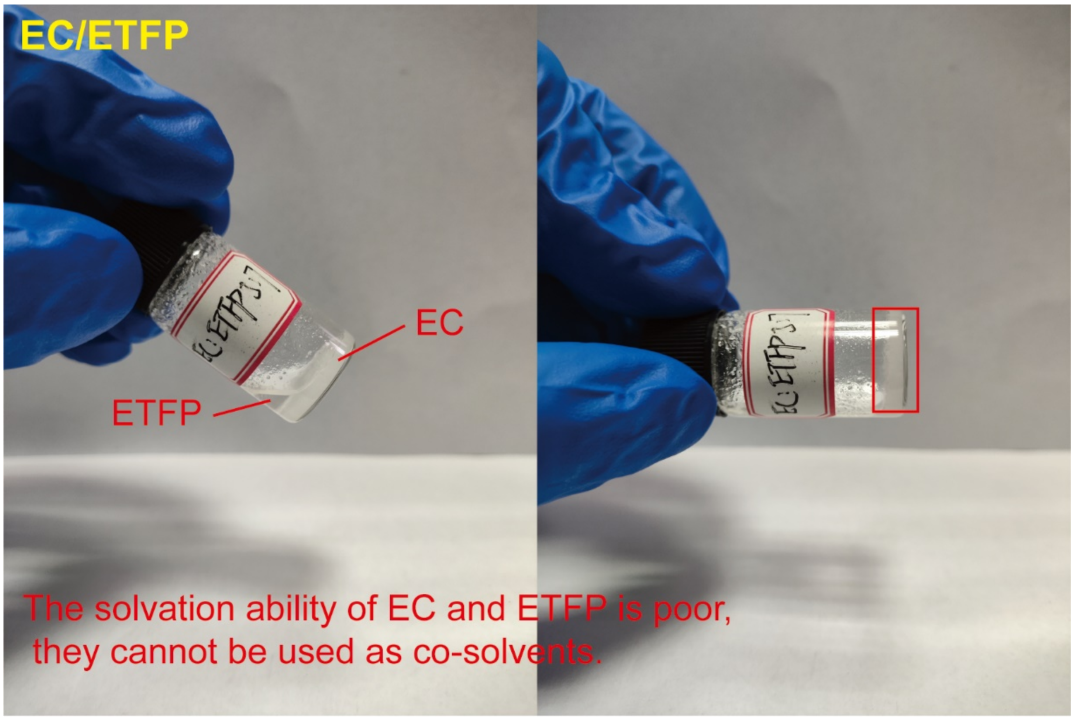

Fig S6 Photograph of the EC/ETFP.

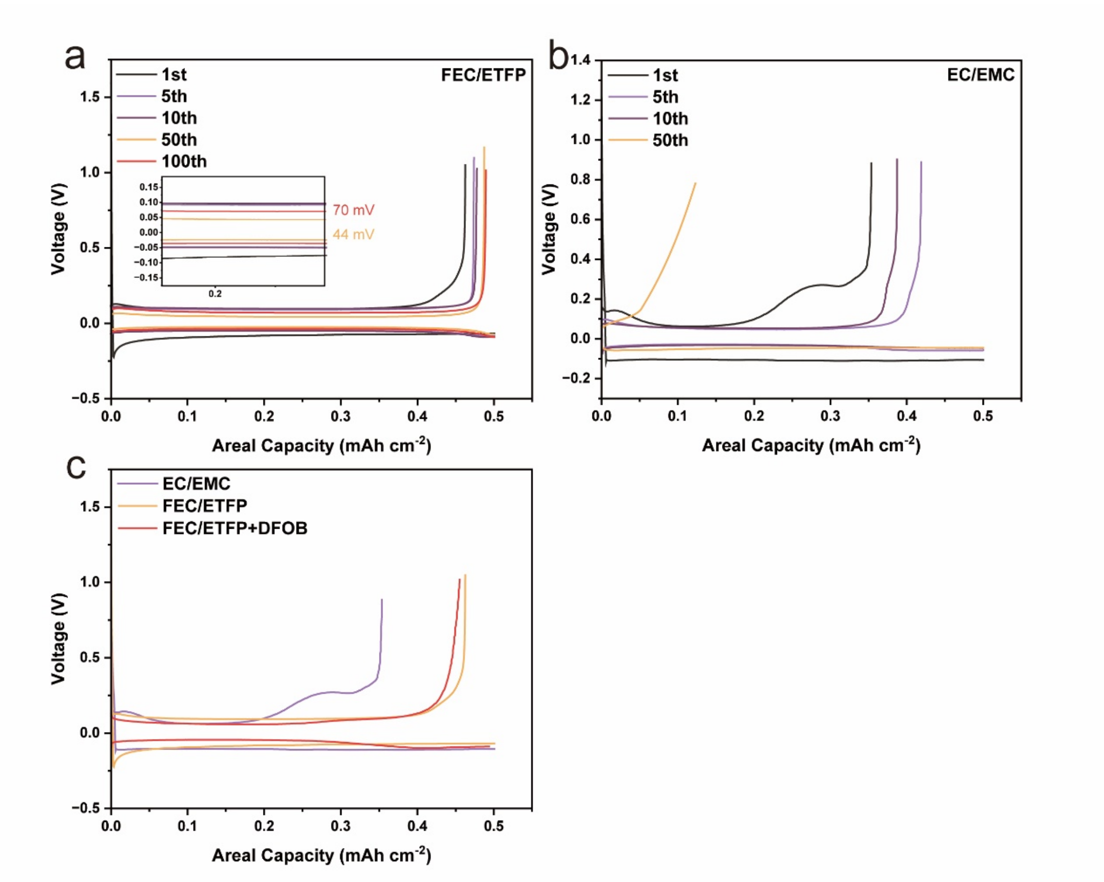

Fig S7 Deposition/stripping curves of Li||Cu batteries using FEC/ETFP (a) and EC/EMC (b). (c) Comparison of polarization voltages during the first cycle.

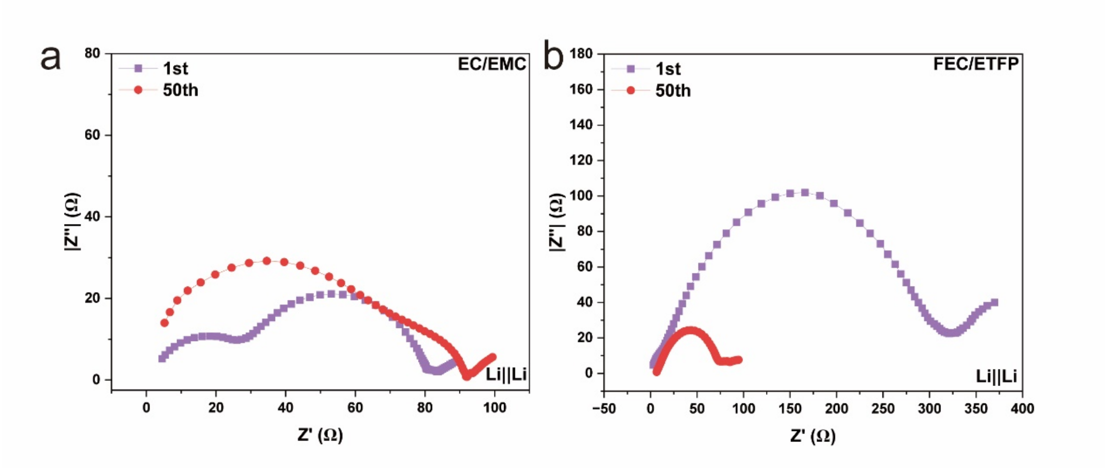

Fig S8 EIS curves of Li||Li batteries with EC/EMC (a) and FEC/ETFP (b).

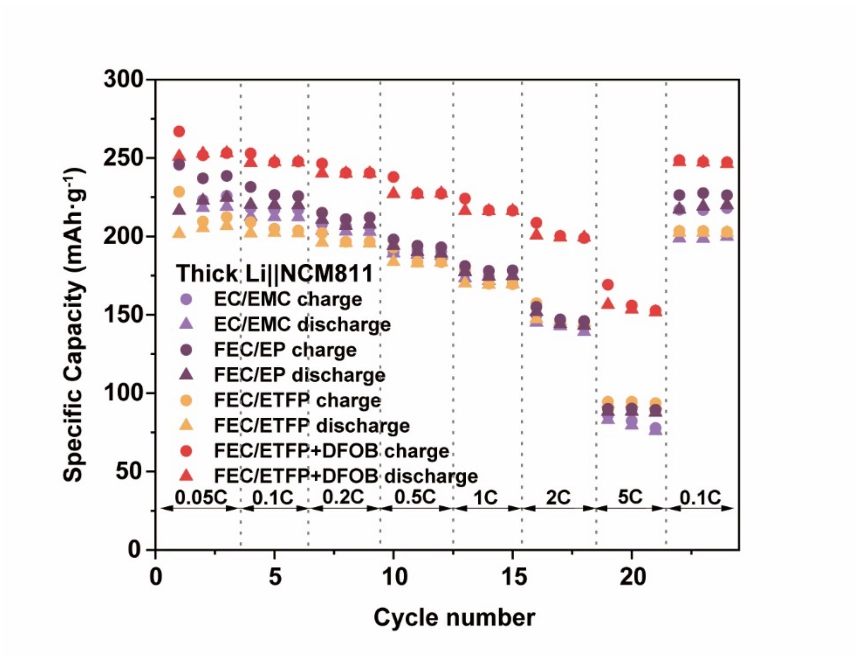

Fig S9 Rate performance of EC/EMC, FEC/EP, FEC/ETFP, and FEC/ETFP+DFOB electrolytes under thick Li conditions.

Table S1 Solvation shell cutoff radius, radial distribution function g(max), and coordination number N(r) for different electrolytes.

Electrolyte	Pair	T/K	r/Å	g(max)	N(r)
EC/EMC	Li-O_{EC}	298K	2.8	32.51	2.64
	Li-O_{EMC}		2.8	43.40	2.05
	Li-P_{PF6}		4.4	8.69	0.59
	Li-F_{PF6}		2.8	9.67	0.85
	Li-F_{PF6}		4.4		2.98
FEC/EP	Li-O_{FEC}	298K	2.8	8.47	0.50
	Li-O_{EP}		2.8	72.14	3.71
	Li-P_{PF6}		4.4	9.09	0.62
	Li-F_{PF6}		2.8	10.99	0.94
	Li-F_{PF6}		4.4		3.16
FEC/ETFP	Li-O_{FEC}	298K	2.8	19.71	1.03
	Li-O_{ETFP}		2.8	58.12	2.90
	Li-P_{PF6}		4.4	21.29	1.18
	Li-F_{PF6}		2.8	19.00	1.52
	Li-F_{PF6}		4.4		5.74
FEC/ETFP+DFOB	Li-O_{FEC}	298K	2.8	17.97	0.95
	Li-O_{ETFP}		2.8	52.42	2.61
	Li-P_{PF6}		4.4	27.13	1.35
	Li-F_{PF6}		2.8	21.26	1.63
	Li-F_{PF6}		4.4		6.51
	Li-F_{LiDFOB}		2.8	25.59	0.05
	Li-B_{LiDFOB}		4.4	16.30	0.06

Table S2 Comparison with the performance of similar studies previously reported.

Electrolyte	Cell condition	Cycling condition &	Ref.

formulation		capacity retention	
1 M $LiPF_6$ + 0.1 M LiDFOB-FEC/ETFP (3:7, v/v)	1.08 mAh·cm^{-2} Cu‖NCM811	3-4.3 V, 0.2C 0.5C, 36.7%@50 cycles	**This work**
	6.6 μm/1.08 mAh·cm^{-2} Li‖NCM811	3-4.3 V, 0.2C 0.5C, 67.35%@100 cycles	
	1.08 mAh·cm^{-2} Li‖NCM811	3-4.3 V, 1C, 90.29%@200 cycles	
1 M LiDFOB + 0.05 M $LiPF_6$-FEC/TTE/DEC (2:2:1, v/v)	2 mAh·cm^{-2} Cu‖NCM523	2.5-4.3 V, 0.1C, 45.52%@35 cycles	1
2 M $LiPF_6$-FEC/DEC (1:1, v/v, diluted by 50% FEC)	2 mAh·cm^{-2} Cu‖NCM111	2.5-4.3 V, 0.1C, 40%@50 cycles	2
4 M LiFSI-PC/FEC (93:7, v/v)	35 μm/4.8 mAh·cm^{-2} Li‖NCM811	3-4.6 V, 0.1C 0.2C, 94%@60 cycles	3
4 vol. %F_{6-0} + 0.08 M LNO + 1 M $LiPF_6$-EC/DMC (3:7, v/v,)	20 μm/210 mAh·g^{-1} Li‖NCM811	2.8-4.5 V, 0.5C, 92.5%@100 cycles	4
1 M $LiPF_6$-MDFA/PFPN/FEC	2.1 mAh·cm^{-2} Graphite‖NCM811	3-4.4 V, 1C, 80.03%@500 cycles	5
1 M $LiPF_6$-MTFP/FEC (9:1, v/v)	1.3 mAh·cm^{-2} Li‖NCM811	3-4.5 V, 0.5C, 80%@250 cycles	6
1.2 M $LiPF_6$-FEC/FEMC/TTE (2:6:2, v/v)	2.5 mAh·cm^{-2} Li‖NCM811	2.7-4.4 V, 1/3C 1C, 86.1%@200 cycles	7
1 M $LiPF_6$-PC/FEMC/DFDEC (3:2:5, v/v)	230 mAh·g^{-1} Li‖NCM811	2.7-4.5 V, 0.2C, 95%@100 cycles	8

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