Stable Lithium Metal Batteries Enabled by Localized High-Concentration Electrolytes with Sevoflurane as a Diluent

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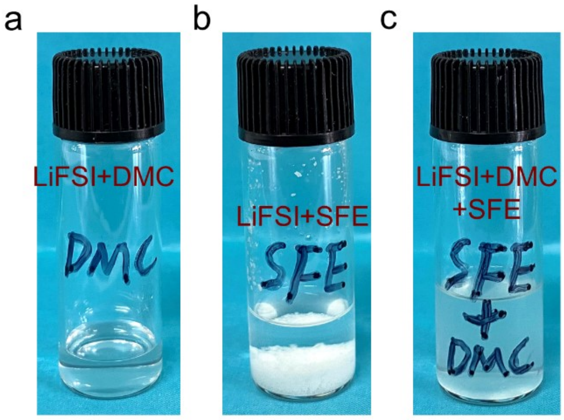


Figure S1. The solubility of LiFSI in SFE and DMC solutions. Photos are taken after 5.0 M LiFSI is added to DMC. (a) LiFSI was completely dissolved immediately. (b) As a sharp contrast, LiFSI was almost completely insoluble in SFE diluent. (c) SFE is highly miscible with a solution of LiFSI in DMC.

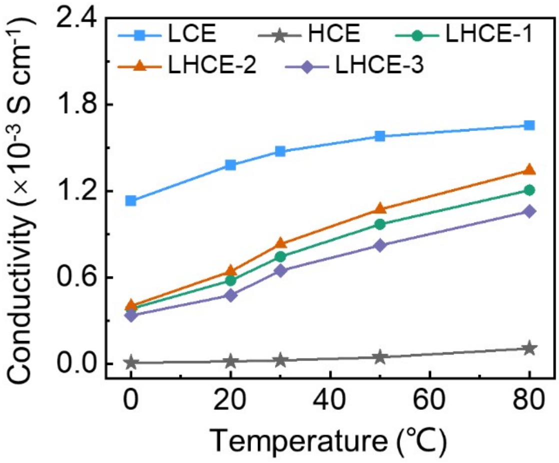


Figure S2. Ion conductivity of the electrolyte combined with 5 separators in LCE, HCE, and LHCEs with different molar ratio of DMC and SFE.

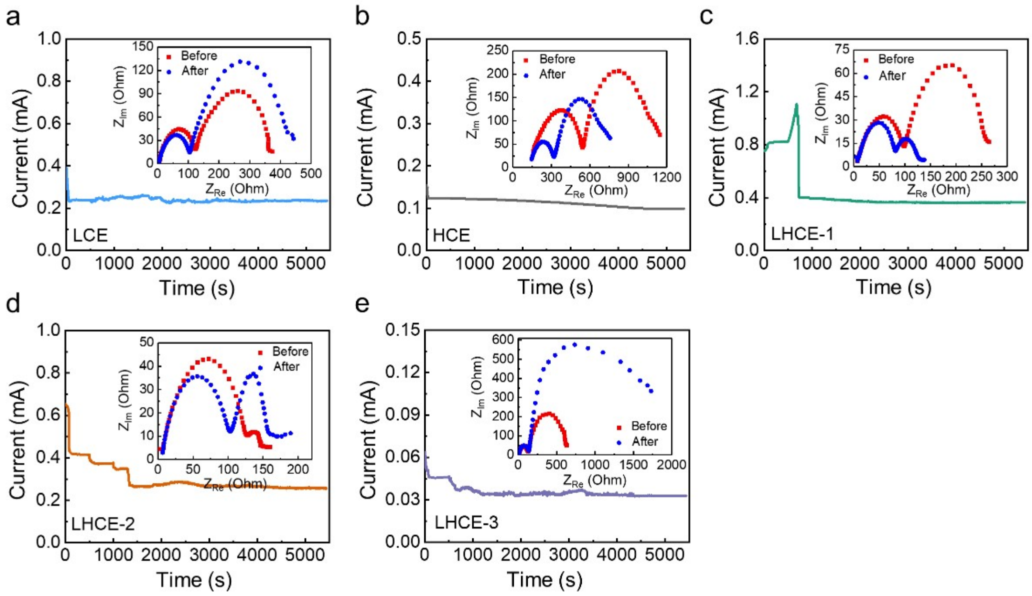


Figure S3. The lithium transference number (LTN) measurement of the (a) LCE, (b) HCE, (c) LHCE-1, (d) LHCE-2, and (e) LHCE-3 in Li||Li symmetric cells.

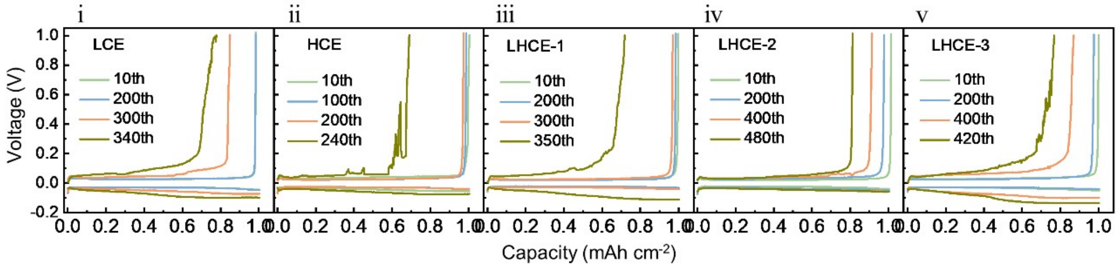


Figure S4. The voltage profiles of Li||Cu cells at selected cycled in different electrolytes.

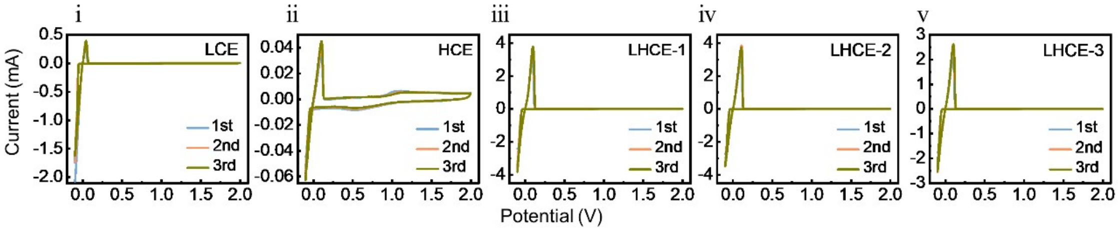


Figure S5. The CV cycles of Li||Cu cells with five different electrolytes (voltage range: -1 V to 2.0 V, scanning rate: 0.1 mV s^{-1}).

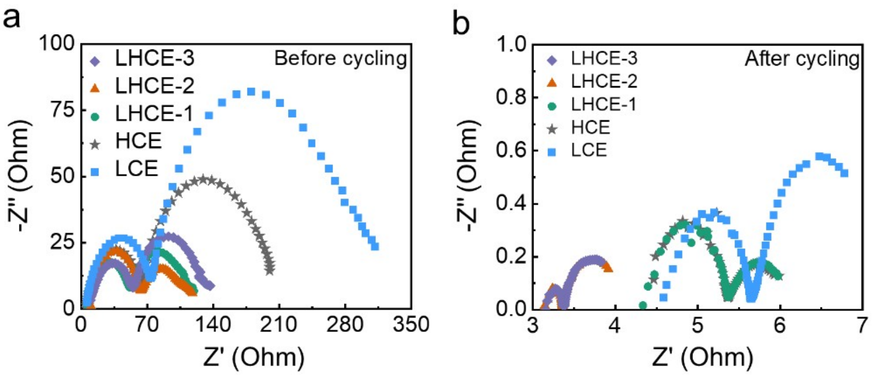


Figure S6. EIS results of Li||Li symmetric cells (a) before cycling, and (b) after long term cycling.

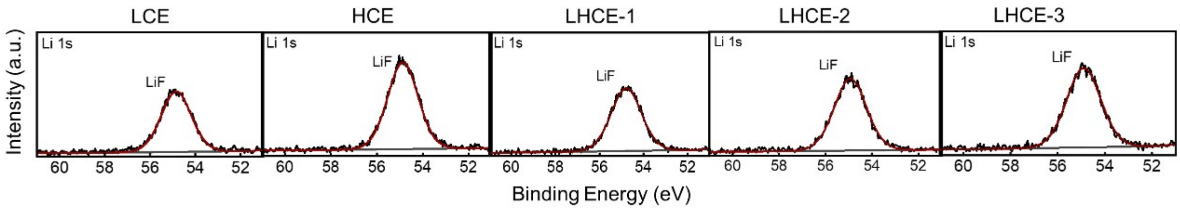


Figure S7. XPS analysis of the SEI composition on Li-metal anodes. Li 1s spectra of the SEI layers on Li electrodes after five cycles in different carbonate-based electrolytes.

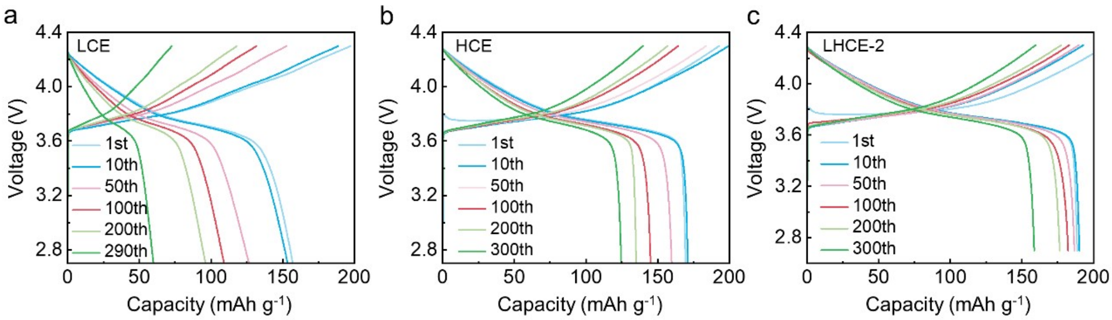


Figure S8. Voltage profiles upon cycling in (a) LCE, (b) HCE, and (c) LHCE-2.

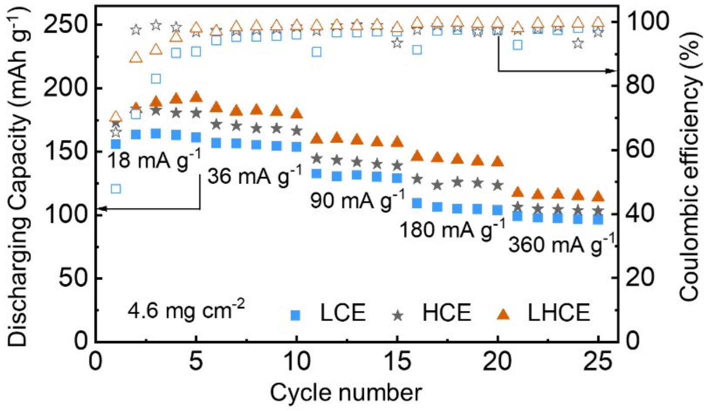


Figure S9. Rate performance of Li||NCM811 full cells using LCE, HCE, and LHCE-2 electrolytes.

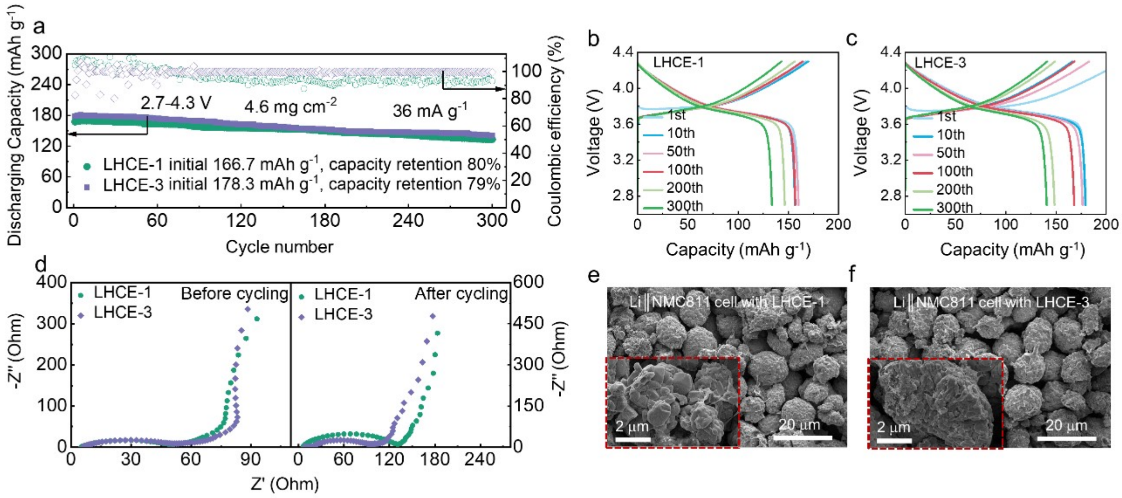


Figure S10. Electrochemical behavior and morphologies of Li||NMC811 full cells in the LHCE-1 and LHCE-3. (a) Cycling performance of Li||NMC811 cells. Voltage profiles of Li||NMC811 cells in (b) LHCE-1 and (c) LHCE-3. (d) EIS comparison of full cells before and after 300 cycles in two electrolytes. SEM images of the cycled cathodes using (e) LHCE-1 and (f) LHCE-3.

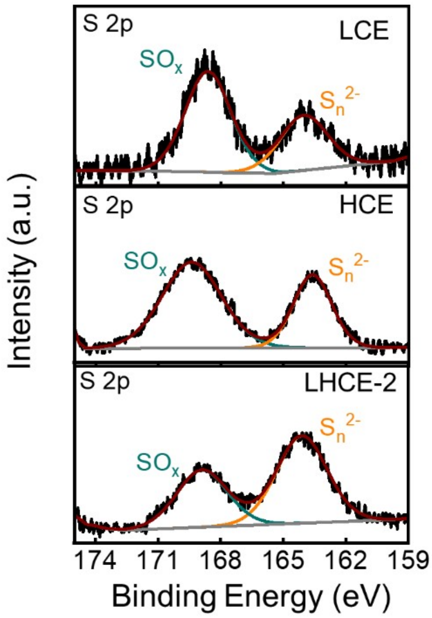


Figure S11. S 2p XPS spectra of the NMC811 cathodes cycled in LCE, HCE, and LHCE-2.

Table S1. Comparison of physical properties of BTFE, TTE, TEEO, and SFE.

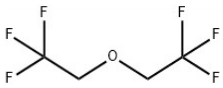
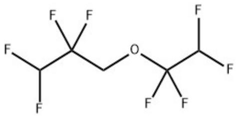
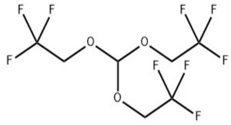
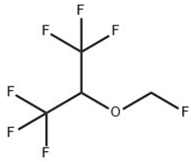
Parameter	BTFE	TTE	TEEO	SFE
Molecular Formula	$C_4H_4F_6O$	$C_5H_4F_8O$	$C_7H_7F_9O_3$	$C_4H_3F_7O$
Structural Formula				
Formula Weight (g mol^{-1})	182.06	232.07	310.12	200.05
Proportion of F (%)	62.62	65.50	55.14	66.48
Boiling point (°C)	63	92	164.7	58
Density (g cm^{-3})	1.404	1.533	1.51	1.505
Price	1g/$63.16	1g/$11.05	1g/$236.85	1g/$44.21
storage temp	-80°C, 6 months; -20°C, 1 month (sealed storage, away from moisture)	Sealed in dry, Room Temperature	storage at -4°C, 1~2 weeks; longer storage period at -20°C, 1~2 years	Refrigerator
Hazard Codes	F, Xi,T	Xi	Xi	Xi
Hazard Class	Flammable/Toxic/ Convulsant	IRRITANT	IRRITANT	IRRITANT

Table S2. Comparison of electrochemical performances of lithium battery using BTFE, TTE, TEEO, and SFE as inert diluents.

Electrolyte	Cell chemistry	Current density	Performances	References
LiFSI/DMC/BTFE (0.41:1:2 by molar)	Li||Cu	1.0 mA cm^{-2}	Avg. CE: 99.4% after 11 cycles	Chen et al, Adv. Mater. 2018, 30, 1706102.
		5.0 mA cm^{-2}	Avg. CE: 92.6% after 11 cycles	
	450 µm Li||NMC333	2.0 mA cm^{-2}	80% capacity retention after 700 cycles	
LiFSI/DME/TTE (1:1.2:3 by molar)	Li||Cu	0.5 mA cm^{-2}	Avg. CE: 99.3% after 300 cycles	Ren et al, Joule, 2019, 3, 1662.
	450 µm Li||NMC811	0.5 mA cm^{-2}	~87% capacity retention after 300 cycles	
LiFSI/DMC/TTE (0.67:1:1 by molar)	Li||Cu	1.0 mA cm^{-2}	Avg. CE: 98.6% after 400 cycles	Piao et al, Adv. Energy Mater. 2020, 10, 1903568.
	Li||NMC622	2.0 C	80.1% capacity retention after 200 cycles	
LiFSI/DME/TEEO (1:1.2:2 by molar)	Li||Cu	0.5 mA cm^{-2}	Avg. CE: 99.2% after 5000 min	Cao et al, Energy Storage Mater. 2021, 34, 76.
	50 µm Li||NMC811	1.4 mA cm^{-2}	80 % capacity retention after 205 cycles	
LHCE-2 (LiFSI/DMC/SFE, 0.42:1:1 by molar)	Li||Cu	1.0 mA cm^{-2}	Avg. CE: 95% after 480 cycles	This work
	Li||Cu	5.0 mA cm^{-2}	Avg. CE: 99.5% after 225 cycles	
	100 µm Li||NMC811	36 mA g^{-1}	84 % capacity retention after 300 cycles	