Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Localized high-concentration electrolyte enabled by a novel ester diluent for lithium metal batteries

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Experimental section

Materials Preparation

Lithium bis(fluorosulfonyl)imide (LiFSI, 99.9%) and dimethyl carbonate (DMC, 99.9%) were purchased from Huizhou City Avenue New Materials Technology Co., Ltd. The diluent, 2,2,2-trifluoroethyl trifluoromethanesulfonate (TFEOTf, 99%), was bought from Sinopharm Chemical Reagent Co., Ltd. All of the materials mentioned above were employed without further purification. Electrolytes were prepared in glovebox (H_2O < 0.01 ppm, O_2 < 0.01 ppm) filled with Ar. The cathode was prepared by blending $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$, Super-P and polyvinylidene fluoride in a mass ratio of 93:5:2 with appropriate amount of N-methyl pyrrolidinone (all from Canrd) as a dispersant, immediately after which the slurry was coated on aluminum foil and then dried in a drying oven. Finally, the prepared electrode was cut into 12 mm diameter disks with an areal density of about 10.8 mg cm^{-2}.

Materials Characterizations

Deposited Li and SEI films, rinsed by DMC for at least 3 times and followed by vacuum drying, were measured on Apreo S (Thermo Scientific) at 2.0 kV to obtain SEM images. Raman spectra were collected by inVia Qontor (Renishaw) using 785 nm laser. XPS for cycled Li anode was tested by K-Alpha (Thermo Scientific). The viscosity and density for laboratory-made electrolytes were measured by Micro Viscometer EDXLovis 2000 M (Anton Paar) equipped with a densitometer. Contact angle tests were carried out on PP separator (Celgard 2400) with different electrolytes through OCA20 (Dataphysics) at 25 °C and the images were analyzed by software Image J.

Electrochemical Measurements

CR2025 coin cells were assembled in a glove box and tested on CT-4008Tn (Neware) for further examination on the electrochemical performances. For Li||Li symmetric cells, EIS was measured on autolab PGSTAT302N (Metrohm) with frequency ranging from 10^6 Hz to 0.1 Hz, and the applied voltage stayed 5 mV. LSV was conducted on the same instrument as EIS, ranging from 3 V to 6 V, with aluminum foil as positive electrode and Li chip as negative electrode, the scanning rate of which was 1 mV s^{-1}. 80 μl electrolyte was added into each CR2025 coin cell if no detailed explanation was mentioned. 1 C is equal to 180 mAh g^{-1}. Li||Cu and Li||Li cells were assembled with regular stainless steel positive electrode shells, while other cells charged over 4 V were assembled with Al-clad ones (Canrd) to avoid the corrosion from electrolyte. For CE tests, Li||Cu cells were adopted following the procedures: (1) Depositing 5 mAh cm^{-2} of Li onto Cu foil and stripping all Li to 1 V to exclude the uncertain factors from Cu substrate; (2) Depositing 5 mAh cm^{-2} of Li onto Cu foil as Li reservoir, based on which cycling in the galvanostatic mode with 1 mAh cm^{-2}; (3) After cycling, then stripping all Li to 1 V. All the current density concerned is 0.5 mA cm^{-2}. The CE was calculated by formula as followed:

$$CE_{avg} = \frac{nQ_C + Q_S}{nQ_C + Q_T}$$

where Q_T is the charge deposited for the second time, n represents the cycling numbers and Q_C refers to charge of each cycle in procedure (2), Q_S is the final stripping charge in procedure (3).

Supplementary Figures

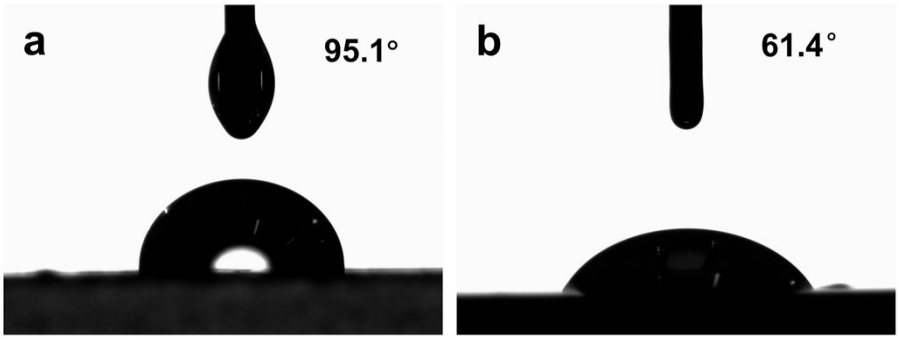

Fig. S1. Contact angle tests of (a) HCE of LiFSI-1.2DMC and (b) LHCE of LiFSI-1.2DMC-0.75TFEOTf on the separator celgard 2400.

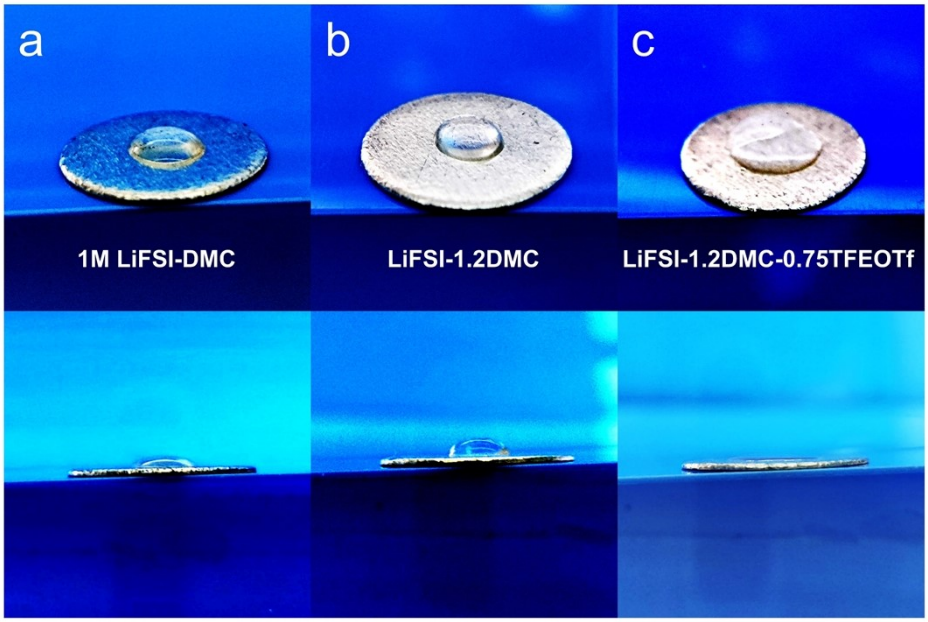

Fig. S2. Optical photos of 20 μl (a) dilute electrolyte 1M LiFSI-DMC, (b) HCE of LiFSI-1.2DMC and (c) LHCE of LiFSI-1.2DMC-0.75TFEOTf on the surface of Li chip.

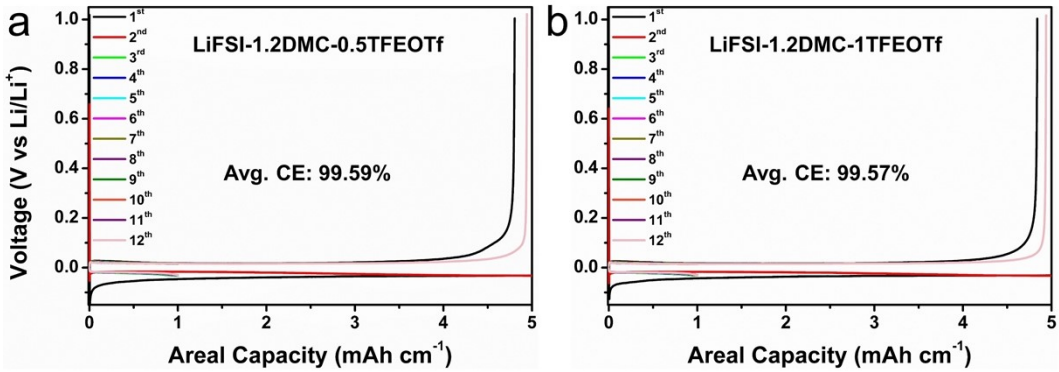

Fig. S3. Coulombic efficiency determined by Li||Cu half cells with LHCE of (a) LiFSI-1.2DMC-0.5TFEOTf and (b) LiFSI-1.2DMC-1TFEOTf.

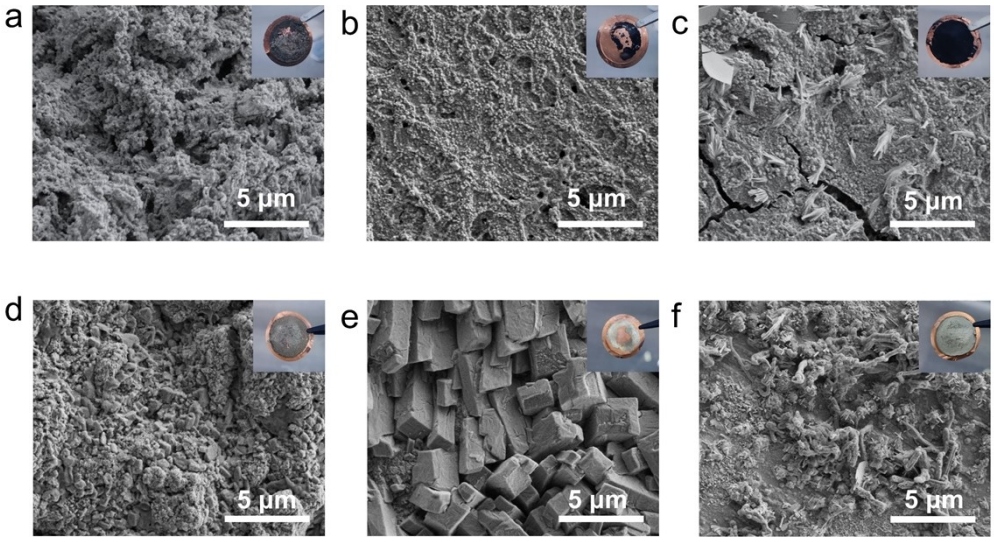

Fig. S4. SEM images for SEI on Cu substrate after cycling for 10 cycles and top view of Li deposition topography with (a)(d) dilute electrolyte 1M LiFSI-DMC, (b)(e) HCE of LiFSI-1.2DMC and (c)(f) LHCE of LiFSI-1.2DMC-0.75TFEOTf. Insets are optical photos of dissembled Cu electrodes.

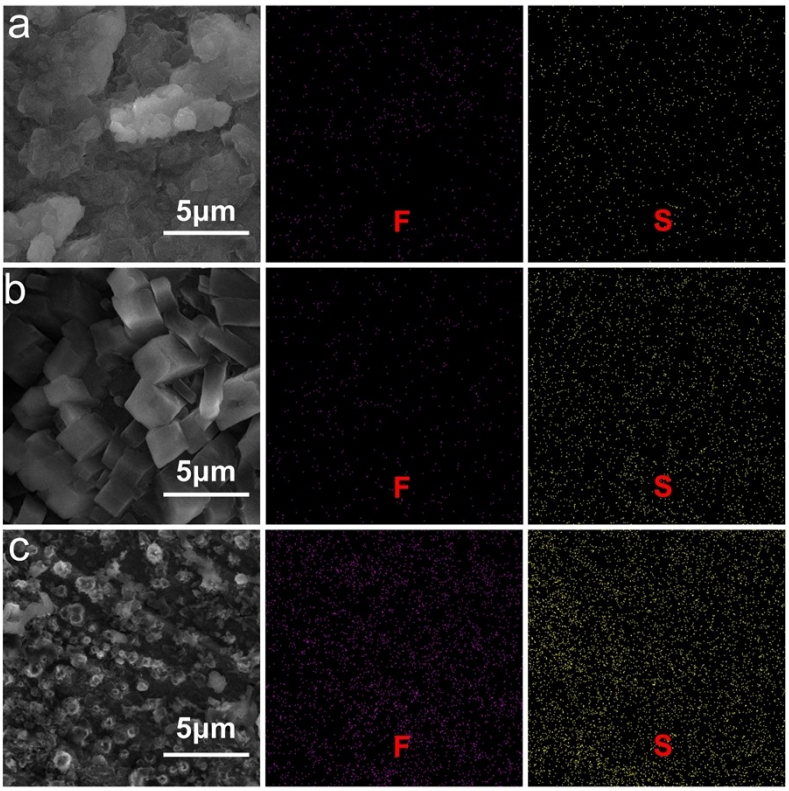

Fig. S5. EDX elemental mappings of deposited Li in electrolyte (a) 1M LiFSI-DMC, (b) LiFSI-1.2DMC and (c) LiFSI-1.2DMC-0.75TFEOTf.

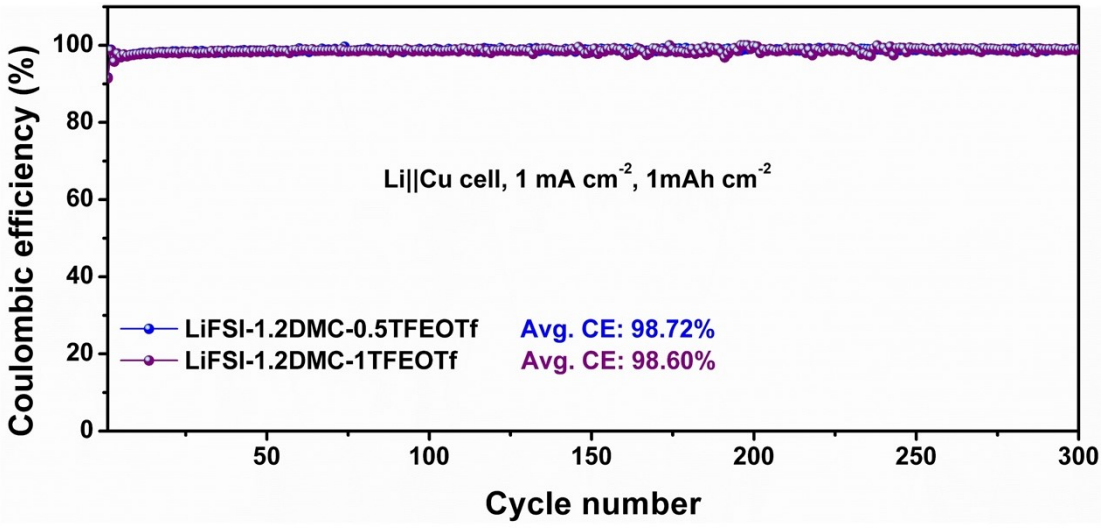

Fig. S6. CE of Li||Cu half cells cycling in LiFSI-1.2DMC-0.5TFEOTf and LiFSI-1.2DMC-1TFEOTf at 1 mA cm^{-2} with areal capacity of 1 mAh cm^{-2}.

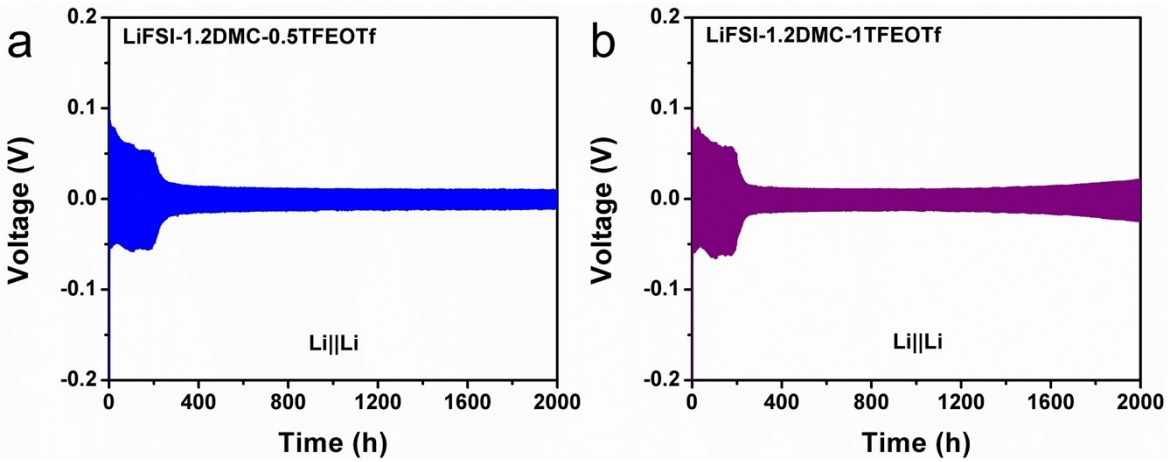

Fig. S7. The voltage curves of (a) LiFSI-1.2DMC-0.5TFEOTf and (b) LiFSI-1.2DMC-1TFEOTf by Li||Li symmetric cells at a current density of 1 mA cm^{-2} with capacity of 1 mAh cm^{-2}.

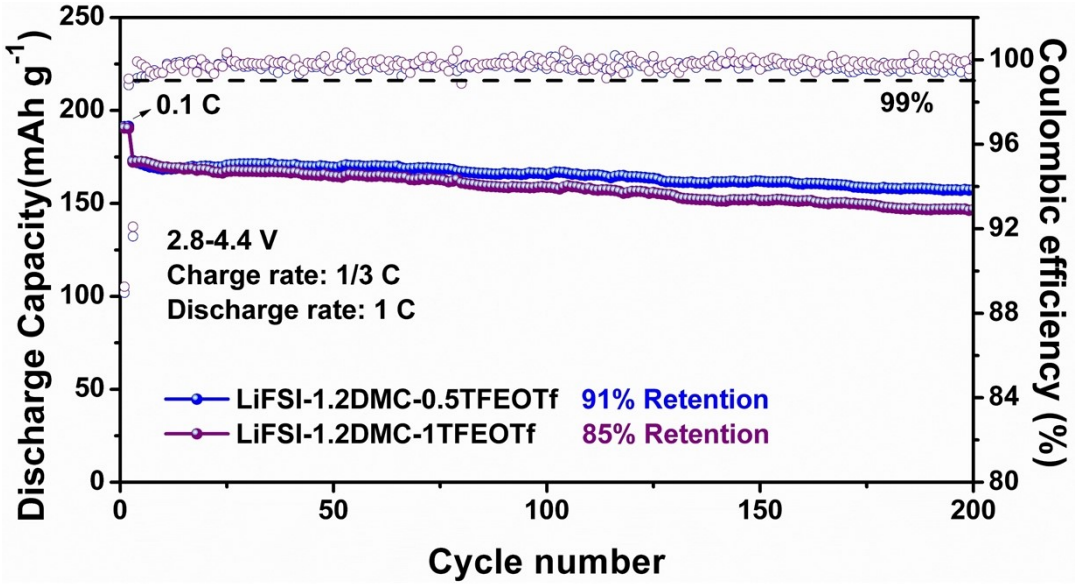

Fig. S8. Cycling stability and CEs of Li||NMC622 cells with LHCEs after two formation cycles at 0.1 C (1 C=180 mAh g^{-1}).

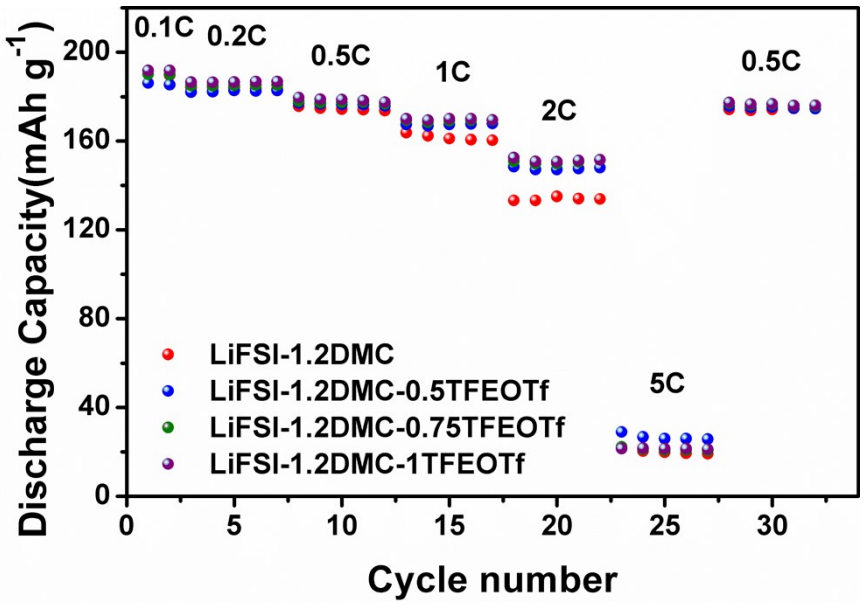

Fig. S9. Rate capability of HCE and LHCEs.

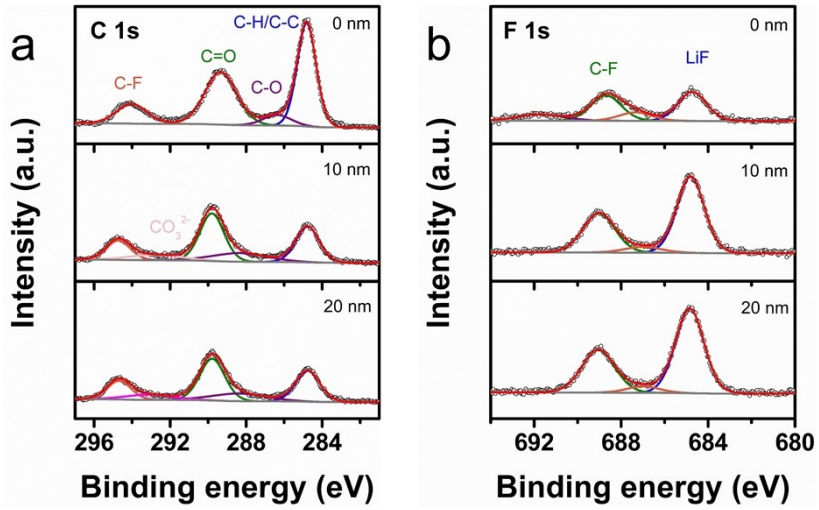

Fig. S10. Depth profiling C 1s (a) and F 1s (b) XPS spectra for SEI on Li surface after 100 cycles in HCE of LiFSI-1.2DMC.

Supplementary Tables

Table S1. Basic physical parameters of different electrolytes.

Electrolyte	Molar ratio	Mass Ratio	Density g/cm^3	Molarity mol/L	Molality mol/kg	Viscosity (25℃) mPa s
1M LiFSI-DMC	1:11.8	1.87:10.69	1.17	0.93	0.94	1.80
LiFSI-1.2DMC	1:1.2	1.87:1.08	1.55	5.25	3.39	220.90
LiFSI-1.2DMC-0.5TFEOTf	1:1.2:0.5	1.87:1.08:1.16	1.57	3.82	2.43	52.37
LiFSI-1.2DMC-0.75TFEOTf	1:1.2:0.75	1.87:1.08:1.74	1.58	3.37	2.13	33.41
LiFSI-1.2DMC-1TFEOTf	1:1.2:1	1.87:1.08:2.32	1.58	3.00	1.90	23.61

Table S2. Excess Li calculation under different conditions (Assume Li could be consumed completely before capacity fading happens in Li||NMC cells).

CE of Li cycling %	Cycling numbers with 90% capacity retention	Requirements of excess Li based on cathode capacity %
99.6	500	190
	1000	390
99.4	500	290
	1000	590
99.2	500	390
	1000	790
99.0	500	490
	1000	990

Table S3. Qualitative analysis of elements on deposited Li surface in LiFSI-1.2DMC-0.75TFEOTf through EDX elemental mapping.

Element	Weight %	Atom %
C	5.65	7.69
N	9.64	11.24
O	55.22	56.38
F	27.62	23.74
S	1.87	0.95
Total	100.00	100.00