

Supporting Information

Stabilization of lithium metal in concentrated electrolytes: effects of electrode potential and solid electrolyte interphase formation

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Table S1 Li electrode potential (E_{Li}) with reference to Fc/Fc⁺ extracted from cyclic voltammograms (Fig. S1) in two or three cells for each electrolyte

LiFSI:DEE molar ratio	Molality (m)	Molarity (M)	E_{Li} (V vs. Fc/Fc ⁺)			
			Cell #1	Cell #2	Cell #3	Average
1:71	0.12	0.10	-3.42	-3.44	-3.47	-3.44
1:14	0.60	0.50	-3.36	-3.35	-3.36	-3.36
1:6.6	1.3	1.0	-3.34	-3.33	-3.33	-3.33
1:4.2	2.0	1.5	-3.31	-3.31	-3.31	-3.31
1:3.0	2.8	2.0	-3.29	-3.28	-3.29	-3.29
1:1.8	4.7	3.0	-3.20	-3.20	-3.20	-3.20
1:1.2	7.1	~4.0	-3.08	-3.06	-3.05	-3.06
1:1.0	8.5	~4.5	-3.00	-3.00	-3.00	-3.00
1:0.85	10	~5.0	-2.95	-2.95	-	-2.95

Table S2 Chemical compositions, Li electrode potential (E_{Li}), Raman peak position of S-N-S vibration of FSI⁻, and average Coulombic efficiency (CE) of Li plating/stripping during 2nd-20th cycles in LiFSI/DEE electrolytes

LiFSI:DEE molar ratio	Molality (m)	Molarity (M)	E_{Li}^* (V vs. Fc/Fc⁺)	FSI⁻ Raman peak (cm⁻¹)	Li CE** (%)
1:71	0.12	0.10	-3.44	-	19.6
1:14	0.60	0.50	-3.36	-	-
1:6.6	1.3	1.0	-3.33	721	93.7
1:4.2	2.0	1.5	-3.31	722	-
1:3.0	2.8	2.0	-3.29	723	95.6
1:1.8	4.7	3.0	-3.20	728	96.3
1:1.2	7.1	~4.0	-3.06	741	96.1
1:1.0	8.5	~4.5	-3.00	744	-
1:0.85	10	~5.0	-2.95	-	96.3

*For E_{Li} , the average values obtained in two or three cells are shown.

**For Li CE, the average values obtained in three cells (Table S3) are shown.

Table S3 Average Coulombic efficiency (CE) of Li plating/stripping during 2nd-20th cycles in three Cu|Li cells for each LiFSI/DEE electrolyte

LiFSI:DEE molar ratio	Molality (m)	Molarity (M)	Average Li CE during 2nd-20th cycles (%)			
			Cell #1	Cell #2	Cell #3	Average
1:71	0.12	0.10	16.6	21.7	20.4	19.6
1:6.6	1.3	1.0	93.6	93.7	93.8	93.7
1:3.0	2.8	2.0	95.4	95.5	96.0	95.6
1:1.8	4.7	3.0	96.1	96.4	96.5	96.3
1:1.2	7.1	~4.0	95.5	95.9	96.8	96.1
1:0.85	10	~5.0	95.6	96.5	96.9	96.3

Table S4 Details of liquid model used in the DFT-MD

	Dilute	Concentrated
LiFSI:DEE molar ratio	10	1:2
Density (g cm ⁻³)	0.92	1.17
# mol. (Solv/Anion)	77 (70/7)	99 (66/33)
#Atoms	1610	1782
Lx (Angstrom)	25.860	22.068

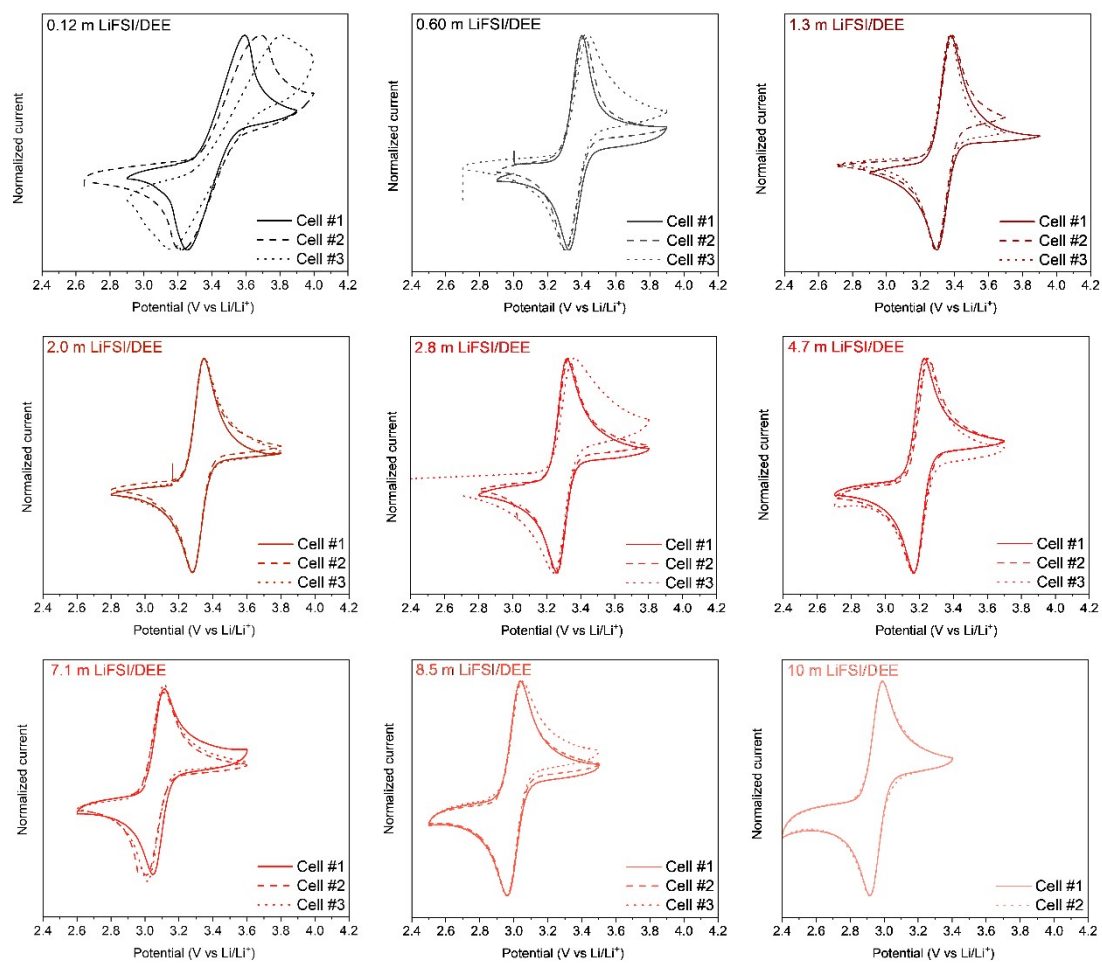


Fig. S1 Cyclic voltammograms (scan rate: 5 mV s^{-1}) of Fc/Fc⁺ redox in LiFSI/DEE at various LiFSI salt concentrations. 1 mM Fc was introduced in each electrolyte. Two or three cells were assembled for each electrolyte and subjected to cyclic voltammetry.

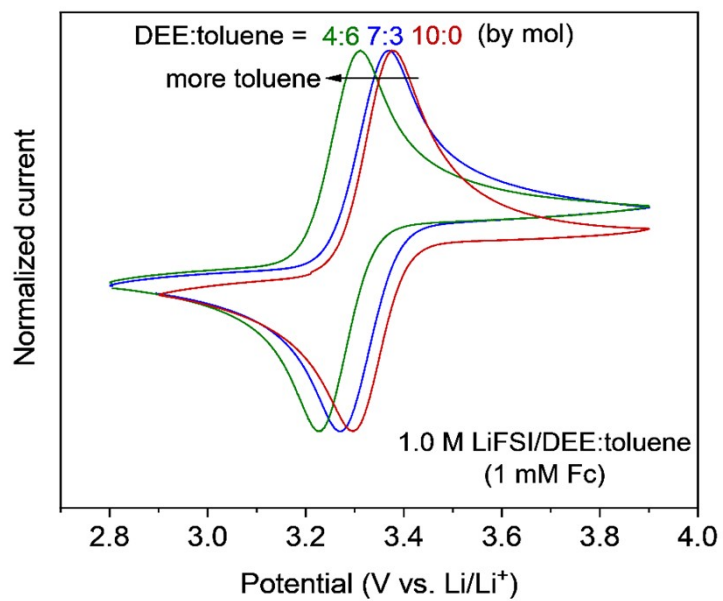


Fig. S2 Cyclic voltammograms (scan rate: 5 mV s⁻¹) of Fc/Fc⁺ redox on Pt electrode in 1.0 M LiFSI/DEE:toluene at various DEE:toluene molar ratios. An electrolyte with the highest amount of non-solvating toluene (DEE:toluene = 4:6 by mol) shows the highest E_{Li} of -3.26 V vs. Fc/Fc⁺.

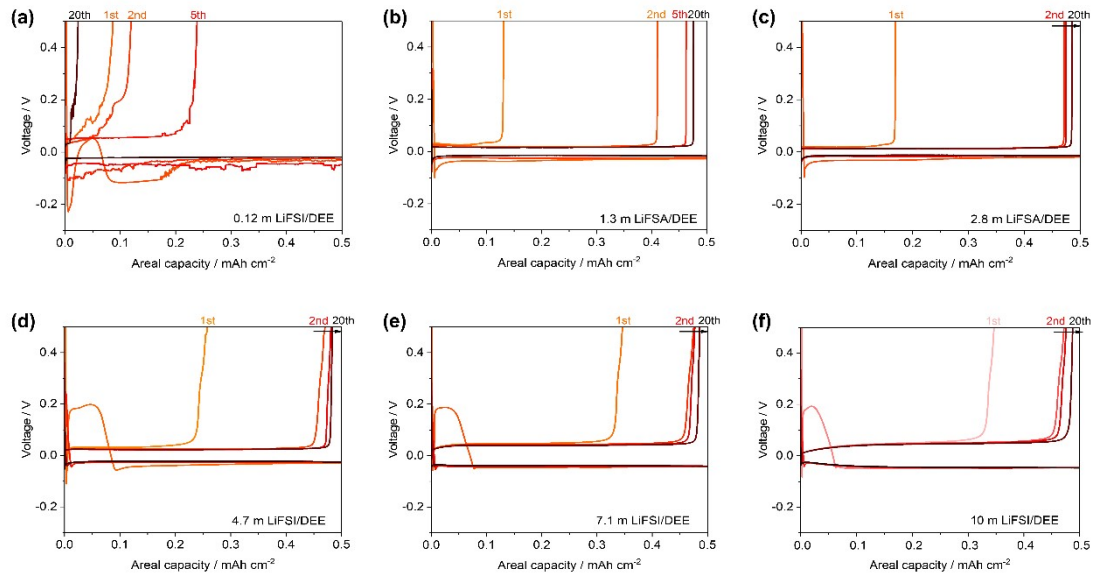


Fig. S3 Charge-discharge curves of Cu|Li cells with (a) 0.12 m, (b) 1.3 m, (c) 2.8 m, (d) 4.7 m, (e) 7.1 m, and (f) 10 m LiFSI/DEE in 1st, 2nd, 5th, and 20th cycles. The applied constant current was 0.5 mA cm⁻². Li was plated for 1 h, followed by Li stripping up to 0.5 V.