# **Supplementary Information**

# Eco-friendly electrolytes via robust bond design for high-

# energy Li-metal batteries

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## **Experimental Methods**

#### Materials

TEOS, MTES, DMES, and DMMS were purchased from Adamas. Battery-grade LiPF<sub>6</sub>, LiFSI, EC, DMC, DME, polyvinylidene difluoride (PVDF) and N-methylpyrrolidone (NMP) were obtained from DodoChem. 1,4-DX was purchased from Aladdin. Thick Li metal anodes (15.6 mm diameter, and 500 µm thick) and thin Li metal anodes plating on Cu collector were received from China Energy Lithium. NCM811 and LCO cathode particles were purchased from Kelude Co, Ltd. Celgard2325 battery separator was bought from MTI and used in all cells. Cu and Al collectors, 2025-type coin-cell cases, springs and spacers were purchased from MTI.

#### Electrolytes

Before using, all solvents were dried by 400 °C pretreatment 4 Å molecular sieves (Aladdin) until water content less than 20 ppm. All electrolyte were prepared in Ar-filled glovebox ( $H_2O < 0.1$  ppm, and  $O_2 < 0.1$  ppm) following corresponding formulas.

### **Electrochemical measurements**

2025-type coin cells components were purchased from MTI. All cells were assembled in Ar-filled glovebox (H<sub>2</sub>O < 0.1 ppm, and O<sub>2</sub> < 0.1 ppm). 75  $\mu$ L electrolyte and a piece of Celgard2400 (25  $\mu$ m monolayer PE) were employed to fabricate a coin cell if not specially indicated. The charge/discharge tests were carried out on the LAND battery test system (Wuhan Land, China). For Li||Cu cells, thick Li metal anode, PE separator, and Cu collector were stacked together. Charge/discharge current was fixed at 0.5 mA/cm<sup>2</sup>. First, plated 4 mAh cm<sup>-2</sup> Li on Cu and charged until 1 V at 0.5 mA/cm<sup>2</sup>. Second, plated 4 mAh cm<sup>-2</sup> Li at 0.5 mA/cm<sup>2</sup> on Cu again. Third, charged to 1 mAh cm<sup>-2</sup> at 1.5 mA/cm<sup>2</sup> and then discharged to 1 mAh cm<sup>-2</sup> at 0.5 mA/cm<sup>2</sup> for 50 cycles. Last, charged to 1V at 0.5 mA/cm<sup>2</sup> and stripped all remaining Li on Cu. For full stripping/plating test, areal electric quantity in every step was controlled as 2 mAh cm<sup>-2</sup> and current was controlled as 0.5 mA/cm<sup>2</sup>. For full cells, thin Li foil, separator, and cathode sheet were assembled. 2.3 mAh cm<sup>-2</sup> NCM811 and 3 mAh cm<sup>-2</sup> LCO cathode sheets were prepared by casting as-prepared NMP slurry (active materials : PVDF :

carbon black = 96: 2: 2, weight ratio) and then oven-dried over-night at 80 °C in a vacuum-oven. 3.5 mAh cm<sup>-2</sup> NCM811cathode sheets (98 wt% active materials) were purchased form Kelude Co, Ltd. Long cycling test was that 0.1C charging and 0.1 C discharging for two activation cycles, 0.333C charging and 0.666C discharging for subsequent cycles (1 C = 200 mAh g<sup>-1</sup> for Li||NCM811 cells with  $2.8 \sim 4.3$  V voltage window, and 1 C = 180 mAh g<sup>-1</sup> for Li||LCO cells with  $3 \sim 4.5$  V voltage window). Dry pouch cells were purchased from LiFun Technology. 2.5 g Ah<sup>-1</sup> electrolyte was added into each cell. The test protocol for Li||NCM811 pouch cells was that 0.1C charging and 0.1 C discharging for two activation cycles, 0.2C charging and 0.5C discharging for subsequent cycles. The test protocol for graphite||NCM811 pouch cells was that 0.1C charging and 0.1 C discharging for two activation cycles, 0.2C charging and 0.3C discharging for subsequent cycles. The rate performance was evaluated by fixing charging current at 0.2 C, varying discharging current from 0.2 C to 4 C respectively for each 5 cycles after 0.1 C/0.1 C two activation cycles. For LSV test, Li||Al cells were assembled of thick Li metal anode, separator, and Al foil. LSV and EIS tests were conducted on Ivium electrochemical workstation (The Netherlands).

#### Materials characterizations

SEM (Hatchi SU-70) was performed to observe Li metal deposition morphology. XPS data were collected by Thermo Scientific ESCALAB 250Xi with 150W Al K<sub>a</sub> 1486.6 eV radiation. All samples were prepared and sealed into XPS transfer chamber in Ar-filled glovebox before XPS measurement. Cryo-TEM samples were prepared and loaded onto the cooling holder in glovebox, and then transferred to field emission gun (FEG) JEM-ARM200F cryo-TEM (200 keV) with continuously flowing Ar gas. The images were recorded at a magnification of ×400,000 with a dose of ~100e Å<sup>-2</sup> s<sup>-1</sup> when the temperature of the samples reached about 100 K. The Raman spectra were obtained by LabRAM HR Evolution Raman spectrometer (Horiba Jobin Yvon, 532 nm). The contact angle measurements were carried on JC2000, Shanghai Zhongchen Digital Technic Apparatus Co., Ltd. Viscosity measurements were performed using Anton Paar MCR102e Rheometer.

#### **Computational methods**

#### Quantum chemistry calculations

All quantum chemistry calculations were performed using the Gaussian 09 package. The geometries of Li-solvent (anion) complexes were firstly optimized using DFT calculations. The B3LYP functional was employed in combination with def2-SVP basis sets. All the optimized structures were confirmed as potential minima, with no frequency modes with imaginary eigenvalues, through frequency analyses following geometry optimizations. The SMD implicit solvation model with acetone ( $\epsilon = 20.4$ ) and ether ( $\epsilon = 4.1$ ) was used to represent different electrolyte environments not explicitly included in quantum chemistry calculations. The frontier orbits and electrostatic surface potential (ESP) of the solvents were rendered using VMD and VESTA programs, respectively. The flexible force constants were calculated by compliance program.

The reduction/oxidation potentials versus Li<sup>+</sup>/Li for various clusters were predicted using a free-energy cycle approach by subtracting 1.4 V from the absolute reduction potentials, as given in equations (1) and (2), respectively<sup>1,2</sup>:

$$E_{\rm ox}(\mathbf{M}) = \left[\Delta G_{\rm e} + \Delta G_{\rm S}(\mathbf{M}^{+}) - \Delta G_{\rm S}(\mathbf{M})\right] / F - 1.4 \,(\mathrm{V}) \tag{1}$$

$$E_{\rm red}(M) = - \left[\Delta G_{\rm e} + \Delta G_{\rm S}(M^{-}) - \Delta G_{\rm S}(M)\right] / F - 1.4 \,(\rm V) \tag{2}$$

In the equations,  $\Delta G_e$  is the ionization free energy or electron affinity in the gas phase at room temperature (298.15 K),  $\Delta G_S(M)$ ,  $\Delta G_S(M^+)$  and  $\Delta G_S(M^-)$  are the Gibbs free energies of solvation for the M, M<sup>+</sup> and M<sup>-</sup> complexes, respectively, and F is the Faraday constant. M05-2X density functional and def2-TZVP basis set were adopted because it precisely predicts electron affinity and ionization potential.

#### **Molecular dynamics simulations**

Molecular dynamics (MD) simulations were performed in LAMMPS using the all-atom optimized potentials for liquid simulations (OPLS-AA) force-field. The force field parameters of Li<sup>+</sup> and FSI<sup>-</sup> were obtained directly from previous publications<sup>3,4</sup> and a charge scaling of 0.9 was adopted to mimic polarization and charge transfer effects. The force field parameters of other organic molecules were generated using LigParGen web server<sup>5</sup>. The 1.2-scaling CM5 charges were based on DFT calculation by Gaussian program and Hirshfeld population analysis by Multiwfn<sup>6</sup>. The electrolyte systems were setup initially with the salt and solvent molecules distributed in the simulation boxes

using Moltemplate (http://www.moltemplate.org/). For each system, an initial energy minimization at 0 K (energy and force tolerances of 10–5) was performed to obtain the ground-state structure. After this, the system was slowly heated from 0 K to room temperature (298 K) at constant volume over 0.2 ns using a Langevin thermostat, with a damping parameter of 100 ps. The system was equilibrated in the constant temperature (298 K), constant pressure (1 bar) (NpT ensemble) for 5 ns before finally being subjected to 5 ns of constant volume, constant temperature dynamics. Snapshots of the Li solvation shells and solvent clusters were also sampled from the simulation trajectory using VESTA. The solvent-centric clusters are classified by the process in the flow chart, as shown in Fig S37. The cluster statistics are obtained by iterating over all solvent molecules in the simulation cell. The Radial distribution functions (RDF) and further statistics results were analyzed from the trajectory data by visual molecular dynamics (VMD) and some scripts written by ourselves.

## **Periodic calculations**

Periodic planewave DFT+U calculations for the electrolyte/cathode interface systems were performed using the Vienna ab initio Simulation Package (VASP) with the spinpolarized Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and the projector-augmented wave (PAW) scheme to treat core electrons. A planewave energy cutoff of 500 eV was employed. For the +U augmented treatment of Ni, Co, and Mn 3d orbitals, we chose a  $U_{\text{eff}}$  (J = 0.0 eV) value of 6.20 eV for Ni, 3.32 eV for Co, and 3.90 eV for Mn. The (001) surface for the 2/3 delithiated Li<sub>0.33</sub>Ni<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> structure (Fig. S30) was generated by removing the Li atoms from the corresponding fully lithiated (LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub>; O termination) slab structure and re-optimizing. The Li<sub>0.33</sub>Ni<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> (001) slab consists of 8 layers and a 15 Å vacuum layer in the z-direction. All selected molecules were placed on the cathode surface in multiple orientations, with some of the H atoms pointing towards surface O atoms. In a second set of calculations, one H atom from the solvent was transferred to the closest surface O, and the geometry was optimized again. We set the energy convergence criteria to  $10^{-6} \text{ eV} \text{ Å}^{-1}$ , and forces were converged below  $0.01 \text{ eV} \text{ Å}^{-2}$  during geometry optimization.

#### Ab initio molecular dynamics calculations

To further investigate the reactivity of the electrolyte with the Li metal surface, Ab initio molecular dynamics (AIMD) simulations using the Born-Oppenheimer approach were further carried out using the freely available CP2K/Quickstep package<sup>7</sup>. The DFT implemented in CP2K is based on a hybrid Gaussian plane wave scheme. The molecular orbitals of the valence electrons are expanded into DZVP-MOLOPT-Goedecker-Teter-Hutter (GTH) basis sets, whereas the interaction with the cores is described through GTH pseudopotentials. The efficient solution of the Poisson equation within the PBC is obtained in the reciprocal space by the expansion of the electronic density into a plane-wave basis set truncated at the energy cutoff of 400 Ry. We used the Perdew-Burke-Ernzerhof functional to describe exchange-correlation effects, and the dispersion correction was applied in all calculations with the Grimme D3 method. Because of the large size of the cells, only the Gamma point in the reciprocal space was used in our calculations. an electronic energy convergence criterion of  $1\times 10^{-5}\,\text{eV},$  and a time step of 1.0 fs were used for ab initio molecular dynamics simulations. A Li metal anode slab structure is created using 7 layers of Li metal exposing the lowest surface energy facet (100) and middle three layers of the slab are fixed to resemble bulk behavior. The total dimensions of the cell including the Li metal slab are 13.7 Å  $\times$  13.7 Å  $\times$  30.3 Å. A vacuum layer of  $\sim$ 20 Å added above the Li metal surface in the Z direction, provides the space where the electrolyte is located. 1.5 M LiFSI DMMS (4 LiFSI and 8 TTMS molecules) electrolyte was tested in this work. Initial geometries of the electrolyte were created with PACKMOL and then quenched using density functional forces. AIMD simulations were then performed at a temperature of 300 K using a Nose thermostat to allow fast equilibration. At least 10 ps of dynamic simulations were performed to analyze the reaction behaviors.

N	Chemical		Product	Price <sup>a</sup>
Name	Formula	CAS number	number	(\$ kg <sup>-1</sup> )
tetraethyl orthosilicate (TEOS)	C <sub>8</sub> H <sub>20</sub> O <sub>4</sub> Si	78-10-4	86578-1L	121
methyltriethoxysilane (MTES)	C7H18O3Si	2031-67-6	175579- 250G	273
dimethydiethoxylsilane (DMES)	C <sub>6</sub> H <sub>16</sub> O <sub>2</sub> Si	78-62-6	40120- 500ML	374
dimethyldimethoxysilica ne (DMMS)	$C_4H_{12}O_2Si$	1112-39-6	24174-1L	151
1,2-dimethoxyethane (DME)	$C_{4}H_{10}O_{2}$	110-71-4	259527-1L	201
1,3-dioxolane (DOL)	$C_3H_6O_2$	646-06-0	271020-1L	161
ethylene carbonate (EC)	$C_3H_4O_3$	96-49-1	676802-1L	175
dimethyl carbonate (DMC)	$C_3H_6O_3$	616-38-6	517127-1L	600
1,1,2,2-tetrafluoroethyl- 2,2,3,3-tetrafluoropropyl ether (TTE)	C5H4F8O	16627-68-2	AMBH93D5 3980	1144
bis(2,2,2-trifluoroethyl) ether (BTFE)	C4H4F6O	333-36-8	287571-5G	20200
1H,1H,5H- octafluoropentyl 1,1,2,2- tetrafluoroethyl ether	$C_7H_4F_{12}O$	16627-71-7	AMBH97B A0A26-25G	3476
lithium bis(fluorosulfonyl)imide (LiFSI)	F2NO4S2Li	171611-11-3	COMH93D5 FEB3-100G	1560
lithium	$C_2F_6NO_4S_2Li$	90076-65-6	544094-	3820

## Table S1 Costs of several electrolyte ingredients.

bis(trifluoromethanesulfo		100G			
n)imide (LiTFSI)					
L:DE.	L;DE.	21224 40 2	450227-	8400	
LIFF6	LIFF6	21324-40-3	500G	8400	

<sup>a</sup>All costs are calculated based on information from Sigma-Aldrich Co. LLC. (https://www.sigmaaldrich.com/US/en).



Fig. S1 Highest occupied molecular orbital (HOMO) and Lowest unoccupied molecular orbital (LUMO) energy levels of solvents and LiFSI.

Name	Structural formula	Melting point (°C)	Boling point (°C)	Dielectric constant	Density (g cm <sup>-3</sup> )
TEOS		-82.5	168.8	2.5	0.933
MTES	H <sub>3</sub> C O O	-46.5	142	3.8	0.895
DMES	H <sub>3</sub> C CH <sub>3</sub>	-87	113	3.2	0.865
DMMS	H <sub>3</sub> C CH <sub>3</sub> O	-80	85	3.7	0.865
DME		-69	85	7.3	0.864
DMC		-1	90.11	3.1	1.064
EC		36.3	246	89.8	1.321

# Table S2 Physicochemical properties of solvent molecules<sup>a</sup>.

<sup>a</sup>Data come from CRC handbook of chemistry and physics<sup>8</sup>.

Electrolyte	1 M LiPF <sub>6</sub> EC/DMC	1.5 M LiFSI DME	LiFSI- DME (1:1, n/n <sup>a</sup> )	LiFSI- DME-TTE (1:1:1, n/n/n)	1.5 M LiFSI DMMS
Density (g mL <sup>-1</sup> )	1.36	1.10	1.87	1.74	0.94

Table S3 Densities of several electrolytes.

<sup>a</sup>molar ratio.



**Fig. S2 Differential scanning calorimetry (DSC) curves of 1 M LiPF<sub>6</sub> EC/DMC electrolyte, and 1.5 M LiFSI DMMS electrolyte.** Inset figure shows optical photo of 1 M LiPF<sub>6</sub> EC/DMC electrolyte (left), and 1.5 M LiFSI DMMS electrolyte (right) at - 60 °C. 1 M LiPF<sub>6</sub> EC/DMC electrolyte was frozen and opalescent, but 1.5 M LiFSI DMMS electrolyte presented as a clear and viscous fluid.



Fig. S3 Ionic conductivities of LiFSI-siloxane mixtures with different concentration. The O atom of the alkoxy group acts as a coordination site for  $Li^+$ , and the alkyl groups possess an increased steric hindrance in the order: isopropyl > ethyl > methyl. Thus, the  $Li^+$  should be most easily accessible to DMMS's two O atoms, and increase the dissociation degree with anions. More  $Li^+$  with higher diffusion ability in DMMS electrolyte render it highest ionic conductivity among a series of siloxane-based electrolytes at the same salt concentration.

Electrolyte	1 M LiPF <sub>6</sub> EC/DMC	1.5 M LiFSI DMMS	LiFSI-DME (1:1, n/n <sup>a</sup> )	LiFSI-DME- TTE (1:1:1, n/n/n)
Viscosity (mPa s)	3.2466	11.099	38.877	11.412

Table S4 Viscosities of different electrolytes.

<sup>a</sup>molar ratio.



Fig. S4 Contact angles of 1 M LiPF<sub>6</sub> EC/DMC electrolyte (a), 1.5 M LiFSI DME electrolyte (b), and 1.5 M LiFSI DMMS electrolyte (c) on the polyethylene separator.

**Table S5 Results of lithium anode stripping/plating Coulombic efficiency (CE) in series of siloxane-based electrolytes.** Referring to Aurbach<sup>9</sup> and Zhang et al.<sup>10</sup> work, a CE test protocol was followed, (1) plate 4 mAh cm<sup>-2</sup> lithium on bare Cu anode under 0.5 mA cm<sup>-2</sup> current and then charge to 1 V for the first cycle, (2) plate 4 mAh cm<sup>-2</sup> lithium on Cu anode under 0.5 mA cm<sup>-2</sup> current again, (3) repeatedly strip/plate 1 mAh cm<sup>-2</sup> lithium under 1.5/0.5 mA cm<sup>-2</sup> current for 50 cycles, (4) finally charge to 1 V and strip all residual lithium.

Electrolyte	X	CE (%)
	0.8	99.074
	1.5	99.317
X WI LIFSI III TEOS	2.0	99.183
	3.0	98.859
	0.8	99.255
	1.5	99.497
x M LIFSI IN MTES	2.1	99.127
	3.0	99.081
	1.5	99.373
	2.1	99.632
x M LIFSI III DMES	3.0	99.411
	3.6	99.348
	0.8	99.759
	1.5	99.805
	2.1	99.658
	3.1	99.426

Electrolyte	Salt	Solvent	Diluent	Fluorine molarity <sup>a</sup> (mol L <sup>-1</sup> )	Fluorine atom ratio <sup>b</sup> (%)	Columbic efficiency of Li anode (%)	Electrolyte amount	Cell conditions	Cycling condition and capacity retention
7 m LiFSI in FEC <sup>11</sup>	Li <sup>†</sup> FNS 0 <sup>× S</sup> 00		None	~27.7	13.4	98.7	Not mentioned	2.5 mAh cm <sup>-2</sup> Li    1.83 mAh cm <sup>-2</sup> LNMO N/P = 1.37	3.2 ~ 5.0 V 0.333 C / 0.333 D cycling, 70% after 140 cycles
1LiFSI- 3TMS- 3TTE <sup>12</sup>	L <sup>i</sup> F <b>N</b> S 0 <sup>5</sup> 00	o S S		31.2	23.8	98.8	40 mL Ah <sup>-1</sup>	50 μm Li    1.5 mAh cm <sup>-2</sup> NMC111 coin cell N/P = 6.67	2.8 ~ 4.3 V 0.333 C / 0.333 D cycling, 80% after 300 cycles
1 M LiFSI in DME- TFEO <sup>13,14</sup>	Li <sup>F</sup> <sup>S</sup> , N, S 000000000000000000000000000000000000	-0-0-		29.0	27.1	99.5	50 g Ah <sup>-1</sup>	50 μm Li    1.5 mAh cm <sup>-2</sup> NMC811 coin cell	2.8 ~ 4.4 V 0.333 C / 0.333 D cycling, 80%

 Table S6 Comparison of the state-of-the-art electrolyte for Li metal battery

								N/P = 6.67	after 300 cycles
11 iFSL								50 µm Li    4.2 mAh	$2.7 \sim 4.4 \; \mathrm{V}$
	Ę ∎i <sup>†</sup> Γ, ¯N Ε		F√F a F√F	20	21.2	00.2	2 41-1	cm <sup>-2</sup>	0.333 C / 0.333 D,
1.2DME-	0 <sup>- \$</sup> 00 <sup>-\$</sup> 0	-0 0-	H F F F F	39	31.2	99.3	3 g An	NMC811 coin cell	80% after 155
$3\mathrm{TTE}^{13}$								N/P = 2.38	cycles
1 M LiPF <sub>6</sub>								$2 \dots \Delta h  \mathrm{cm}^2  \mathrm{Li} \parallel 2$	
in								$2 \text{ mAn cm}^2 \text{ Li} \parallel 2$	
FEC/FEM	F		EF EF					mAh	$2.7 \sim 4.4 \mathrm{V}$
С/ЦЕЕ		-0		34.0	25.8	99.2	50 g Ah <sup>-1</sup>	cm <sup>-2</sup> NMC811 coin	0.5 C/0.5 D, 95%
C/HFE								cell	after 120 cycles
(2:6:2, by		É '						N/P = 1	
weight) <sup>16</sup>									
2.5 m	+								
LiFSI +0.2		<u>o</u> ,					~15 mL	60 μm Li    1.6 mAh <sup>-</sup>	$3.0 \sim 4.3 \text{ V}$
m LiPF cin	0 00 0	F-S-N	None	~16.7	10.2	99.03	Ah <sup>-1</sup>	<sup>2</sup> NCM622 coin cell	0.2 C/0.5 D, 89%
							2 MI	N/P = 7.6	after 200 cycles
FSA''									

1 M I JESI								20 µm Li    1.6 mAh	$2.7 \sim 4.2 \ V$
in In In In In	Li <sup>†</sup> F∖_N, F		Nono	27.5	10.2	00.5	6 a A h <sup>-1</sup>	cm <sup>-2</sup>	0.333 C / 0.333 D
	0 <sup> \$</sup> 00 <sup>-</sup> \$00	F F	None	21.5	18.3	99.5	No g Ali	NMC532 coin cell	cycling, 100%
FDMB								N/P = 2.5	after 210 cycles
3.2 mol kg <sup>-1</sup> LiFSI in C3mpyrFS I/DME (80:20, by weight) <sup>19</sup>	Li F, ⊼N, 5 0 <sup>5</sup> 0000000000000000000000000000000000		None	12.1	10.1	99.2	~21 mL Ah <sup>-1</sup>	50 μm Li    1.3 mAh cm <sup>-2</sup> NMC811 coin cell N/P = 7.69 100 μm Li    3.8 mAh cm <sup>-2</sup> NMC622 coin cell N/P = 5.26	2.8 ~ 4.4 V 0.5 C/0.5 D, 80% after 300 cycles 2.8 ~ 4.3 V 0.25 C/0.25 D, ~94% after 100 cycles
1 M LiPF <sub>6</sub> in FEC/BTC (3:7, by	F-122F F-22F F F			~37.4	~28.6	98.8	11 mL Ah <sup>-1</sup>	50 μm Li    1.7 mAh <sup>-</sup> <sup>2</sup> NCM811 coin cell N/P = 5.88	2.8 ~ 4.7 V 0.2 C/0.5 D, 89.2% after 150 cycles

volume) <sup>20</sup>									
1 M LiPF <sub>6</sub> in EC/DEC+ 0.5 wt% Sn(OTf) <sub>2</sub> + 5wt% LiNO <sub>3</sub> <sup>21</sup>			None	~6	.~3.8	98.4	10 mL Ah <sup>-1</sup>	45 μm Li    3.4 mAh <sup>-</sup> <sup>2</sup> NCM811 coin cell N/P = 2.65	2.8 ~ 4.3 V 0.3 C/0.3 D, 89.6% after 130 cycles
1 M LiFSI in DEE <sup>22</sup>	Li F 0 0 0 0 0 0 0	< <mark>∕</mark> 0	None	2	~1.30	98.9	~13 mL Ah <sup>-1</sup>	40 μm Li    3.5 mAh <sup>-</sup> <sup>2</sup> SPAN coin cell N/P = 2.28	0.5 ~ 3.5 V 0.333 C/0.333 D, 64% after 50 cycles
1 M LiFSI in MeTHF <sup>23</sup>	L <sup>i</sup> F. <mark>,N.</mark> ,F 0 <sup>6</sup> 00	0	None	2	~1.1	98.2	Not mentioned	Not mentioned	Not mentioned

1.7 M LiFSI in MeTHF/T TE (1:1, by volume) <sup>23</sup>	Li <sup>+</sup> 0 <sup>≤ S</sup> ℃ ở 5 0	<b>0</b>		~24.4	~17.5	99.7	~8.5 mL Ah <sup>-1</sup>	50 μm Li    2.7 mAh <sup>-</sup> <sup>2</sup> LiFePO <sub>4</sub> coin cell N/P = 3.7	2.5 ~ 3.75 V 0.5 C/0.5 D, 99.4% after 300 cycles
1 M LiFSI in DME/BTF E (1:5, by volume) <sup>24</sup>	Li <sup>*</sup> <sup>F</sup> S.Ñ.S O <sup>F</sup> OO	-0 0-		42.4	32.6	99.4	~22 mL Ah <sup>-1</sup>	4.2 mAh cm <sup>-2</sup> Li    2.1 mAh cm <sup>-2</sup> NMC811 coin cell N/P = 2	2.7 ~ 4.3 V 0.333 C/0.333 D, 91.4% after 200 cycles
1.2 M LiFSI in F5DEE <sup>25</sup>	Li <sup>†</sup> <sup>F</sup> \s.¯N, y <sup>F</sup> 0 <sup>≤ S</sup> \o o'		None	33.4	22.5	99.74/99. 90±0.10	~8 g Ah <sup>-1</sup>	50 μm Li    4.9 mAh cm <sup>-2</sup> NMC811 coin cell N/P = 2.04	2.8 ~ 4.4 V 0.2 C/0.3 D, 80% after 200 cycles

								25 µm Li    3.8 mAh	
								cm <sup>-2</sup>	$2.8 \sim 4.4 \ V$
							$\sim 2.5 \text{ g Ah}^{-1}$	NMC811 pouch cell	0.2 C/0.5 D, 85%
								(0.13 Ah)	after 150 cycles
								N/P = 1.32	
2 M L'ESI								20 µm Li    1.0 mAh	2.8 ~ 4.3 V
2 M LIF SI	Li <sup>+</sup> F, TN F	FO	Nama	171	26.0	0.9.7	~36 mL	cm <sup>-2</sup>	0.5 C/0.5 D,
111 ETOE <sup>26</sup>	0 <sup>- S</sup> 0 0 S 0	F7 0 0	None	17.1	26.0	98.0	Ah <sup>-1</sup>	NMC811 coin cell	100% after 112
cF1OF <sup>20</sup>								N/P = 4	cycles
								20 µm Li    1.0 mAh	28 12V
2 M LiFSI	Li <sup>†</sup> F, TN /F	FO	Nono	22.4	144	00.2	~24 mL	cm <sup>-2</sup>	$2.6 \sim 4.5$ V
in DTDL <sup>27</sup>	0 <sup>- \$</sup> 00 <sup>5</sup> 0	F7 070-	None	23.4	14.4	99.2	Ah <sup>-1</sup>	NMC811 coin cell	0.3 C/0.3 D, 84%
								N/P = 4	after 200 cycles
1 M LiFSI	+		F F					1 mm Li    1.8 mAh	2.8 ~ 4.2 V
in		_ <b>0</b> _	F F	45.6	42.6	99.0	$> 50 \text{ g Ah}^{-1}$	cm <sup>-2</sup>	0.333 C/0.333 D,
Me <sub>2</sub> O/TE	00 -		F					NMC622	90.4% after 200

E/PFE <sup>28</sup>								customized high- pressure SS cell N/P = 111	cycles
This work 1.5 M LiFSI in DMMS	Li <sup>*</sup> F S.ĨN, F O <sup>r S</sup> O ở S	,_,Si∕	None	3	2.55	99.8	14 g Ah <sup>-1</sup>	20 $\mu$ m Li    2.3 mAh cm <sup>-2</sup> NMC811 coin cell N/P = 1.7 20 $\mu$ m Li    3.5 mAh cm <sup>-2</sup> NMC811 coin cell N/P = 1.1 20 $\mu$ m Li    3.0 mAh cm <sup>-2</sup> LCO coin cell N/P = 1.3	$2.8 \sim 4.3 V$ 0.333 C / 0.666 D cycling, 80% after 350 cycles $2.8 \sim 4.3 V$ 0.333 C / 0.666 D cycling, 88% after 200 cycles $2.8 \sim 4.5 V$ 0.333 C / 0.666 D cycling, 95% after 200 cycles

					20 µm Li    3.0	6 mAh	
					cm <sup>-2</sup>		$2.8\sim 4.3 \ V$
				~2.5 g Ah <sup>-1</sup>	NMC811	pouch	0.2 C/0.5 D, 96%
					cells (1.4 Ah)		after 140 cycles
					N/P = 1.1		

<sup>a</sup> Fluorine concentration is calculated by Fluorine molarity = (mole number of all F atom)/(solution volume)

<sup>b</sup> Fluorine atom ratio is calculated by Fluorine atom ratio = (the number of all F atom)/(the number of all atom in electrolyte)



Fig. S5 Fluorine molarity of state-of-the-art electrolyte and corresponding Li anode Columbic efficiency (CE).



Fig. S6 Capacity-voltage curves of Li||Cu half cells using 1 M LiPF<sub>6</sub> EC/DMC electrolyte (a), 1.5 M LiFSI DME electrolyte (b), and 1.5 M LiFSI DMMS electrolyte (c).



Fig. S7 Cycling performance of Li||Li symmetric cells with 1 M LiPF<sub>6</sub> EC/DMC electrolyte, 1.5 M LiFSI DME electrolyte, and 1.5 M LiFSI DMMS electrolyte. (b) is magnified part of (a) to show details of the overpotentials evolution trends.



**Fig. S8 The EIS results of Li**||**LiNi**<sub>0.8</sub>**Co**<sub>0.1</sub>**Mn**<sub>0.1</sub>**O**<sub>2</sub> (**NCM811**) cells with different electrolytes after 10 cycles (a, c) and 100 cycles (b, d). (c), (d), entire data for 1 M LiPF<sub>6</sub> EC/DMC electrolyte. (e), The EIS fitting model which is employed in impedance analysis.

cycle	Electrolyte	$R_{e}\left(\Omega\right)$	$R_{int1}(\Omega)$	$R_{int2}\left(\Omega\right)$	$\begin{array}{c} R_{int1} + R_{int2} \\ (\Omega) \end{array}$
10	1 M LiPF <sub>6</sub> EC/DMC	4.5	105.3	514.3	619.6
	1.5 M LiFSI DME	2.8	8.4	107.2	115.6
	1.5 M LiFSI DMMS	15.6	19.8	18.4	38.2
100	1 M LiPF <sub>6</sub> EC/DMC	6.7	136.5	1636.0	1772.5
	1.5 M LiFSI DME	7.2	47.8	138.6	185.4
	1.5 M LiFSI DMMS	18.4	21.5	20.2	41.7

Table S7 EIS fitting results of Li||NCM811 cells with different electrolytes after10 cycles and 100 cycles.



Fig. S9 Long-cycling performance of high-loading NCM811||Li full cells with 1 M LiPF<sub>6</sub> EC/DMC electrolyte, 1.5 M LiFSI DME electrolyte and 1.5 M LiFSI DMMS electrolyte. 20  $\mu$ m Li anode and 3.5 mAh cm<sup>-2</sup> industrial NCM811 cathode sheet charge at 0.333 C and discharge at 0.666 C (1 C = 200 mAh g<sup>-1</sup>).



Fig. S10 Long-cycling performance of thin Li||NCM811 cells (20 μm Li anode and 2 mAh cm<sup>-2</sup> NCM811 cathode sheet) with other siloxanes-based electrolytes.



Fig. S11 Long-cycling performance of high-loading NCM811||Li full cells with other siloxanes-based electrolytes. 20  $\mu$ m Li anode and 3.5 mAh cm<sup>-2</sup> industrial NCM811 cathode sheet charge at 0.333 C and discharge at 0.666 C (1 C = 200 mAh g<sup>-1</sup>).



Fig. S12 Photographs of the exploded pouch cell with 1.5 M LiFSI DME electrolyte.



Fig. S13 Photographs of NCM811||Cu pouch cells with 1 M LiPF<sub>6</sub> EC/DMC electrolyte (a), 1.5 M LiFSI DME electrolyte (b), 1.5 M LiFSI DMMS electrolyte (c) after cycling. (d), A pristine dry cell without electrolyte.

	Parameter	Value
NCM811 cathode	Discharge capacity	210 mAh g <sup>-1</sup>
	Active material loading	96.5%
	Areal wight (each side)	17.7 mg cm <sup>-2</sup>
	Areal capacity (each side)	$3.6 \text{ mAh cm}^{-2}$
	Number of layers	6
Al foil	Thickness	12 µm
Li anode	Li thickness (each side)	20 µm
	Areal capacity (each side)	4 mAh cm <sup>-2</sup>
	N/P ratio	1.1
Cu foil	Thickness	8 µm
Electrolyte	E/C ratio	2.5 g Ah <sup>-1</sup>
Separator	Thickness	20 µm
Package foil	Thickness	115 μm
Cell	Average voltage	3.8 V
	Capacity	≥ 1.4 Ah
	Cell energy density	$\geq 340 \text{ Wh kg}^{-1}$

Table S8 Parameters of Li||NCM811 pouch cells with 340Wh kg<sup>-1</sup> at 1.4 Ah level.



Fig. S14 Cycling performances of anode-free pouch cells with 1.5 M LiFSI DMMS electrolyte.



Fig. S15 Fast discharge rate performances of Li||NCM811 cells.



Fig. S16 Long-cycling performance of Li||Graphite (G) half cells with 1.5 M LiFSI TEOS electrolyte. Conditions: 450  $\mu$ m thick Li, 1 mAh cm<sup>-2</sup> G, 75  $\mu$ L electrolyte per coin cell, 0.05~1.2 V, 2 C charge and 2 C discharge (1 C = 375 mAh g<sup>-1</sup>). Replace new Li anodes and separators, and add electrolyte at 717th and 1679th cycle. The average CE of 3000 cycles is 99.96%.



Fig. S17 Long-cycling performance of Li||G half cells with 1.5 M LiFSI MTES electrolyte. Conditions: 450  $\mu$ m thick Li, 1 mAh cm<sup>-2</sup> G, 75  $\mu$ L electrolyte per coin cell, 0.05~1.2 V, 2 C charge and 2 C discharge (1 C = 375 mAh g<sup>-1</sup>). Replace new Li anodes and separators, and add electrolyte at 623th and 1798th cycle. The average CE of 3500 cycles is 99.97%.



Fig. S18 Long-cycling performance of Li||G half cells with 2.1 M LiFSI DMES electrolyte. Conditions: 450  $\mu$ m thick Li, 1 mAh cm<sup>-2</sup> G, 75  $\mu$ L electrolyte per coin cell, 0.05~1.2 V, 2 C charge and 2 C discharge (1 C = 375 mAh g<sup>-1</sup>). Replace new Li anode and separator, and add electrolyte at 1000th cycle. The average CE of 2000 cycles is 99.95%.



Fig. S19 Long-cycling performance of Li||G half cells with 1.5 M LiFSI DMMS electrolyte. Conditions: 450  $\mu$ m thick Li, 1 mAh cm<sup>-2</sup> G, 75  $\mu$ L electrolyte per coin cell, 0.05~1.2 V, 2 C charge and 2 C discharge (1 C = 375 mAh g<sup>-1</sup>). Replace new Li anode and separator, and add electrolyte at 2080th cycle. The average CE of 3100 cycles is 99.98%.



Fig. S20 High temperature (80 °C) cycling performances of Li||G half cells with 1 M LiPF<sub>6</sub> EC/DMC electrolyte and 1.5 M LiFSI MTES electrolyte.



Fig. S21 High temperature (80 °C) cycling performance of Li||LiFePO4 half cells with 1.5 M LiFSI MTES electrolyte.



Fig. S22 Cross-sectional SEM images of thin LMA which retrieved from Li||NCM811 cells with 1 M LiPF<sub>6</sub> EC/DMC electrolyte (a), 1.5 M LiFSI DME electrolyte (b), and 1.5 M LiFSI DMMS electrolyte (c).



Fig. S23 N 1s, and S 2p XPS depth profiles of Li metal surface in 1.5 M LiFSI DMMS.



Fig. S24 Cryo-TEM image (a) and corresponding diffractogram image (b) obtained by fast Fourier Transform (FFT) of freshly deposited Li in 1 M LiPF<sub>6</sub> EC/DMC electrolyte.



Fig. S25 Cryo-TEM image (a) and corresponding diffractogram image (b) obtained by FFT of freshly deposited Li in 1.5 M LiFSI DME electrolyte.



**Fig. S26 Diffractogram image obtained by FFT of freshly deposited Li in 1.5 M LiFSI DMMS electrolyte.** Which is corresponding to Cryo-TEM image Fig. 3f.



**Fig. S27 Representative Cryo-EELS mapping images of Li metal which was deposited in 1.5 M LiFSI DME electrolyte.** The image data contain spatial distribution of C and O element and relative intensity value of each pixel. Only one of five samples detected low intensity and nosing F signals which is full of screen and not related to the shape of Li metal. The possible reason may be less abundant content and an unequal distribution of fluorine in whole SEI.



Fig. S28 Representative Cryo-EELS mapping images of Li metal which was deposited in 1 M LiPF<sub>6</sub> EC/DMC electrolyte. The image data contain spatial distribution of C, O, and F element and relative intensity value of each pixel.



**Fig. S29** The evolution of Li-X RDF during the SEI formation simulation process. X = O (a), C (b), Si (c).



Fig. S30 Snapshots of Li<sub>0.33</sub>Ni<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> model from side view(a) and top view(b). Colorings of atoms are O: red, Li: green, Ni: silver, Co: blue, Mn: purple.



Supplementary Fig.31 H-transfer calculation of EC (a, b) and DME (c, d). a, c, snapshots before H-transfer. b, d, snapshots after H-transfer.

Table S9 Normalized element contents, according to EDS mapping, on the surfaceof lithium metal anode after 100 cycles in 1.5 M LiFSI DMMS electrolyte.

			·	/				J	
Element	С	Ν	0	F	Si	S	Mn	Co	Ni
Mass (%)	5.24	6.75	35.25	20.79	0.99	30.95	0.01	0.00	0.02
Atom (%)	8.36	9.23	42.24	20.98	0.68	18.50	0.00	0.00	0.01

Element	С	0	F	Р	Mn	Со	Ni
Mass (%)	30.16	33.55	29.64	5.95	0.10	0.01	0.59
Atom (%)	39.41	32.91	24.28	3.02	0.03	0.00	0.35

Table S10 Normalized element contents, according to EDS mapping, on the surface of lithium metal anode after 100 cycles in 1 M LiPF<sub>6</sub> EC/DMC electrolyte.

Table S11 Normalized element contents, according to EDS mapping, on the surfaceof lithium metal anode after 100 cycles in 1.5 M LiFSI DME electrolyte.

			v				v	
Element	С	Ν	0	F	S	Mn	Co	Ni
Mass (%)	8.52	5.73	41.98	17.45	25.52	0.14	0.00	0.65
Atom (%)	12.97	7.43	47.99	16.80	14.56	0.05	0.00	0.20



cathode surface in 1.5 M LiFSI DMMS.

**Table S12 MD simulation data for the LiFSI-DMMS mixtures at 300 K.** Note: some of the percentages do not sum to 100% due to the rounding off of the values. "free Li<sup>+</sup> ions" are fully solvated Li<sup>+</sup> cations (not coordinated to anions). "free anions" are uncoordinated (naked) anions which do not contact with Li<sup>+</sup>. "free DMMS" are uncoordinated ether oxygens from the solvent molecules.

Properties	0.8 M	1.5 M	2.8 M	5.0 M
No. solvent in MD box	1728	900	448	686
No. LiFSI in MD box	256	256	256	512
Simulation box length (Å)	73.75	60.49	50.77	58.06
Fraction of free Li <sup>+</sup> ( $r_{Li-O} > 2.80$ Å)	0.002	0.00	0.00	0.00
Fraction of free $FSI^-$ ( $r_{Li-N^*} > 4.80 \text{ Å}$ )	0.00	0.00	0.00	0.00
Fraction of free DMMS ( $r_{Li-Si} > 4.00$ Å)	0.796	0.631	30.5	0.105
Li <sup>+</sup> coordination numbers				
O (within 2.80 Å of $Li^+$ )	2.46	2.27	1.83	1.72
Si (within 4.00 Å of $Li^+$ )	1.36	1.33	1.29	1.32
O* (within 2.80 Å of $Li^+$ )	3.13	3.13	3.18	3.26
N* (within 4.80 Å of $Li^+$ )	2.88	2.88	2.91	2.87

Probability of finding the following number of Li<sup>+</sup> within the given distance from the N\* of FSI<sup>-</sup>

0.015	0.015	0.011	0.011
0.133	0.176	0.105	0.108
0.422	0.359	0.371	0.321
0.355	0.383	0.398	0.398
0.074	0.067	0.109	0.146
0.000	0.000	0.003	0.015
	0.015 0.133 0.422 0.355 0.074 0.000	0.0150.0150.1330.1760.4220.3590.3550.3830.0740.0670.0000.000	0.0150.0150.0110.1330.1760.1050.4220.3590.3710.3550.3830.3980.0740.0670.1090.0000.0000.003



**Fig. S33 Photographs of typical Li<sup>+</sup> primary solvation sheaths in 1.5 M LiFSI DMMS electrolyte.** (a), 3-1 (that is three FSI- and one DMMS). (b), 2-2. (c), 4-1. In ball-and-stick representation, colorings of atoms are H: pink, C: brown, O: red, Si: blue, Li: green, N: purple, S: yellow, F: silver.



Fig. S34 Modified Aurbach's measurement of Li metal CE in Li||Cu half cells using 1 M LiPF<sub>6</sub> in EC/DMC electrolyte.



Fig. S35 Statistical results of anion-solvent number in first solvent sheath of Li<sup>+</sup> in 0.8 M LiFSI DMMS electrolyte (a), 2.8 M LiFSI DMMS electrolyte (b) and 5.0 M LiFSI DMMS electrolyte (c).



Fig. S36 Raman spectrum of 1.5 M LiFSI in DME electrolyte.



Fig. S37 Operating procedure for the classification of solvent-centric clusters.



**Fig. S38 Snapshots of optimized solvent clusters after electron transfer and their oxidation potentials.** (a-e), DMMS. (f-j), DME. (k-o) 1,4-DX. (p-t), EC. (u-y), DMC. In ball-and-stick representation, colorings of atoms are H: pink, C: brown, O: red, Si: blue, Li: green, N: purple, S: yellow, F: silver, P: lilac.



Fig. S39 The proportion and oxidation potentials of five solvent clusters in 1 M LiPF<sub>6</sub> EC/DMC. (a) EC-centric clusters, (b) DMC-centric clusters.



Fig. S40 Long-cycling performance of high-loading NCM811||Li full cells with 1.5 M LiFSI 1,4-DX electrolyte and 1.5 M LiFSI DMMS electrolyte. 20  $\mu$ m Li anode and 3.5 mAh cm<sup>-2</sup> industrial NCM811 cathode sheet, charge at 0.333 C and discharge at 0.666 C (1 C = 200 mAh g<sup>-1</sup>).

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