Support Information

Bridging Thermodynamics and Ion Transport in Lithium Batteries via Molecular Design of High-Entropy Electrolytes

Lun He[1,†], Yiting Lin[1, 2,† *], Jingkun Li[1, 2], Haiping Su[1, 2], Honglai Liu[1, 2], Cheng Yang[3, *],Cheng Lian[1, 2, *]

[1]State Key Laboratory of Chemical Engineering and Low-Carbon Technology, and School of Chemical Engineering, East China University of Science and Technology, Shanghai, 200237, China.

[2]School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai, 200237, China.

[3]State Key Laboratory of Space Power-Source,Shanghai Institute of Space Power-Source, 11 No.2965, Dongchuan Road, Minhang District, Shanghai 200245, China

[*]Corresponding author(s).

E-mail(s): linyiting@ecust.edu.cn; yangcheng811@sina.com;

liancheng@ecust.edu.cn.

[†]These authors contributed equally to this work.

Supplementary Methods

Materials

Ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), fluoroethylene carbonate (FEC), Lithium hexafluorophosphate ($LiPF_6$), lithium bis(fluorosulfonyl)imide (LiFSi), lithium bis(trifluoromethanesulfonyl) imide (LiTFSi), lithium difluoro(oxalato)borate (LiDFOB) and Lithium nitrate ($LiNO_3$) were purchased from Dodochem. All the electrolytes were stored and used in an Ar-filled glovebox with both H_2O and O_2 content below 0.1 ppm.

The NCM811 electrodes were prepared by mixing active material, Super P and PVDF binder in the mass ratio of 8:1:1 in N-methyl-2-pyrrolidone (NMP) solvent and cast on Al foil and then dried at 80 °C for 8 h in a vacuum oven. The loading mass of NCM811 was controlled at ~3.0 mg cm^{-2}.

Electrochemical measurements

For Li||Cu, the copper foils were packed into discs of 19 mm diameter as cathode, while Li metal was used as the anode. During cycles, capacity of 0.5 mAh cm^{-2} lithium was deposited on Cu foils at a current density of 0.5 mA cm^{-2} and then stripped until a cut-off voltage of 1.0 V vs. Li/Li^+. Cyclic voltammetry (CV) of Li||Cu cells with various electrolytes were conducted at a scan rate of 0.8 mV s^{-1} from -0.1 to 2.5 V vs. Li/Li^+.

The Li||Li cells were also exploited to study the cycling stability and kinetic performance in different electrolytes. The method described by Abraham et al. was used to study the Li^+ transfer number (t_{Li^+}) of the different electrolytes[1]. The procedures were as follows: symmetric Li||Li cells were assembled and then the polarization currents at the initial (I^0) and final (I^{ss}), were recorded under a small polarization potential (ΔV) of 10 mV. At the same time, the initial and steady-state values of the bulk resistances (R_b^0 and R_b^{ss}) and interfacial resistances (R_i^0 and R_i^{ss}) were recorded by EIS before and after the polarization. The t_{Li^+} was calculated based on the following equation (1):

$$t_{Li^+} = \frac{\left(\Delta V - I^0 R_i^0\right) I^{SS}}{\left(\Delta V - I^{ss} R_i^{ss}\right) I^0} \quad (1)$$

The measurement of activation energy can also be conducted using Li||Li cells[2]. The following procedures were adopted: symmetric Li||Li cells with various electrolytes were cycled at a current density of 0.5 mA cm^{-2} for 10 cycles, after which they were maintained at temperatures of 303, 313, 323 and 333 K to acquire the

temperature-dependent EISs. By fitting the EISs to the equivalent circuits, the values of the SEI resistance (R_{SEI}). The activation energy (E_a) is then derived from the Arrhenius equation (2) as follows:

$$lnR_{SEI}^{-1} = lnA - \frac{E_a}{RT} \quad (2)$$

Physical characterizations

The morphology of the electrodes cycled with different electrolytes was characterized using a scanning electron microscope (SEM, Helios G4UC). Before being observed, the lithium metal deposited on the copper foil, the copper sheet after lithium stripping, and the NCM811 electrode after rate cycling were disassembled, then rinsed three times with DME to remove residual electrolyte and dried in a glove box to remove solvent residues. For TEM preparation of NCM811 cathodes, Li||NCM811 cells were cycled at 0.5C for 50 cycles in the voltage range of 2.8-4.3 V and then disassembled in glovebox.

The X-ray photoelectron spectroscopy (XPS) analysis was conducted to determine the composition of the Cu cathode. The Li||Cu cells were cycled for 20 cycles after which they were disassembled in an Ar-filled glove box. The harvested electrodes were rinsed three times with DME to remove residual electrolyte and subsequently vacuum dried for 12 hours to remove residual solvent. The elemental composition of the electrode surface was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific) using a monochromatic Al K(α) X-ray source calibrated against carbon (284.8 eV). Peak fitting was conducted using Advantage software.

Theoretical calculations

Atomistic molecular dynamics simulations were conducted in the GROMACS[3] (version 2022.6) simulation package. Molecules and ions were described by the optimized potentials for a liquid simulations all-atom (OPLS-AA) force field[4]. The EL1 system contains 153 EMC molecules, 237 EC molecules, 188 DMC, 34 FEC and 50 $LiPF_6$ molecules. The EL2 system contains 153 EMC molecules, 237 EC molecules, 188 DMC, 34 FEC 30 $LiPF_6$ molecules and 20 LiTFSi molecules. The EL3 system contains 153 EMC molecules, 237 EC molecules, 188 DMC, 34 FEC 30 $LiPF_6$ molecules 10 LiTFSi molecules and 10 LiDFOB molecules. The EL5 system contains 153 EMC molecules, 237 EC molecules, 188 DMC, 34 FEC 30 $LiPF_6$ molecules 5 LiTFSi molecules 5 LiDFOB molecules 5 LiFSi molecules and 5 $LiNO_3$ molecules. The systems were initialized randomly using the Packmol package. The systems were

equilibrated using a simulated annealing protocol consisting of the following steps: (1) energy minimization at 0 K; (2) equilibration at 300 K for 2 ns in the NPT ensemble; (3) heating to 450 K over 1 ns in the NPT ensemble; (4) relaxation at 450 K for 1 ns in the NPT ensemble; (5) cooling to 300 K over 1 ns in the NPT ensemble; and (6) final equilibration at 300 K for 5 ns in the NPT ensemble. The production trajectory was then generated at 300 K for 20 ns in the NVT ensemble. All simulations were performed with a timestep of 1 fs and a pressure of 1 atm. The Parrinello-Rahman barostat and V-rescale thermostat were used to maintain constant pressure and temperature, respectively. To describe van der Waals and Coulomb effects, the cut-off radius was set to 1.0 nm, using the cut-off and PME methods, respectively. The trajectory analysis was conducted using the MD Analysis Python package. Density functional theory calculations are carried out with Gaussian 09[5]. Molecular geometries are optimized at the B3LYP/6-311G(d)[6] level. Single-point energies are calculated using B3LYP/6-311+G (d, p) basis set to improve accuracy. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of each molecule are obtained from Multiwfn 1.5.3[7] and visualized using Visual Molecular Dynamics (VMD) software.

Supporting Figures

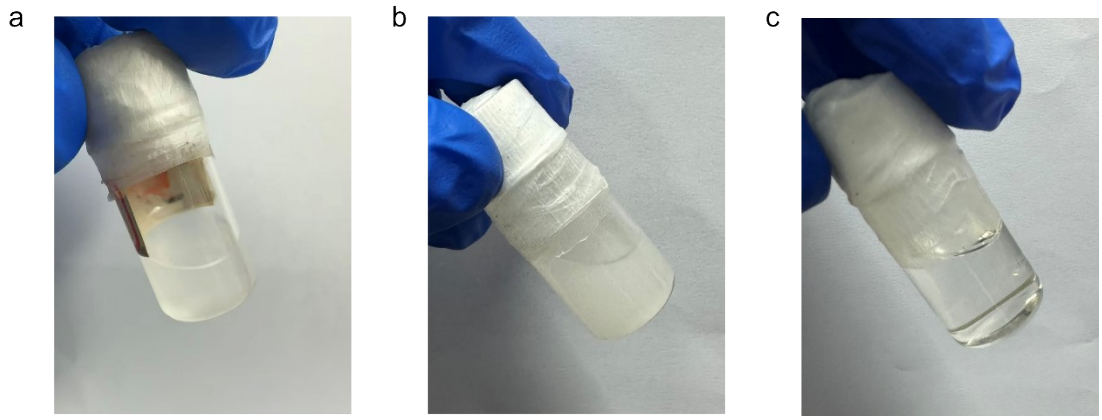


Figure S1. (a) 0.1 M $LiNO_3$/0.6 M $LiPF_6$ in EC/EMC/DMC (1:1:1 by volume) with 5% FEC. (b) 0.1 M $LiNO_3$/0.9 M $LiPF_6$ in EC/EMC/DMC (1:1:1 by volume) with 5% FEC. (c) 0.1 M $LiNO_3$/0.1 M LiTFSi/0.1M LiDFOB/0.1 M LiFSi/0.6 M $LiPF_6$ in EC/EMC/DMC (1:1:1 by volume) with 5% FEC

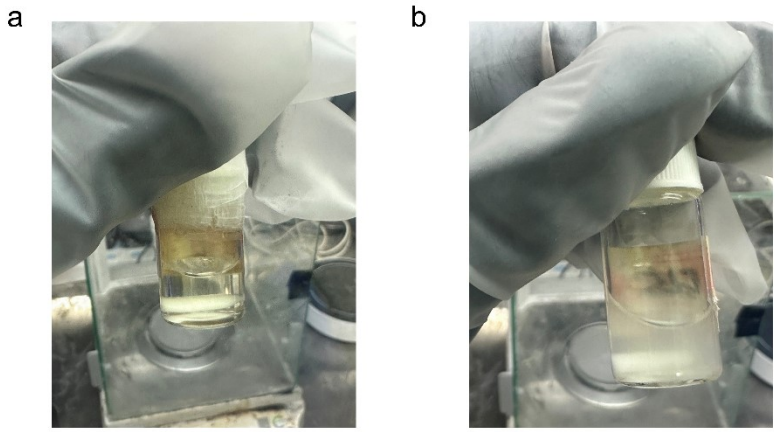


Figure S2. (a) 0.12 M $LiNO_3$/0.1 M LiTFSi/0.1M LiDFOB/0.1 M LiFSi/0.6 M $LiPF_6$ in EC/EMC/DMC (1:1:1 by volume) with 5% FEC. (b) 0.15 M $LiNO_3$/0.1 M LiTFSi/0.1M LiDFOB/0.1 M LiFSi/0.6 M $LiPF_6$ in EC/EMC/DMC (1:1:1 by volume) with 5% FEC

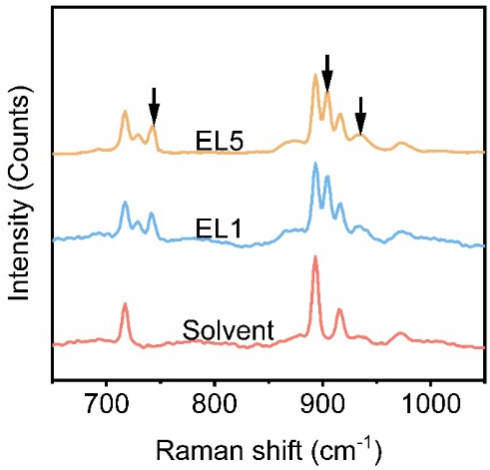


Figure S3. Raman spectra of the solvent, EL1 and EL5.

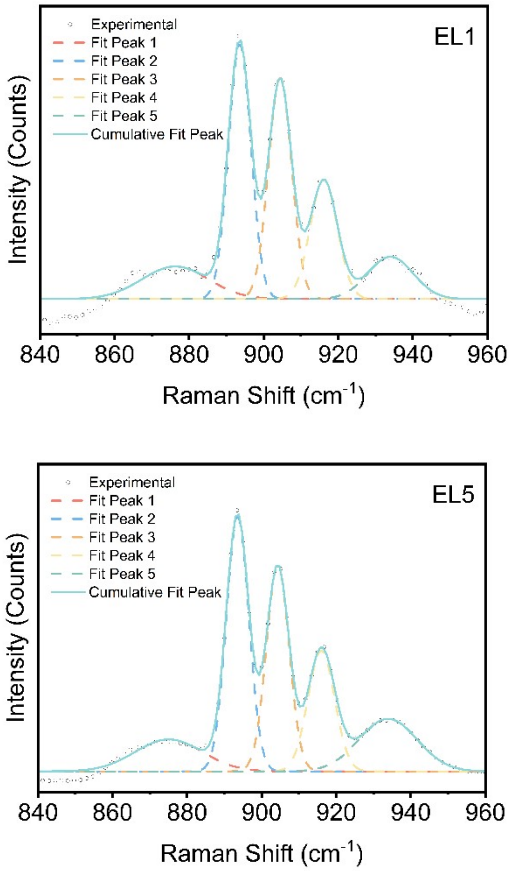


Figure S4. Raman spectra for different electrolytes. The deconvoluted peaks for EL1 and EL5.

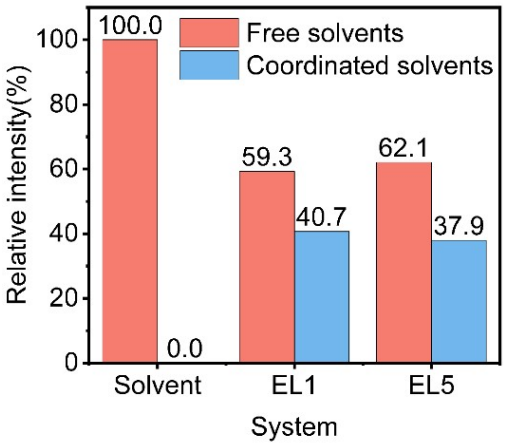


Figure S5. Relative intensity distribution of free and coordinated solvents in EL1 and EL5.

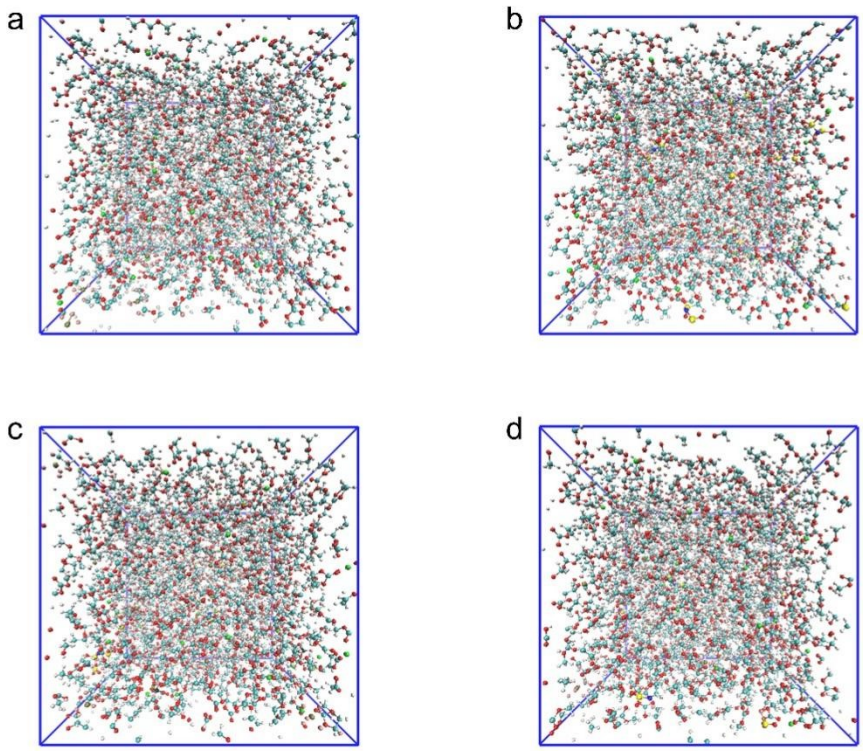


Figure S6. Snapshots of MD simulation boxes for a, EL1, b, EL2, c, EL3 and d, EL5. Li, C, H, O, N, B, F, P, and S atoms are represented by green, cyan, white, red, blue, black, pink, tan, and yellow balls, respectively.

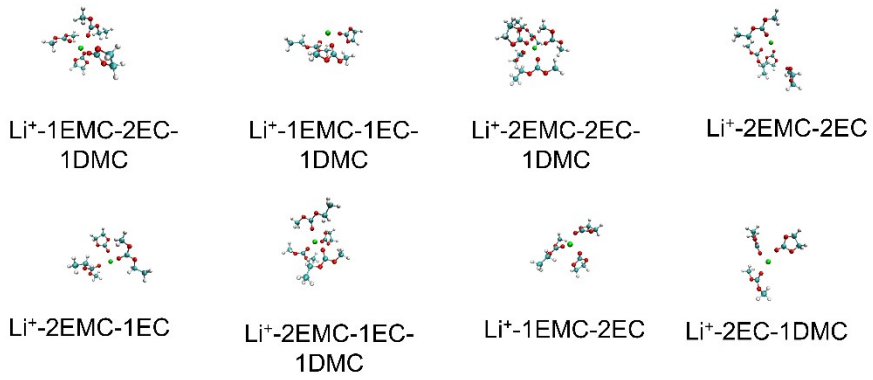


Figure S7. The representative solvation structures from MD simulations for the EL1. Li, C, H, O, N, B, F, P, and S atoms are represented by green, cyan, white, red, blue, black, pink, tan, and yellow balls, respectively.

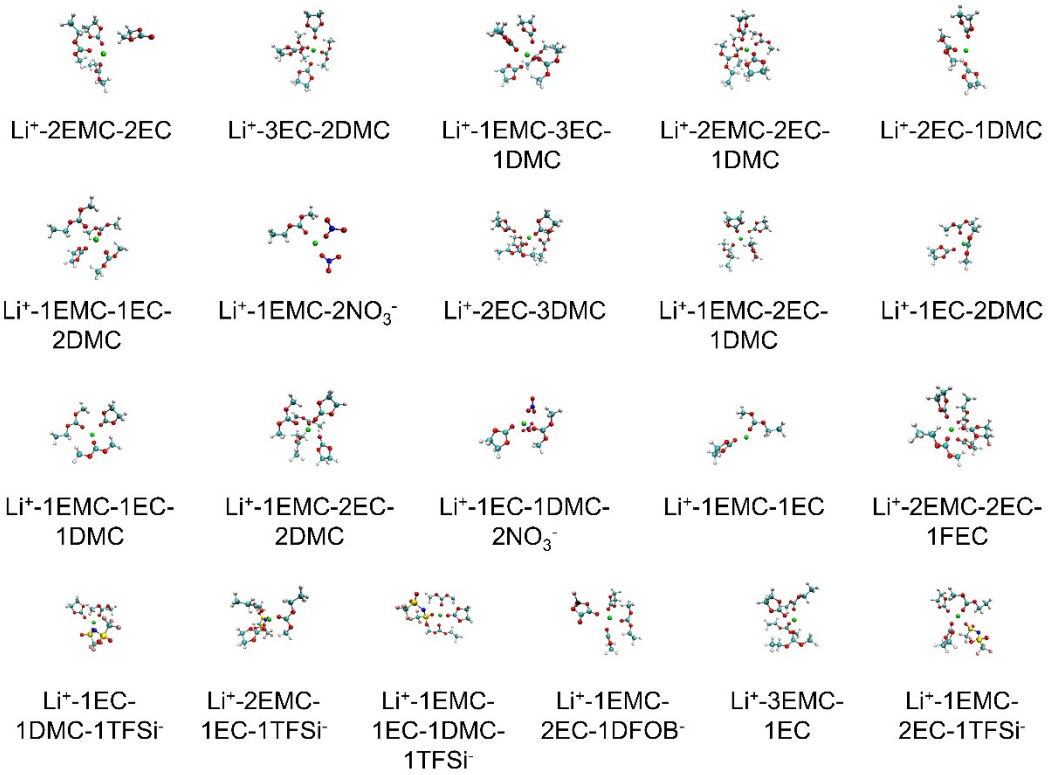


Figure S8. The representative solvation structures from MD simulations for the EL5. Li, C, H, O, N, B, F, P, and S atoms are represented by green, cyan, white, red, blue, black, pink, tan, and yellow balls, respectively.

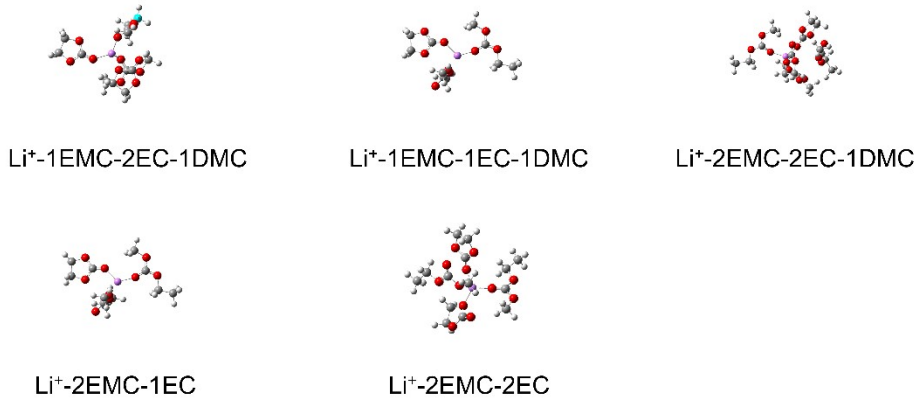


Figure S9. Representative Li^+ solvation structures extracted from MD simulations for EL1 and optimized by DFT. Li, C, H, O, N, P, B, F, and S atoms are represented by purple, gray, white, red, blue, orange, pink, cyan, and yellow balls, respectively.

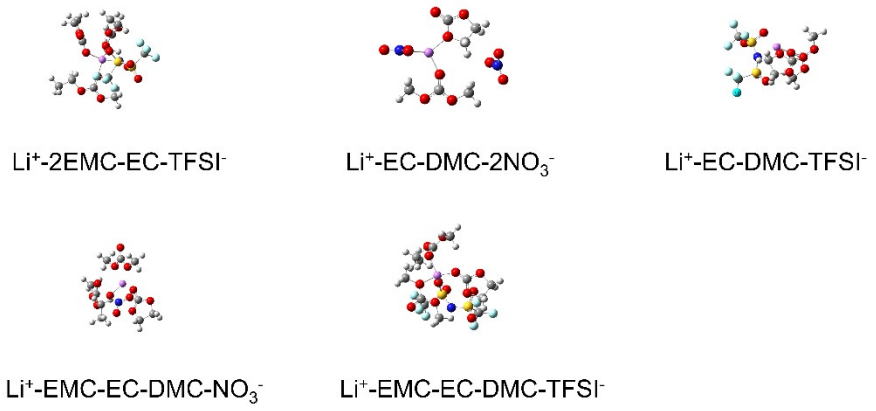
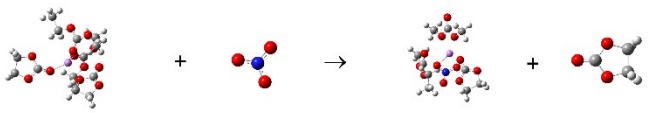


Figure S10. Representative Li^+ solvation structures extracted from MD simulations for EL5 and optimized by DFT. Li, C, H, O, N, P, B, F, and S atoms are represented by purple, gray, white, red, blue, orange, pink, cyan, and yellow balls, respectively.



Li^+-1EMC-2EC-1DMC +NO_3^- → Li^+-EMC-EC-DMC-NO_3^-+EC ΔG=-3.35 eV

Figure S11. Free-energy change for the anion substitution process in the Li^+ solvation structure. Li, C, H, O, N, and F atoms are represented by purple, gray, white, red, blue, and cyan balls, respectively.

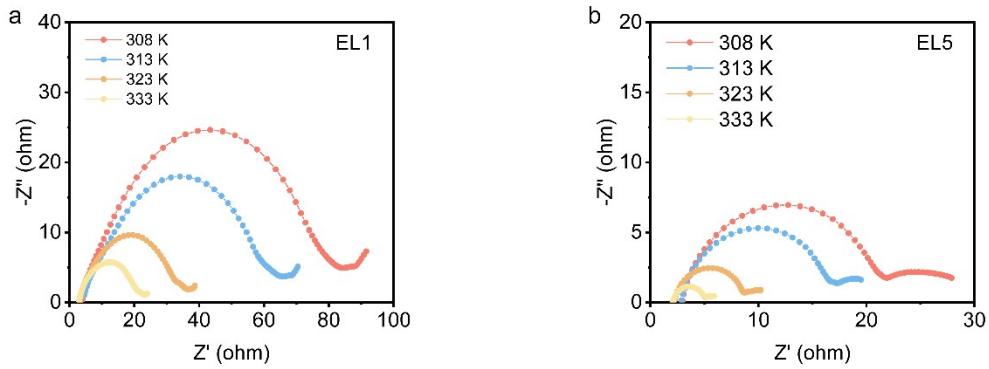


Figure S12. Nyquist plots of Li/Li symmetric cells in the temperature range of 308 to 333 K in (a) EL1, (b) EL5 electrolytes.

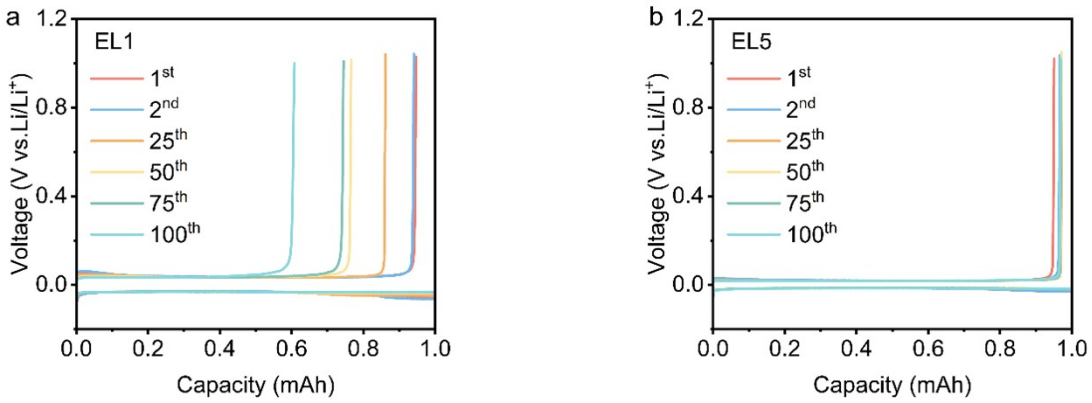


Figure S13. Galvanostatic lithium plating/stripping profiles of Li||Cu cells. a, EL1 and b, EL5 electrolyte of selected cycles at 0.5 mA cm^{-2} and 0.5 mAh cm^{-2}.

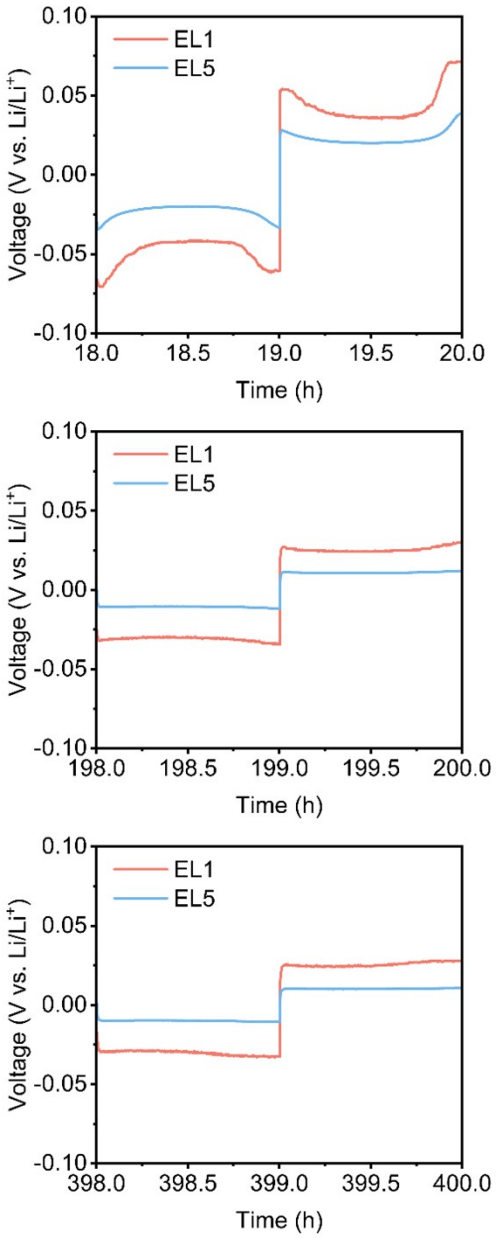


Figure S14. Enlarged voltage profiles of symmetric Li||Li cells cycled in different electrolytes. The Li||Li symmetric were cycled under a current density of 0.5 mA cm^{-2} with each plating/stripping time of 1 h.

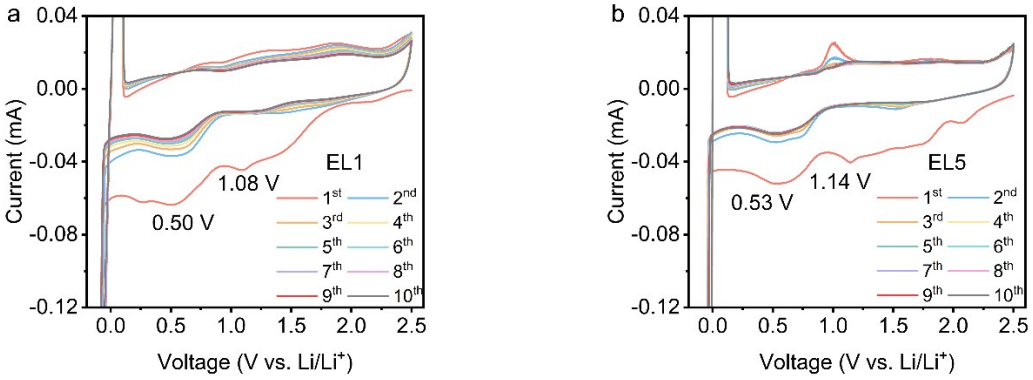


Figure S15. Cyclic voltammetry (CV) curves of Li||Cu cell. The measurements were carried out at a scan rate of 0.8 mV s^{-1} from -0.1 to 2.5 V vs. Li/Li^+ for **a,** EL1 and **b,** EL5.

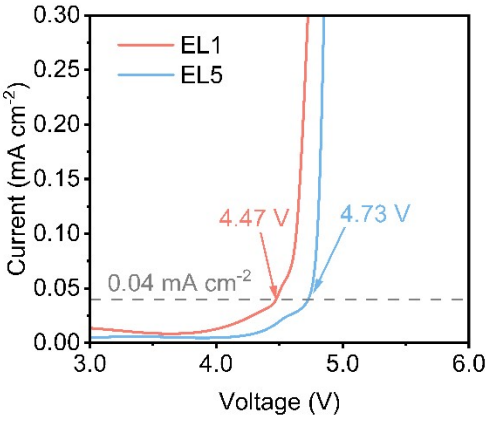


Figure S16. Linear sweep voltammetry (LSV) of Al/C||Li cells to show oxidation stability of different electrolytes. Each cell was scanned from open circuit voltage to 6 V (vs. Li/Li^+).

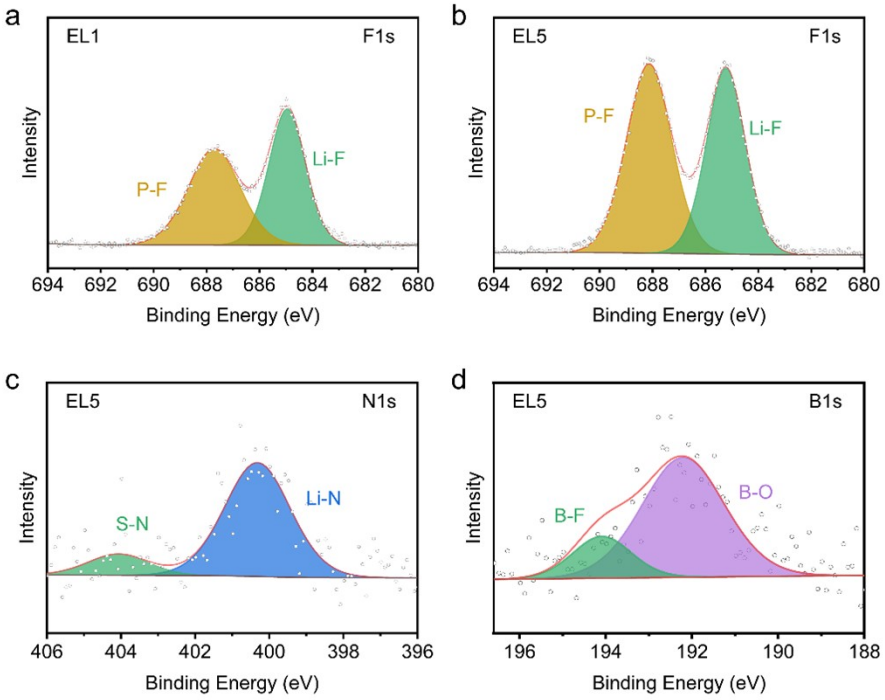


Figure S17. F 1s XPS spectrum of the NCM811 cathode surface after cycling in the (a) EL1 electrolyte and (b) EL5 electrolyte. (c) N 1s XPS spectrum of the NCM811 cathode surface after cycling in the EL5 electrolyte. (d) B 1s XPS spectrum of the NCM811 cathode surface after cycling in the EL5 electrolyte.

Table S1.

The types of solvation structures and their corresponding proportion in the EL1 electrolyte.

EL1	EMC	EC	DMC	FEC	PF_6^-	Ratio
	1	2	1	0	0	0.0628571
	1	1	1	0	0	0.0580952
	2	2	1	0	0	0.0447619
	2	2	0	0	0	0.04
	2	1	0	0	0	0.0371429
	2	1	1	0	0	0.032381
	1	2	0	0	0	0.032381
	0	2	1	0	0	0.0314286
	0	1	1	0	0	0.0304762
	0	2	0	0	0	0.0295238
	3	2	0	0	0	0.0266667
	0	2	3	0	0	0.0266667
	1	2	2	0	0	0.0247619
	0	2	2	0	0	0.0238095
	1	1	0	0	0	0.0219048
	1	1	2	0	0	0.0219048
	1	3	1	0	0	0.0219048
	0	3	2	0	0	0.0209524
	2	3	1	0	0	0.0209524
	1	0	1	0	0	0.02
	3	1	0	0	0	0.02
	0	3	1	0	0	0.0190476
	2	3	0	0	0	0.0161905
	0	1	2	0	0	0.0161905
	3	2	1	0	0	0.0152381
	0	4	2	0	0	0.0152381
	1	3	0	0	0	0.0142857
	0	1	0	0	0	0.012381
	0	2	1	1	0	0.0114286
	0	0	1	0	0	0.0114286
	2	0	1	0	0	0.0114286
	2	1	2	0	0	0.0114286
	1	0	2	0	0	0.0114286
	1	3	2	0	0	0.0104762
	2	2	2	0	0	0.0104762
	3	0	0	0	0	0.0104762
	0	1	3	0	0	0.0095238
	2	0	0	0	0	0.0095238

0	0	0	0	0	0.0085714
1	0	0	0	0	0.0085714
1	4	1	0	0	0.007619
3	3	0	0	0	0.0066667
0	4	1	0	0	0.0066667
1	2	1	1	0	0.0057143
1	3	1	1	0	0.0057143
1	0	2	1	0	0.0047619
3	1	1	0	0	0.0047619
1	1	1	1	0	0.0047619
4	1	0	0	0	0.0047619
2	4	0	0	0	0.0047619
0	3	0	0	0	0.0038095
2	1	0	1	0	0.0038095
0	0	3	0	0	0.0028571
2	2	0	1	0	0.0028571
1	2	2	1	0	0.0028571
0	3	3	0	0	0.0028571
2	0	2	0	0	0.0028571
1	1	2	1	0	0.0028571
1	2	3	0	0	0.0028571
2	0	0	1	0	0.0019048
1	1	3	0	0	0.0019048
0	1	1	1	0	0.0019048
1	0	3	0	0	0.0019048
0	3	2	1	0	0.0019048
1	0	1	1	0	0.0019048
3	2	0	1	0	0.0019048
0	3	1	1	0	0.0019048
1	0	0	1	0	0.0009524
1	1	0	2	0	0.0009524
0	5	1	0	0	0.0009524
0	3	0	1	0	0.0009524
1	3	0	1	0	0.0009524
2	1	1	1	0	0.0009524
4	2	0	0	0	0.0009524
2	3	0	1	0	0.0009524
0	0	1	1	0	0.0009524
0	2	0	1	0	0.0009524
1	2	0	1	0	0.0009524
0	2	2	1	0	0.0009524
0	1	4	0	0	0.0009524
1	1	4	0	0	0.0009524
0	1	0	1	0	0.0009524

0	0	2	0	0	0.0009524
1	1	0	1	0	0.0009524
3	1	0	1	0	0.0009524
1	0	4	0	0	0.0009524
1	4	0	0	0	0.0009524

Table S2.

The types of solvation structures and their corresponding proportion in the EL5 electrolyte.

EL5	EMC	EC	DMC	FEC	PF_6^-	$TFSi^-$	$DFOB^-$	FSi^-	NO_3^-	Ratio
	2	2	0	0	0	0	0	0	0	0.0342857
	0	3	2	0	0	0	0	0	0	0.027619
	1	3	1	0	0	0	0	0	0	0.0247619
	2	2	1	0	0	0	0	0	0	0.0247619
	0	2	1	0	0	0	0	0	0	0.02
	1	1	2	0	0	0	0	0	0	0.0190476
	1	0	0	0	0	0	0	0	2	0.0190476
	2	3	0	0	0	0	0	0	0	0.0190476
	1	2	1	0	0	0	0	0	0	0.0180952
	0	1	2	0	0	0	0	0	0	0.0180952
	1	1	1	0	0	0	0	0	0	0.0161905
	1	2	2	0	0	0	0	0	0	0.0152381
	0	1	1	0	0	0	0	0	2	0.0152381
	1	1	0	0	0	0	0	0	0	0.0142857
	2	2	0	1	0	0	0	0	0	0.0142857
	0	1	1	0	0	1	0	0	0	0.0133333
	2	1	0	0	0	1	0	0	0	0.0133333
	1	1	1	0	0	1	0	0	0	0.012381
	1	2	0	0	0	0	1	0	0	0.012381
	3	1	0	0	0	0	0	0	0	0.012381
	1	2	0	0	0	1	0	0	0	0.012381
	3	2	0	0	0	0	0	0	0	0.012381
	0	2	2	0	0	0	0	0	0	0.012381
	0	2	1	0	0	1	0	0	0	0.012381
	0	2	2	0	0	1	0	0	0	0.0114286
	2	3	1	0	0	0	0	0	0	0.0104762
	1	1	0	0	0	1	0	0	0	0.0104762
	2	1	0	0	0	0	0	0	0	0.0104762
	1	2	1	0	0	0	1	0	0	0.0095238
	0	0	1	0	0	0	0	0	0	0.0095238
	1	2	0	0	0	0	0	0	0	0.0095238
	1	3	0	0	0	0	0	0	0	0.0095238
	1	2	0	0	0	0	0	1	0	0.0095238
	0	1	2	0	0	0	0	1	0	0.0095238
	2	1	0	0	0	0	0	1	0	0.0085714
	0	1	1	0	0	0	1	0	1	0.0085714
	1	3	0	0	0	0	1	0	0	0.0085714
	0	0	2	0	0	0	0	0	0	0.007619
	1	1	0	0	0	0	0	1	0	0.007619
	2	1	1	0	0	0	0	0	0	0.007619

1	1	1	0	0	0	1	0	0	0.007619
2	2	1	0	0	1	0	0	0	0.007619
0	3	1	0	0	0	0	0	0	0.0066667
0	2	0	0	0	0	2	0	1	0.0066667
1	1	0	0	0	0	0	0	2	0.0066667
1	1	2	0	0	0	0	1	0	0.0066667
0	1	1	0	0	0	0	0	1	0.0066667
1	2	2	1	0	0	0	0	0	0.0066667
1	1	0	0	0	0	1	0	0	0.0057143
1	2	1	1	0	0	0	0	0	0.0057143
0	1	1	0	0	0	2	0	1	0.0057143
1	0	1	0	0	0	0	0	0	0.0057143
1	0	1	0	0	0	0	0	1	0.0057143
0	2	0	0	0	0	0	0	1	0.0057143
0	2	0	0	0	0	0	1	0	0.0057143
2	1	1	0	0	0	1	0	0	0.0057143
1	0	0	0	0	0	0	1	0	0.0057143
2	1	0	0	0	0	1	0	0	0.0057143
1	3	2	0	0	0	0	0	0	0.0057143
0	0	1	0	0	0	0	0	2	0.0057143
0	1	2	0	0	0	0	0	1	0.0057143
0	1	2	0	0	0	0	0	2	0.0057143
0	2	3	0	0	0	0	0	0	0.0057143
3	3	0	0	0	0	0	0	0	0.0057143
1	0	0	0	0	0	1	0	2	0.0057143
1	0	0	0	0	0	0	0	0	0.0047619
1	0	0	0	0	0	0	0	1	0.0047619
1	1	1	0	0	0	0	0	1	0.0047619
2	0	1	0	0	0	0	0	1	0.0047619
0	1	2	0	0	1	0	0	0	0.0047619
1	0	1	0	0	0	1	0	1	0.0047619
0	1	0	0	0	1	0	0	0	0.0047619
0	1	0	0	0	0	2	0	1	0.0038095
0	0	1	0	0	0	1	0	2	0.0038095
0	3	0	0	0	0	0	0	0	0.0038095
0	2	2	1	0	0	0	0	0	0.0038095
0	0	2	0	0	0	0	0	2	0.0038095
2	1	0	0	0	1	1	0	0	0.0038095
1	0	2	0	0	0	1	0	0	0.0038095
2	2	1	0	0	0	1	0	0	0.0038095
0	2	3	0	0	1	0	0	0	0.0038095
2	0	0	0	0	0	0	0	0	0.0038095
2	0	0	0	0	0	0	0	1	0.0038095
2	0	0	0	0	0	0	0	2	0.0038095

1	1	2	1	0	0	0	0	0	0.0038095
0	3	0	0	0	0	1	0	0	0.0038095
1	4	0	0	0	0	0	0	0	0.0038095
0	2	1	0	0	0	0	0	2	0.0038095
1	0	0	1	0	0	0	1	0	0.0028571
0	2	0	0	0	0	0	0	2	0.0028571
1	5	0	0	0	0	0	0	0	0.0028571
0	1	0	0	0	0	0	1	0	0.0028571
3	0	0	0	0	0	0	0	0	0.0028571
3	0	0	0	0	0	0	0	1	0.0028571
0	3	0	0	0	1	0	0	0	0.0028571
1	1	1	0	0	0	0	0	2	0.0028571
2	1	1	1	0	0	0	0	0	0.0028571
1	1	0	0	0	0	0	0	1	0.0028571
0	0	1	0	0	0	0	0	1	0.0028571
1	1	1	0	0	0	0	1	0	0.0028571
2	1	2	0	0	0	0	0	0	0.0028571
2	2	0	0	0	0	1	0	0	0.0028571
2	2	2	0	0	0	0	0	0	0.0028571
0	1	0	0	0	0	0	0	0	0.0028571
2	1	0	0	0	0	0	0	1	0.0028571
1	0	2	0	0	0	0	0	0	0.0028571
0	0	0	0	0	0	2	0	1	0.0028571
1	1	0	0	0	1	1	0	0	0.0028571
0	0	2	1	0	0	0	0	0	0.0019048
2	2	0	0	0	1	0	0	0	0.0019048
3	1	0	0	0	0	1	0	0	0.0019048
0	2	0	0	0	0	0	0	0	0.0019048
1	0	1	0	0	0	0	0	2	0.0019048
2	1	1	0	0	0	0	1	0	0.0019048
2	1	0	1	0	0	1	0	0	0.0019048
1	2	0	1	0	0	0	0	0	0.0019048
2	0	1	1	0	0	0	0	1	0.0019048
1	1	2	0	0	0	0	0	1	0.0019048
2	0	1	0	0	0	1	0	0	0.0019048
1	1	0	1	0	0	2	0	0	0.0019048
2	0	0	1	0	0	0	0	0	0.0019048
0	2	0	1	0	0	1	0	0	0.0019048
1	1	0	1	0	0	0	1	0	0.0019048
0	0	3	0	0	0	0	0	0	0.0019048
2	0	0	0	0	0	1	0	0	0.0019048
1	3	0	1	0	0	0	0	0	0.0019048
0	0	2	0	0	1	0	0	0	0.0019048
1	2	1	0	0	1	0	0	0	0.0019048

2	2	0	0	0	0	0	1	0	0.0019048
3	1	0	0	0	0	0	0	1	0.0019048
0	4	0	0	0	0	0	0	0	0.0019048
2	1	0	1	0	0	0	0	1	0.0019048
0	1	0	0	0	0	1	0	1	0.0019048
0	2	1	1	0	0	0	0	0	0.0019048
0	0	3	1	0	0	1	0	0	0.0019048
0	3	0	0	0	0	0	1	0	0.0019048
1	2	0	0	0	0	0	0	2	0.0019048
0	5	0	0	0	0	0	0	0	0.0019048
0	0	0	0	0	0	0	0	0	0.0019048
0	0	0	0	0	0	0	0	2	0.0019048
0	2	0	0	0	0	1	0	0	0.0019048
1	0	1	0	0	0	1	0	0	0.0019048
3	1	0	0	0	0	0	1	0	0.0019048
2	1	1	0	0	1	0	0	0	0.0019048
0	1	1	0	0	0	0	0	0	0.0019048
0	0	2	0	0	0	0	1	0	0.0019048
0	1	0	0	0	0	0	0	2	0.0019048
2	0	0	1	0	0	1	0	0	0.0019048
1	2	2	0	0	0	1	0	0	0.0019048
0	0	0	0	0	0	0	1	0	0.0009524
1	0	1	0	0	1	0	0	0	0.0009524
1	0	1	0	0	0	1	1	1	0.0009524
1	1	3	0	0	0	0	0	0	0.0009524
0	1	0	1	0	0	1	0	0	0.0009524
3	0	1	0	0	0	0	0	0	0.0009524
2	2	0	0	0	0	0	0	1	0.0009524
1	1	1	1	0	0	2	0	0	0.0009524
0	0	1	1	0	0	0	0	0	0.0009524
0	1	2	1	0	1	0	0	0	0.0009524
0	1	2	1	0	0	0	0	0	0.0009524
0	4	2	0	0	0	0	0	0	0.0009524
0	0	0	1	0	0	0	0	2	0.0009524
0	1	2	0	0	0	1	0	0	0.0009524
0	2	1	0	0	0	0	1	0	0.0009524
0	1	1	1	0	1	0	0	0	0.0009524
0	0	0	0	0	0	1	0	0	0.0009524
0	1	1	1	0	0	0	0	0	0.0009524
0	4	1	0	0	0	0	0	0	0.0009524
3	1	0	0	0	1	0	0	0	0.0009524
2	1	1	0	0	1	1	0	0	0.0009524
2	1	1	1	0	0	0	0	1	0.0009524
0	2	0	0	0	0	0	1	1	0.0009524

2	1	0	1	0	0	0	0	0	0.0009524
0	1	0	1	0	0	0	0	2	0.0009524
0	2	2	0	0	0	1	0	0	0.0009524
2	4	0	0	0	0	0	0	0	0.0009524
0	0	1	0	0	1	0	0	0	0.0009524
3	0	0	0	0	0	0	1	0	0.0009524
0	1	0	0	0	0	1	0	2	0.0009524
3	1	0	2	0	0	0	0	0	0.0009524
2	0	1	0	0	0	0	0	0	0.0009524
0	2	1	0	0	0	1	0	0	0.0009524
1	2	0	0	0	0	0	0	1	0.0009524
0	1	1	1	0	0	2	0	0	0.0009524
2	0	1	0	0	0	0	0	2	0.0009524
0	2	1	0	0	0	1	0	1	0.0009524
1	0	2	0	0	0	1	0	1	0.0009524
0	0	0	0	0	1	0	0	0	0.0009524
2	0	0	0	0	1	0	0	0	0.0009524
1	0	0	2	0	0	0	1	0	0.0009524
0	0	2	1	0	0	1	0	0	0.0009524
1	0	1	0	0	0	1	0	2	0.0009524
1	0	0	1	0	0	0	0	1	0.0009524
3	0	0	1	0	0	0	0	0	0.0009524
1	2	1	0	0	0	0	1	0	0.0009524
2	1	0	1	0	0	0	1	0	0.0009524
2	1	1	0	0	0	0	0	1	0.0009524
1	0	0	0	0	0	1	0	0	0.0009524
1	1	1	1	0	0	0	0	0	0.0009524
1	4	1	0	0	0	0	0	0	0.0009524
0	1	0	0	0	0	0	0	1	0.0009524
0	0	0	1	0	0	1	0	1	0.0009524
1	0	1	1	0	0	2	0	0	0.0009524
2	1	0	0	0	0	0	0	2	0.0009524
2	3	0	0	0	0	1	0	0	0.0009524
0	0	3	0	0	0	1	0	0	0.0009524
3	1	0	0	0	1	1	0	0	0.0009524
2	2	1	0	0	0	0	0	1	0.0009524

Table S3.

The types of solvation structures and their corresponding proportion in the EL2 electrolyte.

EL2	EMC	EC	DMC	FEC	PF6	TFSi	Ratio
	0	2	1	0	0	0	0.047619
	1	1	1	0	0	0	0.0361905
	1	2	1	0	0	0	0.0361905
	1	2	0	0	0	0	0.0333333
	1	1	1	1	0	0	0.032381
	1	1	0	0	0	0	0.0314286
	2	1	0	0	0	0	0.0314286
	1	3	1	0	0	0	0.0295238
	0	3	1	0	0	0	0.0228571
	0	1	1	0	0	0	0.0219048
	2	2	0	0	0	0	0.02
	1	2	0	0	0	1	0.0180952
	2	1	1	0	0	0	0.0180952
	2	1	0	0	0	1	0.0180952
	2	3	1	0	0	0	0.0171429
	0	1	0	0	0	0	0.0161905
	0	2	3	0	0	0	0.0161905
	0	2	0	0	0	0	0.0152381
	1	1	1	0	0	1	0.0152381
	1	4	1	0	0	0	0.0133333
	1	1	0	0	0	2	0.0133333
	2	2	1	0	0	0	0.0133333
	2	1	0	0	0	2	0.0133333
	1	0	0	0	0	2	0.012381
	0	2	2	0	0	0	0.012381
	1	4	0	0	0	0	0.0114286
	2	1	1	0	0	1	0.0114286
	1	2	0	0	0	2	0.0114286
	1	0	1	0	0	1	0.0104762
	1	0	0	0	0	0	0.0104762
	1	1	0	0	0	1	0.0104762
	2	2	1	0	0	1	0.0104762
	1	1	1	1	0	1	0.0104762
	0	0	1	0	0	0	0.0104762
	0	3	0	0	0	0	0.0095238
	2	0	0	0	0	0	0.0085714
	1	2	1	0	0	1	0.007619
	1	0	0	0	0	1	0.007619
	1	3	0	0	0	0	0.007619
	0	1	0	1	0	0	0.007619

0	1	2	0	0	0	0.007619
1	0	2	0	0	0	0.007619
3	1	0	0	0	0	0.007619
1	1	2	0	0	1	0.007619
1	0	1	0	0	0	0.0066667
2	0	1	0	0	0	0.0066667
0	1	3	0	0	0	0.0066667
2	0	1	0	0	1	0.0066667
0	2	1	1	0	0	0.0066667
2	3	0	0	0	0	0.0066667
0	2	2	0	0	1	0.0066667
0	3	2	0	0	0	0.0066667
2	4	0	0	0	0	0.0066667
1	2	2	0	0	0	0.0066667
0	4	1	0	0	0	0.0066667
0	0	0	0	0	0	0.0057143
0	2	0	0	0	1	0.0057143
0	4	0	0	0	0	0.0057143
1	1	1	0	0	2	0.0057143
2	1	2	0	0	1	0.0057143
2	2	0	0	0	1	0.0057143
3	2	0	0	0	0	0.0057143
0	3	1	1	0	0	0.0047619
2	0	0	0	0	2	0.0047619
1	0	3	0	0	1	0.0047619
3	0	0	0	0	0	0.0047619
1	1	2	0	0	0	0.0047619
1	2	2	0	0	1	0.0047619
0	1	1	1	0	0	0.0038095
0	2	1	1	0	1	0.0038095
1	3	0	0	0	1	0.0038095
2	0	0	0	0	1	0.0038095
1	2	1	1	0	1	0.0038095
1	1	0	1	0	0	0.0038095
2	0	1	1	0	0	0.0038095
0	2	1	0	0	1	0.0038095
3	1	0	0	0	1	0.0038095
0	0	0	0	0	1	0.0028571
2	2	2	0	0	0	0.0028571
0	0	1	1	0	0	0.0028571
2	0	1	0	0	2	0.0028571
0	0	0	1	0	0	0.0028571
0	0	2	0	0	0	0.0028571
2	1	1	1	0	0	0.0028571

0	3	1	0	0	1	0.0028571
0	5	0	0	0	0	0.0019048
0	1	2	1	0	1	0.0019048
0	3	2	1	0	0	0.0019048
1	0	2	1	0	0	0.0019048
0	1	1	1	0	1	0.0019048
0	0	3	0	0	1	0.0019048
1	5	0	0	0	0	0.0019048
0	2	3	0	0	1	0.0019048
1	0	1	1	0	0	0.0019048
0	0	2	0	0	1	0.0019048
0	1	2	0	0	1	0.0019048
3	1	1	0	0	0	0.0019048
1	2	1	1	0	0	0.0019048
1	1	3	0	0	1	0.0019048
3	1	1	0	0	1	0.0019048
3	2	1	0	0	0	0.0019048
1	0	0	1	0	0	0.0019048
0	1	1	0	0	1	0.0019048
1	0	2	0	0	1	0.0019048
2	0	1	1	0	1	0.0019048
3	3	0	0	0	0	0.0019048
0	1	0	0	0	1	0.0009524
0	0	2	1	0	0	0.0009524
2	1	0	1	0	0	0.0009524
1	0	1	0	0	2	0.0009524
0	0	2	1	0	1	0.0009524
2	2	0	1	0	0	0.0009524
1	0	3	1	0	0	0.0009524
2	0	2	0	0	1	0.0009524
0	2	4	0	0	0	0.0009524
1	0	3	1	0	1	0.0009524
2	1	0	1	0	2	0.0009524
1	3	1	0	0	1	0.0009524
1	1	1	2	0	1	0.0009524
1	0	2	1	0	1	0.0009524
0	1	3	0	0	1	0.0009524
1	4	0	0	0	1	0.0009524
1	2	2	1	0	0	0.0009524
1	1	2	1	0	1	0.0009524
0	2	0	1	0	0	0.0009524
1	0	1	1	0	1	0.0009524
3	0	1	0	0	0	0.0009524
1	0	3	0	0	0	0.0009524

0	3	0	1	0	0	0.0009524
3	0	1	0	0	1	0.0009524
0	4	0	1	0	0	0.0009524
2	3	0	0	0	1	0.0009524
2	2	0	0	0	2	0.0009524
0	0	1	0	0	1	0.0009524
3	0	0	0	0	1	0.0009524
0	2	1	0	0	2	0.0009524
3	2	0	0	0	1	0.0009524

Table S4.

The types of solvation structures and their corresponding proportion in the EL3 electrolyte.

EL3	EMC	EC	DMC	FEC	PF6	TFSi	DFOB	Ratio
	1	2	2	0	0	0	0	0.027619
	1	1	0	0	0	0	0	0.0228571
	0	2	0	0	0	0	0	0.0219048
	1	3	2	0	0	0	0	0.0209524
	1	0	0	0	0	0	0	0.02
	1	0	0	0	0	1	0	0.0190476
	1	2	0	0	0	0	0	0.0190476
	3	2	0	0	0	0	1	0.0190476
	1	1	1	0	0	0	0	0.0180952
	1	1	0	0	0	1	0	0.0171429
	1	1	1	0	0	0	1	0.0161905
	1	2	1	0	0	1	0	0.0152381
	1	1	0	0	0	0	1	0.0142857
	1	2	1	0	0	0	1	0.0142857
	1	3	0	0	0	0	0	0.0142857
	1	3	1	0	0	0	0	0.0142857
	2	2	0	0	0	0	0	0.0142857
	2	2	1	0	0	0	0	0.0142857
	2	1	0	0	0	0	1	0.0133333
	1	0	0	0	0	0	1	0.0133333
	0	2	1	0	0	0	0	0.0133333
	2	2	2	0	0	0	0	0.0133333
	0	3	1	0	0	0	0	0.012381
	2	0	0	0	0	0	0	0.012381
	2	1	0	0	0	0	0	0.012381
	1	2	0	0	0	1	0	0.012381
	2	1	1	0	0	0	0	0.012381
	0	1	1	0	0	1	0	0.012381
	3	0	1	0	0	0	0	0.012381
	1	3	1	0	0	1	0	0.012381
	0	1	0	0	0	0	0	0.0114286
	1	4	0	0	0	0	0	0.0114286
	0	0	0	0	0	0	1	0.0104762
	1	2	1	0	0	0	0	0.0104762
	1	0	1	0	0	0	0	0.0104762
	3	0	0	0	0	0	0	0.0104762
	1	4	1	0	0	0	0	0.0104762
	2	2	0	1	0	1	0	0.0104762
	1	1	2	0	0	0	0	0.0095238
	2	3	0	0	0	0	0	0.0095238

2	2	0	0	0	1	0	0.0095238
0	2	3	0	0	1	0	0.0095238
0	3	2	0	0	0	0	0.0085714
2	0	0	0	0	0	1	0.0085714
0	2	2	0	0	0	0	0.0085714
1	2	0	0	0	0	1	0.007619
1	2	3	0	0	0	0	0.007619
0	1	0	0	0	0	1	0.007619
2	1	1	0	0	0	1	0.007619
1	0	1	0	0	0	1	0.007619
1	2	2	1	0	0	0	0.0066667
1	1	2	0	0	0	2	0.0066667
2	0	0	0	0	0	2	0.0066667
3	1	0	0	0	1	0	0.0066667
0	3	2	0	0	1	0	0.0066667
0	1	1	0	0	0	0	0.0066667
2	1	0	0	0	1	0	0.0066667
3	1	0	0	0	0	0	0.0057143
1	1	2	0	0	0	1	0.0057143
2	3	1	0	0	0	0	0.0057143
2	0	1	0	0	0	0	0.0057143
0	4	0	0	0	0	0	0.0057143
1	2	2	0	0	1	0	0.0057143
0	0	2	0	0	2	0	0.0057143
0	1	2	0	0	1	0	0.0057143
1	1	2	1	0	0	0	0.0057143
0	0	1	0	0	0	0	0.0047619
0	1	1	0	0	0	1	0.0047619
4	0	0	0	0	1	0	0.0047619
2	0	0	0	0	1	2	0.0047619
1	3	0	0	0	1	0	0.0047619
0	3	0	0	0	0	0	0.0038095
1	2	1	1	0	0	0	0.0038095
0	3	2	0	0	0	1	0.0038095
2	2	1	0	0	1	0	0.0038095
2	3	0	0	0	0	1	0.0038095
0	0	0	0	0	0	0	0.0038095
0	0	2	0	0	0	0	0.0038095
4	0	0	0	0	0	0	0.0038095
1	1	1	0	0	1	0	0.0038095
2	4	0	0	0	0	0	0.0038095
1	3	1	1	0	0	0	0.0038095
0	0	1	0	0	1	0	0.0038095
0	1	2	0	0	0	0	0.0038095

2	0	0	0	0	1	0	0.0038095
2	1	2	0	0	0	1	0.0038095
2	1	1	0	0	0	2	0.0038095
0	1	0	0	0	1	0	0.0038095
0	2	1	0	0	0	1	0.0038095
1	0	2	0	0	0	1	0.0038095
0	2	3	0	0	0	0	0.0038095
3	0	0	0	0	1	0	0.0028571
2	0	1	1	0	0	0	0.0028571
3	1	0	0	0	0	1	0.0028571
1	2	0	1	0	0	1	0.0028571
0	2	2	0	0	1	0	0.0028571
0	3	3	0	0	0	0	0.0028571
3	1	0	1	0	1	0	0.0028571
2	1	1	2	0	0	0	0.0028571
3	2	0	0	0	0	0	0.0028571
0	4	2	0	0	0	0	0.0028571
0	0	0	0	0	1	0	0.0028571
0	0	2	0	0	1	0	0.0028571
0	0	2	1	0	2	0	0.0028571
0	1	2	1	0	1	0	0.0028571
2	1	2	0	0	0	0	0.0028571
0	2	0	0	0	0	1	0.0028571
1	1	1	1	0	0	0	0.0028571
2	2	0	0	0	0	1	0.0028571
0	0	0	1	0	0	1	0.0019048
2	0	0	1	0	0	0	0.0019048
0	2	0	0	0	1	0	0.0019048
0	1	1	0	0	2	0	0.0019048
1	0	2	0	0	1	0	0.0019048
0	3	1	0	0	0	1	0.0019048
1	1	3	0	0	0	0	0.0019048
3	1	1	0	0	0	1	0.0019048
0	0	1	0	0	0	1	0.0019048
0	1	1	1	0	0	0	0.0019048
2	0	1	0	0	0	1	0.0019048
1	1	2	0	0	1	0	0.0019048
2	1	0	1	0	0	1	0.0019048
0	1	2	0	0	0	1	0.0019048
2	1	0	1	0	1	0	0.0019048
3	3	0	0	0	0	0	0.0019048
1	0	1	0	0	0	2	0.0019048
0	3	0	1	0	0	0	0.0019048
0	2	2	0	0	0	1	0.0019048

2	1	1	0	0	1	0	0.0019048
2	1	1	0	0	1	1	0.0019048
3	1	0	1	0	0	1	0.0019048
1	0	1	0	0	1	0	0.0009524
0	2	0	0	0	1	1	0.0009524
1	2	0	1	0	0	0	0.0009524
0	1	2	0	0	2	0	0.0009524
1	1	1	0	0	0	2	0.0009524
3	0	0	0	0	1	1	0.0009524
1	1	3	0	0	0	1	0.0009524
3	2	0	1	0	0	0	0.0009524
3	0	0	0	0	1	2	0.0009524
0	1	0	1	0	0	0	0.0009524
0	0	3	0	0	0	0	0.0009524
2	0	2	0	0	0	0	0.0009524
0	1	1	1	0	0	1	0.0009524
2	0	0	1	0	1	0	0.0009524
2	1	0	1	0	0	0	0.0009524
0	4	1	0	0	0	0	0.0009524
2	0	1	0	0	0	2	0.0009524
3	1	1	0	0	1	0	0.0009524
2	2	0	2	0	0	0	0.0009524
1	2	1	0	0	0	2	0.0009524
2	0	0	1	0	1	2	0.0009524
0	0	0	0	0	1	1	0.0009524
1	0	0	1	0	0	0	0.0009524
1	0	1	1	0	0	0	0.0009524
0	1	3	0	0	0	0	0.0009524
0	2	2	1	0	0	0	0.0009524
0	2	1	1	0	0	1	0.0009524
1	3	0	0	0	0	1	0.0009524
4	1	0	0	0	0	0	0.0009524
1	0	2	1	0	0	1	0.0009524
0	1	2	0	0	0	2	0.0009524
2	2	0	1	0	0	1	0.0009524
3	0	0	1	0	0	2	0.0009524
1	1	2	2	0	0	0	0.0009524
3	2	0	0	0	1	0	0.0009524
0	1	0	0	0	1	1	0.0009524
1	0	2	0	0	0	0	0.0009524
1	0	0	1	0	1	0	0.0009524
3	0	0	0	0	0	1	0.0009524
0	3	1	1	0	0	0	0.0009524
1	0	2	0	0	0	2	0.0009524

3	0	0	0	0	0	2	0.0009524
0	2	4	0	0	0	0	0.0009524
2	3	0	1	0	0	0	0.0009524
0	3	2	1	0	0	0	0.0009524
2	2	1	0	0	0	1	0.0009524
1	1	3	1	0	0	0	0.0009524
4	2	0	0	0	0	0	0.0009524

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