Supporting Information

# Tailoring Solvation Chemistry by Hydrogen Bonds in Carbonate

# **Electrolytes for Highly Stable Lithium-Metal Batteries**

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#### **Experimental Section**

*Materials*: LiNO<sub>3</sub> was purchased from Dodo Chem. N-methyl-2-pyrrolidone (NMP) and urea were purchased from Xilong Chemical, Inc (Beijing, China). The baseline electrolytes (1.0 M LiPF<sub>6</sub>-FEC: DMC (v/v=1:2)) were purchased from Songjing New-Energy Co. Ltd (Shanghai, China). Li metal foils (9 mm in diameter and 450  $\mu$ m in thickness, 14 mm in diameter, and 350  $\mu$ m in thickness, 50  $\mu$ m in thickness) were purchased from China Energy Lithium Co. Ltd (Tianjin, China). Powders of LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> (NCM811) were obtained from PULEAD Technology Industry Co. Ltd (Beijing, China). The electrolytes containing additives were prepared by adding 0.1 M urea and 0.05 M LiNO<sub>3</sub> into the baseline electrolytes. The as-obtained electrolytes were stirred to dissolve LiNO<sub>3</sub> completely before being used.

*Electrode preparation and coin cell assembling:* Copper plates were cut into disks with a diameter of 11 mm and immersed in diluted hydrochloric acid (0.1 M) for over 2 h. Thereafter, the copper plates were washed with deionized water and ethanol completely, after that, dried in a vacuum oven (25 °C) overnight. The 90 wt.% NCM811 powders were mixed with 5 wt.% polyvinylidene difluoride (PVDF) (dissolved in NMP) and 5 wt.% carbon black to prepare the uniform slurry. The as-prepared slurry was coated on Al foil and dried at 90 °C. The obtained material was punched into disks ( $\phi$  11 mm) for cathodes and further dried at 120 °C under vacuum before use. The loading mass of active material was controlled at ~ 8.5 mg cm<sup>-2</sup>. The CR-2032 cells were assembled in the glove box filled with Ar (O<sub>2</sub> < 0.1 ppm and H<sub>2</sub>O < 1 ppm). The Li||Li symmetrical cells were assembled with a Li foil (9 mm) as the anode and a Cu foil as the cathode. The full cells were assembled with a Li foil (14 mm) as the anode and the asprepared NCM811 electrode as the cathode. The volume of the electrolyte in all cells was fixed at 75 µL. The Celgard 2400 separators were used in coin cells.

*Materials characterization*: Hitachi-S4800 scanning electron microscopy (SEM) was employed to reveal the morphology of Li anodes. The <sup>1</sup>H and <sup>19</sup>F NMR spectra were collected in Bruker-400 MHz NMR. Fourier transform infrared spectra (FT-IR) of different chemicals were collected in Spotlight 200 FT-IR microscopy (PE). Raman

spectra of different chemicals were collected in Thermo Fisher DXRxi micro Raman imaging spectrometer (532 nm). AXIS supra X-ray photoelectron spectrometer (XPS, Kratos Analytical Ltd.) was used to analyze the SEI and CEI layers on the electrodes. Ar-etching was introduced to investigate the element distributions at various depths. Li anodes and NCM811 cathodes (after 20 cycles at 1 C) were washed with dimethyl carbonate (DMC) to remove the residual Li salts before XPS characterizations. The optical images of Li anodes were obtained in a self-built optical system based on optical microscopy (LW950LJT, Shanghai Cewei Optoelectronic Technology Co., ltd). TOF-SIMS 5 (IONTOF, German) was used to carry out the SIMS analysis of NCM811 cathodes. Before the TOF-SIMS tests. The NCM811 cathodes (after 100 cycles at 1 C) were washed by DMC to remove the residual Li salts before TOF-SIMS characterizations. The CEI layers of cycled NCM811 electrodes were investigated by transmission electron microscope (TEM, JEOL, JEM-2100F).

Theoretical calculations: Gaussian 09 package was used to optimize geometry structures and calculate energy of various molecules at the B3LYP/6-311G+ (d,p) level.<sup>[1, 2]</sup> The solvent effect was considered by SMD implicit solvation model. The molecular dynamics (MD) simulations were conducted with the GROMACS package with cubic periodic boundary conditions.<sup>[3]</sup> All-atom optimized potentials for liquid simulation (OPLS-AA) force field was used to describe the systems, and the parameters of all ions and solvent molecules were obtained from previous work.<sup>[4]</sup> Lorentz-Berthelot combination rule was used to obtain the cross-interaction parameters between different atom types. The equations for the motion of all atoms were integrated by a classic Verlet leapfrog integration algorithm with the time step of 1.0 fs. The cutoff radius of 1.6 nm was used for both short-range van der Waals interactions and realspace electrostatic interactions. Long-range electrostatic interactions in reciprocal space were handled by the particle-mesh Ewald (PME) summation method with an interpolation order of 5 and a Fourier grid spacing of 0.20 nm. All simulation systems were first optimized using a steepest descent algorithm, and then annealed gradually from 600 K to room temperature (300 K) within 10 ns. To maintain the temperature at 300 K and the pressure at 1 atm, an isothermal-isobaric (NPT) ensemble for 20 ns of physical time maintained using a Nosé-Hoover thermostat and a Parrinello-Rahman barostat, with time coupling constants of 0.4 and 0.2 ps, was used for the equilibrium of annealed simulation systems. A canonical ensemble (NVT) for 50 ns was further performed and simulation trajectories were recorded at an interval of 100 fs for structural and dynamical analysis.

*Electrochemical measurements*: All the galvanic charge/discharge cycling tests were conducted on the battery testing system (Land battery tester, Wuhan, China). All the coin-typed cells were allowed to stand for 4 hours before cycling. The Li||Cu half cells for average CE tests were first discharged to plate Li with a capacity of 5.0 mAh cm<sup>-2</sup> on Cu foil at 0.5 mA cm<sup>-2</sup>, then charged to strip all Li reservoir until the voltage reached 1.0 V. After the impurities were removed in the first cycle, the cells were discharged to plate Li reservoir with a capacity of 5.0 mAh cm<sup>-2</sup> on Cu foil at 0.5 mA cm<sup>-2</sup>, then charged in the first cycle, the cells were discharged to plate Li reservoir with a capacity of 5.0 mAh cm<sup>-2</sup> on Cu foil at 0.5 mA cm<sup>-2</sup> for 20 cycles. Finally, the cells were charged at 0.5 mA cm<sup>-2</sup> to strip all the residual Li on Cu foil. The Li||Li symmetrical cells were operated at 0.5 mA cm<sup>-2</sup>/1.0 mAh cm<sup>-2</sup>. The average CE (CE<sub>Avg</sub>) was calculated as follows:

$$CE_{Avg} = [Q_c - (Q_i CE_{Avg} - Q_r)/n]/Q_c \times 100\%$$

Where  $Q_c$ ,  $Q_i$ , and  $Q_r$  are the capacity of a single deposition/stripping process (half cycle), initial depositing Li reservoir, and residual Li, respectively. Li||Cu cells were cycled at 1 mA cm<sup>-2</sup> with a fixed plating/stripping capacity of 1 mAh cm<sup>-2</sup>. Li||NCM811 cell cycling tests were performed within the voltage range of 2.8~4.25 V at 25 °C or 45 °C. The exchange current density tests were conducted on the electrochemical workstation (CHI660e, Chenhua Ltd., Shanghai). The electrochemical impedance spectroscopy (EIS) was conducted by another electrochemical workstation (PGSTAT302N, Metrohm Autolab, The Netherlands) within the frequency range of 10<sup>5</sup> to 10<sup>-2</sup> Hz.



**Figure S1.** The highest occupied molecular orbital (HOMO) energy level and the lowest unoccupied molecular orbital (LUMO) energy level of different components.



Figure S2. Snapshots of different electrolyte obtained by MD simulations.



**Figure S3.** Radial distribution functions (RDFs) and coordination numbers of Li–F and Li–O in (a–b) UNCE and (c–d) UNCE without urea obtained by MD simulations.



**Figure S4.** RDFs of O(DMC)–H(Urea), O(FEC)–H(Urea),  $F(PF_6^-)$ –H(Urea), and F(FEC)–H(Urea) obtained from MD simulation.

Besides the hydrogen bonds formed between H in urea and O in  $NO_3^-$ , there are also certain interactions between H and the electronegative atoms in DMC, FEC, and  $PF_6^-$ .



Figure S5. The RDF of N(NO<sub>3</sub><sup>-</sup>)–N, O, H (Urea) obtained from MD simulations.



Figure S6. FT-IR spectra of different electrolytes and components.



Figure S7. Raman spectra of different electrolytes and components.

UNCE and CE electrolytes exhibit similar FT-IR peak shape because their same main components (Figure S6). In the FT-IR spectra of both UNCE and CE electrolytes, peaks corresponding to FEC and DMC are clearly observed, whereas the peaks of urea are barely detectable due to its low concentration. Both FEC and DMC exhibit shifts in their carbonyl group peaks towards higher wavenumbers. This phenomenon can be mainly attributed to interactions with Li<sup>+</sup>. Furthermore, when comparing the UNCE electrolyte to the CE electrolyte, slight shifts of approximately 1 to 2 cm<sup>-1</sup> are observed in the carbonyl group peaks of FEC and DMC. This observation indicates that FEC and DMC are capable of interacting with urea and LiNO<sub>3</sub> present in the UNCE electrolyte. To better verify the existence of hydrogen bond, we promote the concentration of urea to 0.5 M so as to exhibit the  $-NH_2$  signals in FT-IR spectra (Figure S6d). The shifts of  $-NH_2$  peaks after the addition of LiNO<sub>3</sub> can be attributed to the formation of hydrogen bond between urea and LiNO<sub>3</sub>.

We also employed Raman spectroscopy to analyze the solvation structures of different electrolytes (Figure S7). In the UNCE electrolyte, the ratios of coordinated FEC/free FEC and coordinated DMC/free DMC are higher than those in the CE electrolyte, validating the interaction between FEC, DMC and additives.



Figure S8. The cycling performance of Li||Cu cells with different electrolytes at 1 mA  $cm^{-2}/1$  mAh  $cm^{-2}$ .



**Figure S9.** The morphology of Li deposition on Cu foils with the capacity of (a-b)1.0 mAh cm<sup>-2</sup> and (c-d) 0.5 mAh cm<sup>-2</sup> at 2 mA cm<sup>-2</sup>.



**Figure S10.** (a–b) The morphology of Li deposition on Cu foils with the capacity of  $1.0 \text{ mAh cm}^{-2}$  at 2 mA cm<sup>-2</sup> using the CE electrolyte with 0.1 M urea.

To investigate the effect of urea on the deposition of Li metal, Li||Cu cells were assembled adopting the CE electrolyte with 0.1 M urea. The deposition behavior was observed by SEM. The deposited Li shows a mixed morphology composed of blocky particles and coarser dendrites, which is different from fine dendrites in the CE electrolyte. This indicates that urea has the ability to mitigate the growth of dendritic Li, which is due to the adsorption effect of -C=O and  $-NH_2$  to Li. However, the effect of urea on suppressing dendrite growth is limited without the addition of LiNO<sub>3</sub>.



Figure S11. The EIS measurements of Li||Li cells after 30 cycles at 0.5 mA cm<sup>-2</sup>/1 mAh cm<sup>-2</sup>.



**Figure S12.** The XPS characterizations of Li anodes after 20 cycles. (a) C 1s spectra, (b) F 1s spectra, (c) O 1s spectra of SEI formed in the UNCE electrolyte at different depths. (d) C 1s spectra, (e) F 1s spectra, (f) O 1s spectra of SEI formed in the CE electrolyte at different depths.



Figure S13. The LSV curves of Li||SS cells (scan rate: 5 mV s<sup>-1</sup>).



Figure S14. The EIS measurements of Li||NCM811 cells after 30 cycles at 0.5 C.



Figure S15. The cyclic voltammetry (CV) curves of Li $\|NCM811$  cells with (a) UNCE electrolyte and (b) CE electrolyte at 0.2 mV s<sup>-1</sup>.



Figure S16. TOF-SIMS profiles of (a)  $NiF_3^-$ , (b)  $CoF_3^-$ , (c)  $MnF_3^-$ , (d)  $LiF_2^-$ , (e)  $C_2HO^-$  fragments in CEI layers of NCM811 formed by UNCE and CE electrolytes.



Figure S17. The optical images and pH test of different electrolytes.



**Figure S18.** The <sup>19</sup>F-NMR spectra of CE and UNCE electrolytes after the addition of 1000 ppm  $H_2O$ .

Depths (nm)	Li(%)	C(%)	O(%)	F(%)	P(%)	N(%)
0	35.13	19.86	23.37	18.4	1.5	1.74
5	58.34	6.56	20.96	12.21	0.33	1.61
15	64.58	3.41	19.89	9.36	0.14	2.62
27.5	67.34	3.14	19.89	6.69	0.09	2.86
40	70.43	2.07	19.01	5.05	0.11	3.33

Table S1. The elemental ratios in SEI of Li anodes formed by the UNCE electrolyte.

Depths (nm)	Li(%)	C(%)	O(%)	F(%)	P(%)
0	35.68	22.79	15.13	24.67	1.73
5	53.72	8.91	5.77	30.61	0.98
15	53.69	8.39	9.24	27.72	0.96
27.5	58.84	6.33	14.76	19.28	0.78
40	65.94	4.53	18.19	10.91	0.42

Table S2. The elemental ratios in SEI of Li anodes formed by the CE electrolyte.

Electrolyte	C(%)	N(%)	O(%)	F(%)	P(%)	Li(%)	Ni(%)	Co(%)	Mn(%)
UNCE	38.98	2.36	8.16	35.91	1.08	11.37	1.97	0.02	0.13
CE	40.81	/	7.40	32.39	0.52	17.11	1.72	0.01	0.03

 Table S3. The elemental ratios in CEI of NCM811 formed by UNCE and CE
 electrolytes.

## Reference

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