

## Supplementary Information

## Tuning of hybrid highly concentrated electrolytes and the interfacial building for lithiumbased cells

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## **Experimental Methods**

Chemicals and Materials. Fluoroethylene carbonate (FEC, moisture  $\leq 20$  ppm), acetonitrile (AN, moisture  $\leq 20$  ppm), bis(trifluromethanesulfonyl)imide lithium salt (LiTFSI, purity  $\geq$  99.9%, moisture  $\leq 100$  ppm) were purchased from DodoChem. The conventional carbonate electrolyte for comparison, 1 M LiPF<sub>6</sub>+ EC/DMC/EMC, denoted as CCE, was also purchased from DodoChem. Lithium metal discs with thickness of 1 mm and diameter of 15.6 mm were purchased from China Energy Lithium Co., Ltd. The copper mesh (200 mesh, 100 µm thickness) was purchased from Shanghai Huadong Screen Co., Ltd., which was punched into 16.3 mm diameter discs and cleaned with 1 M HCl solution and ethanol successively, dried under vacuum and stored in argon glove box. The single-crystal LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> (NCM811) cathode material was used as received. The 3501 polypropylene (PP) separator (25 µm thickness) and glass fiber filter (130 µm thickness) was purchased form Guangdong Canrd New Energy Technology Co., Ltd., which was punched into 19 mm diameter discs ready for use.

Preparation of HCEs. All the HCEs were prepared in the argon atmosphere glove box with O<sub>2</sub> content and H<sub>2</sub>O content both below 0.1 ppm. As shown in Table 1, FEC, AN and LiTFSI were weighted and mixed at the fixed mole ratio (2-x):x:1, and stirred for 24 hours to form clear solutions.

Ab Initio Molecular Dynamics (AIMD) Simulation Details. AIMD simulations were performed using the Vienna Ab initio Simulation Package (VASP). The exchange-correlation functional was represented using the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA-PBE). The starting configurations of LiTFSI, FEC and AN were firstly optimized. The initial structures of each HCEs system were set up by randomly placing the molecules on the basis of experimental densities and molar ratios. The shape of simulation box was cubic. The box lengths were 1.611 nm for HiF, 1.569 nm for HiFA-6, 1.554 nm for HiFA-9 and 1.550 nm for HiA, respectively. For AIMD simulations, NVT ensemble was used at 300 K with a time step of 2 fs. A Nose thermostat with a Nose-mass parameter of 1.0 was employed to control the temperature oscillations during the simulations. The systems were preequilibrated at least 60 ps. Then, the production time was 10 ps. The projected density of states (PDOS) were calculated and averaged over five different configurations (extracted from AIMD simulation snapshots) to represent an ensemble average. Radial distribution functions were



obtained by the Visual Molecular Dynamics (VMD) software. The snapshots of the most probable solvation shells were also sampled from the simulation trajectory using VESTA.

Battery Assembly. CR2025-type ionic blocking coin cells were assembled with two stainless steel (SS) discs (1 mm thickness) and glass fiber filter injected with 100  $\mu$ L electrolyte. CR2025-type Li||Li symmetric cells were assembled with two lithium metal discs, a SS discs (500  $\mu$ m thickness) and 3501 PP separator injected with 100  $\mu$ L electrolyte. CR2025-type Li||Cu half cells were assembled with Cu mesh, lithium metal disc, SS discs (1 mm thickness) and 3501 PP separator injected with 100  $\mu$ L electrolyte. NCM811 cathode (2 mg cm<sup>-2</sup>) were prepared with the slurry of NCM811, Super P and PVDF (9:0.5:0.5, wt.) mixture with NMP solvent coated on aluminum foil and dried under vacuum at 120°C for 12 hours, then punched into 13 mm diameter discs. The CR2016-type Li||NCM811 batteries were prepared with lithium metal disc, NCM811 cathode, SS disc (500  $\mu$ m thickness) and 3501 PP separator injected with 100  $\mu$ L electrolyte.

Physical Characterization of HCEs. FT-IR characterization were carried out on a Nicolet iS50 FT-IR spectrometer at transmission mode from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. TG curves were measured on Netzsch STA449F5 thermal analyzer at heating rate of 10°C min<sup>-1</sup> from 30°C to 550°C with N<sub>2</sub>/O<sub>2</sub> mixture as purge gas. The viscosity from 25°C to 70°C were collected on TA Instruments DHR-2 rotational rheometer with accurate temperature control system. Morphology and elements distribution of the deposited lithium were detected on HITACHI S-4800 scanning electron microscope (SEM). The components of SEI at different etching depths were detected on Thermo Fisher Escalab Xi+ X-ray photoelectron spectroscopy (XPS) equipped with Ar ion gun. The flammability tests of electrolytes were carried out in the fume hood. The thermal stability of fully charged NCM811 cathode (4.5 V vs. Li<sup>+</sup>/Li) was measured on Netzsch DSC 214 differential scanning calorimetry (DSC) analyzer at heating rate of 10°C min<sup>-1</sup> from 25°C to 300°C with N<sub>2</sub> as purge gas. All the deposited lithium samples obtained from Li||NCM811 batteries were cleaned with DME and transferred under vacuum to avoid exposure to air.

Electrochemical Characterization. The ionic conductivity ( $\sigma$ ) of HCEs were measured by electrochemical impedance spectroscopy (EIS) tests of the ionic blocking coin cells on Zahner Zennium electrochemical workstation at different temperature controlled by oven and



calculated from Equation S1:

$$\sigma = L/(S \cdot R)$$
 (S1)

where L is the distance between two stainless steel (SS) electrodes, S is the area of SS electrode, and R is the ohmic resistance of the cell obtained from Niquist plot. The Li<sup>+</sup> transference number ( $t_{Li+}$ ) of HCEs were measured by DC polarization (POL) combined with EIS tests of Li||Li symmetrical coin cells on Zaher and calculated from Equation S2:

$$t_{Li^{+}} = I_{s} \cdot R_{1}^{s} (\Delta V - I_{0} \cdot R_{2}^{0}) / (I_{0} \cdot R_{1}^{0} (\Delta V - I_{s} \cdot R_{2}^{s}))$$
(S2)

where  $\Delta V$  is the POL voltage (10 mV), I<sub>0</sub> and I<sub>s</sub> are the response current at the initial and after stabilization, respectively.  $R_1^0$  and  $R_2^0$  are the bulk ohmic resistance and interfacial charge transfer resistance of the Li||Li cells before POL, respectively.  $R_1^s$  and  $R_2^s$  are the bulk ohmic resistance and interfacial charge transfer resistance of the LillLi cells after stabilization. EIS were tested in the frequency range of 1 MHz to 10 mHz at amplitude of 5 mV to obtain Nyquist plots. Cyclic voltammetry of three-electrode cells and LillCu cells were carried out on Bio-Logic VMP3 workstation. The battery performance were tested on Shenzhen Neware battery detection system. The LillLi symmetric cells were cycled at charge/discharge current density of 0.5 mA cm<sup>-2</sup> with controlled capacity of 0.5 mAh cm<sup>-2</sup> per half cycle. Li||Cu half cells were tested by the modified Aurbach method to investigate the coulombic efficiency of lithium plating/stripping. The first cycle of lithium plating/stripping was charge/discharge at 0.5 mA cm<sup>-2</sup> with controlled discharge capacity of 4 mAh cm<sup>-2</sup>. The coulombic efficiency of the first cycle (denoted as CE<sub>1st</sub>) was calculated by dividing the charge capacity (charge to 2 V vs. Li<sup>+</sup>/Li) by the discharge capacity. Next, 4 mAh cm<sup>-2</sup> lithium was pre-deposited, then incomplete plating/stripping were carried out at 0.5 mA cm<sup>-2</sup> with controlled capacity of 1 mAh cm<sup>-2</sup> for 10 cycles. Lastly, fully stripping of lithium were carried out at 0.5 mA cm<sup>-2</sup> charge to 2 V vs.  $Li^+/Li$ . The average coulombic efficiency (denoted as  $CE_{avg}$ ) were calculated by Equation S3:

$$CE_{avg} = (Q_s + n \cdot Q_c) / (Q_p + n \cdot Q_c)$$
(S3)

where  $Q_p$  is the pre-deposited capacity,  $Q_s$  is the lastly fully stripping capacity,  $Q_c$  and n are the controlled capacity and the cycle number of the incomplete plating/stripping process, respectively. Li||NCM811 batteries were tested within the voltage range of 3-4.5 V. The long-term cycle stability of Li||NCM811 batteries were determined through constant current charge/discharge at current density of 1 C (275.5 mA g<sup>-1</sup>) after activation at 0.1 C and 0.5 C for



3 cycles, respectively. In addition, the rate performance of Li||NCM811 batteries were tested at charge/discharge current densities of 0.1 C, 0.5 C, 1 C, 2 C, 3 C 4 C, 5 C and returning to 0.1 C, respectively.

To further characterize the Li<sup>+</sup> solvation structure, especially the first solvation sheath of Li<sup>+</sup> ion, <sup>7</sup>Li-NMR tests were carried out (Bruker, Avance III HD 850MHz). As shown in Fig. S1a, for FEC-based electrolytes, the chemical shift of <sup>7</sup>Li-NMR moved to the high field gradually as the increase of LiTFSI concentration, indicating the shielding effect was enhanced by the increase of electron cloud density around the Li nuclear. It was the evidence of the decrease of FEC solvent molecule and the increase of TFSI<sup>-</sup> anions, which was consistent with the previous reports.<sup>S1</sup> However, as for AN-based electrolytes (Fig. S1b), the chemical shift of <sup>7</sup>Li-NMR moved to the low field gradually. It was mainly related to the quite small steric hindrance of AN molecule. With the increase of LiTFSI concentration, the larger TFSI<sup>-</sup> anions squeezed out some AN molecule and entered the first salvation sheath of  $Li^+$  ions, which would reduce the electron cloud density around Li nucleus and reduce the shielding effect. <sup>S2</sup> Fig. S1c shown the hybrid HCEs based on FEC-AN mixed solvents in this work. With the increase of AN proportion, the chemical shift of <sup>7</sup>Li-NMR moved to the high field gradually, which because the smaller AN molecule was closer to Li+ leading to the increase of the electron cloud density around Li nucleus. Therefore, it's necessary to consider the steric hindrance factor for better understanding about solvation structure and properties of the hybrid HCEs.<sup>S3</sup>





**Fig. S1** <sup>7</sup>Li-NMR spectra of (a) FEC-based electrolytes from low to high concentration, (b) ANbased electrolytes from low to high concentration, (c) FEC-AN mixed solvents based HCEs (FEC:AN:LiTFSI= (2-x):x:1, mol.), respectively.





**Fig. S2** The snapshots of supercells in equilibrium trajectories used for simulations on (a) HiF, (b) HiFA-6, (c) HiFA-9 and (d) HiA, respectively.





**Fig. S3** Flammability tests of (a) The conventional carbonate electrolyte (CCE); (b) HCEs in this work, HiFA-6 (FEC:AN:LiTFSI= 0.8:1.2:1, mol.).



Abbreviation	x in FEC:AN:LiTFSI - = (2-x):x:1, mol.	Viscosity (mPa•s)					
		25°C	40°C	50°C	60°C	70°C	
HiF	0	388.5	164.5	95.3	59.3	40.3	
HiFA-1	0.2	347.4	168.6	103.0	69.0	50.3	
HiFA-2	0.4	329.6	159.1	98.9	68.7	50.0	
HiFA-3	0.6	320.6	150.6	94.5	67.2	48.7	
HiFA-4	0.8	238.7	119.3	79.7	53.7	41.7	
HiFA-5	1	191.4	99.7	65.7	42.1	34.2	
HiFA-6	1.2	166.3	88.6	60.7	43.3	38.0	
HiFA-7	1.4	161.3	89.9	50.5	46.4	39.6	
HiFA-8	1.6	155.6	83.4	54.5	45.6	41.7	
HiFA-9	1.8	151.5	78.7	57.0	44.6	43.7	
HiA	2	148.6	75.4	53.7	44.8	44.3	

 Table S1 Viscosities of HCEs at typical temperature.



Abbreviation	x in FEC:AN:LiTFSI = (2-x):x:1, mol.	Ionic conductivity (mS cm <sup>-1</sup> )					
		25°C	40°C	50°C	60°C	70°C	
HiF	0	0.088	0.166	0.250	0.355	0.513	
HiFA-1	0.2	0.120	0.269	0.427	0.631	0.831	
HiFA-2	0.4	0.148	0.332	0.483	0.727	0.921	
HiFA-3	0.6	0.171	0.378	0.564	0.805	1.032	
HiFA-4	0.8	0.184	0.409	0.642	0.886	1.120	
HiFA-5	1	0.257	0.559	0.801	1.112	1.466	
HiFA-6	1.2	0.288	0.600	0.840	1.153	1.482	
HiFA-7	1.4	0.345	0.685	0.967	1.295	1.613	
HiFA-8	1.6	0.386	0.751	1.059	1.435	1.775	
HiFA-9	1.8	0.425	0.801	1.131	1.526	1.893	
HiA	2	0.425	0.817	1.230	1.669	2.152	

 Table S2 Ionic conductivities of HCEs at different temperature.



Fig. S4 shown the Tafel plots of Li||Li symmetrical cells assembled with HiF, HiFA-6, HiFA-9 and HiA, respectively. Among them, the asymmetry of Tafel curve of HiA indicated the poor reversibility of Li<sup>+</sup> deposition/stripping. The calculation results shown that the exchange current density were 0.18, 0.27, 0.31 and 0.26 mA cm<sup>-2</sup> for HiF, HiFA-6, HiFA-9 and HiA, respectively. Therefore, through the mixed-solvents strategy, the introduction of AN was beneficial to improve the kinetics of lithium deposition/stripping.



**Fig. S4** Tafel plots of Li||Li symmetrical cells assembled with HiF, HiFA-6, HiFA-9 and HiA, respectively, scanning from -0.2 to 0.2 V vs. Li<sup>+</sup>/Li at rate of 1 mV s<sup>-1</sup>. The exchange current densities were calculated with the linear polarization region.





Fig. S5 Current-time profiles of DC polarization tests and Nyquist plots of EIS tests (insertion) of Li||Li symmetric cells assembled with HCEs for  $t_{Li^+}$  calculation.



In addition, longer time DC polarization was applied to measure  $t_{Li^+}$  of HiF, HiFA-6 and HiFA-9, respectively. As shown in Fig. S6, Li||Li symmetrical cell assembled with HiF exhibited low response current and large interface resistance with  $t_{Li^+}$  calculated to be 0.8. The increased resistance after polarization was attributed to the thick passivation layer of lithium metal generated from HiF. For HiFA-9, the response current was relatively high, but was unsteady after 1 hour polarization, indicating the unstable interface of lithium metal with large proportion of AN verified by the significantly decreased resistance. Under the test condition,  $t_{Li^+}$  of HiFA-9 was calculated to be only 0.46. However, for HiFA-6, the response current was slightly lower than that of HiFA-9, but steady-state current and stable interface resistance were obtained after 1 hour polarization, indicating HiFA-6 could generate thin and stable passivation layer on lithium metal. Finally,  $t_{Li^+}$  of HiFA-6 was calculated to be as high as 0.89. Hence that, the introduction of appropriate proportion of AN could promote Li<sup>+</sup> migration and optimize the interface as well.



**Fig. S6** (a) Current-time profiles of 1 hour DC polarization tests and (b) Nyquist plots of EIS tests of Li||Li symmetrical cells assembled with HiF, HiFA-6 and HiFA-9, respectively, for  $t_{Li^+}$  calculation.





Fig. S7 CV curves of (a) HiF, (b-j) HiFA-1~9 and (k) HiA compared with (l) FEC-based low concentration electrolyte "FEC+ 1 M LiTFSI", measured in three-electrode system with platinum as working electrode and lithium metal as counter electrode and reference electrode, at scanning rate of 1 mV s<sup>-1</sup> within -0.2 to 6 V vs. Li<sup>+</sup>/Li.



**Fig. S8** The initial activation scanning of CV tests of Li||Cu cells assembled with (a) FEC+ 1 M LiTFSI, (b) HiF, (c) HiFA-6, (d) HiFA-9 and (e, f) HiA, respectively, within the potential range of 3 V to 0 V vs.  $\text{Li}^+/\text{Li}$  at scanning rate of 1 mV s<sup>-1</sup>.





Fig. S9 Cycle performance of Li||Li symmetric cells assembled with HCEs at galvanostatic charge/discharge current density of 0.5 mA cm<sup>-2</sup> and each half cycle specific capacity of 0.5 mAh cm<sup>-2</sup>.





**Fig. S10** Potential-time curves of Li||Cu half cells assembled with HCEs measured with the modified Aurbach method. (c-e) are the locally enlarged images of (a).





**Fig. S11** Potential-specific capacity curves of Li||Cu half cells at the end of cycle life. (a) Li||Cu half cells cycled at 0.25 mA cm<sup>-2</sup> with controlled specific capacity of 0.25 mAh cm<sup>-2</sup>. (b) Li||Cu half cells cycled at 0.5 mA cm<sup>-2</sup> with controlled specific capacity of 0.5 mAh cm<sup>-2</sup>.





**Fig. S12** SEM images of lithium metal deposition morphology at different magnifications. 4 mAh cm<sup>-2</sup> lithium metal deposited on Cu current collectors were obtained from (a-d) Li|HiF|Cu half cells, (e-h) Li|HiFA-6|Cu half cells and (i-l) Li|HiFA-9|Cu half cells at current density of 0.1 mA cm<sup>-2</sup>, respectively. The insertions in (a), (e) and (i) are optical photographs of the corresponding deposited lithium metal, respectively.



**Fig. S13** C 1s, N 1s and S 2p XPS spectra of in-depth XPS characterization of deposited lithium metal obtained from Li||Cu half cells assembled with (a) HiF, (b) HiFA-6 and (c) HiFA-9, respectively.





**Fig. S14** (a) Coulombic efficiency curves and (b) mid-value potential curves of long-term cycle performance of Li||NCM811 full cells assembled with CCE, HiF and HiFA-6, respectively.



**Fig. S15** Nyquist plots of Li||NCM811 full cells after different cycles at 1 C (fully charged to 4.5 V). (a) CCE; (b) HiF; (c) HiFA-6.

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