Supporting Information

Salt-Rich Solid Electrolyte Interface for Safer High-Energy-Density Li Metal Batteries with Limited Li Excess

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Experimental Section

Chemicals: All the chemicals are used without further purification. The N-methyl-Npropylpiperidium bis(trifluoromethane-sulfonyl)imide (PP13TFSI) was bought from Lanzhou Ionic Liquid Corporation. The ionic liquid was dried at 100 °C under vacuum for 12 h prior to use. Other electrolyte solvents were bought from Shanghai Songjing New-Energy Technology Limited. LiPF₆, NaPF₆, LiTFSI, LiBOB and triethyl phosphate (TEP) were purchased from BASF company. For comparison, the LiPF₆ in EC/DEC(v:v=1:1) was also purchased from Shanghai Songjing New-Energy Technology Limited. Commercialized LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ was purchased from BASF. The optimized electrolyte is consisted of 0.5M LiPF₆ 0.5M LiTFSI 0.2M LiBOB, and 0.15 M NaPF₆ in the mixed solution of PP13TFSI, TEP, PC and FEC. (2:2:3:1) Preparation of NCM811 electrode: the NCM811 cathode was prepared by mixing the commercialized NCM811 powder, Super P and PVDF in a mass ratio of 8:1:1 in the solvent of N-methyl pyrrolidone (NMP). The slurry was then coated on the Al foil and then dried under vacuum at 80 °C for 12h. The average cathode loading is 4 mg cm⁻². The NCM811 with 10 mg cm⁻² was also prepared. To prepare the NCM811 cathode with higher loading, the NCM811powder was mixed with Super P and PVDF in a mass ratio of 9:0.5:0.5. LiNO3 treated glass fiber separators were prepared by immersing the glass fiber in the LiNO₃ solution (1mg LiNO3 in 10ml DME solvent). Then, the glass fiber separators were dried at 80 °C under vacuum overnight.

Preparation of anode: the Li anode was prepared by pairing the Cu foil with Li metal in the optimized electrolyte. the Li||Cu half cells was cycled for 15 times after which the coulombic efficiency of Li||Cu half cells reached 97%. Then, 0.8mAh cm⁻² Li was deposited on the Cu foil to obtain 100% excessive Li anode. The pre-lithiated Cu foil was also prepared by cycling the Li||Cu half cells for 15 times and extracting the Cu foil after recharging to 1V.

Cell assembly: To assemble NCM811||Li full cells, the Li foils (50 mAh cm⁻²), 2 mAh cm⁻² (N/P=1), 0.8 mAh cm⁻² Li on Cu foils (N/P=1), pre-lithiated Cu foil and bare Cu foil were employed as the counterpart electrode. The full cells were assembled by sandwiching the LiNO₃ treated glass fiber separator between NCM811 cathode and different Li metal anodes.

Characterization: The morphologies of NCM811 cathode and Li metal anode were investigated by the Scanning Electronic Microscopic (SEM) (FE-SEM S-4800). The Transmission Electron Microscope (TEM) (JEOL JEM-2100 F microscope (Japan) operated at 200 kV) was also carried out on the NCM811 cathode. X-ray photoelectron spectroscopy (XPS) was carried out on aXSAM800 Ultra spectrometer. Powder X-ray diffraction was carried out on the X-ray diffractometer (Bruker D8 Advance, Germany) with Cu K α radiation (λ = 0.15406 nm).

Computational details: Geometries of the molecules were optimized by using the M08-HX.

exchange-correlation (XC) density functional with the 6-311+G(3df, 2p) all-electron basis. The electronic energies and orbital energies were calculated at the same level of theory. Calculations were performed with the *Gaussian*16 program.



Figure S1. Voltage profile of Li deposition: a) Voltage profiles of the 2nd cycle in different electrolyte; b) Voltage profiles over cycles in optimized electrolyte.

It can be identified that although the controlled electrolyte shows the lowest polarization, the coulombic efficiency is much lower than the optimized electrolyte. In addition, the polarization of the optimized electrolyte remains unchanged over 100 times.



Fig. S2. Average coulombic efficiency of Li plating.

Figure S2 shows the average coulombic efficiency of Li deposition in different electrolyte. As shown in **Figure S2a**, when 5mAh cm⁻² Li was pre-deposited on the Cu foil and 0.5 mAh cm⁻² was utilized for Li-Li symmetric cells, corresponding to 10% Li utilization, a high coulombic efficiency of 99.3% is achieved in our optimized electrolyte. For comparison, the coulombic efficiency of the controlled electrolyte is only 71.88%. When the Li utilization increase to 25%, a high coulombic efficiency of 99.65% is achieved, which is the highest coulombic efficiency.(See **Table S3**)



Figure S3. SEM mapping of Cu foil after plating 0.1 mAh cm⁻² Li: a) EDS image of the mapping area; b,c) Na element EDS mapping; d) Na *1s* XPS spectrum of Cu after deposition of 0.1mAh cm⁻² Li.

Figure S3 shows the SEM mapping of Cu foil after plating 0.1 mAh cm⁻² Li. The signal of Na is clearly found in the SEM mapping. In addition, the X-ray photoelectron spectrum also confirms the presence of Na on the Cu foil. The Na₂O peak is much stronger due to the short exposure to the air before transferring into the vacuum chamber of XPS.



Figure S4. SEM images of Li metal in NCM811 full cells after 50 cycles in different electrolyte:

a,b) in the optimized electrolyte; c,d) in the controlled electrolyte.



Figure S5. XRD pattern of the pristine NCM811 cathode.



Figure S6. Pristine SEM images of NCM811 cathode.



Figure S7. Voltage profiles of Cu||NCM811 full cells.

Two factors contribute to the highly reversible capacities from 2nd to 10th cycle. On the one hand, the initial Coulombic efficiency of NCM811 cathode is only 80%. In other words, 20% of the Li that was deintercalated from the NCM811 cathode during the initial cycles can not be

re-intercalated into the NCM811 cathode. The lithium will remain on the Cu foil. On the other hand, the Cu foil employed in the Figure 2e is not bare Cu foil, but pre-lithiated Cu foils. Prior to assembling into the NCM811||Cu cells, the Cu foil was assembled into Li||Cu half-cells and cycled for 15 time. After that, the Coulombic Efficiency increased to 97%. During the pre-lithiation process, a small amount of Li may also remain on the Cu foil. Those two parts of Li provide the initial Li source for the initial ten cycles. We also paired the bare Cu foil with NCM811 cathode (**Figure S8**). Without pre-lithiation process, both the coulombic efficiency and capacity retention become much inferior.



Figure S8. Electrochemical performance of NCM811|| bare Cu full cell.

We also paired the NCM811 cathode with bared Cu foil. Without pre-lithiation, the NCM811||bare Cu cell decay much rapidly and the coulombic efficiency is also much inferior to the pre-lithiation Cu foil. The result suggests that the pre-lithiation process is important to prolong the cycle life of NCM811||Cu full cells.



Figure S9. Electrochemical performance of NCM811|| Li metal full cell with high cathode loading. (Charge: 0.1C, Discharge: 0.3C, N/P=1)

Even with high cathode loading of 10 mg cm⁻², the NCM811||Li metal also shows stable cycling performance.





Figure S10. The optimized geometries for the salts and solvents in the electrolyte (PS: The balls in red, orange, dark yellow, light yellow, blue, cyan, violet, grey and white are O, P, B, S, N, F, Li, C and H atoms.)



Figure S11. XPS of the Li metal and NCM811 in optimized electrolyte.



Figure S12. XPS of the Li metal and NCM811 in the controlled electrolyte



We also perform Electrochemical Impedance Spectroscopy (EIS) on the Li||Li@Cu symmetric cell. Prior to test, 3 mAh cm⁻² Li was deposited on Cu foil. Then, the Li||Li@Cu symmetric cell was cycled at 0.5mA cm⁻² with a fixed capacity of 0.5mAh cm⁻². **Figure S13** shows the EIS of Li||Li@Cu symmetric cell over cycles. The symmetric cell shows a high initial interface resistance of 101 Ohm, which was then reduced to 19 Ohm after cycling for 20 h. After 60 times, the interface resistance only slightly increases. The result indicates the high stability of the solid electrolyte interphase formed with our electrolyte.



Figure S14. Morphology and structural Characterization of NCM811cathode after cycles; a,b) SEM images of NCM811 cathode after cycling for 50 times in optimized electrolyte; c) HRTEM of the pristine NCM811 cathode; d) HRTEM of NCM811cathode after 50 cycles in the optimized electrolyte; e) HRTEM of NCM811 cathode after 400 cycles in the optimized electrolyte; f) HRTEM of NCM811 cathode after 50 cycles in the controlled electrolyte.

We also studied the microstructure by both high-resolution transmission Electron Microscope (HRTEM) and SEM on cycled NCM811 cathodes. The SEM images in **Figures S11a** and **S11b** show that the secondary particles of NCM811 remain intact in the optimized electrolyte after 50 cycles, whereas the NCM811 secondary particles in the control electrolyte show clear cracks after 50 cycles (**Figure S12**). **Figure S11c** shows the HRTEM images of the pristine NCM811 cathode, where the layered structure of NCM811 is observed in both the marginal surface and the bulk phase. After 50 cycles in the optimized electrolyte, both the marginal surface and the bulk phase of the NCM811 cathode remain as layered structures (**Figure S11d**); even after 400 cycles the bulk phase of NCM811 remains layered, while some rock-like structures are observed on the marginal surface after 400 cycles. In comparison, HRTEM on the NCM811 in the control electrolyte after 50 cycles (**Figure S11e**) shows disordered rock-like phases are observed on the marginal surface. These images confirm that the optimized electrolyte can stabilize the structure of an NCM811 cathode.



Figure S15. SEM images of NCM811 after 50 cycles in the controlled electrolyte.



Figure S16. Differential scanning calorimetry of NCM811 after charging to 4.5V.

Differential scanning calorimetry (DSC) was carried out on the NCM811 cathode after charging to 4.5 V. The exothermic peak of the NCM811 cathode shifts from 223 ^{o}C in the control electrolyte to 236 ^{o}C with less heat generation in the optimized electrolyte, again indicating that the optimized electrolyte can enhance the thermal stability of the NCM811 cathode.

No.	Strategy	Cathode	Electrolyte	Anode	Li excess	Cycle life	Retenti	Refer.
1	MOF separator	LTO	Ether	Thick Li	Large excess	2000	95%	1
2	Alloy Li surface	LTO	Ether	Thick Li	Large excess	1500	90%	2
3	LiPS ₄ SEI Layer	LTO	Ether	Thick Li	Large excess	400	89%	3
4	Cu flower anode	LTO	Ether	20mAh cm ⁻² Li	~6000% excess	1500	73%	4
5	Li ₂ S SEI layer	LTO	Ether	10mAh cm ⁻² Li	1000% excess	900	90%	5
	Li ₂ S SEI layer	LFP	Ether	10mAh cm ⁻² Li	400% Excess	150	80%	5
6	Upright Li anode	LTO	Ether	Thick Li	Large excess	2000	88%	6
7	Li@ 3D Al ₂ O ₃	LTO	Ether	Thick Li	Large Excess	1200	86%	7
	Li@Al2O3	LFP	Ether	Thick Li	Large Excess	200	93.6%	7
8	Li@ CNT/POF	LFP	Ether	10mAh Li	770% Excess	100	80.1%	8
9	MOF electrolyte	LFP	MOF electrolyte	Thick Li	Large Excess	2000	75%	9
10	Thiourea additives	LFP	Ether	Thick Li	Large Excess	650	90%	10
11	Polyurea thin film	LFP	ester	Thick Li	Large Excess	200	92%	11
12	Li@LIGHS@ Cu foil	LFP	Ether	10mAh Li	500% excess	250	90%	12
13	BN coating	LFP	Solid state electrolyte	Thick Li	Large Excess	500	96.6%	13
14	Carbon interlayer	LFP	Ether	Thick Li	Large Excess	800	80%	14
15	High temperature	LFP	Ether	Thick Li	Large Excess	100	>95%	15
16	Fluorinated ether	NCM811	Ether	10mAh cm ⁻² Li	667% Excess	300	80%	16
17	Fluorinated electrolyte	NCM811	ester	Thin Li	100% Excess	120	>97%	17
18	Ternary salt Electrolyte	LFP	Ether	0.5 excess Li	50% Excess	100	83%	18
19	Dual salt electrolyte	NCM111	Ether	Thick Li	Large Excess	300	80%	19
20	Fluorinated ether	NCM811	Ether	10mAh cm ⁻²	200% excess	150	80%	20
	Fluorinated ether	NCM811	Ether	0mAh cm ⁻²	No excess	70	77%	20
21	Fluorinated Ether	NCM622	Ether	10mAh cm ⁻²	260% excess	200	86%	21
22	Li graphene composite	LFP	Ether	10mAh cm ⁻²	500% excess	100	80%	22
23	Fluorinated	NCM622	Ether	10mAh cm ⁻²	270%	200	86%	30
24	Fluorinated	NCM811	Ether	10mAh cm ⁻²	245%	155	80%	31
25	Dual salt	NCM811	carbonate	0	No excess	90	80%	32
23	Optimized electrolyte	NCM811	carbonate	0.8mAh cm ⁻²	100% excess	90	87%	This work

Table S1. Performance of Li metal full cells selected from high impact journals.

Optimized	NCM811	carbonate	0mAh cm ⁻²	No excess	60	50%	This
electrolyte							work

	LFP G	LTO Li	LFP Li	NCM811 Li	NCM811 Li	NCM811 Cu
Cathode	LFP	LTO	LFP	NCM811	NCM811	NCM811
Loading	4 mg cm ⁻²	4 mg cm ⁻²	4 mg cm ⁻²	4mg cm ⁻²	4mg cm ⁻²	4mg cm ⁻²
Working Voltage	3.4 V	1.5 V	3.4 V	3.7 V	3.7 V	3.7 V
Specific	170	170	170	210	210	210
capacity	mAh g ⁻¹	mAh g ⁻¹	mAh g ⁻¹	mAh g ⁻¹	mAh g ⁻¹	mAh g ⁻¹
Anode	graphite	Li	Li	Li	Li	Li
N/P ratio	1.1	10	10	10	1	0
Specific	370	3860	3860	3860	3860	3860
capacity	mAh g ⁻¹	mAh g ⁻¹	mAh g ⁻¹	mAh g ⁻¹	mAh g ⁻¹	mAh g ⁻¹
Anode	1.8	1.8	1.8	2.2	0.22	0
loading	mg cm ⁻²	mg cm ⁻²	mg cm ⁻²	mg cm ⁻²	mg cm ⁻²	mg cm ⁻²
Energy	398	176	398	501	737	840
Density	Wh kg ⁻¹	Wh kg ⁻¹	Wh kg ⁻¹	Wh kg ⁻¹	Wh kg ⁻¹	Wh kg ⁻¹
Energy density of full cell based on total weight	199 Wh kg ⁻¹	88 Wh kg ⁻¹	199 Wh kg ⁻¹	250.5 Wh kg ⁻¹	368.5 Wh kg ⁻¹	420 Wh kg ⁻¹

Table S2: Rough estimation of the energy density of Li metal batteries.

PS: We assume that the cathode loading of the full cell is the same. The weight of electrodes accounts for 50% of the total weight of the full cells.

Table S2 shows the energy density of Li batteries calculated from the weight of cathode and anode. It can be found that when the Li metal anode is ten-fold excess, the advantage of the high energy density of Li metal no longer exists; the energy density of LTO||Li metal batteries with a more than tenfold Li excess is even inferior to commercialized Li ion batteries. Hence, a high energy density cathode with very limited Li metal in the anode is critical to achieve high-energy-density Li metal full cells.

No.	Strategy	Electrolyte	Li utilization ratio	Coulombic efficiency	Refer.
1	Optimized electrolyte	Ether	10%	99.5%	23
2	LiNO ₃ TEP	Ester	10%	97%	24
3	Nano diamond	Ester	10%	96%	25
4	Nonpolar alkines	ether	20%	97%	26
5	Fluorinated ether	ether	20%	99.5%	22
6	Optimized electrolyte	ester	10%	98.7%	
7	Ternary salt electrolyte	ester	25%	99.4%	18
8	LiNO3 additives	ester	5%	98.1%	27
9	Montmorillonite additives	ether	25%	98.3%	28
10	Controlled electrolyte	Ester	10%	71.9%	This work
	Optimized electrolyte	Ester	10%	99.3%	
	Optimized electrolyte	Ester	25%	99.6%	

Table S3. Comparison of the Coulombic Efficiency measured by the method proposed
by Zhang <i>et al.</i> ^[22]

Table S4. The calculated HOMO orbital energy, LUMO orbital energy, and LUMO-

HOMO gap (in eV) for various molecules.

Molecule	HOMO (eV)	LUMO (eV)	LUMO-HOMO

			(eV)
LiBOB	-10.23	-2.83	7.40
NaPF ₆	-12.68	-2.45	10.23
LiTFSI	-10.77	-2.36	8.41
LiPF ₆	-13.28	-2.15	11.13
LiNO ₃	-9.89	-2.08	7.81
[PP13][TFSI]	-9.47	-1.47	7.99
FEC	-10.93	-0.8	10.13
PC	-10.36	-0.78	9.58
EC	-10.53	-0.74	9.79
TEP	-9.93	-0.65	9.28
DEC	-10.17	-0.45	9.72

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