

Solubilized LiNO₃ with CsF of Cationic Size Effect to Protect Lithium Metal Anode and Prevent the Dendrite in Carbonate Electrolyte

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Experimental section:

1.1 Preparation of electrolyte:

The basic electrolyte (BE) was 1 M lithium hexafluorophosphate (LiPF₆) in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, v/v). 0.5 wt% lithium nitrate (LiNO₃) and 0.5 wt% cesium fluoride (CsF) as additives mixed in basic ester-based electrolyte promoting dissolution mutually in an Ar-filled glove box (O₂<0.1 ppm, H₂O<0.1 ppm).

1.2 Preparation of cathodes:

Polyacrylonitrile (PAN) and sulfur were mixed then thermally polymerized at the temperature 330 °C in atmosphere of Ar, and the black powder of sulfurized polyacrylonitrile (SPAN) was obtained (sulfur by weight: 45 wt%).

The SPAN was mixed with super P and poly(vinylidene fluoride) (PVDF) solution (5 wt% PVDF in NMP) at a mass ratio of 8:1:1, some amount of N-methylpyrrolidone (NMP) was added to disperse the mixture for the homogeneous slurry. The slurry was coated onto carbon coated aluminum foil, vacuum-dried at 60°C for 24 h and cut into electrode with a diameter of 12 mm. The areal mass loadings of the electrodes are 4.8 - 5.0 mg/cm². The high loading LiFePO₄ (LFP) and

$\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523) cathodes were bought from Guangdong Canrd New Energy Technology Co.,Ltd., and the weight ratio of LiFePO_4 and $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ were 10.2 mg/cm^2 and $8 - 9 \text{ mg/cm}^2$ respectively.

1.3 Cell Assembling:

The cells were assembled for Lithium metal foil ($450\mu\text{m}$, 15.6 mm) and polypropylene microporous film (Celgard 2400, 19 mm) were used as anodes and separator in 2025 type button cells respectively. $\text{Li} \parallel \text{Li}$, $\text{Li} \parallel \text{Cu}$ and full batteries were injected $60 \mu\text{L}$ electrolyte and assembled for electrochemical tests in an argon-filled glove box. Li-Li symmetrical battery cycled with current density 1 mA/cm^2 for 1mAh/cm^2 . $\text{Li} \parallel \text{SPAN}$ battery cycled at a 0.1 C and 1 C ($1\text{C} = 600 \text{ mA/mg}$) with a cutoff voltage of $1 - 3 \text{ V}$; $\text{Li} \parallel \text{LFP}$ battery cycled at a 0.1 C and 1 C ($1\text{C} = 150 \text{ mA/mg}$) with a cutoff voltage of $2.5 - 4.0 \text{ V}$; $\text{Li} \parallel \text{NCM523}$ battery cycled at a 0.1 C and 1 C ($1\text{C} = 165 \text{ mA/mg}$) with a cutoff voltage of $3.0 - 4.4 \text{ V}$.

1.4 Characterizations and tests:

The galvanostatic charge/discharge experiments and rate performance tests were carried out on a LAND CT2001A battery-testing system. EIS measurements with the frequency ranging from 0.1 Hz to 100 kHz , Chronoamperometry (CA) of lithium anode with an overpotential of -130 mV vs. Li^+/Li . Tafel polarization curves with a voltage range of -0.3 V to 0.3 V vs. Li^+/Li and linear sweep voltammetry (LSV) of $\text{Li} \parallel \text{Cu}$ battery with a voltage range of 0 V to 2.0 V , were conducted on CHI 660E electrochemical workstation. Cyclic voltammetry (CV) test was conducted on Solartron 1470E MutiStat instrument. The lithium deposition process was observed by In-situ optical microscopy observation (LIB MS) equipped with glassy carbon electrodes and Au electrodes (Beijing Scistar technology Co.,Ltd). The morphologies were observed by a field-emission scanning electron microscope (FESEM, SU8010, HITACHI) equipped with X-ray spectroscopy (EDX) for elemental analysis. X-ray photoelectron spectroscopy (XPS) data was collected through ESCALAB.

1.5 Computational methods

The Molecular Dynamics (MD) simulations of the electrolytes were carried out by the Gromacs (version 2020.6) program suite¹ with General Amber force

field(GAFF). The force field parameters of organic molecules were obtained by Sobtop program². The Restrained Electro Static Potential (RESP) charges^{3, 4} were based on DFT calculation by the ORCA program⁵ and wavefunction analysis by Multiwfn⁶. The solution systems were built through randomly placing 826 DEC, 1498 EC molecules and 200 LiPF₆, and then added 190 LiNO₃ and 86 CsF molecules into the corresponding systems, respectively. The initial simulation boxes of dimensions 100×100×100 Å³ packed with electrolyte components were constructed using the packmol program⁷. These structures were first relaxed by energy minimizing calculations and then undergo annealing from 0 to 298.15 K with the time step of 1 ps during 1ns to reach the equilibrium state. Velocity-rescale thermostat with a relaxation constant of 1 ps was used to control the temperature at 298.15 K. Parrinello-Rahman barostat with isothermal compressibility constant of 4.5×10⁻⁵ was used to control the pressure at 1.01325×10⁵ Pa. Periodic boundary conditions were applied in all directions. Particle-mesh Ewald (PME) method with a cut-off distance of 12 Å was applied to treat the electrostatic interactions and the van der Waals forces.

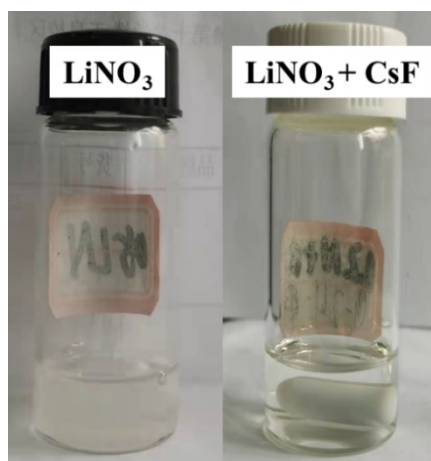


Fig. S1 Photo of LiNO₃ and LiNO₃ + CsF in carbonate electrolyte.

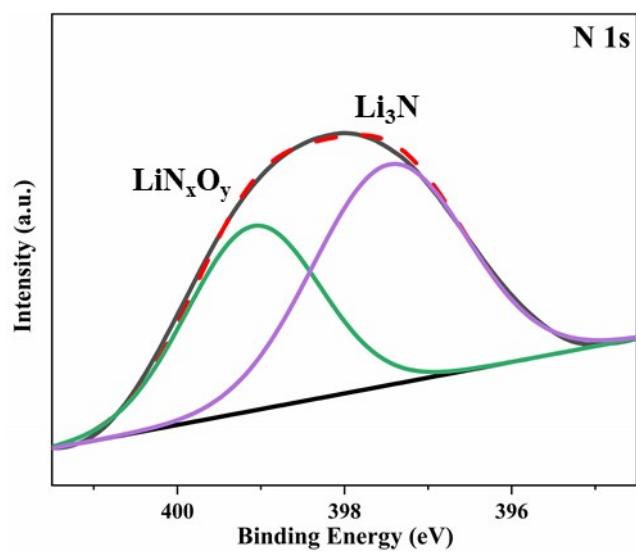


Fig. S2 XPS spectrum of the N 1s in the electrolyte with LiNO_3 and CsF additives after 5 cycles.

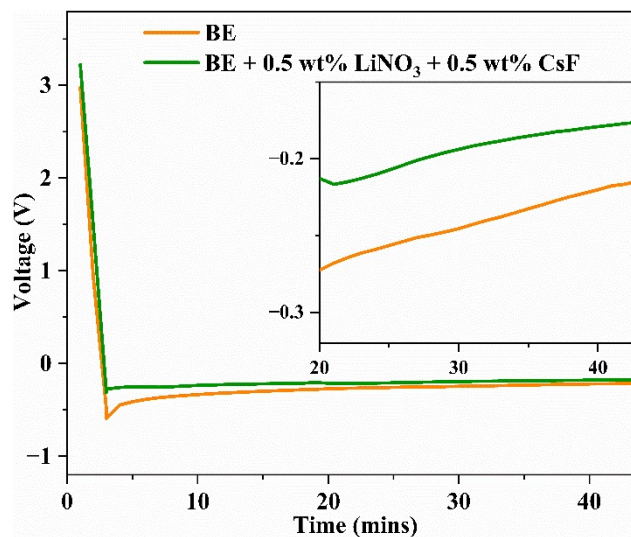


Fig. S3 Discharge voltage profiles of in-situ optical visualization Li || Cu cells during Li⁺ deposition on the Cu substrate with 12 mA/cm² in different electrolytes.

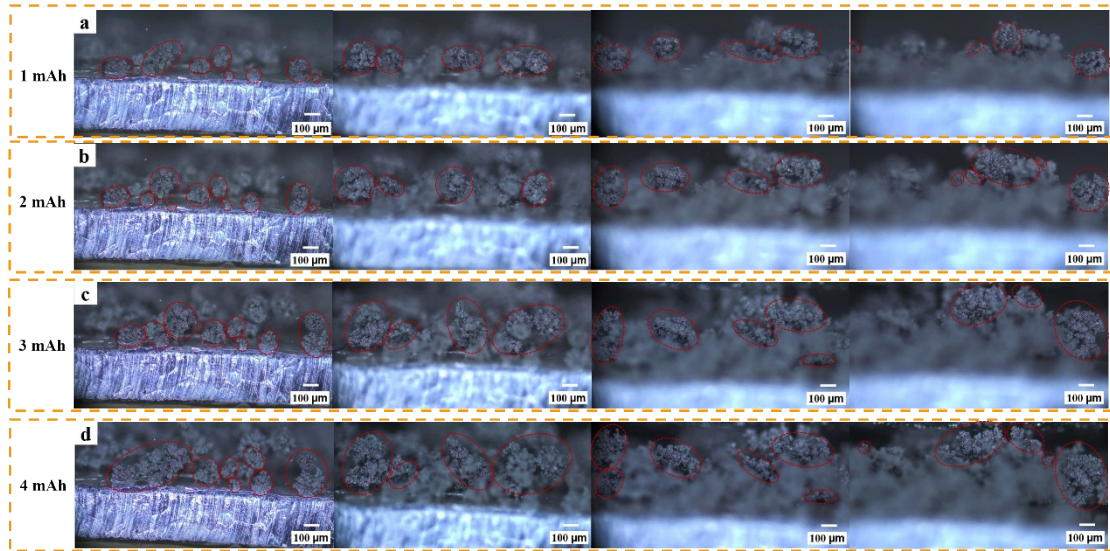


Fig. S4 In-situ optical visualization microscopy for the lithium metal symmetrical cell during deposition of Li⁺ with 12 mA/cm² in (a-d) electrolyte without additive;

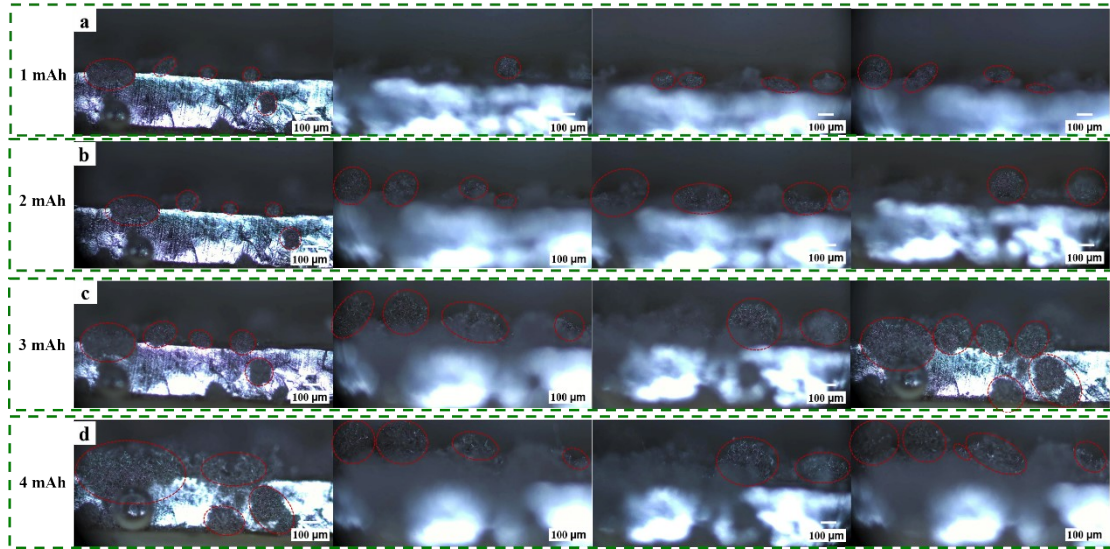


Fig. S5 In-situ optical visualization microscopy for the lithium metal symmetrical cell during deposition of Li⁺ with 12 mA/cm² in the (a-d) electrolyte with LiNO₃ and CsF additives.

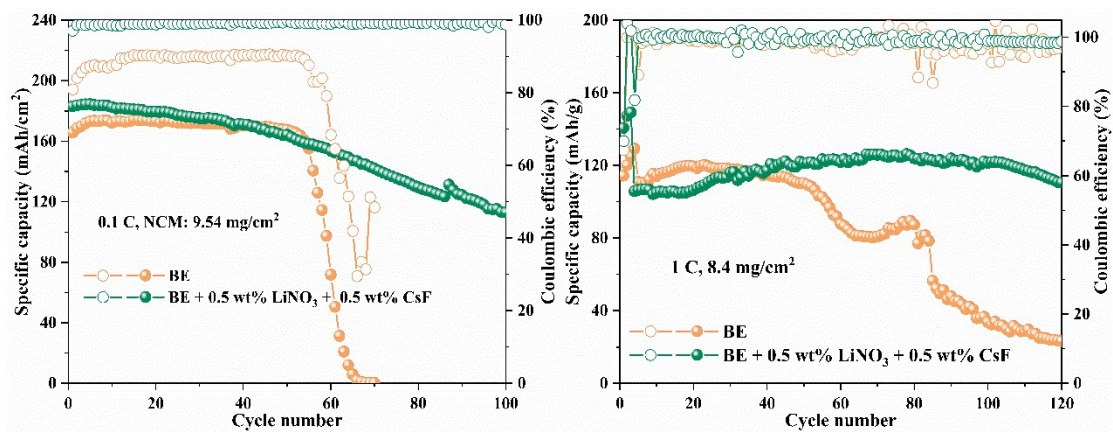


Fig. S6 (a) Cycling performances of the Li || LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ cells with 3.0 – 4.4 V cutoff voltage (a) at the rate of 0.1 C; (b) at the rate of 1 C.

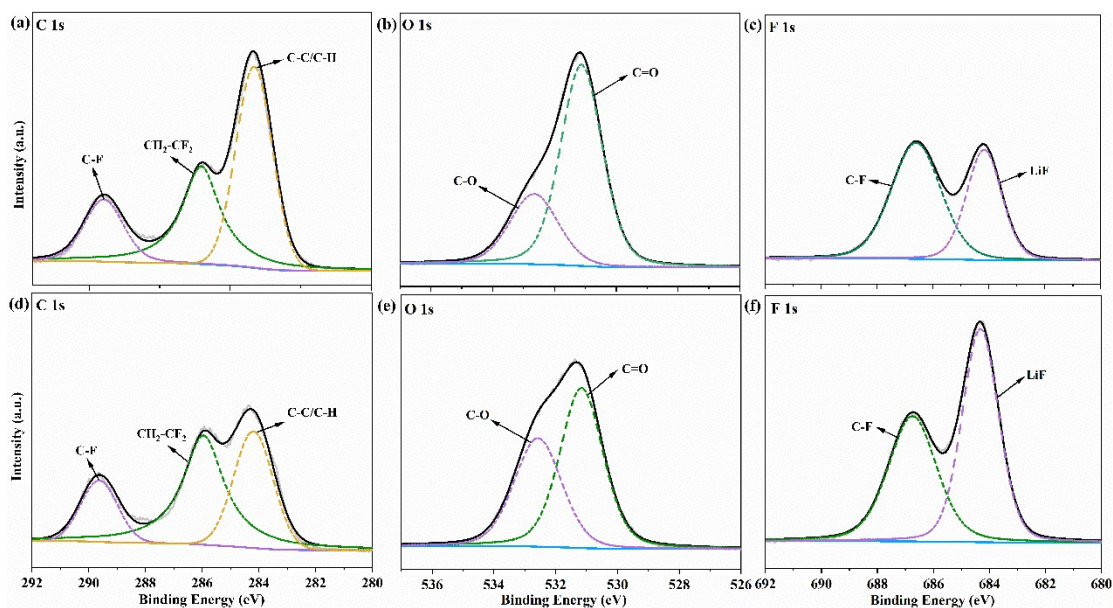


Fig. S7 C 1s, O 1s, and F 1s XPS spectra of the cycled SPAN cathode in (a-c) electrolyte without additive and (d-f) with LiNO_3 and CsF additives after 5 cycles at 0.1 C.

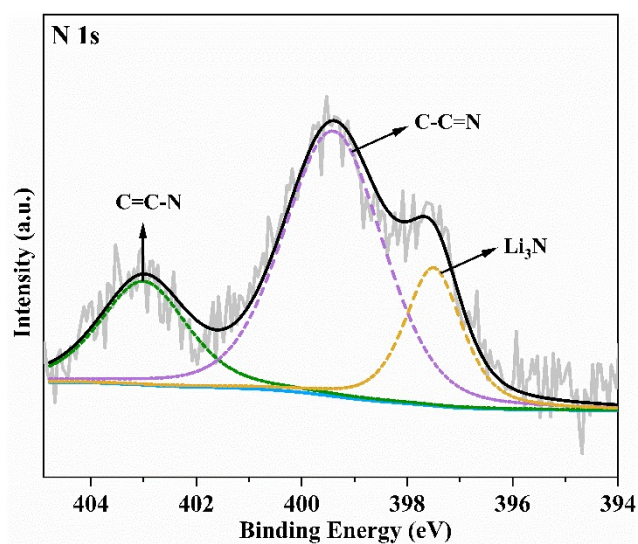


Fig. S8 N 1s XPS spectrum of the cycled SPAN cathode in the electrolyte with LiNO_3 and CsF additives after 5 cycles at 0.1 C.

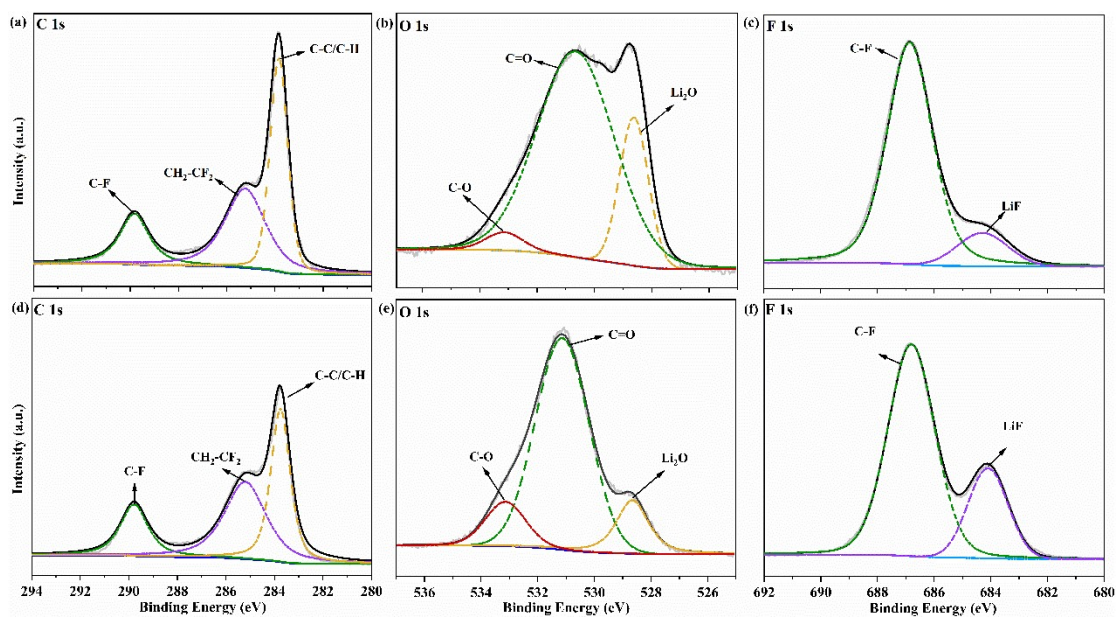


Fig. S9 C 1s, O 1s, and F 1s XPS spectra of the cycled NCM523 cathode in (a-c) electrolyte without additive and (d-f) with LiNO₃ and CsF additives after 5 cycles at 0.1 C.

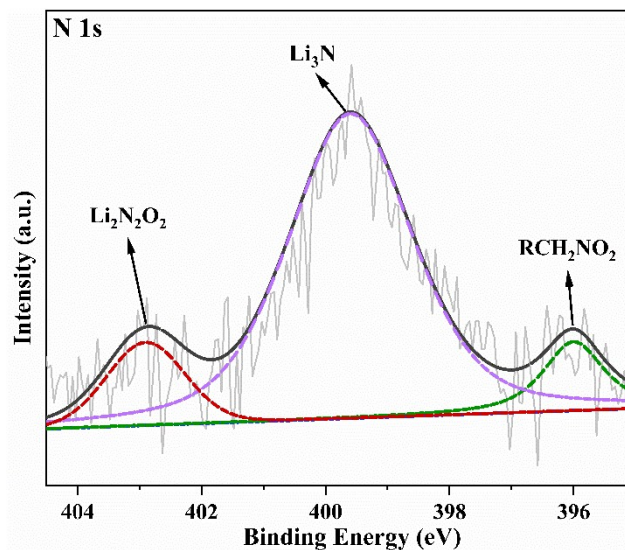


Fig. S10 N 1s XPS spectrum of the cycled NCM523 cathode in the electrolyte with LiNO₃ and CsF additives after 5 cycles at 0.1 C.

Table S1The comparison of dissolution results of LiNO₃ in the carbonate electrolyte with other literatures

Electrolyte	Solubilizer	LiNO ₃	Li Cu Coulombic Efficiency	Cycles	mA/cm ² , mAh/cm ²	Reference
1 M LiPF ₆ in EC/DEC (v/v, 1:1)	0.5 wt.% CsF	0.5 wt.%	98 %	200	1, 1	This work
1 M LiPF ₆ in EC/DEC (v/v, 1:1)	0.5 wt.% Sn(OTf) ₂	1 wt.%, 5 wt.%	96.7 % 98.4 %	80 300	1, 1 1, 1	8
1 M LiPF ₆ in EC/DEC (v/v, 1:1)	0.2 wt.% CuF ₂	1 wt.%	98.1 %	18	0.5, 0.5	9
1 M LiPF ₆ in EC/EMC (v/v, 1:1) + 2wt.% FEC	180 μL tetramethylurea in 1 mL electrolyte	20.7 mg	98.19%	10	1, 1	10
1 M LiTFSI in FEC/DMC (v/v, 1:4)	3.5 wt.% N-N-Dimethylacetamide	0.5 wt.%	98%	300	0.5, 0.5	11

Reference

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