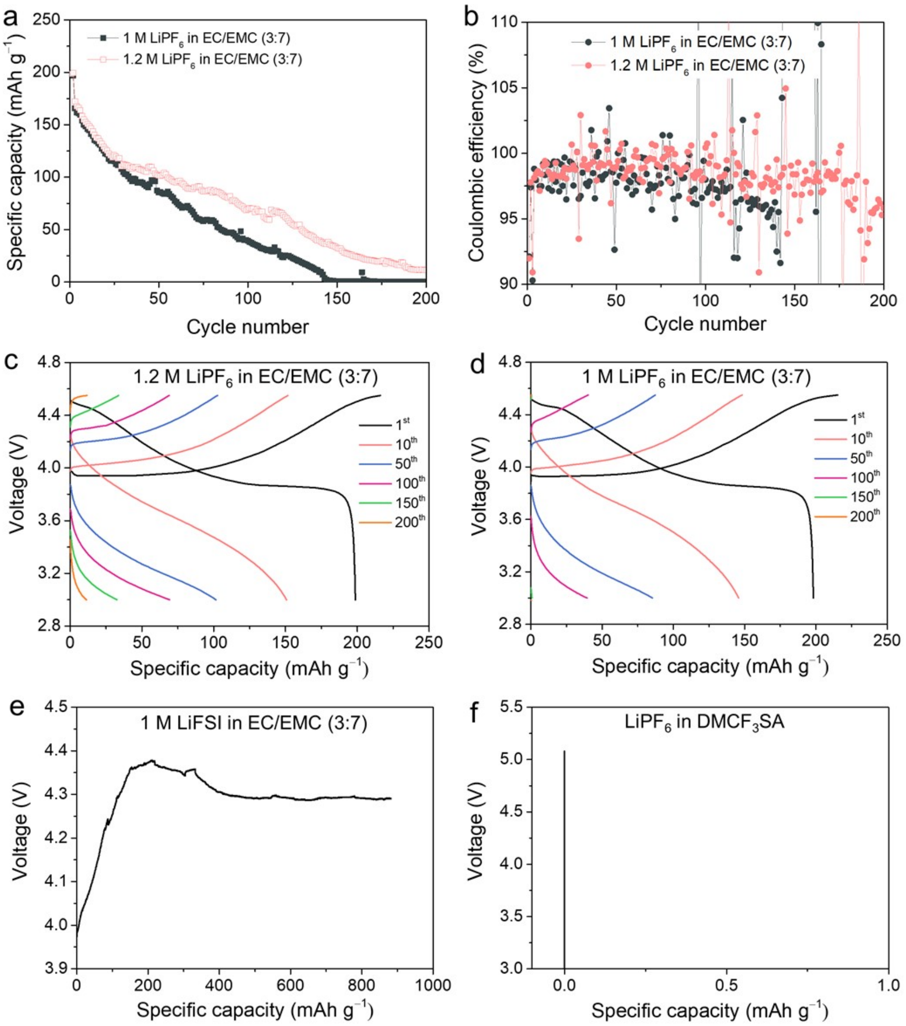
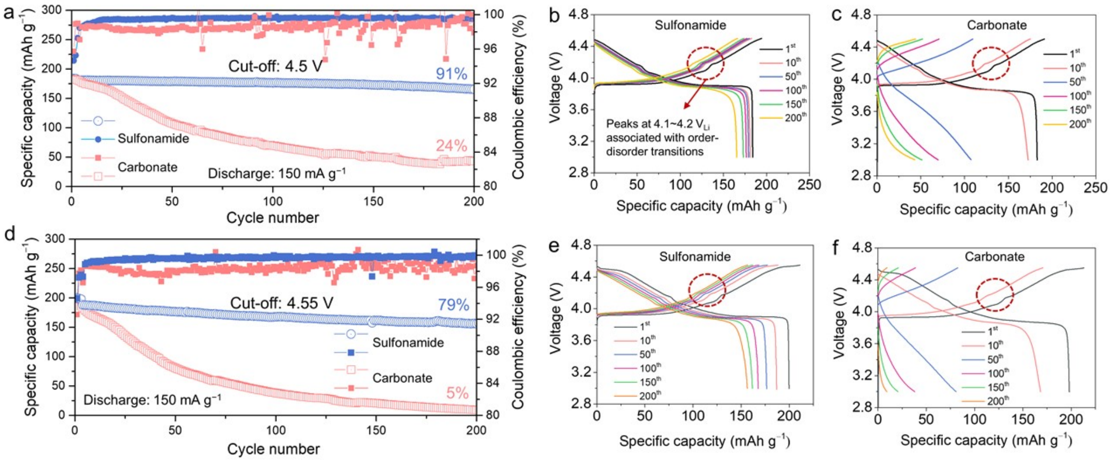


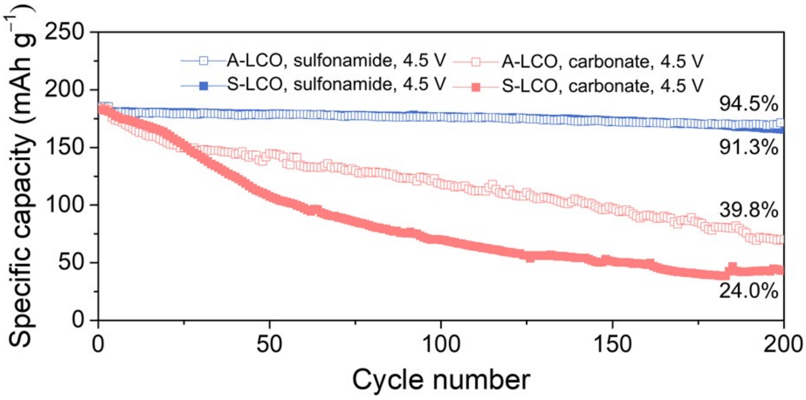
Supplementary Fig. 1 Electrochemical performance of the Li||A-LCO cells with different electrolytes. The specific capacities (a), Coulombic efficiencies (b), and corresponding voltage profiles (c, d) as a function of cycle number with 1 M $LiPF_6$ in EC/EMC (3:7 wt) and 1.2 M $LiPF_6$ in EC/EMC (3:7 wt) electrolytes. (e, f) Voltage profile of the Li||A-LCO cell with 1 M LiFSI in EC/EMC (3:7 wt) and $LiPF_6$ in $DMCF_3SA$ electrolytes, respectively.

As shown in (a~d), we compared the cycling performance of the LCO cathode using 1 M $LiPF_6$ in EC/EMC (3:7 wt) and 1.2 M $LiPF_6$ in EC/EMC (3:7 wt) electrolytes. Better capacity retention and slightly higher CE were noted for 1.2 M $LiPF_6$ in EC/EMC (3:7 wt) electrolyte.

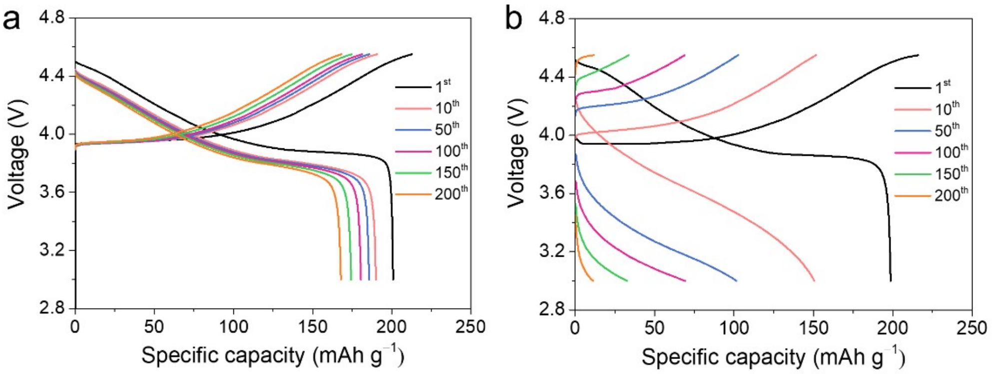
We also conducted further experiments trying to fix the salt in both carbonate and sulfonamide solvents. If 1 M LiFSI salt was used in carbonate, yielding 1 M LiFSI in EC/EMC (3:7 wt) electrolyte, Al corrosion by LiFSI salt cannot be avoided (e). $LiPF_6$-sulfonamide combination does not have Li-ion conductivity because $LiPF_6$ cannot be dissolved in $DMCF_3SA$ (f).



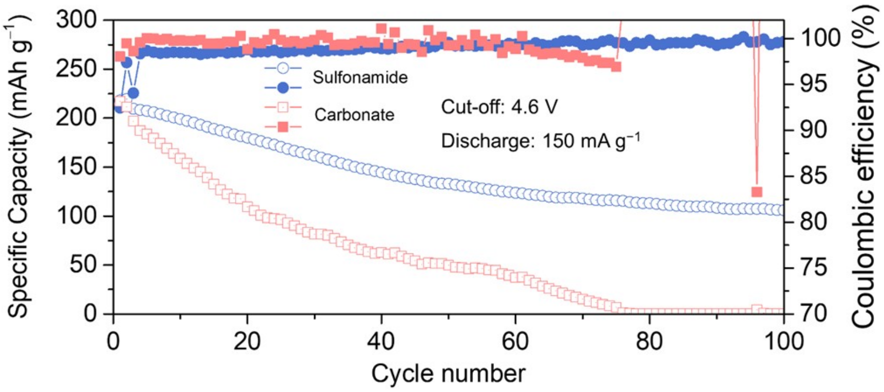
Supplementary Fig. 2 Electrochemical performance of Li||S-LCO cells with different electrolytes. Cycling performance and corresponding voltage profiles with upper cut-off voltages of 4.5 V_{Li} (a, b, c) and 4.55 V_{Li} (d, e, f), respectively. The current densities for charging and discharging were 50 mA g^{-1} and 150 mA g^{-1}, respectively. 10 mA g^{-1} charging-discharging was used for the initial 1^{st} cycle. Minor peaks at 4.1~4.2 V_{Li} in voltage profiles (b, c, e, f) were indicated by red circles, which are associated with order-disorder transitions of undoped LCO materials.



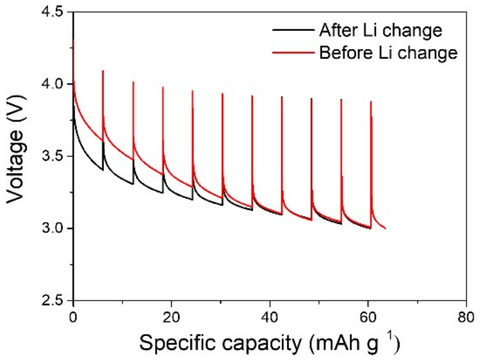
Supplementary Fig. 3 Cycling performance of the Li||A-LCO and Li||S-LCO cells with an upper cut-off voltage of 4.5 V_{Li} using the sulfonamide-based and carbonate-based electrolytes. A-LCO is a commercial LCO from BTR, China with doping and coating. S-LCO has no doping or coating purchased from Sigma Aldrich.



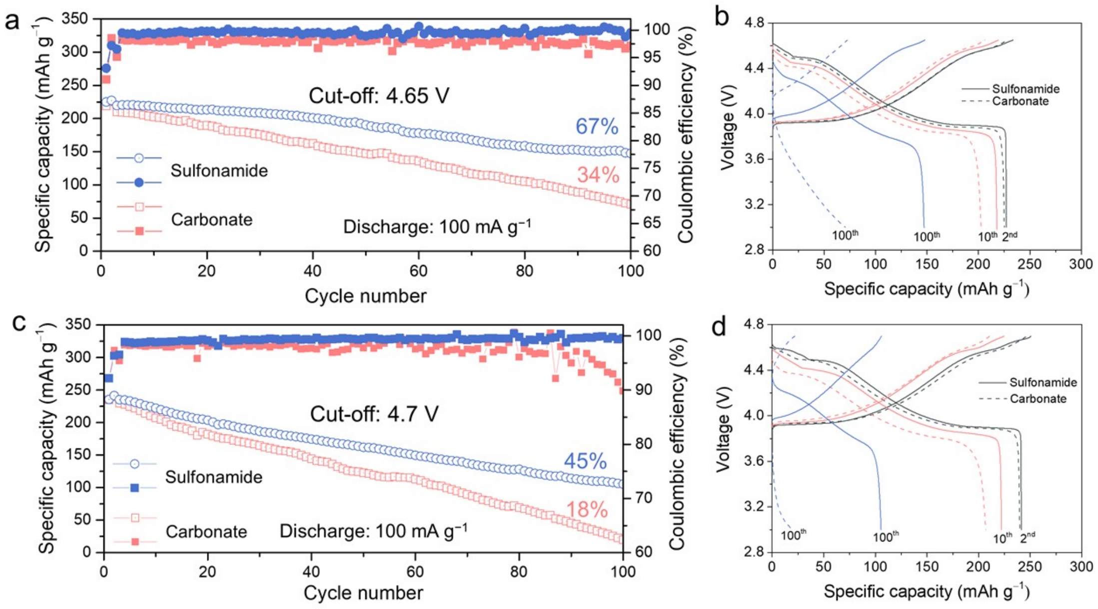
Supplementary Fig. 4 Voltage profiles of the Li||A-LCO cells with the sulfonamide-based (a) and carbonate-based (b) electrolytes. The cells were cycled at an upper cut-off voltage of 4.55 V_{Li} and charging/discharging rates of 50/150 mA g^{-1}. 10 mA g^{-1} charging-discharging was used for the initial 1st cycle. The amounts of the sulfonamide-based and carbonate-based electrolytes were 15 μL and 50 μL per cell, respectively. 350 μm Li foils were used.



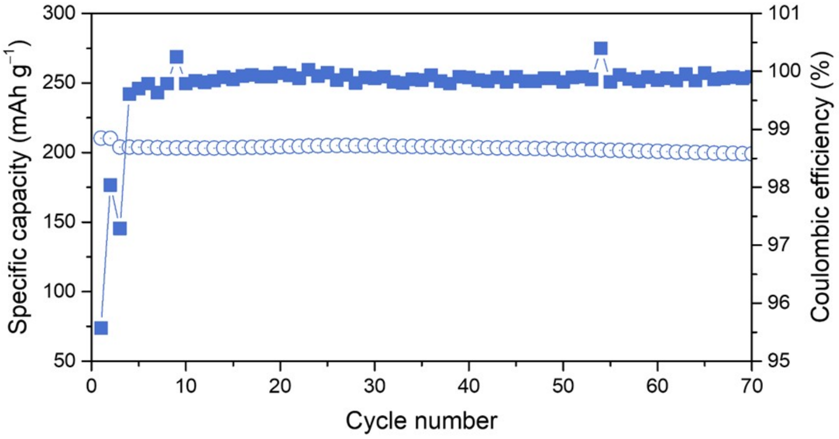
Supplementary Fig. 5 Cycling performance of the Li||A-LCO cells with different electrolytes under an upper cut-off voltage of 4.6 V_{Li}. The current densities for charging and discharging were 50 mA g^{-1} and 150 mA g^{-1}, respectively. 10 mA g^{-1} charging-discharging was used for the initial two cycles.



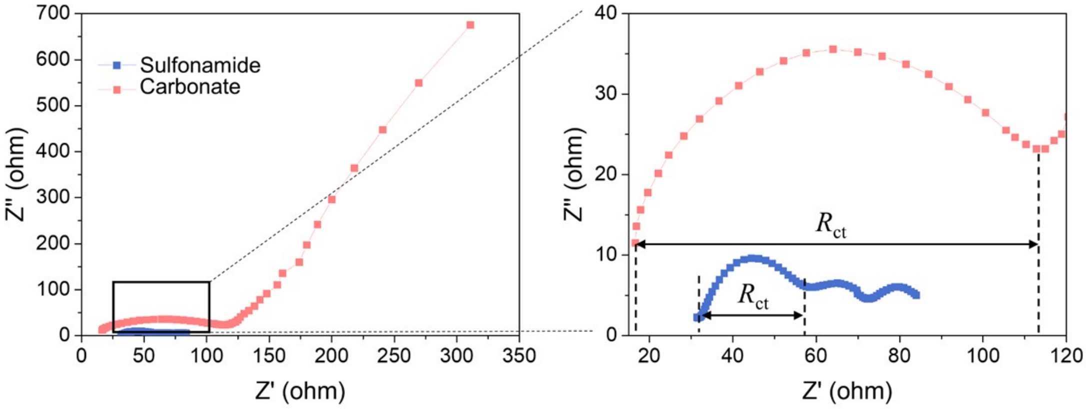
Supplementary Fig. 6 GITT plots of the Li||A-LCO cell with the carbonate electrolyte after 100 cycles (4.55 V_{Li} cut-off and 50/150 mA g^{-1} for charging/discharging) before and after changing a fresh Li metal and refilling with fresh electrolyte. The almost identical plots indicate that with abundant Li metal anode (350 μm Li foil), electrolyte (50 μL) and a slow charging rate of 50 mA g^{-1} (~0.63 mA cm^{-2}), the capacity decay and overpotential growth are mostly from the cathode side. The degradation of Li metal anode has almost no influence on the performance, which makes the comparison with the sulfonamide-based electrolyte sufficiently fair.



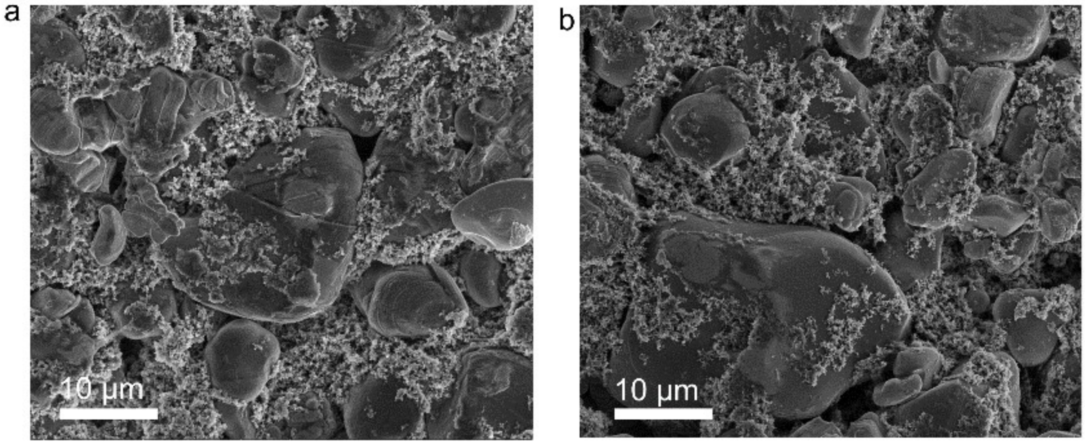
Supplementary Fig. 7 Electrochemical performance of Li||T-LCO cells with different electrolytes. Cycling performance and corresponding voltage profiles with upper cut-off voltages of 4.65 V_{Li} (a, b) and 4.7 V_{Li} (c, d), respectively. The current densities for charging and discharging were 50 mA g^{-1} and 100 mA g^{-1}, respectively. 10 mA g^{-1} charging-discharging was used for the first 2 cycles. The amounts of the sulfonamide-based and carbonate-based electrolytes were 15 μL and 50 μL per cell. respectively. 350 μm Li foils were used.



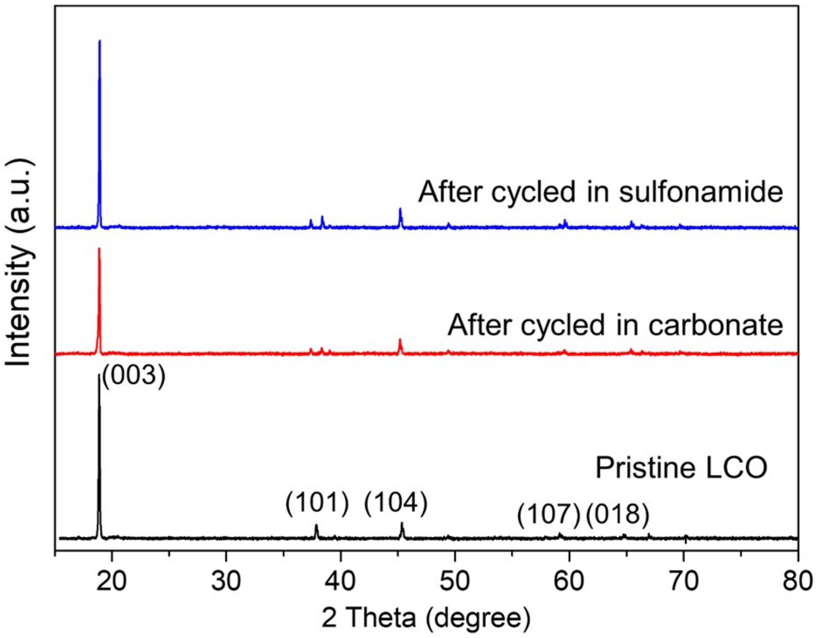
Supplementary Fig. 8 Electrochemical performance of Li||T-LCO cells with the sulfonamide-based electrolyte with an upper cut-off voltage of 4.55 V_{Li} and discharging rate of 100 mA g^{-1} at 45 °C (20 mA g^{-1} charging/discharging for the first two cycles). The capacity retention is 97.6% and the average CE is 99.88% calculated from the 3rd cycle to the 70th cycle.



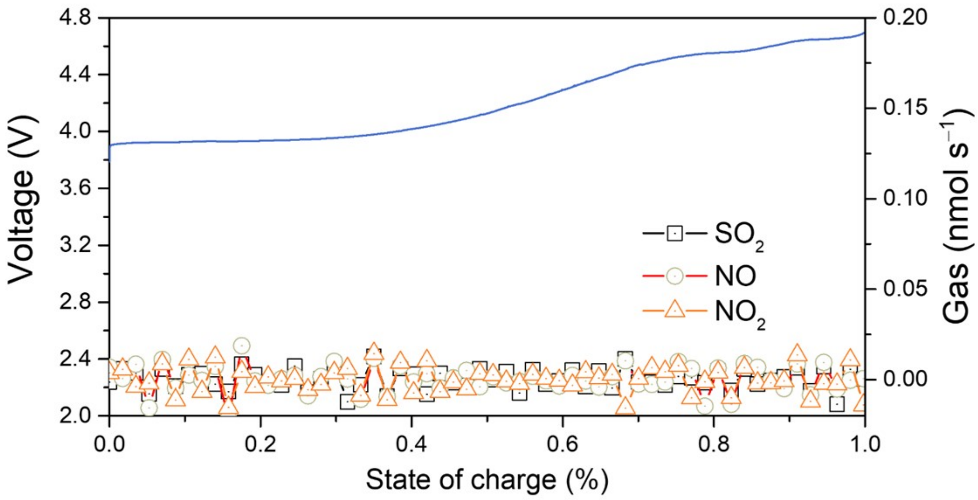
Supplementary Fig. 9 EIS plots of the Li||A-LCO cells after 200 cycles in different electrolytes with an upper cut-off voltage of 4.55 V_{Li}. The enlarged high-frequency area on the right side clearly indicates a much smaller charge transfer resistance (R_{ct}) of the cell cycled in the sulfonamide-based electrolyte than the one cycled in the carbonate-based electrolyte.



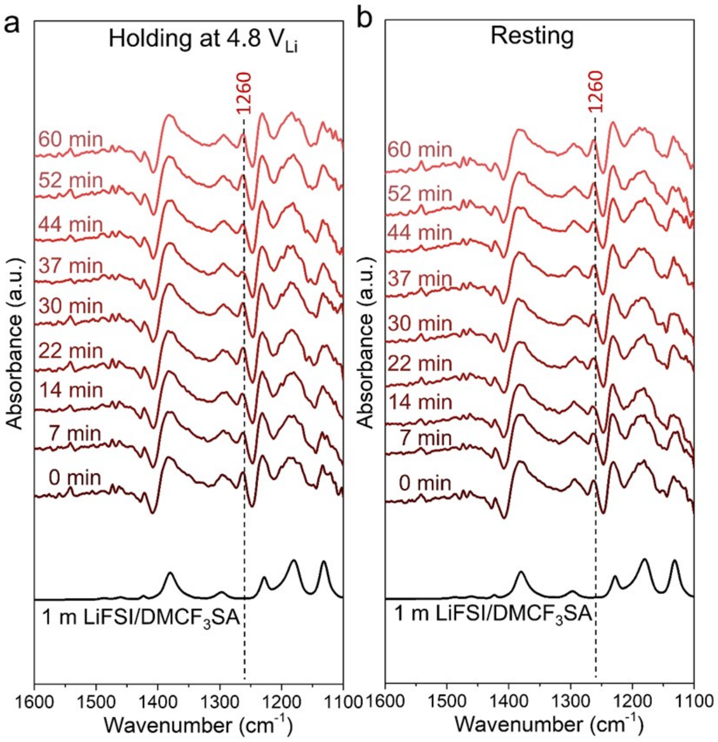
Supplementary Fig. 10 Low-magnification SEM images of the A-LCO cathodes after 200 cycles in the carbonate-based (a) and sulfonamide-based (b) electrolytes at 4.55 V_{Li} cut-off voltage.



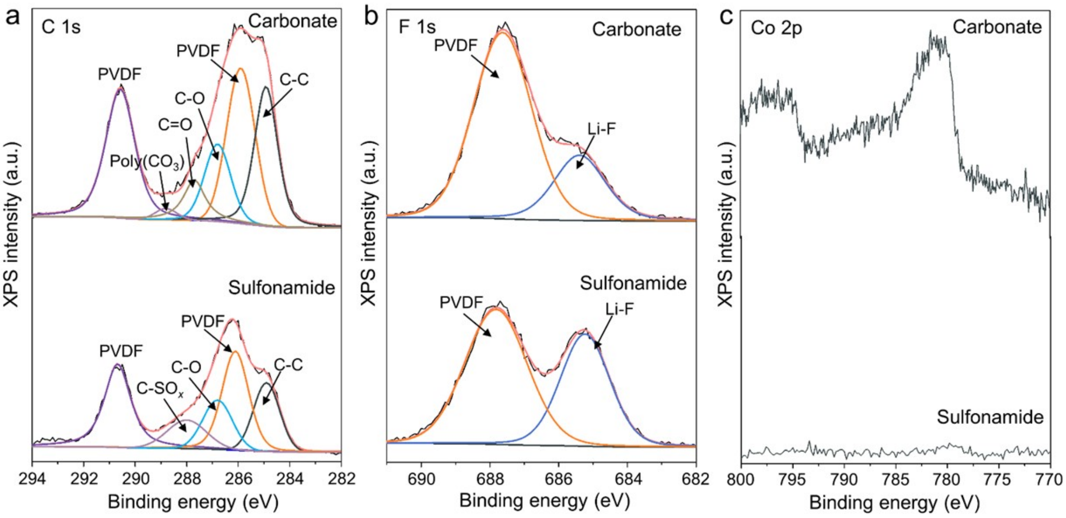
Supplementary Fig. 11 XRD patterns of pristine A-LCO cathodes after cycling in different electrolytes with an upper cut-off voltage of 4.55 V_{Li}.



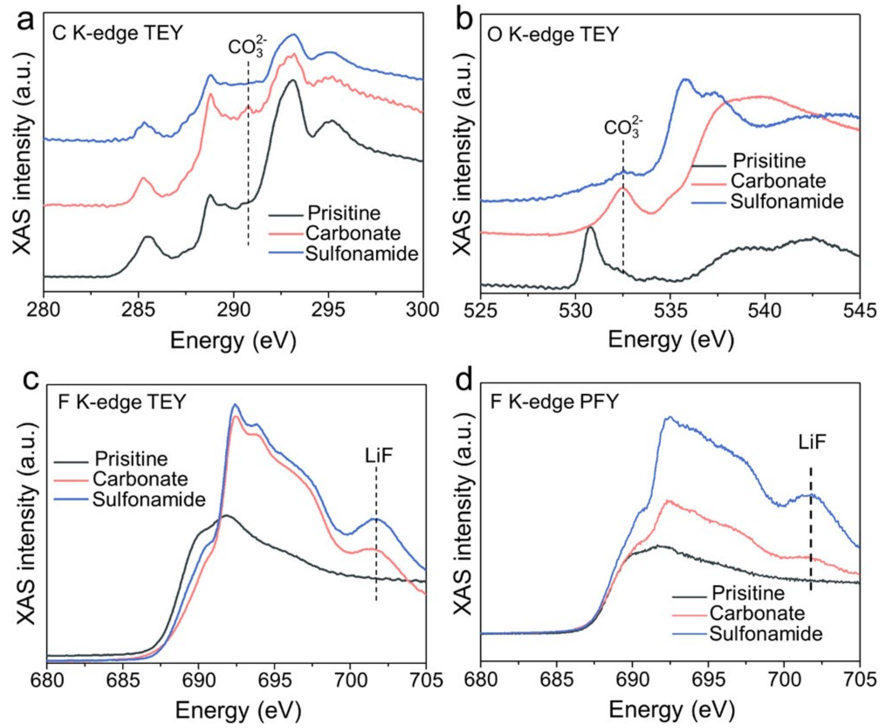
Supplementary Fig. 12 *In-situ* DEMS analysis of the SO$_2$, NO, and NO$_2$ evolution during first charging the A-LCO to 4.7 V$_{Li}$ in the sulfonamide-based electrolyte.



Supplementary Fig. 13 *In-situ* FT-IR spectra on LCO surfaces in the sulfonamide-based electrolyte at regular intervals during holding the potential at 4.8 V_{Li} (a) (after charging to 4.8 V_{Li} in Fig. 4c, d) and subsequent resting at open circuit potential (b).

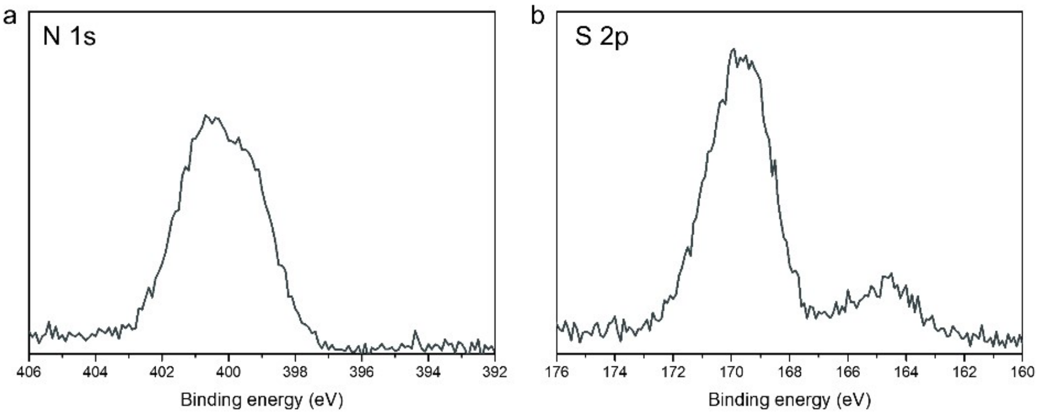


Supplementary Fig. 14 XPS analysis of the CEIs retrieved from the Li||A-LCO cells at 4.55 V_{Li} for 100 cycles for C 1s (a), F 1s (b), and Co 2p (c).

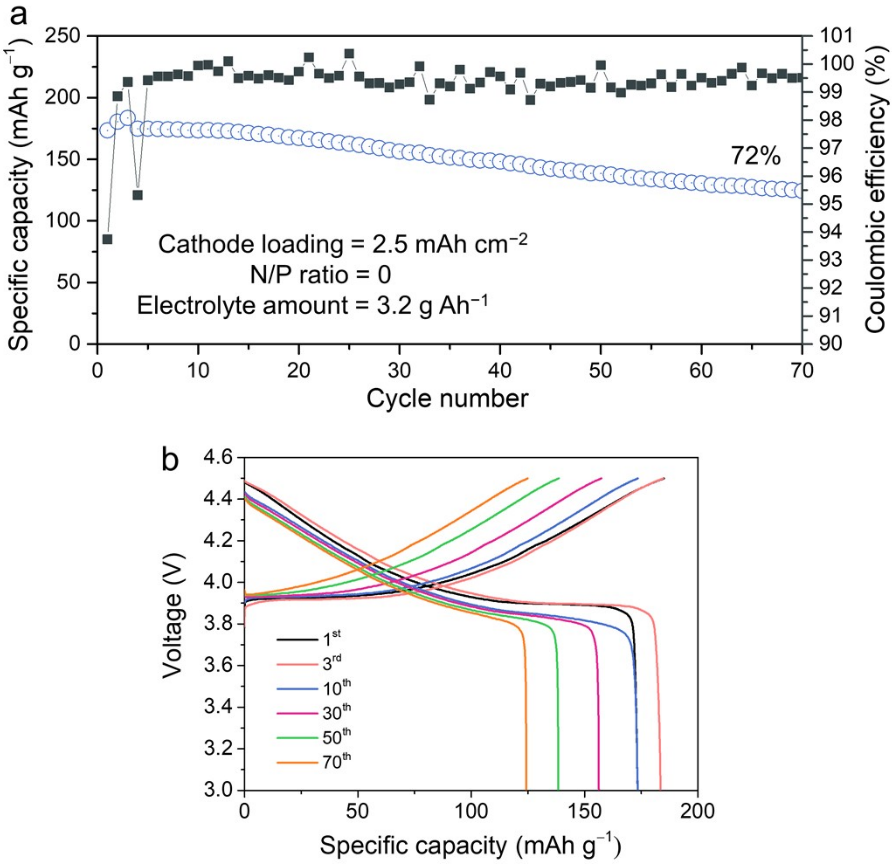


Supplementary Fig. 15 C K-edge (a), O K-edge (b), and F K-edge (c) sXAS TEY spectra and F K-edge PFY spectra (d) of the pristine and cycled A-LCO cathodes in different electrolytes with an upper cut-off voltage of 4.55 V_{Li}.

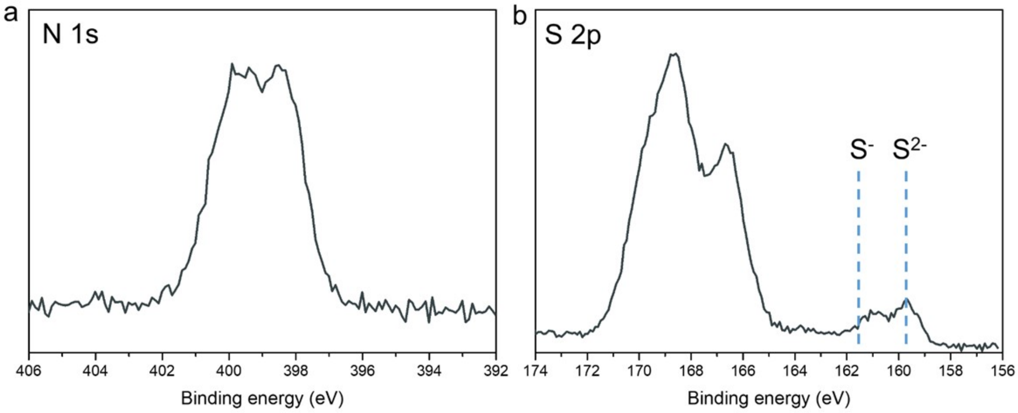
The evolution of CEIs formed on A-LCO cathode surfaces in different electrolytes was examined by XPS and sXAS. XPS and the total electron yield (TEY) mode of sXAS are sensitive to the surface (~5 nm) and the partial fluorescence yield (PFY) mode of sXAS can collect information from the bulk (~100 nm). Such a combination will provide more information on the CEI structure and underneath.



Supplementary Fig. 16 XPS spectra of the CEI formed on the A-LCO cathodes after 100 cycles in the sulfonamide-based electrolyte at an upper cut-off voltage of 4.55 V_{Li}. (a) N 1s and (b) S 2p.



Supplementary Fig. 17 Cycling performance (a) and corresponding voltage profiles (b) of an anode-free A-LCO||Cu cell in 1 m LiFSI/DMCF$_3$SA electrolyte with a bare Cu as the anode. 2.5 mAh cm^{-2} LCO cathode and lean electrolyte (electrolyte/capacity ratio, E/C ratio ~3.2 g Ah^{-1}) were used with C/5 charging and C/2 discharging (C/10 charging-discharging for the initial 3 cycles) between 3~4.5 V at room temperature.



Supplementary Fig. 18 XPS spectra of the SEIs on Li metal anode retrieved from the Li||A-LCO cells after 100 cycles in different electrolytes with an upper cut-off voltage of 4.55 V_{Li}. (a) N 1s and (b) S 2p.

Supplementary Table 1 Comparison of our work with recent electrolyte works on high-voltage LCO

Composition	**Cathode side**				**Cyclability**	**Li-Anode**
	Cathode	**Cut-off voltage**	**Highest capacity**	**CE**		**CE (Li-Cu)***
1 m LiFSI/DMCF$_3$SA (our work）	**Commercial LCO (BTR, China and Targray. Co)**	**4.55 V$_{\text{Li}}$** **4.6 V$_{\text{Li}}$**	**200.8 mAh g^{-1}** **219.6 mAh g^{-1}**	**~99.84%** **~99.55%**	**89% (200 cycles)** **85% (100 cycles)**	**~99.7%**
1.2 M LiPF$_6$ in FEC/DMC/HFE (1:1:1 v)[1]	LCO (unspecified source)	4.5 V$_{\text{Li}}$	~184 mAh g^{-1}	——	83.6% (300 cycles)	~98%
LiFSI-1.0 DME-3 TTE (mol ratio)[2]	Commercial LCO (BTR, China)	4.5 V$_{\text{Li}}$	~184 mAh g^{-1}	~99.9%	92.9% (300 cycles)	——
poly (butyl vinyl ether-alt-maleic anhydride) based polymer electrolyte[3]	Commercial LCO (CATL, China)	4.45 V$_{\text{Li}}$	~181 mAh g^{-1}	——	96% (150 cycles)	——
FN + 1 M LiPF$_6$-EC/EMC/DEC[4]	Commercial LCO (Hunan Shanshan)	4.5 V$_{\text{Li}}$	~188 mAh g^{-1}	——	95.7% (120 cycles)	——
PPFPN+1 M LiPF$_6$-EC/DMC[5]	Commercial LCO (Hunan Shanshan)	4.5 V$_{\text{Li}}$	~185 mAh g^{-1}	——	90% (300 cycles)	——
ADN+THFPB+CHB+1 M LiPF$_6$+EC+EMC+DEC[6]	Commercial LCO (CATL, China)	4.45 V$_{\text{Li}}$	~174 mAh g^{-1}	——	77% (100 cycles)	——
0.4 M LiODFB +0.6 M LiPF$_6$-(TMTA–TFSI)/DMC[7]	Commercial LCO (Amperex Technology Co. China)	4.4 V$_{\text{Li}}$	~143 mAh g^{-1}	——	105% (90 cycles)	——

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Supplementary Table 2 Costs of the chemicals used for DMTMSA solvent synthesis

	Formula	**Role**	**Price**	**Vendor**
Dimethylamine	$(CH_3)_2NH$	Raw material	\$600/ton	Industry
Trifluoromethanesulfonyl chloride	CF_3SO_2Cl	Raw material	\$2,670,000/ton	Aaron Chemicals
Dichloromethane	CH_2Cl_2	Solvent	\$615/ton	Industry
Tetrahydrofuran	C_4H_8O	Solvent	\$1,700/ton	Industry
Triethylamine	$N(C_2H_5)_3$	Removing byproduct HCl	\$1,400/ton	Industry
LiFSI	$LiF_2NO_4S_2$	Salt	\$150,000/ton	Industry

The cost of carbonate-based electrolytes is around ~\$6,000/ton.