Supporting information for

Enhanced Cycling Stability of High-Voltage Lithium Metal Battery with Trifunctional Electrolyte Additive

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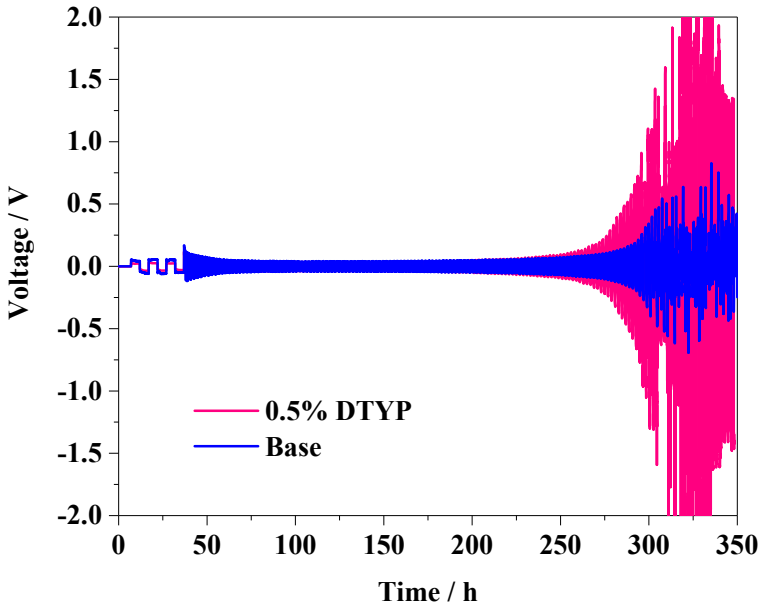

Fig. S1 Voltage profiles of the Li//Li symmetric cells during the stripping-plating test with a capacity of 0.7 mAh cm^{-2} at a current density of 0.14 mA cm^{-2} for the initial 3 cycles and at a current density of 0.7 mA cm^{-2} for subsequent cycles in base and 0.5% DTYP-containing electrolytes.

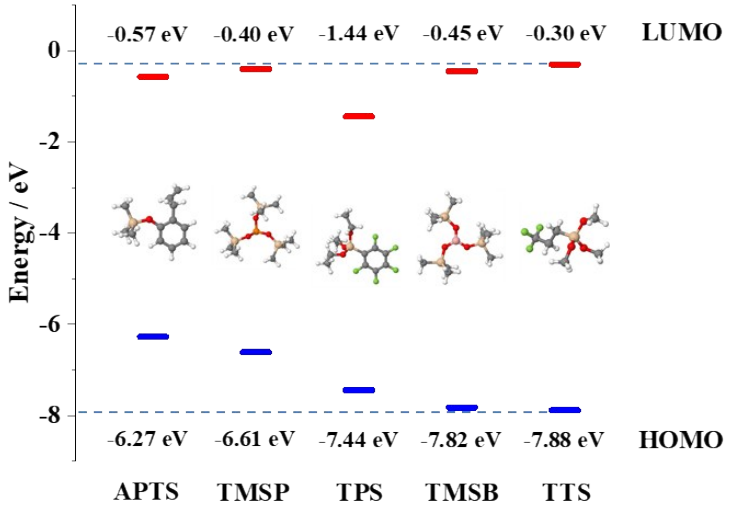

Fig. S2 Calculated HOMO and LUMO energy levels of APTS, TMSP, TPS, TMSB and TTS molecules.

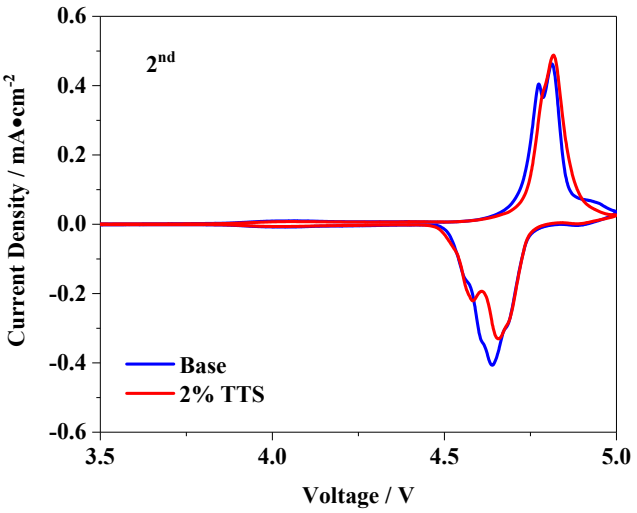

Fig. S3 Second cyclic voltammograms (CV) curve of H-LNMO/Li cells operated in base and 2% TTS-containing electrolytes at a rate of 0.1 mV s^{-1}.

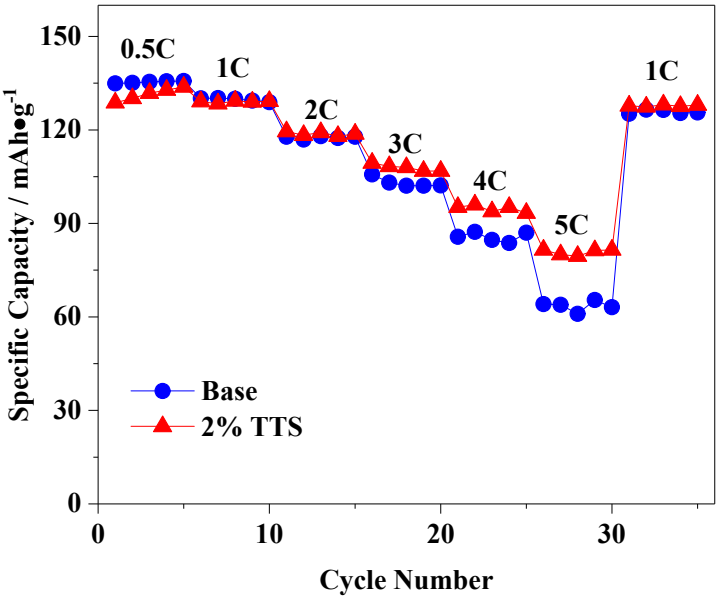

Fig. S4 Rate capability of H-LNMO/Li cells operated in base and 2% TTS-containing electrolytes in the voltage range of 3.0 - 4.9 V.

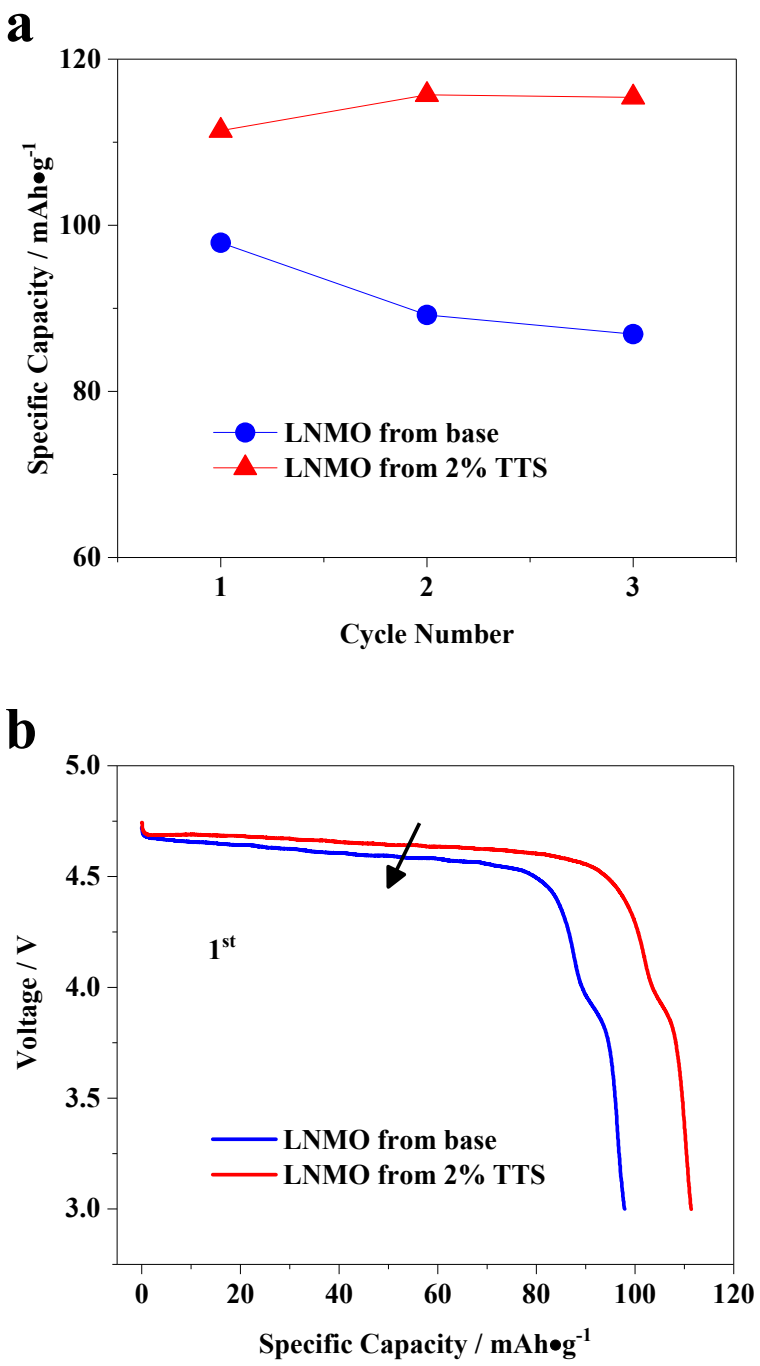

Fig. S5 (a) Cycling stability of reassembled L-LNMO/Li cells at 1 C within the voltage range of 3.0 - 4.9 V in base electrolyte, and corresponding (b) the first discharge curves. The LNMO electrodes are respectively taken from the L-LNMO/Li cells after 500 cycles in base and 2% TTS-containing electrolyte, matching with fresh Li electrodes to form reassemble L-LNMO/Li cells.

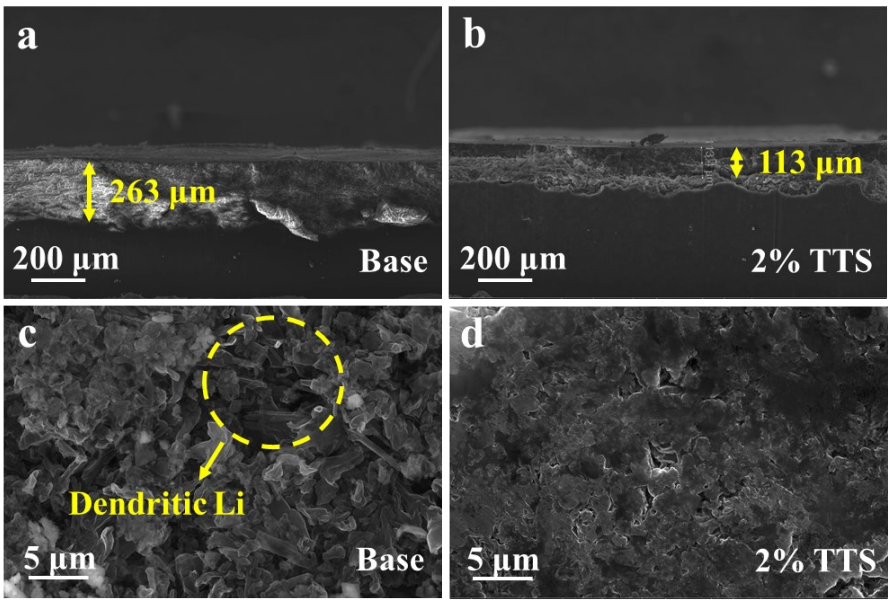

Fig. S6 Cross-sectional and surface SEM images of Li electrodes from Li//Li symmetric cells after the stripping-plating test for 550 hours in (a, c) base and (b, d) 2% TTS-containing electrolytes.

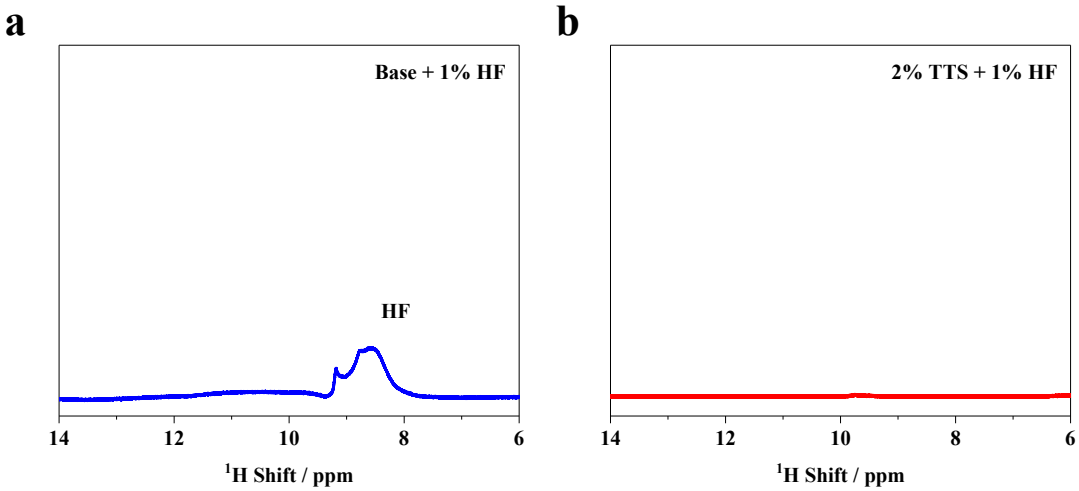

Fig. S7 ^{1}H NMR spectra of (a) base and (b) 2% TTS-containing electrolytes after adding 1% HF aqueous solution.

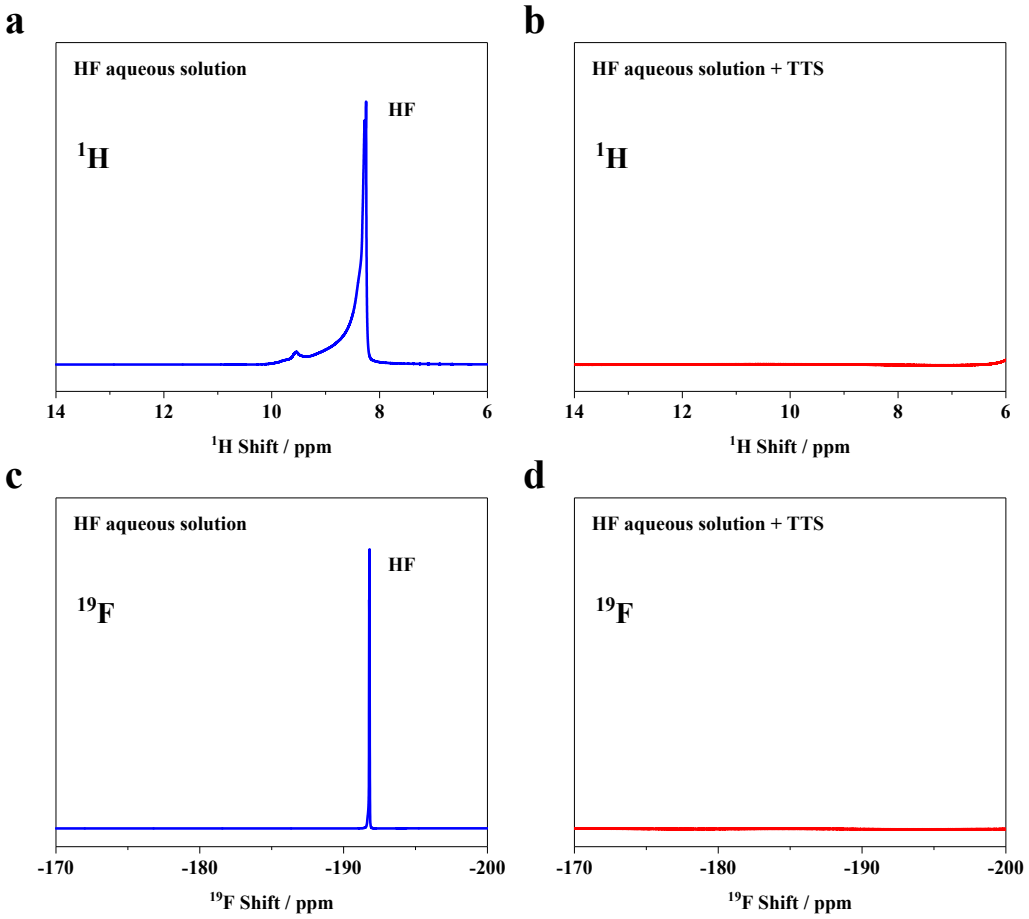

Fig. S8 ^{1}H and ^{19}F NMR spectra of HF aqueous solution (a, c) before and (b, d) after introducing TTS. The mass ratio of HF aqueous solution to TTS is 1 to 2.

Table S1 Comparison of electrochemical performance of Li//Li symmetric cell performed by TTS with the other additives.

Electrolyte additive	Current density / mA cm^{-2}	Capacity / mAh cm^{-2}	Cycling performance / hours
0.2 wt.% P123[1]	1	1	180
5 wt.% LiBOB[2]	1	1	350
10 wt.% FEC[3]	0.75	1.5	350
0.5 wt.% DPS[4]	1	2	360
0.15 M LiDFP[5]	0.5	0.5	500
0.3 wt.% TAEC[6]	0.5	0.5	500
5 mM $C_{60}(NO_2)_6$[7]	0.5	0.5	600
2 wt.% TTS (this work)	0.7	0.7	550

Table S2 Comparison of improved electrochemical performance of high voltage cathodes by TTS with the other additives.

Electrolyte additive	Cathode material	Charging Voltage / V	Cycle number	Current / C	Capacity retention improvement / %
10 vol.% ADN[8]	$LiNi_{0.5}Mn_{1.5}O_4$	5.0	50	0.5	4
0.075 wt.% Qc[9]	$LiNi_{0.5}Mn_{1.5}O_4$	4.9	100	1	6
0.5 wt.% DMPP[10]	$LiNi_{0.5}Mn_{1.5}O_4$	4.95	145	1	9
0.5 wt.% 4-TB[11]	$LiNi_{0.5}Mn_{1.5}O_4$	4.9	300	1	16
0.25 wt.% 3THP[12]	$LiNi_{0.5}Mn_{1.5}O_4$	4.9	350	1	41
1 wt.% PES[13]	$LiNi_{0.5}Mn_{1.5}O_4$	4.95	400	1	41.7
2 wt.% TTS (this work)	H-$LiNi_{0.5}Mn_{1.5}O_4$	4.9	100	1	63
2 wt.% TTS (this work)	L-$LiNi_{0.5}Mn_{1.5}O_4$	4.9	500	1	44

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