Supporting information

Enhancing high-voltage solid-state lithium-metal battery performance through stable solid-electrolyte interphase

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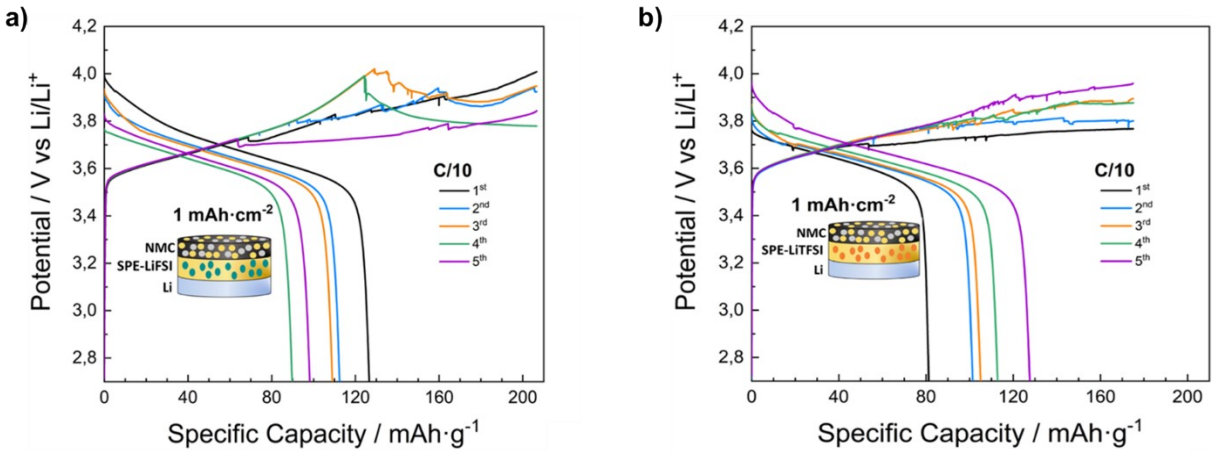

Fig. S1. Long cycling performance at 0.1C and RT of NMC622-based full cells assembled with (a) SPE-LiFSI and (b) SPE-LiTFSI as SPE.

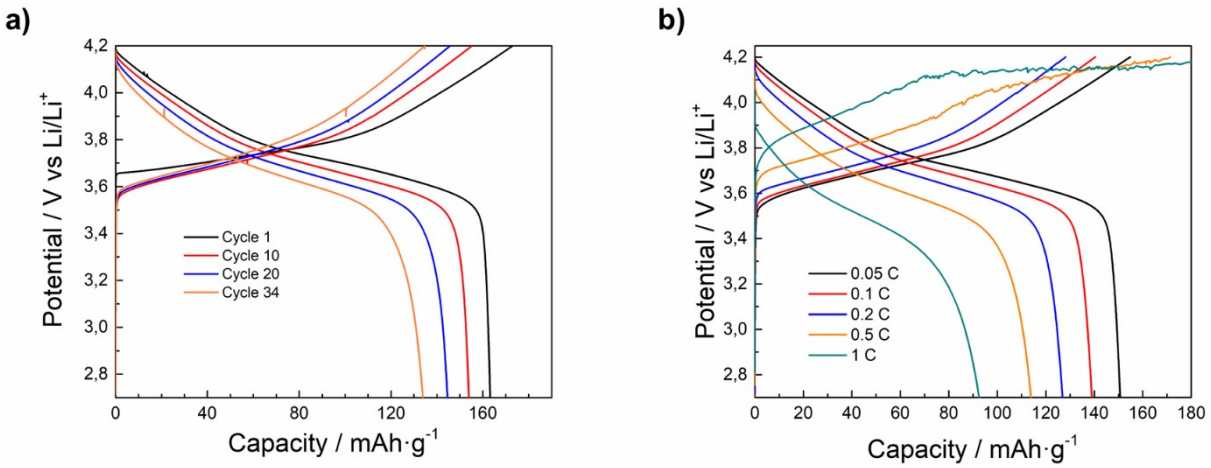

Fig. S2. (a) Voltage galvanostatic profiles at 0.1C and (b) voltage galvanostatic profiles at different current rates of NMC622|SPE-LiBOB|Li metal cells with 1 mAh·cm^{-2} loading.

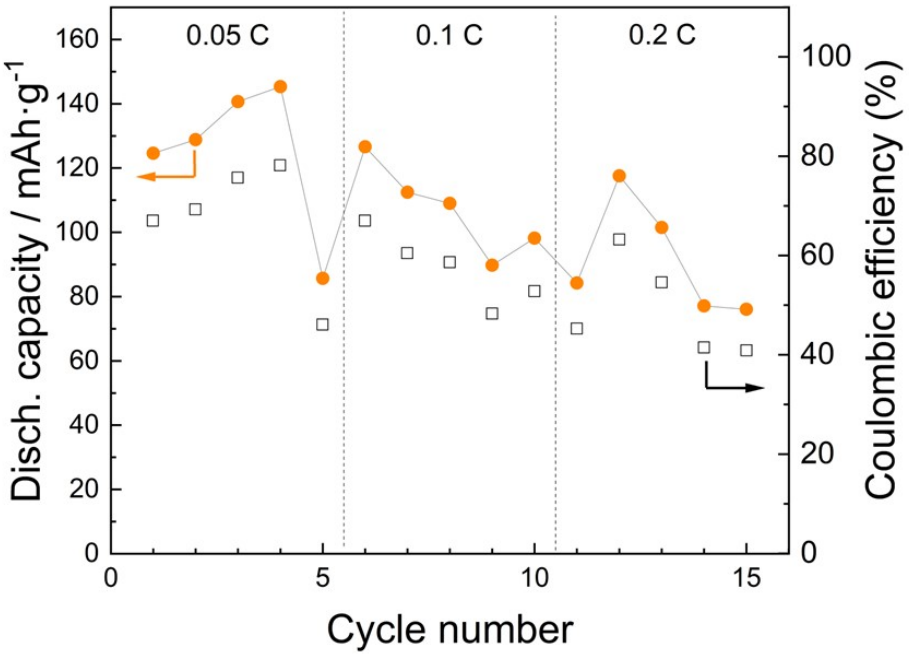

Fig. S3. C-rate capability test of NMC622|SPE-LiFSI|Li metal cell at 70 °C for a cathode loading of 1 mAh·cm^{-2}.

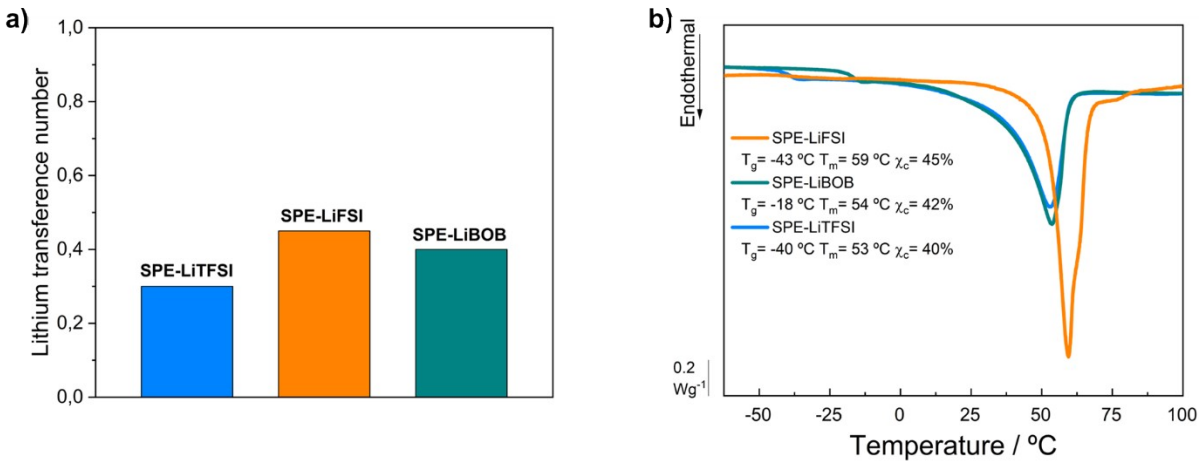

Fig. S4. (A) Lithium transference number and (b) DSC thermograms of Li-based containing SPE.

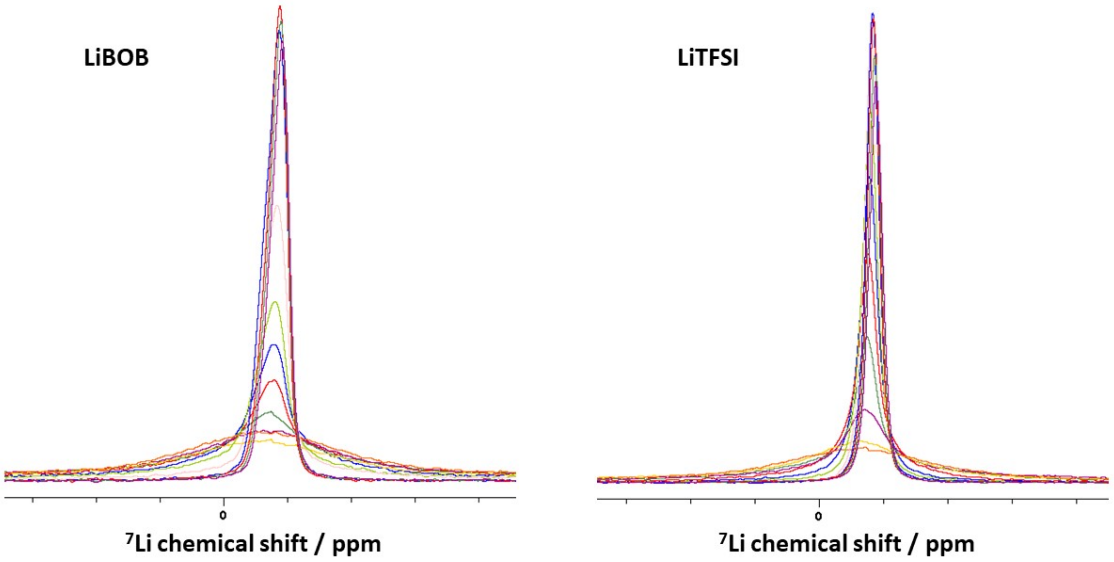

Fig. S5. ^{7}Li signals at different temperature for SPE-LiBOB (left) and SPE-LiTFSI (right)

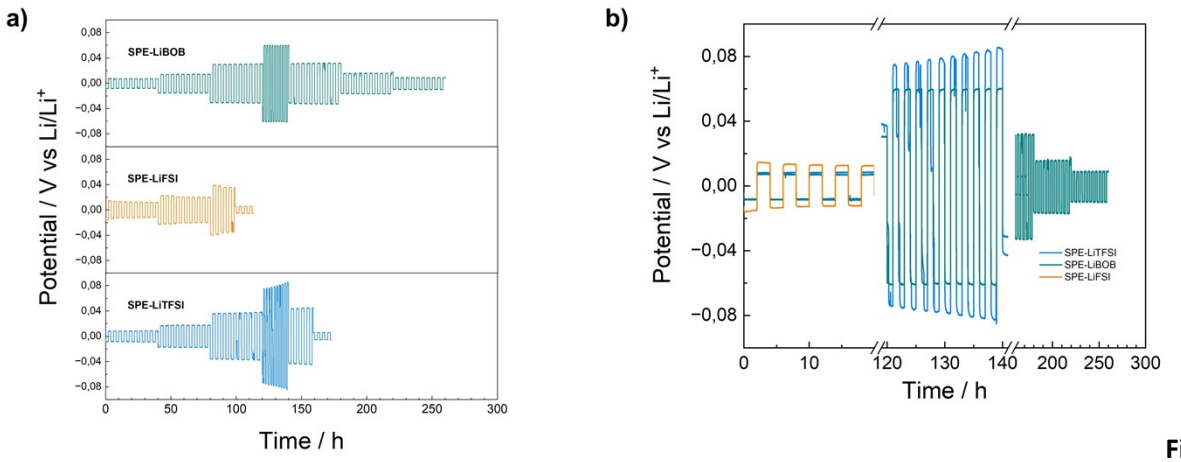

Fig. S6. (a) C-rate capability of symmetric lithium cells assembled with different SPE and (b) inset of C-rate capability test.

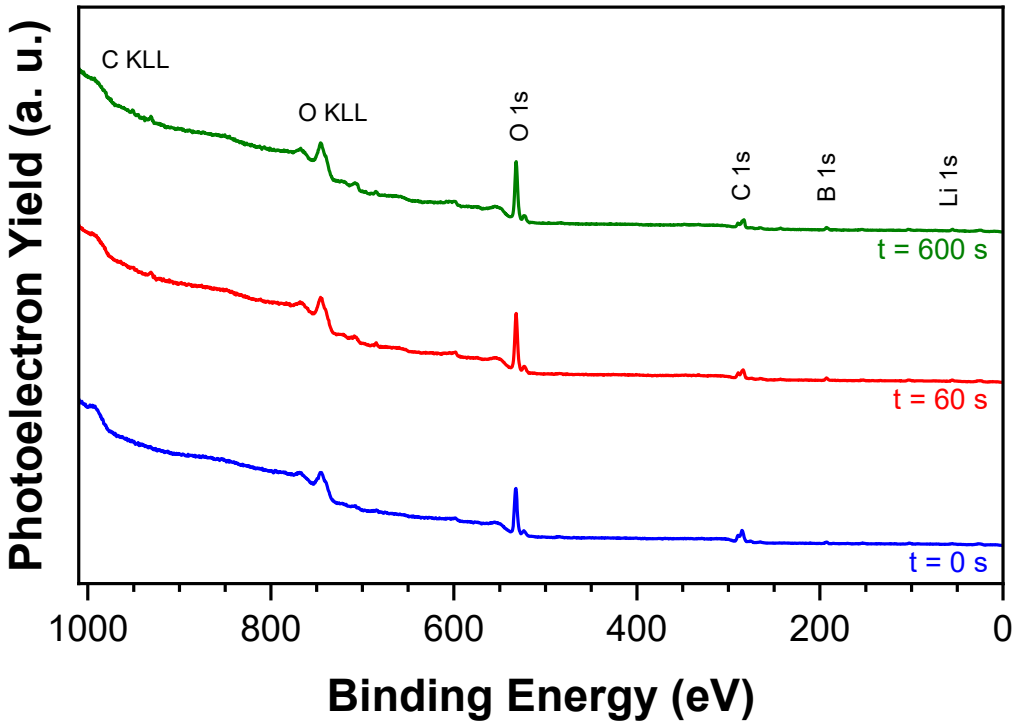

Fig. S7. Survey scan spectra of the Li deposits using LiBOB salt at different sputtering times.

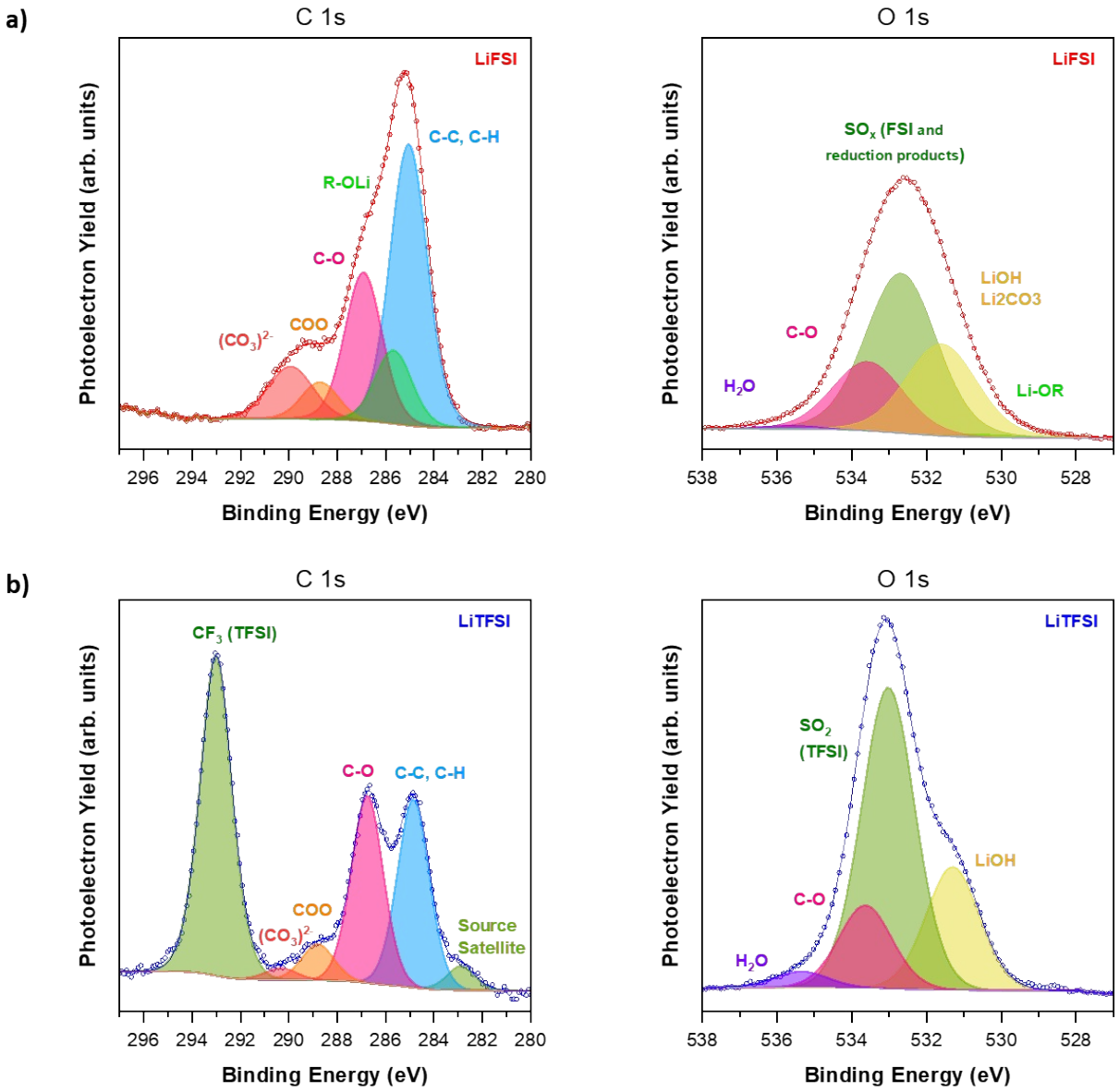

Fig. S8. C 1s and O 1S spectra of the outermost surface of SEI formed on plated Li metal with (a) LiFSI and (b) LiTFSI containing electrolyte

2. Supplementary Tables

Table S1. Estimated resistances and capacitances of the different elements after being fitted to the EC model.

Sample	R_b (Ohm)	CPE_{int} ($F \cdot s^{(a-1)}$)	R_{int} (Ohm)	CPE_{ct} ($F \cdot s^{(a-1)}$)	R_{ct} (Ohm)	W_s ($Ohm \cdot s^{-1/2}$)
Before cycling	14.5	6.71×10^{-6}	19.0	---	---	17.5
At 80% DoD	17.3	1.81×10^{-5}	22.3	1.65×10^{-5}	27.2	99.9

Table S2. Activation energy (Ea) and ionic conductivity (σ) of SPEs with different Li-based salts.

Sample	$\sigma_{25\,°C} \times 10^6$ ($S \cdot cm^{-1}$)	Ea1 (eV)	$\sigma_{70\,°C} \times 10^4$ ($S \cdot cm^{-1}$)	Ea2 (eV)
SPE-LiBOB	0.9	1.8	3.7	0.4
SPE-LiTFSI	6.5	1.1	4.4	0.3
SPE-LiFSI	1.8	1.2	2.0	0.3