Supporting information

Enhancing the polymer electrolyte – Li metal interface on high-voltage solid-state batteries with Li-based additives inspired by the surface chemistry of $Li_7La_3Zr_20_{12}$

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1. Supplementary Figures

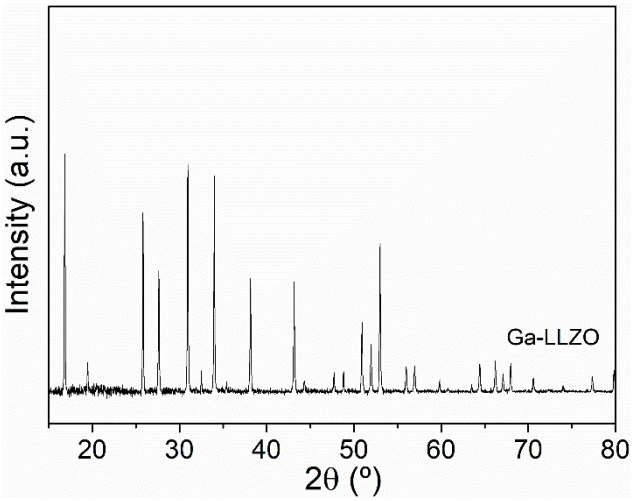
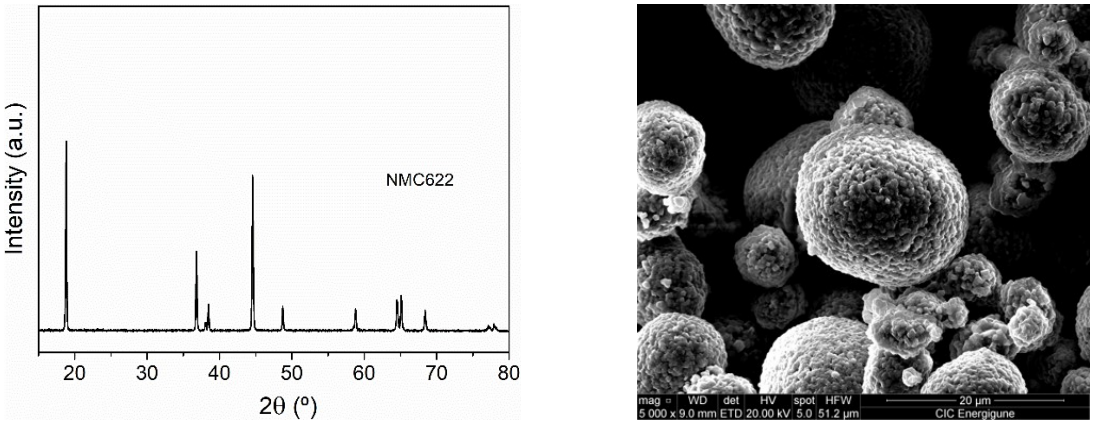


Fig. S1. XRD of the pure cubic Ga-substituted LLZO ($Li_{6.55}Ga_{0.15}La_3Zr_2O_{12}$) powder.



(A) **(B)**

Fig. S2. (A) XRD and (B) SEM micrograph of NMC622 powder.

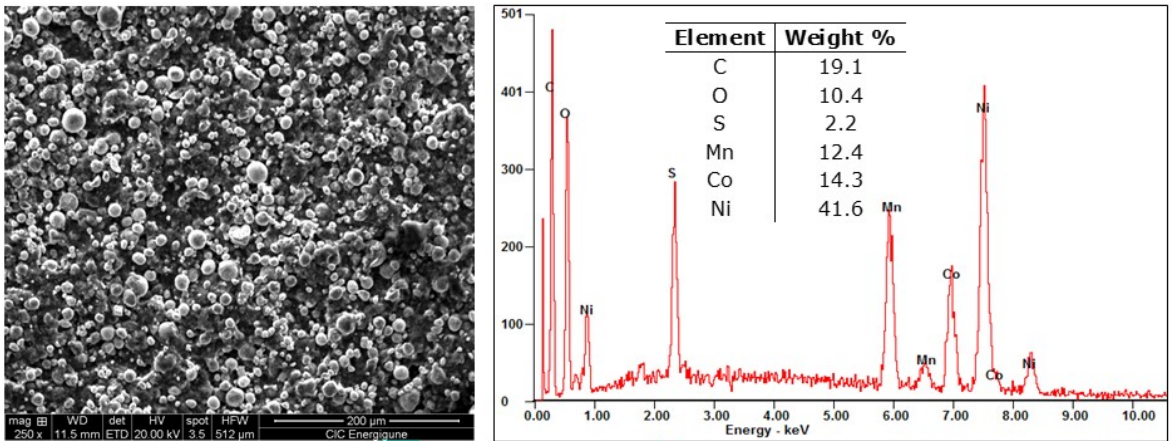


Fig. S3. SEM micrograph and EDX analysis of NMC622 electrode.

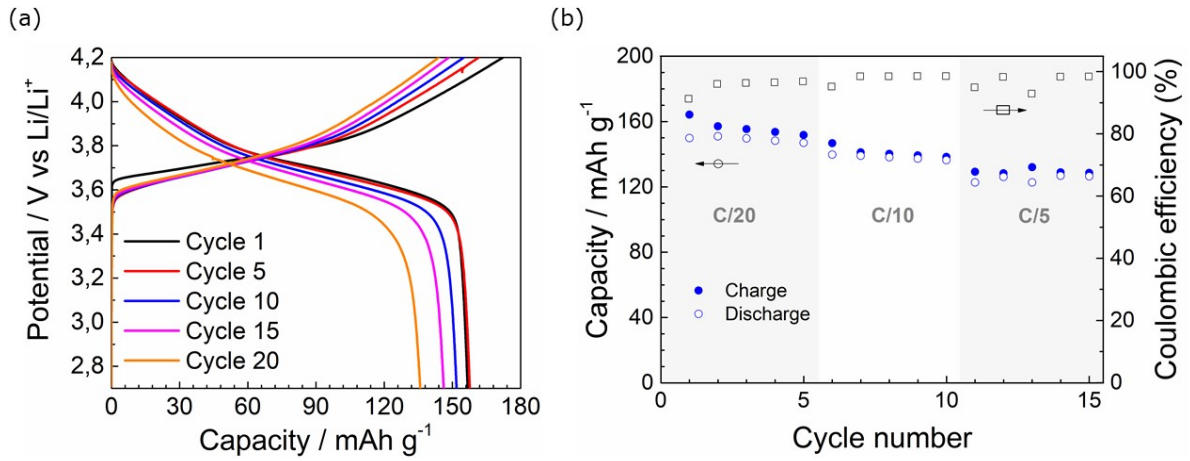


Fig. S4. (a) Voltage galvanostatic profiles at C/10 of the NMC622 cathode with Li metal anode at different cycles and (b) Rate capability at 70 °C of NMC622 | SPE-LiOH | Li metal cells with 1 mAh·cm^{-2} loading.

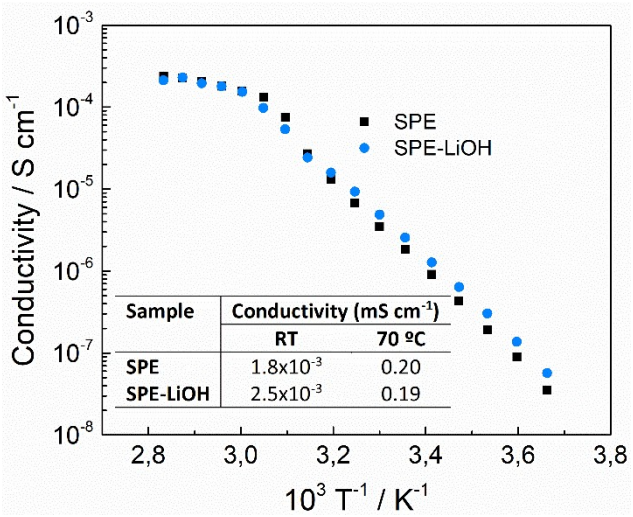


Fig. S5. Arrhenius plot of SPE and SPE-LiOH between 0-80 °C.

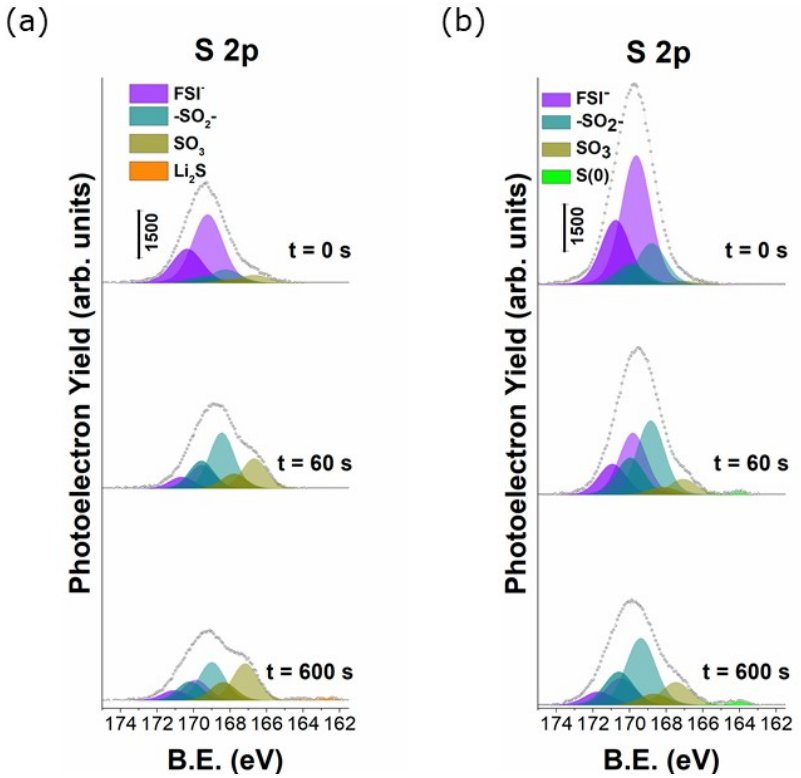


Fig. S6. S 2p spectra of the outermost surface of SEI layer formed on plated Li metal with (a) pristine electrolyte and (b) LiOH containing electrolyte at different depths.

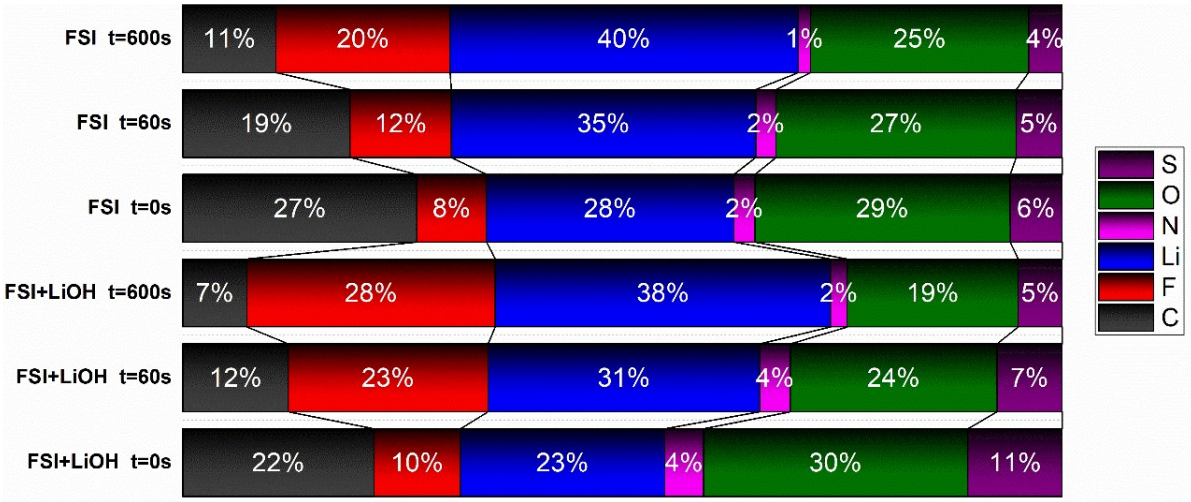


Fig. S7. Distribution of different elements (represented in atomic percent) formed in the SEI layer at different depth and calculated based on XPS results.

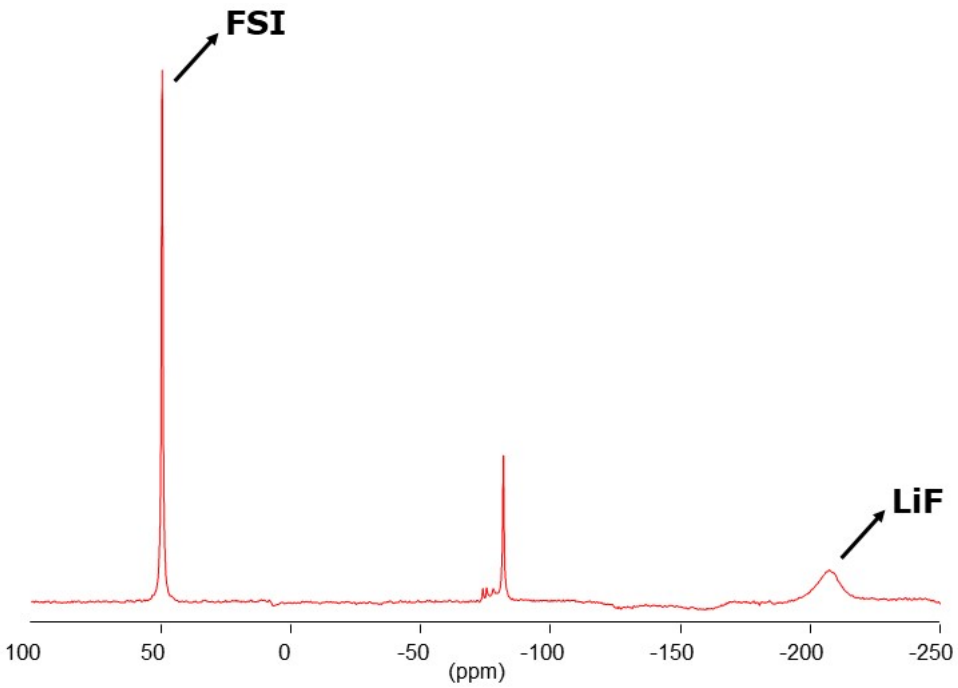


Fig. S8. ^{19}F solid-state NMR spectra of CPE after conditioning the sample at 70 °C for 48 h.

2. Supplementary Tables

Table S1. Resistances of the different components obtained from Li metal cells assembled with NMC electrode: ionic bulk conductivity, (R_B), electrode interfaces (R_{int}), cathode solid electrolyte interface resistance (R_{CEI}) and charge transfer resistance for electrochemical reactions (R_{CT}). All resistances are calculated from the equivalent circuit before cycling and after 20 cycles of cycling. Values are given Ω.

Sample	R_b	R_{int}	R_{CEI}	R_{CT}
Before Cycling	19	25	<1	13
After 20 cycles	26	156	20	20

Table S2. Resistances of the different components obtained from symmetric Li metal cells: ionic bulk conductivity (R_b) and electrode interfaces (R_{int}). All resistances are calculated from the equivalent circuit after conditioning the cells at 70 ^{o}C for 24h. Values are given Ω.

Sample	R_b	R_{int}
SPE	10	15
SPE-LiOH	10	7