Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information: Redox active cathode interphases in solid-state batteries

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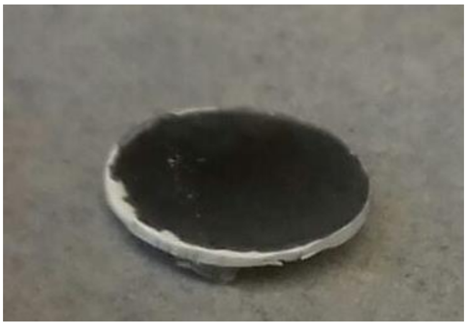
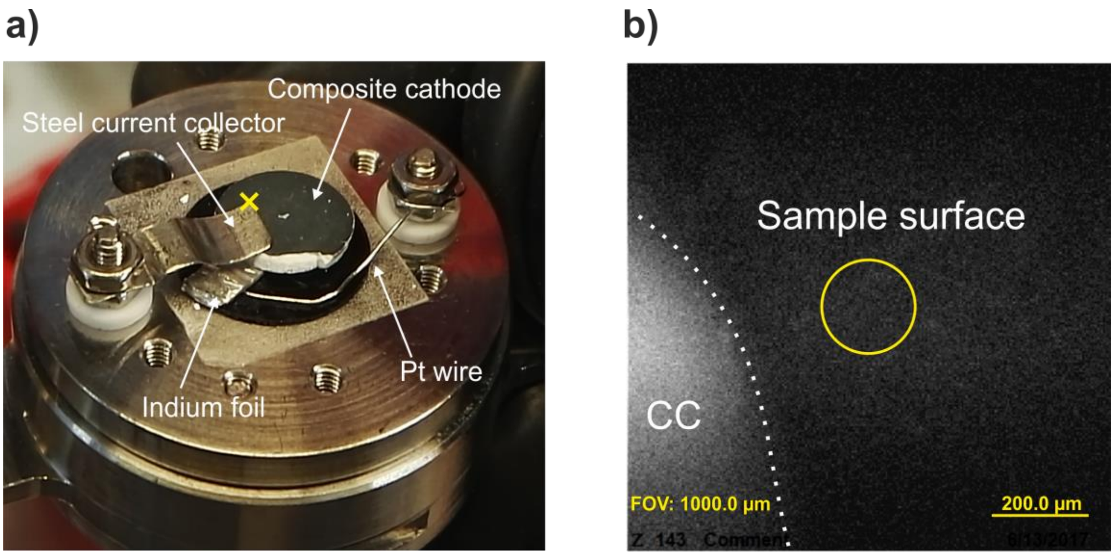
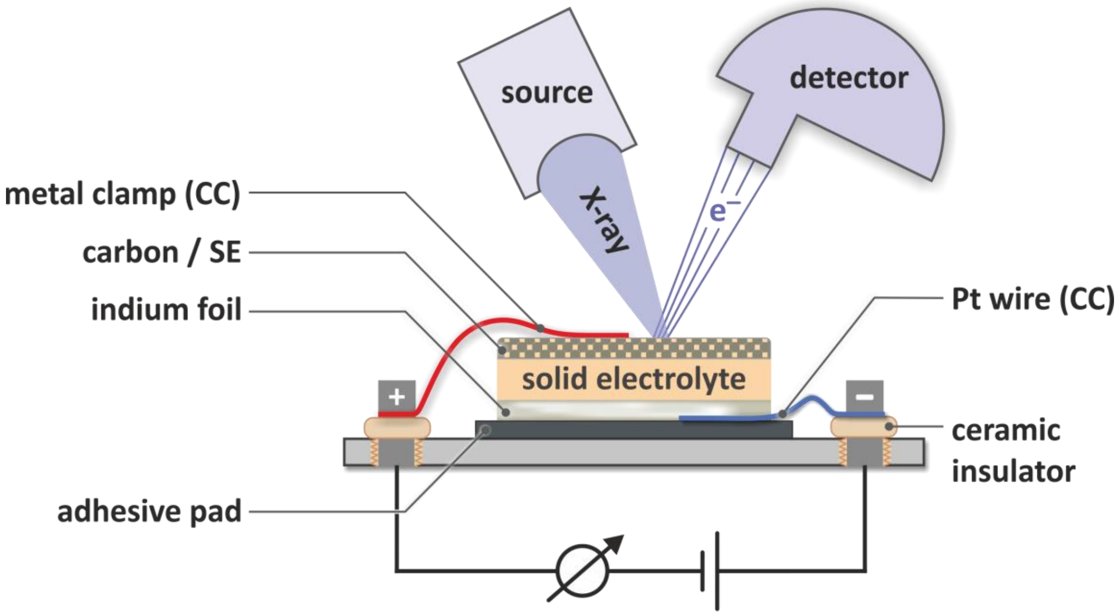


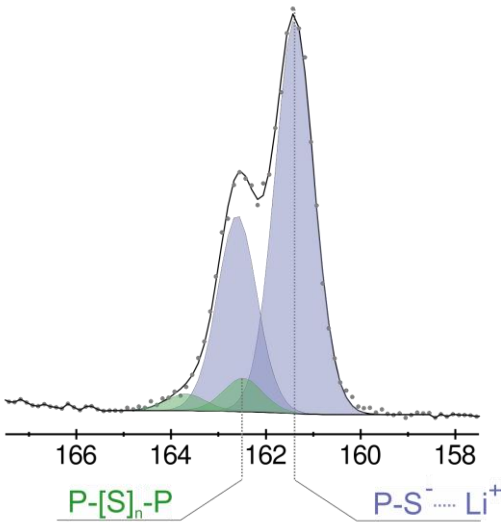
Supplementary Figure S1: Example of an extracted SSB pellet of a NCM-811 / β-Li_3PS_4 | β-Li_3PS_4 | Li-In battery, which was used for XPS depth profiling.



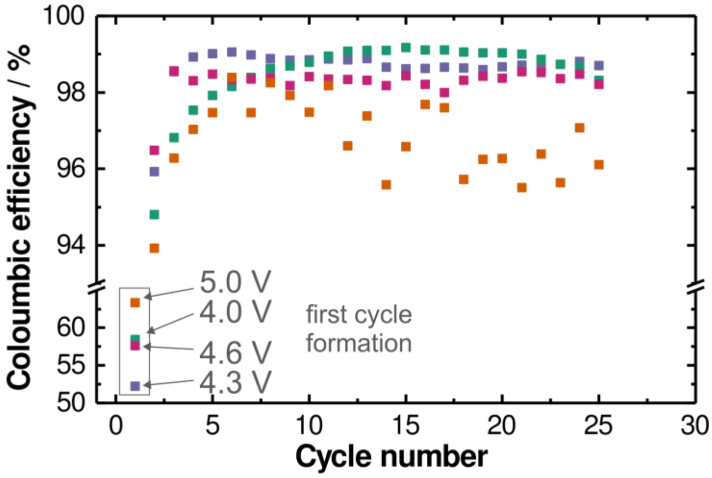
Supplementary Figure S2: (a) XPS sample preparation. The sample pellet is placed onto an adhesive carbon pad. The indium foil on the bottom is contacted using a platinum wire. The top side of the pellet is pressed onto the holder by a stainless-steel sheet, which serves as the positive current collector. (b) SXI of the sample surface near to the current collector (CC). The measurement spot is marked in yellow.



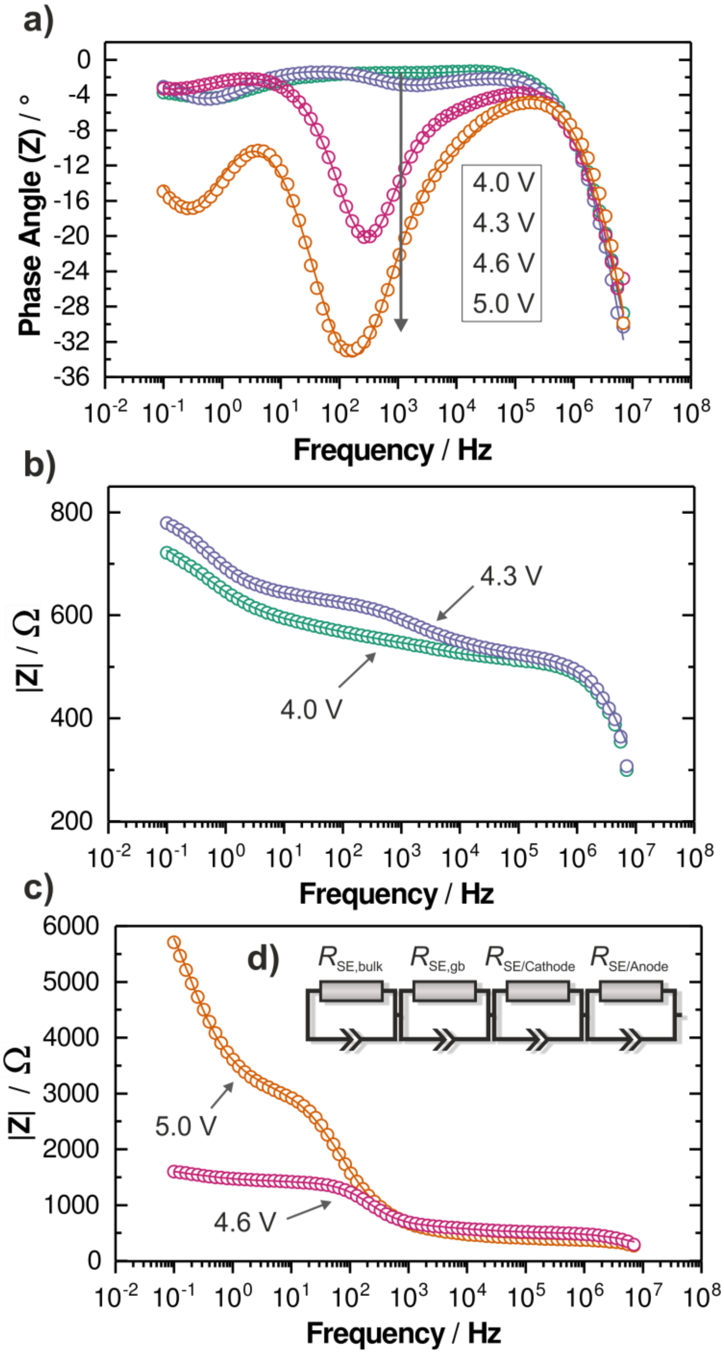
Supplementary Figure S3: Schematic of the measurement setup for in situ XPS of SSLB.



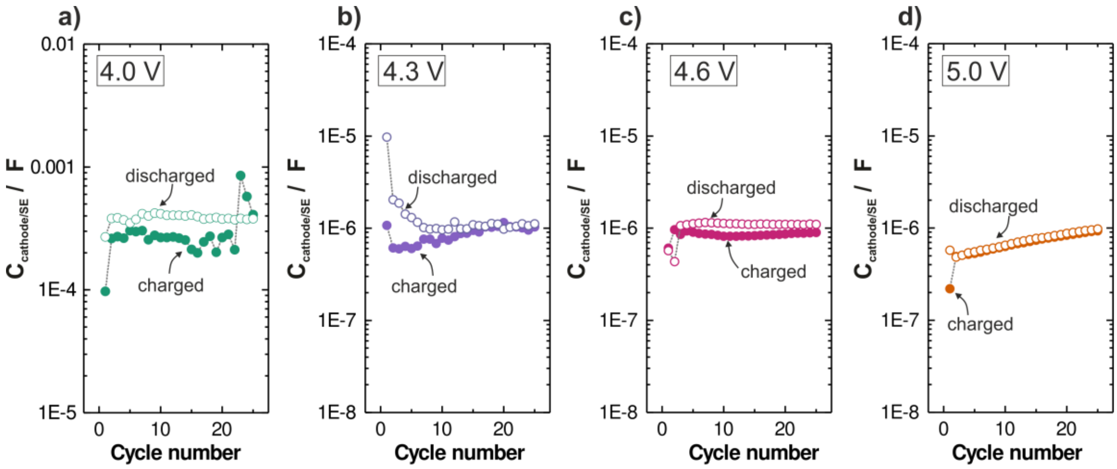
Supplementary Figure S4: Peak deconvolution of the S 2p spectra of pristine β-Li_3PS_4. Two species are needed to provide a sufficient fit. Blue peaks are attributed to equivalent $P^{\delta+}-S^{\delta-}$ bonds. Green peaks were correlated to bridging $P-[S]_n-P$ units.



Supplementary Figure S5: Coulombic efficiency f of Li-In | β-Li_3PS_4 | NCM-811 /β-Li_3PS_4 cells when charged to cutoff voltages of 4.0, 4.3, 4.6 and 5.0 V. Cells cycled to 4.0 and 4.3 V are cycled stable above 98 %. When charged to a voltage limitation of 5.0 V, the Coulombic efficiencies are scattered and exhibit lower values. The solid grey box indicates the values for the first discharge cycle.



Supplementary Figure S6: Bode plot of the NCM-811 / β-Li_3PS_4 | β-Li_3PS_4 | Li-In cells cycled at 213 μA/cm² to different upper cutoff voltages between 4.0 and 5.0 V. (a) Phase angle diagram, (b) Bode magnitude plot of the cells charged to 4.0 and 4.3 V and (c) when charging to 4.6 and 5.0 V, respectively. Spectra recorded in the discharged state after 25 cycles and a 24 hour OCV period. Open circles indicate the measured data, solid lines represent the resulting fit using an equivalent circuit of (RQ)(RQ)(RQ)(RQ) as seen in d).



Supplementary Figure S7: Evolution of the capacitance $C_{cathode/SE}$ upon cycling for Li-In | β-Li_3PS_4 | NCM-811+β-Li_3PS_4 batteries charged to different upper cutoff voltages between 4.0 V and 5.0 V (a-d). Filled circles represent the charged, open circles the discharged state. The capacitances (4.0 – 5.0 V) for the other circuit elements are in the approximate range of $C_{SE,bulk}$ ~ 0.05 nF, $C_{SE,grain}$ ~ 0.1 µF and $C_{anode/SE}$ ~ 0.3 mF.

Table S8: Quantification (atom fractions x(i)) of the S 2p signal from XPS measurements of the cathode-current collector surface cycled to different upper voltage limitations between 4.0 and 5.0 V.

Sample	*x*(P-S-Li) / at-%	*x*(P-$[S]_n$-P) / at-%	*x*(S^0) / at-%
4.0 V	66	17	17
4.3 V	70	17	13
4.6 V	66	20	14
5.0 V	42	32	26