Supporting Information

Understanding solid electrolyte interphase formation in hydroborate-based solid-state batteries

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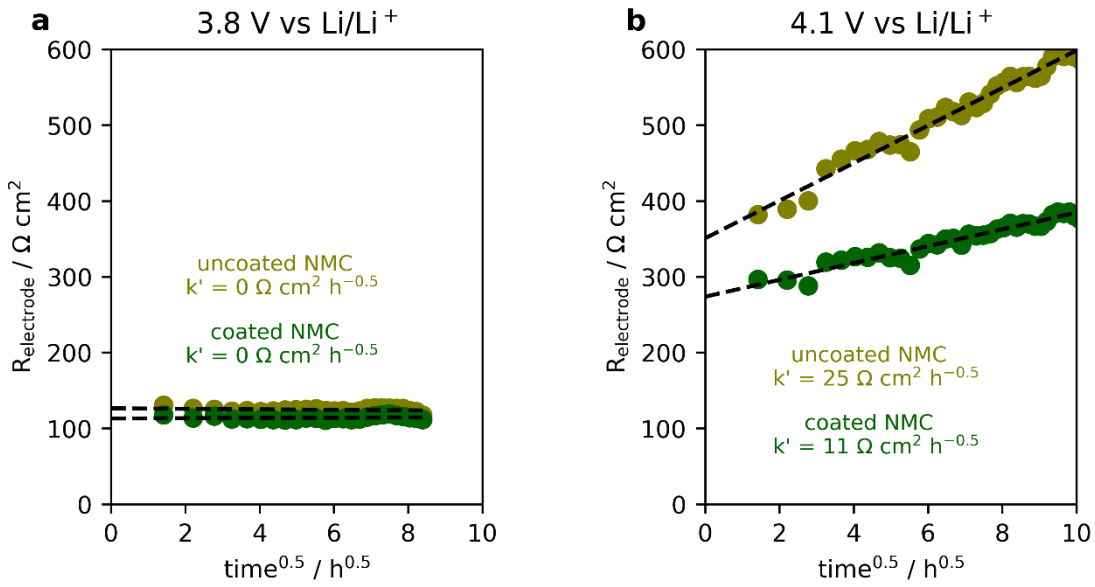

Figure S1. Evolution of the electrode resistance of NMC811-$Li_3(CB_{11}H_{12})_2CB_9H_{10}$ composite electrodes after delithiation to an open-circuit potential of (a) 3.8 V vs Li/Li^+ and (b) 4.1 V vs Li/Li^+. The dashed black lines represent linear fits to the linear square-root of time dependence with the corresponding slope k' indicated as well Results with uncoated and coated NMC811 active material are displayed in olive and green color, respectively. The fitted impedance spectra and equivalent circuits can be found in Figures S3-S6.

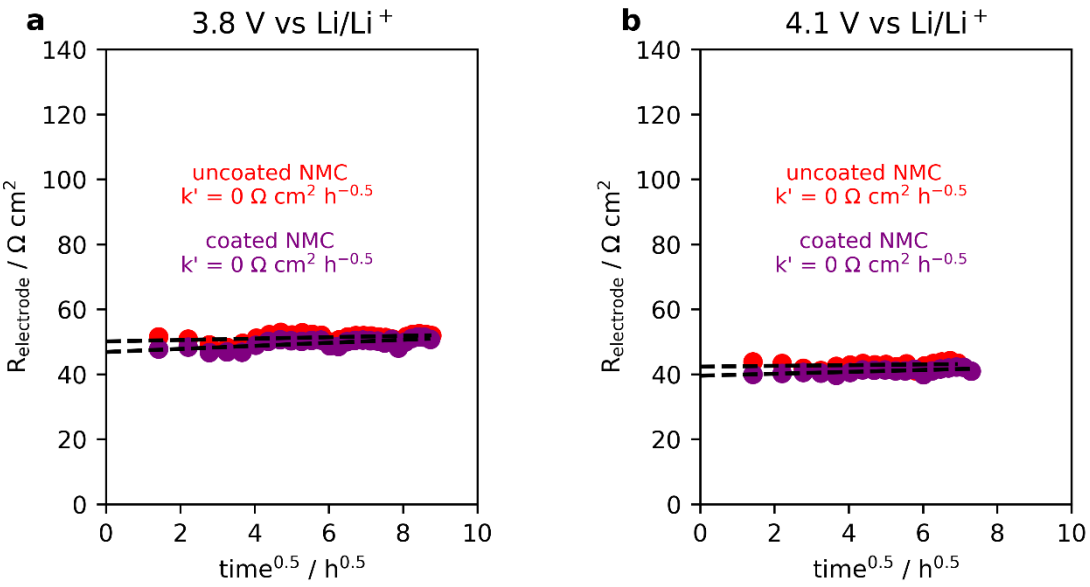

Figure S2. Evolution of the electrode resistance of NMC811-Li_6PS_5Cl composite electrodes after delithiation to an open-circuit potential of (a) 3.8 V vs Li/Li^+ and (b) 4.1 V vs Li/Li^+. The dashed black fitting lines with the square-root of time are indicated along with the corresponding slope k'. Results with uncoated and coated NMC811 active material are displayed in red and purple color, respectively. The fitted impedance spectra and equivalent circuits can be found in Figures S7-S10.

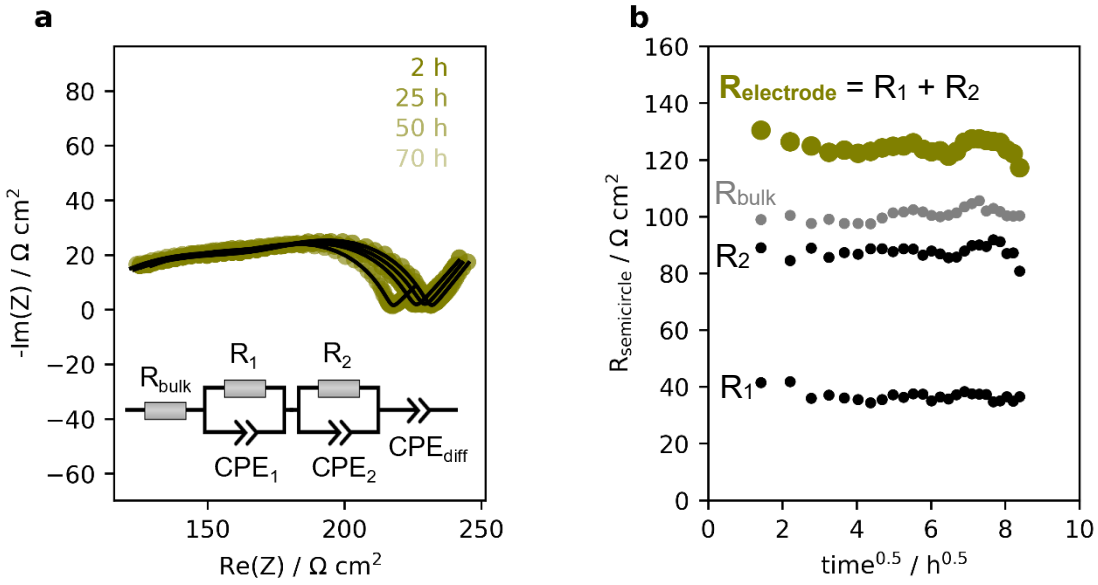

Figure S3. (a) Exemplary impedance spectra of the NMC811-$Li_3(CB_{11}H_{12})_2CB_9H_{10}$ composite electrode after delithiation to an open-circuit potential of 3.8 V vs Li/Li^+ (olive, uncoated NMC811) and their fit with the equivalent circuit presented in the inset (black). (b) Time evolution of the fitted resistances.

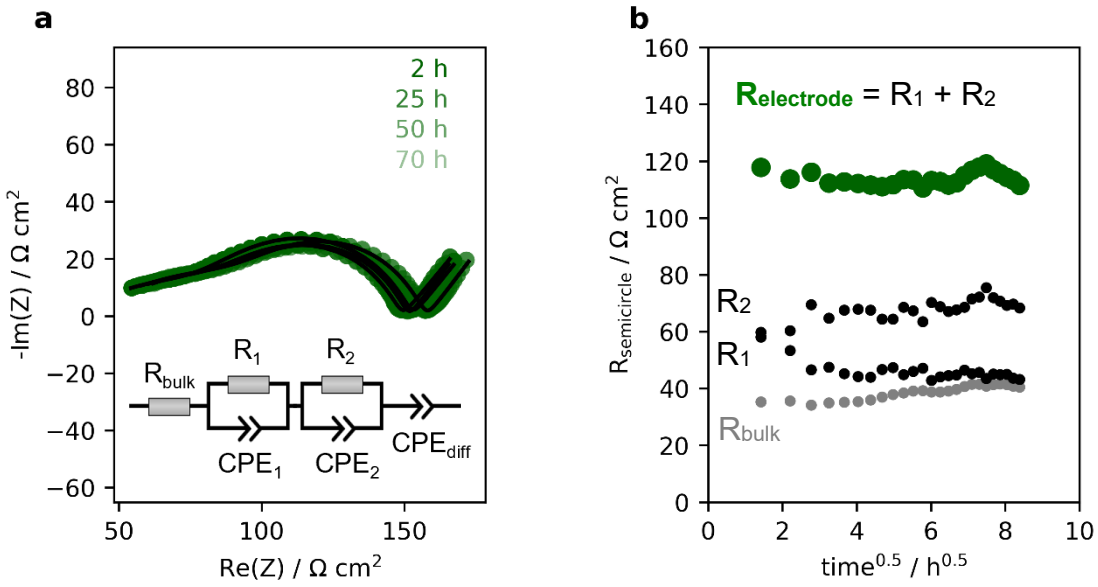

Figure S4. (a) Exemplary impedance spectra of the NMC811-$Li_3(CB_{11}H_{12})_2CB_9H_{10}$ composite electrode after delithiation to an open-circuit potential of 3.8 V vs Li/Li^+ (green, coated NMC811) and their fit with the equivalent circuit presented in the inset (black). (b) Time evolution of the fitted resistances.

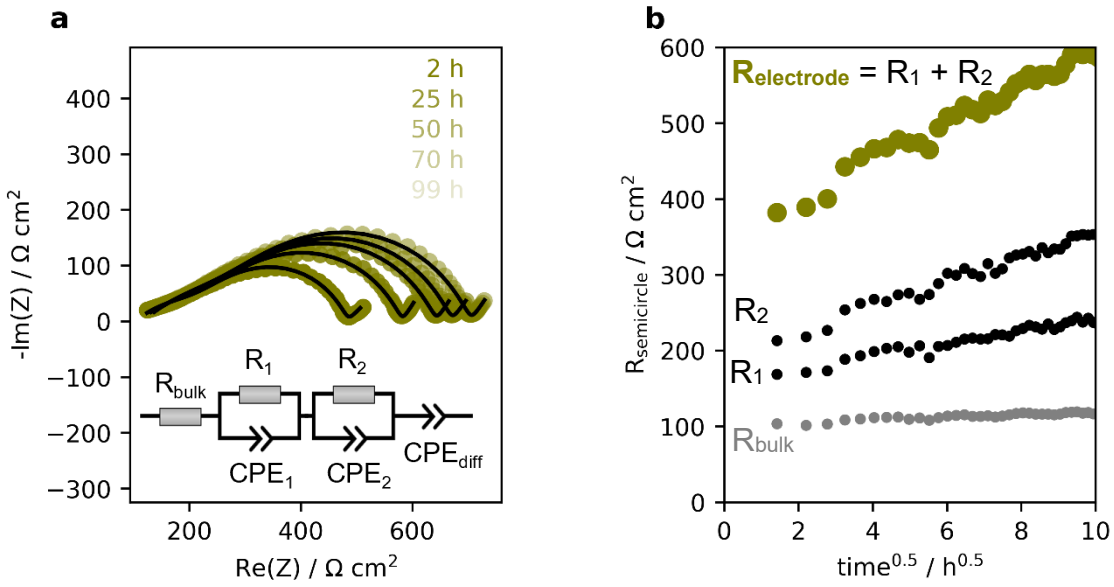

Figure S5. (a) Exemplary impedance spectra of the NMC811-$Li_3(CB_{11}H_{12})_2CB_9H_{10}$ composite electrode after delithiation to an open-circuit potential of 4.1 V vs Li/Li^+ (olive, uncoated NMC811) and their fit with the equivalent circuit presented in the inset (black). (b) Time evolution of the fitted resistances.

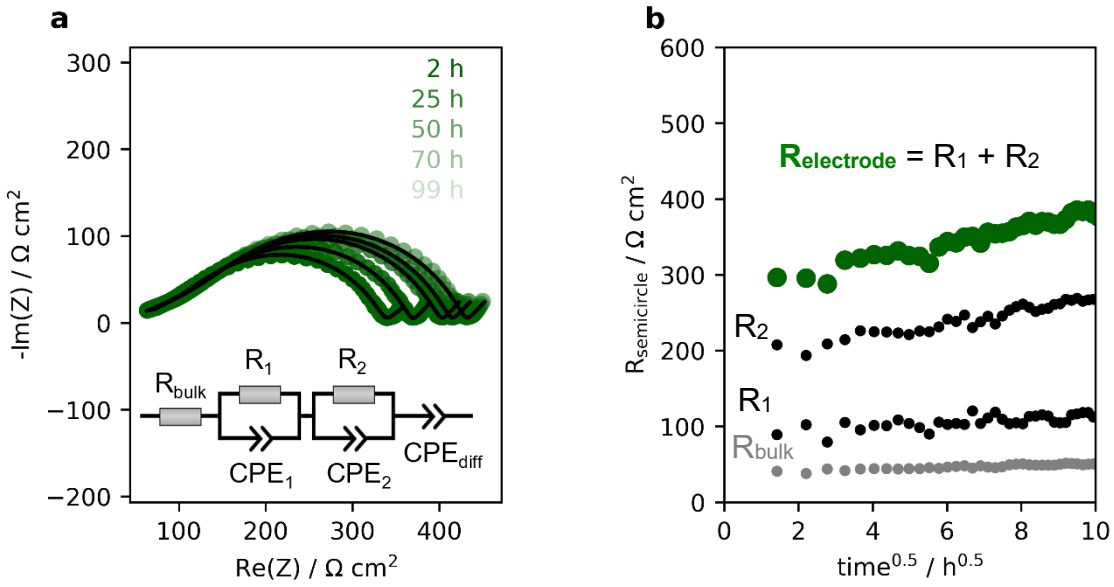

Figure S6. (a) Exemplary impedance spectra of the NMC811-$Li_3(CB_{11}H_{12})_2CB_9H_{10}$ composite electrode after delithiation to an open-circuit potential of 4.1 V vs Li/Li^+ (green, coated NMC811) and their fit with the equivalent circuit presented in the inset (black). (b) Time evolution of the fitted resistances.

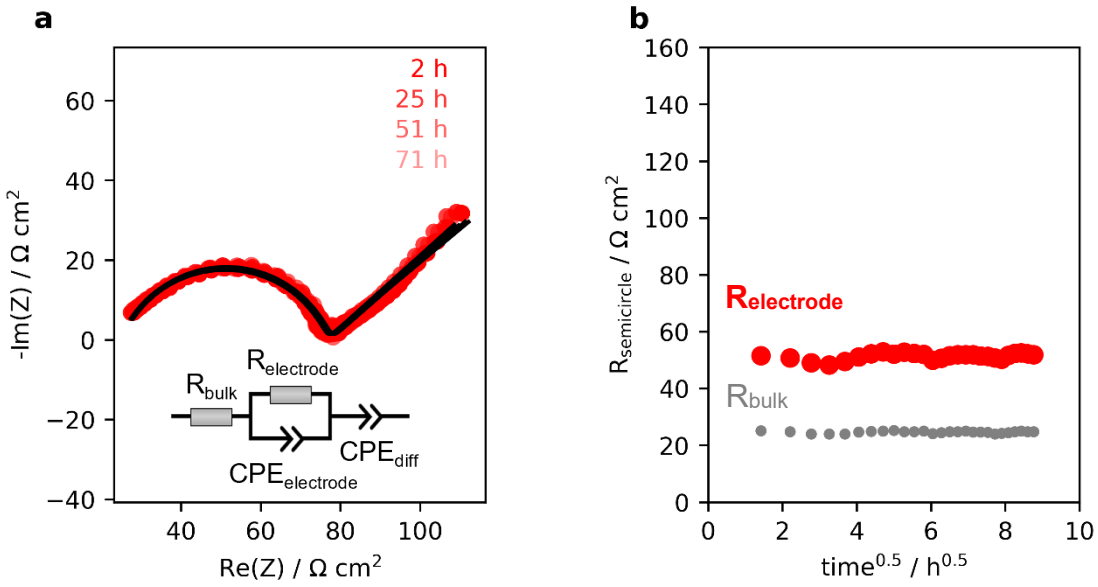

Figure S7. (a) Exemplary impedance spectra of the NMC811-Li_6PS_5Cl composite electrode after delithiation to an open-circuit potential of 3.8 V vs Li/Li^+ (red, uncoated NMC811) and their fit with the equivalent circuit presented in the inset (black). (b) Time evolution of the fitted resistances.

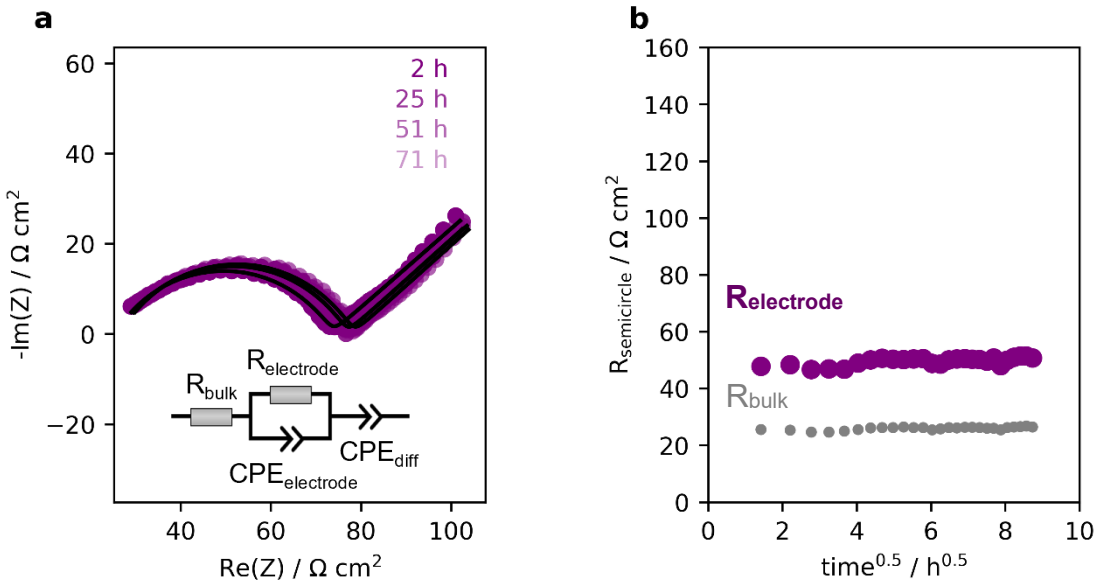

Figure S8. (a) Exemplary impedance spectra of the NMC811-Li_6PS_5Cl composite electrode after delithiation to an open-circuit potential of 3.8 V vs Li/Li^+ (purple, coated NMC811) and their fit with the equivalent circuit presented in the inset (black). (b) Time evolution of the fitted resistances.

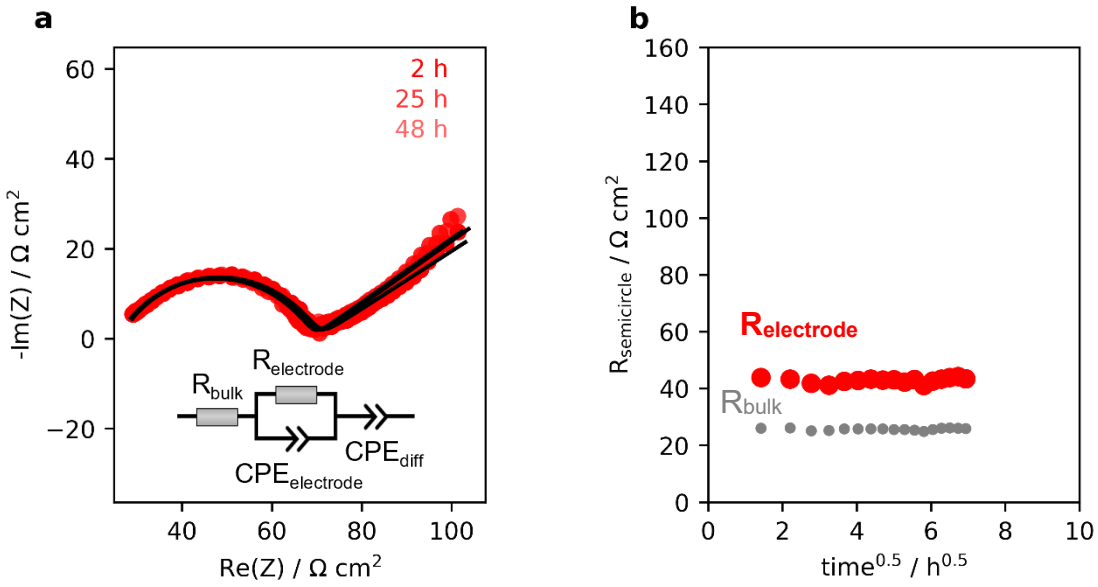

Figure S9. (a) Exemplary impedance spectra of the NMC811-Li_6PS_5Cl composite electrode after delithiation to an open-circuit potential of 4.1 V vs Li/Li^+ (red, uncoated NMC811) and their fit with the equivalent circuit presented in the inset (black). (b) Time evolution of the fitted resistances.

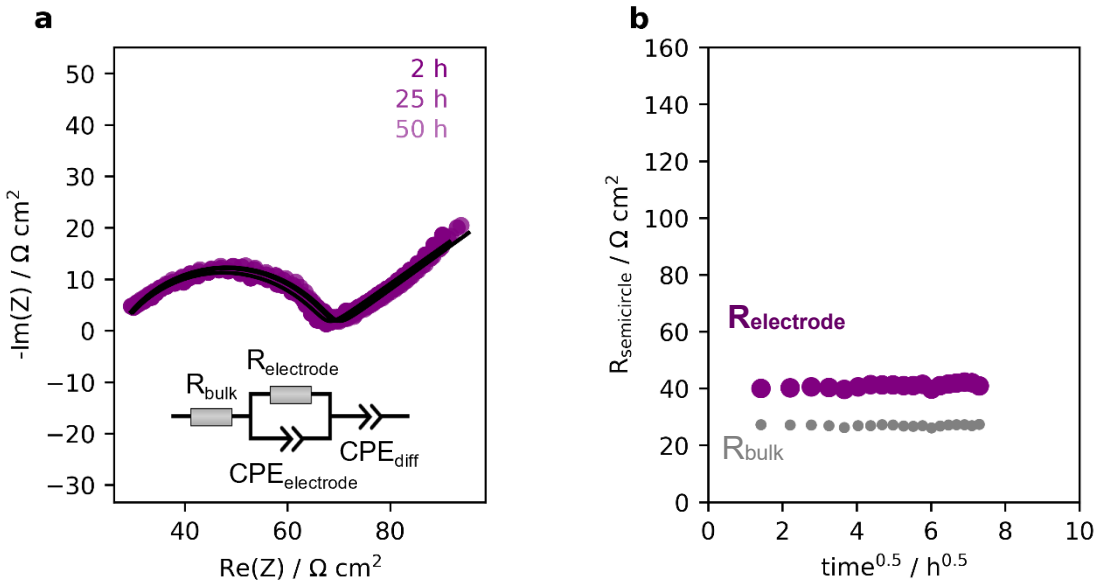

Figure S10. (a) Exemplary impedance spectra of the NMC811-Li_6PS_5Cl composite electrode after delithiation to an open-circuit potential of 4.1 V vs Li/Li^+ (purple, coated NMC811) and their fit with the equivalent circuit presented in the inset (black). (b) Time evolution of the fitted resistances.

METHODS

Materials

All material preparation, electrode preparation, cell assembly, and electrochemical testing was carried out in an argon-filled glovebox (MBraun, H_2O and O_2 < 0.1 ppm). Hydrated $LiCB_{11}H_{12}$-xH_2O (KatChem) and $LiCB_9H_{10}$-xH_2O (KatChem) were dried under vacuum (10^{-3} mbar) at 180 °C and 230 °C for 12 h, respectively. $Li_3(CB_{11}H_{12})_2(CB_9H_{10})$ was prepared by ball milling of dried $LiCB_{11}H_{12}$ and $LiCB_9H_{10}$ in a molar ratio of 2:1 in argon for 4 × 15 min in a sample-to-ball weight ratio of 1:40 using a shaker mill (Spex 8000M). Li_6PS_5Cl (NEI Corporation, particle size ~5 μm) was used as received. NMC811 was synthesized and either used directly or coated with TiO_2 and Li_2CO_3, as described in Ref. 1.

NMC811 electrode preparation

For the composite electrodes, NMC811, solid electrolyte, and vapor-grown carbon fibers (Sigma Aldrich 719781, dried at 120 °C under vacuum for 5 h) were mixed with a mortar and pestle in a weight ratio of 80:15:05 ($Li_3(CB_{11}H_{12})_2(CB_9H_{10})$ electrolyte) and 75:21:4.7 (Li_6PS_5Cl electrolyte), corresponding to an identical volume ratio of 50.7:41.3:8 for both electrolytes. 2 wt% of polytetrafluoroethylene binder (Goodfellow FP30-PD-000110) were added and fibrillated at 60 °C in a heated mortar and pestle. The resulting flakes were then crushed to a powder in a laboratory mixer (IKA Tube Mill control) at 10'000 rpm for 3 min. (11.8 ± 0.2) mg of this powder for the $Li_3(CB_{11}H_{12})_2(CB_9H_{10})$-based composites, and (12.6 ± 0.2) mg for the Li_6PS_5Cl-based composites was then laminated onto an aluminum current collector coated with a thin carbon layer (MSE Supplies BR0125) in a stainless-steel die of 8 mm diameter under uniaxial pressure of 390 MPa for 3 min, after heating the tool with the powder to 60 °C for 1h. The areal loading is (18.4 ± 0.4) mg_{NMC} cm^{-2} for both composites.

Cell Assembly

Three-electrode pressure cells were prepared in a custom-made setup described in more detail in Ref. 1. First, the pre-laminated NMC811 electrode was placed centrally in the pressure cell, which was taped with a ring-shaped polyimide tape (Kapton) with inner diameter of 8 mm to center the electrode and to avoid direct contact between the electrolyte and the steel plunger of 12.5 mm diameter. Then, (100 ± 0.5) mg of $Li_3(CB_{11}H_{12})_2(CB_9H_{10})$ electrolyte or (156.2 ± 0.5) mg of Li_6PS_5Cl electrolyte were added and pressed under 160 MPa for 3 min, resulting in a pellet, serving as separator, of approximately 900 µm thickness. As a reference electrode, an indium ring (15 ± 1 mg) with an outer diameter of 11 mm and an inner diameter 10 mm was punched out from an indium foil (> 99.995 %, 0.1 mm in thickness, Sigma Aldrich) and added on top of the electrolyte pellet (the indium is lithiated electrochemically, see below). The hollow steel cylinder contacting the reference electrode with a hollow polyether ether ketone isolation (8 mm inner diameter) were then inserted into the cell. Subsequently, (20 ± 0.2) mg of $Li_3(CB_{11}H_{12})_2(CB_9H_{10})$ electrolyte or (31.2 ± 0.2) mg of Li_6PS_5Cl electrolyte were inserted and pressed uniaxially under 160 MPa for 3 min. Finally, In/InLi counter electrodes were fabricated by adding (44 ± 1) mg rolled-out indium foil (> 99.995 %, 0.1 mm in thickness before rolling out, 8 mm diameter, Sigma Aldrich) and (1.75 ± 0.25) mg rolled-out lithium foil (purity 99.9 %, 0.75 mm in thickness before rolling out, Alfa Aesar) and pressing the cell stack under 160 MPa for 3 min. The weight ratio of indium to lithium was chosen such that a molar ratio of 30-45 at% lithium in the In/InLi alloy is achieved. The cells were then exposed to an initial stack pressure of 8 ± 1 MPa in a custom-built pressure frame, as validated with force sensors.

Electrochemical characterization

Electrochemical characterization was carried out with a multichannel potentiostat (BioLogic VSP-3e) with electrochemical impedance capabilities. Unless explicitly stated otherwise, all measurements

were conducted at room temperature (25 °C). First, the indium ring was electrochemically lithiated to form the In/InLi reference electrode, by connecting it to the working electrode cable and applying a bias of – 0.2 V vs. the In/InLi counter electrode until 15 at% lithium in the In/InLi reference electrode was achieved. Subsequently, the NMC811 working electrode was delithiated at 0.3 mA cm^{-2} with a constant potential hold at 3.578 V vs In/InLi (4.2 V vs Li^+/Li) until a capacity of 120 mAh g_{NMC}^{-1} (for the cells at an open-circuit potential of 3.8 V vs Li^+/Li) or a capacity of 185 mAh g_{NMC}^{-1} (for the cells at an open-circuit potential of 4.1 V vs Li^+/Li) was reached. Then, the cells were rested at open-circuit condition, with potentiostatic electrochemical impedance spectroscopy measurements carried out from 1 MHz to 5 mHz with 10 mV amplitude every 2 hours. The impedance spectra were fitted using the impedance.py python module using the data points from 60 kHz to 5 mHz.[2] For the argyrodite-based electrodes, a single R/CPE element was sufficient to obtain a good fit to the impedance spectra. For the hydroborate-based electrodes, two R/CPE elements are fitted, because a single element was insufficient to obtain a good fit.

References

1. H. Braun, C. Bürgel, E. Quérel, A. Remhof and C. Battaglia, *EES Batteries*, 2026, **2**, 597–608.
2. M. D. Murbach, B. Gerwe, N. Dawson-Elli and L.-K. Tsui, *Journal of Open Source Software*, 2020, **5**, 2349.