Supporting information

The Interplay between (Electro)chemical and (Chemo)mechanical Effects in the Cycling Performance of Thiophosphate-based Solid-State Batteries

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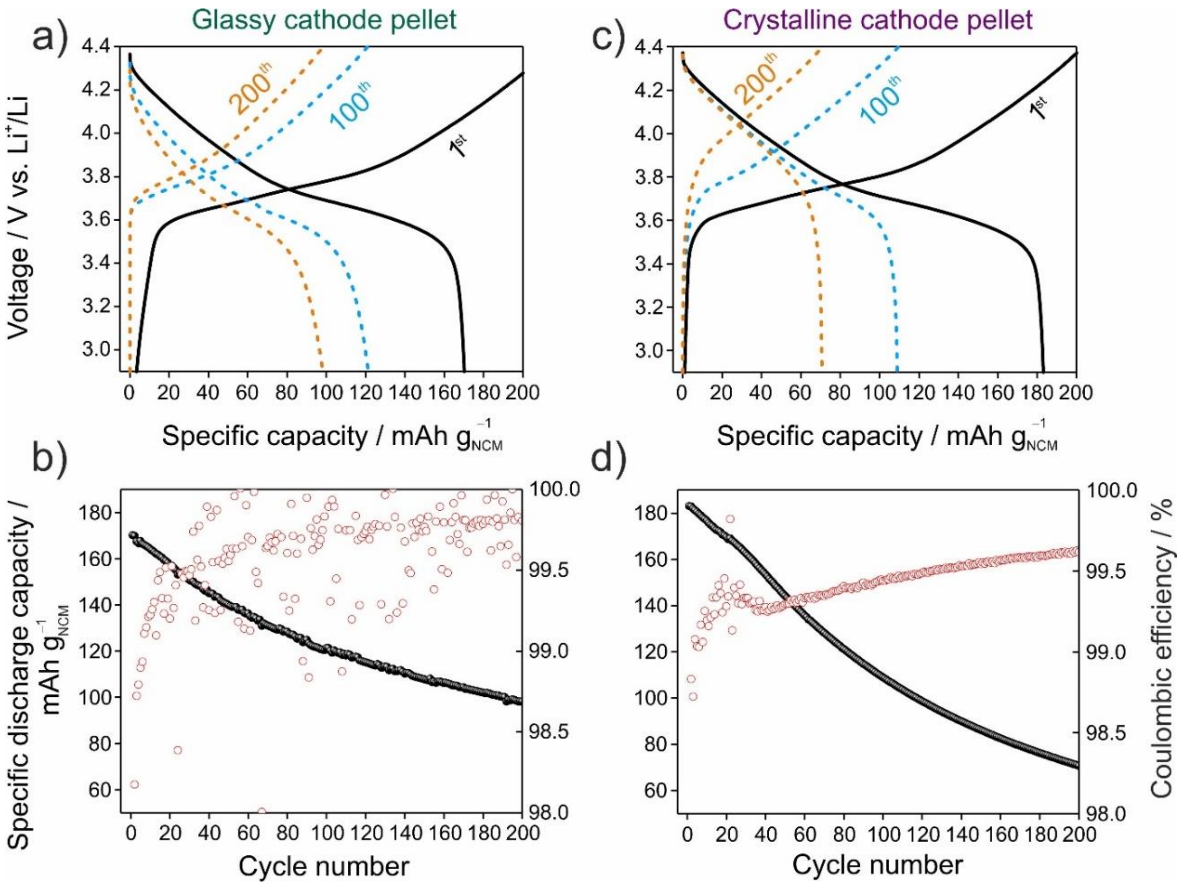

Figure S1. Representative 1st, 100th, and 200th cycle charge/discharge curves at a rate of C/5 and 45 °C of pelletized SSB cells with (a) glassy SE ($1.5Li_2S$-$0.5P_2S_5$-LiI) and (c) crystalline SE (Li_6PS_5Cl) and (b, d) corresponding specific discharge capacities and Coulombic efficiencies over 200 cycles.

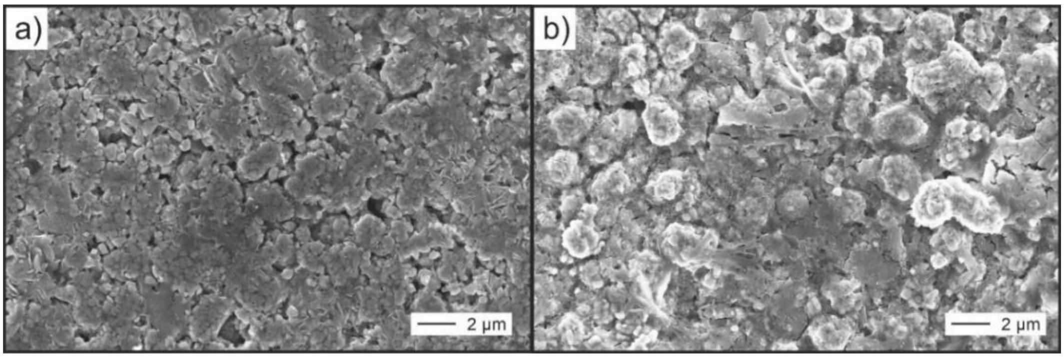

Figure S2. Top-view SEM images of the cathode of SSB cells in (a) pelletized and (b) slurry-cast setups.

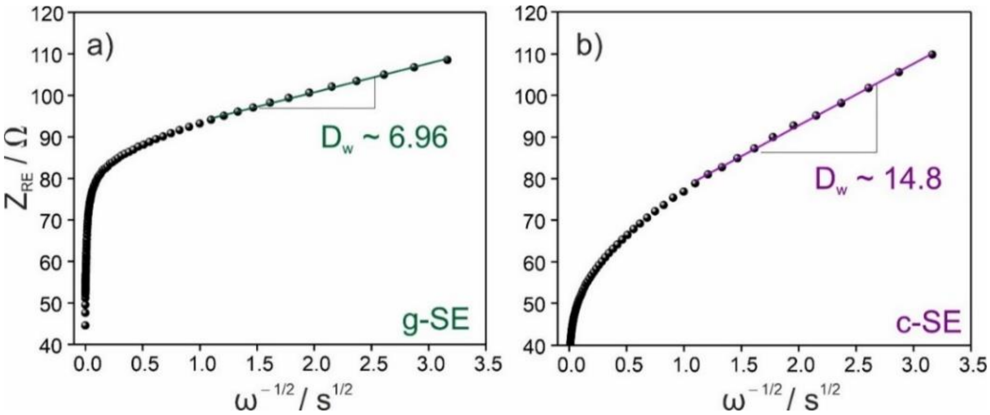

Figure S3. The real part of impedance data plotted versus the (frequency)$^{-1/2}$ and corresponding linear fit at low frequencies for (a) the g-SE cell and (b) the c-SE cell after 200 cycles at a rate of C/5 and 45 °C.

The following equations correlate the Warburg coefficient to the contact area at the CAM/SE interface:[1-3]

$$Z_{\mathrm{RE}}(\omega) = R_{\mathrm{SE}} + R_{\mathrm{CT}} + D_{\mathrm{W}} \cdot \frac{1}{\sqrt{\omega}} \qquad (\textbf{Eq. S1}),$$

with $Z_{\mathrm{RE}}(\omega)$ being the real part of the impedance, R_{SE} the SE bulk resistance, R_{CT} the charge-transfer resistance, D_{W} the Warburg coefficient, and ω the frequency.

$$D_{\mathrm{w}} = \frac{RT}{n^2F^2A\sqrt{2}}\left(\frac{1}{c_{\mathrm{i}}\sqrt{D_{\mathrm{i}}}}\right) \qquad (\textbf{Eq. S2})$$

R is the gas constant, *T* the absolute temperature, *n* the number of electrons exchanged in the redox process, *F* the Faraday constant, *A* the contact area, D_i the lithium-diffusion coefficient in the bulk electrode material, and c_i represents the concentration of lithium ions in the bulk electrode material.

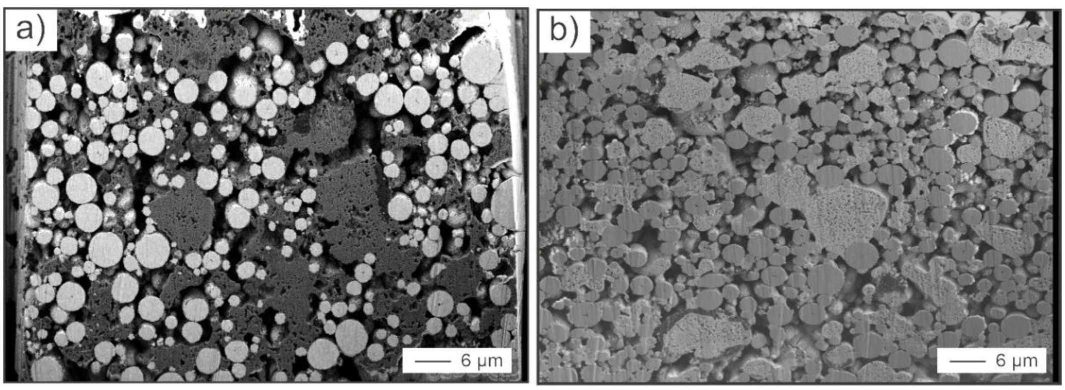

Figure S4. Cross-sectional FIB-SEM slice images of slurry-cast cathodes with (a) glassy SE ($1.5Li_2S$-$0.5P_2S_5$-LiI) and (b) crystalline SE (Li_6PS_5Cl). Note that the cathode was not cold-pressed prior to the measurement. More pores within the SE particles are observed for the c-SE cell than the g-SE cell. Panel (a) shows a backscattered electron image and panel (b) is a secondary electron image.

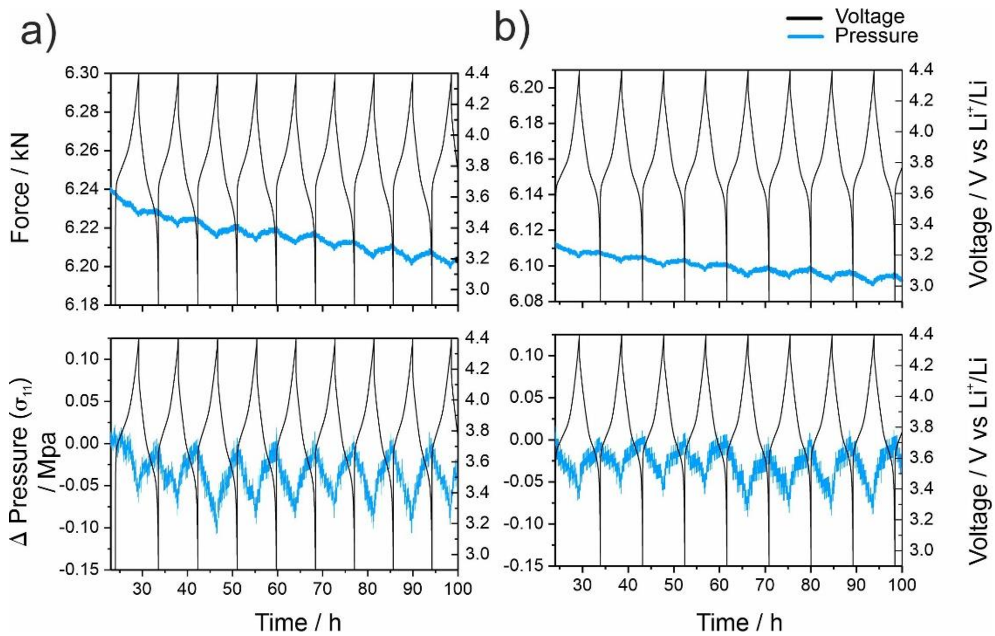

Figure S5. Raw data of the uniaxial force of slurry-cast cathodes with (a) glassy SE ($1.5Li_2S$-$0.5P_2S_5$-LiI) and (b) crystalline SE (Li_6PS_5Cl) recorded during cycling and the corresponding change in uniaxial stress (σ_{11}) after baseline correction. SSB cells tested at 45 °C, C/5, 2.9-4.4 V vs Li^+/Li.

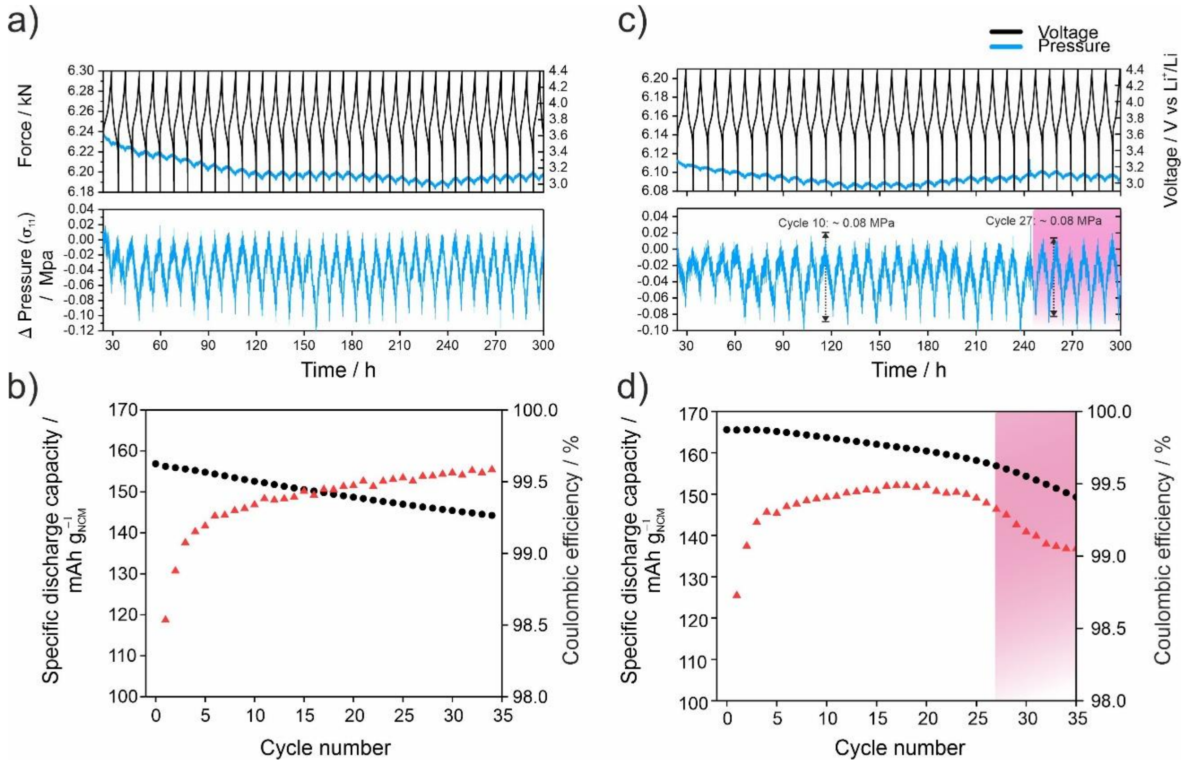

Figure S6. Force and pressure response during cycling of slurry-cast cathodes with (a) glassy SE ($1.5Li_2S$-$0.5P_2S_5$-LiI) and (c) crystalline SE (Li_6PS_5Cl) and (b, d) corresponding specific discharge capacities and Coulombic efficiencies over 35 cycles. SSB cells tested at 45 °C, C/5, 2.9-4.4 V vs Li^+/Li.

Electrochemical decomposition of Li_2CO_3 impurities:

$$2Li_2CO_3 \rightarrow 4Li^+ + 4e^- + 2CO_2 \uparrow + O_2 \uparrow \qquad (\textbf{Eq. S3})$$

References

[1] Wang S, Zhang W, Chen X, Das D, Reuss R, Gautam A, Walther F, Ohno S, Koerver R, Zhang Q, Zeier W G, F H Richter, Nan C-W and Janek J. 2021 *Adv. Energy Mater*. **11** 2100654.

[2] Wang P-P, Xu C-Y, Li W-D, Wang L and Zhen L. 2015 *Electrochim. Acta* **169** 440-446.

[3] Xiao P, Lv T, Chen X and Chang C. 2017 *Sci. Rep.* **7** 1408.