Electronic Supplementary Information (ESI)

Investigations into the Superionic Glass Phase of Li_4PS_4I for Improving Stability of High-Loading All-Solid-State Batteries

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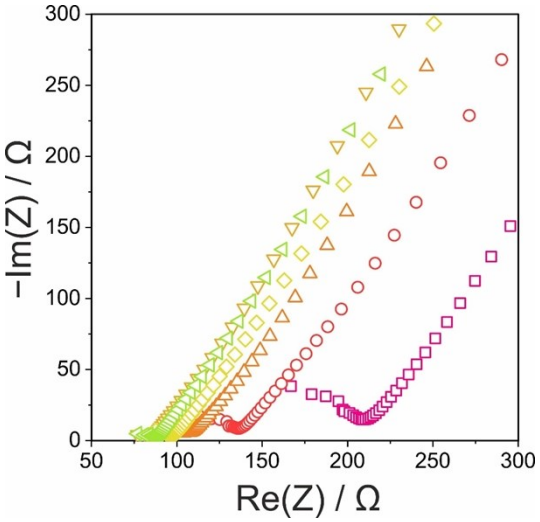

Fig. S1 Nyquist plots of the electrochemical impedance (at 25 °C) for the precursor mixture after different milling times ranging from 7 to 12 h (color scheme as in Fig. 1).

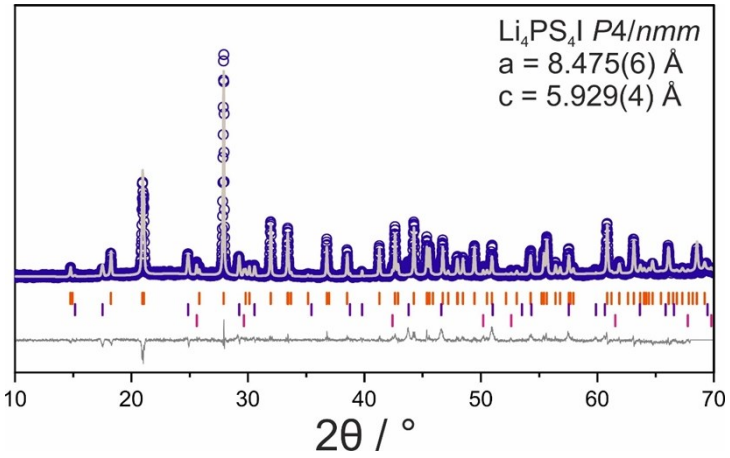

Fig. S2 Rietveld plot for the PXRD refinement of the glassy $1.5Li_2S$-$0.5P_2S_5$-LiI (obtained after 12 h ball-milling) annealed for 12 h at 250 °C. Blue circles and gray lines represent the measured, calculated and difference profiles, respectively. Bragg reflections for Li_4PS_4I (*P*4/*nmm* space group), Li_6PS_5I (*F*–43*m* space group) and LiI (*Fm*–3*m* space group) are denoted by orange, purple and pink vertical lines (tick marks), respectively. An average (primary) crystallite size of 390 nm was calculated for Li_4PS_4I.

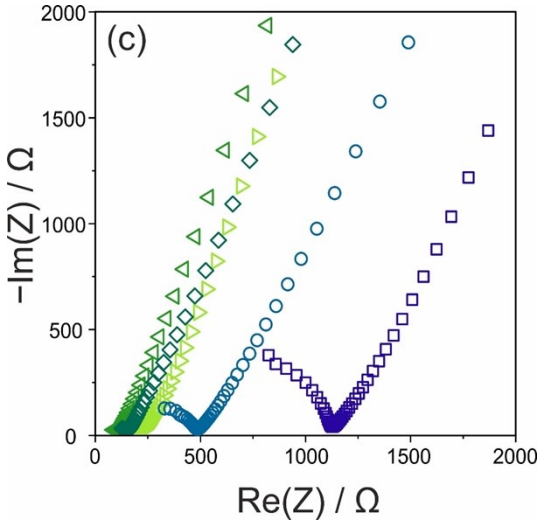

Fig. S3 Nyquist plots of the electrochemical impedance (at 25 °C) for the glassy $1.5Li_2S$-$0.5P_2S_5$-LiI (obtained after 12 h ball-milling) after annealing for 12 h at different temperatures ranging from 155 to 250 °C (color scheme as in Fig. 2).

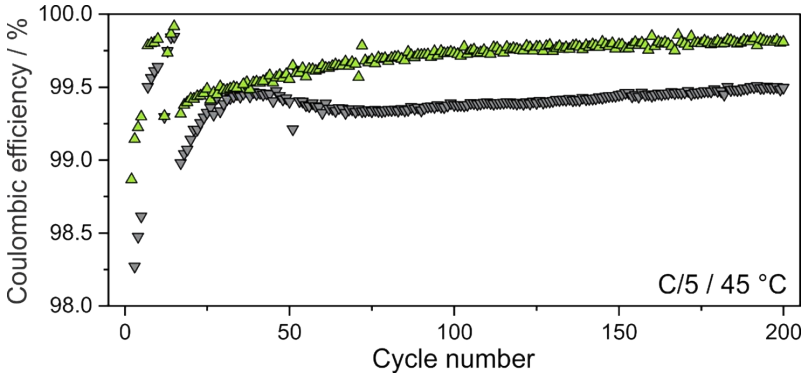

Fig. S4 Coulombic efficiency of SSB cells using the glassy $1.5Li_2S$-$0.5P_2S_5$-LiI or Li_6PS_5Cl solid electrolyte (color scheme as in Fig. 3). After rate performance testing (five cycles each at C/5, C/2, and 1C), the cycling was continued at C/5 and 45 °C in the voltage range between 1.35 and 2.85 V versus $Li_4Ti_5O_{12}$/$Li_7Ti_5O_{12}$.

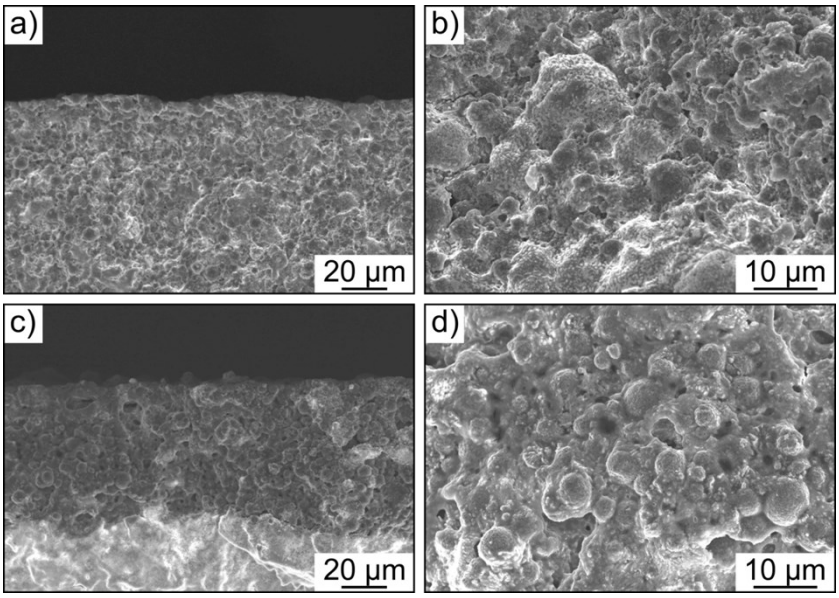

Fig. S5 Cross-sectional SEM images at different magnifications of the cathode layer of SSB cells using the glassy $1.5Li_2S$-$0.5P_2S_5$-LiI solid electrolyte (a, b) before and (c, d) after 200 cycles.

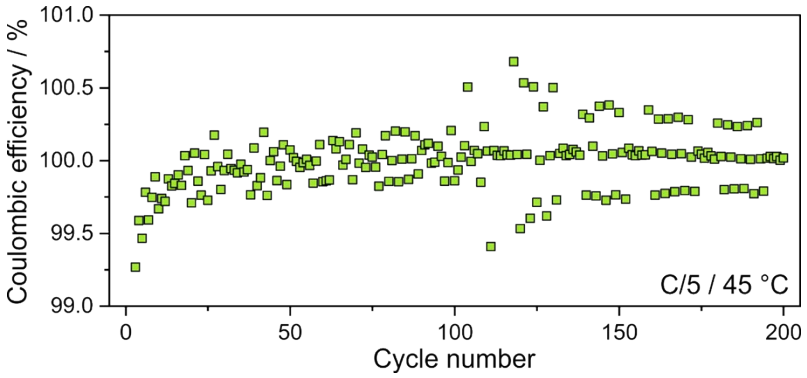

Fig. S6 Coulombic efficiency of a high-loading SSB cell with slurry-cast cathode and the glassy $1.5Li_2S$-$0.5P_2S_5$-LiI solid electrolyte cycled at C/5 rate and 45 °C in the voltage range between 1.35 and 2.85 V versus $Li_4Ti_5O_{12}/Li_7Ti_5O_{12}$.