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Pressure Effects on Sulfide Electrolytes for All Solid-State Batteries

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Supplementary information

Material & Methods

All materials synthesis, testing and processing was conducted in an Argon-filled glovebox (mBraun MB 200B and LC Technology LC-180) with O_2 and H_2O levels below 0.5 ppm.

Synthesis

Argyrodite Li_6PS_5Cl was bought from NEI Corporation (USA) and used as-is, without further purification. Lithium Indium (Li-In) alloy was prepared from stabilized lithium nano powder (FMC) and indium powder (Sigma Aldrich, 99.99%) by mixing with a vortex mixer until homogenized. The NCA cathode ($LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$, Toda Chemicals) was coated with amorphous $LiNbO_3$ (LNO – 2 wt. %) with a wet chemical method: NCA powder was first stirred for one hour in an ethanol solution containing Li and Nb ethoxide (both from Sigma Aldrich). Then, the solvent was dried in a rotary evaporator, before heat treatment in air at 450 °C for one hour in a box furnace (Lindberg Blue M).

Pressure monitoring and control

To allow control of the stack pressure during EIS measurement and cycling, the solid-state electrolyte pellets and batteries were placed in the cell holder described in the Figure 1. A 1-ton load cell mounted at the bottom of the holder allows direct measurement of the uniaxial stack pressure applied to the cell. The load cell was calibrated with a 100 kN Instron 5982 Universal Testing System mechanical testing frame, by applying a load equivalent to 100% of the load cell capacity. The accuracy and linearity of the load cell response was then controlled over the whole range of the load cell, i.e. between 0 and 125 MPa.

Electrochemical measurements

The electrolyte pellets were prepared using a 10 mm custom-made polyether ether ketone (PEEK) die mold and titanium plungers: 70 mg of the electrolyte powder was pressed at the fabrication pressure (50, 150, 250 or 370 MPa as specified in the main text) for 3 minutes with a hydraulic press. Then, the titanium plungers were used as current collectors while the pellet was measured at a varying stack pressure. To study the effect of the current collector material, around 3 mg of acetylene black was added on both side of the pellet and pressed at the fabrication pressure before remeasuring the conductivity of the pellet. The ionic conductivity of the electrolyte

pellets was evaluated by electrochemical impedance spectroscopy (EIS) using a Solartron 1260 Impedance Analyzer, with a 10 mV excitation potential between 1 MHz and 1 Hz. Each EIS measurement has been repeated on 4 different samples and the average value is reported with the standard deviation as error bars.

All solid-state batteries were made in the same die mold, with the same mass of electrolyte powder. On the cathode side, 12 mg of LNO-coated NCA/Li_6PS_5Cl/Acetylene black composite (11:16:1) was added and pressed at the fabrication pressure. Then, on the anode side, 40 mg of Li-In alloy was added, covered with a 10 mm diameter copper foil, and pressed at 150 MPa (for cells made with a fabrication pressure of 150, 250 and 370 MPa) or 50 MPa (for cells made at a fabrication pressure of 50 MPa). Cells were cycled at a rate of C/10 for the cycling stability study and at C/5, C/2, C and 2C for the rate performance study, between 2.5 and 4.25 V vs. Li/Li^+. All cells were cycled using Neware CT-4008 cyclers.

Focused Ion Beam (FIB) and 3D reconstruction

Focused Ion Beam (FIB) – Scanning Electron Microscopy (SEM) (FEI Scios DualBeam FIB/SEM) was applied at room temperature to explore the morphology of the cross-section and bulk structure of Li_6PS_5Cl electrolyte with different fabrication pressures. To prepare cross-sectional images, samples were rough milled (around 50 µm*50 µm) with a cross-sectional cut (30 kV, 5 nA) followed by a cleaning cut (30 kV, 0.5 nA). To further explore the 3D bulk structure, a 10 µm by 4 µm Pt protective layer with a 500 nm thickness was deposited on the top of electrolyte pellet, to protect the sample from the ion beam. Then, the left and right sides around the Pt layer were milled out to define the acquisition region. Finally, cross-sectional images were sequentially collected while continuously milling through the defined area (10 µm*8 µm*4 µm). 40 slices (100 nm thickness for each slice) were acquired (**Figure S2)**. The FIB milling current used was 0.5 nA at 30 kV and the SEM imaging current was 0.1 nA at 5 kV. Using Amira-Avizo software, these images were segmented to generate a 3D reconstruction model.

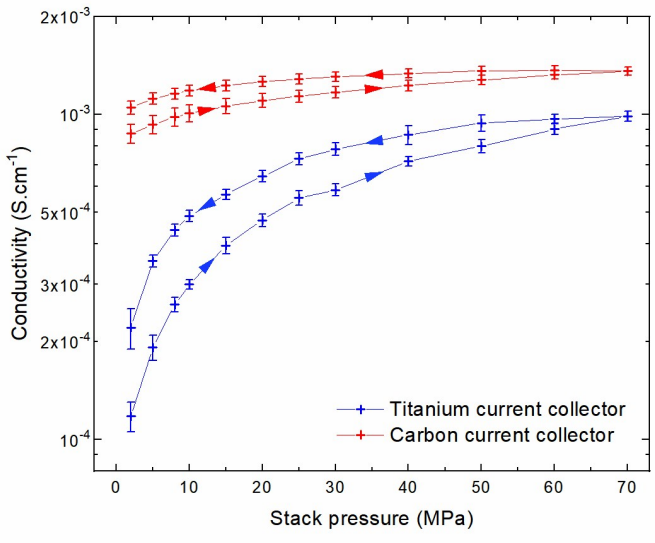

Figure S1. *Ionic conductivity of $Li_7P_3S_{11}$ with increasing and subsequent decreasing of stack pressure, using titanium plungers or pressed carbon powder as electrodes. Error bars represent the standard deviation on 4 samples.*

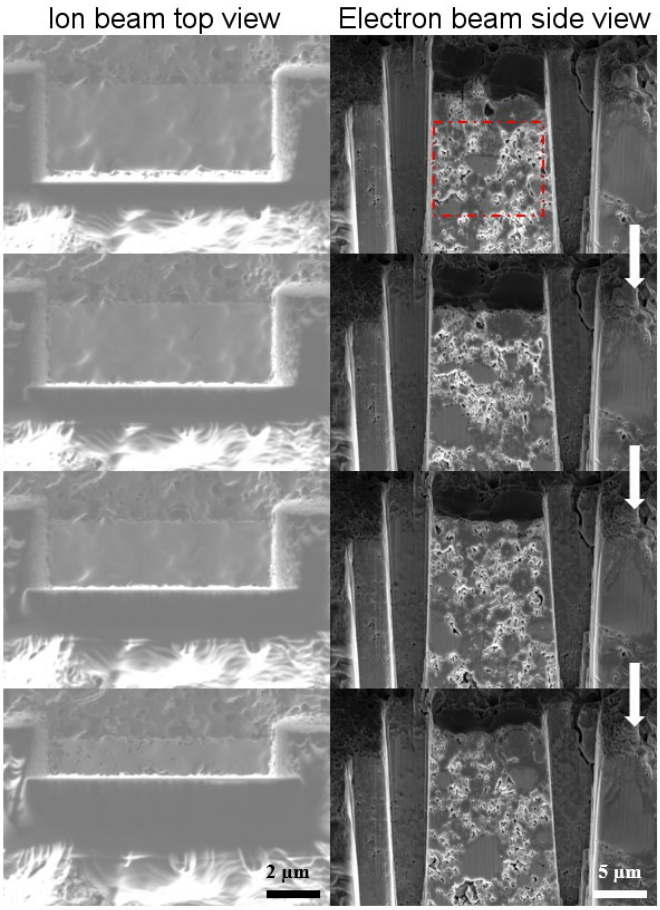

Figure S2. *Continuous FIB milling of Li_6PS_5Cl with 50 MPa fabrication pressure. 40 slices were milled with a step size of 100 nm. The ion beam image is on the left and the electron beam image is on the right. The reconstruction area is labeled by the red dashed box.*

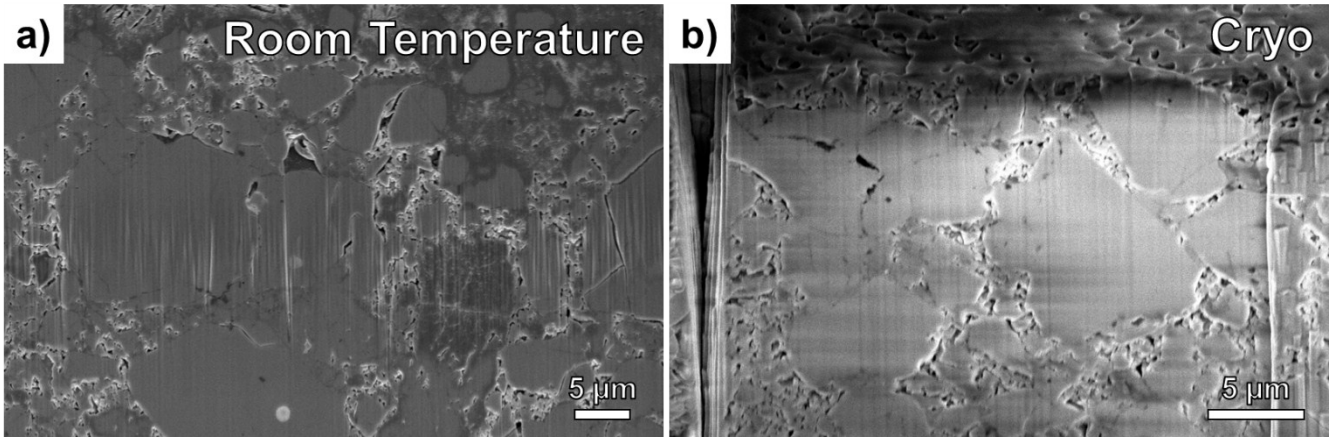

Figure S3. *FIB cross-section of a Li_6PS_5Cl electrolyte pellet made at a fabrication pressure of 370 MPa. The FIB milling process was performed at a) Room temperature and b) under cryogenic conditions. The*

similar morphology indicates that no degradation of the electrolyte by beam damage was observed when ion milling at room temperature.

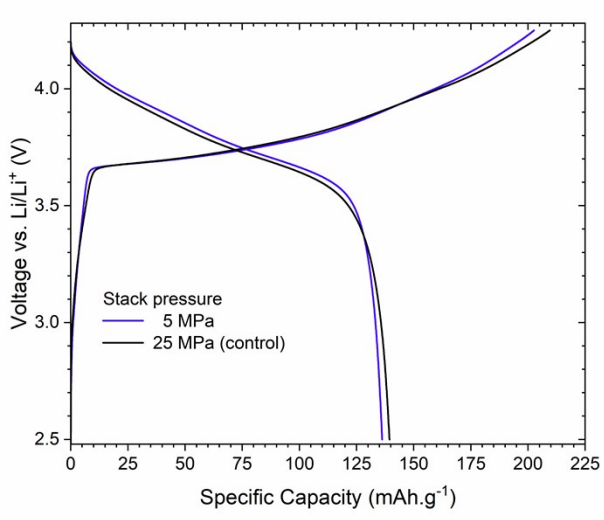

Figure S4. *First voltage profile of the cells shown on Figure 2b, cycled at stack pressure of 5 and 25 MPa.*

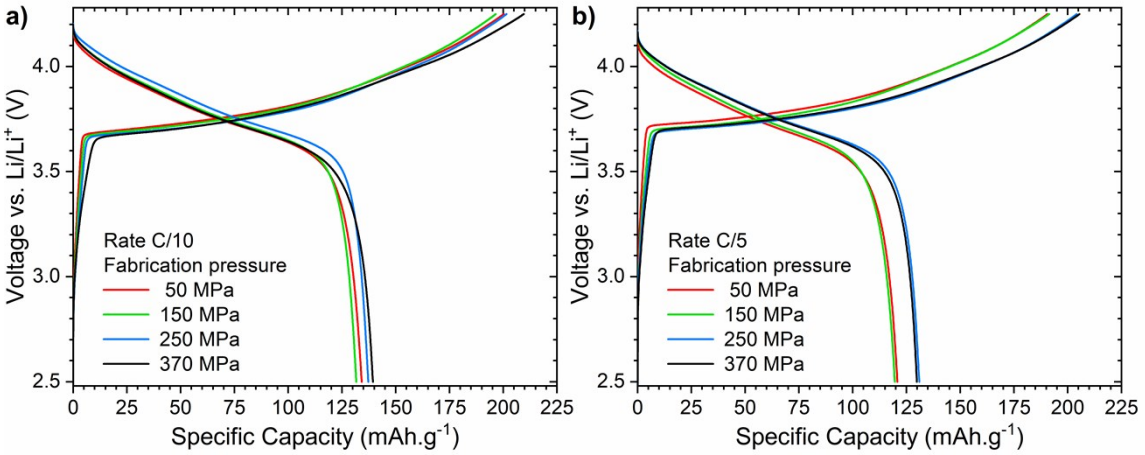

Figure S5. *First voltage profiles of ASSBs made at fabrication pressure of 50, 150, 250 and 350 MPa at a rate of a) C/10 and b) C/5.*

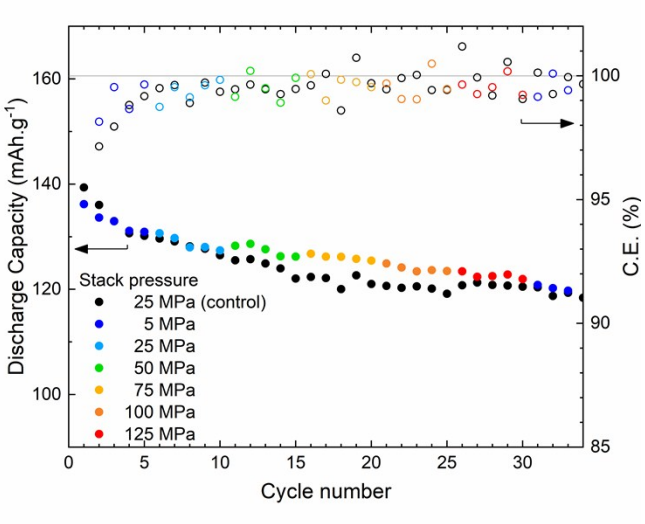

Figure S6. *Effect of stack pressure on the cycling stability (at room temperature) of LiIn | LPSCl | NCA solid-state batteries. Axis scales have been increased to allow to see small differences. First cycle Coulombic efficiencies were 66.5% (25 MPa, control) and 67.2% (5 MPa).*

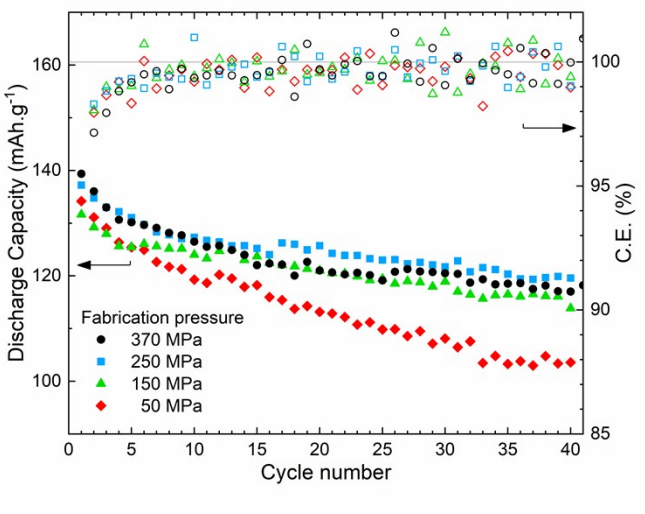

Figure S7. *Room temperature cycling stability at C/10 as a function of the fabrication pressure of LiIn | LPSCl | NCA solid-state batteries. Axis scales have been increased to allow to see small differences. First cycle Coulombic efficiencies were respectively 67.0%, 67.0%, 68.1% and 66.5% at fabrication pressures of 50, 150, 250 and 370 MPa.*