Supporting Information

Unraveling the Reversible Redox Mechanism of Li_6PS_5Cl Solid Electrolyte in All-Solid-State Lithium-Sulfur Batteries

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Experimental Section

1. Solid electrolyte synthesis

Li_6PS_5Cl (LPSCl) solid electrolyte is prepared based on the method reported by Shuo Wang et al.[1] The LPSCl is synthesized by ball milling and annealing method in argon (Ar) gas atmosphere using Li_2S (Sigma-Aldrich, 99.98%), LiCl (Sigma-Aldrich, 99%) and P_2S_5 (Sigma-Aldrich, 99%) powders with a molar ratio of 5:2:1, respectively. The powders prepared based on 9 g are mixed by ball milling at 450 rpm for 60 hours (20 min run, 40 min pause) with zirconia balls using a planetary mill apparatus (Fritsch Pulverisette 5, premium line). The ball-to-powder ratio is 130 and the diameter of zirconia ball used is 10 mm. After that, the mixture is annealed for 5 hours in a quartz tube at 550 ℃. The temperature of furnace is raised for 260 minutes at a rate of 2 ℃/min from room temperature to 550 ℃ and then maintained for 5 hours. After slowly cooling at room temperature, the synthetic powder is pulverized using mortar and sieve to control the particle size. The entire processes are carried out in conditions where atmospheric exposure is thoroughly prevented.

2. LPSCl-based composite cathode (LPSCl-C)

LPSCl is mixed with multi-wall carbon nanotube (MWCNT) in a weight ratio of 4:1 by ball milling at 250 rpm for 6.5 hours (30 min run, 10 min pause) with zirconia balls (diameter, 10 mm) using a planetary mill apparatus (Fritsch Pulverisette 7). The mixture is prepared based on 0.5 g and the ball milling process is performed under Ar gas atmosphere.

3. Sulfur-based composite cathode (S-C)

Commercialized sulfur-based materials such as sulfur (S_8), lithium sulfide (Li_2S) and mixture ($S_8 + Li_2S$) are adopted as cathode active materials. Cryo-milling method is employed to control the particle size uniformly. The sulfur-based cathode active material is mixed with multiwall carbon nanotube (MWCNT) in a weight ratio of 3:2 by ball milling at 250 rpm for 6.5 hours (30 min run, 10 min pause) with zirconia balls (diameter, 10 mm) using a planetary mill apparatus (Fritsch Pulverisette 7). Thereafter, the compound is mixed with LPSCl in a weight ratio of 1:1 by ball milling at 300 rpm for 1 hour (30 min run, 10 min pause). The total mixture is prepared based on 0.5 g and the entire ball milling processes are conducted under Ar gas atmosphere.

4. All-solid-state lithium-sulfur (ASSLS) cell manufacture

The pellets for the ASSLS cells are created by the cold-press method under Ar gas atmosphere (Glove box). First, 140 mg of LPSCl powder is pressed with 4 tons for 30 seconds to form an intermediate solid electrolyte layer. Second, 6 mg of composite cathode powder is applied to one side of the solid electrolyte pellet and pressed with 4 tons for 30 seconds. Lastly, 60 mg of Li-In alloy powder or Li metal foil is added on the other side of the pellet and pressed with 2 tons for 3 seconds. The finished pellet has a diameter of 15 mm and a thickness of less than about 800 μm.

Material Characterization

X-ray diffraction (XRD) patterns are recorded on the R-AXIS IV++, Rigaku, with Mo-Kα radiation (wavelength of 0.7107 Å). The materials for XRD measurement are placed in a quartz tube and sealed using vacuum grease under Ar atmosphere to minimize the risk of atmospheric exposure. The spectra are converted into Cu-Kα radiation (wavelength of 1.5418 Å) for easy comparison with existing literatures. Electrochemical measurement is conducted on a multichannel battery tester (Maccor version 4000) and the cyclic voltammogram (CV) curves

are obtained using a biologic potentiostat/galvanostat model VMP3 (Biolab, Inc.). X-ray photoelectron spectroscopy (XPS) measurement is performed using PHI 5000 Versa probe (Ulvac-PHI) equipment with a monochromator of Al-Kα (1486.6 eV). *In-situ* XRD measurement is carried out at the 6D bend-magnet X-ray beamline at Pohang Light Source (PLS). For this experiment, ASSLS cells are manufactured using cell parts with holes in order to X-ray beam to penetrate, and the holes are sealed with the polyimide film under Ar atmosphere to avoid damage caused by atmospheric exposure. Among the X-ray absorption spectroscopy (XAS) analysis results, K-edge spectra are acquired from 16A1 bend-magnet tender X-ray beamline at Taiwan Light Source (TLS), and L-edge spectra are obtained at the 10D bend-magnet X-ray beamline at Pohang Light Source (PLS).

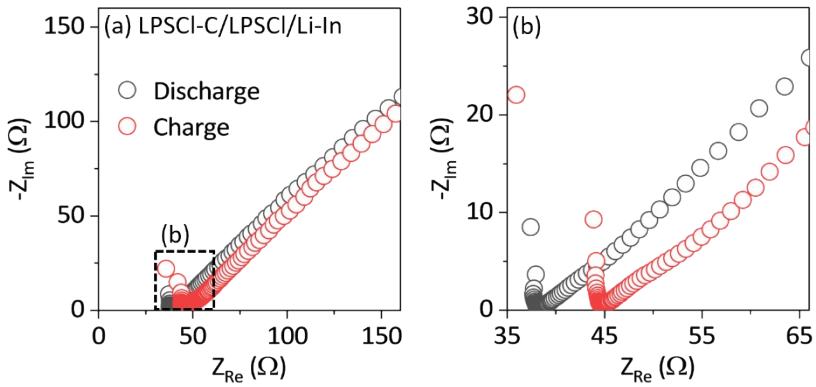

Fig. S1 Cell impedance measurement results of the LPSCl-C/LPSCl/Li-In configuration. (a) The impedance spectra of the cell after first discharge and charge. (b) The magnifying impedance spectra of the dashed region in (a).

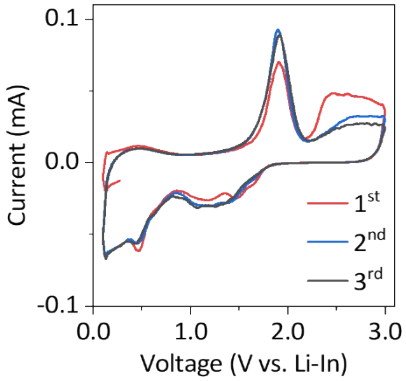

Fig. S2 Cyclic voltammogram curves at initial cycling (50 μV/s) of the LPSCl-C/LPSCl/Li-In cell.

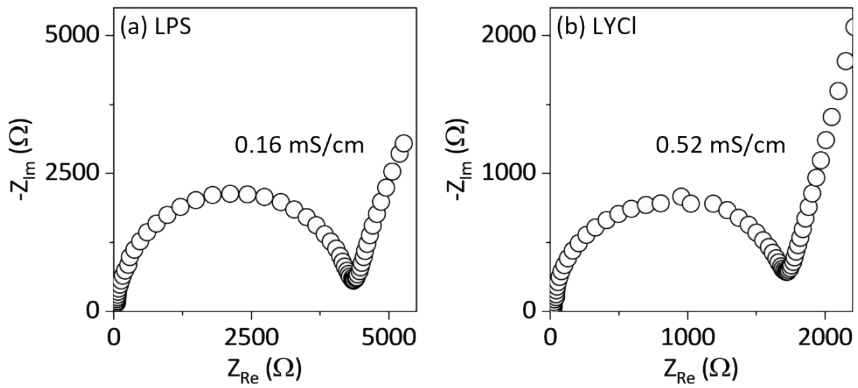

Fig. S3 Nyquist plots with ion conductivities of (a) Li_3PS_4 (LPS) and (b) Li_3YCl_6 (LYCl) solid electrolytes.

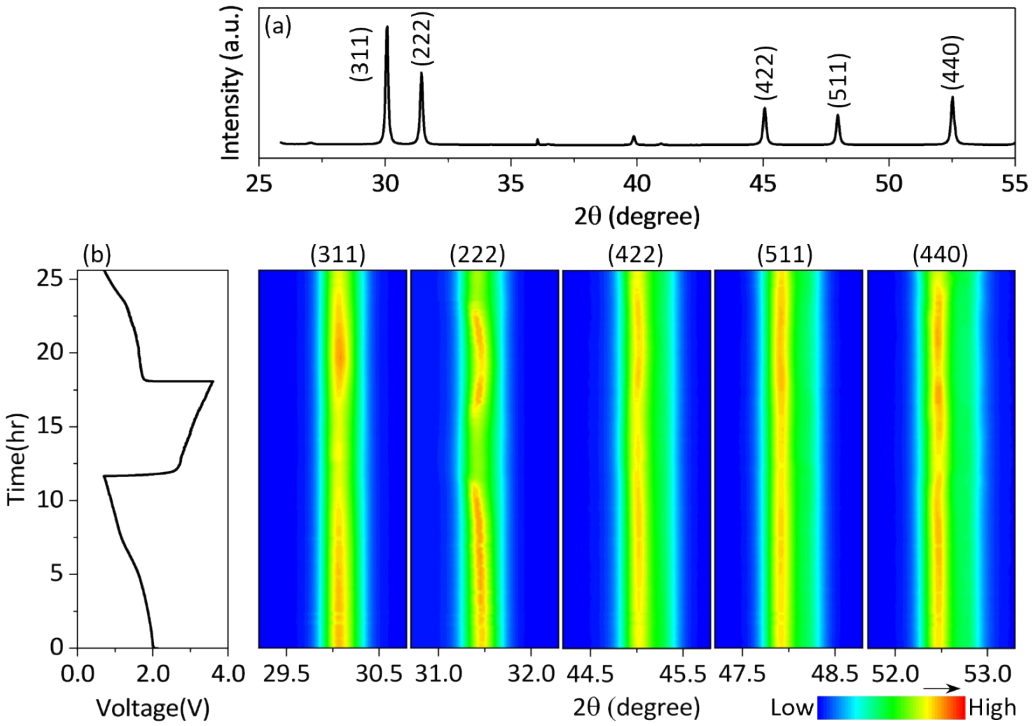

Fig. S4 (a) The XRD patterns of LPSCl in the ASSLS cell (S-C/LPSCl/Li-metal). (b) *In-situ* XRD measurement result of the ASSLS cell (S-C/LPSCl/Li-metal) during initial cycling and contour plots of the (311), (222), (422), (511), (440) diffraction peaks of LPSCl.

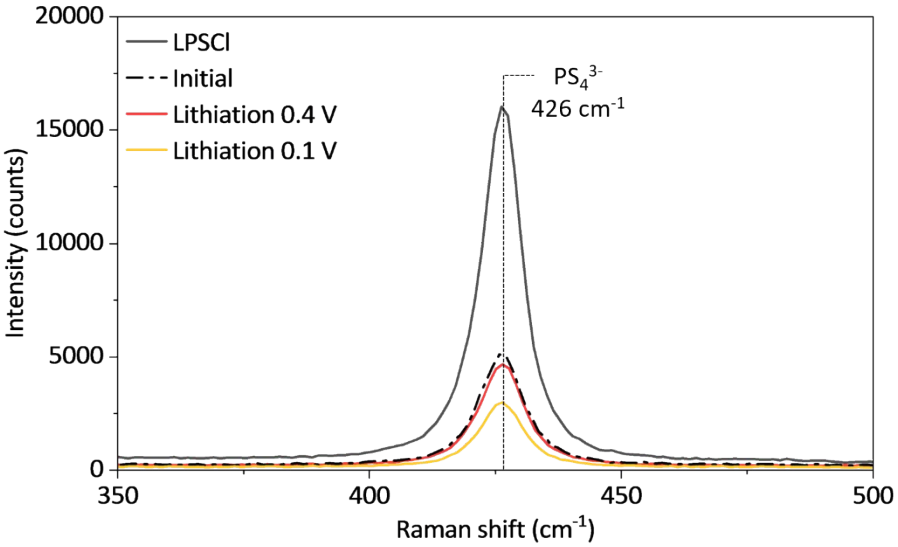

Fig. S5 Raman spectra of LPSCl and sulfur-based composite cathodes of the ASSLS cell (S-C/LPSCl/Li-In) during initial discharge.

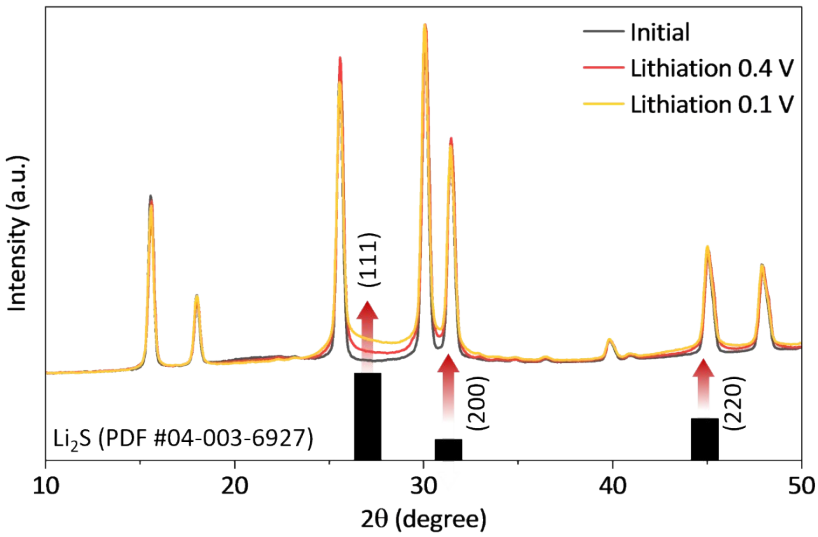

Fig. S6 *Ex-situ* XRD measurement results of the LPSCl-based composite cathodes (LPSCl-C/LPSCl/Li-In) during initial discharge and the standard powder diffraction file (PDF) patterns of the Li_2S pristine material.

Reference

1. S. Wang, Y. Zhang, X. Zhang, T. Liu, Y.-H. Lin, Y. Shen, L. Li and C.-W. Nan, *ACS applied materials & interfaces*, 2018, **10**, 42279-42285.