

Supporting Information

**Multi-step charging/discharging protocol enables stable cycling for lithium
argyrodite-based all solid-state lithium batteries**

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Experimental Procedures

1 Synthesis of lithium argyrodite electrolyte

Argyrodite sulfide solid electrolyte was prepared via a mechanical ball milling technique and subsequent heat treatment process. Reagent-grade P_2S_5 (99%, Aladdin), Li_2S (99.9%, Aladdin), $LiCl$ (99%, Aladdin) crystalline powders were used as starting materials. The required amount of each starting material was calculated based on the composition $Li_{7-x}PS_{6-x}Cl_x$ ($x=1.0, 1.3, 1.5, 1.7$) and then sealed in ZrO_2 pot containing 50 ZrO_2 balls with a diameter of 5 mm and 20 ZrO_2 balls with a diameter of 10 mm in an Argon filled glovebox ($H_2O, O_2 < 0.01$ ppm) due to the oxygen- and moisture-sensitive of the raw materials. The total weight of the starting mixture was almost 5.0 g. The sealed pot was rotated at a speed of 500 r/min for 10 h with a planetary ball mill. Then the electrolyte precursor was annealed at 460 °C for 10 h, and finally the $Li_{7-x}PS_{6-x}Cl_x$ was obtained.

2 Materials characterization

XRD measurements of the $Li_{7-x}PS_{6-x}Cl_x$ electrolyte were carried out using Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å, RIGAKU D/MAX 2550/PC) from 10° to 80°. SEM and EDS mapping images were obtained with a Hitachi S-8100 scanning electron microscope. XPS was performed using a Thermo Scientific K-Alpha Spectrometer with a monochromatic Al $K\alpha$ source.

3 Electrochemical measurements

The ionic conductivity of $Li_{7-x}PS_{6-x}Cl_x$ was tested with a Biologic VSP-300 electrochemical workstation from 0.1 Hz to 7 MHz at 25 °C. Solid electrolyte powders were positioned between two stainless steel cylinders of the mold and pressed into electrolyte sheets under a pressure of 300 MPa. Formula 1 was utilized to calculate the ionic conductivity (σ). R denotes the resistance value, L is the thickness of the electrolyte sheets, and S is the area of the electrolyte sheets. The activation energy (E_a) was calculated using the Formula 2, where σ denotes the ionic conductivity, A refers to the prefactor, T stands for the absolute temperature, and kB represents the Boltzmann constant. Formula 3 was used to calculate the electronic conductivity (σ), with Δd represents the thickness of the electrolyte sheet, S represents the area of the electrolyte sheet, U is the polarization voltage, and I represents the steady-state current.

$$\sigma = L/(R \cdot S) \quad (1)$$

$$\sigma = A/T \cdot e^{-E_a/kBT} \quad (2)$$

$$\sigma = \Delta d/U/(I \cdot S) \quad (3)$$

To evaluate the electrochemical stability of the LPSCl_x, LPSCl_x and VGCF were mixed at a weight ratio of 9:1 and manually ground in an agate mortar for 15 min. CV measurement was performed on a LPSCl+VGCF/LPSCl/Li cell under a pressure of 300 MPa using a Biologic VSP-300 at a scan rate of 0.5 mV s⁻¹ from 2.1 to -0.1 V at room temperature.

For symmetric Li/Li cells, 150 mg of solid electrolyte powder was pressed under 500 MPa, and two pieces of treated lithium foil with a diameter of 12 mm were applied to both sides of the pellet. For all-solid-state NMC/Li cells, a composite cathode consisting of NMC811, solid electrolyte, and vapor-grown carbon fibers (VGCF) at a weight ratio of 75: 25: 2 was prepared by mixing in an agate mortar. The mixed cathode powder, with a loading of 5~6 mg cm⁻², was then pressed onto one side of the electrolyte pellet under 400 MPa, with the treated lithium foil pressed against the other side. Long-term lithium plating/stripping tests of Li/Li cells at different current densities were conducted using a LAND battery test system at 50 °C, and all-solid-state NMC/Li cells were tested from 2.8 to 4.2 V at 30 or 50 °C with 10 MPa stack pressure.

4 Figures and Tables

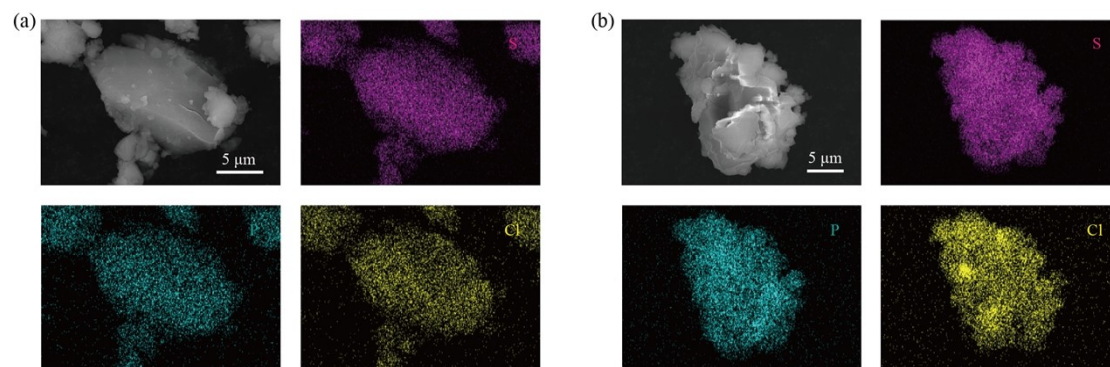


Figure S1. SEM and EDS of (a) LPSC11.0, (b) LPSC11.5 power.

Table S1 Crystallographic data of LPSC11.0 obtained from Rietveld refinement.

Atom	Wyckoff site	x	y	z
Li	48h	0.3187	0.0268	0.6813
Cl	4a	0	0	1
S1	4c	0.25	0.25	0.75
P	4b	0	0	0.5
S2	16e	0.1196	-0.1425	0.6196

Table S2 Cell parameters of LPSC11.0 obtained from Rietveld refinement.

x	y	z
9.8526 (17)	9.8526 (17)	9.8526 (17)

Table S3 Crystallographic data of LPSC11.5 obtained from Rietveld refinement.

Atom	Wyckoff site	x	y	z
Li1	48h	0.3313	0.0076	0.6687
Li2	24g	0	0	0
Cl1	4a	0	0	0
Cl2	4c	0.5	0.5	0.5
S1	4c	0.25	0.25	0.75
P	4b	0	0	0.5
S2	16e	0.1195	-0.1195	0.6195

Table S4 Cell parameters of LPSC11.5 obtained from Rietveld refinement.

x	y	z
9.7833 (16)	9.7833 (16)	9.7833 (16)

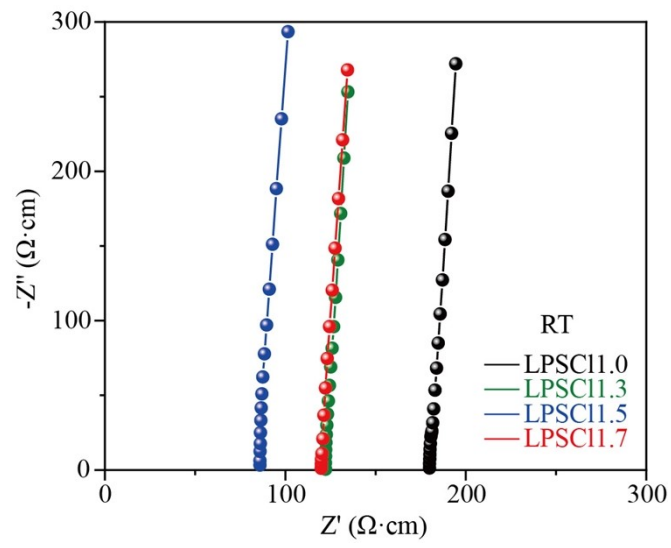


Figure S2. The impedance plots of the $\text{Li}_{7-x}\text{PS}_{6-x}\text{Cl}_x$ ($x = 1.0, 1.3, 1.5, \text{ and } 1.7$).

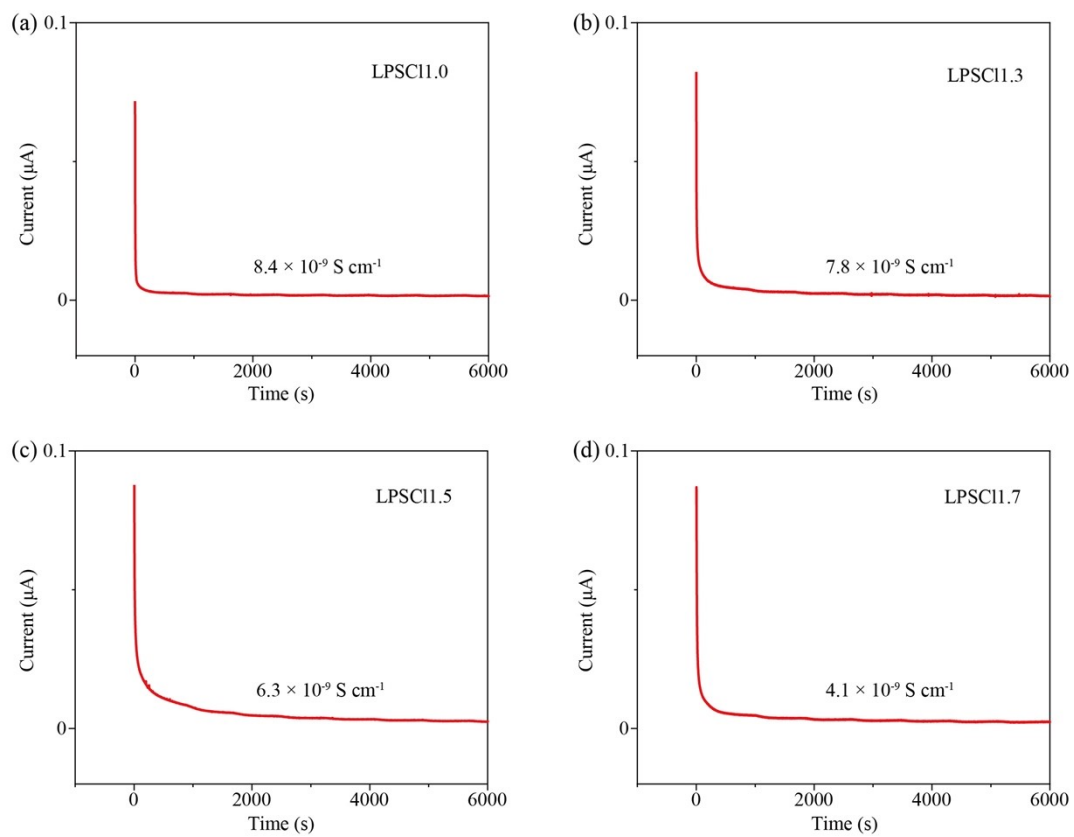


Figure S3. Current–time curve of the $\text{Li}_{7-x}\text{PS}_{6-x}\text{Cl}_x$ ($x = 1.0, 1.3, 1.5, \text{ and } 1.7$) sandwiched between two pieces of stainless steel.

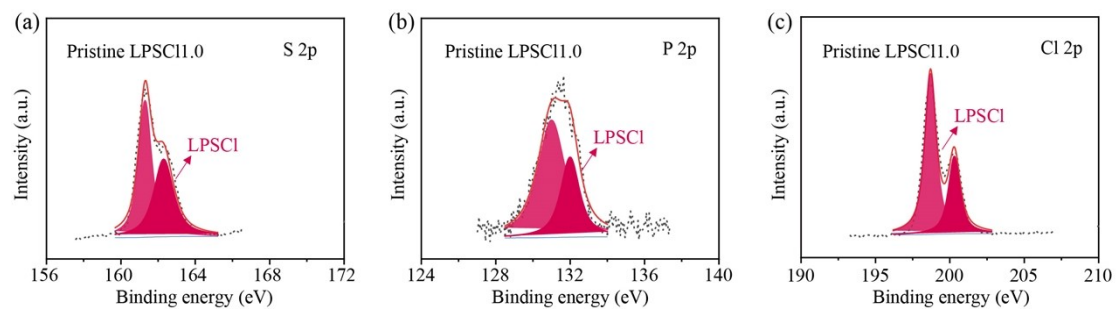


Figure S4. XPS spectra of pristine LPSC11.0.

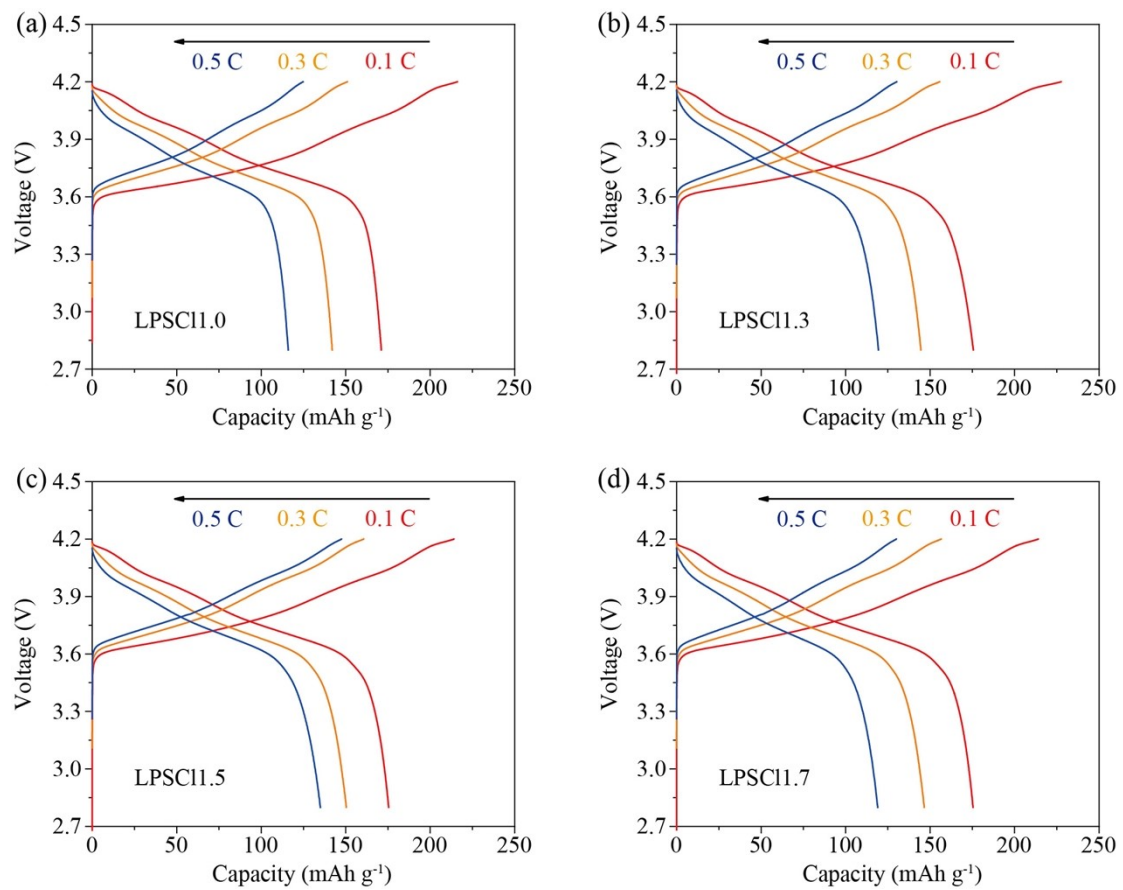


Figure S5 Charge–discharge curves at different rates of the $\text{Li}_{7-x}\text{PS}_{6-x}\text{Cl}_x$ (x = 1.0, 1.3, 1.5, and 1.7).

Table S5 Test matrix with different charging/discharging protocols.

	2.8–3.6 V	3.6–3.9 V	3.9–4.2 V	4.2–4.0 V	4.0–3.5 V	3.5–2.8 V
CCCD	0.3 C	0.3 C	0.3 C	0.3 C	0.3 C	0.3 C
MCCCD	0.3 C	0.5 C	0.2 C	0.3 C	0.5 C	0.2 C

Table S6 The total time of charging/discharging of MCCCCD and CCCD protocols in the 5th cycle (ICE > 99.9%).

	charging	discharging	total
CCCD	3.1 h	3.1 h	6.2 h
MCCCCD	2.6 h	2.4 h	5.0 h