

A “Solo-Solvent *de novo* Liquid-Phase” Method for Synthesizing Sulfide Solid Electrolyte $\text{Li}_6\text{PS}_5\text{Cl}$

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1. Experimental Details

Materials: Molecular sieves (4Å, Shanghai Ailan) were activated in a muffle furnace at 400°C for 12 hours before use. Tetrahydropyrrole (Anhydrous, 99%), tetrahydrothiophene (Anhydrous, 99%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd and were dried by refluxing in the presence of sodium and benzophenone, then distilled out after the solution turned dark blue.

Li foil (99.9%, Alfa Aesar), In foil (99.9%, Alfa Aesar), LiCl (Shanghai Aladdin, 99.9%), P_2S_5 (LuoEn, 99.9%), and Li_2S (Shanghai Aladdin, 99.9%) were used as received. The anhydrous Na_2S powder was obtained by heating the raw material $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$ (Tianjin Damao, 99.5%) under vacuum at 90 °C for 2 h and then at 220 °C for 4 h. $\text{LiNi}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$ (NCM721) is provided by Guilin Electrical Equipment Scientific Research Institute Co., Ltd.

*Synthesis of $\text{Li}_6\text{PS}_5\text{Cl}$ by the “Solo-Solvent *de novo* Liquid-Phase” method:* Three precursors of LiCl, Na_2S and P_2S_5 at the molar ratio of 12:5:1+x ($x = 0 - 0.2$) together with 30 mL of tetrahydropyrrole were added into a PTFE lined stainless steel reactor. The reactor was heated at 140 °C under stirring for 3 hours, and then cooled naturally. Next, the suspension mixture was transferred into a centrifuge tube and centrifugated for 6 minutes at 10,000 rpm to remove the solid byproduct. Then, the supernatant was heated by a rotovap at 130°C for 5 h to obtain a dry powder. Last, the collected powder was heated at 550°C for 5 h under argon to produce the targeted electrolyte $\text{Li}_6\text{PS}_5\text{Cl}$.

Materials Characterization: The X-ray diffraction (XRD) was carried out on an X-ray diffractometer (Rigaku Smartlab9KW, Japan), which uses Cu K_α radiation ($\lambda = 0.15406$ nm) as the X-ray source. To prepare the XRD samples, a small amount of sample powder was spread onto an XRD substrate, which was covered with a dome-like polyimide film. The scanning 2θ -angle was typically 10 – 80° with the rate at 15°/min. Scanning electron microscope (FEI Apreo S LoVac, Czech) was employed to measure sample morphologies. The X-ray photoelectron spectrometer

(ESCALAB 250Xi, English) was used to reveal the materials identities and the elemental oxidation states therein. Before taking XPS spectra, sample surfaces were bombarded with Ar⁺-ions to etch off about 50-nm top layer. Raman spectra were collected on a Raman spectroscopy (Renishaw, inVin reflex, English), whose laser power is 8 mW and laser wavelength is 785 nm.

To measure the ionic conductivity of Li₆PS₅Cl, 130 mg of sample powder was first placed in a polyaldehyde mold and then pressed into a pellet under a pressure of 360 MPa. The thickness of electrolyte pellet was measured by a vernier caliper; and the cross-sectional area was set as 1 cm. Next, the mold was fastened with screws, which were isolated from the stainless-steel rods through Teflon (or polyaldehyde) washers. Next, a sealed box holding the assembled electrolyte set was put inside a thermostatic oven whose temperature was controlled at 30°C. An electrochemical workstation (CHI 660E) was employed to measure the electrochemical impedance spectra (EIS), using the alternating voltage of 10 mV in amplitude and 1 - 10⁶ Hz in frequency. The ionic conductivity (σ) was calculated according to the equation of $\sigma = d/AR$, where d was the pellet thickness, A was the pellet cross-section area and R was the pellet resistance read from the EIS. Afterwards, the electronic conductivity was measured via chronoamperometry with the direct voltage (V) of 1 V and the recording duration of 35000 s. The finally steady current (I) was plugged into the equation of $\sigma = dI/AV$, to calculate out the electronic conductivity.

To assess the battery performance of Li₆PS₅Cl, all solid-state lithium batteries in full-cell configuration was used, with the assembling procedure as follows. First, 70 mg of Li₆PS₅Cl powder was placed into a polyaldehyde mode and pressed under 360 MPa for 10 seconds. Then, another portion of Li₆PS₅Cl powder together with NCM721 in a mass ratio of 7:3 was manually ground together for 5 minutes to obtain a composite cathode mixture. Next, 40 mg of the composite cathode mixture (corresponding to a mass loading of 9 mg/cm²) was spread on one side of the electrolyte pellet and pressed under 360 MPa for 20 seconds. On the other side of the pellet, a piece of indium foil (aladdin, 99.99%, $\phi = 10$ mm, $d = 0.1$ mm) was attached. Afterwards, 1 mg of Li foil (aladdin, 99.9%) was pressed into a thin layer (around 5 mm diameter) and placed over the indium foil. Subsequently, all the components were compressed together under 360 MPa, and an ASSLB for tests would be ready after the mold was tightened with metal screws. For the cyclability tests, galvanostatic charging/discharging process was performed at 60 °C on LAND battery analyzers by using 0.2 C rate for the first three cycles and then using 1 C rate for the rest cycles. The charging/discharging voltage was 2.10 - 3.78 V.

2. Additional Results and Discussion

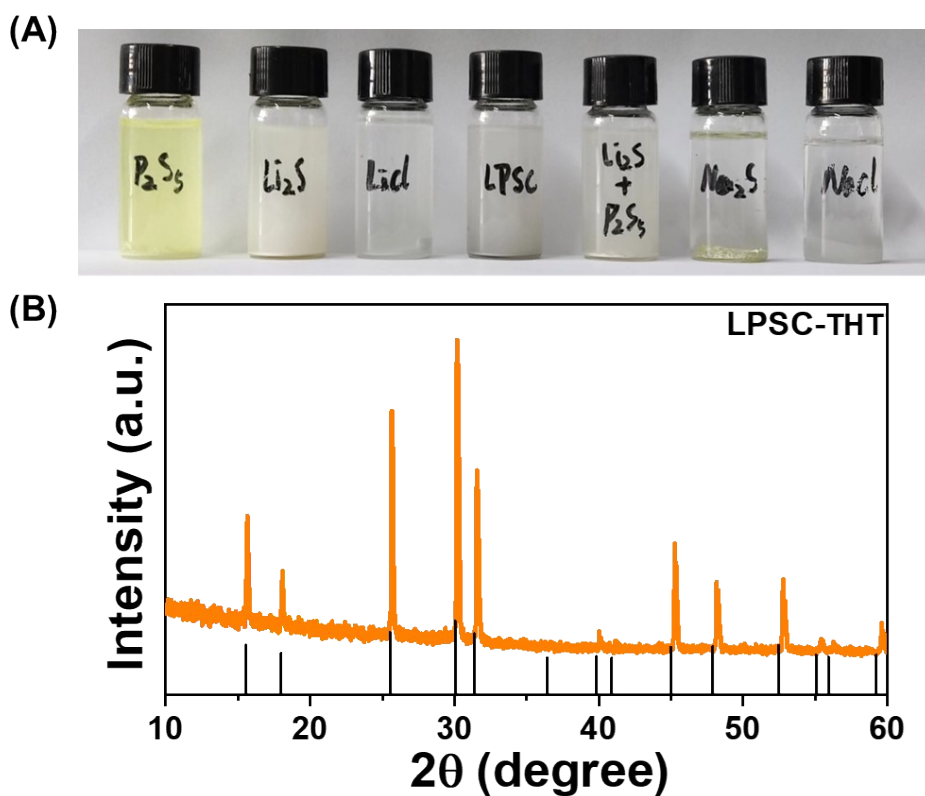


Fig. S1. (A) Optical images showing the solubility tests for some chemicals in THT. (B) XRD data for LPSC prepared with THT as the solvent.

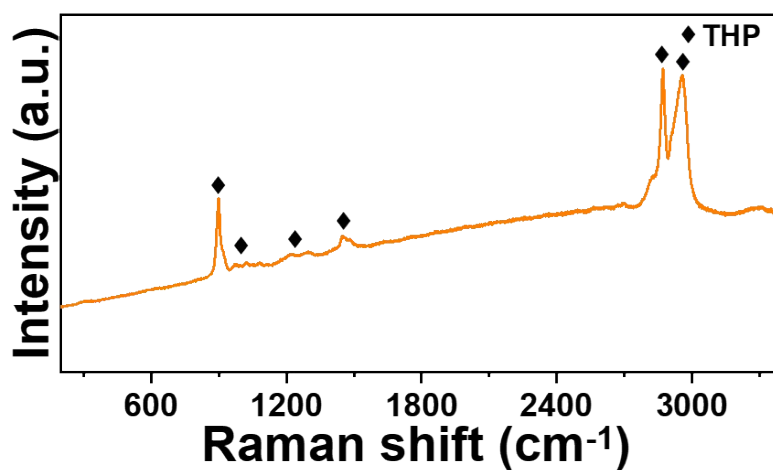


Fig. S2. Raman spectrum of the reaction solution after the solvothermal process for synthesizing LPSC.

Fig. S3 illustrates the typical synthesis procedure of the developed SoSo-*dn*-LiP method. A brief description for making $\text{Li}_6\text{PS}_5\text{Cl}$ is elaborated below. Firstly, the needed precursors of LiCl , Na_2S and P_2S_5 together with an appropriate amount of THP are added into a solvothermal jar made of Teflon. Secondly, the jar is sealed inside a stainless coat and then

put in a metal-beads bath to conduct the solvothermal reaction at 140°C for 3 h. Thirdly, the turbid reaction mixture is centrifuged (or filtrated) to collect the liquid-phase solution and separate off the solid byproduct NaCl. Fourthly, the solution is heated on a rotary evaporator to remove the solvent THP under vacuum for collecting the precipitate. Fifthly, the collected solid is calcined under Ar at 550°C for 5 h, producing the targeted material LPSC to be characterized and assessed later. The typical production yield was 76.6%.

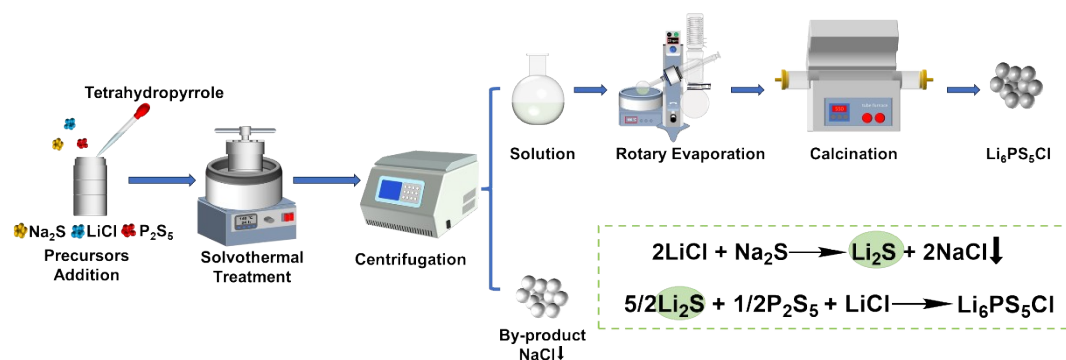


Fig. S3. The conceptual flowchart for the synthetic procedure of the SoSo-dn-LiP method.

The EDS mappings of LPSC- $X\%$ P₂S₅ all show that the spatial distributions of strong signals for P, S and Cl elements are consistent with the SEM images (**Fig. S5 – S8**). In addition, tiny amounts of Na are also detected in the range of 0.22 - 0.60 atom% for LPSC- $X\%$ P₂S₅ samples, as shown by the EDS spectra in **Fig. S5 – S8**. Then, the LPSC-20%P₂S₅ sample is selected as a representative for ion chromatography to quantify the proportion of Na, which is found to be 0.62%, consistent with the EDS result. Correspondingly, the mass fraction of NaCl impurity in the sample is 0.93%, matching well with the Rietveld-refinement result.

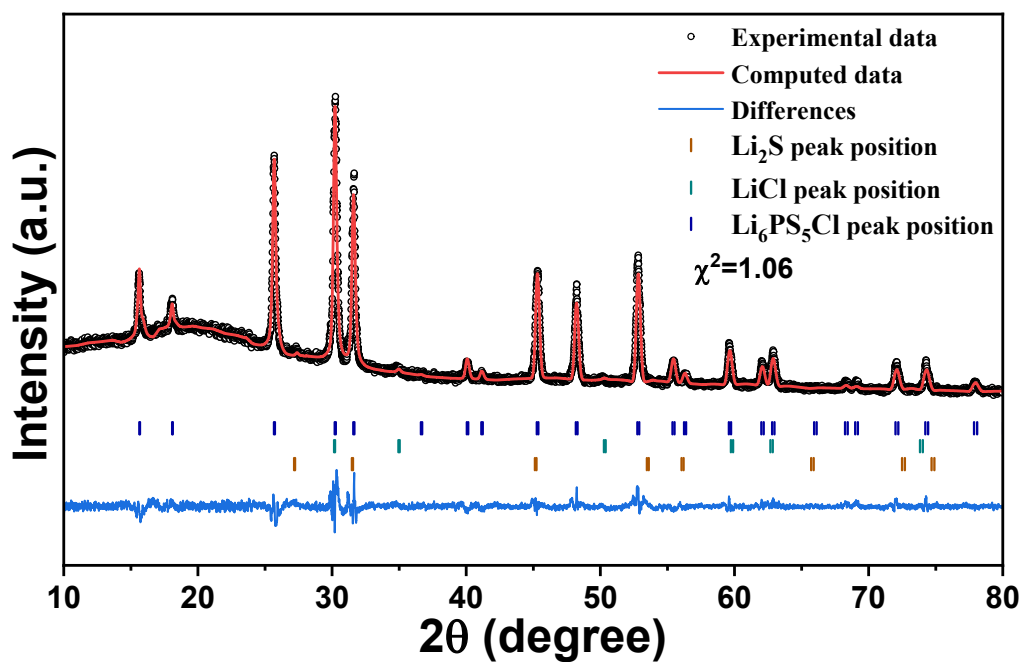


Fig. S4. XRD Rietveld refinement results of LPSC-20% P₂S₅.

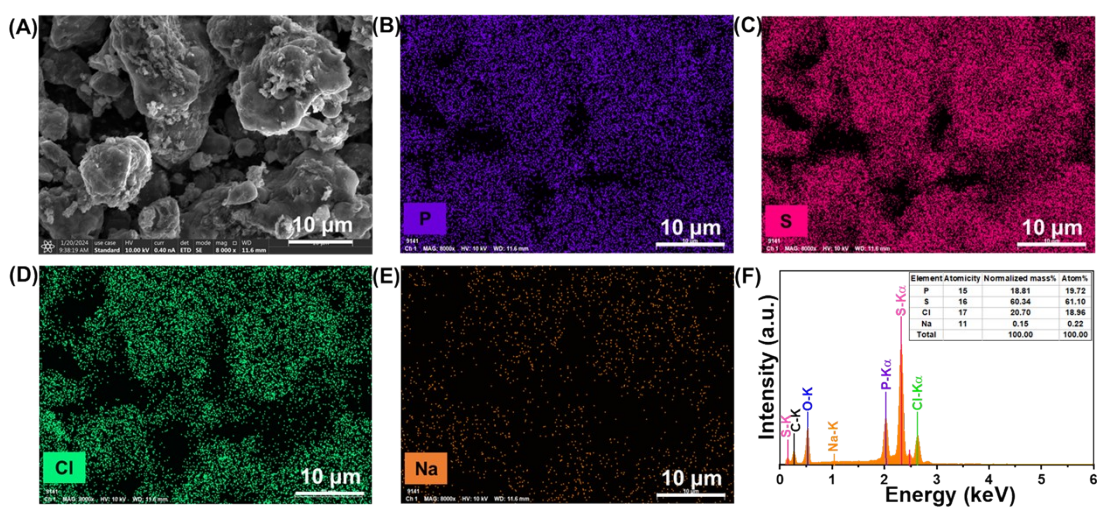


Fig. S5. SEM image (A), EDS mappings (B-E) and EDS spectrum (F) of LPSC-0%P₂S₅.

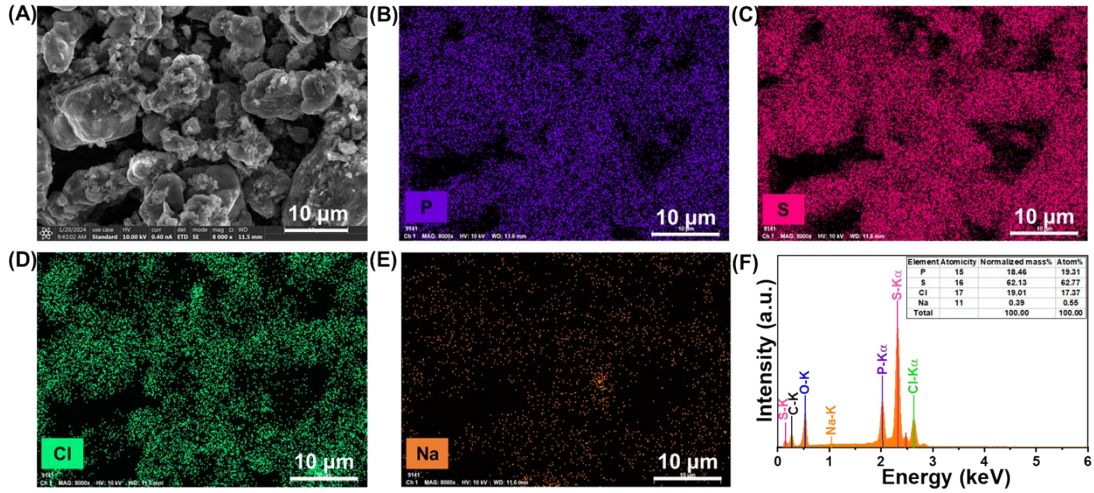


Fig. S6. SEM image (A), EDS mappings (B-E) and EDS spectrum (F) of LPSC-10%P₂S₅.

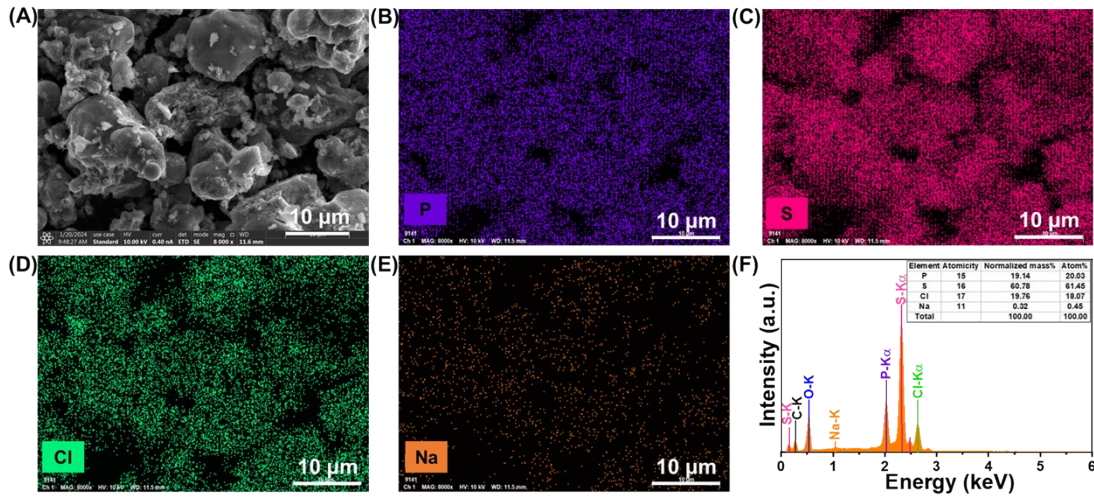


Fig. S7. SEM image (A), EDS mappings (B-E) and EDS spectrum (F) of LPSC-15%P₂S₅.

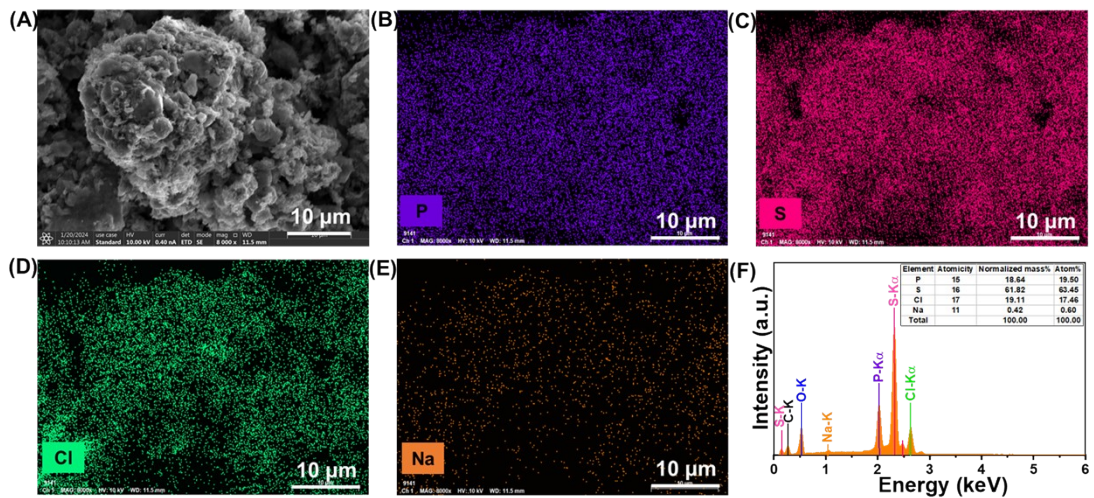


Fig. S8. SEM image (A), EDS mappings (B-E) and EDS spectrum (F) of LPSC-20% P₂S₅.

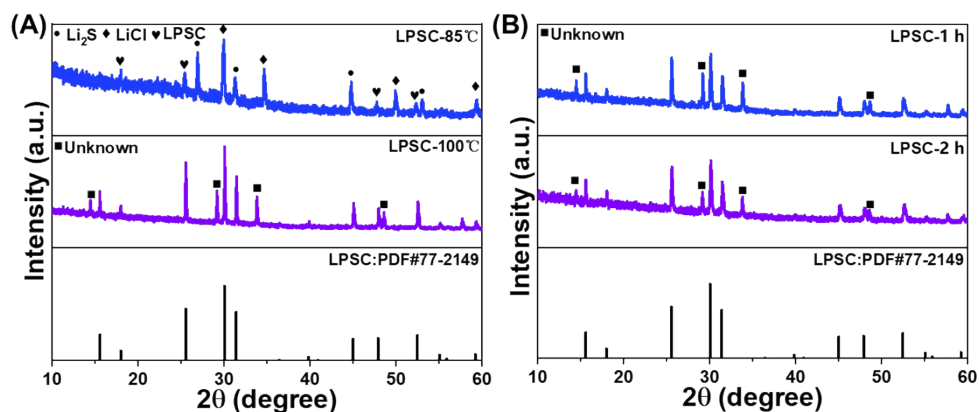


Fig. S9. XRD pattern of LPSC prepared by decreasing the solvothermal temperature (A) and shortening the solvothermal duration (B).

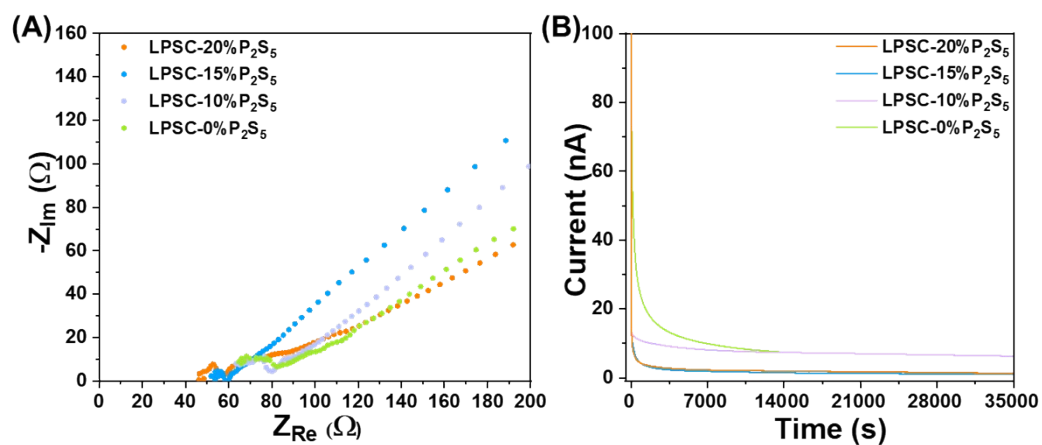


Fig. S10. (A) The electrochemical impedance spectra for extracting ionic conductivity (σ_{Li^+}) and (B) The chronoamperometric curves for extracting electronic conductivity (σ_e) of LPSC-X%P₂S₅.

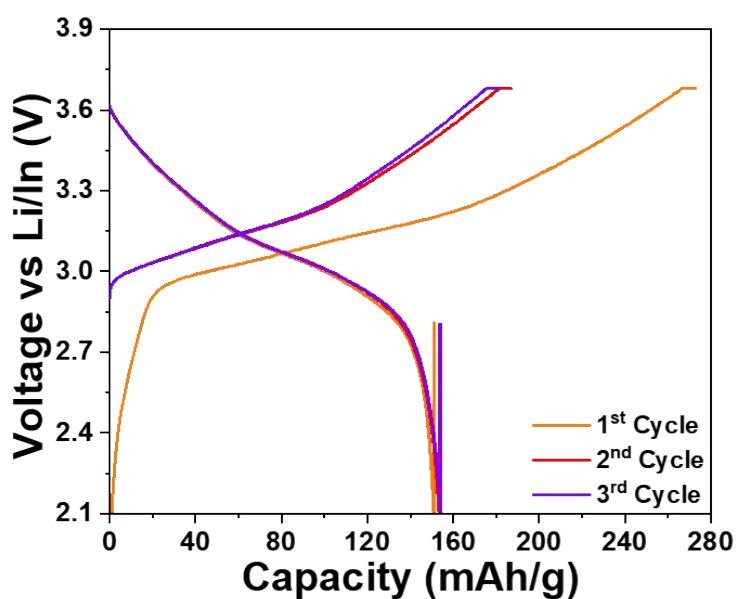


Fig. S11. Voltage - capacity profiles of an all-solid-state battery assembled from the synthesized-LPSC.

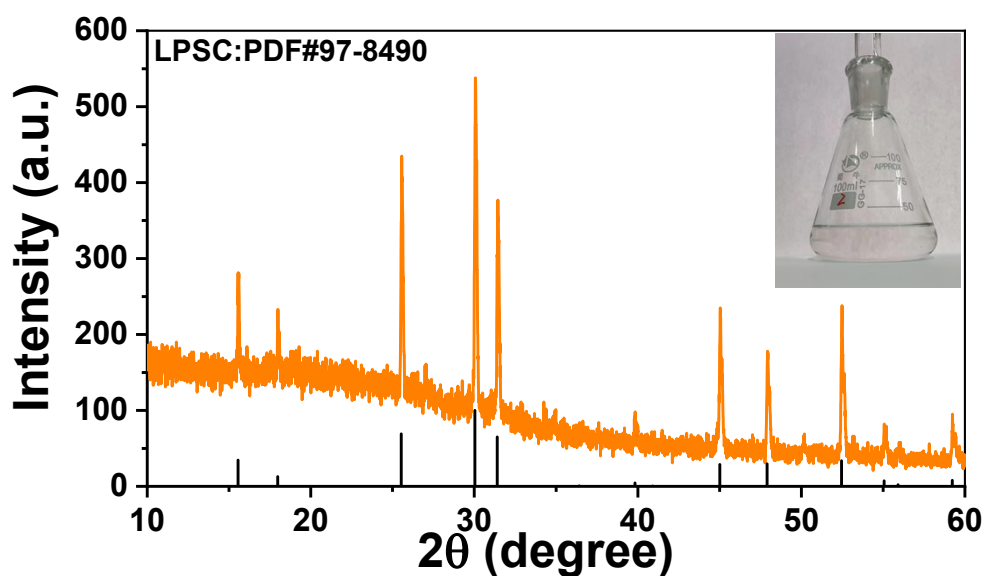


Fig. S12. The XRD patterns of LPSC-20%P₂S₅ prepared with the recovered THP, with the inset showing the visual appearance of the recycled THP.

Table S1. Properties comparison of THP with EtOH and THF.

Solvent	Properties	Price	Risk Description
Tetrahydropyrrole (THP)	b.p. = 88°C Flammable	\$55.5/kg 99%	R11 (Highly flammable), R20/21/22 (Harmful by inhalation, in contact with

			skin and if swallowed), R35 (Causes severe burns).
Ethanol (EtOH)	b.p. = 78.5°C Flammable	\$8/kg 99%	R11 (Highly flammable)
Tetrahydrofuran (THF)	b.p. = 66°C Flammable	\$24/kg 99.5%	R11 (Highly flammable), R20/21/22 (Harmful by inhalation, in contact with skin and if swallowed), R36/38 (Irritating to eyes and skin), R52/53 (Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment)