

Anomalous high ionic conductivity of nanoporous β -Li₃PS₄

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Methods

Synthesis and structural analysis: In a typical synthesis, Li₂S (Aldrich, 99%) and P₂S₅ (Sigma-Aldrich, 99%) with a stoichiometry of 3 to 1 were mixed in anhydrous THF (Sigma-Aldrich, >99.9%) at room temperature in an argon-filled glove box. The mixture was then stirred overnight. The white precipitation was separated by centrifuge and washed with THF three times before collecting for characterization. As-synthesized precipitation was heated under house vacuum at 80 °C for the removal of THF. Heat treatments of samples at 100, 140, 160, 180, and 200 °C were conducted in the same manner as the removal of THF. The compositions of all samples were analyzed at Galbraith Laboratories (a commercial analysis service). SEM images were conducted on a field-emission scanning electron microscopy (SEM, Zeiss Merlin®) that was equipped with a specially designed stage for handling air-sensitive samples. N₂ adsorption/desorption isotherms were measured using a Micromeritic Gemini 275 system. Powder XRD patterns were collected on X'pert Pro Powder Diffractometer (PANalytical) with copper K α line. Small-angle x-ray scattering data were collected using a SAXSess instrument

(Anton-Paar) with Cu K α radiation in line mode. Raman spectra were conducted on an Acton Trivista 555 spectrometer (Princeton Instruments). All characterizations were handled with special care to avoid contact with air and moisture.

Ionic conductivity measurements: All materials have been pressed into dense pellets with sufficient mechanical strength for the measurements of ionic conductivity. Pellets (diameter 12.5 mm, thickness ~1 mm) were prepared by pressing the powder with carbon-coated aluminum foils (a free sample from Exopack) on both sides in an argon-filled glove box. The pellets have a density of 95% of the reported bulk materials. The carbon-coated aluminum foils served as blocking electrodes. Electrochemical impedance spectroscopy (EIS) measurements were carried out using a specially designed air-tight cell. The a.c. impedance measurements were conducted in the frequency range of 1 MHz to 1 Hz with the amplitude of 100 mV by using a frequency response analyzer (Solartron 1260). The temperature was controlled between -20 to 100 °C in a temperature chamber (Maccor, ± 0.5 °C). The EIS presents a semi-arc at high frequencies and a straight line at lower frequencies, an expected characteristic of a pure ionic conductor in nature (Fig S6). The intercept of straight line at the axis of Z_R was employed to determine the total ionic conductivity.

Electrochemical characterization: The cyclic voltammogram (CV) was measured on the Li/Li₃PS₄/Pt cell at a scan rate of 100 mVs⁻¹ between -0.2 and 5 V at room temperature by using a potentiostat (EG&G, 263A). The Li/Li₃PS₄/Li symmetric cells were cycled on a battery test system (Maccor 4000) with a current density of 0.1 mAcm⁻² at room temperature and 80 °C.

Supplementary Figures

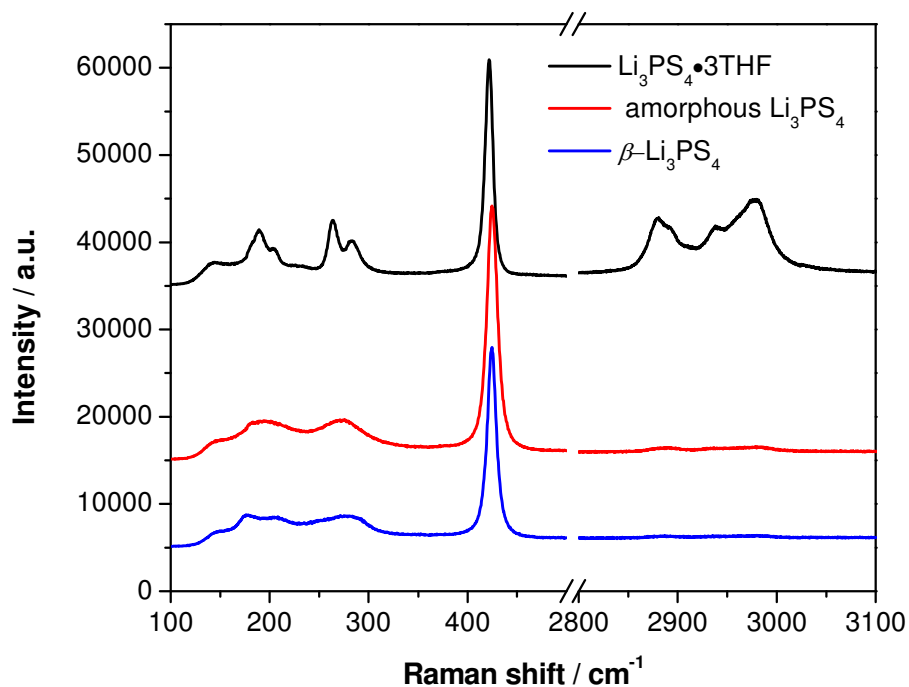


Fig S1 Raman spectra of $\text{Li}_3\text{PS}_4 \cdot 3\text{THF}$ (as-synthesized particles), amorphous Li_3PS_4 (heated at 80 °C), and nanoporous $\beta\text{-Li}_3\text{PS}_4$ (heated at 140 °C). All spectra show the characteristic peak of $\nu_s(\text{PS}_4)$ at 422 cm⁻¹. The C-H vibration peaks between 2850-3050 cm⁻¹ disappear after the removal of THF.

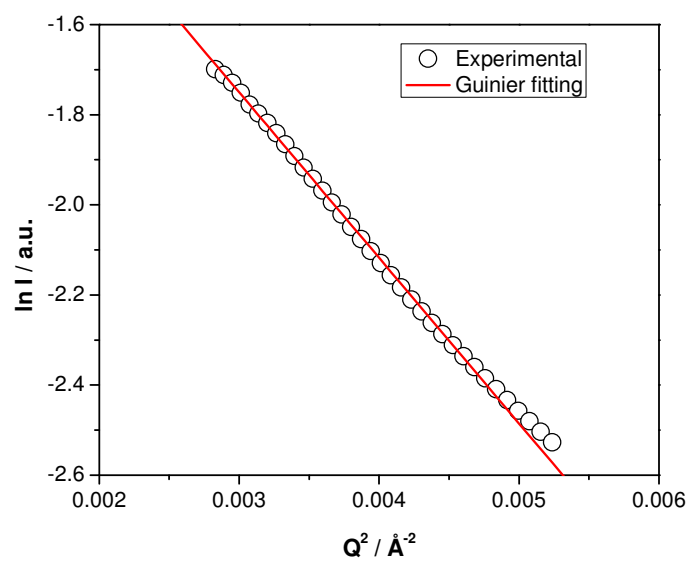


Fig S2 Small angle X-ray scattering of nanoporous β - Li_3PS_4 . The Guinier fitting of the SAXS data gives an estimated pore size of approximately 33 nm.

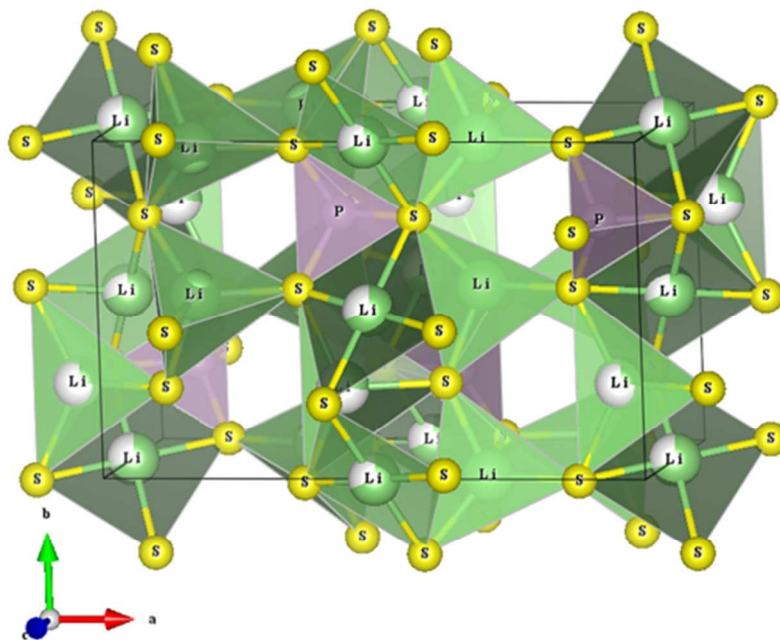


Fig S3 Crystal structure of β - Li_3PS_4 showing the interstitials along the c axis.

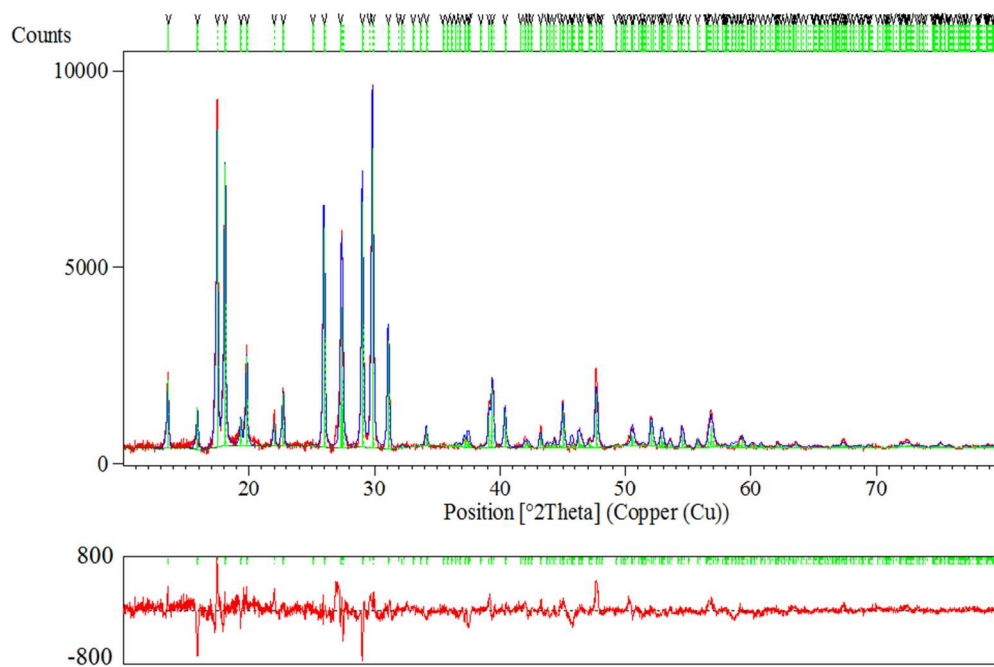


Fig S4 Rietveld refinement of XRD pattern of nanoporous β -Li₃PS₄. The X-ray diffraction pattern is indexed to orthorhombic β -Li₃PS₄ (space group *pnma*, $a=12.9857(8)$, $b=8.0559(5)$, $c=6.1380(3)$). Red: measured intensity; blue: fitted intensity; and green line: the position of the diffraction peak. The bottom shows the difference plot.

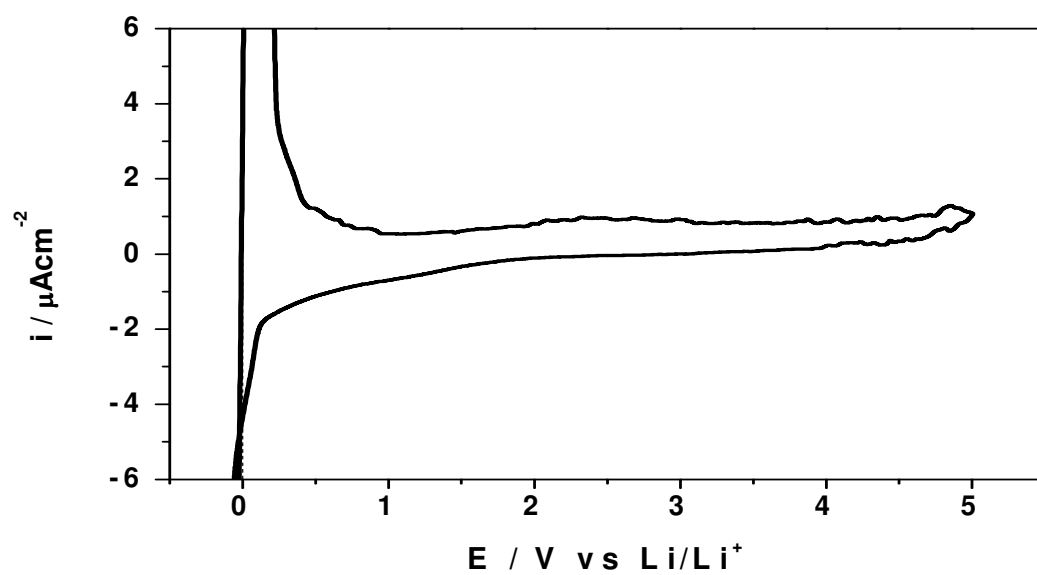


Fig S5 Cyclic voltammogram (CV) of the Li/ β -Li₃PS₄/Pt cell with 10 times amplification of the current scale

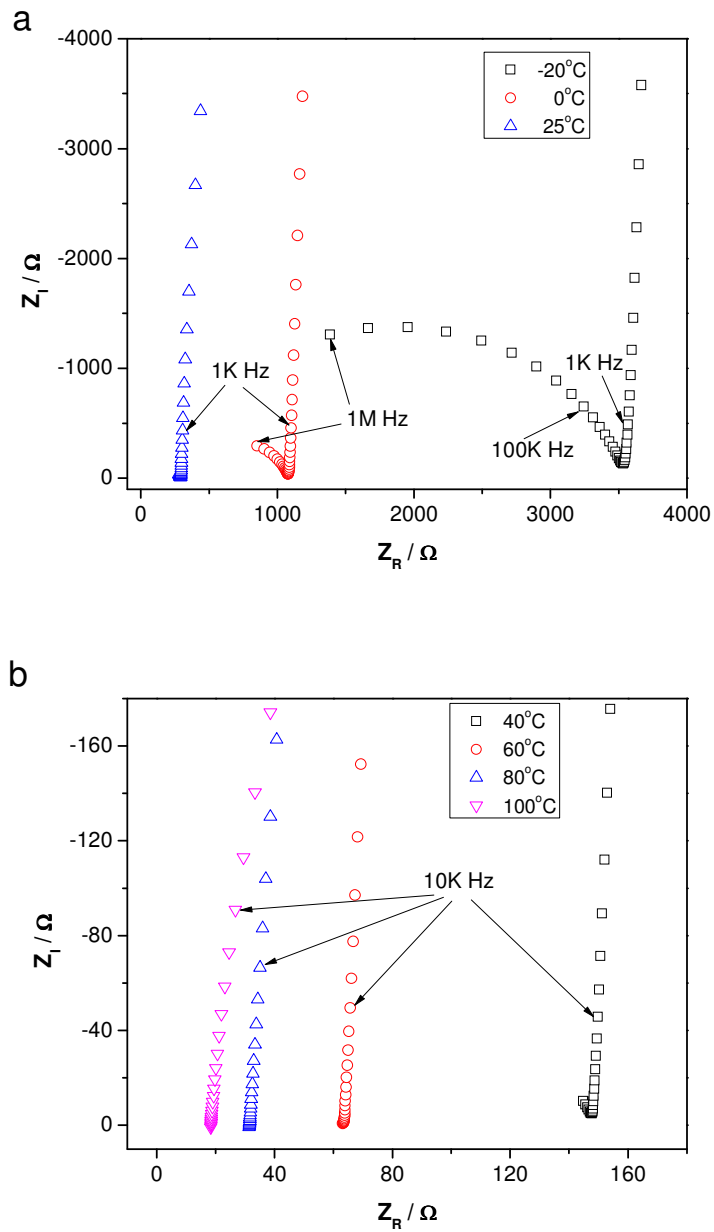


Fig S6 Impedance spectra of nanoporous β -Li₃PS₄ measured at (a) -20 to 25 °C and (b) 40 to 100 °C. The total conductivity is determined by using the intercept between the semi-arc and straight line as the total resistance.