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*Electronic Supplementary Information for:*

## **Microwave aided synthesis of lithium thiophosphate solid electrolyte**

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**General experimental methods.** Due to the air sensitivity of lithium thiophosphates, all sample synthesis, handling and characterization was performed under argon gas in a glove box with H<sub>2</sub>O and O<sub>2</sub> levels below 0.1 ppm. All reagents were commercially available and used without further purification. Microwave syntheses were performed using an Anton Paar Monowave 300.

**A typical experimental procedure for the synthesis of amorphous Li<sub>3</sub>PS<sub>4</sub>.** Into a 10 mL silicon carbide microwave vial (Anton Paar), anhydrous THF (Manchester Organics, 3 mL) and a stir bar were added. To the vial, Li<sub>2</sub>S (Aldrich, 99.98%, 41.4 mg, 0.900 mmol) and P<sub>2</sub>S<sub>5</sub> (Sigma-Aldrich, 99%, 66.7 mg, 0.3 mmol) powder were added. The vial was immediately capped and vortexed. The vial was then transferred from the glove box to the microwave reactor. The mixture was heated to 100°C for 3 hours with a stir rate of 1200 rpm. Due to the air sensitivity of the lithium thiophosphates, the IR temperature sensor was used to control the temperature. After the synthesis was complete, the vial was returned to the glove box and the white insoluble product was removed using suction filtration. After the solvent was removed, the residue was slurried in anhydrous heptane (10 mL) and the insoluble product was collected by suction filtration. The coordinated solvent (i.e. THF) was removed from the insoluble product by heating it to 124°C on a hot plate in the glove box for 3 hours.

**A typical experimental procedure for the synthesis of amorphous Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> pre-cursor.** Into a 10 mL quartz microwave vial (Anton Paar), anhydrous acetonitrile (ACN) (Manchester Organics, 3 mL) and a stir bar were added. To the vial, Li<sub>2</sub>S (Aldrich, 99.98%, 48.2 mg, 1.05 mmol) and P<sub>2</sub>S<sub>5</sub> (Sigma-Aldrich, 99%, 100 mg, 0.45 mmol) powder were added. The vial was immediately capped and vortexed. The vial was then transferred from the glove box to the microwave reactor. The mixture was heated to 100°C for 3 hours with a stir rate of 1200 rpm. Due to the air sensitivity of the lithium thiophosphates, the IR

temperature sensor was used to control the temperature. After the synthesis was complete, the vial was returned to the glove box and the acetonitrile was removed at 50°C under vacuum, leaving behind a white product. After the bulk solvent was removed, the coordinated solvent (i.e. ACN) was removed from the powder product by heating it to 200°C in a Buchi B-585 glass oven for 1 hour.

**TGA Analysis.** TGA analysis was performed within an Ar glove box ( $\text{H}_2\text{O}$ ,  $\text{O}_2 < 0.1$  ppm) using a Netzsch Luxx STA 409 PC. About 8 mg of sample powder was loaded into a cold-sealable, DSC pan with a 75  $\mu\text{m}$  diameter hole in the lid. The DSC pan was crimped, loaded into the Netzsch Luxx and heated at 2°C/min. The reference was an empty, crimped DSC pan with a hole in the lid.

**Raman Analysis.** Raman spectroscopy was performed with a Horiba LabRAM HR spectrometer equipped with an inverted optical microscope. A 50x lwr objective lens was used to focus a 532 nm laser onto the powder sample, which was pressed against the inside surface of a sealed cuvette to protect it from air. The back-scattered light was dispersed using a 600 grating/mm grating onto a CCD camera. Spectra were collected by performing 20 sequential scans, each with a 1 second duration. Spectra were collected from four different spots on each sample and compared to confirm sample homogeneity.

**SEM Analysis.** SEM images were collected using a JEOL 7800 FLV at a magnification of 500x with an acceleration voltage of 5 kV and a beam current of 8 (43 pA).

**Powder XRD Analysis.** A Rigaku SmartLab 3kW fitted with an Anton-Paar HTK 1200N oven chamber and capillary extension was used to collect the XRD patterns. The 0.3 mm diameter quartz capillary was filled

with dried, amorphous  $\text{Li}_3\text{PS}_4$  and sealed with epoxy in the glove box before transferring it to the diffractometer. Patterns were collected with a  $0.035^\circ$  step size at a rate of  $0.4167^\circ/\text{min}$ . After the amorphous material was scanned, the capillary was heated to  $150^\circ\text{C}$  to crystallize the material into  $\beta\text{-Li}_3\text{PS}_4$ . Multiple scans were performed so that the first and final patterns could be compared to confirm that the pattern did not change with time and, therefore, that the sample was successfully protected from air. The repeated scans were then added together to form the final XRD patterns.

**Conductivity Measurement.** Into a Macor pellet die, 100 mg of  $\text{Li}_3\text{PS}_4$  powder was added and then pressed at 66.4 bar for 1 min to form an 11.28 mm diameter pellet (i.e.  $1.0\text{ cm}^2$ ). Then, carbon-coated aluminum foil (MTI corp.) was pressed into both sides of the pellet. This stack of materials was compressed at about 88 MPa in an air-tight cell, attached to a Bio-logic VMP3 potentiostat, and placed into a temperature-controlled oven. Electrochemical impedance spectroscopy was performed using a Bio-logic VMP3 potentiostat between 100 mHz and 10 kHz at increasing temperatures from  $-10^\circ\text{C}$  to  $80^\circ\text{C}$ . The potential amplitude was 10 mV. The electrolyte resistance was determined from the EIS plots by extrapolating the low-frequency, linear section of the curves down to the x-axis, as described by Minami *et al.*<sup>1</sup>

**Electrochemical Cycling.** Into a Macor pellet die, 100 mg of  $\text{Li}_3\text{PS}_4$  powder was added and then pressed at 66.4 bar for 1 min to form an 11.28 mm diameter pellet (i.e.  $1.0\text{ cm}^2$ ), 596  $\mu\text{m}$  thick. Then, polished and flattened lithium foil discs (99.8%, Honjo Metal) were applied to both sides of the pellet, followed by 508  $\mu\text{m}$ -thick 400 nickel spacers (McMaster-Carr) and 0.9 cm diameter wave springs (McMaster-Carr). The spring/spacer/Li/solid electrolyte/Li/spacer/spring stack was compressed to 8.8 MPa in a cell,

transferred to a 25°C oven and cycled in an air-tight container using a Bio-logic VMP3 potentiostat. The cell was cycled galvanostatically at 100  $\mu\text{A}/\text{cm}^2$  with 0.2  $\text{mAh}/\text{cm}^2$  half-cycles.

### Supplementary Figures

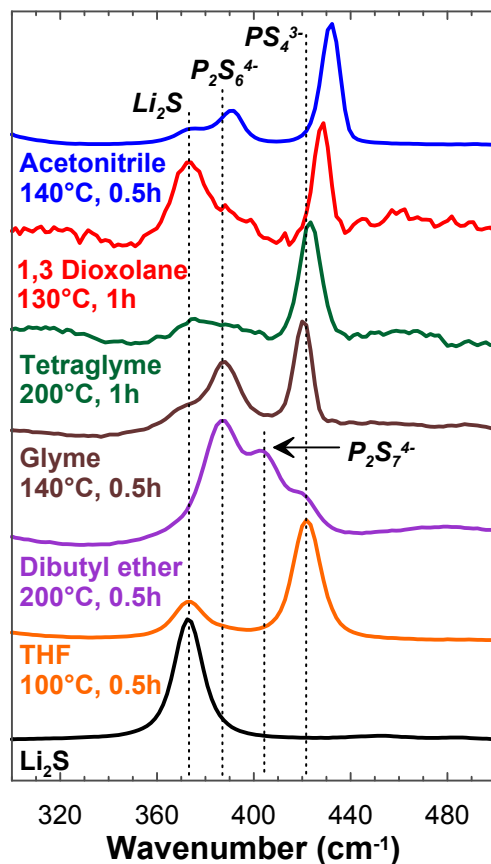


Figure S1: Raman spectra of 3Li<sub>2</sub>S:P<sub>2</sub>S<sub>5</sub> samples microwaved in various solvents, including acetonitrile (blue), 1,3 dioxolane (red), tetraglyme (green), glyme (brown), dibutyl ether (purple) and tetrahydrofuran (THF, orange). The Raman spectrum of pure Li<sub>2</sub>S (black) is shown to demonstrate that some of the microwave syntheses did not react to completion. In this case, any P<sub>2</sub>S<sub>6</sub><sup>4-</sup>, P<sub>2</sub>S<sub>7</sub><sup>4-</sup>, or Li<sub>2</sub>S in the product signal is undesirable.

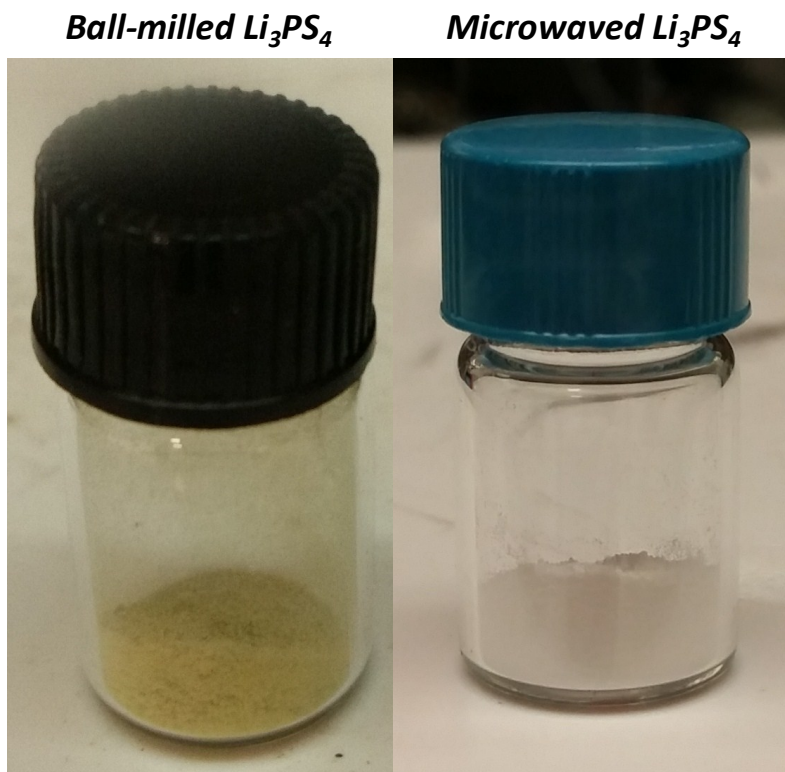


Figure S2: Pictures of  $\text{Li}_3\text{PS}_4$  made via ball-milling (left) and microwave-assisted solution synthesis in THF (right). The THF has been removed from the white, microwaved powder by heating it to 124°C.

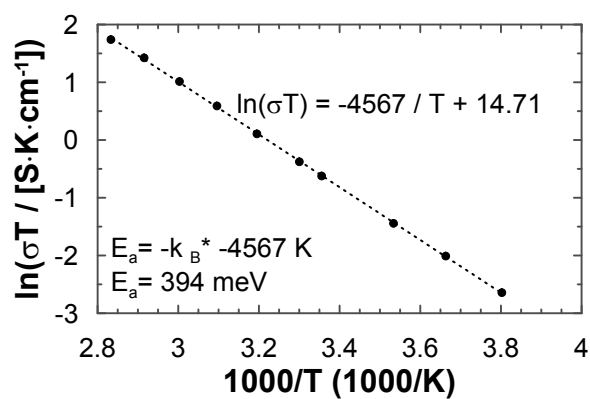


Figure S3: Arrhenius plot of the natural logarithm of ionic conductivity ( $\sigma$ ) × temperature ( $T$ ) vs inverse temperature. The slope of the fitted line is equal to  $-E_a/k_B$ , allowing the  $\text{Li}^+$  diffusion activation energy ( $E_a$ ) to be determined using the Boltzmann constant ( $k_B$ ).

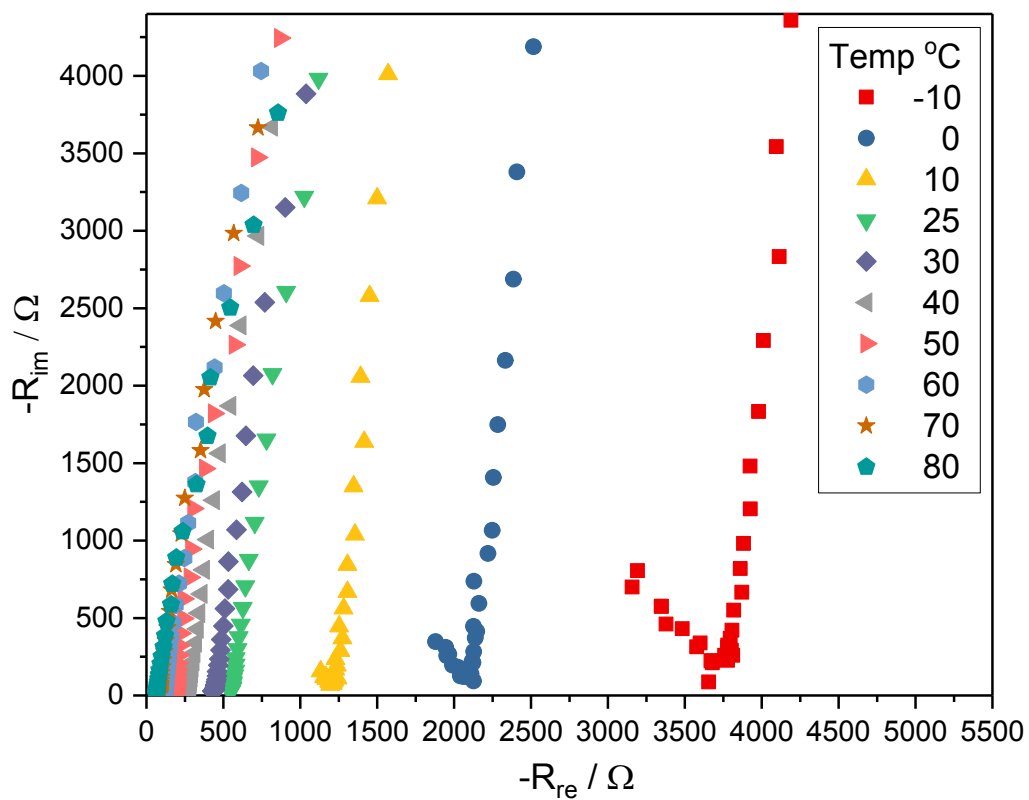


Figure S4: Complex plane plots for the EIS obtained for a symmetric cell consisting of microwave-synthesized, amorphous  $\text{Li}_3\text{PS}_4$  with carbon coated Al electrodes pressed into opposing sides of the solid electrolyte pellet. The data sets vary in temperature from  $-10^\circ\text{C}$  to  $80^\circ\text{C}$  as shown in the legend.

## Reference

1 K. Minami, F. Mizuno, A. Hayashi and M. Tatsumisago, *Solid State Ion.*, 2007, **178**, 837–841.