# Supporting Information

## Solvent-Mediated Synthesis of Amorphous $Li_3PS_4$/PEO Composite Solid Electrolytes with High $Li^+$ Conductivity

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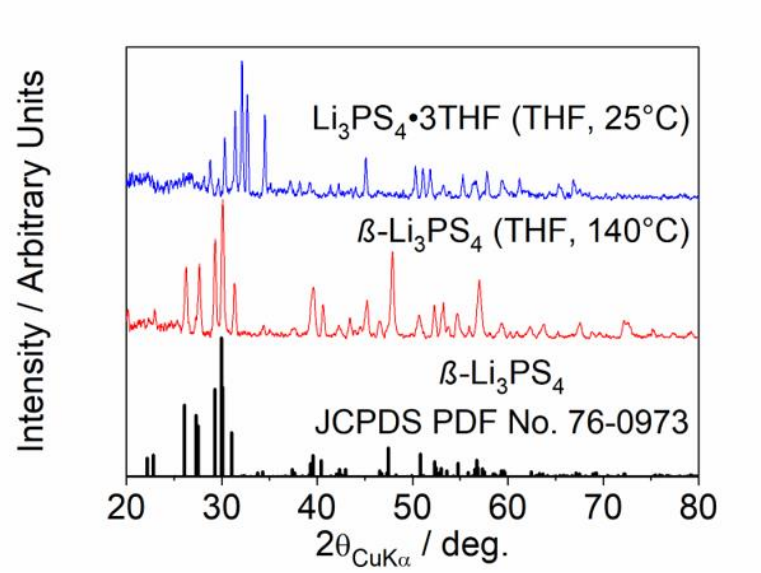


**Figure S1.** Powder XRD patterns of $Li_3PS_4$ powders synthesized from THF dried under vacuum overnight at room temperature and 140 °C. Kapton background was manually subtracted.

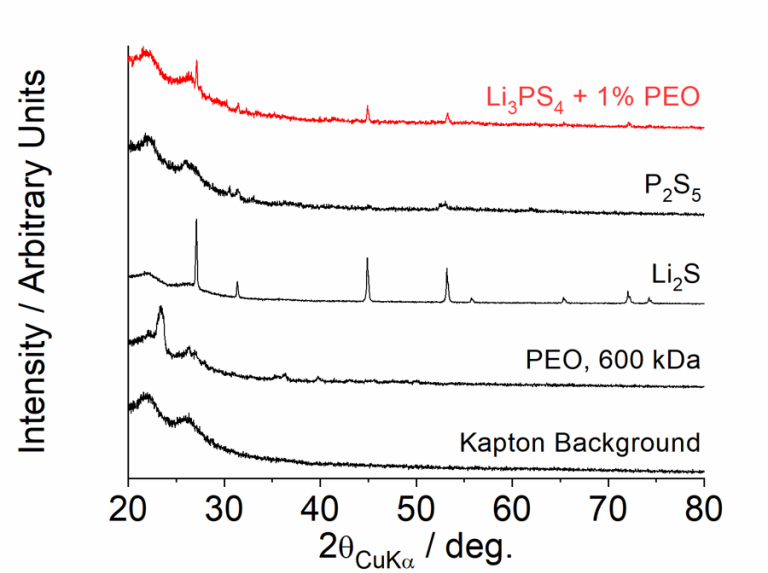


**Figure S2.** Powder XRD patterns of $Li_3PS_4$ + 1% PEO, precursor materials ($Li_2S$, $P_2S_5$, and PEO), and Kapton tape used to mitigate sample exposure during XRD measurements.

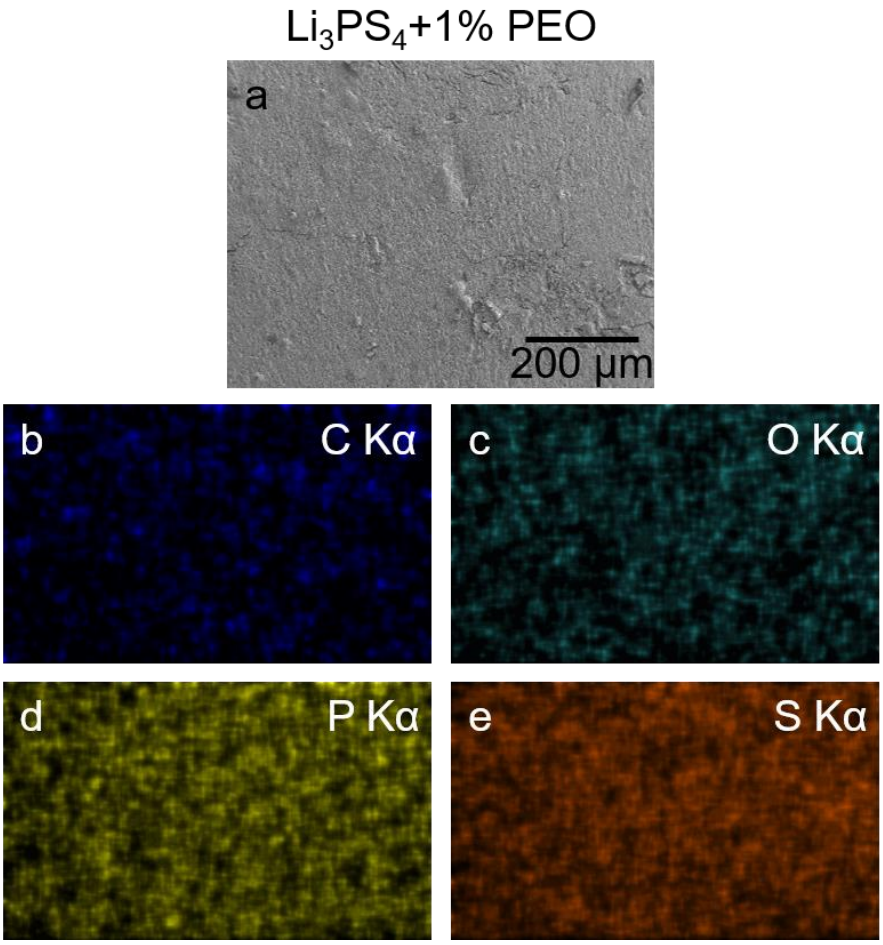


**Figure S3.** SEM image and corresponding EDX maps of an amorphous $Li_3PS_4$ + 1 wt.% PEO composite showing the elemental distribution of C/O (associated with PEO) and P/S (associated with $Li_3PS_4$).

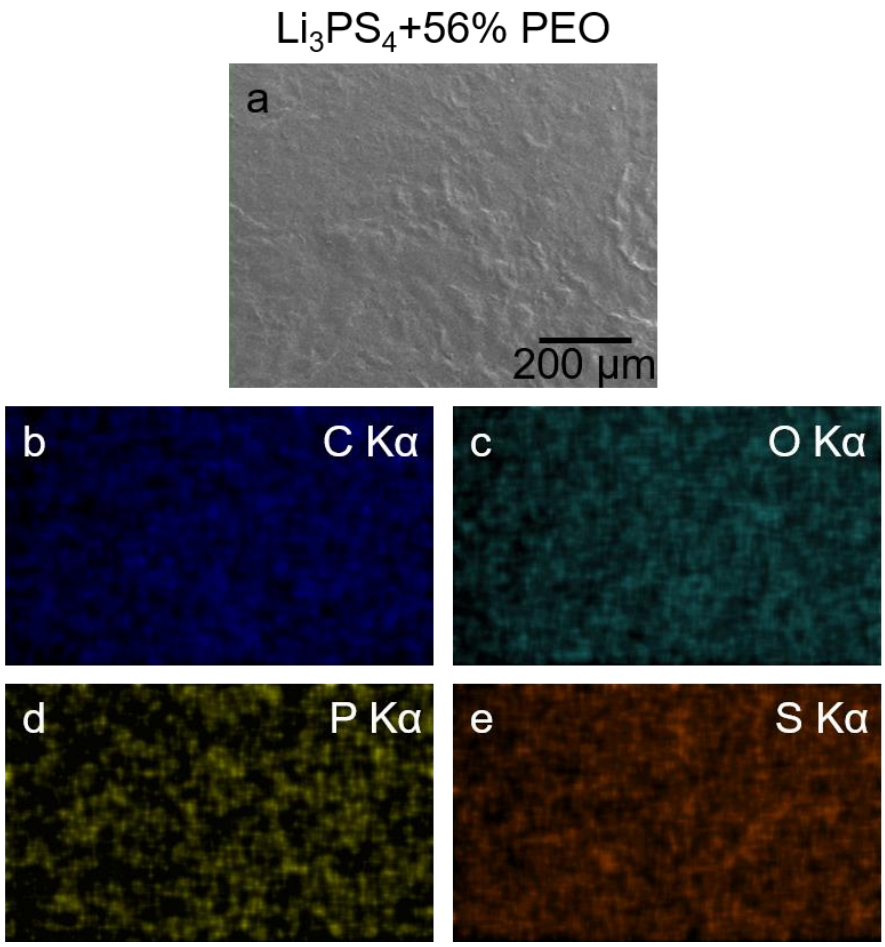


**Figure S4.** SEM image and corresponding EDX maps of an amorphous $Li_3PS_4$ + 56 wt.% PEO composite showing the elemental distribution of C/O (associated with PEO) and P/S (associated with $Li_3PS_4$).

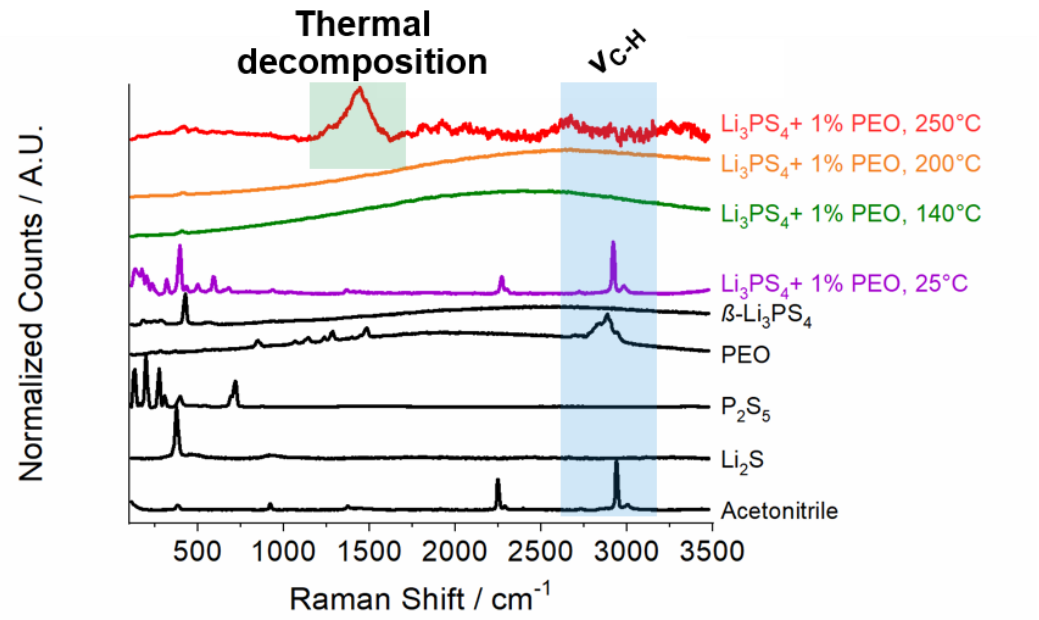


**Figure S5.** Raman spectra of $Li_3PS_4$ + 1 wt.% PEO dried overnight at 25 – 250 °C. Fluorescence background was subtracted for the sample heated to 250 °C. Reference data for *ß*-$Li_3PS_4$ and precursor materials ($Li_2S$, $P_2S_5$, PEO, and acetonitrile) are shown for comparison.

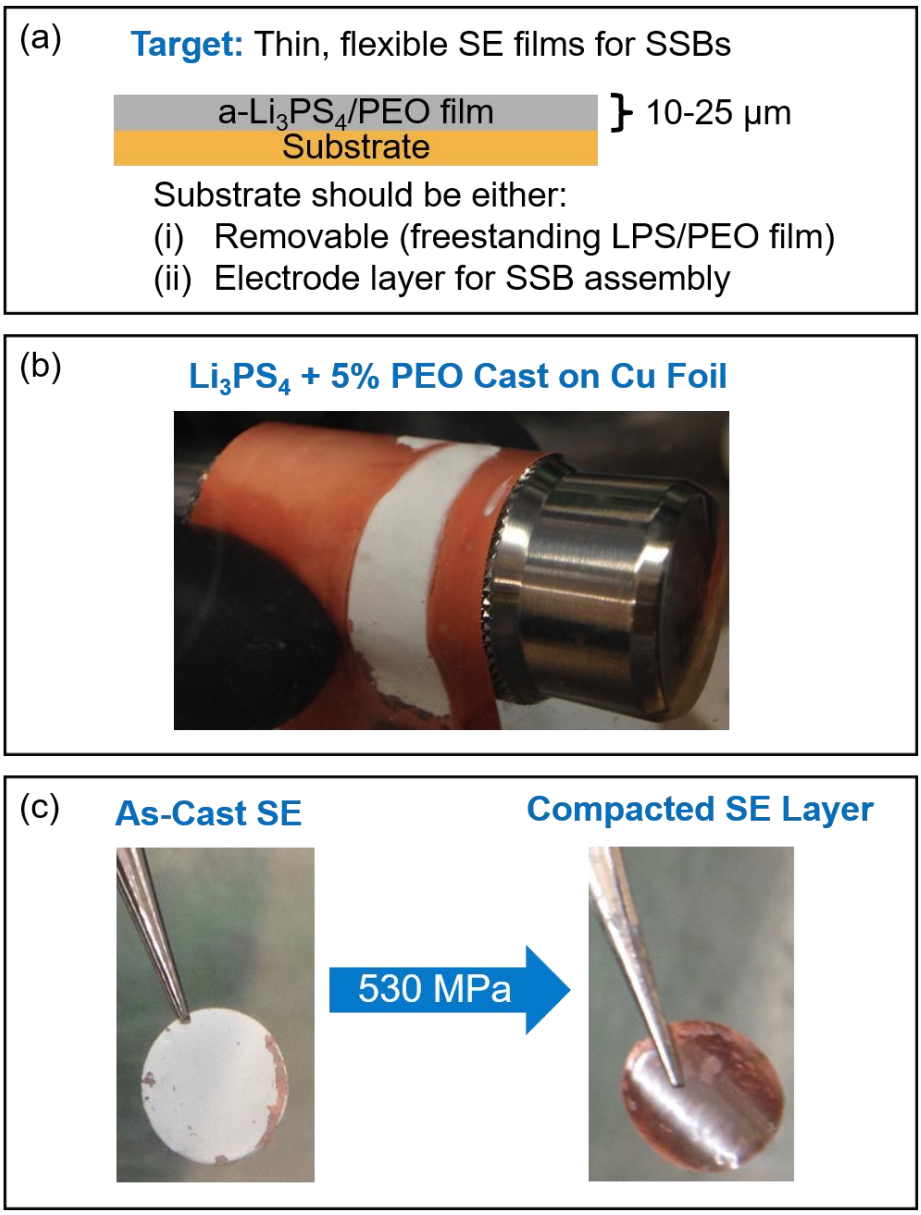


**Figure S6**. Preliminary investigations of slurry cast $Li_3PS_4$/PEO solid electrolytes showing (a) targeted structure containing a thin (10 – 25 µm) solid electrolyte layer deposited on a substrate, (b) $Li_3PS_4$ + 5% PEO cast onto Cu foil, and (c) solid electrolyte disks (1/2" diameter) on Cu foil before and after cold-pressing at 530 MPa. Further optimization of the electrolyte and slurry composition is required before testing these thin solid electrolytes in all-solid-state batteries.

**Table S1.** Properties of the $Li_3PS_4$ + 5% PEO SE layers cast onto Cu foil shown in Figure S6.

| Sample | Thickness (μm) | Loading ($mg/cm^2$) | Density ($g/cm^3$) | Porosity* (%) |
|---|---|---|---|---|
| As-Cast | 32 | 1.82 | 0.57 | 70 |
| Cold-Pressed (530 MPa) | 10 | 1.82 | 1.82 | 3 |

* Porosity estimated assuming a theoretical density of 1.87 $g/cm^3$ for *ß*-$Li_3PS_4$.