

# **Spectroscopic characterization of lithium thiophosphates by XPS and XAS – a model to help monitor interfacial reactions in all-solid-state batteries**

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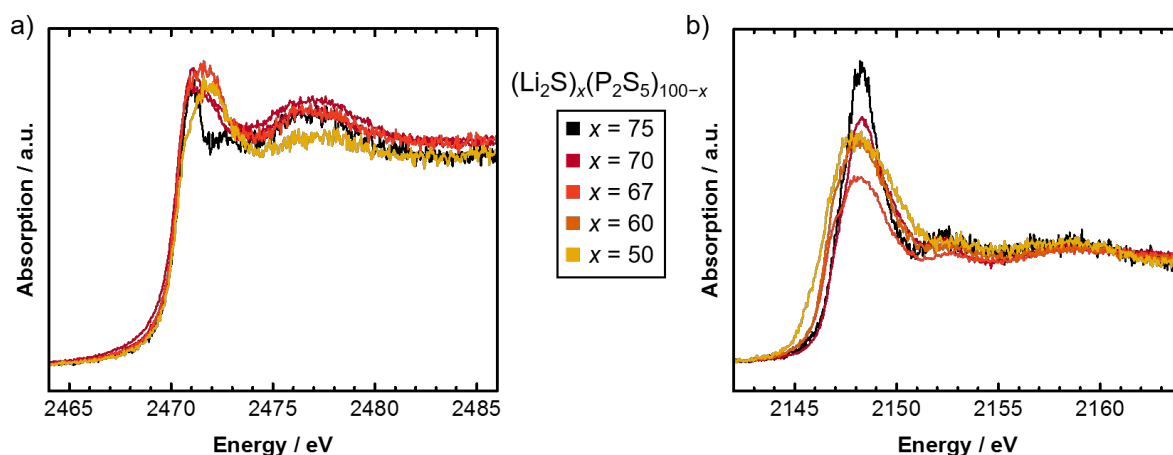


Figure S1: XANES of LPS glasses at the S K edge (a) and P K edge (b) measured in fluorescence yield (FLY). Compared to spectra collected in total electron yield (TEY), spectra collected in FLY mode are less resolved but not affected by surface oxidation.

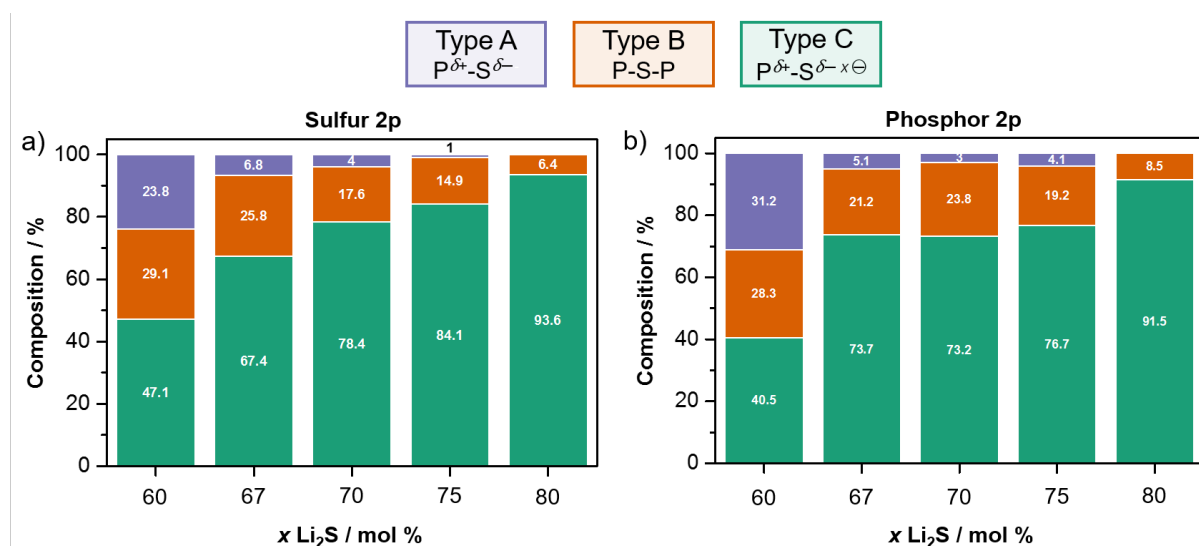


Figure S2: Quantitative compositional results of the XPS peak fitting of S<sub>3/2</sub> 2p (a) and P<sub>3/2</sub> 2p (b). A strong correlation of increasing fractions of type C bonds with the Li<sub>2</sub>S composition are found, while type A and B bonds diminish.

**Raman spectroscopy.** A Senterra Raman spectrometer (Bruker, USA) with an excitation wavelength of 532 nm was used to collect Raman spectra from 55 to 1555 cm<sup>-1</sup> using a 20x objective and 0.2 mW of power. Samples were placed on glass substrates in the glovebox and sealed airtight by a cover glass and silicon vacuum grease.

**Solid-State Nuclear Magnetic Resonance (NMR) Spectroscopy.** <sup>31</sup>P magic angle spinning (MAS) NMR experiments were carried out on a Bruker Avance 500 MHz spectrometer equipped with a commercial 2.5 mm MAS NMR double-resonance probe (ZrO<sub>2</sub> rotor was filled in the glovebox) at a spinning speed of 30 kHz. The magnetic field strength was 11.7 T

corresponding to a Larmor frequency of 202.4 MHz. A rotor-synchronized Hahn-echo pulse sequence was used for data acquisition with a  $\pi/2$  time of 2  $\mu\text{s}$  and recycle delays of 60 s.

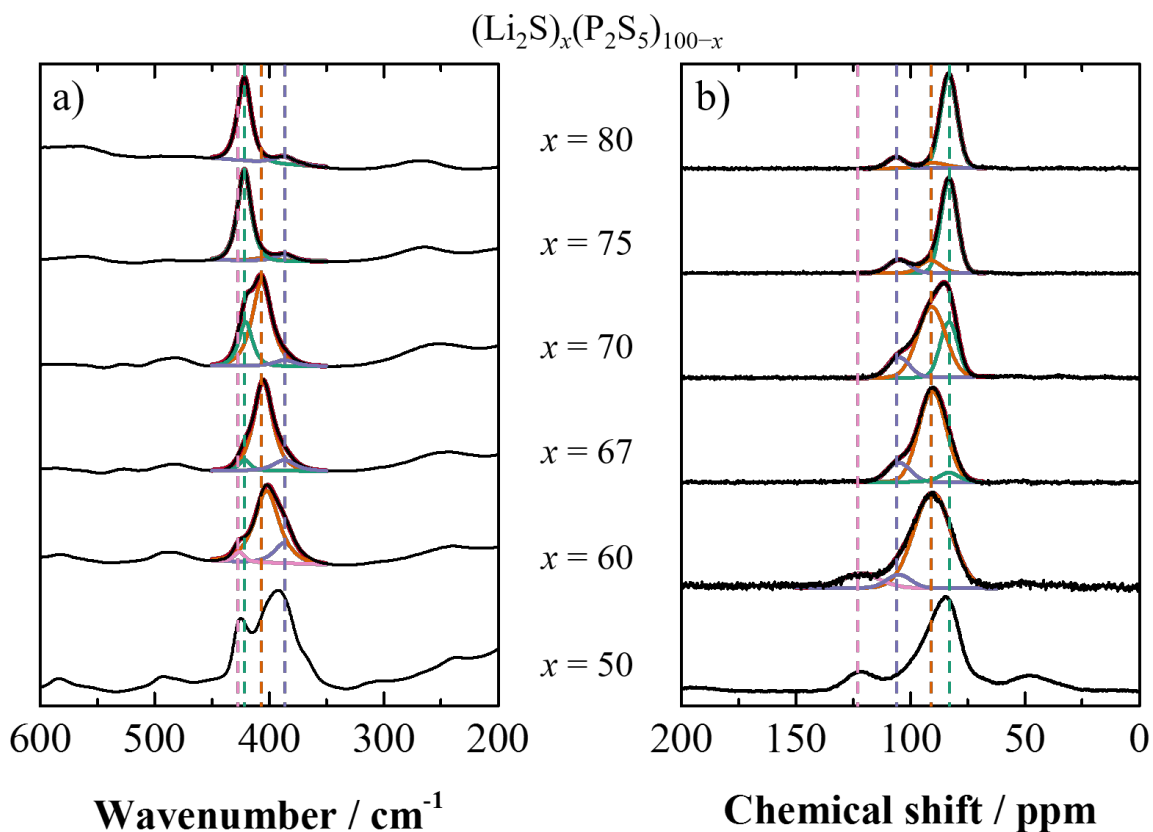


Figure S3: Overview of fitted Raman (a) and  $^{31}\text{P}$  MAS NMR (b) spectra of LPS glasses (fitted data was reproduced from Dietrich et. al)<sup>1</sup>. According to the general trend peaks of  $(\text{Li}_2\text{S})_{50}(\text{P}_2\text{S}_5)_{50}$  are expected at lower wavenumber and higher isotropic chemical shift, while the opposite is observed.

## References

- (1) Dietrich, C.; Weber, D. A.; Sedlmaier, S. J.; Indris, S.; Culver, S. P.; Walter, D.; Janek, J.; Zeier, W. G. *J. Mater. Chem. A* **2017**, *5*, 18111.