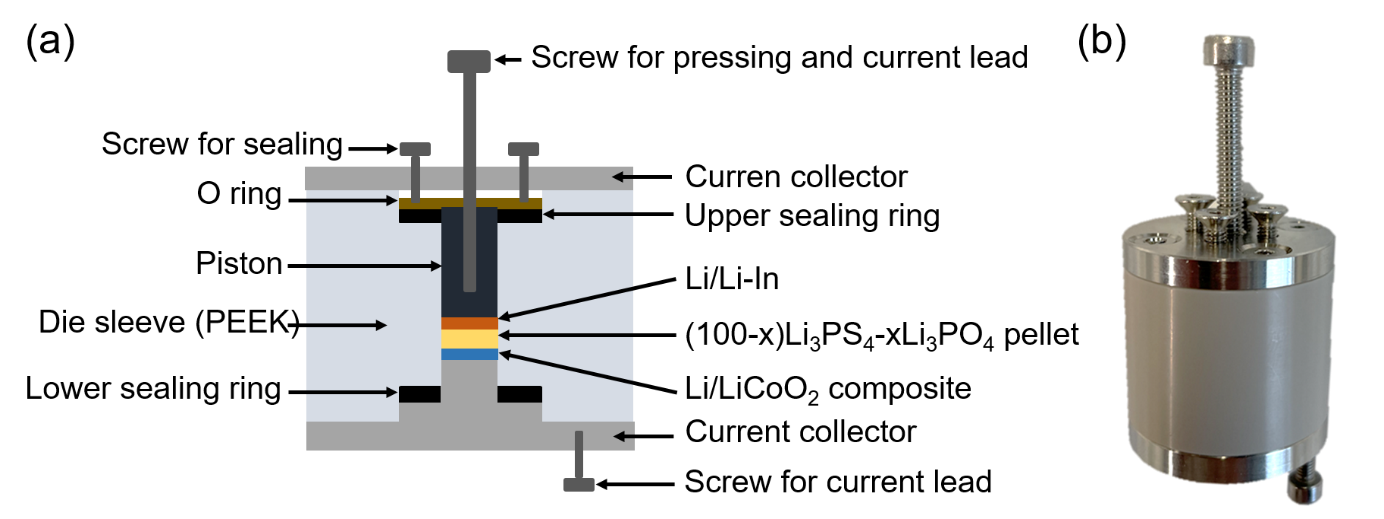
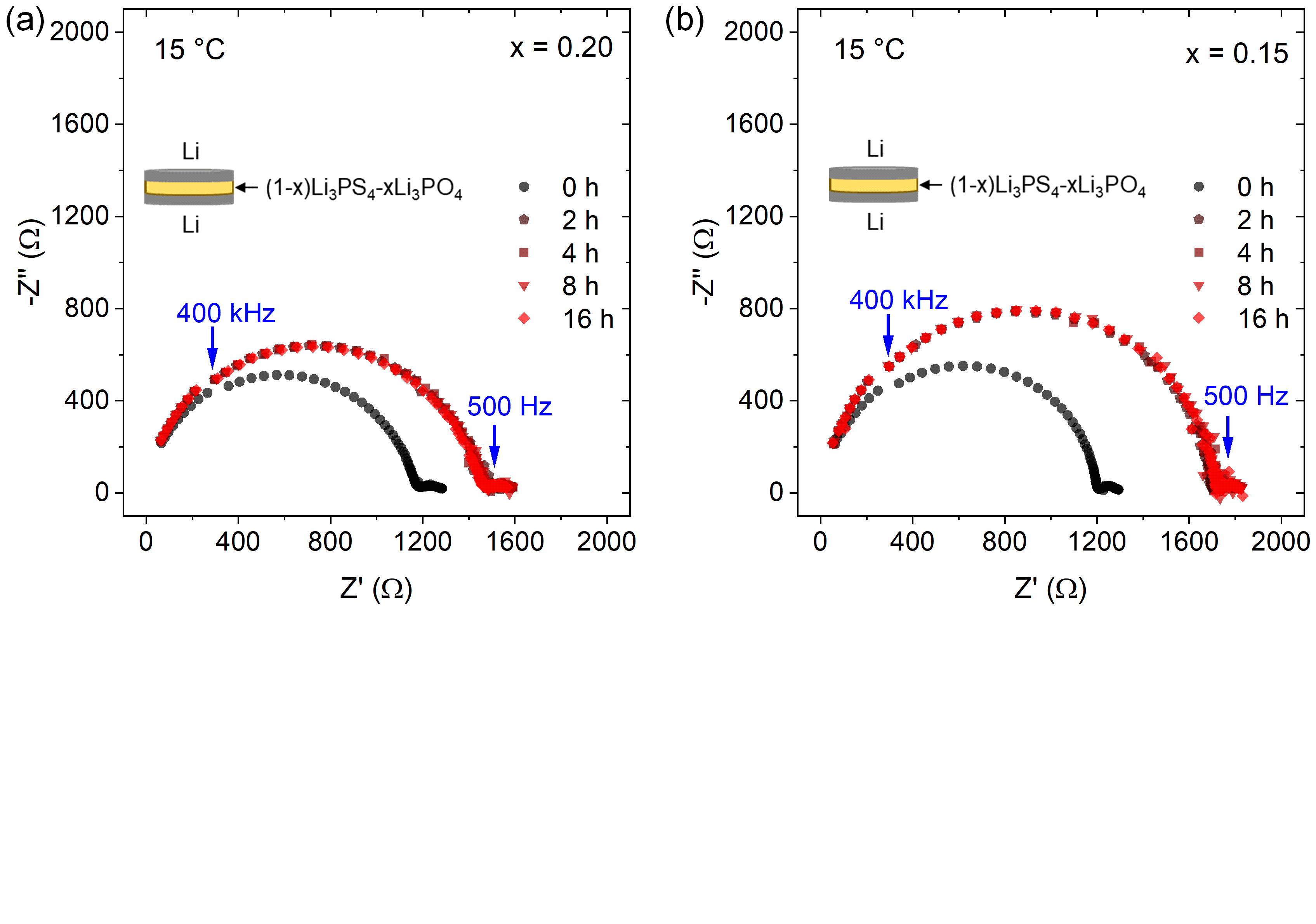
Supporting Information

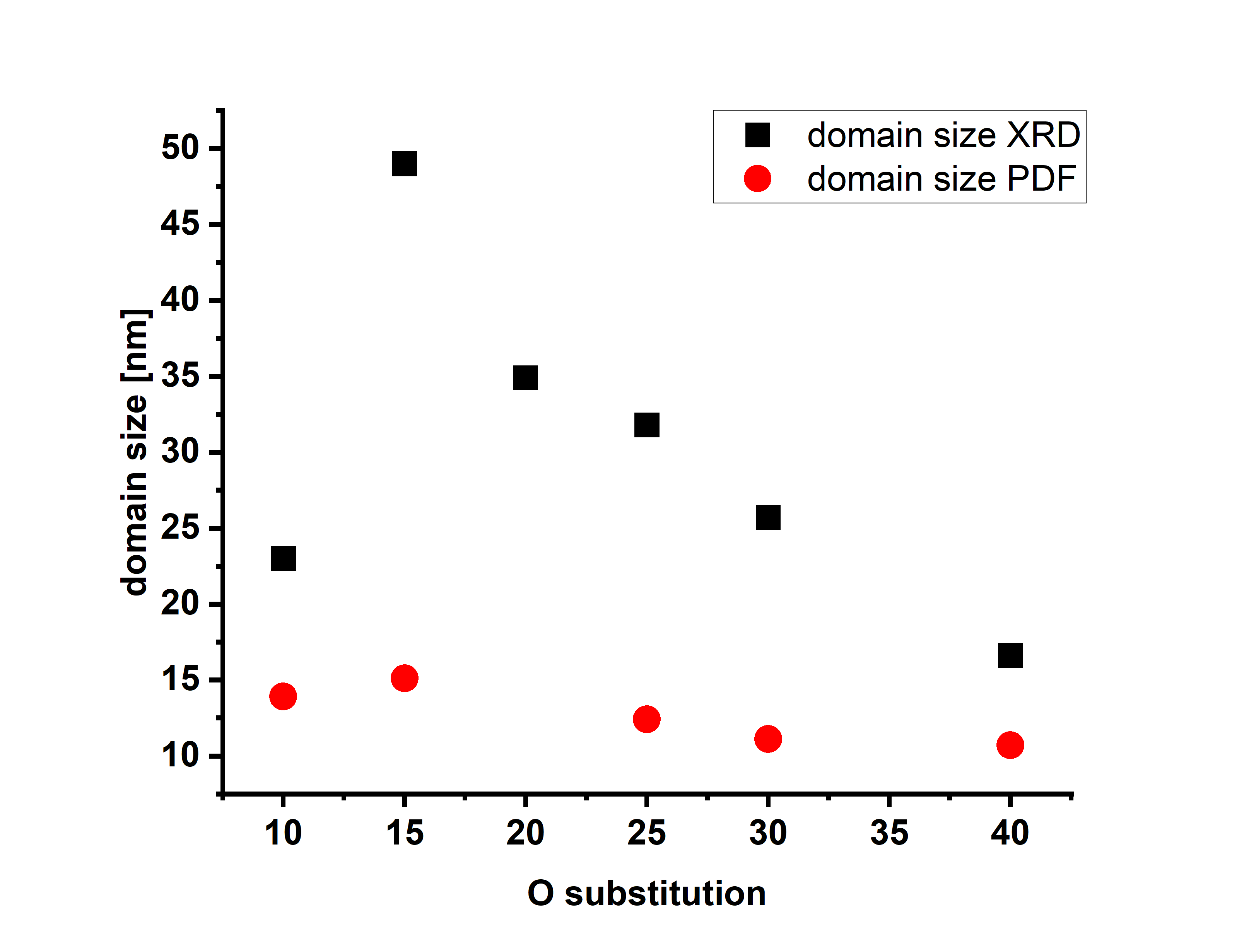


**Figure S1**: Scheme (a) and picture (b) of the measurement cell for SSEs.

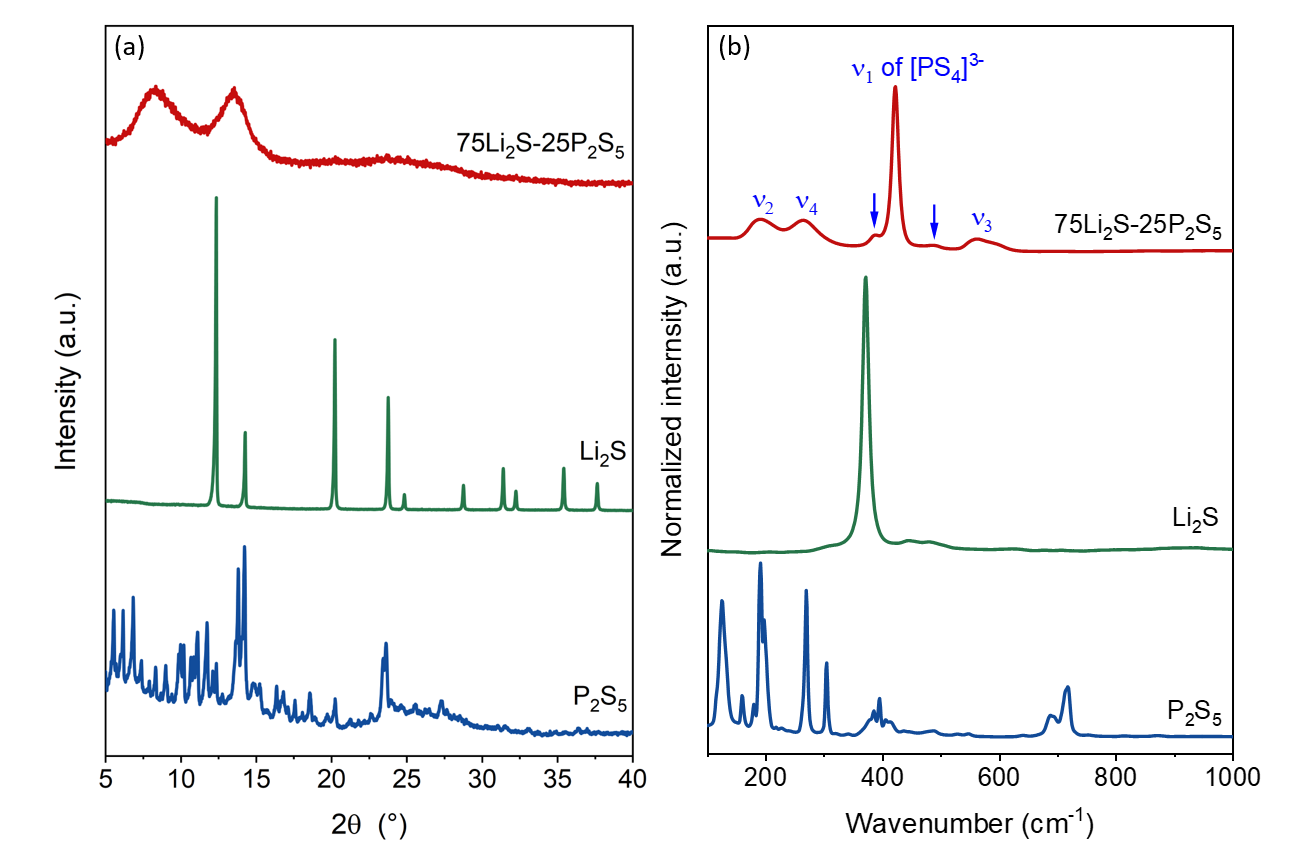
SSE pellet is prepressed with 50 MPa and loaded into cell. Then the pallet is pressed again with a final pelleting pressure of ca. 400 MPa before the cell is closed. Pressure can be applied by adjusting the torque on the top screw.



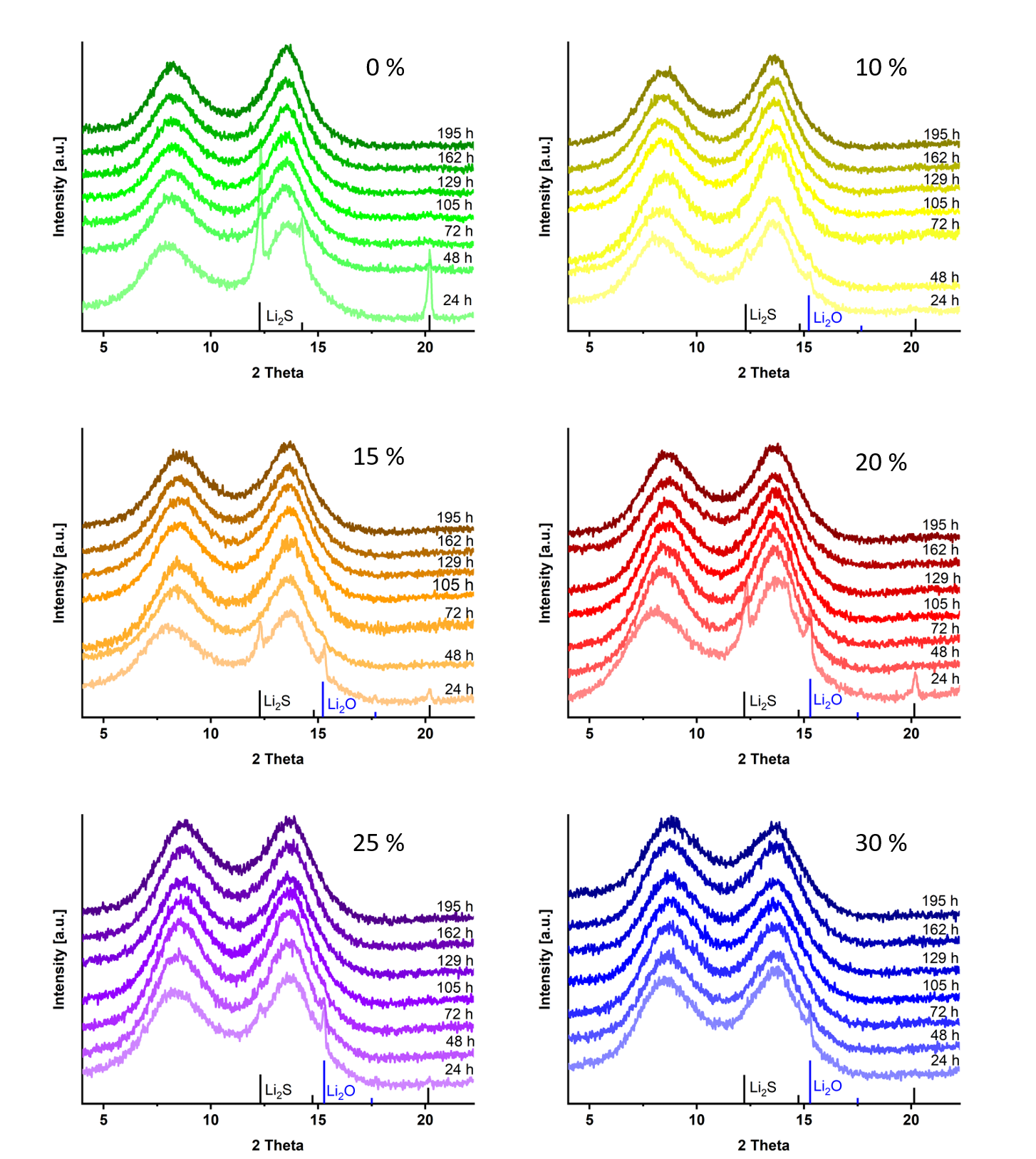
**Figure S2:** Exemplary impedance spectra of Li symmetric cells Li/Li3POxS4-x/Li after different waiting times between assembly and measurement.



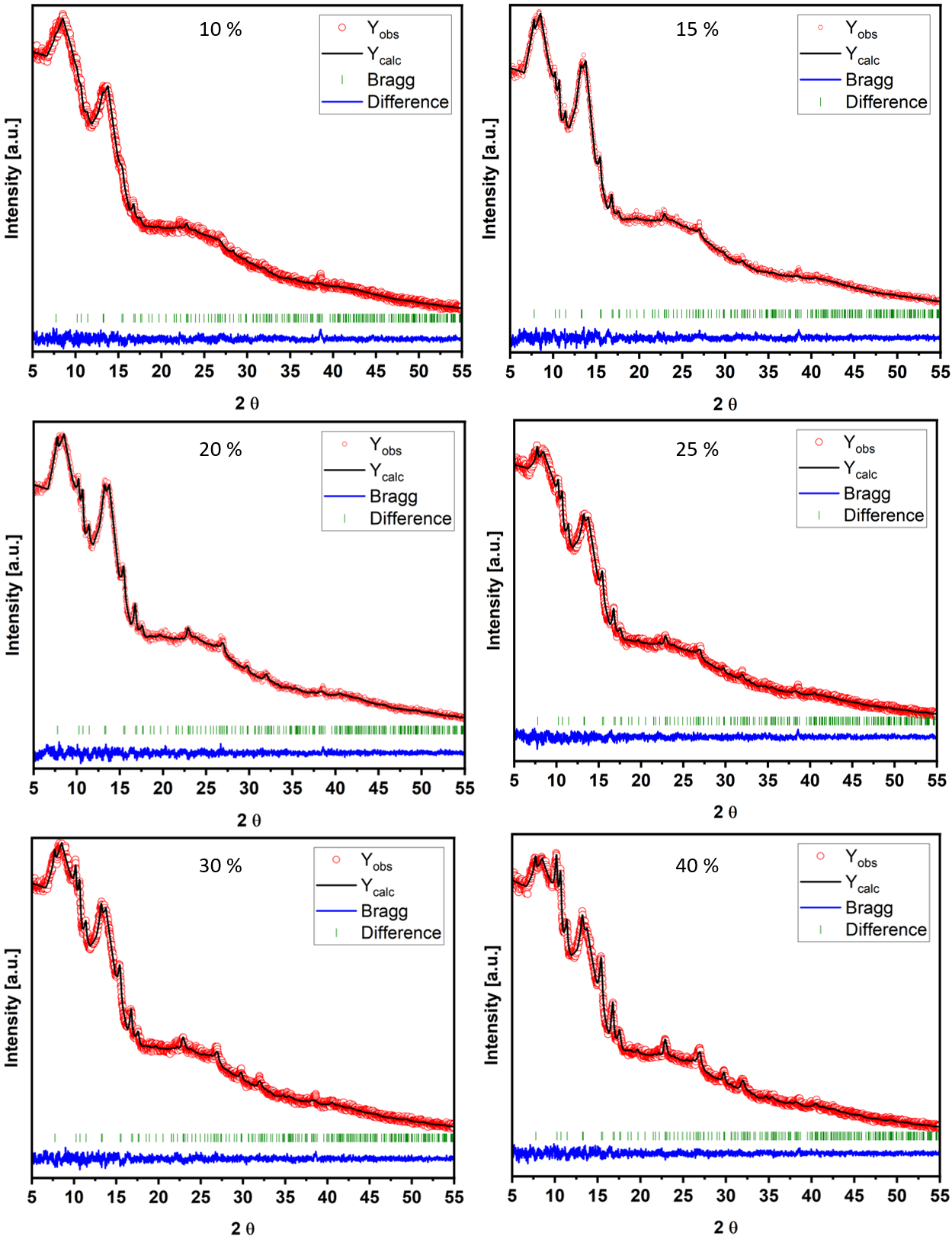
**Figure S3**: Domain size of LPO crystallites determined by fitting of XRD and PDF data.

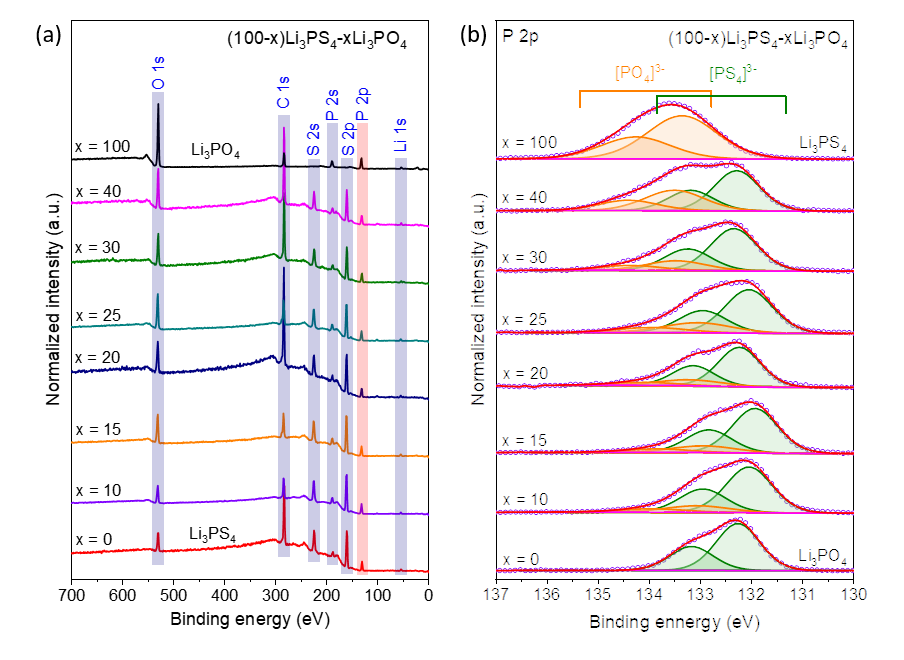
**Figure S4**: XRD patterns (a), and Raman (b) of starting materials Li2S, P2S5, and glass 75Li2S-25P2S5 (Li3PS4) after mechanical milling.Ɵ

All precursors are phase pure. After milling, the thiophosphates are x-ray amorphous, meaning no Bragg reflections can be found.

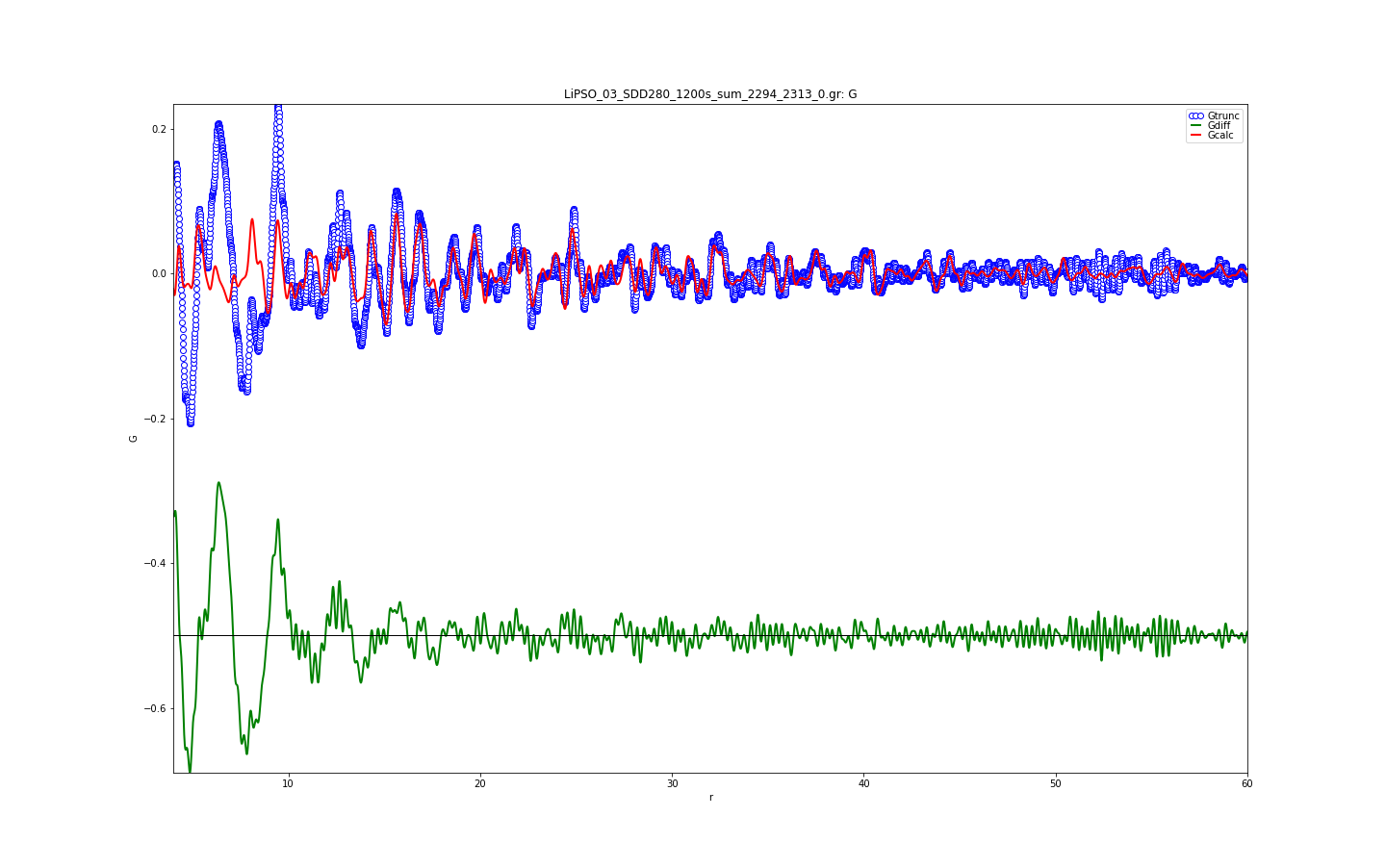


**Figure S5**: X-ray diffractograms of (3-x)Li2S + xLi2O + P2S5 (0 ≤ x ≤ 2.4) powders between synthesis steps, percentages denote the level of oxygen substitution.

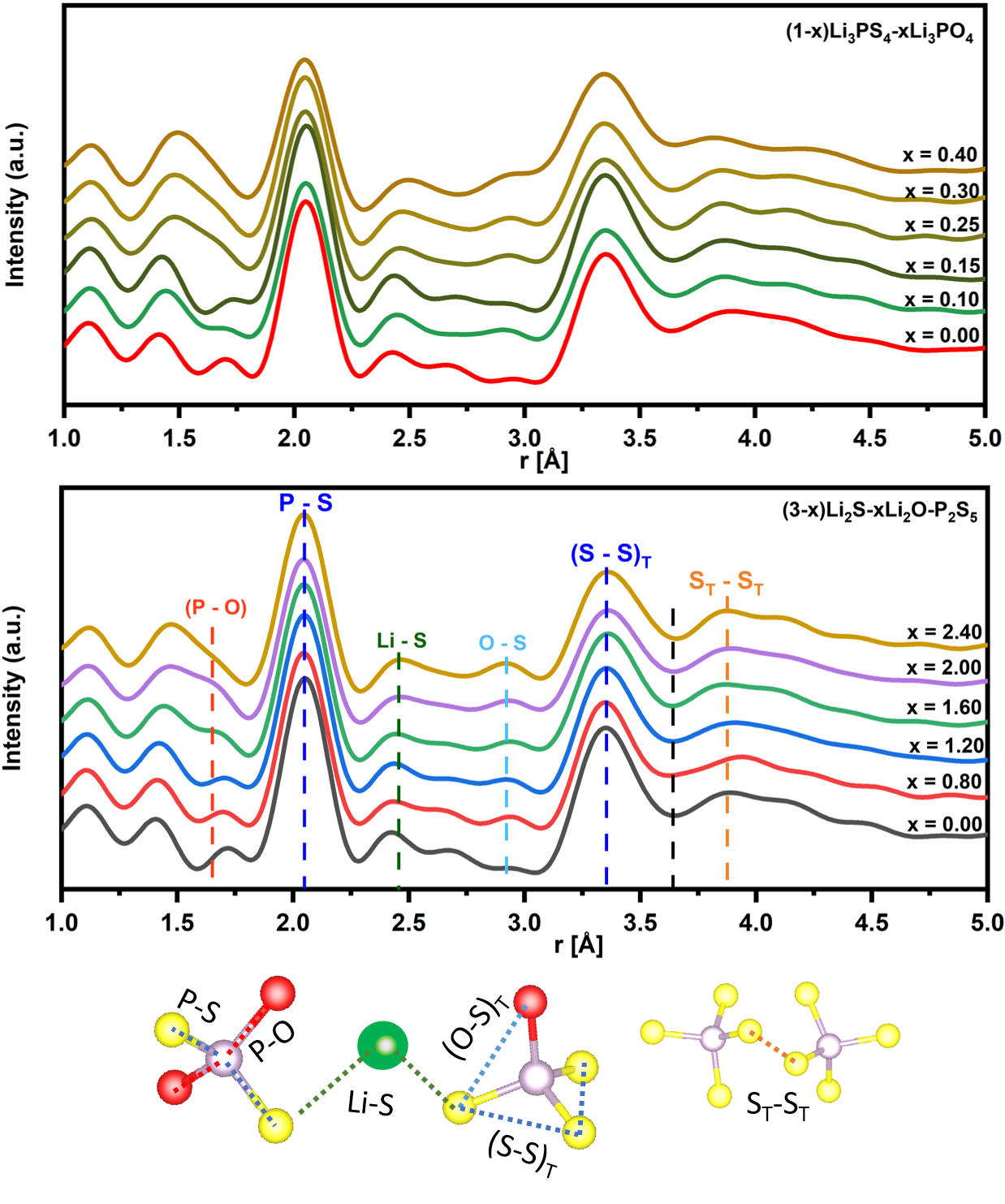
 **Figure S6**: Rietveld refinements of the LIPOS samples. Only β-Li3PO4 phase was refined, percentages denote the level of oxygen substitution.



**Figure S7**: XPS survey spectra (a) and high-resolution P 2p spectra (b) of starting materials of Li3PO4, Li3PS4, and oxysulfide mixtures (1-x)Li3PS4-xLi3PO4 (0.10 ≤ x ≤ 0.40) after mechanical milling.



**Figure S8**: PDFgui fit of LIPSO x = 0.3 with β-Li3PO4. Fit range from 4 – 60 Å.



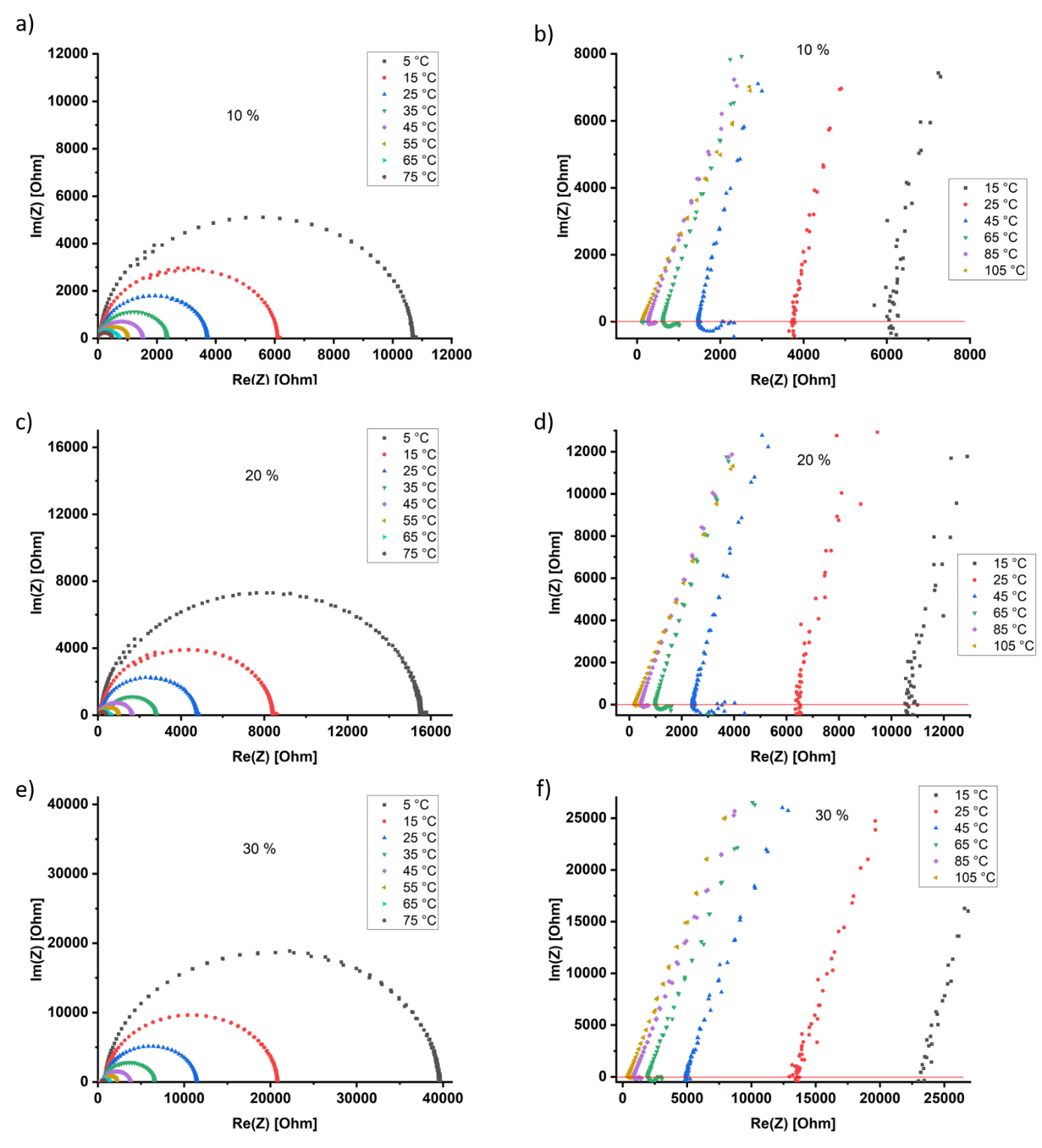
c

b

a

**Figure S9**: Zoom in on the low r region (r ≤ 5) of LIPSO (a) and LiO (b) with peak assignment and schematic representation of atom pairs found in the structures (c).

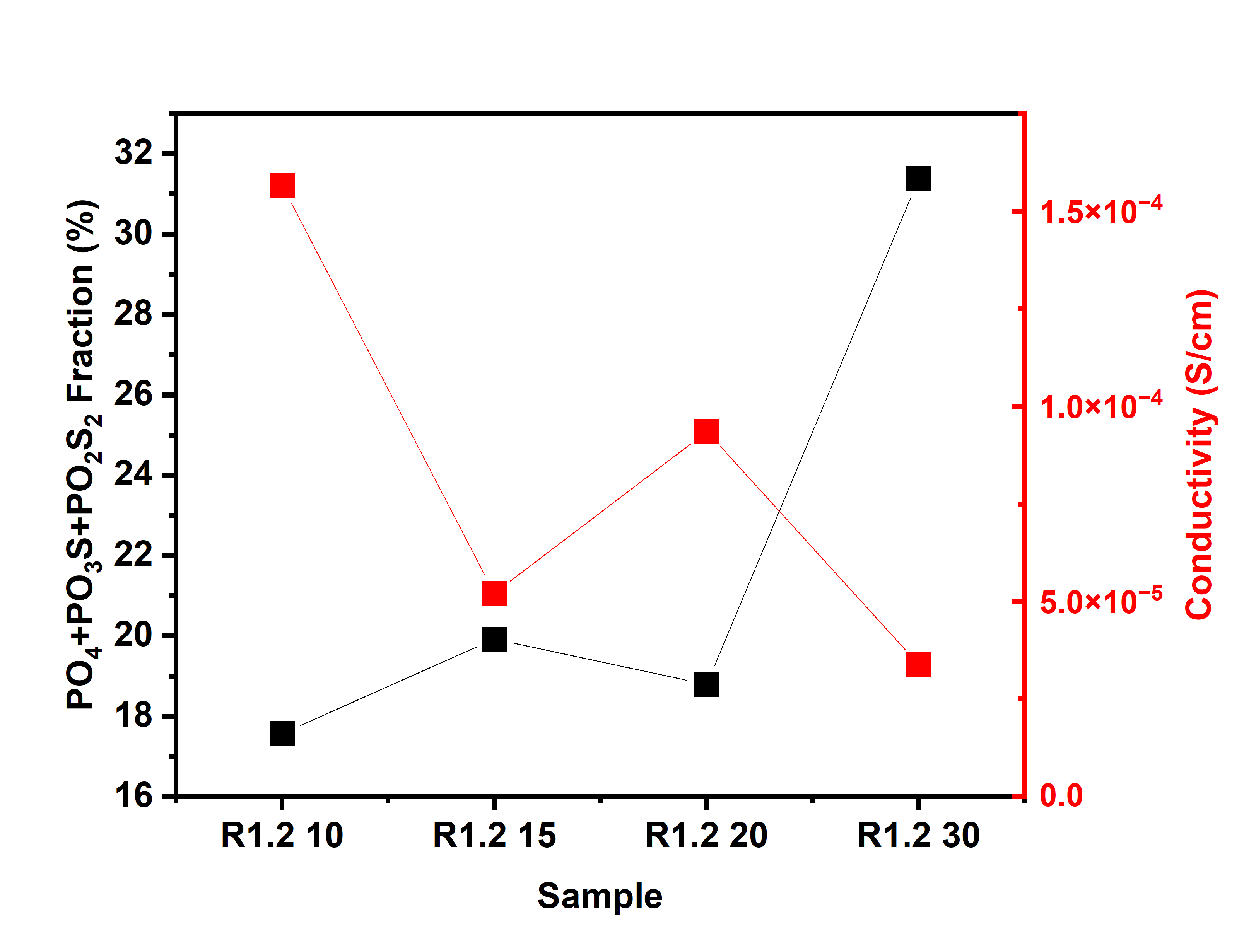
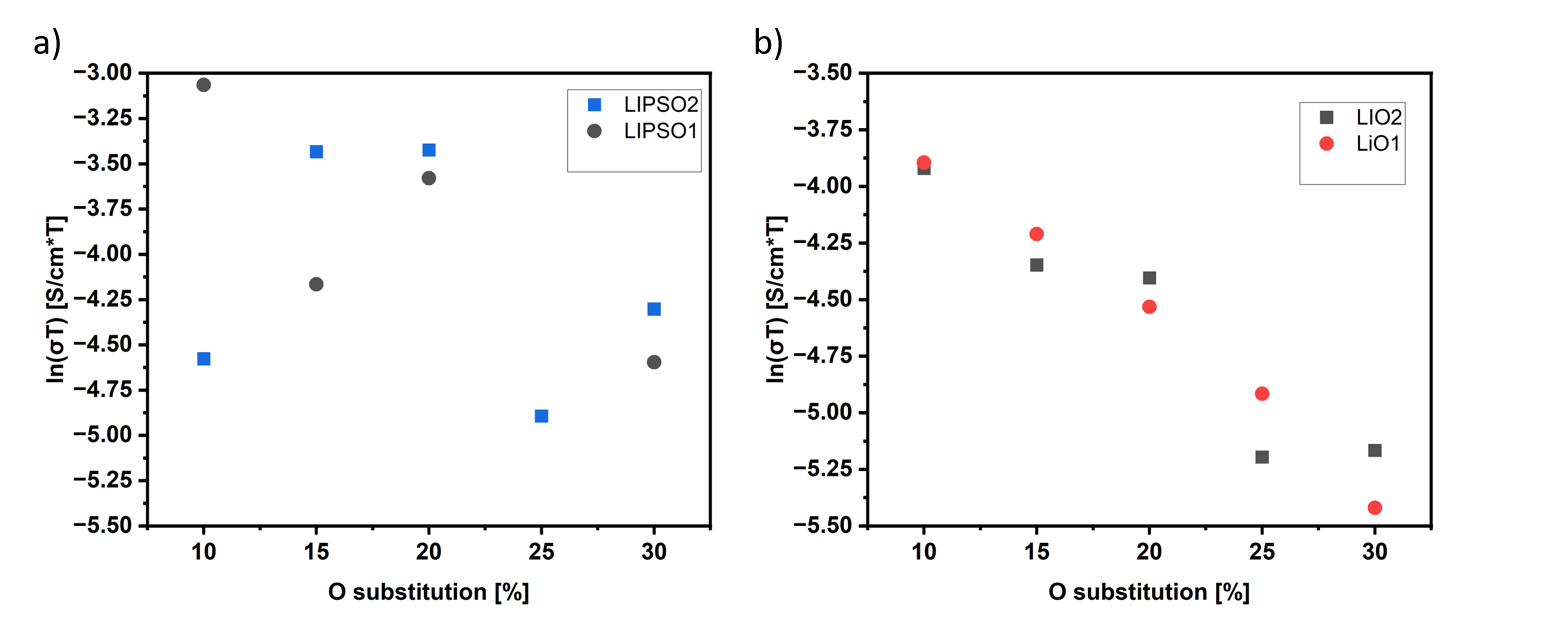
The P – O peak is not clearly visible and the region is overlayed by termination ripples. These ripples originate from the finite Qmax and can not be avoided. Similarly, the peaks for Li – S and O – S pairs cannot be undoubtedly assigned because their intensity is weak and its not clear that the peaks appearing in the PDFs are actually due to the named pair correlations, or ripples which coincidentally lie in the region where Li – S and O- S respectively are expected to be found.



**Figure S10:** Exemplary Nyquist plots impedance data from LiO samples with 10 (a, b), 20 (c, d), and 30 % (e, f) oxygen substitution. Plots on the left side present data from measurements with the in-house cell. Plots on the right present data from measurements with the CompreDrive setup.

The variations in resistance values for the same composition at a specific temperature in the impedance complex plane plots are a result of minor differences in the sample preparation and measurement conditions. The pellets measured with the in-house cell had a diameter of 8 mm, whereas the CompreCell fits pellets with a 6 mm diameter, therefore the absolute impedance values differ between the two measurements. Additionally, the pressure in the in-house cells cannot be adjusted as precisely as in the CompreCell. The thickness of both pellets was in the range of 0.7 mm.

Regarding the visibility of the Warburg impedance at low frequencies for the data collected with the in-house cell, we would like to clarify that the in-house cell has a different geometry and electrode material compared to the commercial cell, which can result in slight variations in the impedance spectra. To reduce the effects of pressure and ensure better contact between electrolyte pellet and electrodes, Li foil was added in the in-house cells on both sides of the pellet. As a result, a second semicircle can be identified at low frequencies and low temperatures, which as attributed to the charge transfer kinetics between electrolyte pellet and Li foil.

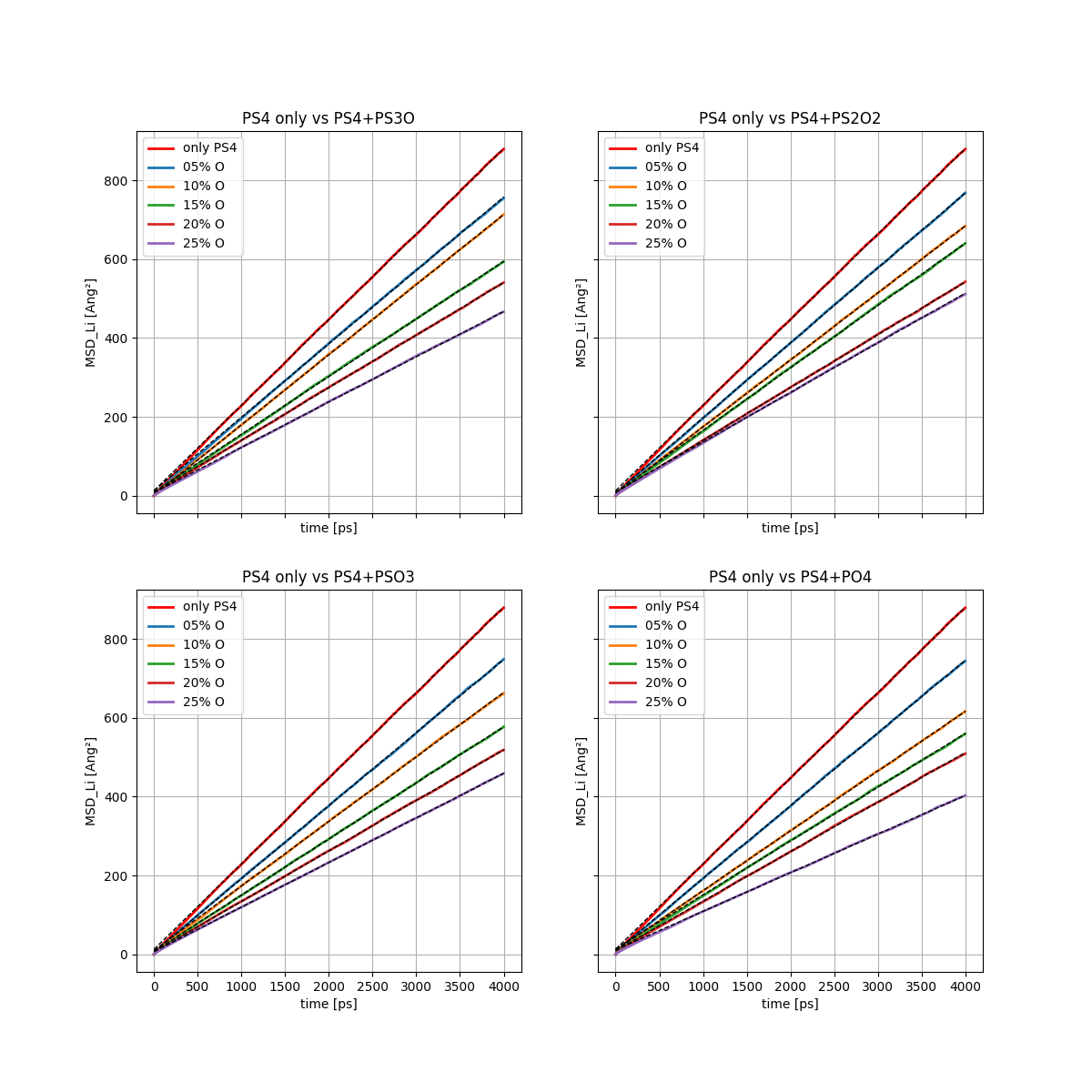


B

A

c

**Figure S11**: RT conductivity values against P – O content for LiPSO (a) and LiO (b) compared with their respective control experiment and the combined fraction of all tetrahedra with nO > 2 vs Li-ion conductivity for the LiPSO control experiment (c).



**Figure S12**: MSD curves for different structural composition and oxygen content with linear regressions (dotted black lines).

Ein Bild, das Text, Diagramm, Reihe, Screenshot enthält.

Automatisch generierte Beschreibung

**Figure S13**: Parity plot of predicted energies and forces with the fitted ACE potential versus the underlying DFT reference data of the training set.

Ein Bild, das Text, Diagramm, Reihe, Screenshot enthält.

Automatisch generierte Beschreibung

**Figure S14**: Parity plot of predicted energies and forces with the fitted ACE potential versus the underlying DFT reference data of the test set.

**Table S1**: Fractions of different structural units found in oxy-sulfide glasses based on NMR analysis and calculated statistical distribution.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Structure unit/** | **P2S7** | **P2S6** | **POS3/PS4** | **PO2S2** | **PO3S** | **PO4 (cryst)** | **PO4 (am)** | **P2O7** |
| **Sample** |
| LIPSO 0.10 | 13.74 | 7.10 | 50.14 | 9.76 | 9.5 | 1.59 | 4.06 | 4.11 |
| LIPSO 0.15 | 13.92 | 9.53 | 67.59 | 2.56 | 2.04 | 1.61 | 1.96 | 0.8 |
| LIPSO 0.20 | 14.66 | 3.83 | 66.28 | 3.89 | 3.78 | 1.65 | 2.65 | 3.27 |
| LIPSO 0.25 | 13.02 | 6.05 | 53.34 | 10.76 | 7.7 | 2.47 | 4.39 | 2.27 |
| LIPSO 0.3 | 14.14 | 6.97 | 51.54 | 6.78 | 8.31 | 2.5 | 4.03 | 6.06 |
| LIPSO 0.4 | 10.42 | 3.17 | 52.02 | 8.27 | 8.54 | 4.53 | 7.02 | 6.01 |
| LIO 0.8 | 16.71 | 10.51 | 58.22 | 10.41 | 3.15 | - | 0.58 | 0.43 |
| LIO 1.2 | 16.43 | 9.64 | 50.65 | 10.31 | 8.65 | - | 1.53 | 2.79 |
| LIO 1.6 | 17.14 | 11.73 | 43.37 | 11.18 | 9.84 | - | 2.33 | 4.40 |
| LIO 2.0 | 17.45 | 7.58 | 41.96 | 13.46 | 10.65 | - | 2.21 | 6.68 |
| LIO 2.4 | 17.08 | 5.25 | 38.84 | 12.08 | 12.92 | - | 2.84 | 10.98 |
| Stat. 10 % P-O | - | - | 94.77 (65.61/29.16) | 4.86 | 0.36 | - | 0.01 | - |
| Stat. 15 % P-O | - | - | 89.05 (52.2/36.85) | 9.75 | 1.15 | - | 0.05 | - |
| Stat. 20 % P-O | - | - | 81.92 (40.96/40.96) | 15.36 | 2.56 | - | 0.16 | - |
| Stat. 25 % P-O | - | - | 73.83 (31.64/42.19) | 21.09 | 4.69 | - | 0.39 | - |
| Stat. 30 % P-O | - | - | 65.17 (24.01/41.16) | 26.46 | 7.56 | - | 0.8 | - |
| Stat. 40 % P-O | - | - | 47.52 (12.96/34.56) | 34.56 | 15.36 | - | 2.56 | - |

**Table S2**: Final results of the ACE potential fitting for atomic energies E and forces F of the training and test set. RMSE = Root mean square error, MAE = mean absolute error, MAX\_AE = maximum absolute error. Elow and Flow indicate energies and forces.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | ***E***  **[eV/atom]** | ***E*low**  **[eV/atom]** | ***F***  **[meV/Å]** | ***F*low**  **[meV/ Å]** |
| Training Set: | | | | |
| RMSE | 1.07 | 0.88 | 45.99 | 43.35 |
| MAE | 0.75 | 0.65 | 31.21 | 29.90 |
| MAX\_AE | 7.55 | 3.87 | 1502.89 | 1258.56 |
| Test Set: | | | | |
| RMSE | 1.10 | 0.92 | 47.18 | 43.10 |
| MAE | 0.78 | 0.69 | 31.49 | 29.45 |
| MAX\_AE | 5.26 | 4.08 | 1625.11 | 1625.11 |