

Gently Does It!: In Situ Preparation of Alkali Metal - Solid Electrolyte Interfaces for Photoelectron Spectroscopy – Supporting Information

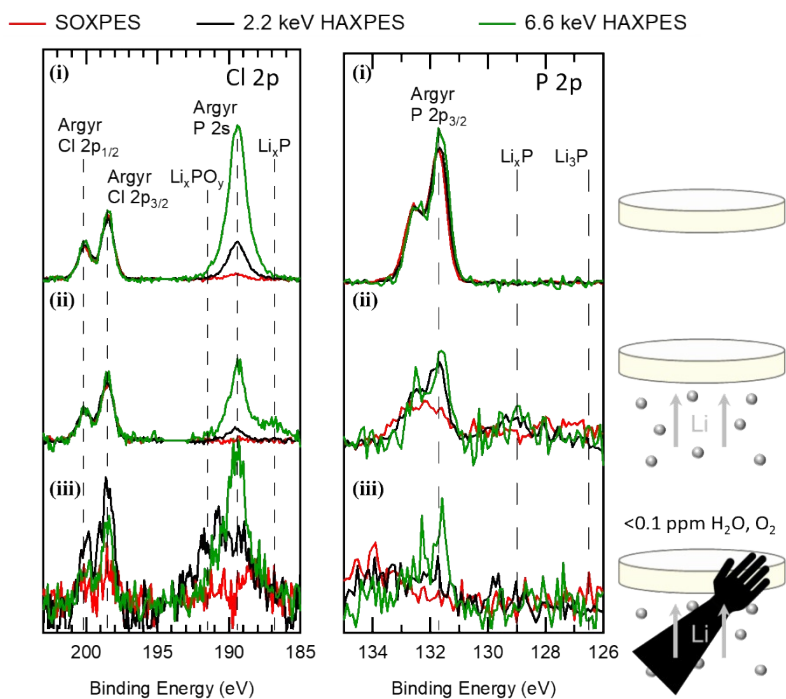
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**Supporting Information 1 – SOXPES and HAXPES data for Cl 2p and P 2p**

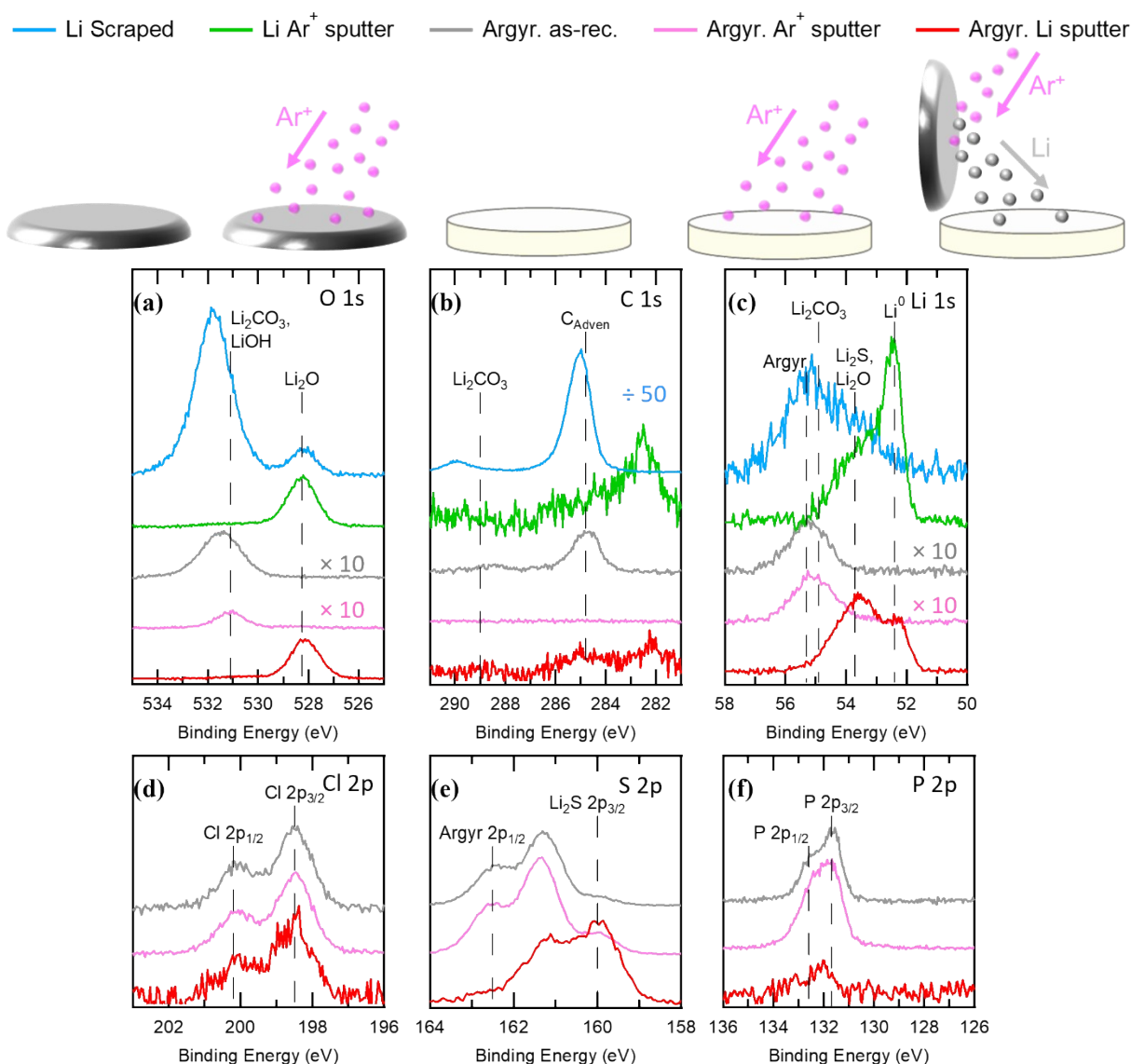


**Figure S1:** Synchrotron HAXPES ( $h\nu = 2.2$  keV, black and 6.6 keV, green) and SOXPES (kinetic energy = 315 eV, red) data for (i) as-received bare  $\text{Li}_6\text{PS}_5\text{Cl}$  argyrodite, (ii) 20 nm Li evaporated on  $\text{Li}_6\text{PS}_5\text{Cl}$  in situ and (iii) 20 nm of Li on  $\text{Li}_6\text{PS}_5\text{Cl}$  after inert transfer through an Ar glovebox atmosphere. Data has been normalised such that the Cl 2p and P 2p peak areas are unity, with the binding energy calibrated such that the Cl  $2p_{3/2}$  sits at 198.5 eV.

As is the case in the main text, the Cl  $2p_{3/2}$  peak has been used as an internal reference at 198.5 eV, with the Cl environment unchanged as a consequence of lithium evaporation or glovebox exposure. Recoil effects on the heavier P and Cl atoms are not sufficient to affect the binding energies of any of the spectra in fig S1, as described in the main text. The spectra shown in the top row, figure S1 (i), display only one chemical environment for each element with Cl 2p and P 2p peaks at  $\approx 198.5$  eV and  $\approx 131.7$  eV, respectively, both corresponding to the pristine  $\text{Li}_6\text{PS}_5\text{Cl}$  argyrodite. The Cl 2p and P 2p peaks display a doublet due to spin-orbit splitting of the p-orbital electrons, with the peak splitting observed consistent with literature values [1]. Within the Cl 2p region the P 2s photoelectron peak can be observed at  $\sim 189.4$  eV, also displaying a single chemical environment. With increasing photon energy from SOXPES (315 eV KE, red) to 6.6 keV (green) there is an increase in the ratio of the P 2s to the Cl 2p. This change can be rationalised by the differences in the absorption cross sections with photon energy. The absorption cross section for the 2p orbital decays much more rapidly than that of the 2s orbital, with increasing photon energy, resulting in a greater relative signal arising from the 2s orbital, compared to the 2p orbitals, at high photon energies (6.6 keV) compared to low ones (SOXPES) [1]. Consequently, this change should not be interpreted as a greater quantity of phosphorus in the near-surface region than in the bulk.

The second row of data for the in situ UHV evaporated sample, figure S1 (ii), displays an increased quantity of noise due to the expected attenuation of the emitted photoelectrons through the Li overlayer. The low signal to noise ratio supports the claim that the lithium overlayer does not contain high concentrations of Cl or P species. The P 2s and P 2p show evidence of some partially reduced phosphorous species,  $\text{Li}_x\text{P}$ , for the 2.2 keV and 6.6 keV data, indicating that these species exist at a buried interface, rather than at the outermost surface. The spectra the third row of fig S1 (iii), show the Cl and P data for an in situ deposited Li film after ‘inert’ transfer in a glovebox-like environment using a polymer gasket sealed inert transfer device. Although the data is very noisy it may be possible to observe some oxidised lithium phosphate ( $\text{Li}_x\text{PO}_y$ ) on the high binding energy side of the P 2s and P 2p data. The greater quantity of noise observed for these spectra compared to the data in the second row can be rationalised by the fact that lithium carbonate attenuates photoelectrons to a greater degree than lithium metal (inelastic mean free paths of 41.08 Å and 55.70 Å at 1500 eV, respectively), despite the same nominal film thicknesses [2]. Consequently, the photoelectrons are not able to escape as efficiently through the lithium carbonate layer that has formed from the reaction of Li metal with contaminants during this ‘inert’ transfer.

## **Supporting Information 2 – Comparison of Li metal sputtered argyrodite and argon ion sputtered argyrodite and Li metal surfaces**

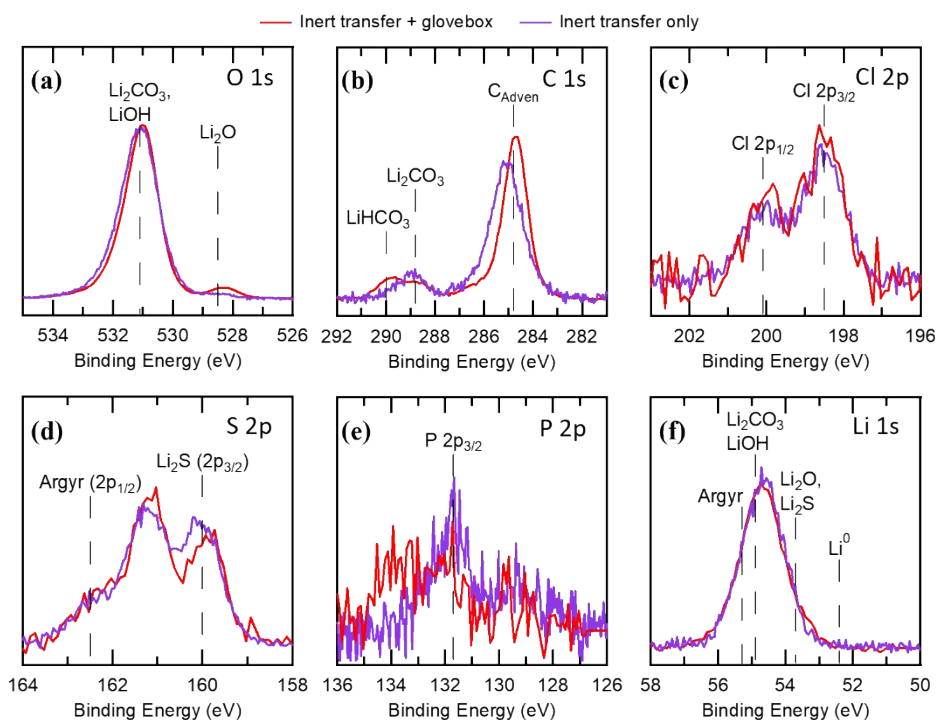


**Figure S2:** Photoelectron spectra comparing sputtering induced effects following  $\text{Ar}^+$  and lithium metal sputtering. Spectra have been collected for Li metal mechanically scraped clean in a glovebox (blue) and after  $\text{Ar}^+$  sputtering (green). Data for an as-received  $\text{Li}_6\text{PS}_5\text{Cl}$  argyrodite (grey), after sputtering with  $\text{Ar}^+$  (pink) and after sputter deposition of Li metal (red). Core level spectra are shown for (a) O 1s, (b) C 1s, (c) Li 1s, (d) Cl 2p, (e) S 2p and (f) P 2p. For argyrodite containing surfaces data has been normalised to the Cl peak area with the binding energy calibrated such that the Cl  $2p_{3/2}$  sits at 198.5 eV. For Li metal surfaces data has been normalised to the Li peak area with the binding energy calibrated such that the  $\text{Li}_2\text{O}$  sits at 528.3 eV. Spectra are offset for clarity. For added clarity the O 1s and Li 1s the spectra for as-received and  $\text{Ar}^+$  sputtered  $\text{Li}_6\text{PS}_5\text{Cl}$  have been multiplied by a factor of 10 and the C 1s spectrum of the scraped Li chip has been reduced by factor 50.

The spectra in figS2 compare the sputtering induced effects for  $\text{Ar}^+$  and Li metal beams on  $\text{Li}_6\text{PS}_5\text{Cl}$  (fig. S2, pink and red, respectively), and  $\text{Ar}^+$  beam on Li metal (fig. S2, green). Irradiation of Li metal with  $\text{Ar}^+$  ions is seen to decrease the  $\text{Li}_2\text{CO}_3$  /  $\text{LiOH}$  peak at  $\sim 531$  eV, however the  $\text{Li}_2\text{O}$  at  $\sim 528.3$  eV is seen to increase, in accordance with previous reports [3]. The C 1s data shows that irradiation of a Li metal surface with  $\text{Ar}^+$  removes the  $\text{Li}_2\text{CO}_3 \approx 289$  eV and adventitious carbon at  $\approx 285$  eV. For the Li metal surface the Li 1s spectra show an increase in the metallic Li component at  $\approx$

52.4 eV with Ar<sup>+</sup> etching, as well as evidence of Li<sub>2</sub>O at ≈ 53.7 eV. Irradiation of Li<sub>6</sub>PS<sub>5</sub>Cl with Ar<sup>+</sup> ions for 30 minutes results in a reduction of the Li<sub>2</sub>CO<sub>3</sub> / LiOH peaks present in both the O 1s and the C 1s region, as well as the C<sub>adven</sub> environment. Sputter deposition of 10 nm Li metal onto the Li<sub>6</sub>PS<sub>5</sub>Cl surface also causes a removal of the Li<sub>2</sub>CO<sub>3</sub> / LiOH and C<sub>adven</sub> peaks as well as an increase in the Li<sub>2</sub>O peak, due to reaction of the Li metal with trace oxygen in the UHV chamber. These results show that irradiation of the Li<sub>6</sub>PS<sub>5</sub>Cl surface with the high energy Ar<sup>+</sup> ions or Li metal have a similar effect, with both removing surface adsorbed Li<sub>2</sub>CO<sub>3</sub> / LiOH and C<sub>adven</sub>. The Li 1s core level for the Li<sub>6</sub>PS<sub>5</sub>Cl surface does not appear to undergo any changes as a result of Ar<sup>+</sup> sputtering, but for Li metal sputtering an increase in the Li peak is expected, as described in the main text. The Cl 2p spectra, fig S2 (d), are very similar for the as-received, Ar<sup>+</sup> sputtered and Li sputtered Li<sub>6</sub>PS<sub>5</sub>Cl surfaces, with the reduced signal to noise ratio, observed for the Li coated surface, due to attenuation through the Li metal overlayer. For the S 2p spectra, fig S2 (e), the Li sputtered surface shows Li<sub>2</sub>S as the majority component, rather than the Li<sub>6</sub>PS<sub>5</sub>Cl component, as seen in the as-received and Ar<sup>+</sup> sputtered surfaces. The P 2p data, fig S2 (f), appears to present a lower proportion of phosphorous in the near surface region, compared to the Cl species to which the data is normalised, for the Li sputtered surface. Additionally, the spin-orbit peaks for the P 2p data for the Ar<sup>+</sup> sputtered Li<sub>6</sub>PS<sub>5</sub>Cl appears to be less well resolved than for the bare as-received pellet. These observations, namely the loss of surface chemical species and the generation of damaged environments, are consistent with effects expected from sputter damage of the surfaces by the incoming Ar<sup>+</sup> ions or Li metal particles.

### **Supporting Information 3 – Comparison of Direct inert transfer to XPS with Glovebox exposed samples**



**Figure S3:** Photoelectron spectra comparing the surfaces obtained for Li evaporated on  $\text{Li}_6\text{PS}_5\text{Cl}$  after inert transfer directly into the XPS analysis chamber (purple,  $h\nu = 1.486$  keV) and transfer via a glovebox (red,  $h\nu = 2.2$  keV). Core level spectra are shown for (a) O 1s, (b) C 1s, (c) Cl 2p, (d) S 2p, (e) P 2p and (f) Li 1s. For each core level, data has been normalised have equal areas to negate differences in escape depth. Binding energy calibrated such that the Cl  $2p_{3/2}$  sits at 198.5 eV.

The data shown in figure S3 show photoelectron spectra for Li evaporated under UHV onto  $\text{Li}_6\text{PS}_5\text{Cl}$ . The purple data shows the data following direct transfer (time in transfer device < 10 minutes) to the analysis instrument via an inert transfer in a device sealed with a polymer O-ring, whilst the data in red shows a sample which has been transferred into a glovebox, through use of a polymer sealed inert transfer device, prior to analysis (total time in glovebox and transfer device ~6 hours). The purple data were collected in a lab-based XPS (Al  $K\alpha$ ,  $h\nu = 1486$  eV) whilst the red data were collected at the Diamond Light Source synchrotron ( $h\nu = 2200$  eV). For the photon energy used here recoil effects are not significant (less than 0.1 eV), as described in the main text. There is a similarity in many of the core levels, with evidence of  $\text{Li}_2\text{CO}_3$  /  $\text{LiOH}$  species having formed on both surfaces, as shown in the O 1s and C 1s data at ~531 eV and ~289 eV, respectively. The surface that has been exposed to a glovebox for a longer period has evidence of  $\text{LiHCO}_3$  formation, as discussed in the main text. In both cases the evaporated lithium layer can be seen to attenuate the P 2p and the Cl 2p signals, as evidenced by the reduced signal-to-noise ratio. Both surfaces show evidence of  $\text{Li}_2\text{S}$  being the predominant sulphur species in the near surface region, whilst neither of the samples show any evidence of a metallic Li peak, with the  $\text{Li}_2\text{CO}_3$  /  $\text{LiOH}$  species at ~54.7 eV dominant. It is likely

that the slight differences observed in the O 1s, C 1s and S 2p data may be a result of the different probing depths afforded by the use of the two different photon energies. These data show that the use of inert transfer devices, even for short periods of time, can result in the reaction and passivation of surface layers, especially for alkali metals.

## References

- [1] Albert C. Thompson, *et al.*, *X-ray Data Booklet*. Eds., Lawrence Berkeley National Laboratory, California, (2009)
- [2] A. Jablonski and C.J. Powell *NIST Standard Reference Database 71: NIST Electron Inelastic-Mean-Free-Path Database Version 1.2*, (accessed 2021)
- [3] Otto, S.-K., Moryson, Y., Krauskopf, T., Pepler, K., Sann, J., Janek, J. and Henss, A., *In-Depth Characterization of Lithium-Metal Surfaces with XPS and ToF-SIMS: Toward Better Understanding of the Passivation Layer*. *Chemistry of Materials*, **33**, (2021), pp. 859-867.