Supporting Information for "Electro-Chemo-Mechanical Evolution of Sulfide Solid Electrolytes/ Li Metal Interfaces: Operando analysis and ALD Interlayer Effects"

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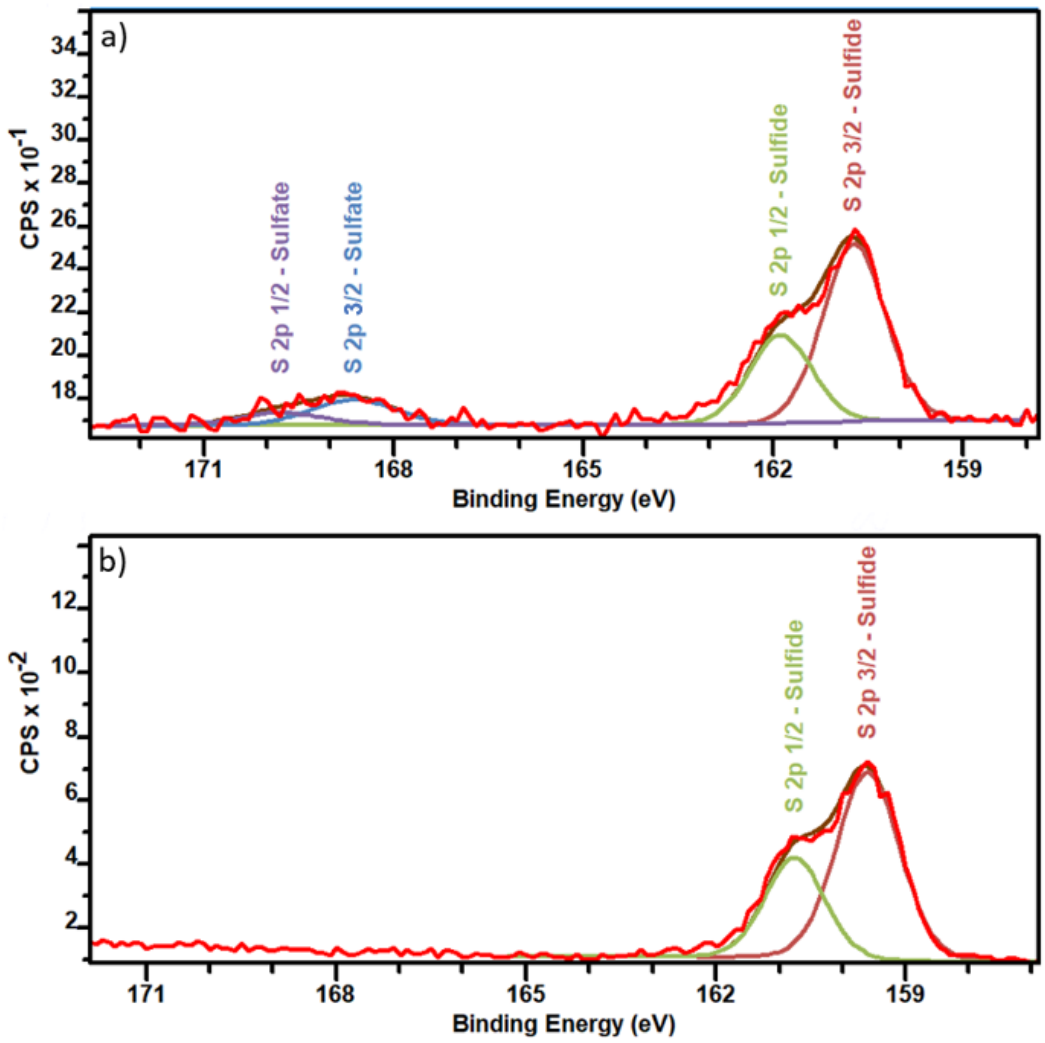

Figure S1. XPS analysis of the ALD/LGPS interface. a) S 2p peaks showing LGPS through 30x (3 nm) of ALD Al_2O_3. b) S 2p peaks of the uncoated LGPS surface.

As can be seen in the ALD-coated sample, a small peak associated with sulfate species forms at the ALD/LGPS interface, which is attributed to bonding between sulfur species in the LGPS and oxygen in the Al_2O_3. However, the majority of the sulfur at the interface remains in the sulfide phase, with only 15% of the sulfur at the interface associated with sulphate. This demonstrates that while there is some very slight oxidation of the sulfur during deposition, it is highly localized to the first few atomic layers of the interface.

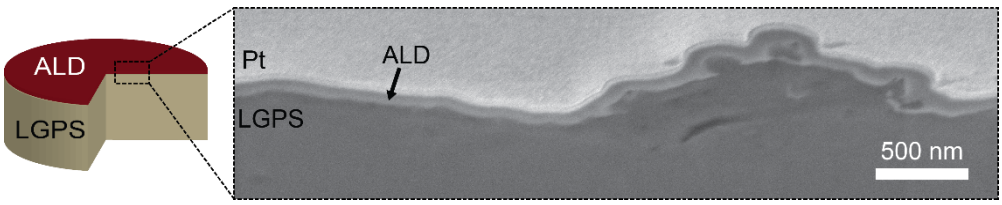

Figure S2. FIB-SEM cross section of the ALD coated LGPS surface. The ALD conformally coats the LGPS. Growth rates measured by SEM match those measured by elipsometry on adjacent Si samples. Pt was deposited in the SEM to achieve a clean cross section of the ALD.

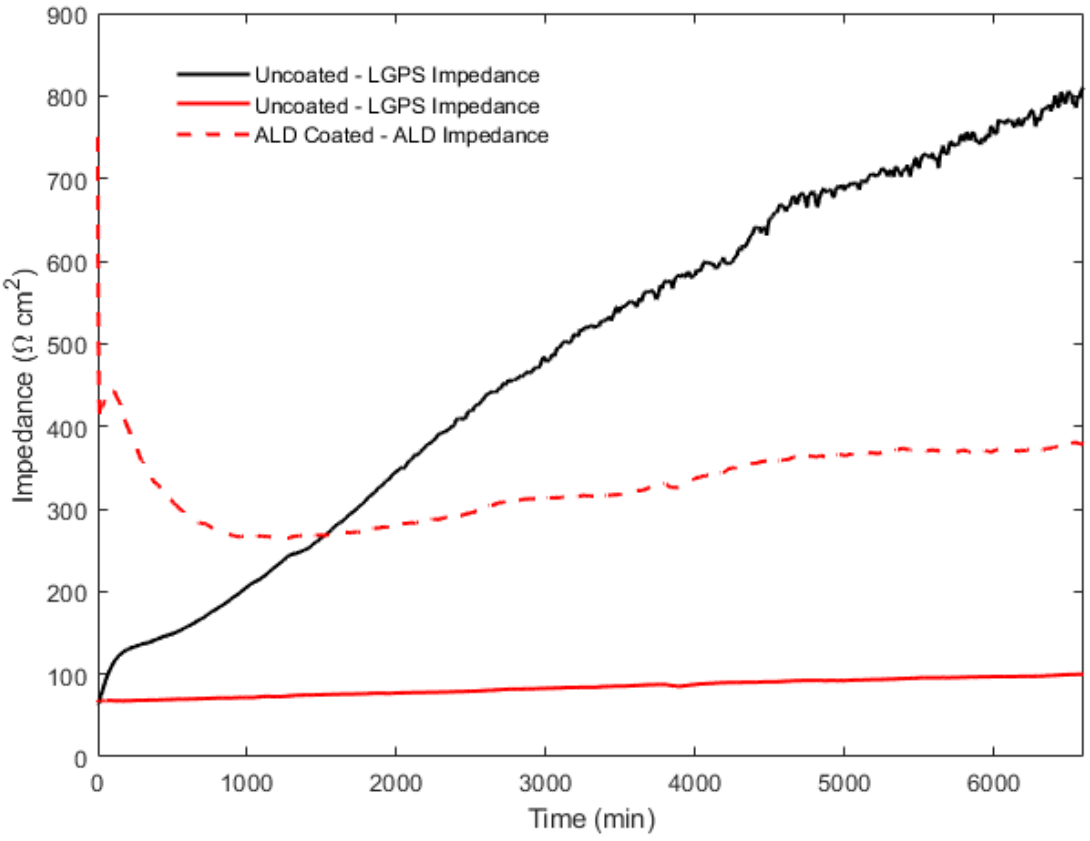

Figure S3. Fits of semicircles from Nyquist plots in Figure 1c-d.

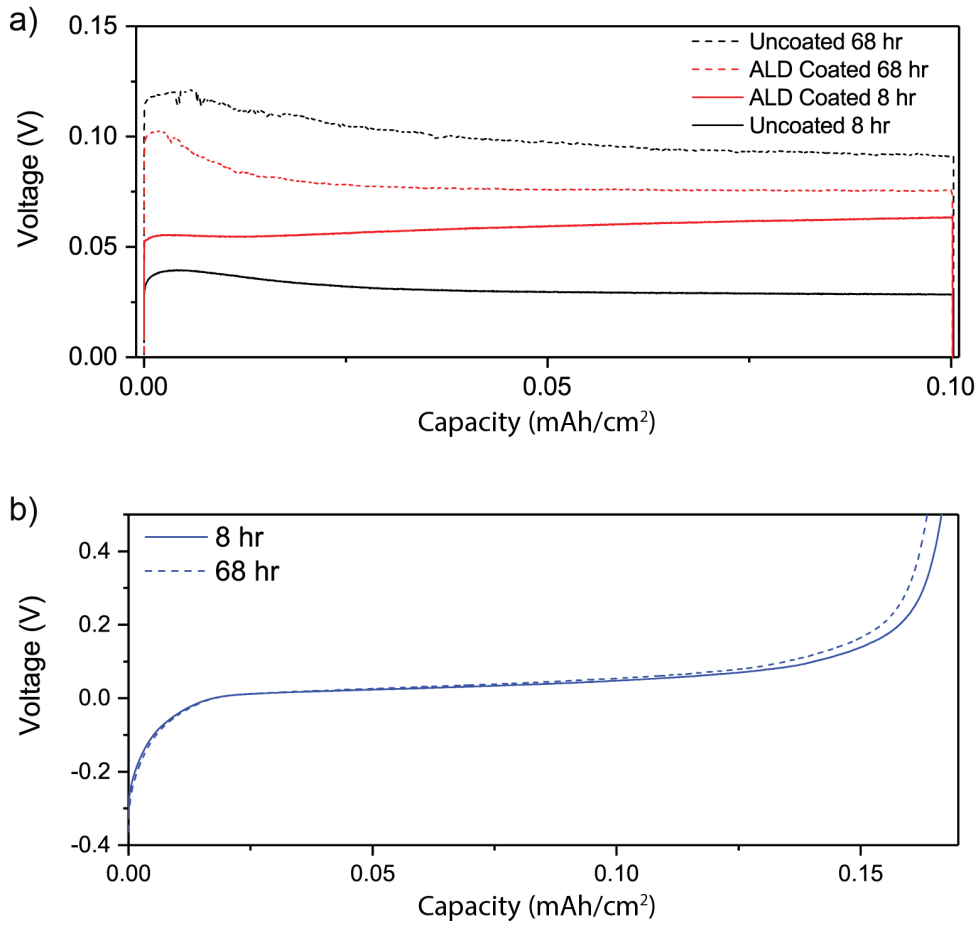

Figure S4. (a) Voltage profiles of uncoated and ALD coated Li-Li symmetric cells at 8 hrs and 68 hrs of cycling. (b) LTO/LGPS/LTO symmetric cell charging cycles with a current density of 0.02 mA/cm^2. Little change is observed after formation cycles (8 hrs after start of cycling) and after significant cycling (after 68 hrs of cycling).

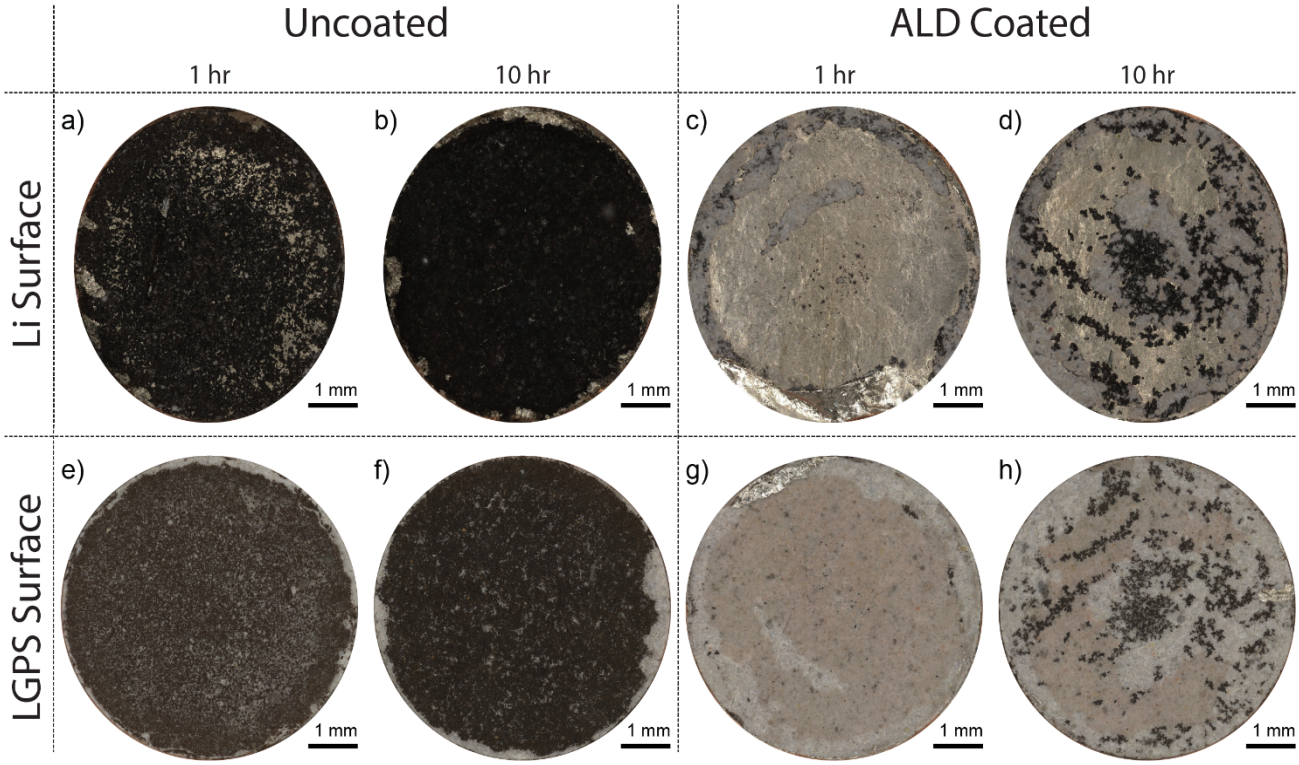

Figure S5. (a-d) Optical images of the Li surfaces after cell disassembly when the Li is peeled off of the LGPS surface. (e-h) Optical images of the corresponding LGPS surfaces from Figure 2 are included here for comparison. In the uncoated samples the entire surface of both the Li and the LGPS is covered in blackened areas indicating significant reduction of the LGPS has occurred. Reduced LGPS debris easily breaks away and sticks to the Li surface during disassembly. In the ALD coated case, after 1 hr of Li contact, little reduced LGPS debris is visible on either the Li metal or LGPS surfaces. Due to this lack of reduced LGPS, the Li remains tightly adhered to the LGPS surface and is significantly more difficult to remove. Because of this increased adhesion, a few chunks of the bulk LGPS are ripped out of the pellet and remain adhered to the Li metal. The most visible of these chunks is the lighter crescent shape visible in (c) and (d) and is shown in more detail in Figure S6.

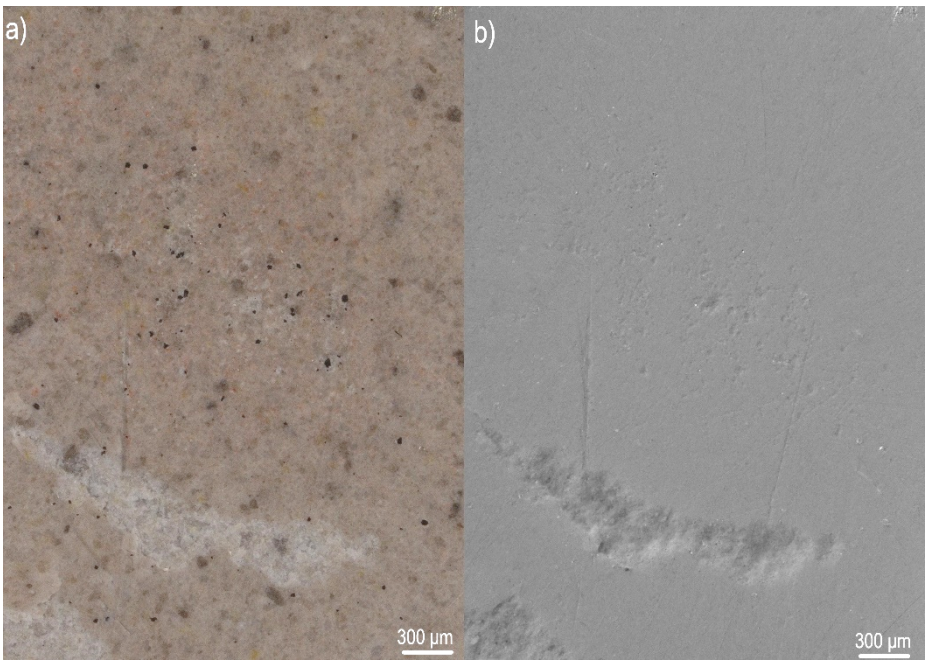

Figure S6: (a) Optical image showing higher magnification view of LGPS surface from Figure S5g. (b) Optical shadow effect mode image showing the LGPS surface 3D topography. Pits are visible where chunks of LGPS were ripped out of the LGPS pellet during cell disassembly.

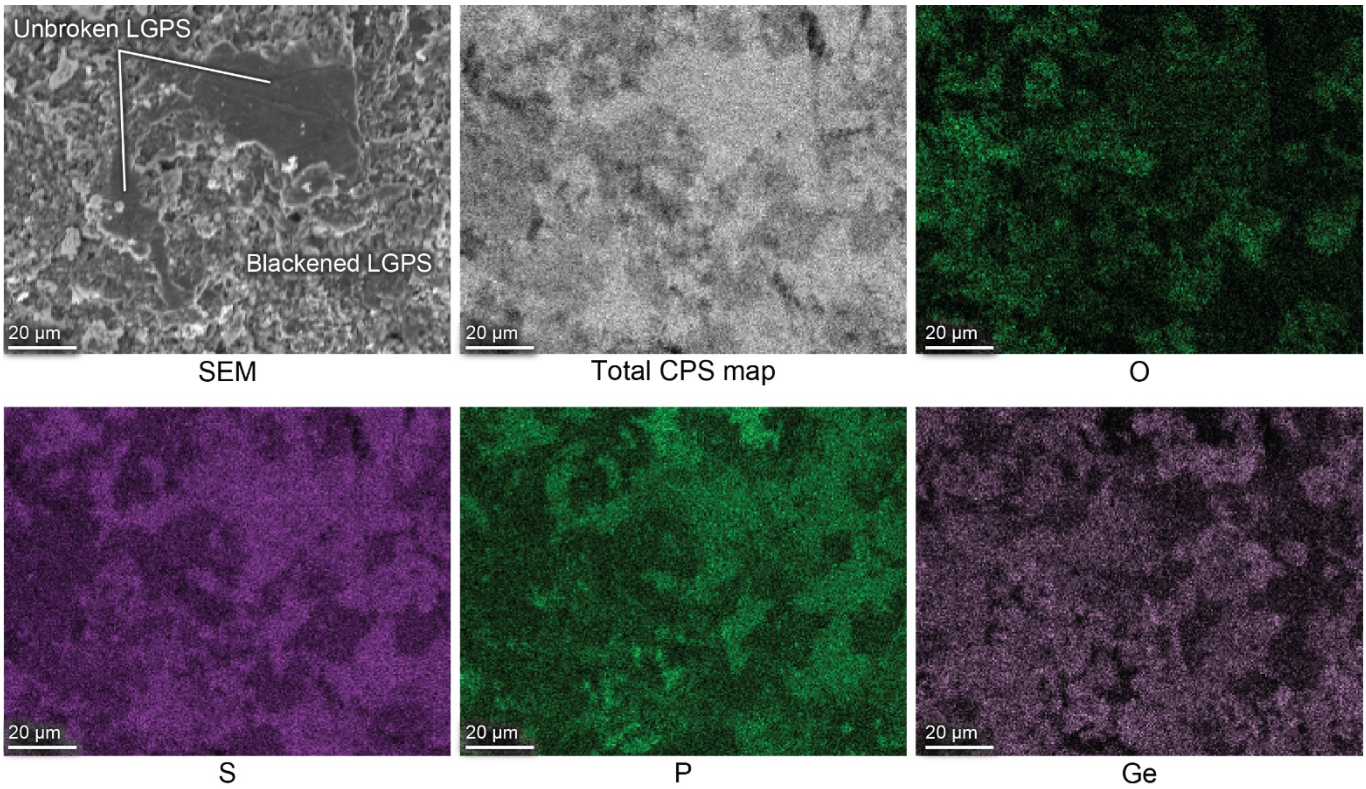

Figure S7: EDS elemental maps of the uncoated sample after contact with lithium metal. Texturing in the blackened LGPS region leads to non-uniform signal intensity but does not show consistent differences in elemental composition.

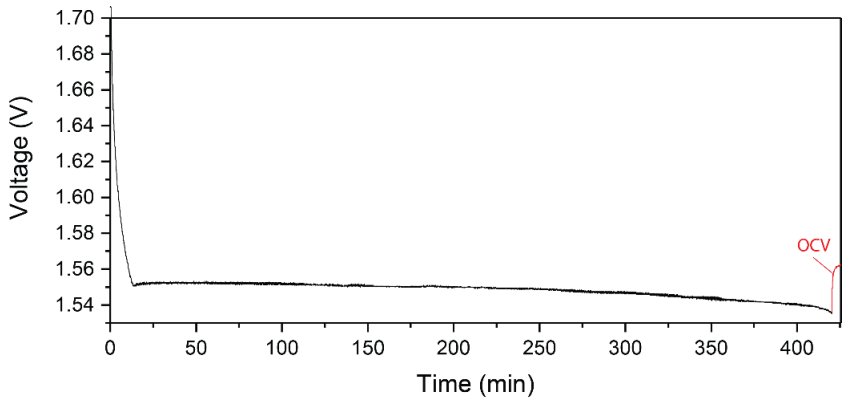

Figure S8. Final lithiation cycle and following OCV rest of LTO electrode in liquid electrolyte coin cell.

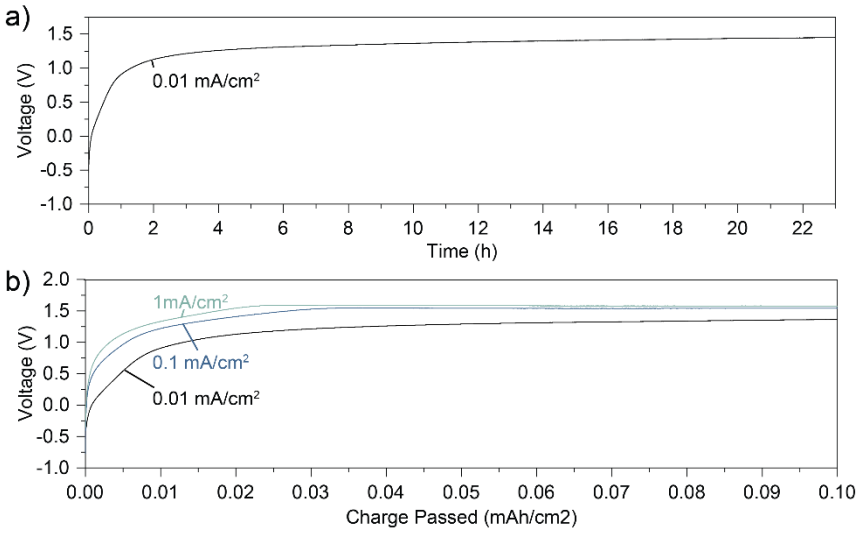

Figure S9. (a) Extended voltage trace of 0.01 mA/cm^2 uncoated half cell shown in Figure 7. Even after 23 hr the cell has not reached 1.53 V (the Li/LTO OCV potential). (b) Voltage traces from Figure 7l plotted with respect to charge passed. At higher current densities Li metal plating occors with less total charge passed.

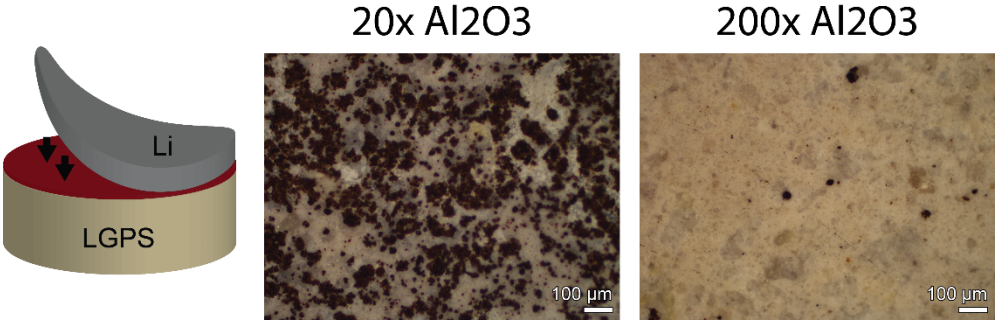

Figure S10. Optical microscopy of ALD coated LGPS surfaces with different numbers of ALD cycles after 1 hr of contact with Li. 200 cycles of Al_2O_3 showed significantly better stabilization than 20 cycles.

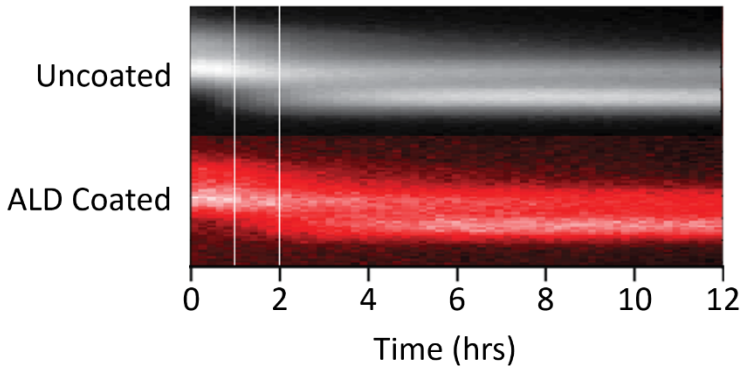

Figure S11. OpXPS S 2p spectra from Figure 4. Spectra have been aligned to show onset times for peaks corresponding to Li_2S.

References

1 K. N. Wood, K. X. Steirer, S. E. Hafner, C. Ban, S. Santhanagopalan, S.-H. Lee and G. Teeter, *Nat. Commun.*, 2018, **9**, 2490.