

## Characterising and Minimising Damage Effects in Air- and Beam-sensitive Solid-state Li-ion Battery Materials

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Solid-state Li-ion batteries (SSLIBs) have potential to revolutionise the electric-vehicle industry due to both their superior capacity and improved safety relative to conventional liquid cells. However, commercialisation of SSLIBs is at present hindered by the side reaction which occurs at the electrode-electrolyte interface. This reaction leads to voltage hysteresis and capacity fading, and subsequently to degraded battery performance [1].

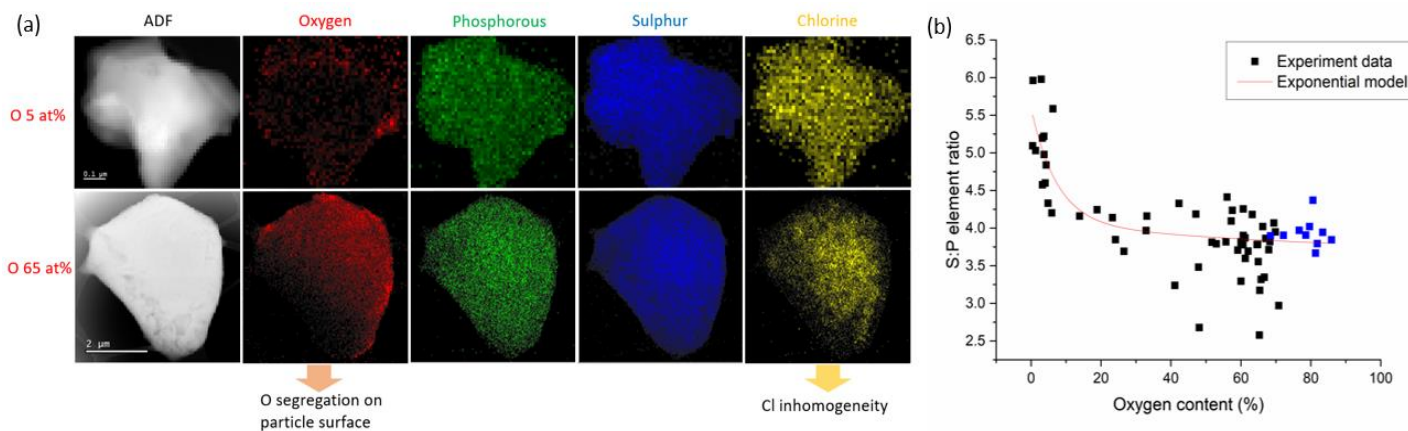
Understanding this electrochemical performance decay at the nanoscale requires the use of high-resolution characterisation techniques such as transmission electron microscopy (TEM). However, TEM studies of SSLIBs are complicated due to the extreme air- and electron-beam sensitivity of battery materials. It is therefore important to understand the effects of such damage to the native interface structure, and operate below these thresholds and/or identify the onset of damage during high-resolution imaging and spectroscopy experiments.

Initial observations showed that air exposure of the solid-state electrolyte argyrodite ( $\text{Li}_6\text{PS}_5\text{Cl}$ ) is characterised by inhomogeneity of chemical elements such as Cl and O (Fig.1(a)), along with significant changes in sample morphology. Deliberate exposure of argyrodite particles to oxygen-rich environments showed a trend of sulphur deficiency with increasing oxygen contamination (Fig.1 (b)). To mitigate these effects on studies of the argyrodite- $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  (NMC622) cathode interface, we developed an anaerobic sample transfer protocol which minimised air exposure and therefore prevented oxygen-related sample degradation.

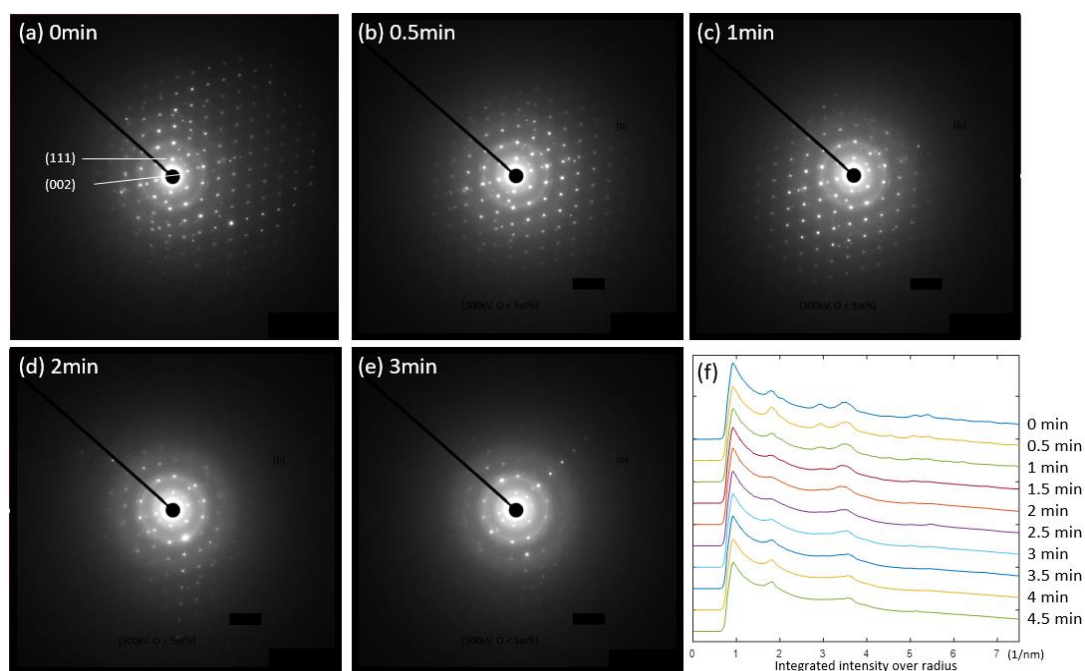
We proceeded to characterise the effects of electron beam damage by observing changes in the argyrodite in-situ diffraction pattern (DP). Particle tilting can be observed as a result of beam damage from the Laue Zone shift from top right to bottom left in Fig. 2 (a)-(e). Critical dose thresholds were calculated by monitoring of the diffraction spots intensity measured with time (and therefore increasing electron dose), as shown in Figure 2(f).

By combining this anaerobic sample transfer and knowledge of critical electron dose limits, it was possible to study the argyrodite-NMC622 spontaneous redox side reaction at the interface in its near-native state. Scanning transmission electron microscopy (STEM) EDS and annular dark field (ADF) imaging allowed characterisation of chemical elemental distributions and particle morphology respectively. Electron energy loss spectroscopy (EELS) was also used to map the Ni oxidation state, using the L<sub>2,3</sub> white line ratio and by development of a quantification routine based on model fitting in Hyperspy [2] of raw experimental data with low signal-to-noise ratios.

The ability to characterise air- and electron beam-damage is key to managing the particular experimental challenges relating to (S)TEM studies of solid-state battery materials. Such challenges are of particular importance for high-resolution characterisation, as needed to further our understanding of, for example, the argyrodite-NMC622 interface. Such work has exciting potential to guide future materials selection and interface design, by correlating microstructure, composition and electrochemical performance.



**Figure 1.** (a) EDS elemental map of O, P, S and S on argyrodite at oxygen content of 5 at% and 65 at% (b) S: P element ratio against oxygen content (blue data points were acquired with cryogenic holder).



**Figure 2.** Diffraction pattern of argyrodite at 300kV at (a)  $t=0$  min, (b)  $t=0.5$  min, (c)  $t=1$  min, (d)  $t=2$  min, (e)  $t=3$  min; (f) integrated diffraction spots intensity over radius

## References:

- [1] JM Tarascon and M Armand in "Materials for sustainable energy: a collection of peer-reviewed research and review articles from Nature Publishing Group" (2011), p. 171. doi: 10.1142/9789814317665\_0024
- [2] F de la Peña et al., *hyperspy/hyperspy: v1.6.5*. 2021: Zenodo.
- [3] The authors acknowledge use of characterization facilities within the David Cockayne Centre for Electron Microscopy, Department of Materials, University of Oxford and in particular the Faraday Institution (FIRG007, FIRG008), the EPSRC (EP/K040375/1 "South of England Analytical Electron Microscope") and additional instrument provision from the Henry Royce Institute (Grant reference EP/R010145/1).