

## Batteries

### *Imaging degradation*

***The degradation and failure of Li-ion batteries is strongly associated with electrode microstructure change upon (de)lithiation. Now, an operando X-ray tomography approach is shown to correlate changes in the microstructure of electrodes to cell performance, and thereby predict degradation pathways.***

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Li-ion batteries have revolutionised modern life, most notably through their use in consumer electronics, but also powering applications as diverse as medical implants, grid scale storage and satellites. In the future, battery technologies will continue to shape the way we live, from post Li-ion batteries for automotive applications, to off grid micro-generation systems to power our homes. However, with increasing concern regarding the safety and durability of batteries, fuelled by recent high profile failures, it is essential that materials scientists and engineers understand the fundamental degradation mechanisms. Writing in Nature Communications, Vanessa Wood and co-workers from Switzerland and Germany now report an advanced 3D X-ray imaging technique to explore the relationship between performance and microstructure for current and future generation battery materials [1].

Porous materials are commonly used as electrodes in Li-ion batteries, but they often have complex and heterogeneous microstructures. Historically, these electrodes have been described using macro-homogenous porous electrode theories, for example, the models of Newman and co-workers [2] which laid the foundation for Li battery electrode design. In spite of the success of these models in predicting electrode performance, their estimation of battery lifetime and durability has been problematic; this is in part due to their limited ability to describe microstructural heterogeneities [3].

The recent advent of 3D imaging techniques, including high resolution X-ray tomography and focused ion beam slice-and-view, has provided unprecedented insight into the microstructure of materials. These techniques have been widely adopted by the battery community, revolutionizing our understanding of complex real-life electrodes for a range of battery chemistries, and more recently these investigations have been extended to operando studies, to examine the evolution of electrode microstructures [4-7].

In this work Wood and co-workers have utilized operando X-ray computed tomography (CT) to create time-lapse images in three dimensions of working Li-ion battery electrodes, using both graphite and composite graphite-silicon formulations.

Graphite electrodes are overwhelmingly the most popular anode in commercial cells, but have been challenging to image using conventional techniques [8]. This is because conventional absorption imaging typically provides insufficient contrast between the weakly absorbing graphite particles and the electrolyte in the filled pore space. Using synchrotron phase contrast imaging techniques, which enrich the image contrast, Wood and co-workers have been able to image the local expansion of graphite electrodes as they accept lithium ions during charging. This investigation is further extended by the use of digital volume

correlation techniques (DVC) which can help identify local strains in the electrode and link the microstructure to electrochemical performance. Whilst previously digital image correlation has revealed the local strains during charging in graphite electrodes in two-dimensions [9], information in the third-dimension is obtained in this work. The combination of operando X-ray CT and DVC allows direct observation of the distribution of state-of-charge within the electrode.

Graphite electrode particles are typically 'flake' like in morphology and aligned parallel to the current collector. Consequently the expansion of the electrode during lithiation is highly anisotropic, significantly favoring the 'through-plane' direction. Indeed, the researchers observed that the expansion starts at the electrode/separator interfaces and progresses towards the current collector along the 'through-plane' direction. They also showed that this expansion, over a single charge cycle has limited impact on the electrode porosity and tortuosity. However, the impacts of these strains may be more significant over extended cycle life, or for different electrode chemistries. A schematic of electrode structural expansion is shown in Fig. 1.

The graphite-silicon composite electrode has gained increasing attention in recent years as a way of incorporating high-capacity silicon into an electrode, whilst mitigating against the extreme volume expansion which drives degradation in pure silicon electrodes [10]. By applying the same operando CT and DVC tools as for the graphite electrodes, Wood and co-workers have examined the more significant microstructure evolution effects in these composite electrodes. As expected the silicon phase of the composite electrode dominates the expansion, and the graphite particles may even be compressed by this expansion. Although the polycrystalline silicon particles are spherical, and therefore are expected to expand isotropically, a strong directional dependence in electrode expansion is observed. For these electrodes, this is attributed to the macroscopic confinement effects of the cell housing, emphasizing the importance of cell architecture in determining electrode performance.

The approach of Wood and co-workers forms part of a growing body of work on the application of tomography and DVC to explore materials and architectures for high performance batteries. The non-destructive nature of X-ray imaging provides a powerful platform to explore the evolution and degradation of battery materials over a wide range of time and length scales. With the increasingly widespread adoption of tomography techniques, which is also aided by the translation of synchrotron tools to the lab environment, the battery community is now equipped with a powerful tool to observe battery materials in their operating environment. In particular, the potential to track microstructural degradation of battery electrodes over extended lifetime cycling, provides a compelling opportunity to understand the fundamental driving forces for capacity fade, and failure. This will provide key information to optimize the materials design. This feedback process will be particularly valuable to accelerate the deployment of novel materials. In the future, it is expected that these tools will form part of the materials characterization toolbox enabling scientists and engineers to develop the next generation of safer, longer-lasting cells for a range of demanding applications.

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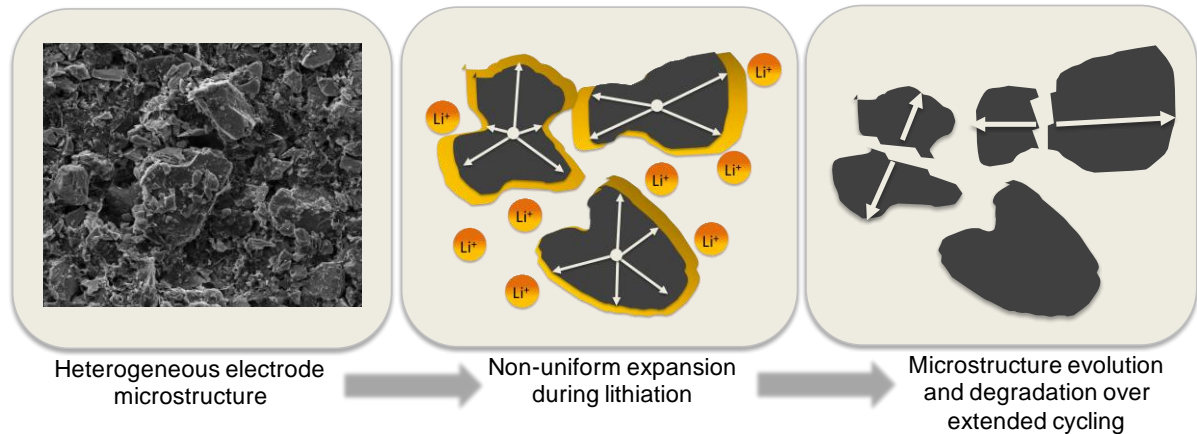


Figure 1: **Schematic of structural expansion during de/lithiation.** The expansion and contraction of electrode particles can generate strain across the electrode, indicated by arrows. The extent of the volume change will depend on the battery chemistry, and can drive microstructural degradation during repeated cycling, leading to capacity fade. The far left images shows an SEM image taken at UCL of a graphite electrode, the middle panel shows, schematically, the expansion of the graphite during Li intercalation indicated by the yellow regions. The right hand panel shows possible microstructure evolution and fracture as a result of cycling