Understanding Chemomechanical Li-ion Cathode Degradation through Multi-Scale, Multi-Modal X-ray Spectromicroscopy

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In a transitioning energy landscape, the demand for Li-ion based Electric Vehicles (EVs) and Plug-in Hybrid Electric Vehicles (PHEVs) has been and will continue to grow exponentially. Coinciding with this growth, there has been a significant reduction in the cost of batteries while energy density has seen a similar positive trend due largely to decreasing manufacturing costs [1]. However, going forward, the expectation is that cost reduction will be sustained by improvements in current and next generation Li-ion battery materials which possess higher capacity, energy density and better safety characteristics. Therefore, a fundamental understanding of Li-ion intercalation and degradation is required in order to provide promising avenues towards the rational design of next generation Li-ion battery materials.

Li-rich and Ni-rich transition metal (Ni, Mn, Co; NMC) layered oxide cathode materials represent some such promising next generation battery materials as they exhibit a high theoretical capacity (∼220 mAh g⁻¹), high tap density and good rate capabilities while possessing comparatively low raw and manufacturing costs. Despite these advantageous properties, significant capacity fade and poor cycle life have impeded these materials from achieving commercial realization. In spite of these noted issues, and in accordance with their significant potential as commercial cathodes, high capacity layered oxide materials have been subject to a substantial research effort to understand and mitigate the associated degradation phenomena and provide potential pathways towards commercial realization. To this end, studies on NMC cathode materials have shown that the capacity fade can be, in part attributed to (1) multiple length-scale strain-induced morphological modifications through anisotropic volume expansion during intercalation [2] (2) localized chemical phase changes resulting in heterogeneous intercalation [3], and (3) the thermal instability of the material [4]. Due to the inter-relatedness of these degradation phenomena, a full (electro)chemomechanical understanding spanning length-scales from the electrode (few cm) to the atomic (few Å) length scale is crucial for determining the best strategies to mitigate these effects. The challenges in undertaking such a multi-faceted approach must therefore be met with an equally comprehensive characterization platform. Central to this are X-ray microscopy (XRM) techniques, which offer high resolution imaging, large field-of-view and provide detailed and localized chemical and microstructural information.

In this study, we utilized both hard and soft X-ray microscopy to track the local chemical, morphological and structural changes in Li-rich and Ni-rich layered oxides across several important length-scales (Figure 1). Combined with electrochemical measurements and chemomechanical modelling, we have sought to provide comprehensive mechanistic insights into the degradation pathways of promising layered oxide...
cathode materials. Using full-field Transmission X-ray Microscopy (TXM) (beamline 6-2C, SSRL) in the hard X-ray regime, we investigated the microstructural evolution of NMC cathodes. X-ray tomography data at various states-of-charge show how the particle microstructural evolves during charge and discharge. We observed intergranular fracturing, primarily at the particle core which corresponds well with the lattice expansion/contraction as a function of voltage as determined by in-situ XRD. Complementary thermodynamic modelling correlates significant strain buildup within a single NMC secondary particle due to the anisotropic volume expansions of randomly oriented grains. Using 2D TXM spectromicroscopy, we observed compositional heterogeneities, which persist after long relaxation suggesting that these heterogeneities and internal strain evolution are intrinsically linked [3] and dictate the bulk electrochemical properties of the system. Furthermore, to investigate the spatial distribution of transition metal redox of NMC, we employed Scanning Transmission X-ray Microscopy (STXM) and ptychography (beamlines 11.0.2 and 7.0.1, ALS) in the soft X-ray regime [5]. In this regard, we developed a dry sample ultramicrotomy technique that allows for sub-100 nm sample thicknesses making them suitable for investigation by soft X-ray spectromicroscopy. This ultramicrotomy methodology has been employed to understand promising cathode materials at several important length-scales. The combination of these techniques allows for understanding the chemomechanical behaviour of Li-ion intercalation at multiple, relevant length-scales.

**Figure 1.** TXM tomography and STXM/ptychography spectromicroscopy were used to investigate battery degradation mechanisms in NMC layered oxide cathode materials. Combined with electrochemistry and (electro)chemomechanical modelling, this imaging platform has been used to obtain a comprehensive understanding of NMC degradation.

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