Operando Spectroscopic Microscopy of $LiCoO_2$ Cathodes Outside Standard Operating Potentials

The ever-growing demand for more energy storage capacity for portable electronics and electric vehicles has increased the frequency of catastrophic battery failure and the need to mitigate or prevent it entirely. Over-lithiation (or over-discharge) of the cathode during discharge is just one possible failure mechanism and safety concern. Over-lithiation can occur due to inadequate battery management when multiple cells are placed in parallel or are cascaded. If a battery management system is not conservative enough, a battery pack could appear to be working within a safe voltage window while the cell with the lowest capacity may experience over-lithiation.

In a recent study, researchers from SSRL used *operando* x-ray absorption spectroscopy (XAS) and *operando* spectroscopic transmission x-ray microscopy (TXM) to understand the chemical and morphological changes that occur during over-lithiation of standard $LiCoO_2$ cathodes. The studies reveal a core-shell conversion pathway from $LiCoO_2$ to Li_2O and Co metal during over-lithiation (Figures 1 and 2). This conversion reaction is accompanied by a delayed, irreversible mechanical degradation with micron-sized particles cracking and pulverizing, allowing Li-ions access to the core of the particles (Figure 2). Because of the delay, the mechanical degradation is likely avoided in brief over-lithiation events, where only the surface of the particles would convert to Co. The use of nano-sized $LiCoO_2$ could decrease the morphological changes occurring during over-lithiation, which may improve the lifetime of the battery after an accidental deep discharge. Further studies are necessary to determine in particle degradation can be avoided and if the mitigation of the microscopic

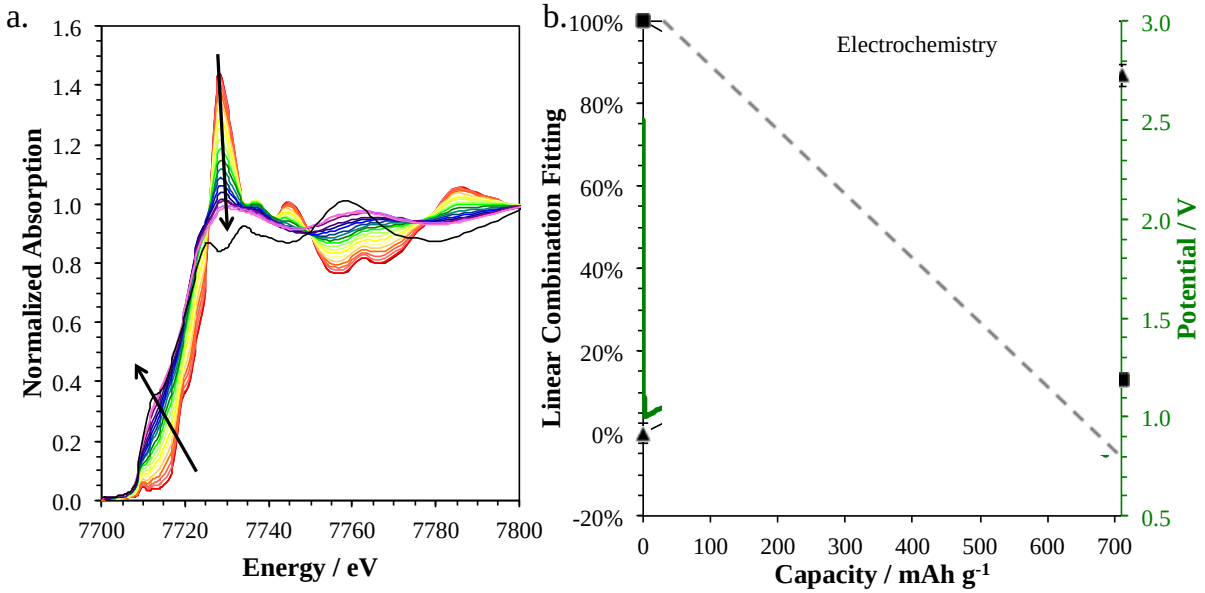

Figure 1. a) X-ray absorption spectroscopy of the $LiCoO_2$ cathode during over-lithiation. The spectra are colored from red to violet starting with OCV and ending in the over-lithiated state. The spectrum for Co metal is black. Two arrows indicate the reaction direction. b) Linear combination fitting plotted with the cell's electrochemistry (green) shows $LiCoO_2$ conversion to Co metal with approximately 13% $LiCoO_2$ remaining at the 0.8 V cutoff. A dashed line has been added to aid in distinguishing the linear and nonlinear regions of the conversion reaction, which directly correlate with the voltage plateau. The error bars indicate the uncertainty in the fitting percentages.

mechanical degradation improves capacity retention and cycle lifetime after over-lithiation. This work demonstrates the value in linking chemical and morphological dynamics using complementary x-ray characterization techniques to understand electrode failure mechanisms.

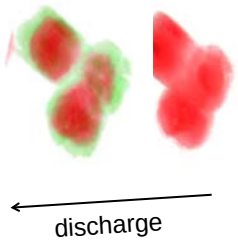

Figure 2. Schematic of the transmission x-ray microscope with selective maps of showing the Co chemistry during over-lithiation (discharge). Color is used to indicate the percentage of each chemical state (red for $LiCoO_2$ and green for Co). The transparency of a pixel indicates the total content of Co in the pixel.

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