Li rich oxides $x\text{Li}_2\text{MnO}_3(1-x)\text{LiMO}_2$, ($M=\text{Ni, Co, Fe, Al, Cr}$ etc.) have attracted significant attention in recent years as the promising cathodes for Li-ion batteries because of their higher energy storage capacity, thermal stability, and lower costs. These materials are structurally integrated composites of two phases: monoclinic C2/m $\text{Li}_2\text{MnO}_3$ phase and trigonal R-3m $\text{LiMO}_2$ phase [1]. The $\text{Li}_2\text{MnO}_3$ phase provides structural integrity to the $\text{LiMO}_2$ during Li intercalation and also can be activated to $\text{Li}_x\text{MnO}_y$ at potentials higher than 4.5 V to further boost the energy storing capacity [2]. The reported performance of $\text{Li}[\text{Li}_1/6\text{Fe}_{1/6}\text{Ni}_{1/6}\text{Mn}_{1/2}]\text{O}_2$ cathode is 282 mAh/g at first discharge [3], which is double the capacity of $\text{LiCoO}_2$ cathode currently utilized in commercial Li ion batteries. However, before those cathodes could replace traditional materials, two issues with Li-rich cathodes need to be resolved: gradual capacity loss (71% of capacity after 50 cycles [3]), and drop off in discharge voltage upon cycling (3.57 V of midpoint voltage at the 4th discharge decreases to 3.38 V at the 100th discharge [4]). Both degradation phenomena are closely related to structural changes within the cathode materials during cycling. It has been proposed that the transition metal ions migrate to Li site upon cycling and the layered structure transforms to spinel or distorted spinel, however complete picture of the structural changes in Li rich layered-layered oxides isn’t clear yet.

To improve the performance of Li-rich cathode, detailed understanding of the degradation mechanisms in those materials is required. This talk will focus on the results of x-ray diffraction (XRD) and in situ x-ray absorption spectroscopy (XAS) to examine the role of the monoclinic $\text{Li}_2\text{MnO}_3$ phase in low cost, Li rich, Co free $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6-x}\text{Fe}_{0.10}]\text{O}_2$ 0.15$<x<0.25$ layered-layered oxide. Our study employs XRD with Rietveld analysis for crystallographic phase information, and in-situ XAS for probing the oxidation state and local structure from extended x-ray absorption fine spectroscopy (EXAFS) within the materials during charge and discharge cycles.

References: