(Student Research Award of the Battery Division) Characterization of Structural Changes in Layered Li-Excess Nickel Manganese Oxides in High Voltage Lithium-Ion Batteries during the First Electrochemical Cycle

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Characterization of Structural Changes in Layered Li-excess Nickel Manganese Oxides in High Voltage Lithium Ion Batteries During the First Electrochemical Cycle

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The lithium-excess layered oxide compounds $Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O_2$ ($0 < x < 1/2$) are of great interests as a new generation of positive electrode materials for high energy density lithium-ion batteries. This series of layered lithium transition metal oxides is attractive because of higher energy density and lower costs. The structure of these compounds differs from conventional layered oxides such as $LiCoO_2$ because additional Li is present in the transition metal (TM) layer inducing cation ordering in the TM layers. During the initial charging region up to 4.4 V, the capacity originates from the oxidation of Ni^{2+} to Ni^{4+}. Lithium may continue to be extracted from these materials despite the fact that all the manganese and nickel ions are in their fully charged (+4) oxidation state, which is associated with a plateau region at 4.45V. The source of the anomalous capacities have been attributed either to an irreversible oxygen loss from the lattice accompanied by Li removal or to a surface reaction through electrode/electrolyte reduction and or hydrogen exchange. Regardless of the source of the anomalous capacity, previous work has shown significant structural changes following electrochemical cycling including superlattice disappearance, surface and bulk cation migration as well as second phase formation. Our previous research combined experimental and computational methods to identify a new spinel-like solid phase on the surface of the electrode and tetrahedral Li formation following high voltage cycling.

Although we demonstrated this new surface layer forming on the surface of the material, it is still unclear when this phase forms, how it affects the structure and when the unique cation migration occurs. Detailed investigation to identify structural changes associated with cation migration in the pristine layered lithium-excess oxides during the first electrochemical cycle. In this work we carried out Synchrotron X-ray Diffraction (XRD), aberration corrected Scanning transmission electron microscopy (*a*-S/TEM) at different states of charge during the first electrochemical cycle in $Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O_2$ (x=1/5) compounds to identify when changes occur in the surface and bulk.

We identified that during the first charge, the electrochemical impedance increases between the pristine particles and surface phase during plateau region of the first electrochemical cycle as identified below in figure 1. The low frequency second loop corresponds to changes in the surface film and the $Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2$ particle interface. HRTEM images show that during the first electrochemical cycle, large strains are introduced into the structure during the voltage plateau at 4.5V. Synchrotron x-ray diffraction also shows increases in microstrain and unique cation migration during the first electrochemical cycle, specifically the plateau region.

Analysis of strain occurring in this material has not previously been quantified and can provide further understanding of the delithiation mechanism. It is proposed that such changes are one of the factors contributing to the first cycle irreversible capacity and the main reason for the *intrinsic* poor rate capability of these materials.

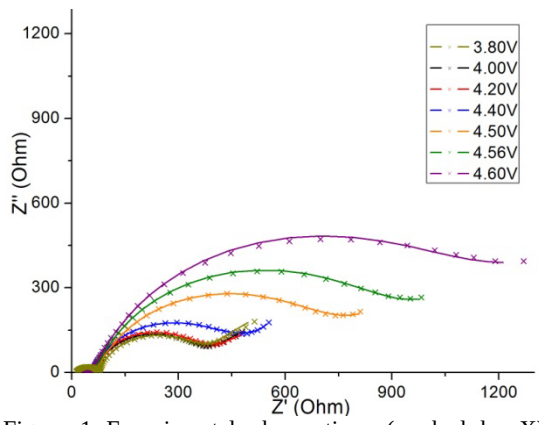

Figure 1 Experimental observations (marked by X) of electrochemical impedance spectroscopy (EIS) of $Li[Ni_{1/5}Li_{1/5}Mn_{3/5}]O_2$ during the first electrochemical charging cycle at different states of charge (SOC).

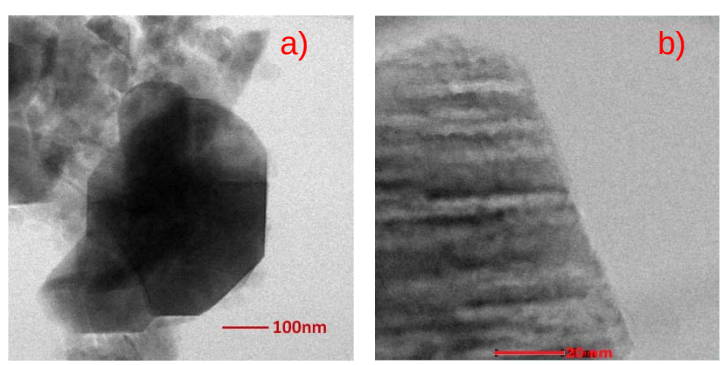

Figure 2 High resolution TEM images of bulk $Li[Ni_{1/5}Li_{1/5}Mn_{3/5}]O_2$ before electrochemical cycling (a) and during the first charge to 4.60 V (b) showing large cracks and strains.