STEM/EELS Analysis of Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2 Held at High Voltages

P. Mukherjee¹, D. Su², N. Pereira¹, G Amatucci¹, and F. Cosandey¹
¹ Department of Materials Science & Engineering, Rutgers University, Piscataway, NJ
² Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY

Ni rich Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2 commonly known as NCA is being used commercially as Li-ion battery cathode material for its high discharge capacity. [1] The stability and related safety concerns at high voltage limit the use of NCA at 3.6V, where only 50% of Li can be extracted. Thus, only a part of theoretical capacity is achieved in this process. At high voltages (>4V), the layered structure of the bulk NCA does not change, however new surface phases are formed. To utilize the full potential of this material, high-voltage studies of surface phases, their chemical evolution and their mechanisms are needed. We present here the evolution of surface phases in NCA held at a constant voltage up to 4.75V.

The surface phases of NCA were observed in a cold cathode field emission aberration corrected JEOL ARM STEM (at Lehigh University). The spatial resolution of the STEM system was 0.07 nm. EELS chemical analysis as well as HAADF STEM imaging were carried out using aberration corrected HITACHI HD2700C TEM and GATAN Enfina EELS spectrometer with an energy resolution of 0.5 eV. A HAADF STEM image of a NCA particle (held at 4.75V for 2 weeks) oriented along [010] zone axis of layered (R-3m) structure is shown in Figure 1. Atomic–resolution images from different regions of the particle were obtained revealing structural inhomogeneity with two different surface phases. The HAADF STEM image from region 1 (Figure 2a) shows that the bulk layered structure (R-3m) is maintained up to the surface, but almost 1/3 of transition metal (TM) ions (mostly Ni) have migrated to the Li layer as determined from the intensity profile (Figure 2b). In region 2 the surface is fully transformed to a rocksalt (RS) type (Fm-3m) phase (Figure 2c). The contrast between Li and TM layer is uniform and the spacing between them is ~0.23nm (d_{111} of Fm3m phase). The presence of two different phases within the same particle shows that the surface of NCA particles is highly inhomogeneous. Also, this large scale migration of TM ions (1/3 of TM moving to Li layer) from its original octahedral site to a tetrahedral Li site is accompanied by creation of oxygen vacancies. This is consistent with the earlier report which shows that the diffusion barrier for TM migration is reduced when initial configuration of TM octahedron is five coordinated (MO_{5}, deficient in one O) instead of regular six coordinated (MO_{6}).[2] Chemical analysis was done on these particles and indeed oxygen loss accompanied these surface phase transformations.

A characteristic EELS feature of pristine NCA is the presence of O-pre-peak, 12.0 eV from the main O peak, which occurs due to a transition from O 1s to a hybridized state formed by O 2p and Ni 3d states. For NiO, the pre-peak is smaller and located 7.5 eV from the main O peak. This pre-peak is almost missing in the surface phases from sample held at 4.75V (Figure 3a). The O edge at this voltage resembles that of NiO phase (Figure 3b) with a lower pre-peak intensity and average energy position of 7.5 eV. The O/TM atomic ratio of 1.6 measured for the surface phases and averaged over several particles show that the surface is oxygen deficient as compared to pristine NCA (2). Also, a reduction in Ni valence, measured from Ni L3/L2 ratio is observed at the surface (Ni^{2+} as compared to pristine NCA (Ni^{3+}). Both of these values are between pristine NCA and NiO (O/TM ratio of 1 and Ni^{2+} valence state). The surface phases at 4.75V is spread over 20 nm from the edge and it is extremely difficult to obtain any bulk EELS information at this voltage. So, the reduction in Ni observed at 4.75V is corroborated by a shift of Ni L edge with respect to bulk NCA at 4.5V, where surface phases span up to 10 nm (Figure 3c). [3]
References:

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Fig. 1. (Left) STEM image of a NCA particle oriented along [010] zone axis of R-3m

Fig. 2. (Right) HAADF-STEM image of NCA along [010] zone axis of layered structure. (a) Atomic-resolution HAADF image from region 1 of the particle show layered (R-3m) structure with partially occupied Li layer and (b) corresponding intensity profile. (c) Region 2 of the particle has rocksalt structure (Fm-3m) and (d) corresponding intensity profile.

Fig. 3. (a) O-edge of EELS spectra of NCA at 4.75V (solid) compared with pristine NCA (dash) and NiO (dot). (b) The ratio of O pre and main peaks plotted as a function of their energy difference (red dots) show their proximity to NiO. The blue square represents the same for bulk NCA. (c) The shift in Ni L lines at 4.5V from surface to NCA bulk shows a reduction in Ni.