Determination of Al location in Ni-rich layered oxide Li-ion cathode by combined atomic resolution X-ray EDS and EELNES

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Ni-rich $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, commonly known as NCA, is one of the highest capacity cathode materials currently being used commercially. This structural stability of NCA at high charge voltage is unlike its parent compounds $LiNiO_2$ and $LiCoO_2$, both of which degrade rapidly above 4.5 V. It has long been argued that Al plays a critical role in structural stability of NCA, but the exact manner in which Al stabilizes the structure is not known yet. In this work, we have studied the distribution of Al by X-ray energy-dispersive spectroscopy (EDS) at both nanometer and atomic levels in $LiNi_{0.8}Al_{0.2}O_2$ (LNA), and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA). We also determined the Al location (octahedral versus tetrahedral occupancy) by electron energy loss near edge structure (EELNES). This study includes pristine condition as well as electrochemically stressed at high charge voltages.

Atomic resolution EDS measurements and HAADF STEM images were obtained in a FEI Titan G2 80-200 STEM with a Cs probe corrector at Sandia National Laboratories. The spatial resolution of the STEM microscope was 0.07 nm. Chemical analysis and EELNES were performed in an aberration corrected FEI Titan microscope (TEAM I at Lawrence Berkeley National Laboratory) using a GATAN Enfina EELS spectrometer with an energy resolution of 0.8 eV.

The Al distribution as a function of distance from the edge has been determined for pristine NCA and for electrochemically stressed NCA at 4.75V. In all cases there is Al enrichment at the surface. This kind of preferential distribution of Al is also observed in pristine LNA. The Al is distributed preferentially at the corners and some facets of the particle while the core of the particle remains essentially Al deficient. The atomic resolution HAADF STEM image of one such particle is shown in the attached Figure. The layered LNA compound is electron beam sensitive and in order to obtain sufficient X-ray counts for obtaining atomic resolution EDS maps, summations over multiple acquisition maps as well as summation of all unit cells within the map have been performed. The averaged HAADF STEM image is shown in Figure b with the corresponding atomic-scale EDS maps for (c) O-K, (d) Ni-K and (e) Al-K. It can be seen that Ni and Al occupy the same octahedral sites. The X-ray intensity profiles for Ni and Al are shown in Figure f. For Ni, the intensity profile is sharp while some broadening in the Al position is observed which could be due to smaller Al-O distance for some Al positions as compared to Ni-O distance. After the second EDS acquisition from the same region, some Ni atoms have migrated (induced by the electron beam) to the Li layer position as revealed by the small peak between the Ni positions. Additional work has been performed to determine by EELNES the chemical state of Al from the Al-K edge in the same area of the particles and under low dose conditions. A single peak at 1573 eV is observed which is attributed to Al in the octahedral site.

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