Investigation of Local Changes in Crystal and Electronic Structures of Charged Li$_{1-x}$Ni$_x$Co$_{0.05}$Al$_{1-x}$O$_2$ Cathode Materials for Li-Ion Batteries by TEM-EELS

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In recent years, rechargeable Li-ion batteries (LIBs) have been widely investigated and developed for the large scale applications such as hybrid electric vehicle (HEV), plug-in hybrid electric vehicle (PHEV) and electric vehicle (EV). For the commercialization of LIBs in transportation applications, the development of electrode materials with high capacity, higher power, longer cycle life, and in particular, lower cost and better safety characteristics is required. The Ni-based layered cathode materials, LiNi$_{1-x}$Co$_{0.05}$Al$_{1-x}$O$_2$, are promising alternatives with their high discharge capacities ~200 mAhg$^{-1}$. However, LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ electrodes have several disadvantages such as drastic capacity fading and impedance rise with cycling in addition to poor thermal stability. Developing electrochemically inactive NiO-like phase on the surface has been attributed for low retention and high impedance. In-depth consideration on surface changes in crystal structure and correlating phenomena of charged LiNi$_{1-x}$Co$_{0.05}$Al$_{1-x}$O$_2$ is highly required.

We investigated both electronic and crystal structures of charged Li$_{1-x}$Ni$_x$Co$_{0.05}$Al$_{1-x}$O$_2$ cathode materials as a function of state of charge by transmission electron microscopy (TEM) coupled with electron energy loss spectroscopy (EELS), namely TEM-EELS. Bulk measurements by X-ray diffraction and spectroscopy (XRD, XAS) are very powerful in examining the structural and chemical changes of the bulk electrodes, but often inefficient in studies of local structural disorder or reorganization. On the other hand, superior spatial resolution of TEM provides nanoscale observation of the phase transitions that occur in individual particles, allowing us to distinguish subtle changes in crystal structure at the surface from the interior region after electrochemical delithiation. Electronic structure of electrode materials has been mostly investigated by x-ray absorption so far; but, it is difficult to select the area of interest, e. g. surface region. EELS combined with TEM can give great site selectivity and a chance to acquire an image, diffraction pattern, and electron energy loss spectrum simultaneously, making thorough understanding on charged state of cathode possible.

In this study, we present surface modification in crystal structure and chemical bonding of Li$_3$Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ cathode after mild (half) charging and severe (over) charging.Phase transitions take place with cation re-arrangement around oxygen; thus electronic structure of oxygen is important to understand. Figure 1 shows representative oxygen K-edge electron energy loss spectra from pristine (x=1), half charged (x=0.5), and overcharged (x=0.1) Li$_{1-x}$Ni$_x$Co$_{0.05}$Al$_{1-x}$O$_2$ particles, respectively. To investigate any kinetic effects, two sizes of selective area (SA) apertures were used to define the area to be analyzed: one is an aperture with diameter of 325 nm at image plane for bulk analysis and the other is an aperture with diameter of 180 nm for more surface-dependent analysis. The regions where spectra came from are represented with BF images of each particle as an inset of Figs. 1(a)~(c). Typical spectra of oxygen K-edge display two distinct peaks such as pre-edge peak around 528~530 eV and main peak around 540 eV regardless of surface or bulk.

Oxygen pre-edge peak is known to be attributed to the transition of 1s core state to unoccupied 2p states hybridized with transition metal (TM) 3d states and main peak is known to originate from a transition of 1s to the hybridized states of O 2p and metal 4sp state. As lithium is removed from the original state, intensity of pre-edge peak changes interestingly, that is pre-edge peak is increasing at both surface and bulk when 50 % of lithium is removed but decreasing at surface in case of over charged state with positive shift while bulk particle keeps comparable intensity to half charged sample. This interesting behavior in oxygen pre-edge peak is attributed from charge compensation with charging, and phase transitions. All the details will be available at the meeting.

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Figure 1. Electron energy loss spectrum of oxygen K-edge of (a) pristine (x=1), (b) half charged (x=0.5) and (c) overcharged (x=0.1) Li$_{1-x}$Ni$_x$Co$_{0.05}$Al$_{1-x}$O$_2$ cathode

References