Abnormal Cracking of Layered $LiCoO_2$ Particle during Extreme Lithium Extraction

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$LiCoO_2$, Lithium cobalt oxide (LCO) has been one of the most common materials for lithium-ion battery cathode. Recently, safety issues of lithium-ion batteries have attracted much media and public attention mainly caused by incendiary incident of electronics. Overcharge, which means charging more than a normal charging range, is one of the major sources of thermal runaway due to a vicious cycle in which the heating and the exothermic acceleration are repeated. Compared to the well-known electrochemical process of LCO in a normal operation range, knowledge on overcharging process is still limited and superficial. [1, 2] By virtue of its layered structure accommodating two-dimensional lithium layer between cobalt oxide octahedron slabs, LCO is known to reversibly turn into $Li_{0.5}CoO_2$ in a normal charge range. [3] Here, we investigate the structural change in LCO during extreme extra lithium extraction from $Li_{x<0.5}CoO_2$ to reveal the irreversible reaction mechanism and to suggest the approach to improve safety of LCO.

We conducted an overcharge test up to 6 V in contrast to the normal charge range of 4.4 V. The cell charging was performed under coin cell configuration with a commercial cathode of LCO particles and a lithium metal anode. For the comparative analysis, samples under pristine cell, normal charge (4.4 V) and overcharge (6 V) conditions were examined, mostly with transmission electron microscopy (TEM). To overcome the limits of local TEM analysis, other multiscale analytical techniques such as X-ray diffraction, scanning electron microscopy (SEM) and Raman spectroscopy were performed simultaneously.

As a result, we found unreported damage occurred during overcharge as shown in the SEM and TEM image, Figure 1. These abnormal cracks are distinguished by the feature that they propagated perpendicularly to $(003)_{LCO}$ layer from the common in-plane gaps, mainly due to strain induced by the volume change during charging. Additionally, by investigating the crack region with scanning transmission electron microscopy as in Figure 2, we confirmed that original layered phase and newly derived cobalt oxide phase were separated by the crack boundary. This indicates that extreme lithium extraction results in instability of $Li_{x\sim0}CoO_2$ structure, i.e., making cobalt oxide slab to face directly oxygen to oxygen without the lithium layer. Accordingly, structural collapse toward Co_2O_3 has been induced by the cobalt ion migration into adjacent lithium ion position of LCO. Here we suggest that these microscopic irreversible structural change causes the macroscopic physical damage mentioned above. Furthermore, as in Figure 3, overcharging was also accompanied by the formation of Co_3O_4 which supports that layered structure hardly remains the original feature during lithium extraction with the reaction: [4]

$$Li_xCoO_2 \rightarrow \frac{(1-x)}{3}Co_3O_4 + xLiCoO_2 + \frac{(1-x)}{3}O_2$$

These experimental results lead us to reveal the relation between these microscopic cracking of intriguing shape and the actual battery performance and to understand detailed overcharge mechanism of layered LCO particle.

[1] T. Ohsaki et al., Journal of Power Sources 146 (2005) 97-100

[2] R. Hausbrand et al., Materials Science and Engineering B 192 (2015) 3-25

[3] J. N. Reimers and J. R. Dahn, Journal of the Electrochemical Society 139, 8 (1992) 2091-2097

[4] J. R. Dahn et al., Solid State Ionics 69 (1994) 265-270

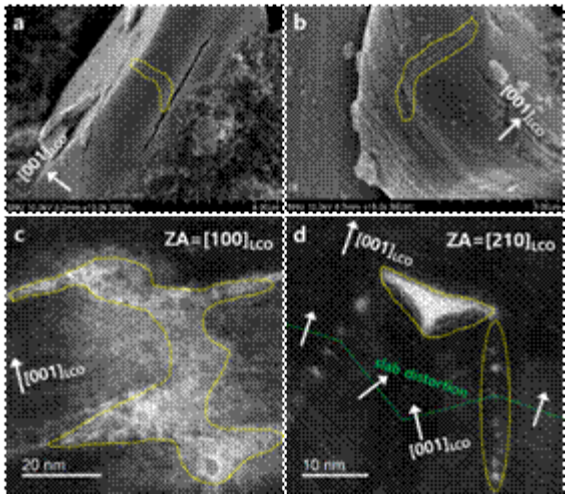

Figure 1. Abnormal cracking of $LiCoO_2$ after 6 V cut-off shown in (a, b) SEM image and in (c, d) TEM image. Yellow dot lines indicate the crack region of the particle. White parts of the TEM image shows real cavity (not graphically drawn).

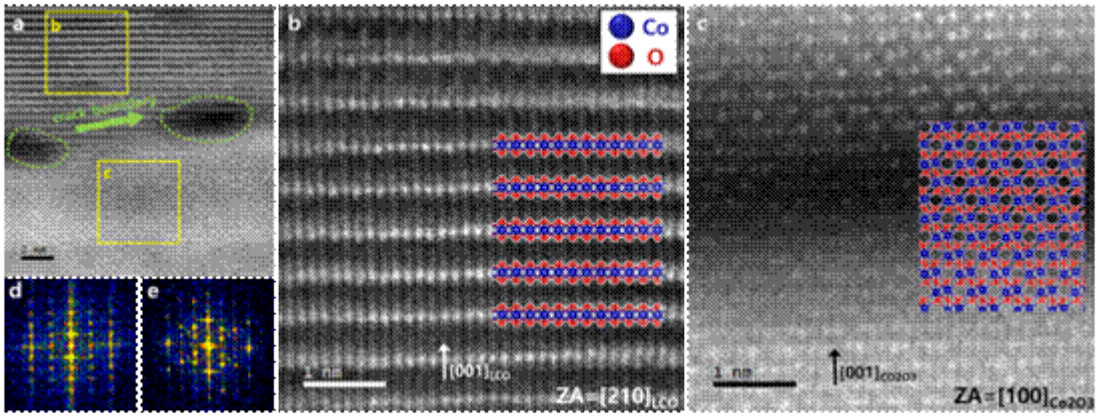

Figure 2. Atomic-scale resolution annular dark-field STEM image of overcharged $LiCoO_2$. (a) Different phases are separated by crack boundary. Detailed image of upper region and lower region of (a) are shown in (b) and (c), respectively. (d, e) FFT patterns which agree with the atomic structure drawn in (b) and (c). Unlike the layered structure (Li_xCoO_2) shown in (b), (c) indicates newly induced cobalt oxide phase (Co_2O_3).

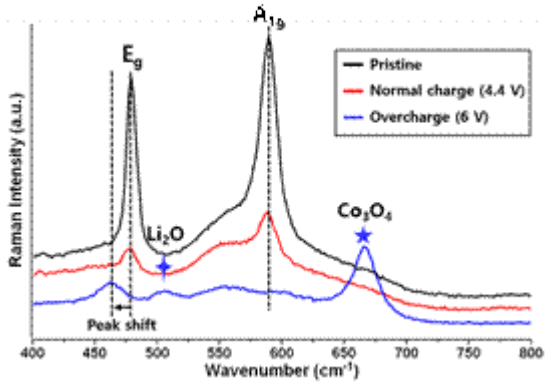

Figure 3. Raman spectra of $LiCoO_2$ particles at different charge conditions. The pristine particle shows two distinct peak in E_g (479 cm^{-1}, O-Co-O bending) and A_{1g} (589 cm^{-1}, Co-O stretching). Contrastively, after overcharging, main bands weakening with peak shift of E_g ~ 461 cm^{-1} and newly induced peaks (i.e. Li_2O and Co_3O_4) are shown.