Understanding Surface Modification and Electrochemical Cycling Stability of Oxide Cathode Materials for Li-Ion Batteries by Advanced Analytical Transmission Electron Microscopy

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Oxides are of great interest being used as Cathode materials in Li-Ion Batteries, which are the source of lithium and therefore determine the energy density of a Lithium ion cell. In particular, lithium manganese oxides ($Li_x(TM_yMn_{1-y})O_2$) have being attracting significant attention because they are cheap, plentiful, non-toxic, and environmentally benign. During the charge/discharge cycle, Li^+ ions leave/enter the lattice of oxide, while charge neutrality is preserved by oxidation/reduction of transition metal (TM) ions (for example Ni^{2+}/Ni^{4+}). Structural and compositional stability under electrochemical cycling limits the useful capacity of the oxides for practical applications because material degradation could result in declining performance and safety concerns. Studying the surface region of these oxide grains in this aspect is of particularly importance since it does not only experience Li insertion/extraction as the bulk, but also serves as the interface between cathode and electrolyte.

Advanced analytical transmission electron microscopy is an ideal technique for such detailed local structural and compositional study because of its unique capability of simultaneously probing atomic arrangements and investigating electronic structure and composition. For example, atomic rearrangements at surface can be clearly revealed by aberration corrected Z-contrast imaging; possible TM dissolution to electrolyte can be studied by atomic resolution chemical analysis, including electron dispersive x-ray (EDX) and electron energy loss spectroscopy (EELS); oxidation state evolution of TM elements while can be tracked by fine EELS fine structures. In particular, Li composition and its chemical bonding, which is one of the key parameters determining the battery performance, can be well monitored by using EELS. Furthermore, these techniques can be combined with in-situ capabilities, such as heating, biasing and liquid cell to observe dynamic structural and compositional evolutions under real-time performing conditions.

$Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ was chosen as a representative model compound in the presented work because of its relatively high capacity. $Li[Li_{1/3-2x/3}Ni_xMn_{2/3-x/3}]O_2$ system contains a layered structure and Li diffuses along {0001} planes.[1-3] The material was synthesized from mixed nickel-manganese carbonate precursors, prepared by a co-precipitation method, and lithium carbonate as the lithium source. The as-prepared sample was mixed with carbon black and a PVDF binder for electrochemical testing in 2016 type coin cells. The coin cell was cycled between 2.5 and 5.0 V for one and ten cycles for comparison. An aberration-corrected FEI-Titan S 80-300 STEM equipped with a Gatan Image Filter (GIF) Quantum 865 was used to correlate the observed structural changes with electrochemical behavior.

Although bulk crystalline structure and composition remains the same, surface structure modifications for the $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ particles were observed by atomic-resolution high angle annular dark field (HAADF) STEM imaging before and after electrochemical cycling (Fig.1). Most of Li sites were occupied by TM elements on the outermost 4-5 atomic layers of the surface in the cycled samples. The oxidation state of Mn in this surface region was analyzed to be Mn^{3+} rich based on EELS results, while that of Ni remains 2+. Fine structures of both O-K edges and Mn-L edges clearly show the modified

electronic structure in the surface region compared to that of the bulk and of the pristine sample. Detailed structure analysis shows that this structure can be referred to a spinel-like structure. Combining our experimental observations with first principles computational investigation, a detailed lithium de-intercalation mechanism is proposed. Interestingly, such surface structural modification was even observed on the sample after one cycle and the thickness of such surface region does not change significantly with electrochemical cycling times. We propose that such surface phase transformation is one of the factors contributing to the first cycle irreversible capacity and the main reason for the intrinsic poor rate capability of these materials. We further investigated the structural and compositional stability of spinel-structured $LiNi_{0.45}Mn_{1.55}O_4$, in which Li diffuses 3-dimentionally during charge/discharge cycles. No obvious surface structural modification has been observed. This fact further supports our proposition that the modified surface layer formed in the layered structured material most likely contributes to the unique phenomenon of the first cycle irreversible capacity in the layered LNMO. In-situ experiments observing the structure change of surface on layered material will also be performed by using a biasing holder and solid electrolyte, the detailed results will be presented. [4]

References
[1] Hong, Y.S., Park, Y.J., Ryu, K.S. & Chang, S.H. (2005). Solid State Ionics **176**(11-12), 1035-1042.
[2] Kang, S.H., Kempgens, P., Greenbaum, S., Kropf, A.J., Amine, K. & Thackeray, M.M. (2007). Journal of Materials Chemistry **17**(20), 2069-2077.
[3] Jiang, M., Key, B., Meng, Y.S. & Grey, C.P. (2009). Electrochemical and Structural Study of the Layered, Chemistry of Materials **21**(13), 27332745.
[4] Research at the ORNL SHaRE User Facility supported by the Division of Scientific User Facilities, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy.
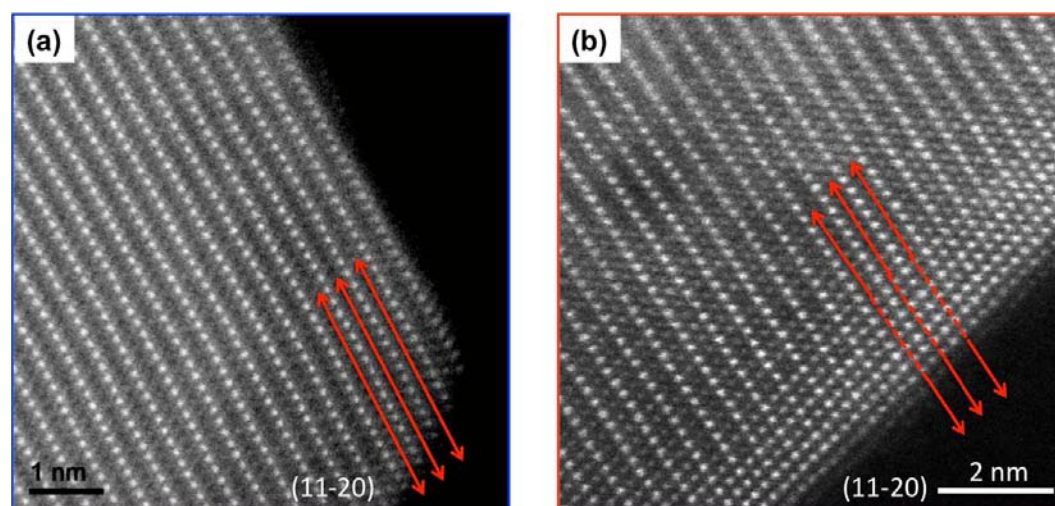

Figure 1, comparison of atomic structures of pristine (a) and ten times cycled $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$.(b) Arrowed lines shows the Li diffusion pathway.