doi:10.1017/S143192761005974X
Microsc. Microanal. 16 (Suppl 2), 2010

An Investigation of Structure and Electrochemical Cycling Stability of $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ using Aberration-Corrected Z-contrast Imaging and EELS

Miaofang Chi*, Christopher Fell** and Shirley Meng**

*Materials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
**Department of Materials Science and Engineering, University of Florida, Gainesville, FL, 32611

Layered lithium nickel manganese oxide $Li[Li_{1/3-2x/3}Ni_xMn_{2/3-x/3}]O_2$ ($0 \leq x \leq 0.5$) has attracted interest as a strong candidate for use as a cathode material in Li-ion batteries due to its high discharge capacity of more than 200mAh/g when operated between 2.5-4.6V.[1,2] Compared to $LiCoO_2$, which is the most commonly used positive electrode material in commercial Li-ion batteries, $Li[Li_{1/3-2x/3}Ni_xMn_{2/3-x/3}]O_2$ has a lower cost, and higher safety and abuse tolerance. However, this large capacity cathode material continues to degrade during rapid charge-discharge cycling, rendering it somewhat impractical for real-life, long-term applications. [3,4] The possible reasons proposed for these durability issues are oxygen loss and/or cation re-arrangement during cycling. Unfortunately, neither experimental data nor theoretical calculations have solidly proven these propositions yet. Here, scanning transmission electron microscopy (STEM) combined with electron energy loss spectroscopy (EELS) have been used to study the structural and compositional changes for $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ as a function of electrochemical cycles.

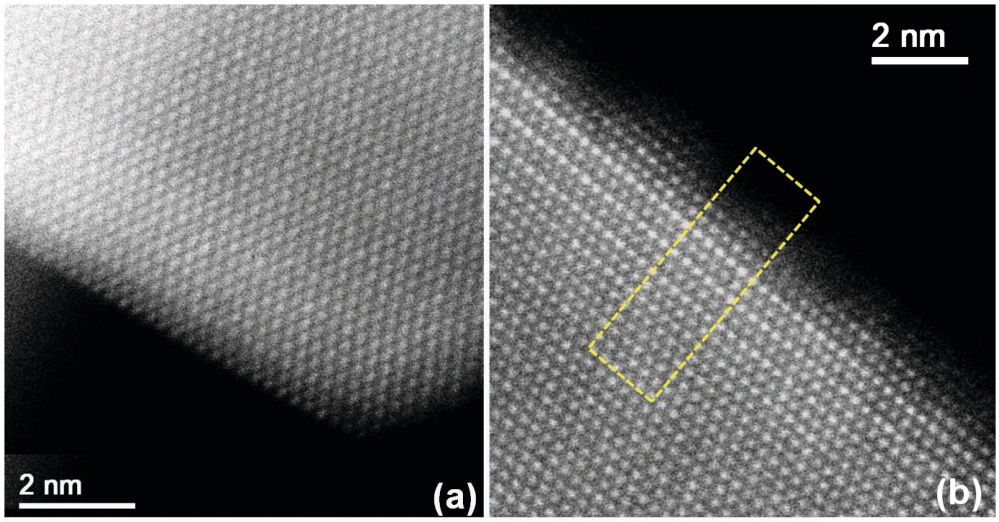
$Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ was chosen as a representative model compound for this study because of its reported high capacity within the $Li[Li_{1/3-2x/3}Ni_xMn_{2/3-x/3}]O_2$ system. The material was synthesized from mixed nickel-manganese carbonate precursors prepared by a co-precipitation method [5] and lithium carbonate was used 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. A lithium metal ribbon and $LiPF_6$ with EC/DEC (1:1 volume%) were used as the anode and the electrolyte, respectively. The coin cell was cycled between 2.5 and 5.0 V for 5-10 cycles. An aberration-corrected FEI-Titan S 80-300 STEM equipped with a Gatan Image Filter (GIF) was used to correlate the observed structural and chemical changes with electrochemical behavior.

Surface structure modifications for the $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ particles were observed by sub-Å-resolution high angle annular dark field (HAADF) STEM imaging before and after electrochemical cycling The as-processed atomic structure of the $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ surface is shown in Fig. 1a and the surface following ten (10) charge-discharge cycles is shown in Fig. 1b. The outermost 2-3 atomic layers of the surface were very rough and were somewhat amorphized, whereas the inner ~8-10 layers of the surface exhibited an alternating periodic intensity of the [11-1] planes, indicative of an ordered structure (Fig. 1c). The atomic structure of the surface layers was analyzed in detail by combining the images acquired from different orientations and was consistent with an ordered octahedral spinel crystal structure. EELS analyses showed a Li-deficiency associated with the surface, which was accompanied by modifications of the oxidation state for both Mn and Ni. The structural and compositional/chemical evolution of these surface structures during electrochemical cycling may play an important role on the amount and mechanism of degradation for this family of cathode materials in Li-ion batteries. Detailed analyses of such structural alterations for different cycles and cycling rates will be discussed and we will also present results from *in-situ* heating

experiments on these materials assessing structural and chemical changes as a function of temperature using aberration corrected STEM imaging and EELS.

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] Kang, S.H., Sun, Y.K. & Amine, K. (2003). Electrochemical and Solid State Letters **6**(9), A183-A186.
[4] Lu, Z.H., MacNeil, D.D. & Dahn, J.R. (2001). Electrochemical and Solid State Letters **4**(12), A200-A203.
[5] Jiang, M., Key, B., Meng, Y.S. & Grey, C.P. (2009). Electrochemical and Structural Study of the Layered, "Li-Excess" Lithium-Ion Battery Electrode Material Li[Li1/9Ni1/3Mn5/9]O-2. Chemistry of Materials **21**(13), 2733-2745.
[6] 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.



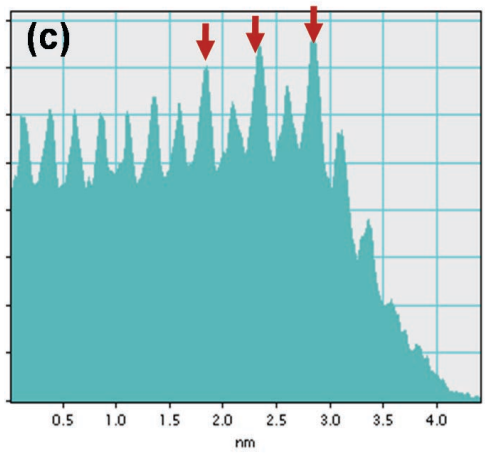


Fig. (a) 1 A typical HAADF-STEM image shows that the surface contains the same atomic structure as its bulk in the pristine $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ sample, (b) surface layer modification (ordering) is observed in the sample after ten (10) charge-discharge cycles, and (c) the intensity profile from the boxed region marked in (b) reveals ordering of the atomic structure near the surface.

https://doi.org/10.1017/S143192761005974X Published online by Cambridge University Press