

Ordering and Phase Transformation in $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{1-x}\text{O}_2$ Battery Electrode Material

K.S. Rao¹, N. Pereira^{1,2}, G. Amatucci^{1,2} and F. Cosandey¹

¹ Department of Materials Science & Engineering, Rutgers University, Piscataway, NJ 08854.

² Energy Storage Research Group (ESRG), Rutgers University, North Brunswick, NJ 08902.

Layered lithium nickel manganese oxides have attracted interest as possible alternatives to LiCoO_2 , the material that is most commonly used as positive electrode in commercial Li-ion batteries, because of their lower cost and higher safety and abuse tolerance. The series of compounds $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{1-x}\text{O}_2$ were first reported by Ohzuku et al. [1] in 2001. These layered structures have similar space group as LiCoO_2 (space group $R\bar{3}m$).

There have been many studies on how the crystal structure evolves over one charge-discharge cycle. On the other hand, there have been few studies on how the crystal structure evolves after extensive electrochemical cycling. $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{1-x}\text{O}_2$ was chosen as a representative model compound in this work, in order to investigate the structural changes that occur after charge-discharge cycles. Selected area electron diffraction patterns (SAED) and high resolution transmission electron microscope (HRTEM) images were obtained from both the as-prepared powders and from powders taken from the positive electrode after many charged-discharged cycles. These powder samples were suspended on lacey carbon films and investigated using a JEOL 2010F microscope operating at 200kV. Several particles of the as-prepared and cycled material were viewed along various low-index zone axes. These experimental studies were accompanied by simulations of diffraction patterns for various possible crystal structures using the JEMS (Java EMS) software program developed by P. Stadelmann (version 2009).

A typical TEM image of as-prepared $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{1-x}\text{O}_2$ powder is shown in Figure 1 (a) with in Figure 1 (b)-(c) two electron diffraction patterns obtained along the $[\bar{1}\bar{1}\bar{2}]$ and $[001]$ zone axes respectively. These fundamental reflections and zone axes are indexed as the parent trigonal phase with a space group of $R\bar{3}m$. Additional weak reflections are also observed whose first order superlattice reflections are marked by open circles in Fig. 1(b) and (c), which indicate the presence of cation ordering in the transition metal layer [2,3]. These superlattice reflections (marked by open circles) observed in Fig. 1(b) and (c) can be indexed to $\sqrt{3}a_r \times \sqrt{3}a_r \times c_r$ superstructure with space group $P3_1I2$. Superlattice reflections unique to this superstructure were found in all as synthesized particles.

Figure 2 (a) shows the bright-field TEM image of cycled $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{1-x}\text{O}_2$ sample. Fig. 2(b) and (d) shows the SAED patterns taken from the particle interior and edge respectively. The SAED pattern from the particle interior is in good agreement with the simulated electron diffraction pattern shown in Figure 2c with space group $R\bar{3}m$ ($[100]$ zone axis). Superlattice reflections corresponding to the ordered $P3_1I2$ phase are not observed after cycling. However, additional reflections are observed in Figure 2d which could be indexed as the cubic $Fd\bar{3}m$ phase ($[110]$ zone axis) as shown in Fig. 2 (e). This indicates the presence of cubic phase on the particle surface. These results are further evidenced by HRTEM image and FFT pattern shown in Fig. 2(f) indicative of a cubic surface phase.

References

- [1] T. Ohzuku, Y. Makimura, *Chem. Lett.* 30 (2001) 744.

- [2] Y.S. Meng, G. Ceder, C.P. Grey *et al.*, *Chem. Mater.* 17 (2005) 2386.
 [3] F. Weill, N. Tran, L. Croguennec, C. Delmas, *J. Power Sources* 172 (2007) 893.
 [3] The authors would like to acknowledge the Institute of Advanced Materials, Devices and Nanotechnology (IAMDN), Rutgers University for the use of microscopy facility.

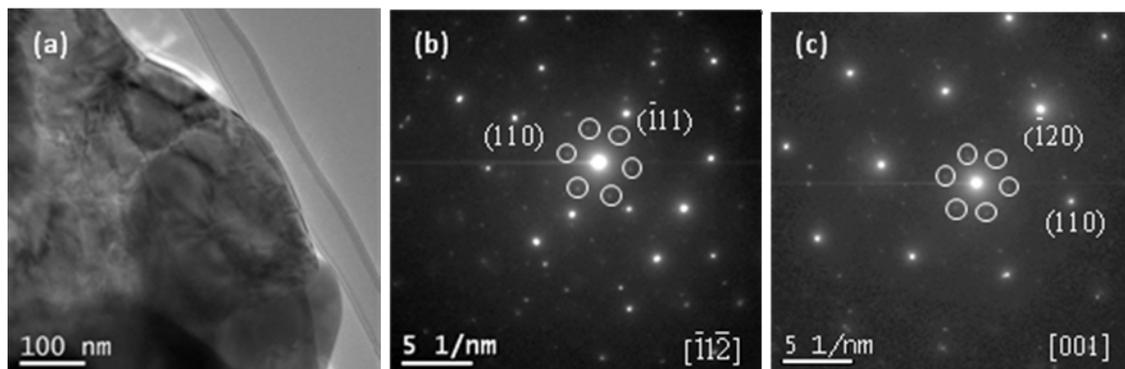


Fig.1. (a) Bright-field TEM image of the as prepared $\text{Li}_{1+x}(\text{Ni}_{0.3}\text{Mn}_{0.3}\text{Co}_{0.3})_{1-x}\text{O}_2$ particle, (b)-(c) SAED patterns collected along the $[\bar{1}1\bar{2}]$ and $[001]$ zone axes respectively. First order superlattice reflections marked by open circles are from cation ordering.

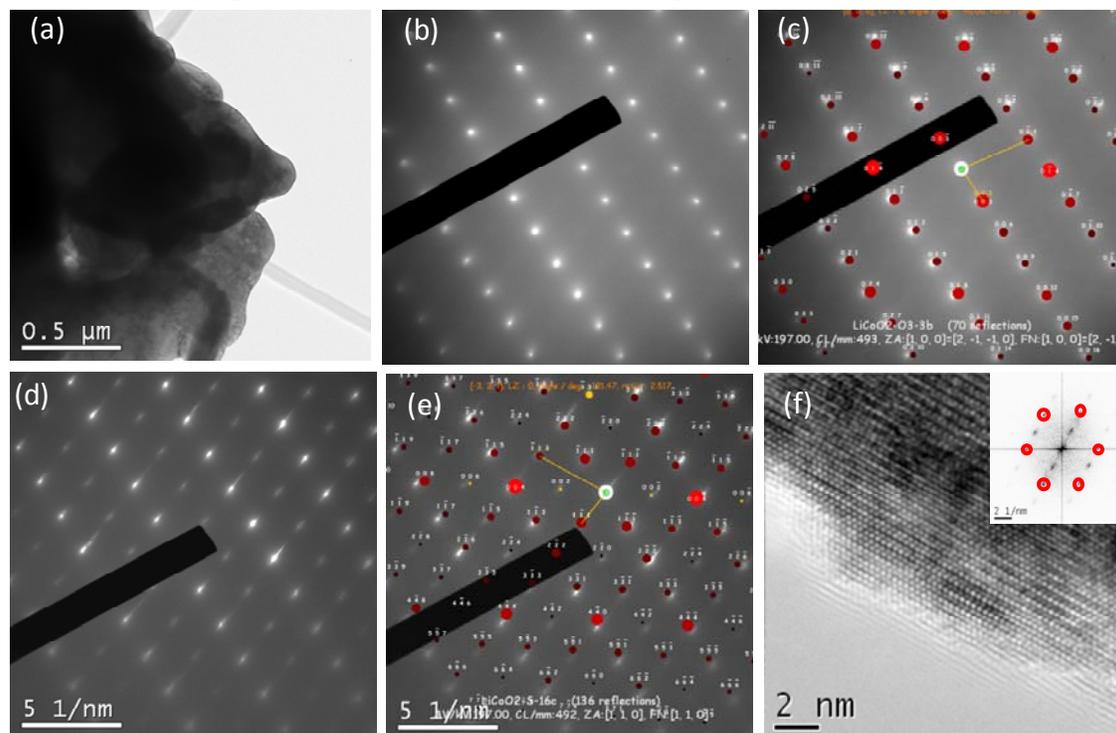


Fig.2. (a) Bright-field TEM image of cycled material, (b) Experimental electron diffraction pattern collected from the interior of the $\text{Li}_{1+x}(\text{Ni}_{0.3}\text{Mn}_{0.3}\text{Co}_{0.3})_{1-x}\text{O}_2$ particle, (c) Simulated $[100]_{\text{T}}$ zone axis pattern with a space group $R\bar{3}m$. (d) Experimental electron diffraction pattern collected from the edge of the particle (a), (e) Simulated $[110]_{\text{cubic}}$ zone axis pattern with a space group of $Fd\bar{3}m$, (f) High resolution electron microscope image collected near the particle edge, with the corresponding FFT pattern with reflections from the cubic phase in the insert.