

## Lithium Ordering in Next-Generation High-Voltage Lithium-Rich Layered Oxide Cathode Battery Materials

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Lithium-rich layered oxide cathode materials, with general formula  $\text{Li}_{1+\alpha}\text{MO}_2$  (M = transition metal or combination of metals), represent the next generation of high-voltage, high-capacity Li-ion battery cathode materials for plug-in electric vehicle applications. These materials offer up to ~90% increased lithium capacity, increased safety, and lower cost potential compared to incumbent  $\text{LiMO}_2$  positive electrode active materials such as  $\text{LiCoO}_2$  or  $\text{Li}[\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y}]\text{O}_2$ .

In this study, transmission electron microscopy (TEM), electron diffraction (ED), x-ray energy-dispersive spectroscopy (XEDS) and x-ray diffraction (XRD) techniques were used to characterize these structurally-complex materials both in their pristine as-synthesized state, and after extensive electrochemical cycling. As synthesized, both ED and XRD reveal the overall monoclinic C2/m symmetry, indicating the presence of lithium ordering in transition-metal layers, similar to its parent  $\text{Li}_2\text{MnO}_3$  crystal structure. However, it was found that this lithium ordering is not uniformly present throughout the sample. Convergent-beam electron diffraction (CBED) obtained from numerous nanometer-size regions across single nanoparticles reveal the presence of domains with trigonal R-3m symmetry, indicating disordered transition metal layers similar to the  $\text{LiCoO}_2$  structure. Additional high-resolution imaging confirms that ordered lithium-rich domains are inter-grown with Li-poor domains, over length scales ~1-3 nm, and randomly distributed throughout the sample. Upon electrochemical cycling, conversion from a layered crystal structure to spinel-like structure was captured as a function of number of cycles using both dark-field imaging and CBED.

Cathode nanoparticles were synthesized from Ni, Mo, and Co metal and lithium carbonate precursors. Precursor powders were mixed together using ball-milling processes, and then heat-treated at 850 – 1050 °C for ~10 hours to convert to ~100-200 nm particles  $\text{Li}_{1+\alpha}[\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y}]\text{O}_2$ .

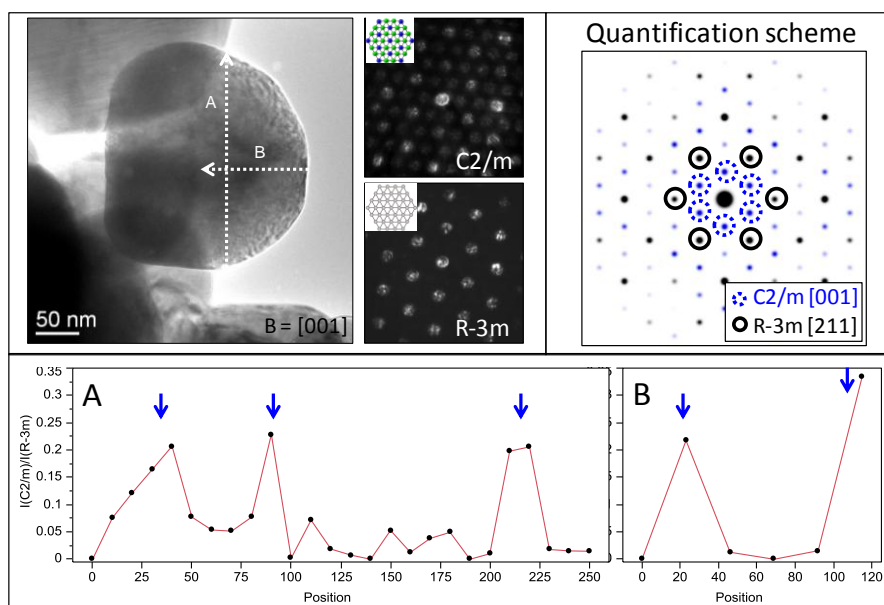
Figure 1 shows the inter-grown C2/m and R-3m structures present within a single nanoparticle of as-synthesized  $\text{Li}_{1+\alpha}[\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y}]\text{O}_2$ . Nanometer size regions exhibiting either monoclinic or trigonal character were observed by CBED patterns collected from the nanocrystal. Specifically, CBED patterns were collected from regions spaced ~10 nm apart along the indicated lines from a [001]-oriented nanoparticle. The relative intensities of the unique C2/m (blue) and R-3m (black) diffraction spots were evaluated for each diffraction pattern, and their ratio ( $I_{\text{C2/m}}/I_{\text{R-3m}}$ ) is plotted as a function of probe position across the nanoparticle. As is evident from this plot, nanometer size regions of R-3m and C2/m symmetry are present and distributed randomly throughout the nanocrystal. Blue arrows indicate regions with high C2/m diffraction spot intensity, and thus indicate high levels of Li content and ordering. The variation in intensity ratio further indicates that lithium content and ordering varies continuously throughout the nanoparticle, consistent with a solid-solution of these two phases. This finding is consistent with previous findings that the stochastic distribution of C2/m and R-3m local structures is determined both by the Li/Me ratio, and (Ni+Co)/Mn ratio [1,2].

Figure 2 shows images and diffraction patterns of materials cycled for 2 and 200 cycles. Upon

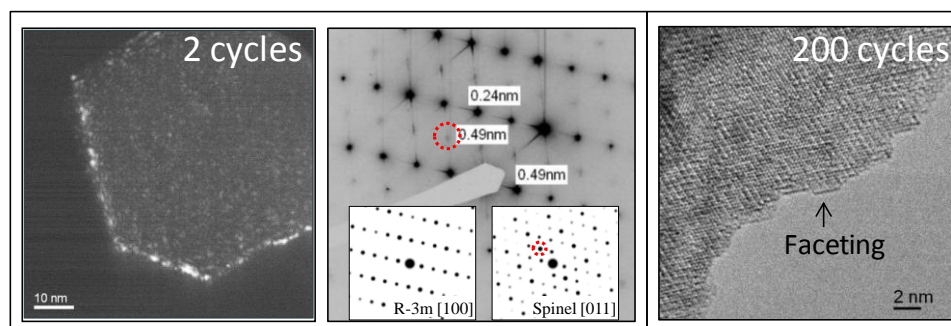
electrochemical cycling, diffraction patterns reveal the appearance of new diffraction spots, whose spacings and symmetries are consistent with that of  $Fd\bar{3}m$  spinel. After two cycles, dark-field images show that nanoparticle surfaces exhibit spinel-like structure, yet the layered  $R\bar{3}m$  and  $C2/m$  structures remain throughout the bulk. However, after 200 cycles, only  $R\bar{3}m$  and spinel-like diffraction patterns are observed, indicating the loss of Li ordering, and migration of transition metal ions into the Li layers. In addition, new nm-size crystalline facets are observed, indicating migration and recrystallization.

## References

- [1] M. Gu *et al*, *Nano Letters* **12** (2012), p. 5186.  
 [2] J. Barenó *et al*, *Chemistry of Materials* **23** (2011), p. 2039.



**Figure 1.** (upper left) Bright-field TEM image of a single cathode nanoparticles with representative  $C2/m$  and  $R\bar{3}m$  CBED patterns obtained along the indicated lines. (upper right) The quantification scheme used to evaluate the degree of  $C2/m$  character from each CBED pattern. (bottom) Intensity ratio  $I_{C2/m}/I_{R\bar{3}m}$  plotted as a function of



**Figure 2.** (Left) Dark-field image of nanoparticle after 2 cycles produced with weak spinel diffraction spot indicated (simulated spinel and  $R\bar{3}m$  pattern shown in inset) shows spinel phase distributed on the surface of the nanoparticles. (Right) HRTEM image of nanoparticles surface after 200 cycles shows formation of new facets.