

Structural Characterization of Powders and Thin Films of Layered $\text{Li}_{1.2}\text{Mn}_{0.55}\text{Ni}_{0.15}\text{Co}_{0.1}\text{O}_2$ Cathode Materials

Aaron C. Johnston-Peck¹, K. Kamala Bharathi^{1,2}, Saya Takeuchi¹, Igor Levin¹, Andrew A. Herzing¹ and Leonid A. Bendersky¹

¹ Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, 20899, USA

² Department of Materials Science and Engineering, University of Maryland, College Park, Maryland, USA

Layered, lithium and manganese rich transition metal oxides are becoming the next generation high energy cathode material for lithium ion batteries with superior performance including high capacity (>200 mAh/g), low cost, and better thermal stability. A thorough atomic-level structural understanding of these materials is needed to understand and improve their electrochemical properties. To this end, we have studied a layer cathode material with a composition of $\text{Li}_{1.2}\text{Mn}_{0.55}\text{Ni}_{0.15}\text{Co}_{0.1}\text{O}_2$ (HE5050, TODA Inc.) [1]. A commercially available powder can provide a common platform for study in a field where differences of compositions and processing methods can make comparisons between studies difficult. In addition to the powders, pulse laser deposition (PLD) was used to grow epitaxial thin films on single-crystal SrTiO_3 substrates. The targets for growth were made from the HE5050 powder.

The samples were characterized using multiple techniques that probe over a variety of length scales. High angle annular dark field scanning transmission electron microscopy (HAADF STEM) was used to characterize the local structure. Selected area electron diffraction (SAED) provides structural information from entire particles or grains while X-ray diffraction (XRD) complements these localized measurements with a global measure. Careful examination of these materials is necessary due to their complex structure, which can consist of multiple phases based on different ordering of Li and transition metals on the same oxygen sublattice. A trigonal $R\bar{3}m$ phase can form which is comprised of a repeating layer sequence of a Li-O-M-O-Li. Yet, depending on preparation conditions and precise composition, a monoclinic $C2/m$ phase may form where lithium atoms are incorporated in the transition metal layer in an ordered manner. In this case the stacking sequence is the same however the transition metal atoms are periodically replaced by Li atoms. The results of structural characterization reported in the literature have been mixed. Some observe a composite type structure [2] where small regions of trigonal and monoclinic structures coexist, while others report a solid solution of a single monoclinic phase [3]. Structural characterization based on diffraction results alone can be quite difficult because the monoclinic phase is an ordered structure derived from the parent trigonal structure. Defects may further convolute interpretation of diffraction data. HAADF-STEM, while limited in its ability to sample large areas, can unambiguously differentiate between the trigonal and monoclinic phase. When used together we can begin to create a structural model to describe the sample with an increased degree of confidence.

Characterization of the particles from the HE5050 powder suggests that the structure is primarily in the monoclinic phase; both diffraction and HAADF-STEM support this designation (Figure 1). No long range ordering of the trigonal phase was observed. However, at the surfaces of the particles a spinel phase was found to form along specific facets. Measurements by energy dispersive X-ray spectroscopy (EDS) indicate the spinel phase was enriched in Ni relative the particle (Figure 2). Along other facets the spinel phase did not form but there was still a local increase in the concentration of transition metal

atoms.

The thin films were successfully grown in the monoclinic phase. It was noted that the quality of the underlayer could influence the structure of the as-grown films and in certain cases the trigonal and spinel phases were observed in addition to the monoclinic. Characterization of the film samples before and after electrochemical testing revealed a change in the structure of the samples as well as a migration of the elements revealed by EDS.

References:

[1] Certain commercial equipment and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendations by the National Institute of Standards and Technology nor does it imply that the material or equipment identified is necessarily the best available for this purpose. The HE5050 powder and sintered pellet for PLD were kindly provided by B. Polzin and A. Jansen from Argonne National Lab.

[2] J. Bareño *et al.*, Chem. Mater. **23** (2011), p.2039.

[3] K.A. Jarvis *et al.*, Chem. Mater. **23** (2011), p.3614.

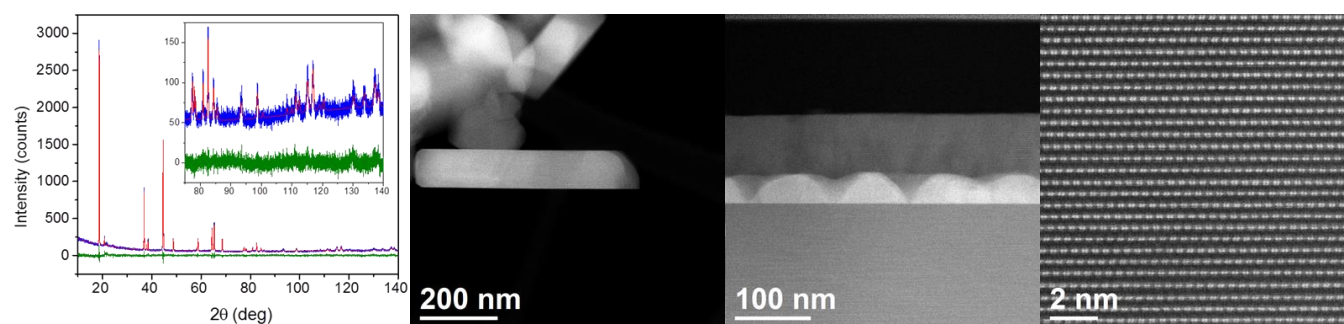


Figure 1. Experimental (blue) and calculated (red) X-ray diffraction profiles, the calculated profile is for the monoclinic phase. HAADF STEM images of the powder and thin film samples. A representative HAADF STEM image along [1-10] revealing ordering in the transition metal atom layer, indicating formation of the monoclinic phase.

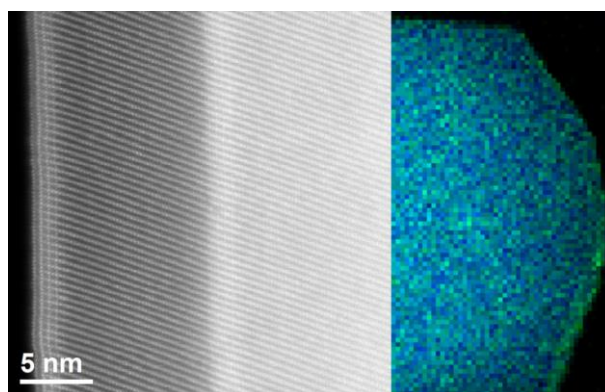


Figure 2. HAADF STEM image of a particle edge that has reconstructed to spinel. EDS map demonstrates the spinel phase is Ni-enriched (Ni = green, Mn = blue).