Published in final edited form as:

Mater Charact. 2016 September ; 119: 120–128. doi:10.1016/j.matchar.2016.07.013.

Structural studies of $\text{Li}_{1.2}\text{Mn}_{0.55}\text{Ni}_{0.15}\text{Co}_{0.1}\text{O}_2$ electrode material

Aaron C. Johnston-Peck, Igor Levin, Andrew A. Herzing, and Leonid A. Bendersky

Materials Measurement Laboratory, National Institute of Standards Technology, Gaithersburg, MD 20899 USA

Abstract

A pristine Li-rich layered electrode material with composition $\text{Li}_{1.2}\text{Mn}_{0.55}\text{Ni}_{0.15}\text{Co}_{0.1}\text{O}_2$ was characterized by X-ray diffraction, transmission electron microscopy, and scanning transmission electron microscopy to determine whether it is a coherent mixture of monoclinic $C2/m$ Li_2MO_3 and trigonal $R\bar{3}m$ LiMO_2 phases or a solid solution of the monoclinic phase. Contradictory results have been previously reported which can be attributed to the complexity and structural similarity of the monoclinic and trigonal phases. We resolved this uncertainty by combining diffraction and imaging techniques that probe complimentary length scales. Our results demonstrate that the structure is primarily monoclinic, supporting the solid solution model, although near surface structural alterations were also observed.

Keywords

Lithium Battery Material; Scanning Transmission Electron Microscopy; X-ray Diffraction

Introduction

Design and manufacturing of next generation batteries require comprehensive understanding of the structure and electrochemical processes in the materials involved. Positive electrode materials for high-voltage Li-ion batteries based on chemical formulations $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M = \text{Mn}, \text{Ni}, \text{Co}$) are currently under worldwide development.[1-4] It was demonstrated that these materials can provide a reversible capacity of 230 mAh/g or more, which is significantly higher than the capacity offered by state-of-the-art layered $\text{Li}_{1-x}\text{CoO}_2$ (≈ 140 mAh/g) or spinel $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ (≈ 110 mAh/g) electrodes. These layered materials are anticipated by design to be a coherent mixtures comprising two end-members – layered monoclinic $C2/m$ Li_2MO_3 and layered trigonal $R\bar{3}m$ LiMO_2 . [5] Also in the literature are reports describing these materials as a single phase solid solution. [6] This discrepancy is not easily addressed because of the structural similarity between the $C2/m$ and $R\bar{3}m$ phases. Disparities in synthetic conditions (composition, temperature profiles, etc.) that influence structure [7-9] further complicate the situation and create the possibility that both structural interpretations are correct. The complexity of this situation emphasizes the importance of being able to accurately and confidently characterize the structure of these materials to elucidate the interplay of processing and electrochemical behavior.

The monoclinic phase is an ordered structure derived from the parent trigonal phase. In the stoichiometric trigonal structure (LiMO_2) alternating layers of LiO_6 and MO_6 octahedrals are present along the c axis. In the lithium-rich monoclinic structure, the Li layer octahedral sites are occupied exclusively by lithium ions whereas the transition metal layer octahedral sites are now occupied by both lithium and transition metal ions in a -Li-M-M-Li- arrangement (both the monoclinic and trigonal unit cells are depicted in the Supporting Information Figure S1). It is this similarity between the two phases that hinders structural characterization that is both accurate and representative. Diffraction methods struggle because the reflections of $R\bar{3}m$ phase are a subset of those for the lower symmetry $C2/m$ phase and it has been reported refinements of the same material can be satisfactorily fitted using either 100 % monoclinic Li_2MO_3 or a composite structure consisting of Li_2MO_3 and LiMO_2 intergrowths.[10] Additionally, in these material systems, the presence of defects, such as stacking faults, can further complicate interpretation of diffraction data.[11-13] High-resolution transmission electron microscopy (HRTEM) images should be able to accurately identify the phases present in these materials; however interpreting phase contrast images can be difficult because the image contrast is a complex result depending on parameters of both the specimen and microscope. Image simulation and the use of focal series improves reliability of HRTEM image interpretation. Atomic-resolution high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) – with its strong sensitivity to atomic number – can differentiate between these two phases. When the materials are observed along select crystallographic directions the presence (or lack) of chemical ordering on the transition metal layer will be observable enabling the $C2/m$ and $R\bar{3}m$ phases to be distinguished.[6] Although STEM provides excellent insight into which phase has formed locally, the results may not be completely representative of the entire sample because of sampling limitations.

While a large number of research groups are investigating these materials, it is difficult to compare the results. Differences in compositions and processing parameters between materials may influence the structure.[7-9] Widely available materials, such as a commercially available product, can provide a platform to compare results. For instance, a material has been developed and manufactured by TODA Inc; this material has composition $\text{Li}_{1.2}\text{Mn}_{0.55}\text{Ni}_{0.15}\text{Co}_{0.1}\text{O}_2$ (hereafter referred to as HE5050). The performance of HE5050 was studied using electrochemical methods.[14-17] In addition, the structure of HE5050 powder was investigated recently by X-ray diffraction (XRD),[15, 18] neutron scattering, [10] electron diffraction,[16, 18] magnetic susceptibility techniques,[10] and HRTEM.[18] Mohanty et al.[10] used temperature-dependent magnetic susceptibility measurements to complement diffraction data. These measurements revealed a paramagnetic response at higher temperature with a magnetic transition at $T_N = 50$ K. The paramagnetic behavior was believed to be the response of the trigonal phase while the transition was attributed to the presence of Li/M cation ordering, a feature of the monoclinic phase. Together the results of magnetic measurements and neutron diffraction data were attributed to the presence of two phases, supporting the coherent mixture structural model.[10] To this point, the coherent mixture structural model has been used to describe the structure of HE5050[10, 18] but reports detailing its characterization by HAADF-STEM have not been made.

It is clear that proper interpretation of the structure requires careful consideration. In particular, relying on a single technique may not be suitable to capture all the nuances of these materials. The complexity of this system demands the use of complementary techniques that are able to measure the sample both macroscopically and locally. Therefore, we will describe the characterization of a single material (HE5050) using a combination of XRD, selected area electron diffraction (SAED), and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) to arrive at an interpretation of the structure.

Experimental

HE5050 powder was provided by Argonne National Laboratory and acquired from TODA America, Inc. The composition of the powder, $\text{Li}_{1.2}\text{Mn}_{0.55}\text{Ni}_{0.15}\text{Co}_{0.1}\text{O}_2$, has been reported elsewhere.[18-20] Samples for TEM were prepared by directly depositing the powder onto a support (Cu grid supported C film or a SiN membrane) without any further modification or treatment. The data shown in Figure 8 is an exception and was exposed to a 5 kV Argon ion beam for 200 minutes.

Phase assemblages were characterized using X-ray diffraction performed in a Panalytical X-ray powder diffractometer equipped with an incident-beam monochromator ($\text{Cu K}_{\alpha 1}$ radiation) and a position sensitive Pixcel detector. Rietveld refinements of structural models were performed using the TOPAS software package. A FEI Titan 80-300 was used to acquire scanning/transmission electron microscopy (S/TEM) data. The microscope has an aberration corrector for the probe-forming optics. High angle annular dark field (HAADF) images and electron energy loss spectroscopy (EELS) data were acquired at 300 kV with probe currents over the range of ≈ 25 pA to ≈ 35 pA. Some of the images (Figure 7c, 8c, and S6) included are the sum of a series of images that were aligned using a rigid body registration routine, StackReg,[21] supported in FIJI.[22] A raw unprocessed image of the same region can be found in Supporting Information. Accelerating voltages of 80 kV and 150 kV were used to acquire energy dispersive X-ray spectroscopy (EDS) data. In STEM, probe forming convergence semi angles of ≈ 14 and ≈ 23 mrad were used primarily for imaging and EDS, respectively. A detector inner collection angle of ≈ 71 mrad was primarily used for HAADF imaging.

Results and Discussion

The XRD patterns (blue profile of Figure 1) were fit using models which contained varying amounts of monoclinic and trigonal phase (details can be found in the Supplementary Information). The results suggest that the particles contain exclusively the monoclinic ($C2/m$) phase. Rietveld refinements indicate partial substitution of Li on the 2b site by the transition metal atoms with an occupancy of 0.35(5). The other Li sites, 2c and 4h, are fully occupied while Li may also partially occupy (≈ 0.2) the transition metal sites. The distribution of the transition-metal cations cannot be refined using the XRD data because of the similar X-ray scattering cross-sections for these species.

To unambiguously rule out the presence of the $R\bar{3}m$ phase, we also employed more local measurements of the structure by SAED and HAADF-STEM. A complex structure such as requires careful analysis HE5050 to prevent erroneous interpretations. To illustrate this complexity, consider the particle shown in Figure 2a and the corresponding SAED pattern (Figure 2b) which shows both fundamental and superlattice reflections. The fundamental reflections can be indexed to the [001] zone of the trigonal phase but superlattice reflections indicate there is chemical ordering and suggest the presence of the monoclinic phase. The simulated pattern of the [103] monoclinic zone axis shown in Figure 2c provides a partial match; all the fundamental reflections are accounted for but not all of the superlattice reflections. This inconsistency can be resolved by atomic resolution HAADF-STEM imaging (Figure 2f-i). The contrast in HAADF-STEM images is proportional, to a first-order approximation, to the average projected atomic number of the column. For example, atomic columns of transition metal atoms will have much higher intensities than those containing oxygen or lithium atoms. In Figure 2f, the atomic resolution image matches well with the monoclinic structure oriented along the [103] zone axis. Comparisons of both the image and its FFT with the simulated diffraction pattern as well as the multislice image simulation (Figure 2c) correspond well. However, different regions of the particle are not identical to that shown in Figure 2f. Figure 2g has a similar striped appearance but the orientation has changed by $\approx 120^\circ$, while other regions have a honeycomb-like appearance as shown in Figure 2h and 2i. This can be explained by the projection nature of the TEM images and the formation of variants along the stacking of the (001) planes i.e., the [103] direction. These variants form at 120° rotations with respect to one another, such that their effect in projection can be simulated by overlaying the [103] diffraction pattern with itself after 120° and 240° rotations about the central (000) point (Figure 2d and 2e, respectively). After accounting for the orientation variants the simulated pattern (Figure 2e) successfully matches all reflections in the experimental data (Figure 2b). Furthermore, the multislice image simulations reproduce the image intensity observed in Figures 2h and 2i. Details of these simulations are in the Supporting Information. Residual differences in intensity between experiment and simulation may be due to differences in thickness and/or subtle chemical deviations from the perfectly ordered model used for the simulation.

The ordered arrangement of the Li and M ions reduces the symmetry from the trigonal to the monoclinic point group.[23] Van Tendeloo and Aemelinckx determined that the number of orientation variants, n , formed in an ordered alloy is given by:

$$n = \frac{p}{q}$$

where p and q are, respectively, the orders of the point groups of the disordered and ordered phases.[24] The order of the trigonal phase is 12 (point group $\bar{3}2/m$) while the order of the monoclinic phase is 4 (point group $2/m$). The higher symmetry order of the trigonal structure is due to the additional three-fold axis of rotation about the c axis that is not present in the

monoclinic structure. It has been identified that the $[100]$, $\begin{bmatrix} \bar{1} & 10 \end{bmatrix}$, $\begin{bmatrix} \bar{1} & \bar{1} & 0 \end{bmatrix}$ are related to one

another by orientation variants.[25-27] Practically this means domains of $[100]$, $\begin{bmatrix} \bar{1} & 10 \end{bmatrix}$, $\begin{bmatrix} \bar{1} & \bar{1} & 0 \end{bmatrix}$ oriented material can be simultaneously observed when oriented along any one of these respective zone axes (e.g., Figure 3a or S4 and see the aforementioned references).

The presence of orientation variants has implications for interpreting data viewed along numerous other zone axes as well. By picturing the $[103]$ (equivalent to the $[001]$ in the trigonal structure) as a three-fold axis of rotation it becomes clear that certain zone axes will be near coincidence with one another. A stereogram has been constructed (Supporting Information Figure S3) to illustrate this relationship. The presence of orientation variants may cause discrepancies between experimentally acquired diffraction patterns or images and simulated data built from models assuming a defect free monoclinic structure. These discrepancies can include extra reflections in diffraction patterns or altered contrast in HAADF-STEM images, both due to the projective nature of S/TEM and overlapping orientation variants along the viewing direction. This behavior is exemplified by the example shown in Figure 2. To outline which zones are potentially susceptible to variation in appearance due to orientation variants, calculations were performed to determine groups of three zone axes that are separated by an equal angular distance from one another as well as having the same angular separation from the $[103]$ zone axis. This list, presented in Table 1, is not exhaustive (for a more complete version see Table S2 in the Supporting Information) but should be sufficient to aid in the interpretation of situations where uncertainties exist. Additionally, tilting the specimen to neighboring zone axes and acquiring diffraction and/or image data can help resolve uncertainties. The stereogram (Supporting Information Figure S3) visualizes these relationships identified in Tables 1 and S2.

Taking into account the role structural variants can have on the electron microscopy results, several particles were analyzed by SAED in conjunction with bright field/dark field (BF/DF) TEM and HAADF-STEM imaging. Figures 3 and 4 present images acquired from two

particles oriented along the $\begin{bmatrix} \bar{1} & \bar{1} & 0 \end{bmatrix}$, $\begin{bmatrix} 0 & \bar{1} & 0 \end{bmatrix}$, and $\begin{bmatrix} 1 & \bar{1} & 0 \end{bmatrix}$, and $\begin{bmatrix} \bar{1} & 00 \end{bmatrix}$, $\begin{bmatrix} \bar{3} & 10 \end{bmatrix}$, and $\begin{bmatrix} \bar{3} & \bar{1} & 0 \end{bmatrix}$ zone axes, respectively. The images from the $\begin{bmatrix} \bar{1} & 00 \end{bmatrix}$, $\begin{bmatrix} \bar{1} & \bar{1} & 0 \end{bmatrix}$, and $\begin{bmatrix} 1 & \bar{1} & 0 \end{bmatrix}$ orientation show long range ordering of the transition metal ions indicating the monoclinic phase and orientation variants can be observed as well (see Supporting Information Figure S4 for additional data). The presence of orientation variants is reflected in the SAED patterns where extra reflections are present. Streaking in the patterns may be a shape effect from the stacking of small domains along the $[103]$ direction. Bright and dark field TEM images (in the Supporting Information, Figure S5) from each particle demonstrate that the orientation variants are frequently observed and are regularly distributed throughout the particles. To improve the limited sampling that is associated with S/TEM analysis an additional fifteen particles were examined by HAADF-STEM. Each particle was tilted to an orientation that provided unambiguous identification (e.g., $[100]$) of the structure and images were acquired from several regions of the particle. Zone axes like $\begin{bmatrix} 0 & \bar{1} & 0 \end{bmatrix}$, $\begin{bmatrix} \bar{3} & 10 \end{bmatrix}$, and $\begin{bmatrix} \bar{3} & \bar{1} & 0 \end{bmatrix}$ (Figures 3b, 4a, 4c) cannot be used to differentiate between the monoclinic and trigonal phases because the

projected structure will not show evidence of ordering of the metal ions if it exists, that is, the trigonal and monoclinic structure will appear approximately the same along these zone axes. All the particles observed had roughly the same structure, that is, predominately monoclinic with no large and/or regular domains of the trigonal phase observed. This suggests there is little interparticle variability with respect to crystallographic phase.

The particles are primarily monoclinic phase; however some noteworthy deviations are present. Along certain edges of the particles there is a pronounced increase in the HAADF STEM signal as seen in Figures 3b, 4a and 4c. The HAADF contrast indicates a new arrangement of the transition metal ions and suggests a spinel phase has formed that is approximately 1 nm to 2 nm wide, as seen in Figure 5a. This formation was observed only

along the $\left\{13\bar{1}\right\}$ terminations. A combination of HAADF-STEM, diffraction, EELS, and EDS were used to interrogate these formations. This spinel phase was not detected in the XRD measurements, likely due to a combination of the small amount and its nanocrystallinity. EDS measurements indicate the spinel is enriched in Ni relative to the monoclinic portion. EELS spectra recorded from the spinel region and the bulk of the particle have notable differences. The relative intensity of the Ni $L_{2,3}$ -edge has increased suggesting the region is enriched in Ni supporting the observations made by EDS. As shown in Figure 6a the fine-structure of the O K-edge changes suggesting differences in local bonding environment between the surface and core. Additionally, the onset of the Mn $L_{2,3}$ -edge shifts to a lower energy suggesting a reduction in valence from the +4 state. Local diffraction measurements performed using a STEM probe with a small convergence angle and HAADF-STEM images (Figure 6c-f and Supporting Information S6) acquired in several zone-axis orientations support the spinel ($Fd\bar{3}m$) structure. Although, some data suggests there may be a high concentration of point defects disrupting the order of the spinel structure altering its symmetry towards the rock salt phase. A diffraction pattern (Supporting Information S5b) reveals rows of reflections are periodically absent, suggesting that there may be a degree of ordering amongst the defects, and the HAADF image also deviates from what would be expected for that particular zone axis.

The segregation of Ni in pristine material has been observed in $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{M}_{0.6}]\text{O}_2$ materials that are predominately the trigonal phase.[28, 29] Of note, it was reported when the monoclinic phase was observed Ni-enrichment did not occur at the surface,[28] this is contrary to what is observed here, where a clear indication of Ni segregation was observed in particles with the monoclinic symmetry.

These structural observations have important implications for material performance, as the rate of lithium diffusion is structure dependent. The origin of these near-surface formations in these materials is poorly understood at present. One possibility is that it is thermodynamically driven because of differences in the transition metal oxidation states. In the perfectly ordered structure of Li_2MO_3 , the metal cations are in the +4 oxidation state, while Ni and Co are more stable in oxidation states of +2 and +3, respectively. Therefore, mechanisms that lower the Co and Ni valence to a more favorable state may influence what phases are present in HE5050. Intermixing of transition metal ions to the 2b Li (observed by XRD) sites could be one way to reduce the energy of the system. Alternatively, formation of

spinel, where the oxidation state of the cations is lower than +4, might be another mechanism to lower energy. If this is the case, eliminating inhomogeneity in the as-synthesized product might be achieved by careful control of synthetic parameters such as cooling rates or the ratio of Ni and Co to Mn.

Another deviation from the monoclinic structure was a limited amount of atomic rows displaying an apparent increase in intensity on the 2b sites, which are Li-occupied in the ordered monoclinic phase. The comparatively increased intensity on these sites suggests an increasing concentration of transition metals at these positions. This relationship between increasing concentration of transition metals on the 2b sites and HAADF image contrast is demonstrated by the multislice image simulations shown in Figure 7a. Without the lithium atoms periodically arranged in the transition-metal atomic layer the high symmetry degenerates back to the structure characteristic of the trigonal phase. These regions with apparent increases in transition metal ion disorder were confined primarily to 1 or 2 adjacent atomic layers and did not occur with any regular periodicity. In Figure 7c two atomic layers are marked by blue arrows, in this case the 2b intensity has increased slightly but is still small relative to the transition metal columns. In the atomic row marked with a red arrow the 2b intensity is approximately the same suggesting a single layer of trigonal phase. In addition to these regions, other areas exhibit unique contrast indicated by the red box in Figure 7d. This region has a structure that does not correspond to the monoclinic or trigonal phases. Regions such as these were also limited in size and did not occur with any regular periodicity. Multislice simulations provide an interpretation of the HAADF image intensity. When two monoclinic slabs overlap with an appropriate sub-unit-cell shift the projected image of the structure reproduces this contrast (Figure 7e). The contrast (Figure 7e) can be generated by combinations of overlapping slabs of like orientations (e.g., [100] with [100])

or unlike orientations (e.g., [100] with $\begin{bmatrix} 1 & \bar{1} & 0 \end{bmatrix}$). This behavior suggests that these regions with unique contrast are in fact the monoclinic structure and the apparent deviation is a projection artifact of the STEM imaging process. This phenomenon raises the question of whether other regions with an apparent increase in disorder are also due to projection artifacts. This idea is further supported by the fact that these regions of apparent disorder can be found at junctions between variants where overlapping variants could occur. For example, in Figure 7c the regions marked by blue arrows also mark the boundary between different variants.

Taken all together, the characterization by XRD, TEM, and STEM points to a structure that is monoclinic with orientation variations and that has a small degree of intermixing between the lithium and transition metal atoms. Additionally, there is limited formation of spinel at surface terminations. This data supports the general scheme of a single-phase solid solution monoclinic material rather than the proposed composite scheme of coherent intergrowths of trigonal and monoclinic phase. Previous studies on HE5050 interpreted the structure as a composite based on the interpretation of various combinations of neutron, X-ray, and electron diffraction, TEM imaging (this did not include HR-STEM), and magnetic susceptibility measurements.[10, 15, 18] While substantial data was provided to suggest the presence of the monoclinic phase no irrefutable evidence was provided to establish that regions of the trigonal phase were present. Without direct identification by a compositionally

sensitive imaging technique it is difficult to distinguish the contributions of these similar phases to global measures. It is advisable to use HAADF-STEM in conjunction with other characterization techniques.

Finally, when analyzing these materials it is important to take precautions to limit exposure to the high energy particle beams. Electrons beams used in STEM imaging can result in disruption of the chemical ordering of the monoclinic phase, reduction in the oxidation state of the transition metal ions, and sputtering of oxygen and lithium atoms.[30] Electron beam damage has also been reported to transform the trigonal phase into the rock salt phase.[31] This consideration is also important for sample preparation when ion milling is employed. In Figure 8, the sample was exposed to a low energy (5 kV) argon ion beam for 200 min. After exposure the particles have inhomogeneous contrast and a highly textured surface. Dark regions at both the edges and center of the particles likely indicate loss of material due to sputtering. Inspection of these regions reveals that the crystal structure has changed from the layered structure to a rock salt phase. Also, at the edges of the pore-like defect formation a spinel phase is found. It is believed that for the monoclinic structure the Li and O atoms, whose displacement threshold is below the maximum energy transfer from the electron and ion beams, are being displaced from the lattice thereby restructuring the particle.[32, 33] This behavior is also similar to the effects caused by heating.[34] Accordingly, when imaging these materials the dose should be limited by operating at lower beam currents (dose rate) and reducing total exposure time (dose). During sample preparation preferably select minimally invasive techniques, or when using an invasive technique like ion milling identify best practices to minimize damage or remove damage through additional processing (e.g., chemical etches).

Conclusions

A lithium-rich cathode material, HE5050, in its pristine state was characterized using multiple characterization tools that sample over a complimentary range of length scales. Both diffraction and imaging indicates a structure comprised of primarily the monoclinic phase with three orientation variants. Convincing evidence in support of the mixture model containing coherent intergrowths of the monoclinic and trigonal phases was not observed.

HAADF-STEM and EDS indicated the formation of Ni enriched spinel along $\left\{ \begin{smallmatrix} 13 \\ 1 \end{smallmatrix} \right\}$ surface terminations. Changes to processing conditions may be able to eliminate these formations. There were limited observations of small regions with apparent increased concentration of transition metal ions on the $2b$ site. These regions may be a result of projection artifacts rather than formation of the trigonal phase. Thorough characterization of the pristine material will allow for an improved understanding between structure and the electrochemical performance

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

We thank Bryant J. Polzin and Andrew N. Jansen (Argonne National Laboratory) for providing the HE5050 powder. This research was performed while A.C.J.-P. held a National Research Council Research Associateship Award at the National Institute of Standards and Technology. 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.

References

1. Thackeray MM, Johnson CS, Vaughey JT, Li N, Hackney SA. Advances in manganese-oxide 'composite' electrodes for lithium-ion batteries. *Journal of Materials Chemistry*. 2005; 15:2257–2267.
2. Johnson CS, Li N, Lefief C, Thackeray MM. Anomalous capacity and cycling stability of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ electrodes (M = Mn, Ni, Co) in lithium batteries at 50 °C. *Electrochemistry Communications*. 2007; 9:787–795.
3. Bréger J, Meng YS, Hinuma Y, Kumar S, Kang K, Shao-Horn Y, Ceder G, Grey CP. Effect of high voltage on the structure and electrochemistry of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$: A joint experimental and theoretical study. *Chemistry of Materials*. 2006; 18:4768–4781.
4. Johnson CS, Li N, Lefief C, Vaughey JT, Thackeray MM. Synthesis, characterization and electrochemistry of lithium battery electrodes: $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMn}_{0.333}\text{Ni}_{0.333}\text{Co}_{0.333}\text{O}_2$ ($0 \leq x \leq 0.7$). *Chemistry of Materials*. 2008; 20:6095–6106.
5. Bareño J, Balasubramanian M, Kang SH, Wen JG, Lei CH, Pol SV, Petrov I, Abraham DP. Long-range and local structure in the layered oxide $\text{Li}_{1.2}\text{Co}_{0.4}\text{Mn}_{0.4}\text{O}_2$. *Chemistry of Materials*. 2011; 23:2039–2050.
6. Jarvis KA, Deng Z, Allard LF, Manthiram A, Ferreira PJ. Atomic structure of a lithium-rich layered oxide material for lithium-ion batteries: Evidence of a solid solution. *Chemistry of Materials*. 2011; 23:3614–3621.
7. McCalla E, Lowartz CM, Brown CR, Dahn JR. Formation of layered-layered composites in the Li–Co–Mn oxide pseudoternary system during slow cooling. *Chemistry of Materials*. 2013; 25:912–918.
8. McCalla E, Rowe AW, Brown CR, Hacquebard LRP, Dahn JR. How phase transformations during cooling affect Li–Mn–Ni–O positive electrodes in lithium ion batteries. *Journal of The Electrochemical Society*. 2013; 160:A1134–A1138.
9. Jarvis KA, Wang C-C, Manthiram A, Ferreira PJ. The role of composition in the atomic structure, oxygen loss, and capacity of layered Li–Mn–Ni oxide cathodes. *Journal of Materials Chemistry A*. 2014; 2:1353–1362.
10. Mohanty D, Huq A, Payzant EA, Sefat AS, Li J, Abraham DP, Wood DL, Daniel C. Neutron diffraction and magnetic susceptibility studies on a high-voltage $\text{Li}_{1.2}\text{Mn}_{0.55}\text{Ni}_{0.15}\text{Co}_{0.10}\text{O}_2$ lithium ion battery cathode: Insight into the crystal structure. *Chemistry of Materials*. 2013; 25:4064–4070.
11. Bréger J, Jiang M, Dupré N, Meng YS, Shao-Horn Y, Ceder G, Grey CP. High-resolution X-ray diffraction, DIFFaX, NMR and first principles study of disorder in the Li_2MnO_3 – $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ solid solution. *Journal of Solid State Chemistry*. 2005; 178:2575–2585.
12. Boulineau A, Croguennec L, Delmas C, Weill F. Structure of Li_2MnO_3 with different degrees of defects. *Solid State Ionics*. 2010; 180:1652–1659.
13. Weill F, Tran N, Croguennec L, Delmas C. Cation ordering in the layered $\text{Li}_{1+x}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{1-x}\text{O}_2$ materials ($x = 0$ and 0.12). *Journal of Power Sources*. 2007; 172:893–900.
14. Gowda SR, Dees DW, Jansen AN, Gallagher KG. Examining the electrochemical impedance at low states of charge in lithium- and manganese-rich layered transition-metal oxide electrodes. *Journal of The Electrochemical Society*. 2015; 162:A1374–A1381.

15. Mohanty D, Kalnaus S, Meisner RA, Rhodes KJ, Li J, Payzant EA, Wood Iii DL, Daniel C. Structural transformation of a lithium-rich $\text{Li}_{1.2}\text{Co}_{0.1}\text{Mn}_{0.55}\text{Ni}_{0.15}\text{O}_2$ cathode during high voltage cycling resolved by in situ X-ray diffraction. *Journal of Power Sources*. 2013; 229:239–248.
16. Mohanty D, Sefat AS, Li J, Meisner RA, Rondinone AJ, Payzant EA, Abraham DP, Wood Iii DL, Daniel C. Correlating cation ordering and voltage fade in a lithium-manganese-rich lithium-ion battery cathode oxide: a joint magnetic susceptibility and TEM study. *Physical Chemistry Chemical Physics*. 2013; 15:19496–19509. [PubMed: 24129599]
17. Trask SE, Li Y, Kubal JJ, Bettge M, Polzin BJ, Zhu Y, Jansen AN, Abraham DP. From coin cells to 400 mAh pouch cells: Enhancing performance of high-capacity lithium-ion cells via modifications in electrode constitution and fabrication. *Journal of Power Sources*. 2014; 259:233–244.
18. Mohanty D, Sefat AS, Kalnaus S, Li J, Meisner RA, Payzant EA, Abraham DP, Wood DL, Daniel C. Investigating phase transformation in the $\text{Li}_{1.2}\text{Co}_{0.1}\text{Mn}_{0.55}\text{Ni}_{0.15}\text{O}_2$ lithium-ion battery cathode during high-voltage hold (4.5 V) via magnetic, X-ray diffraction and electron microscopy studies. *Journal of Materials Chemistry A*. 2013; 1:6249–6261.
19. Li Y, Bettge M, Polzin B, Zhu Y, Balasubramanian M, Abraham DP. Understanding long-term cycling performance of $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ -Graphite lithium-ion cells. *Journal of The Electrochemical Society*. 2013; 160:A3006–A3019.
20. Gallagher KG, Croy JR, Balasubramanian M, Bettge M, Abraham DP, Burrell AK, Thackeray MM. Correlating hysteresis and voltage fade in lithium- and manganese-rich layered transition-metal oxide electrodes. *Electrochemistry Communications*. 2013; 33:96–98.
21. Thevenaz P, Ruttimann UE, Unser M. A pyramid approach to subpixel registration based on intensity. *IEEE Transactions on Image Processing*. 1998; 7:27–41. [PubMed: 18267377]
22. Schindelin J, Arganda-Carreras I, Frise E, Kaynig V, Longair M, Pietzsch T, Preibisch S, Rueden C, Saalfeld S, Schmid B, Tinevez J-Y, White DJ, Hartenstein V, Eliceiri K, Tomancak P, Cardona A. Fiji: an open-source platform for biological-image analysis. *Nat Meth*. 2012; 9:676–682.
23. Strobel P, Lambert-Andron B. Crystallographic and magnetic structure of Li_2MnO_3 . *Journal of Solid State Chemistry*. 1988; 75:90–98.
24. van Tendeloo G, Amelinckx S. Group-theoretical considerations concerning domain formation in ordered alloys. *Acta Crystallographica Section A*. 1974; 30:431–440.
25. Jarvis KA, Deng Z, Allard LF, Manthiram A, Ferreira PJ. Understanding structural defects in lithium-rich layered oxide cathodes. *Journal of Materials Chemistry*. 2012; 22:11550–11555.
26. Boulineau A, Simonin L, Colin J-F, Canévet E, Daniel L, Patoux S. Evolutions of $\text{Li}_{1.2}\text{Mn}_{0.61}\text{Ni}_{0.18}\text{Mg}_{0.01}\text{O}_2$ during the initial charge/discharge cycle studied by advanced electron microscopy. *Chemistry of Materials*. 2012; 24:3558–3566.
27. Gu M, Belharouak I, Zheng J, Wu H, Xiao J, Genc A, Amine K, Thevuthasan S, Baer DR, Zhang J-G, Browning ND, Liu J, Wang C. Formation of the spinel phase in the layered composite cathode used in Li-ion batteries. *ACS Nano*. 2012; 7:760–767. [PubMed: 23237664]
28. Zheng J, Gu M, Genc A, Xiao J, Xu P, Chen X, Zhu Z, Zhao W, Pullan L, Wang C, Zhang J-G. Mitigating voltage fade in cathode materials by improving the atomic level uniformity of elemental distribution. *Nano Letters*. 2014; 14:2628–2635. [PubMed: 24707978]
29. Gu M, Genc A, Belharouak I, Wang D, Amine K, Thevuthasan S, Baer DR, Zhang J-G, Browning ND, Liu J, Wang C. Nanoscale phase separation, cation ordering, and surface chemistry in pristine $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ for Li-ion batteries. *Chemistry of Materials*. 2013; 25:2319–2326.
30. Phillips PJ, Iddir H, Abraham DP, Klie RF. Direct observation of the structural and electronic changes of Li_2MnO_3 during electron irradiation. *Applied Physics Letters*. 2014; 105:113905.
31. Lin F, Markus IM, Doeff MM, Xin HL. Chemical and structural stability of lithium-ion battery electrode materials under electron beam. *Scientific Reports*. 2014; 4:5694. [PubMed: 25027190]
32. Egerton RF, McLeod R, Wang F, Malac M. Basic questions related to electron-induced sputtering in the TEM. *Ultramicroscopy*. 2010; 110:991–997.
33. Egerton RF, Li P, Malac M. Radiation damage in the TEM and SEM. *Micron*. 2004; 35:399–409. [PubMed: 15120123]
34. Hwang S, Kim SM, Bak S-M, Cho B-W, Chung KY, Lee JY, Chang W, Stach EA. Investigating local degradation and thermal stability of charged nickel-based cathode materials through real-time

electron microscopy. ACS Applied Materials & Interfaces. 2014; 6:15140–15147. [PubMed: 25101895]

NIST Author Manuscript

NIST Author Manuscript

NIST Author Manuscript

Highlights

- Complimentary techniques study the microstructure of a Li-rich electrode material.
- The structure is a solid solution rather than a coherent mixture of two phases.
- A spinel phase is observed at surface terminations.
- Ion irradiation transforms the crystallographic phase of the material.

Figure 1.

XRD experimental (blue) and calculated (red) X-ray diffraction profiles for the $\text{Li}_2\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_3$ (nominal) sample. The calculated pattern corresponds to the $C2/m$ model, which accounts for all the reflections. The fitting statistics are $R_{\text{wp}} = 7.36\%$, $R_{\text{p}} = 5.74\%$, where R_{wp} and R_{p} are the weighted-profile and profile R -factors, respectively. The entire pattern (a) and enlarge regions at low (b) and high (c) angles.

Figure 2.

Single particle orientated along the [103] zone axis. (b) SAED pattern diffraction pattern does not completely match with a simulated pattern (c) of monoclinic [103] but does with a manually constructed pattern (d, e) once variants have been accounted for. HAADF-STEM images corroborate the monoclinic phase designation (f, g) as well as highlight the presence of variants which give a honeycomb like appearance when multiple are viewed in projection (h and i). Multislice image simulations confirm these interpretations when 1 (c), 2(d), or 3 (e) variants are viewed in projection. The inset in (f) is a FFT of the image, cropped for size, which matches well with the simulated diffraction pattern in (c).

Figure 3.
HAADF-STEM images and SAED of a single particle oriented to three different zones axes,
(a) $[\bar{1}\bar{1}0]$ (b) $[0\bar{1}0]$ (c) $[1\bar{1}0]$.

Figure 4. HAADF-STEM images and SAED of a single particle oriented to three different zones axes, (a) $[\bar{3}10]$ (b) $[\bar{1}00]$ (c) $[\bar{3}\bar{1}0]$. Red arrows highlight the presence of spinel formation at the particle surface.

Figure 5. HAADF-STEM images of particles with spinel (a) forming at the particle surface. The surface terminations are indicated in the image. Image intensity profiles from images (a) along the transition metal ion layer (b) and lithium ion layer (c). The red arrows indicate the specific row. HAADF-STEM image (d) and EDS map of a particle edge with the individual elemental components separated, Mn (e), Co (f), Ni (g), and a colorized overlay (i), blue = Mn and green = Ni.

Figure 6.

EELS spectra from the core and edge of a particle where spinel is present (a) the HAADF-STEM image (b) indicates the location from where the spectra were acquired.

Complimentary HAADF-STEM and diffraction patterns from particles with spinel formation acquired along the [110] (c and d) and [121] (e and f) directions. The directions indicated are that of the spinel not the monoclinic core.

Figure 7.

Multislice image simulations of the Li_2MnO_3 monoclinic structure with increasing concentrations of the Mn located on the 2b site. HAADF-STEM images (c, d) of particles oriented along the [100] or an orientation variant thereof. The image contains regions, marked by arrow or box, of apparent increased intermixing on the 2b sites. A multislice image simulation (e) of a two overlapped variants which matches the intensity profile of the boxed region in (d).

Figure 8.
HAADF-STEM image of a Ar ion irradiated sample. Spinel (c) and rock salt (d) formations can be observed.

Table 1

Zone axes that are coincident though an orientation variant about the $[103]$ axis. Specific directions are provided, however this list can be extended to the entire family of directions.

$[103]$	*	*
$[100]$	$[\bar{1}10]$	$[\bar{1}\bar{1}0]$
$[101]$	$[013]$	$[0\bar{1}3]$
$[\bar{3}1\bar{6}]$	$[00\bar{1}]$	$[\bar{3}1\bar{6}]$
$[301]$	$[\bar{3}43]$	$[\bar{3}43]$
$[\bar{1}01]$	$[3\bar{2}3]$	$[323]$
$[213]$	$[2\bar{1}3]$	$[\bar{1}03]$
$[510]$	$[\bar{2}10]$	$[\bar{1}\bar{3}0]$
$[310]$	$[\bar{3}10]$	$[0\bar{1}0]$
$[\bar{7}10]$	$[5\bar{3}0]$	$[120]$
$[\bar{5}3\bar{6}]$	$[\bar{5}3\bar{6}]$	$[20\bar{3}]$
$[\bar{7}1\bar{6}]$	$[11\bar{3}]$	$[\bar{1}3\bar{6}]$
$[\bar{5}1\bar{6}]$	$[11\bar{6}]$	$[\bar{1}1\bar{3}]$
$[\bar{1}1\bar{6}]$	$[\bar{2}0\bar{3}]$	$[\bar{1}1\bar{6}]$