In-situ Energy Dispersive X-ray Diffraction Study of Prototype LiMn$_2$O$_4$- and LiFePO$_4$-based Coin Cell Batteries

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This in-situ study demonstrates the feasibility of using energy dispersive x-ray diffraction (EDXRD) to characterize the internal structure and chemical composition of coin cell type Li-ion batteries. CR2032 coin cell batteries containing Li$_{1-3x}$Cr$_x$FePO$_4$ (with x = 0.015) or Li$_x$Mn$_{1.42}$Ni$_{0.42}$Co$_{0.16}$O$_4$ cathode were studied by EDXRD measurement. EDXRD patterns with 50 to 70 scans were made between top and bottom of charged or discharged coin cells of about 3.2 mm thickness. The seven different layers of materials contained in the Li$_{1-3x}$Cr$_x$FePO$_4$ coin cell can be clearly identified from the measured 50 in-situ EXRD patterns. For the Li$_x$Mn$_{1.42}$Ni$_{0.42}$Co$_{0.16}$O$_4$ cell, the Bragg lines shift to higher energy in the charged cathode consistent with a lattice contraction with decreased Li content. The charged spectrum Bragg lines are broadened due to two phase behavior. The detailed electrochemical phases of the cathode materials and other layers of materials in this prototype LiMn$_2$O$_4$-based coin cell have been profiled, using EDXRD, as a function of state of charge and as a function of z-position in the interior of the cell. Our results demonstrate that in-situ EDXRD characterization of the crystal structures and phase distribution of coin cell batteries in space and time is feasible under different charge/discharge conditions.

1. Introduction

Lithium-ion batteries (LIB) are the power source of choice for future portable electronic devices, large-scale stationary energy storage, and electric or hybrid electric vehicles (EV and HEV). The advancement of LIB technologies, such as enhancing LIB’s power, energy density, life time, and safety level, largely depend on our in-depth understanding of the mechanism of charge transport, chemical reactions, and the phase changes that occur during electrochemical cycling processes. In-situ characterization of cathode, anode, separator, spacer, electrolyte materials as a function of charging/discharging state and other battery operational conditions is particularly important for both the understanding of the electrochemical processes in cathode materials and the technology development of LIBs.
In last two decades, to study the phase distribution and chemical reactions during recycling processes, great effort was made on the in-situ synchrotron x-ray studies (including x-ray diffraction measurement) of cathode materials for LIB cells with x-ray transparent windows such as Mylar windows (1-3). However, all these windowed LIB cells (specifically designed for in-situ studies) have some obvious drawbacks. For example, the window materials could add complicating factors to the cycling conditions and the commercial cell geometries are changed after such windows are made on the cells. In addition, batteries with such windows sometimes cannot be operated under some conditions such as at elevated temperatures. The primary purpose of this paper is to demonstrate the feasibility of studying the layer structure and phase changes in coin cell batteries (without x-ray transparent windows) by high energy in-situ energy dispersive x-ray diffraction (EDXRD) technique. The coin cell batteries are selected for this study due to the material alignment simplicity that all the materials (cathode, anode, separator, etc.) in the cell are basically parallel each other and thus the EDXRD patterns obtained for each material layer can be easily indexed and analyzed. Such demonstration can provide valuable information such as how the charging/discharging state of cathode varies as a function of crystal structure, spatial phase distribution and cycling conditions. This information should be very important for future application of the EDXRD technique to the study of various commercial LIB systems and for the battery design optimization process.

2. Experimental

The Li$_x$Mn$_{1.42}$Ni$_{0.42}$Co$_{0.16}$O$_4$ spinel and Li$_{1-3x}$Cr$_x$FePO$_4$ with $x = 0.015$ cathodes were made by mixing active material (75 wt.%), conductive carbon (20 wt.%) and polytetrafluoroethylene binder (PTEF; 5 wt.%), rolling the mixture into thin sheets, and cutting the material into circular disks. The CR2032 coin cells with about 3.2 mm thickness were assembled with the stainless steel caps, Ni sponge, cathode disc (~ 0.1 mm thick) , lithium ribbon anode, 1M LiPF$_6$ in 1:1 ethylene carbonate/diethyl carbonate electrolyte, and Celgard polypropylene separator. Liu et al. previously carried out an extensive charge/discharge characterization (between 3.4 and 5.0 V) on the electrochemical performance of the Li$_x$Mn$_{1.42}$Ni$_{0.42}$Co$_{0.16}$O$_4$ cathode material (4).

The energy dispersive x-ray diffraction (EDXRD) measurements in this work were performed at the Brookhaven National Synchrotron Light Source (NSLS) on the superconducting wiggler beam line X17B1 (5-8). In general, EDXRD has proven highly effective for strain and phase mapping in engineering applications (5-9). The experimental setup (1-4) involves “white beam” incident radiation with scattering at a fixed angle $2\theta$ ($2\theta = 4^\circ$ in the present work). Schematic transmission diffraction geometry and incident/scattered beam collimation slits can be found in the references of this paper (5, 7, 8, 10). A schematic of the experimental geometry in these coin cell experiments is shown in Figure 1.

A high resolution Germanium detector measures the intensity versus energy of the scattered beam. The energies, $E$, of the scattered Bragg peaks are given by $E = b/[d_{hkl} \sin(\theta)]$ where $d_{hkl}$ is the spacing associated with a specific inter-atomic plane labeled by the Miller indices (hkl). Here $b = hc/2$ where $h$ is Plank’s constant, and $c$ is the speed of light. In the conventional units, where $d_{hkl}$ is measured in Angstroms and $E$ in keV, one
has $b=6.199$ Å keV. As in typical x-ray diffraction, a chemical phase will exhibit a unique “fingerprint” pattern of Bragg reflections in its EDXRD spectrum. The relative intensity variations, in space (or charge state), of these reflections can be used to profile the relative abundance of the respective chemical phases in an electrochemical cell. (see for example reference 10). For our purposes, simple comparison of the intensities of selected Bragg lines yields a satisfactory picture of the relative phase variations.

The intersection of the collimated incident and diffracted beam paths defines the gauge volume (GV) over which the crystalline scattering is averaged (5,7,8). In this work the GV dimensions were: 70 μm along the profile, z-direction (see Figure 1) and 1 mm in width in the y-direction transverse to the profile. Along the incident beam, x-direction, the small angle leads to spreading of the GV into a flattened parallelogram with cross section of 2 mm total length (5,8). These GV dimension choices were made with the planar geometry of the coin cell in mind. When studying such planner systems [a shot peened near surface layer (7) is another example], the long dimension (the x direction here) of the GV is aligned parallel to the symmetry plane. The dimension of the GV in the z, profile direction (perpendicular to the plane) is kept small for good profiling resolution. Finally the other GV dimension parallel to the plane (y here) is enlarged to increase the scattered intensity signal.

### 3. Results and Discussion

Figure 2 displays 50 EDXRD patterns taken at equal increments through a 3.2 mm thick coin cell containing a fully discharged Li$_{1-3x}$Cr$_x$FePO$_4$ with $x = 0.015$ cathode. Each
pattern was taken with step $\Delta z = 3.2/50 \text{ mm} = 64 \mu\text{m}$. The spectrum number or pattern numbers (PN) for these 50 patterns are labeled at the right end of the patterns. This coin cell battery contains 7 layers of materials from the top to bottom: Stainless steel (S.S or Fe) bottom cap, Ni sponge spacer, Li metal disc, separator film, cathode disc, titanium disc, and S.S (Fe) top cap. Indeed, by comparing the patterns in Fig. 2 with the XRD patterns of standards, the following material classification can be made for these 50 patterns: air for PN 1-2, Fe (S.S) cap for PN 3-6, Ni spacer for PN 7-38, Li metal layer for PN 39-43, $\text{Li}_{1-3x}\text{Cr}_x\text{FePO}_4$ ($x = 0.015$) cathode disc for PN 44-47, Li net for PN 48, and Fe (S.S.) cap for PN 49-50.

Figure 3 displays 70 diffraction patterns taken in equal increments through a 3.2 mm thick coin cell containing a fully discharged $\text{Li}_x\text{Mn}_{1.42}\text{Ni}_{0.42}\text{Co}_{0.16}\text{O}_4$ (labeled as $\text{Li}_x(\text{Mn,Ni,Co})\text{O}_4$ in Fig. 3-12) cathode. Each pattern was taken with step $\Delta z = 3.2/70 \text{ mm} = 46 \mu\text{m}$. The EDXRD patterns for spectrum numbers or pattern numbers (PN) 57-59 are for the cathode material and can be indexed with the LiMn$_2$O spinel crystal structure. Note that the channel number $N$ is related to the photon energy $E$ of the x-ray beam by a linear relationship: $E = 0.0024779N - 1.025$ (eV). As discussed in reference 10, it is useful to present a phase distribution profile in a 2-D contour plot format which allows comparison of multiple Bragg line intensities from multiple phases as a function of depth in an electrochemical cell. Such a plot is presented in Figure 4 for the fully discharge cell.

Figure 2. 50 diffraction patterns taken in equal increments through a 3.2 mm thick fully discharged coin cell containing a fully discharged $\text{Li}_{1-3x}\text{Cr}_x\text{FePO}_4$ with $x = 0.015$ cathode. The EDXRD patterns with scan numbers 44-47 are for the cathode material.
containing the Li$_x$Mn$_{1.42}$Ni$_{0.42}$Co$_{0.16}$O$_4$ cathode. Here the diffracted x-ray intensity appears in gray scale, the diffracted energy (E) is on the abscissa, and the spectrum number (or equivalently the depth in the cell) is on the ordinate. The cathode layer of this discharged cell can be seen to manifest sharp spinel phase diffraction lines (see Miller indices). The diffraction pattern of the fcc steel cell-body/external electrodes and the Ni-sponge layer can also be clearly seen.

In Figure 5 the diffraction contour profile of a charged cell containing Li$_x$Mn$_{1.42}$Ni$_{0.42}$Co$_{0.16}$O$_4$ cathode is shown. Again the cathode layer of this cell can be nicely indexed with the spinel phase lines. Two points should, however, be noted for the spinel phase layer in the charged cell. Firstly, the Bragg lines of the charged cell are shifted to higher energy (smaller lattice parameter and lower Li content) relative to those of the discharged cell. Since this shift is not easily apparent from the contour plots, Figure 6 compares the EDXRD spectra of the charged and discharged cells. The shift in all of the Bragg lines is dramatically clear in Figure 6.

Secondly detailed inspection of the charged cell lines in Figure 5 reveals a shift in the

![Figure 3](image)

Figure 3. 70 diffraction patterns taken in equal increments through a 3.2 mm thick fully discharged coin cell containing a fully discharged Li$_x$Mn$_{1.42}$Ni$_{0.42}$Co$_{0.16}$O$_4$ cathode. The EDXRD patterns with scan numbers 57-59 are for the cathode material. The photon energy E of the x-ray beam has a linear relationship with the channel number N as: E = 0.0024779N – 1.025 (eV).
Bragg line across the cathode region. This is consistent with a gradient in the Li content across the cathode in the charged cell. No such effect is visible in the discharged cell. Indeed Figure 7 provides a typical illustration of how all of the spinel Bragg lines for the discharged cell can be fitted to a single Gaussian peak.

In contrast Figure 8 shows that the spinel (400) Bragg lines for the charged cell are bimodal and can be fitted with a superposition of two Gaussian peaks ($A_2$ and $A_3$). Here the Fityk fitting program was used for both background and Gaussian fitting. After initial choices of the two line parameters fits alternately holding the line 1 and line 2 parameters constant were alternated until the fits converged.

Inspection of the spectra and fits clearly show that: the $A_3$ phase is dominant adjacent to the Li layer; a $A_3$ phase to $A_2$ phase conversion occurs as one proceeds deeper into the cathode; and the cathode region adjacent to the steel electrode is entirely of $A_2$ phase. To quantify this Li gradient Figure 9 shows the relative fraction $f_i$ of the fitted (400) area of the $A_i$ line plotted versus the position in the cathode. Here fraction was determined by the fitted area of the $i$'th line divided by the sum of the line 1 plus line 2 areas. The $A_3$ phase to $A_2$ phase conversion with increasing $z$ (depth into the cathode starting from the Li side) is clear in Figure 9.
Figure 5. As above, the diffraction contour plot through the charged cell. The layers and indexing are as in the previous figure. One should note that the spinel phase Bragg lines in the charged cell shift in energy across the cathode indicating a gradient in Li content across the cathode.

Figure 6 EDXRD patterns at points near the center of the cathodes for the charged and discharged coin cells. Note that the Bragg lines shift to higher energy in the charged cathode consistent with a lattice contraction with decreased Li content. Note also that the charged spectrum Bragg lines are broadened due to two phase behavior as will be analyzed below.
Figure 7. Fitted (400) Bragg line near the center of the cathode of the discharged cell (with background subtracted). Note that all of the discharged cell Bragg lines were well fitted with a single Gaussian peak.

Figure 8. A sequence (400) Bragg lines across the cathode of the charged cell (with background subtracted). These Bragg lines were fitted with a superposition of two Gaussian peaks $A_1$ and $A_2$. Both the fitted $A_2$ and $A_3$ components and the total fit are shown in the figure. The vertical intensity scale factor is the same for each Bragg line.
Annamalai’s (11) results for the lattice parameter variation with Li content in the 
$Li_xMn_{1.42}Ni_{0.42}Co_{0.16}O_4$ [abbreviated here as $Li_x(Mn,Ni,Co)O_4$] system, shown in Figure 
10, provide a useful comparison to our results. Figure 11 shows our results for the spatial 
variation across the cathode of the lattice parameter in the charged and discharged coin 
cells. Here the lattice parameters were determined from the $(400)$ Bragg line positions 
derived from the fits discussed above. For the discharged cell the lattice parameter 
variation shows a week positional change (see A1 in figure) and is consistent with a large 
lattice parameter/Li content. As noted above the charged cell manifests two phase A2-A3 
behavior. The A2 phase has a higher lattice parameter/Li-content and the A3 phase has a 
lower lattice parameter/Li content. The presence of a discontinuity between the A2 and 
A3 systems is similar to the results of Annamalai (11) although our discontinuity is 
somewhat larger. The labeling of the various phases in our results is in analogy to those 
chosen by Annamalai (11), however our in situ conditions and detailed differences in the 
precise lattice parameters preclude a direct phase association. However using 
Annamalai’s (11) results as guidelines it would appear that: our A3 phase has Li content 
of $x\approx0.2$; our A2 phase has $x\approx0.6$; and our A1 phase also has $x\approx0.6$.

Referring back to Figure 8 one can see a substantial variation in the intensity of the 
spinel (400) Bragg line across the cathode of the charged cell. This effect is caused by the 
finite sized GV dimension in the $z$ direction (70 $\mu$m) entering and leaving the cathode 
layer. Indeed the stainless steel (111) Bragg line in the $z=160$ $\mu$m spectrum (in Figure 8) 
reflects the GV straddling the spinel-cathode/steel-electrode interface. In Figure 12 the 
total A2 plus A3 area/intensity of the (400) line is plotted versus the coin cell position in 
the $z$-direction. The $z=0$ position was chosen so as the point where the (400) intensity 
extrapolates to zero (on the Li layer side of the cathode) as indicated in the figure. Thus 
the $z$-positions used throughout this paper are referenced to the position where the edge 
of the GV first enters the cathode. A similar (400) intensity versus position relation is

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Figure 9. The variation of the fractional $A_2$ and $A_3$ phase components across the charged-cell cathode. Here the phase fraction of the $i$’th phase is the area of that Gaussian component (see Figure 8) divided by the summed area of both components.
Figure 10. The literature variation of the lattice parameter variations in the Li$_x$Mn$_{1.42}$Ni$_{0.42}$Co$_{0.16}$O$_4$ system. (Abbrivated here as Li$_x$(Mn,Ni,Co)O$_4$). Note the three phases characterizes as a1, a2, and a3.

Figure 11. The spatial variation of the lattice parameters across the cathodes of the discharged cell (A$_1$), and the charged cell (A$_2$ and A$_3$).
observed for the discharged cell and the \( z=0 \) position is similarly defined as illustrated in Figure 12.

The total extrapolated \( z \)-cell-position variation that these cells exhibit the spinel cathode scattering is about 192 \( \mu \text{m} \) (see Figure 12). Using a simple rectangular GV cross section, of width \( w \), and a simple sharp cathode layer thickness \( t \), one would calculate the total extent of the spinel cathode scattering to be \( w+t \). The incident beam collimation slit width defines \( w=70 \ \mu \text{m} \). Thus the nominal thickness \( t \approx 122 \ \mu \text{m} \). In discussing the phase variation across the cathode it must be emphasized that the \( z \)-translation step size had the course 46 \( \mu \text{m} \) value. Hence the phase variation results across the cathode region are blurred by the convolution of the overlap between the GV and the cathode. Nevertheless, the clear indication of a systematic gradient in the phase content across the cathode of the charged cell is reflected in the data. Much higher spatial resolution experiments are clearly necessary in future experiments.

4. Conclusions

In this paper the detailed electrochemical phases of the cathode material and other layers of materials in a prototype LiMn\(_2\)O\(_4\)-based and LiFePO\(_4\)-based coin cells have been profiled, using EDXRD, as a function of state of charge and as a function of \( z \)-position in the interior of the cell. Our results have demonstrated that in-situ high energy x-ray diffraction characterization of coin cells in space and time is feasible under different charge/discharge conditions and on a routine basis. Such in-situ EDXRD measurement will advance battery technology by providing a powerful characterization method for studying the fundamental mechanism and chemical processes occurring inside battery cells.

![Figure 12. The spatial variation of the (400) Bragg line areas/intensities for: the A\(_1\) phase (for the discharged cell), and the summed A\(_2\) plus A\(_3\) areas for the charged cell).](image)
Acknowledgments

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