IN-SITU ANALYSIS of LiFePO₄ BATTERIES:
SIGNAL EXTRACTION BY MULTIVARIATE ANALYSIS

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ABSTRACT

Electrochemical reaction behavior of a commercial Li-ion battery (LiFePO₄-based cathode, graphite-based anode) has been measured via in-situ neutron diffraction. Multivariate analysis was successfully applied to the neutron diffraction dataset facilitating in the determination of Li-bearing phases participating in the electrochemical reaction in both the anode and cathode as a function of state-of-charge (SOC). Analysis resulted in quantified phase fraction values for LiFePO₄ and FePO₄ cathode compounds as well as identification of staging behavior of Li₆, Li₁₂, Li₂₄ and graphite phases in the anode. An additional Li-graphite phase has also been tentatively identified during electrochemical cycling as LiC₄₈ at conditions of ~5 to 15% SOC.

INTRODUCTION

In an age where access to energy has concurrent national-security and environmental implications, development of battery technology for energy storage and distribution is of critical importance (Conte et al., 2004; Arico et al., 2005). Recent advancements in cathode materials such as the olivine-type LiFePO₄ have demonstrated the co-existence of an environmentally-friendly rechargeable Li-ion battery that has adequate functionality for consumer demands along with the added advantage of a relatively low cost cathode material (Ravet et al., 2001; Arico et al., 2005). One of many goals regarding research and development of battery technologies is to characterize the entire battery system during electrochemical cycling. This type of experiment is best performed in-situ using test cells that match (as close as possible) the constituents and duty cycles of the actual deployed cell. One of the challenges regarding structure/property relationships of electrochemical systems such as a battery is that these energy storage devices have many constituents, most of which do not undergo significant chemical change during cell cycling. Therefore, in-situ structural characterization proves difficult because scattering occurs from the entire interrogated cell (i.e. cathode, anode, separator, electrolyte, current collectors and outside housing). Recently, we performed in-situ XRD characterization of a specially designed "coffee-bag" test battery (Rodriguez et al., 2007) where afore-mentioned complications of the dataset were overcome by the use of multivariate analysis (MVA).
using MVA for the examination of the XRD dataset (which was collected as a function of battery discharge) it was possible to decompose the dataset into "components" that significantly aided data interpretation. Our success in this arena suggested that similar measurements using neutron scattering could be performed in-situ on commercially available Li-ion cells. The highly penetrating neutron beam, along with enhanced sensitivity to Li scattering could perhaps serve well for the characterization of the entire electrochemical battery system with minimal modification to the existing battery design. We present results for just such a neutron scattering experiment, employing a commercial Li-ion battery and utilizing MVA for data-reduction and as an aide to interpretation of the cell behavior.

![Battery State-of-Charge](image.png)

**Figure 1.** Battery State-of-Charge for assigned experimental step number (see text for details).

**EXPERIMENTAL**

**Data collection**

A cylindrical Li-ion battery (type 18650, 2600mAh, LPF-1350) was used as received. The battery was wired to a potentiostat and lowered into the sample chamber of the HIPPO neutron spectrometer at LANSCE/LANL (Wenk *et al.*, 2003). The initial condition of the cell was 100% state-of-charge (SOC) and ~3.2 DCV. The cell was systematically discharged so as to remove ~10% SOC within 30 minutes. These were not exactly 10% SOC steps because we discharged based on coulombic content. After arriving at the designated SOC, the potentiostat was turned off and the cell was allowed several minutes to equilibrate at the new SOC prior to collection of neutron diffraction data; each neutron diffraction dataset required ~1 hr at a given SOC. Data were collected from 100% (fully charged) to 0% SOC (fully discharged) followed by a recharge cycle to 100% SOC. Another discharge cycle was then performed, thus generating a total of 30 SOC steps. Figure 1 illustrates the SOC for each experimental step where the downward pointing triangles are discharge steps and the upward pointing triangles are for the charging
steps. Star symbols on the plot denote fully-charged or discharged conditions. Note that while there are 30 total steps, the step values are labeled with only the odd numbers, and therefore range from 1 to 59. We chose this designation because scattering data were also collected during applied bias of the potentiostat. These data are the even-numbered-steps that represent conditions between each SOC and are not reported here.

Data Reduction and Analysis

Similar to our past in-situ experiment on XRD data (Rodriguez et al., 2007), we employed common forms of multivariate analyses, termed Principal Component Analysis (PCA) and Multivariate Curve Resolution (MCR) to examine our in-situ neutron diffraction dataset. Full details on the use of PCA/MCR are beyond the scope of this paper and we refer the reader to existing references on this topic (e.g. Jollife, 2002; Keenan & Kotula, 2004; Rodriguez, et al. 2007; Van Bethem et al., 2002). In brief, MVA is typically used to reduce the dimensionality of large data sets, retaining as much information as possible (while excluding noise), in the hope that one can successfully isolate the essential signal of the convoluted dataset. In the case of this in-situ battery experiment, neutron diffraction patterns from the 150° banks of the HIPPO spectrometer were used exclusively as they provided the highest resolution of diffraction peaks. Treatment of the neutron diffraction dataset was first performed on a very large Time-Of-Flight (TOF) range (2-24 msec) for the 150° bank histograms. This resulted in isolation of anode components. A second treatment of the neutron dataset was performed on a much more limited TOF range (10.6 to 16 msec) resulting in diagnosis of cathode behavior. All calculations were performed with MATLAB (The Mathworks, 2008) using constrained least squares routines that were developed in-house (Keenan & Kotula, 2004; Van Benthem & Keenan, 2004). Approximately 100 iterations were required for convergence to the final components. In addition, standard Rietveld structure refinement was also performed using GSAS (Larson & Von Dreele, 1986; Toby, 2005) for the purposes of determining phase fraction of the cathode constituents and for validation of MVA results.

Figure 2. Stack plot of raw data from in-situ neutron diffraction experiment. See text for details.
RESULTS AND DISCUSSION

Figure 2 shows a stack plot of the raw histograms for the 150° banks as a function of SOC step. This series of histograms reveal several things. First, the patterns are dominated by scatter from the nickel-plated-iron container of the battery. Fortunately, we also obtain electrochemical information from inside the battery as demonstrated by significant peak changes occurring in the TOF = 16-20 msec range during charge and discharge. These peaks describe behavior of the graphitic anode; the 16-20 msec range shall therefore be referred to as the "anode-window" because it illustrates changes associated with the anode phases with relatively few obstructing peaks from other cell constituents. Also note the range from 10.6-16 msec. This region shall likewise be referred to as the "cathode-window" because this range contains numerous, albeit weak, LiFePO4/FePO4 peaks. Finally, it needs to be noted that there is significant background scatter in this experiment, likely associated with the hydrogen containing materials present in the cell as well as the naturally occurring fraction of 6Li isotope. Background noise was one of the reasons that long count-times were employed at a given SOC, so as to improve success of in-situ analysis without deuteration of all hydrogen and lithium containing constituents. Moreover, the use of MVA facilitated diagnosis of electrochemical behavior even with the high-background nature of the observed data.

Figure 3. Derived components from PCA/MCR analysis of full histograms and their corresponding scores with step number. See text for details.

Initial PCA/MCR attempt (full histograms) – anode behavior

In PCA the term "component" refers to a subset of data (e.g. histogram) that represents an isolated portion of the entire dataset and that behaves according to a determined "score" function. For brevity, we shall discuss this score function in terms of its correlation to phase fraction of a given battery constituent. With this said, we now move on to the discussion of PCA analysis on the full histograms. This initial data treatment, employing PCA/MCR for data reduction, revealed a six component system. The first component (not shown) was designated as
the inert component and appeared to be mostly due to scatter from the nickel-plated-iron casing and background noise. It is worth noting that no attempt was made to determine amorphous content, the presence of which would likely be relegated to the inert component. The other five components are shown in figure 3. These components and their associated scores are shown as a stacked series. The isolated components we obtain are almost exclusively representative of various forms of lithium-intercalated graphite. This intercalation process, often referred to as "staging", has been previously documented (Billaud et al., 1979) and the TOF peak positions of the above major reflections in the histogram plot (Figure 3, right) convert to d-spacings consistent with known phases; namely, LiC_6 (d_{001} = 3.70 Å), LiC_{12} (d_{002} = 3.52 Å), LiC_{24} (d_{003} = 3.47 Å), and graphite (d_{002} = 3.36 Å). Interestingly, we see one more component (Labeled LiC_?) between LiC_{24} and graphite. The main peak for this phase is located at d = 3.43 Å which does not match any of the reported intercalation compounds for graphite (Billaud et al., 1979). The plot showing the histogram scores vs. step number (Figure 3, left) indicates that the various LiC_x forms vary in concentration, with LiC_6 dominating at the initial 100% SOC (step 1) and graphite dominating at ~0% SOC (step 23). The LiC_{12} phase looks to be the major phase in the anode at step 9 and 10 (62 and 53.5% SOC, respectively). Likewise, LiC_{24} looks to dominate at ~24% SOC (step 17) and LiC_7 shows a maximum at ~15% SOC (step 19). A mirror-like symmetry in the scores is seen for the charging process (step 23-41).

With respect to the LiC_7 phase, there are three likely scenarios that exist to explain its origin. The first scenario is that this is an ordered form of lithium-intercalated graphite with a composition near LiC_{48} that has not been previously reported. This is possible in that LiC_7 appears to exist only in a narrow range of SOC (i.e. 5 to 15% SOC). Additionally, in the raw data the LiC_7 peak is overlapped with the graphite and LiC_{24} reflections and it is only via PCA/MCR that this possible phase becomes isolated as a separate histogram. The second scenario is that the LiC_7 phase is actually the LiC_{24} composition and the as-labeled LiC_{24} histogram (d = 3.47 Å) is an intermediate composition between LiC_{24} and LiC_{12} (e.g. LiC_{16}). Such a scenario seems less likely in that this would mean an error of 0.04 Å for the LiC_{24} peak position as measured by Billaud (1979). This would be a significant error considering the other reported values for LiC_6 and LiC_{12} are within 0.01 Å of our measured peak locations. The third scenario is that the LiC_7 component is an artifact of our analysis. It is possible that the LiC_7 component results from intensity that would have been better assigned to the graphite and LiC_{24} components, but was inadvertently isolated as a separate component in our analysis. While this too is a possibility, it seems unlikely because the LiC_7 scores show its existence on either side of 0% SOC in figure 3. Regardless of the actual explanation regarding LiC_7, the PCA/MCR results for the full histograms strongly suggest staging behavior in the anode, and the isolated histograms likely represent various compositions of these lithium-intercalated graphite compounds.

Cathode-Window Analysis: Structure refinements

The initial PCA/MCR of the neutron data was dominated by signal associated with the anode. The weak signals from the cathode peaks were unfortunately not of sufficient magnitude to be isolated as independent components, due to the overwhelming priority of the many anode components. However, careful evaluation of the raw patterns especially in the 10.6 – 16 msec range (cathode-window) did reveal peaks from the expected LiFePO_4 (Triphylite) and FePO_4.
(Heterosite) phases. It was also clear that these peaks varied in intensity with step (SOC). One of our goals regarding the in-situ experiment was to derive the phase fraction of LiFePO₄/FePO₄ as a function of SOC as this would help in understanding the cathode performance and its correlation to the anode. Regrettably, full Rietveld structure refinement of this limited range was not possible due to the large number of parameters required as compared to the observed reflections, as well as the significant noise level in the measured histograms. Fortunately, the behavior of the LiFePO₄/FePO₄ conversion has been previously measured and documented by Andersson et al., (2000) using ex-situ cathode specimens. They note that during charge and discharge there is relatively little change in the structures of Tripylite and Heterosite in terms of atom positions and lattice parameters and that the phases display phase-separation behavior during Li-shuttling. In other words, there is no constantly varying gradient of LiₓFePO₄ composition during charge or discharge, but instead the cathode phases exist as either Triphylite or Heterosite with only a very thin interface between the two compounds. Armed with this knowledge, attempts at phase fraction quantification of the cathode-window data were straightforward because the number of variables in the refinement could be greatly reduced to strictly background, scale factor, and phase fraction parameters.

Figure 4 shows a typical fit of the cathode-window data. The histogram shows weak peaks for LiFePO₄ and FePO₄ phases along with an Al (111) peak (from the current collector). The Al (111) peak was employed as an internal standard for the refinement. It was possible to fit these data with a three phase model (Al, LiFePO₄ and FePO₄) to obtain useful phase fraction results. Figure 5 shows a summary of these refinements as a function of step number. This figure shows the systematic conversion of FePO₄ to LiFePO₄ during discharge until step 23 (0% SOC) where we can see a significant portion of the FePO₄ still unconverted. Recharging restores the cathode to nearly full FePO₄ content (step 43). It is worth noting here that while these data were possible to obtain by Rietveld structure refinement, the process of refining histograms of a large
dataset typical of in-situ measurements becomes laborious even with existing batching procedures and software improvements.

![Diagram](63.png)

Figure 5. Phase fraction LiFePO$_4$ (circles) and FePO$_4$ (triangles) as a function of step number as derived from Rietveld structure refinements on cathode-window data.

**Cathode-Window Analysis: PCA**

The second attempt at PCA analysis of the neutron diffraction dataset was attempted on the cathode-window data to see if the analysis could derive any meaningful results from data sensitive to the cathode phases. Figures 6 and 7 present the resulting components and scores for the cathode-window analysis. The results were definitive in terms of component determination, yielding a simple two-component system. The first component histogram and its corresponding score values with step are shown in figure 6 (note: histograms for step 19 and 57 suffered reduced counts and required rescaling prior to analysis). The component histogram appears to represent the average pattern for a mixture of LiFePO$_4$ and FePO$_4$ phases. This can be deduced by the fact that the scores for this histogram are nearly constant with step (SOC). Also notice that this histogram has significantly reduced noise as compared to the measured histogram in figure 4. PCA has served well to reduce the noise level because it derives components from all measured histograms while screening out Poisson noise. Figure 7 shows the second component obtained by PCA along with its score values. Just as the first component looks to be an average pattern for the series, the second component appears to represent the way in which the first component varies with step (SOC). Viewing the histogram in figure 7 (right) we see intensity deviating above and below zero. When viewed carefully and in comparison to figure 4 one observes that the peaks on the positive side of the scale are major peaks from the LiFePO$_4$ phase while peaks on the negative side of the y-axis are associated with the FePO$_4$ phase. When we consider the scores for the second component as shown in figure 7 (left) it is clear that this component oscillates with charge and discharge in similar fashion to figure 5. In fact, the scores observed in figure 7 match almost perfectly to the observed phase fraction behavior of LiFePO$_4$. 
One can think of the second component as the magnitude of variation of the peak intensity away from the average histogram (component 1). If we consider step 11 on figure 7 the score for the second component is near zero which means there is essentially no variation of peak intensity at this 53.5% SOC condition, hence the component 1 histogram looks essentially unchanged. However, if we look at step 23, the score is strongly positive and component 2 acts to enhance the LiFePO₄ peaks while removing intensity from FePO₄ peaks of the average histogram. PCA has therefore effectively diagnosed and quantified the cathode electrochemical behavior derived by iterative Rietveld refinements. This well demonstrates the utility of PCA for analysis of large datasets involving in-situ analysis.

Figure 6. First component from PCA of cathode-window data (right) and the corresponding score values with step number (left). See text for details.

Figure 7. Second component from PCA of cathode-window data (right) and the corresponding score values with step number (left). See text for details.
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REFERENCES


