IN-SITU ENERGY-DISPERSIVE X-RAY DIFFRACTION STUDY OF A COMMERCIAL LITHIUM IRON PHOSPHATE / GRAPHITE 18650 CELL

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ABSTRACT

A commercial lithium iron phosphate 18650 cell was probed in situ while discharging using ultrahigh energy white synchrotron radiation at the NSLS X17B1 beamline at Brookhaven National Laboratory. Time-resolved energy-dispersive X-ray diffraction (EDXRD) spectra were collected using a germanium energy detector at a fixed angle of 3 degrees. The data show the full evolution of lithium-ions moving from the graphite negative electrode to the lithium iron phosphate positive electrode. A qualitative depiction of both the iron phosphate to lithium iron phosphate phase transformation and the lithium staging process in graphite is shown. Based on the results, the graphite electrode appears to not be fully utilized. The results highlight the power and versatility of energy dispersive X-ray diffraction at the X17B1 beamline.
This document was presented at the Denver X-ray Conference (DXC) on Applications of X-ray Analysis.

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1. INTRODUCTION

Lithium-ion batteries (LIB) have revolutionized the consumer electronics industry and are beginning to be used in automobiles. (Scrosati and Garche, 2010) Lithium-ion batteries are desirable for applications in hybrid-electric and fully-electric vehicles, however many challenges still exist which prevent a more wide-spread adoption of electric vehicles. (Armand and Tarascon, 2008) Both the desirable and limiting traits of LIBs dominated by the chemical and physical characteristics of the electrode and electrolyte materials of which the LIB are composed. When packaged together and electrochemically-cycled, LIBs experience degradation processes which are further influenced by these characteristics. (Ebner et al., 2013)

It is imperative that scientists and engineers have better tools for nondestructive monitoring battery behaviors and characteristics. Traditionally, the only feedback mechanism to a cell's performance is the voltage between its two terminals. Methods such as impedance spectroscopy have allowed for more information to be collected from cells but impedance and current-voltage curves are only sensitive to an entire cell. (Reddy, 2010) These traditional methods are limited in their ability to measure smaller-scale mechanisms on which the batteries' performance is so dependent. Although it allows for a more detailed analysis, disassembly of cycled batteries changes the context of the material and can distort or obfuscate important results.

Diffraction using X-rays, and sometimes neutrons, has been a preferred method for in-situ experimentation because of its ability to provide data on structural changes. Furthermore, in-situ diffraction experiments on batteries date back as far as 1992 and continue to advance the field of battery research today. (Liu et al., 2014; Rodriguez et al., 2004; Morcrette et al., 2002; Amatucci et al., 1996) Some of the first in-situ diffraction experiments on lithium ion batteries, carried out by Amatucci et al., were able to isolate a new phase in the LiCoO₂ solid solution by constructing a cell that would allow for the penetration of X-rays. Later, in 2002, M. Morcrette, along with others including Amatucci, published their novel in-situ X-ray cell using Bellcore's plastic laminate electrodes. Using their specially constructed cell, they were able to screen new materials including different phosphate-based electrodes. Further advances in low-Z packaging materials and instrumentation, mainly synchrotron radiation, have allowed for a stronger understanding of the structural evolution of electrode materials.
Energy dispersive X-ray diffraction (EDXRD) is well suited for in-situ experimentation because of its fixed geometry and ability to collect a full spectrum in parallel. (Kämpfe et al., 2005) As a result, EDXRD has been used with both laboratory and synchrotron sources to study lithium batteries. Ronci et al. were able to show structural changes in a LiNi$_{4/5}$Co$_{1/5}$O$_2$ positive electrode in situ using a half-cell with a special geometry to allow the X-rays to penetrate the electrode. (1999) Later, the same group studied Li$_{1/3}$Ti$_{5/3}$O$_4$ for its zero-strain be behavior using the same laboratory setup. (Panero et al., 2001) Harnessing the highly-penetrative nature synchrotron radiation, Rijssenbeek et al. were able to probe sodium metal-halide cells during charge and discharge cycles. (2011) From their experiments they were able to show a reaction front within the cell and, to their advantage, discovered intermediate phases which were negatively affecting the cell’s performance.

In this paper we use EDXRD to study the discharge process of a commercial lithium iron phosphate cylindrical cell. Recent battery research has shown that lithium iron phosphate has desirable advantages over now-ubiquitous cobalt oxide materials. The low raw-materials cost, environmental friendliness, long cycle lifetime, and thermal stability make it a desirable cathode material for use in electric and hybrid-electric vehicle applications. (Padhi, 1997) We take advantage of the highly penetrative nature of the X-rays at NSLS X17B1 to probe a cell without any special sample modifications; we literally just take the commercial cell from the manufacturer and place it in the beam. By using EDXRD to study the discharge process, we study the reaction process under real-world conditions. We hope to show the flexibility of the technique and elucidate the otherwise hidden-behavior of the electrode materials in the cell.

2. EXPERIMENTAL

Experiments were carried out at the National Synchrotron Light Source located at Brookhaven National Laboratory in Upton, NY. The X17B1 beamline uses a 7-pole superconducting wiggler insertion device to create a high-brilliance high-energy broad-spectrum X-ray beam with energies up to 200 keV. The beam is collimated using a series of tantalum slits and focused on a sample which rests on a computer-controlled micro-positioning stage. Positioned at a fixed angle (3° for this experiment) a germanium broadband energy-detector collects the scattered X-rays
that have been transmitted through the sample (Laue geometry.) The photons are then counted and binned in an 8192 channel analyzer and plotted using a custom graphical user interface. A schematic of the experiment is shown in Figure 1. The volume in which scattering is measured is called the gauge volume and occupies a fixed position in space.

![Figure 1. Schematic of the EDXRD experimental configuration at NSLS X17B1](image)

The battery used in this study was a commercially produced cylindrical lithium iron phosphate (LiFePO₄) rechargeable cell (Model 30072-0, Tenergy Corporation.) The battery was connected to a battery cycler (BT2000, Arbin) and mounted lengthwise in the beam path as shown in Figure 1. A copper filter was applied to the incoming beam to absorb lower energy photons and reduce potential damage to the cell. The battery was positioned such that the gauge volume encompassed a significant portion (10-20%) of the active material. Diffraction spectra were collected every 60 seconds as the battery was discharged at 1.5A (approximately \( \frac{4}{3} \) C rate) for a total of 33 spectra.

3. RESULTS AND DISCUSSION

Figure 2a shows the time-resolved diffraction contour plot of the EDXRD data. Selected Bragg lines are indicated. The phases identified in the spectra correspond as follows: (lithium) iron phosphate as the positive electrode; aluminum as the positive current collector; graphite as the
negative electrode; and copper as the negative current collector. No unexpected phases were detected. Additionally, no peaks pertaining to separators or electrolytes were detected.

Figure 2b shows the galvanic cell potential during discharge. The capacity observed was in line with the manufacturer’s specification. The flat voltage profile confirms that a first order (biphasic) phase transformation is occurring.

A more detailed depiction of the phase change processes occurring in both the negative and positive electrodes is presented in Figure 3. Figure 3a shows the time-resolved diffraction contour plot of the energy range where the graphite (002) reflections lie. Similarly, Figure 3b shows the energy range where lithium iron phosphate reflections with good line resolution lie.
The commercial 18650 cell has a negative electrode that consists of graphitic carbon. When the cell is fully charged, lithium ions are incorporated into the planar structure of the graphite. This process is well understood and occurs in a multi-phase reaction progression known as lithium staging. (Ohzuku et al., 1993) A schematic depiction of the lithium staging process is shown in Figure 4. The most basic unit in graphite is a single sheet known as graphene. When multiple sheets of graphene are present, and stacked together, they are said to compose graphite. Now, the maximum amount of lithium incorporation in graphite occurs when each gap between graphene sheets is occupied by a lithium ion; this is known as Stage 1. Between the maximum concentration and absence of lithium ions, however, are three more thermodynamically stable phases. These additional stages, 2-4 exist from the stacking sequences shown in Figure 4.
In our experiment, we observe the fully charged cell starting with multiple stages present (Figure 3a.) While the phase amounts were not determined quantitatively, the presence of the Stage 1, 2, 3, 4, and graphite peaks indicate that the graphite negative electrode is not fully occupied with lithium. In other words, there is excess capacity on the negative side of the cell. We understand this to be common practice to accommodate for heterogeneity in cell manufacturing.

As the cell is discharged, we observe the decrease in intensities of first the Stage 1 peak, then the Stage 2 and Stage 3 peaks, until we are left with pure graphite and Stage 3 and 4. It is important to note that the Stage 3 and 4 peaks lie close together and are difficult to differentiate. The behavior we observe is what we expected based on prior knowledge of lithium staging in graphite.

With the cell is in the fully-charged state, we observed the positive electrode to be composed entirely of iron phosphate. During the course of discharge, the in-situ data show an increasing presence of lithium iron phosphate peaks and a decreasing presence of iron phosphate peaks. Upon full discharge, the only peaks present are lithium iron phosphate. While a quantitative analysis is desirable, unfortunately the counting statistics did not justify such an exercise.
CONCLUSIONS

A commercial lithium iron phosphate / graphite 18650 cell was probed in-situ using energy dispersive X-ray diffraction. Time-resolved spectra were collected while discharging the cell at a constant current. The full discharge process in both positive and negative electrodes is observed. A qualitative analysis of lithium staging in graphite shows an over capacity in the negative electrode. Additionally, a qualitative analysis of the positive electrode shows full completion of the reaction from iron phosphate to lithium iron phosphate. The results are what is expected from a commercial cell and highlight the versatility of the energy-dispersive X-ray diffraction technique.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge and Dr. E. Koray Akdoğan, İlyas Şavkliyıldız, and Shivani McGee for their support in the laboratory. Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

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