In situ XANES & XRD Study of interphasial reaction between uncharged \( \text{Li}_2\text{FeSiO}_4 \) cathode and \( \text{LiPF}_6 \)-based electrolyte

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Abstract. In situ synchrotron radiation XANES and XRD have been carried out on \( \text{Li}_2\text{FeSiO}_4 \) cathode material in a lithium-ion-battery (LIB) cell. The evolution of the long range lattice structure and the local iron oxidation state has been observed at a charging rate of C/20 for the formation cycle for one Lithium extraction; additional ex situ measurements of the pristine cathode material were taken for comparison. The observed spontaneous interaction between the cathode and the fluorinated electrolyte and the impact of subsequent cycling are discussed.

1. Introduction

The ubiquity of Lithium Ion Batteries (LIBs) has brought with it a surge in rapid battery prototyping. Synchrotron radiation techniques have been widely applied in this field to gain insight into the electrochemical/solid state phase transition processes that accompany the formation cycle of electrode materials. These processes are believed to be a key aspect of designing high-performance lithium ion batteries [1-3]. A quick perusal of the current literature reveals that in situ studies using both XRD and XANES abound. However, due to various limitations, these two techniques are usually performed independently on electrochemical cells of the same prototype. In such cases, the hope is that enough controls have been put in place that the results from the two techniques are comparable. In an effort to alleviate concerns over sample reproducibility, a setup for the rapid measurement of \( \text{Li}_2\text{FeSiO}_4 \) (LFS) cathode material within a single active cell by both XANES and XRD has been constructed. The two measurements can be performed sequentially on the same sampling area, with less than 100-micron spatial uncertainty, in less than 30 minutes. In this study, the pristine material, uncharged constructed cell and cycled cell have each been measured using this combined technique (the latter two in situ). The results of our observations are reported here.

2. Experimental

XANES and XRD data were collected at 06ID-1 Hard X-ray Micro-Analysis (HXMA) beamline [4] at the Canadian Lightsource (CLS). The beamline optics were optimized to allow rapid movement between 7112 eV (nominal Fe K-edge) and 17 keV without sample re-alignment. The setup within the experimental hutch is shown in Figure 1. The reproducibility of the beam location was confirmed by scanning the center of X-ray slits with a 100 micron opening both vertically and horizontally. The setup (Figure 1) consists of a fast photon shutter, followed by a He beam-pass, at the end of the He pass JJ X-ray \(^*\) slits (beam defining; ca. 0.5x 0.5 mm\(^2\) aperture under He flow), and connected downstream to this aperture a (independent) He gas flowed ion chamber. In an effort to further improve the diffraction signal, a 2 mm W pinhole collimator was placed downstream of the ion chamber, directly adjacent to the LIB in situ cell. Downstream of the in situ LIB cell, a photo-diode detector served a dual purpose, both as a transmitted XANES detector and as a beam stop for the mar345\(^*\) image plate detector positioned at 252.58(8) mm downstream of the sample (Figure 1). The XRD patterns were collected in the Debye-Scherrer geometry at 17 keV, and the Fe K-edge XANES were collected using the photo-diode and ion chamber in transmission mode. When detector linearity was not achievable (i.e. crystal glitches not normalizing out), a short (4") ion chamber was used in lieu of the photo-diode (not pictured in Figure 1).
The in situ battery sample cells were modified CR2032 battery cells, having 10 mm through holes punched on the beam exiting side and 4 mm holes on the beam incident side of the cell casing. Both holes were covered with Kapton® tape from inside and outside the cell. The assembled cells were sealed inside a glove box under an argon atmosphere. The LFS cathode consisted of \( \text{Li}_2\text{FeSiO}_4 \) nanoparticles (80% LFS, 10% acetylene black and 10% polyvinylidene fluoride) and were prepared via an organic-assisted hydrothermal-annealing (180°C and 400°C, respectively) synthesis method [5].

The electrochemical in situ cell consisted of \( \text{Li}_2\text{FeSiO}_4 \) nanoparticle aggregates rolled onto Al foil; 25 \( \mu \text{m} \) Celgard® 2325 separators; a lithium anode; and 1M of LiPF\(_6\) in ethylene carbonate and dimethyl carbonate (EC/DMC) electrolyte (Figure 1: bottom right). The ex situ battery cathode was prepared by removing the cathode from an assembled cell in a glove box under high purity N\(_2\) atmosphere, after being carefully washed using EC/DMC solvent they were hermetically sealed until the XANES and XRD measurements.

XANES data reduction was performed using Athena software [6]. The XANES data were normalized to the edge jump size as determined by using the post-edge data from approximately 70 eV up to 250 eV. The photon energy calibration was carried out by defining the Fe metal foil inflection point at 7112 eV. Calibration of the mar345® detector to sample distance was completed using a NIST LaB\(_6\) sample mounted inside a CR2032 cell casing and FIT2D’s calibration routine [7]. XRD two-dimensional patterns were processed using FIT2D, and integrated into 2\( \theta \) diffraction patterns [8]. The Debye-Scherrer ring pattern for the pristine LFS material can be seen in Figure 1 (bottom left). The pristine XANES spectrum for the same material at the same location is provided in Figure 1 (bottom middle).

### 3. Results and Discussions

In situ XANES and XRD measurements of the cathode were performed on the initially uncharged battery 96 hours after the coin cell was assembled. From the time of assembly LFS remained in contact with 1M of LiPF\(_6\) in EC/DMC electrolytic solution. Measurements were also carried out after cycling the cell at a rate of C/20 for a single Li extraction (i.e. the formation cycle). These cells will be referred to as the “uncharged” cell and the “cycled” cell, respectively. The ex situ measurement is directly comparable to the “uncharged” in situ measurement in terms of state-of-charge (SOC) and interaction with the electrolyte for ca. 90 hours before disassembly.
Figure 2a depicts the three LFS XANES spectra, capturing the pristine material state (black), the uncharged state (red) and the cycled state (blue). From comparison between the uncharged and pristine states, it is apparent that the 96-hour interaction with the fluorinated electrolyte had already caused changes to the iron site local atomic structure; in the region around 7140 eV of the \textit{in situ} uncharged spectrum (red; Figure 2a), there is broadening of features and an intensity increase as compared to the pristine spectrum (black). This is consistent with an increase in short-range disorder following an interphasial reaction between the cathode and the electrolyte. Evidence of this spontaneous interphasial reaction is almost completely lost from the \textit{ex situ} uncharged spectrum (purple), in fact upon washing it appears that the \textit{ex situ} cathode is indistinguishable from the pristine.

More distinct spectral changes related to this interphasial reaction can be observed in the comparison of the background removed pre-edge spectra (inset; Figure 2a). Here, the uncharged spectrum (red trace) is of larger intensity than that of either the pristine or cycled traces. This is an indicator of larger Jahn-Teller distortions of the Fe tetrahedra [9]. The Fe K pre-edge features in the tetrahedral ferrous and ferric iron complexes have been identified [10]. They include primarily dipole transitions to: \(^4\)T\(_2\) and \(^4\)T\(_1\) (both low & high energy states) in the ferrous case; and to \(^5\)T\(_2\) in the ferric case [10]. This means for a ferrous iron tetrahedral complex the pre-edge possesses an apparent “two-peak” pattern; while for a ferric iron tetrahedral complex the pre-edge has a single peak [10]. However, the energy location of the ferrous pre-edge \(^4\)T\(_1\) (high energy state) feature coincides with that of the ferric \(^5\)T\(_2\) feature. As a result, for a system with both ferrous and ferric contents the overall pre-edge appears to still have an apparent “two-peak” pattern as shown in Figure 2a(insert). Therefore when comparing the \textit{in situ} uncharged (red) to the pristine (black) (Figure 2a insert), the observed change in the apparent “two-peak” intensity ratio indicates a change in the ratio of underlying components, i.e. the ferrous and ferric content of the sample changes during the 96 hours interaction between the cathode and the electrolyte. This phenomenon is again almost invisible in the relaxed \textit{ex situ} uncharged state (purple). Also shown in Figure 2a(insert): after the formation cycle (blue), the aforementioned ratio between the apparent “two peaks” is largely restored to that similar to the pristine case (black).

The \textit{in situ} XRD patterns depicted in Figure 2b reveal the long-range structural differences among the pristine, “uncharged” and “cycled” states. The as-prepared pristine material was found to be a mixture of approximately 3:2 of monoclinic P2\(_1\)/n (\(\gamma\)) and the “low temperature” orthorhombic Pmn\(_2\)\(_1\) (\(\beta\)) phases, determined respectively through Rietveld refinement [12, 13]. Upon reaction with the electrolyte in the uncharged cell, a new phase was formed. This can be observed in the birth of a new peak around 10\(^o\), and the increase in peak intensity around 22\(^o\). These indicators of phase change are not present in the \textit{ex situ} uncharged XRD patterns (Figure 2b; purple). The XRD pattern for the uncharged cell also exhibits broadening in the features associated with P2\(_1\)/n (\(\gamma\)) and Pmn\(_2\)\(_1\) (\(\beta\)) phases, as well as decreased intensity. In terms of peak intensity and broadening, once again the
cycled state has been partially restored to the pristine state. However, the new spontaneous phase formation that occurred in the uncharged state persisted in the cycled cathode. Additionally, in the multi-phase mixture the relative ratio of $P_{2}/n (\gamma_{1})$ to $P_{mn2} (\beta_{II})$ may not be assumed constant in this case.

3. Conclusions

A rapid XANES and XRD mode-switching setup has been implemented at the HXMA Beamline at the CLS, employing in situ spectroscopy and diffraction studies of same-sample areas of lithium-ion batteries. Use of both in situ XANES & XRD in this way has allowed a spontaneous reaction to be observed between the Li$_2$FeSiO$_4$ cathode and LiPF$_6$-based electrolyte in the uncharged lithium-ion battery state which was not otherwise observable in the ex situ measurements. This reaction results in partial oxidation of the ferrous content in the cathode material; however, for the cycled battery state (formation cycle), the ferrous content is then partially restored. This local structural phenomenon is accompanied by the emergence of a new crystalline phase as indicated by the in situ XRD.

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