Soft X-ray Characterization Technique for Li Batteries under Operating Conditions

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Synopsis A novel solid state lithium battery design enables surface- and bulk-sensitive soft X-ray absorption spectroscopy of battery materials under operating conditions.

Abstract O K edge and Co L edge near edge X-ray absorption fine structure (NEXAFS) was used to examine the cathode of an intact solid-state lithium ion battery. The novel technique allowed for the simultaneous acquisition of partial electron yield and fluorescence yield data during the first charge cycle of a $LiCoO_2$-based battery below the intercalation voltage. The chemical environments of oxygen and cobalt at the surface are shown to differ chemically from those in the bulk. The present design enables a wide variety of *in situ* spectroscopies, microscopies, and scattering techniques.

Keywords: NEXAFS, XANES, Li ion battery, in situ, $LiCoO_2$

1. Introduction

The excellent energy density (Tarascon et al. 2001) of rechargeable lithium batteries make them the preeminent energy storage technology for portable electronics and electric vehicles. Still, the safety and cycle life of intercalation cathodes are in doubt. Without direct measurements of the intercalation reaction as a function of cell potential over multiple cycles, selection of the best cathode material is guesswork. While it is known that a lithium ion leaving the cathode, upon charging, must be balanced by the loss of an electron, it is not known whether this electron comes from the transition metal ion alone or also from oxygen. Even for the dominant commercial cathode material, $LiCoO_2$, it is not clear whether the electron is taken from cobalt to form a Co^{4+} ion or from oxygen to produce O^- ions or oxygen gas (Dahn et al. 1994). Although Co^{4+} has been detected by EPR in coordination complexes (Koikawa et al. 1989), Co(IV) compounds are quite rare in nature and therefore may be highly reactive in a charged lithium battery. For mixed transition metal oxides, the picture is even more complex and interesting because multiple 3d metals with multiple oxidation states are reacting simultaneously, and influencing each other (Deb et al. 2004). Any additional electron donation by oxygen ions would result in highly reactive species which may encourage the gradual combustion, or the violent explosion, of nonaqueous electrolytes. A method for detecting gas evolution and measuring the oxidation state of oxygen and the 3d transition metals *in situ* is presented.

Battery researchers have long sought to characterize cathode materials with X-rays *in situ* rather than *ex situ* because the requisite disassembly and washing of a cathode may change the bulk or surface composition significantly and eliminate internal

electric fields. Furthermore, only one sample need be prepared to characterize an intercalation cathode at multiple cell potentials which not only reduces the work required, but also eliminates variations due to sample preparation. *Ex situ* methods become cumbersome when investigating the effects of multiple cycles. Only *in situ* cells can be measured over multiple cycles, enabling life cycle studies of cathodes. Extensive *in situ* X-ray Absorption Near Edge Spectroscopy (XANES) work has successfully characterized these materials at the metal K edges using hard X-ray energies above 4 keV with the use of Kapton windows and standard nonaqueous electrolytes. With this method, the oxidation states of transition metal ions in intercalation cathodes have been characterized as a function of state-of-charge (Deb et al. 2004; Alamgir et al. 2005). In these studies, a shift in the XANES spectra to higher energies is attributed partly to an increase in the 1s binding energy due to a loss of 3d electrons which would otherwise shield the nucleus.

Unfortunately, the dipole selection rule allows only 1s $\rightarrow$ 4p transitions at the K edge. The occupancy, configurations and energies of the 3d orbitals of the first row transition metals, which form bonds with O in most Li battery cathodes, are not measured. The L edge spectra, by contrast, arise due to 2p $\rightarrow$ 3d transitions. The amplitudes of some near edge features are proportional to the number of empty 3d states, while changes in the 2p binding energy still cause energy shifts in the spectra. *In situ* XANES (called NEXAFS, Near Edge X-ray Absorption Fine Structure in the soft-X-ray context) of transition metal L edges can provide more direct oxidation information than can K edge XANES. In addition, hard X-ray *in situ* studies are seldom surface sensitive; the present method can show surface-to-bulk differences at the metal L edges that could not be seen at the K edges.

Additionally, soft X-ray NEXAFS spectroscopy accesses the 1s $\rightarrow$ 2p transitions of lighter elements including C, O, S, and P. The loss of O 2p electrons on deintercalation has been speculated to contribute to the capacity of $LiCoO_2$ (Montoro et al. 2000; Yoon et al. 2002; Alamgir et al. 2005). Theoretical calculations (Ceder et al. 1998) and hard X-ray EXAFS experiments (Alamgir et al. 2005) suggest that oxygen contributes some of the capacity of $LiCoO_2$, possibly by forming O^- ions during the deintercalation of lithium. Also, the irreversible formation of Li_2O can be detected by its characteristic absorption spectrum. NEXAFS at the O K edge, therefore, provides a great deal of information on intercalation reactions. Many *ex situ* studies (Montoro et al. 2000; Uchimoto et al. 2001; Yoon et al. 2002), have shown $LiCoO_2$ and other cathodes at multiple states of charge by chemically or electrochemically adjusting the lithium content. Changes in both the oxygen K edge and transition metal L edges have been detected as a function of lithium content, but without the electric fields of a battery. These studies have been unable to show oxygen's K edge spectrum in an assembled battery due to design difficulties. X-rays below 1 keV in energy have attenuation lengths of ~500 nm in solid materials; such a thin X-ray window cannot contain the pressure of a liquid electrolyte. Instead, a vacuum-compatible cell is required.

Only an *in situ* soft X-ray electrochemical cell, lacking windows or liquids, allows for surface sensitive and bulk sensitive spectroscopy over a continuous range of cell voltages and at multiple cycles. Recent advances in X-ray focussing can even enable spectromicroscopy at solid electrochemical interfaces on the top surface and along the outer profile of the cell. The exposure of the cell to vacuum allows mass spectroscopic methods and gas-exposure experiments. For example, the effect of water vapor and oxygen on the electronic structure of the cathode and anode at various voltages can be studied in such a packaging-free cell by adjusting the partial pressures of these gases in the vacuum chamber.

In the present study, surface-sensitive and bulk-sensitive NEXAFS measurements of the cathode of an intact, packaging-free solid state lithium battery are presented. Partial electron yield and fluorescence yield techniques reveal that the chemical environments of oxygen and of cobalt at the surface differ from those in the bulk in $LiCoO_2$. The cell was successfully charged in a vacuum synchrotron endstation under high vacuum conditions with simultaneous collection of surface-sensitive and bulk-sensitive signals. This is the first-ever reported *in situ* soft X-ray absorption study of a working lithium battery.

2. Experiment

2.1. Cell Design and Assembly

The solid state lithium battery consisted of a three-layer powder compact, shown schematically in Figure 1b. The cathode layer consisted of a mixture of 14 wt% $LiCoO_2$ (7-10 μm, Sigma-Aldrich) 41 wt% solid electrolyte powder and 45 wt% acetylene black (Sigma-Aldrich) mixed in a SPEX 8000 planetary ball mill but without grinding media. The electrolyte layer consisted of partially amorphized lithium phosphorous sulfide glass of the formula $75Li_2S \cdot 25P_2S_5$. The electrolyte was mixed in an argon-filled glovebox, vacuum sealed into an agate vial equipped with Viton^{TM} o-rings and three 12 mm agate balls, and amorphized in a SPEX 8000 mill for 20 hours. XRD showed the powder to contain a large amorphous fraction, indicating its lithium ion conductivity (Hayashi et al. 2001).

The cathode and electrolyte layers were pressed in a 13mm die at 2050 kg/cm^2 in an argon-filled glovebox containing less than 1 ppm of moisture. An 11mm diameter piece of scraped lithium foil served as the anode. A pair of aluminum plates served as current collectors. An 8 mm countersunk hole in the cathode current collector allowed for a wide collection angle. A shallow counterbore held the pellet in position while nylon screws held the current collector plates together. Figure 1a shows the assembly without the screws. The assembly was inserted into the loadlock of the analysis chamber at the beamline via a nitrogen-filled glovebag.

2.2. Electrochemical Cycling

The battery was transferred from the loadlock to the soft x-ray analysis chamber and pumped down to 3×10^{-8} torr. It was charged via a feedthrough by a Solartron 1287 potentiostat. The initial voltage of the as-prepared battery was 1.9V. It was later charged at 10 microamps to 2.5V for 10.5 h, followed by a second charging to 3.15V at 25 microamps for 5 h. At all times the battery remained below the onset voltage of approximately 3.9V. (Alamgir et al. 2005)

2.3. X-ray Absorption Measurements

NEXAFS spectra were taken at the NIST soft x-ray beamline U7A of the National Synchrotron Light Source at Brookhaven National Laboratory. The incident beam irradiated the sample at 38º from the sample normal. Data were simultaneously collected in 0.2 eV steps from a partial electron yield (PEY) detector, held 35º below the sample normal, and from a fluorescence yield detector positioned perpendicular to the incident beam, or 52º from the sample normal. The PEY detector was biased at -250V to reject low-energy electrons. The fluorescence yield (FY) data were filtered to include only O K edge transitions, or only the fluorescence from cobalt in Co L edge spectra. A clean, high-transmittance gold mesh was used to calibrate the oxygen spectra and to normalize spectral intensity while an FeNiCrCo alloy mesh was used to calibrate cobalt spectra.

3. Results

NEXAFS spectra at the O K edge in Figure 2a, in both PEY and FY modes, show a sharp resonance at 530 eV and broad pair of resonances around 540 eV with a shoulder feature at ~535 eV. Relative to the PEY spectrum, the FY spectrum contains a more intense 530 eV resonance and a stronger 540eV resonance. The shoulder resonance at 535 eV is lower in energy in the bulk-sensitive FY spectrum than in the PEY spectrum.

Figure 3 shows the O K edge at its initial voltage of 1.9V, and also while charging the cell past 2.3V and 3.1V. A small feature at 533 eV was seen when no current was flowing at cell potentials of 1.9V and at 2.5V. While charging, the feature was temporarily reduced in size.

Co L edge spectra in Figure 2b show more dramatic peak height differences between the surface-sensitive PEY data and the bulk-sensitive FY data. The peak area ratios (L_3 vs. L_2) also differ; PEY scans show the 2:1 area ratio, which was expected based on spin considerations (Leapman et al. 1982), while FY scans indicate a 1.5:1 ratio. Additionally, the FY L peaks are broader than the PEY peaks.

4. Discussion

Soft X-ray NEXAFS indicates that no permanent chemical changes occur between 1.9V and 3.15V. This is in accordance with cyclic voltammetry data (Alamgir et al. 2005) showing that intercalation begins at 3.9V or higher in $LiCoO_2$. The present design will allow for extensive *in situ* studies at higher voltages and over the course of many cycles. However, the present samples utilized an incompletely amorphized solid electrolyte, leading to a very high internal resistance in the cell. Together with an imperfect electrolyte-lithium-metal interface, the poorly-amorphized solid electrolyte limited the speed of operation of the battery. In the best case, the sulfide electrolyte conductivity has been reported to reach $2.0\ 10^{-4}$ S/cm at 75% $Li_2S\bullet25\%P_2S_5$.

(Hayashi et al. 2001) Polyethylene oxide composites can reach 1.4×10^{-4} S/cm (Pitawala et al. 2008), but only with the addition of lithium salts, 15% ceramic filler as well as 50 wt% aprotic solvents, making them unsuitable for vacuum work.

The pre edge peak corresponds to molecular orbitals formed from O 2p and Co 3d orbitals, while the 540 eV peaks represent transitions from O 1s to molecular orbitals between O 2p and hybridized Co 4sp orbitals. (de Groot et al. 1989) The Co L edge is split into the L_3 (780 eV) and L_2 (~795 eV) resonances, both of which correspond to transitions from Co 2p states to O 2p-Co 3d molecular orbitals.

Historically, soft X-ray studies have used *ex situ* samples and total electron yield detection (Montoro et al. 2000; Uchimoto et al. 2001; Yoon et al. 2002), in which the drain current resulting from photoemission is measured. This method suffers from background noise and a lack of data from the bulk. In partial electron yield detection, a bias grid reduces the background by rejecting low energy electrons from other elements in the sample. PEY and TEY are surface sensitive due to the low inelastic mean free path of electrons.

Oxygen K edge NEXAFS data show that, in the bulk, the O 2p-Co 3d molecular orbitals are less filled than at the surface. In the bulk, this resonance is broader, indicating that a wider variety of energy levels is present. Separately, the O 2p-Co 4sp molecular orbitals are more filled in the bulk than at the surface, leaving fewer unoccupied bound states for X-ray absorption. Because the cell was below the deintercalation onset potential, these differences are likely due to a difference in bond symmetry at the surface. However, transient effect was seen wherein a small resonance at 533 eV was suppressed by the flow of current through the cell. This effect proves that the proportions of conductive additives and solid electrolyte in the composite cathode layer are at least sufficient for battery operation, if not more so. Also, such changes to the electronic structure of oxygen may tend to stabilize or destabilize oxygen ions in the lattice of $LiCoO_2$, thereby affecting oxygen gas emissions.

Both FY and PEY O K edge spectra differ considerably from *ex situ* results in TEY mode in that the pre edge peak is less intense than the post edge peaks. While the spectra in Figure 2 resolve the peak at 540 eV, the feature at 536 eV appears as only a thin shoulder on the peak. To date, only one bulk sensitive *ex situ* spectrum has shown the oxygen K edge in Li_xCoO_2 where x was 0.35 (Yoon et al. 2004).

Yoon et al. (2004) found that in PEY spectra of $Li_{0.4}Mn_2O_4$, the broad peaks near 540 eV were lower in intensity compared to the 530 eV peak. Simultaneously collected FY spectra showed the 530 eV peak to have a comparable intensity to the broad peaks near 540 eV; in this work, the same surface-to-bulk trend is seen in $LiCoO_2$. Yoon et al. (2007) found the same trend of a reduced peak height in the bulk of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, yet bulk-sensitive data on $LiCoO_2$ has been missing from the literature until now.

Cobalt L edge fluorescence yield data is vulnerable to self absorption whereby the photons emitted from the bulk are partly absorbed before they escape the sample. Because absorption is nonlinear, taller peaks such as the L_3 tend to be attenuated more than would the L_2. This may explain the discrepancy in peak area ratios as well as the lower peak intensities in fluorescence yield data. However, the broader FY peaks are indicative of a wider range of transition energies in the bulk compared to the surface. On the other hand, deviations in the expected 2:1 peak area ratios have been observed for several transition metals and their oxides. The ratio is influenced by the 3d band occupancy, and is therefore sensitive to the chemical state of the transition metal ion. (Leapman et al. 1982) The observed differences in this ratio between the PEY and FY spectra can point to real differences in the chemical state of the transition metal ion in the surface as compared to the bulk.

The partial electron yield Co L edge spectrum matches the total electron yield results of Yoon et al. (2002), but the fluorescence yield data show peak area differences. This may indicate an increased occupancy of Co 3d states in the bulk as compared to the surface. Fluorescent self absorption may also play a role in reducing peak heights.

As in *ex situ* soft X-ray spectroscopy at the oxygen K edge, the present samples are vulnerable to oxygen vacancies near the surface of each cathode particle. However, the vacancy concentration at room temperature will be too low to affect the spectrum.

Solid state pellet batteries described in the present work are especially useful for *in situ* surface sensitive techniques. While this paper demonstrates the viability of direct soft X-ray spectroscopy on $LiCoO_2$, the novel cell design allows any powdered electrode material to be studied under *in situ* conditions. Also, *in situ* XRD is feasible with some modifications. Thin film solid state batteries also have potential for *in situ* measurements. However, thin film batteries are limited to cathode compositions which can be deposited in thin film form and heat treated while attached to a substrate, and the anode layer may be concealed. Pellet batteries can incorporate any powdered cathode, including sol-gel-derived ceramics, and the cell can be reversed for direct spectroscopic measurements on the anode.

5. Conclusions

An all-solid-state, packaging-free spectroelectrochemical cell has been designed to enable simultaneous, *in situ* surface-sensitive and bulk-sensitive soft X-ray absorption measurements together with mass spectroscopic measurements. The soft X-ray design allows studies complementary to those carried out at hard X-ray energies.

Fluorescence yield data, for the first time, shows that in $LiCoO_2$, O and Co experience different electronic environments in the bulk as compared to the surface. This difference is a key to understanding electrochemical reactions in $LiCoO_2$ particles. Additionally, PEY spectra show that the flow of current has a transient effect on the electronic structure of oxygen. These changes may affect the evolution of oxygen gas.

The present design allows both O K edge and transition metal L edge NEXAFS spectra to be obtained with a single sample at a soft X-ray synchrotron beamline. While previous *in situ* methods only measured the energy of the transition metal 4p orbitals, the current method measures the transition metal 3d orbitals and the O 2p orbitals, which form molecular orbitals in Li battery cathodes. *In situ* soft X-ray NEXAFS using this battery design can, therefore, detect the occupancies of all the relevant molecular orbitals in transition metal oxide intercalation cathodes.

Figure 1   a) The sample holder b) an enlarged cutaway view of the solid state battery

Figure 2   Normalized Fluorescence Yield and Partial Electron Yield NEXAFS spectra of $LiCo_{O2}$ at the a) O K edge, 3.1V and b) Co L edge, 2.5V

Figure 3   Partial Electron Yield NEXAFS at the O K edge at 1.9V, 2.3V, and 3.1V

References

Alamgir F.M., Strauss E., Greenbaum S., Whitacre J.F., Kao C.-C., Neih S., (2005) Journal of the Electrochemical Society **152**, A845

Ceder G., Chiang Y.-M. , Sadoway D.R., Ayindol M.K., Y.-I. Jang & Huang B., (1998) Nature **392**, 694

Dahn J.R., Fuller E.W., Obrovac M., von Sacken U., (1994) Solid State Ionics **69**, 265

Deb A., Bergmann U., (2004) J.S.R. **11**, 497

de Groot, F.M.F., Grioni M., Fuggle J.C., Ghijsen J., Sawatzky G.A., Petersen H., (1989) Physical Review B **40**, 5715

Hayashi A., Hama S., Morimoto H., Tatsumisago M., Minami T., (2001) J. Am. Ceram. Soc. **84**, 477

Koikawa M., Gotoh M., Ôkawa H., Kida S., Kohzuma T., (1989) J. CHEM. SOC. DALTON TRANS., 1613

Leapman R.D., Grunes L.A., Fejes (1982) P.L., Phys. Rev. B **26** p614

 Montoro L.A., Abbate M., Rosolen J.M., (2000) Electrochemical and Solid State Letters **3**, 410

Pitawala H.M.J.C., Dissenanayake M.A.K.L., Seneviratne V.A., Mellander B.-E., Albinson I. (2008) J. Solid State Electrochemistry **12** p783

Tarascon J.-M., Armand M., (2001) Nature 414, 359

Uchimoto Y., Sawada H., Yao T., (2001) J.S.R. **8,** 872

Yoon W.-S., Kim K.-B., Kim M.-G., Lee M.-K., Shin H.-J., Lee J.-M., Lee J.-S., Yo C.-H., (2002) J. Phys. Chem. B, **106**, 2526

Yoon W.-S., Balasubramanian M., Yang X.-Q., Fu Z., Fischer D.A., McBreen J., (2004) Journal of the Electrochemical Society **151**, A246

Yoon W.-S., Chung K., McBreen J., Fischer D.A., Yang S., (2007) Journal of Power Sources **174**, 1015

a)

b)

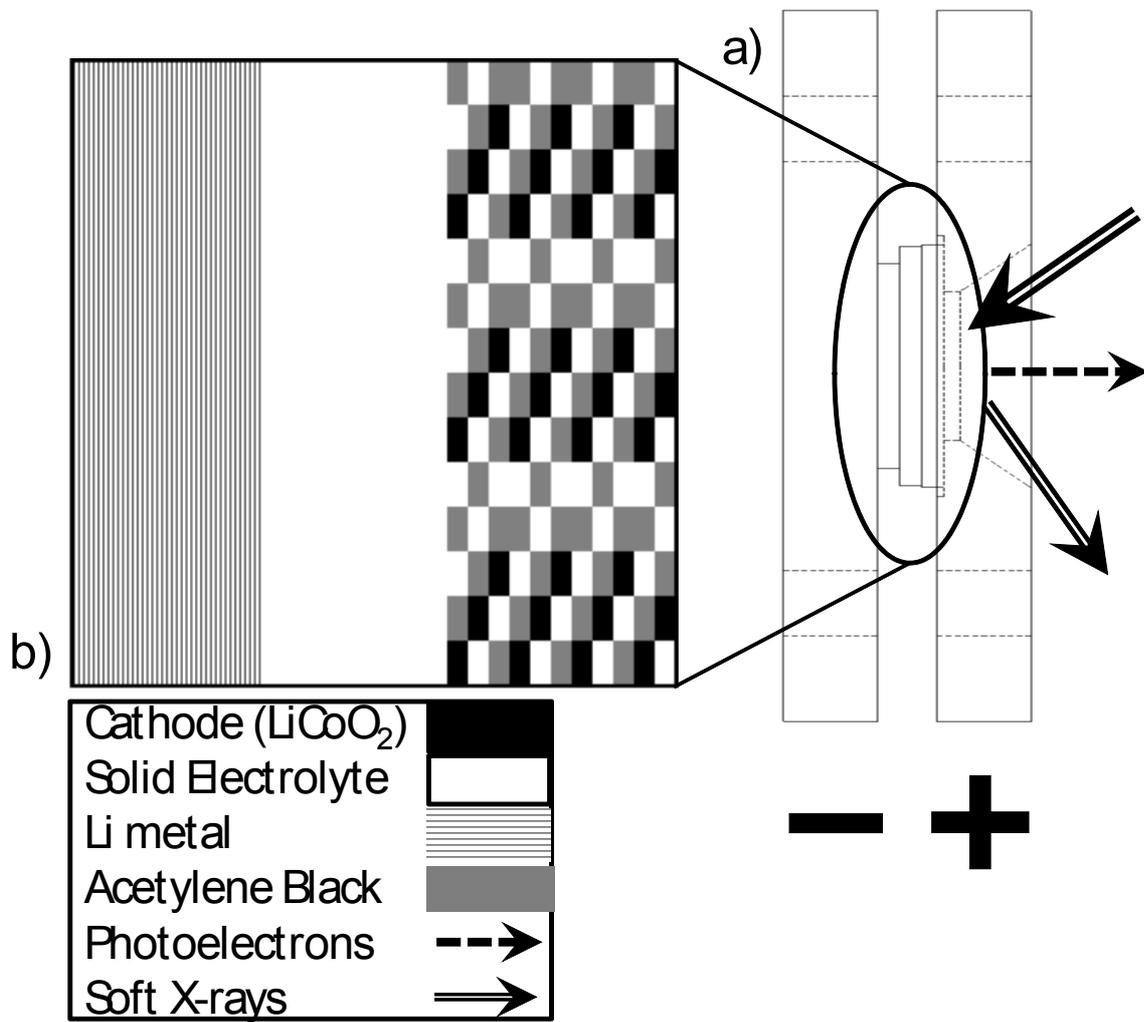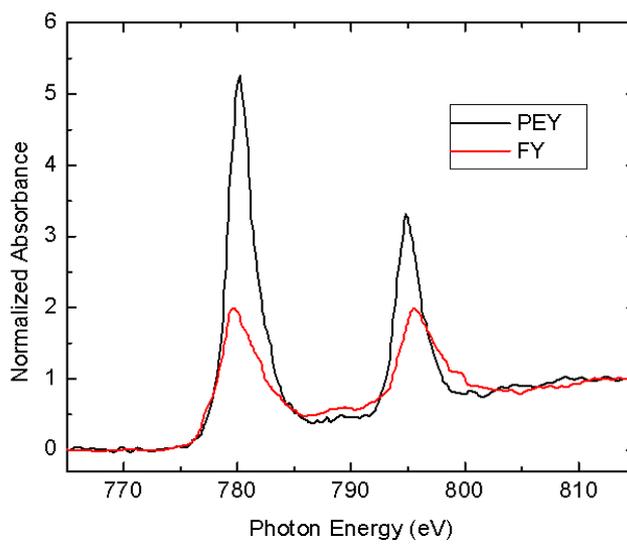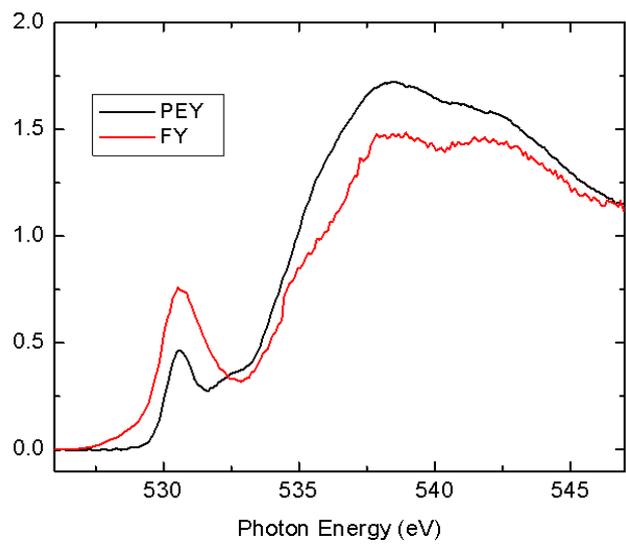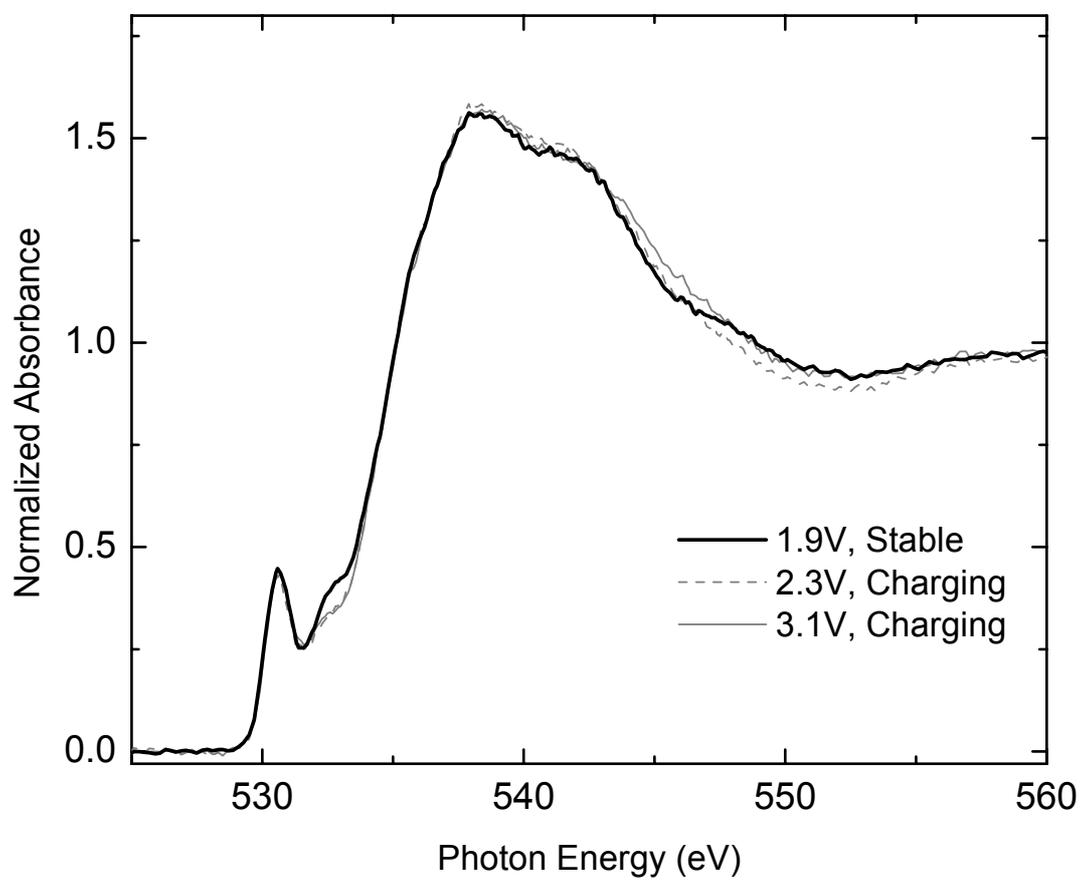| Cathode (LiCoO$_2$) | ■ |
Solid Electrolyte	□
Li metal	▤
Acetylene Black	▨
Photoelectrons	⇢
Soft X-rays	⇒

− +

Figure 1

Figure 2

Figure 3