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Characterization of Electrode Materials for Lithium Ion and Sodium Ion Batteries using Synchrotron Radiation Techniques

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Abstract:	Intercalation compounds such as transition metal oxides or phosphates are the most commonly used electrode materials in Li-ion and Na-ion batteries. During insertion or removal of alkali metal ions, the redox states of transition metals in the compounds change and structural transformations such as phase transitions and/or lattice parameter increases or decreases occur. These behaviors in turn determine important characteristics of the batteries such as the potential profiles, rate capabilities, and cycle lives. The extremely bright and tuneable x-rays produced by synchrotron radiation allow rapid acquisition of high-resolution data that provide information about these processes. Transformations in the bulk materials, such as phase transitions, can be directly observed using X-ray diffraction (XRD), while X-ray absorption spectroscopy (XAS) gives information about the local electronic and geometric structures (e.g., changes in redox states and bond lengths). In situ experiments carried out on operating cells are particularly useful because they allow direct correlation between the electrochemical and structural properties of the materials. These experiments are time-consuming and can be challenging to design due to the reactivity and air-sensitivity of the alkali metal anodes used in the half-cell configurations, and/or the possibility of signal interference from other cell components and hardware. For these reasons, it is appropriate to carry out ex situ experiments (e.g., on electrodes harvested from partially charged or cycled cells) in some cases. Here, we present detailed protocols for the preparation of both ex situ and in situ samples for experiments involving synchrotron radiation and demonstrate how these experiments are done.
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	Hugues Duncan Chunjoong Kim Kinson C Kam Thomas Conry
Author Comments:	I have described two types of complementary beam line experiments that we commonly do at the synchrotron to characterize our materials. As a rule, these are not done simultaneously; we either have XRD or XAS time scheduled on any given week, rarely both and never on the same day. In the protocol, I have highlighted the in situ XRD work for filming, because we generally obtain more shifts for this type of work than for the XAS, so it is more likely that we will be doing this. However, depending on the timing, we can consider filming XAS experiments instead. Scheduling at the beam lines is done several times a year. We have assigned times for winter and early spring and are waiting to hear about late spring and summer sessions. Part of the article will be filmed at Lawrence Berkeley Nat'l Lab and part at SSRL, which is about a 75 minute drive from LBNL. We will want to film on days where we have scheduled beam time. We will communicate the available dates when we are farther along in the process.

Cover Letter

December 7, 2012

Dear JoVE Editors,

We would like to submit our manuscript entitled “Characterization of Electrode Materials for Lithium Ion and Sodium Ion Batteries using Synchrotron Techniques” to the Journal of Visual Experimentation for consideration. I, and the co-authors listed on the manuscript, are all involved in the use of this method or have been involved in it in the recent past. Currently, Drs. Mona Shirpour, Hugues Duncan and Chunjoong Kim are carrying out the experiments, but I relied heavily on previous work that Dr. Thomas Conry and Kinson Kam did while they were at LBNL (both left the lab in 2012 to pursue new careers) for the manuscript. Drs. Guoying Chen, Jordi Cabana, Thomas Richardson and I oversee the work, suggest experiments, and help with data analysis and interpretation. Dr. Apurva Mehta is a beam line scientist at SSRL who works closely with us. His help in setting up beam line experiments and with data interpretation and analysis is invaluable.

I have described two types of complementary beam line experiments that we commonly do at the synchrotron to characterize our materials. As a rule, these are not done simultaneously; we either have XRD or XAS time scheduled on any given week, rarely both and never on the same day. In the protocol, I have highlighted the *in situ* XRD work for filming, because we generally obtain more shifts for this type of work than for the XAS, so it is more likely that we will be doing this. However, depending on the timing, we can consider filming XAS experiments instead.

This manuscript is not under consideration for publication in another journal. We have been working with associate editor Rachelle Baker, who requested this article. Possible reviewers include Xiao-Qing Yang at Brookhaven National Lab (xyang@bnl.gov), Shirley Meng at the University of California at San Diego (shirleymeng@ucsd.edu), Hironori Kobayashi at AIST, (hironori-kobayashi@aist.go.jp), Yang-Shao Horn at MIT ((shaohorn@mit.edu), Won-Sub Yoon at Sungkyunkwan University, South Korea (wsyoon@skku.edu), and Christian Masquelier at the University of Picardie (christian.masquelier@u-picardie.fr).

Sincerely,

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Electrode materials, Li ion battery, Na ion battery, X-ray Absorption Spectroscopy (XAS), *in situ* X-ray diffraction (XRD)

Short Abstract

We describe the use of synchrotron X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) techniques to probe details of intercalation/deintercalation processes in electrode materials for Li ion and Na ion batteries. Both *in situ* and *ex situ* experiments are used to understand structural behavior relevant to the operation of devices.

Long Abstract

Intercalation compounds such as transition metal oxides or phosphates are the most commonly used electrode materials in Li-ion and Na-ion batteries. During insertion or removal of alkali metal ions, the redox states of transition metals in the compounds change and structural transformations such as phase transitions and/or lattice parameter increases or decreases occur. These behaviors in turn determine important characteristics of the batteries such as the potential profiles, rate capabilities, and cycle lives. The extremely bright and tunable x-rays produced by synchrotron radiation allow rapid acquisition of high-resolution data that provide information about these processes. Transformations in the bulk materials, such as phase transitions, can be directly observed using X-ray diffraction (XRD), while X-ray absorption spectroscopy (XAS) gives information about the local electronic and geometric structures (e.g., changes in redox states and bond lengths). *In situ* experiments carried out on operating cells are particularly useful because they allow direct correlation between the electrochemical and structural properties of the materials. These experiments are time-consuming and can be challenging to design due to the reactivity and air-sensitivity of the alkali metal anodes used in the half-cell configurations, and/or the possibility of signal interference from other cell components and hardware. For these

reasons, it is appropriate to carry out *ex situ* experiments (e.g., on electrodes harvested from partially charged or cycled cells) in some cases. Here, we present detailed protocols for the preparation of both *ex situ* and *in situ* samples for experiments involving synchrotron radiation and demonstrate how these experiments are done.

Introduction

Lithium ion batteries for consumer electronics presently command an $11 billion market worldwide (http://www.marketresearch.com/David-Company-v3832/Lithium-Ion-Batteries-Outlook-Alternative-6842261/) and are the premier choice for emerging vehicular applications such as plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs). Analogs to these devices utilizing sodium ions rather than lithium are in earlier stages of development, but are considered attractive for large scale energy storage (i.e., grid applications) based on cost and supply security arguments.[1, 2] Both dual intercalation systems work on the same principle; alkali metal ions shuttle between two electrodes acting as host structures, which undergo insertion processes at different potentials. The electrochemical cells themselves are relatively simple, consisting of composite positive and negative electrodes on current collectors, separated by a porous membrane saturated with an electrolytic solution usually consisting of a salt dissolved in a mixture of organic solvents (Figure 1). Graphite and $LiCoO_2$ are the most commonly employed negative and positive electrodes, respectively, for lithium ion batteries. Several alternative electrode materials have also been developed for specific applications, including variants of $LiMn_2O_4$ spinel, $LiFePO_4$ with the olivine structure, and NMCs ($LiNi_xMn_xCo_{1-2x}O_2$ compounds) for positives, and hard carbons, $Li_4Ti_5O_{12}$, and alloys of lithium with tin for negatives.[3] High voltage materials like $LiNi_{0.5}Mn_{1.5}O_4$, new high capacity materials such as layered-layered composites (e.g., $xLi_2MnO_3{\cdot}(1-x)LiMn_{0.5}Ni_{0.5}O_2$), compounds with transition metals that can undergo multiple changes in redox states, and Li-Si alloy anodes are currently subjects of intense research, and, if successfully deployed, should raise practical energy densities of lithium ion cells further. Another class of materials, known as conversion electrodes, in which transition metal oxides, sulfides, or fluorides are reversibly reduced to the metallic element and a lithium salt, are also under consideration for use as battery electrodes (primarily as replacements for anodes).[4] For devices based on sodium, hard carbons, alloys, Nasicon structures, and titanates are being investigated for use as anodes and various transition metal oxides and polyanionic compounds as cathodes.

Because lithium ion and sodium ion batteries are not based on fixed chemistries, their performance characteristics vary considerably depending on the electrodes that are employed. The redox behavior of the electrodes determines the potential profiles, rate capabilities, and cycle lives of the devices. Conventional powder x-ray diffraction (XRD) techniques can be used for initial structural characterization of pristine materials and *ex situ* measurements on cycled electrodes, but practical considerations such as low signal strength and the relatively long times needed to collect data limit the amount of information that can be obtained on the discharge and charge processes. In contrast, the high brilliance and short wavelengths of synchrotron radiation (e.g., λ=0.97 Å at the Stanford Synchrotron Radiation Lightsource's beamline 11-3), combined with the use of high throughput image detectors, permit acquisition of high-resolution data on samples in as little as 10 seconds. *In situ* work is performed in transmission mode on cell components undergoing charge and discharge in hermetically sealed pouches transparent to x-rays, without having to stop operation to acquire data. As a result, electrode structural changes can be observed as "snapshots in time" as the cell cycles, and much more information can be obtained than with conventional techniques.

X-ray absorption spectroscopy (XAS), also sometimes referred to as X-ray Absorption Fine Structure (XAFS) gives information about the local electronic and geometric structure of materials. In XAS experiments, the photon energy is tuned to the characteristic absorption edges of the specific elements under investigation. Most commonly for battery materials, these energies correspond to the K-edges (1s orbitals) of the transition metals of interest, but soft XAS experiments tuned to O, F, C, B, N and the $L_{2,3}$ edges of first row transition metals are also sometimes carried out on *ex situ* samples.[5] The spectra generated by XAS experiments can be divided into several distinct regions, containing different information (see Newville, M., Fundamentals of XAFS. http://xafs.org/Tutorials?action=AttachFile&do=get&target=Newville_xas_fundamentals.pdf). The main feature, consisting of the absorption edge and extending about 30-50 eV beyond is the X-ray Absorption Near Edge Structure (XANES) region and indicates the ionization threshold to continuum states. This contains information about the oxidation state and coordination chemistry of the absorber. The higher energy portion of the spectrum is known as the Extended X-ray Absorption Fine Structure (EXAFS) region and corresponds to the scattering of the ejected photoelectron off neighboring atoms. Fourier analysis of this region gives short-range structural information such as bond lengths and the numbers and types of neighboring ions. Pre-edge features below the characteristic absorption energies of some compounds also sometimes appear. These arise from dipole forbidden electronic transitions to empty bound states for octahedral geometries, or dipole allowed orbital hybridization effects in tetrahedral ones and can often be correlated to the local symmetry of the absorbing ion (e.g., whether it is tetrahedrally or octahedrally coordinated).[6]

XAS is a particularly useful technique for studying mixed metal systems such as NMCs to determine initial redox states and which transition metal ions undergo redox during delithiation and lithiation processes. Data on several different metals can be obtained rapidly in a single experiment and interpretation is reasonably straightforward. In contrast, Mossbauer spectroscopy is limited to only a few metals used in battery materials (primarily, Fe and Sn). While magnetic measurements can also be used to determine oxidation states, magnetic coupling effects can complicate interpretation particularly for complex oxides such as the NMCs.

Well-planned and -executed *in situ* and *ex situ* synchrotron XRD and XAS experiments give complementary information and allow a more complete picture to be formed of the structural changes occurring in electrode materials during normal battery operation than what can be obtained via conventional techniques. This, in turn, gives a greater understanding of what governs the electrochemical behavior of the devices.

Protocol

1. Planning of Experiments

1.1 Identify beam line experiments of interest. Refer to beam line webpages as guides. For SSRL XAS and XRD, these are: http://www-ssrl.slac.stanford.edu/beamlines/bl4-1/ and http://www-ssrl.slac.stanford.edu/beamlines/bl4-3/ and http://www-ssrl.slac.stanford.edu/beamlines/bl11-3/

1.1.1 Contact beam line scientist and discuss details of experiment.

1.2. Check deadlines and requirements for proposals by going to the relevant website.

1.3. Write beam time proposal and submit.

1.4. After the proposal has been scored, schedule beam time.

1.5. Follow instructions provided by the facility to prepare for beam time. Consider the details of the experiment, transport of materials (especially of devices containing alkali metals) and equipment, and any safety concerns. Safety training is generally required for new users.

2. Preparation of Materials, Electrodes, and Cells

2.1. Synthesize or obtain active material of interest.

2.2. Characterize material by conventional x-ray powder diffraction, using steps 2.2.1-2.2.9.

2.2.1. Grind powder and sieve to ensure uniform particle size distribution.

2.2.2. Load sample into sample holder. Remove backplate from holder and place it against a glass slide. Fill cavity with powder, then attach backplate, flip holder and remove slide. This ensures that the powder is even with the surface of the holder and that the surface is flat.

2.2.3. Log into logbook for the diffractometer.

2.2.4. Insert sample holder into diffractometer and align.

2.2.5. Close doors of diffractometer.

2.2.6. Using Data Collector program on computer attached to Panalytical diffractometer, increase voltage and current to values appropriate for measurement. Select slits and beam masks for the experiment. Select or modify program for scan.

2.2.7. Start program and name datafile. Lock diffractometer doors by swiping badge when prompted by the program. Collect data.

2.2.8. Analyze pattern using High Score program. In particular, look for the presence of impurities (extra reflections) and whether pattern matches that of reference materials or calculated patterns.

2.2.9. Remove sample from diffractometer. Turn down current and voltage, and close doors. Log out, noting any unusual conditions.

2.3. Obtain scanning electron micrographs to assess particle morphologies, using steps 2.3.1.-2.3.10.

2.3.1. Prepare sample by attaching carbon tape to an aluminum stub, and sprinkling sample powder onto sticky side. Test for magnetism by holding a kitchen magnet over the sample.

2.3.2. Insert sample into SEM chamber via airlock.

2.3.3. Once vacuum is established, turn accelerating voltage on.

2.3.4. In low magnification mode, adjust contrast and brightness. This is most conveniently done using the ACB button.

2.3.5. Find area of interest by manually scanning in the x and y directions.

2.3.6. Switch to SEM or gentle beam modes if higher magnification is desired. Select desired detector, and set working distance to values appropriate for the experiment.

2.3.7. Adjust contrast and brightness using ACB knob.

2.3.8. Focus image with stage z control.

2.3.8. Align beam, correct astigmatism and focus using x and y knobs.

2.3.9. Take pictures as desired, using photo button, and save to appropriate folder on the computer.

2.3.10. When finished, turn off accelerating voltage. Move sample to exchange position and remove from chamber via airlock.

2.4. Conduct elemental analysis by ICP if needed, and characterize materials with any other desired techniques such as IR or Raman spectroscopy.

2.5. Fabricate electrodes, using steps 2.5.1.-2.5.8.

2.5.1. Make a solution of 5-6 wt. % polyvinylidene fluoride (PVDF) in N-methylpyrolidinone (NMP).

2.5.2. Mill together active material and conductive additive (acetylene black, graphite, etc.).

2.5.3. Add NMP solution from step 2.3.1 to dry powder from step 2.3.2 and mix. Proportions vary depending on the nature of the active material, but a final dry composition of 80:10:10 (active material:PVDF:conductive additive) is common.

2.5.4. Using a doctor blade and (optionally) a vacuum table, cast electrode slurry onto an Al or Cu current collector. Carbon coated Al foil may be used for Li ion battery cathode materials and all Na ion electrode materials, and Cu foil is used for Li ion anode materials.

2.5.5. Allow electrodes to air-dry.

2.5.6. Dry electrodes further using an IR lamp, hot plate, or vacuum oven.

2.5.7. Cut or punch electrodes to the size needed. Weigh electrodes.

2.5.8. Transfer electrodes to an inert atmosphere glovebox. An additional drying step using a vacuum heated antechamber attached to the glovebox is recommended to remove all residual moisture.

2.6. Assemble electrochemical devices (usually coin cells, but other configurations can be used for electrochemical characterization) for initial characterization, *ex situ* samples, and/or beam line experiment, using steps 2.6.1-2.6.7.

2.6.1. Gather all needed components in the inert atmosphere glovebox.

2.6.2. Cut lithium or sodium foil to the desired size.

2.6.3. Cut microporous separator to the desired size.

2.6.4. Layer components in this order in the device: electrode, separator, electrolytic solution, and Li or Na foil.

2.6.5. Add spacers and wave washers as needed.

2.6.6. Seal cell using a coin cell press.

2.6.7. For *in situ* XRD experiments, attach tabs to either side of coin cell and seal device in polyester pouch.

2.7. Perform electrochemical experiment for initial characterization or *ex situ* work, using steps 2.7.1-2.7.6.

2.7.1. Connect leads from the potentiostat/galvanostat or cycler to device and measure open circuit potential.

2.7.2. Write program for the electrochemical experiment desired or select an archived program.

2.7.3. Run experiment and collect data.

2.7.4. For *ex situ* experiments, disassemble the device in glovebox, taking care not to short-circuit it. For coin cells, use either a coin cell disassembler tool or pliers wrapped with Teflon tape.

2.7.5. Rinse electrodes with dimethylcarbonate to remove residual electrolyte salt. Allow them to dry.

2.7.6. Cover electrodes for *ex situ* study with Kapton foil for XRD experiments or scotch tape for XAS and store in the glovebox until the experiment is carried out.

2.8. Powders intended for study by XAS should be sieved to ensure particle size homogeneity. They may then be sprinkled onto several pieces of scotch tape. A series of samples can then be prepared by stacking progressively more numerous pieces of the powdered tape together. This is particularly useful if the user is uncertain about the amount of powder needed for the optimal signal.

2.8.1. Alternatively, powders for XAS measurements may be diluted with BN if the user is confident about what will result in the optimum signal.

3. Performance of Experiments at the Synchrotron Facility

3.1. Several days before the experiment is to begin, plan transport of materials and equipment to the facility.

3.1.1. For devices containing alkali metal anodes, shipping is required to avoid hazards associated with transportation in personal or public vehicles.

3.1.2. Equipment such as portable galvanostat/potentiostats and laptop computers and nonhazardous samples such as electrodes for *ex situ* work may be brought to the facility by the individual carrying out the experiments in any convenient fashion.

3.2. Check in and register at the facility.

3.3 For both *in situ* and *ex situ* XRD experiments, take a reference pattern of LaB_6 for purposes of calibration.

3.3.1. Contact beamline scientist and personnel for instructions.

3.3.2. Calibrate beam to find right beam conditions.

3.3.3. Measure reference pattern of LaB_6.

3.4. For *in situ* XRD experiments, set up device and start experiment following steps 3.4.1-3.4.6.

3.4.1. Insert pouch into Al pressure plates and ensure that holes are properly aligned to allow the x-ray beam to transmit.

3.4.2. Find optimum beam position and exposure time. Prolonged exposure can lead to oversaturation. Decide whether sample will be rocked or stationary.

3.4.3. Take initial pattern before electrochemistry is started.

3.4.4. Attach leads from galvanostat/potentiostat to device.

3.4.5. Start electrochemistry experiment.

3.4.6. Obtain data. Once experiment is under way, data collection is automatic, and user need only to oversee to make sure experiment is going as planned.

3.5. Set up XAS experiments.

3.5.1. Check in and contact beamline scientist and personnel for instructions.

3.5.2. Insert sample and foil reference material (depending on metal that is being measured; e.g., Ni for Ni K edge).

3.5.3. Align sample.

3.5.4. Determine energy of specific metal edge using IFEFFIT's Hephaestus. Tune monochromator, then de-tune by about 30% to eliminate higher order harmonics. Change gains to adjust I_1 and I_2 measure offsets.

3.5.5. Take measurement. Two or more scans should be taken and merged for the element of interest.

3.5.6. Repeat steps 3.5.3 to 3.5.5 for additional elements, as needed.

4. Data analysis

4.1. For XRD work, calibrate the LaB_6 image

4.1.1. Download Area Diffraction Machine, which is available through the google code (http://code.google.com/p/areadiffractionmachine/).

4.1.2. Open the image for LaB_6 diffraction and use initial calibration values from the file header

4.1.3. Open the reference Q ($=2\pi/d$) values of LaB_6

4.1.4. Calibrate the LaB_6 diffraction image with the Q values and the initial guess of the calibration values**.**

4.1.5. Obtain correct calibration values by image fitting.

4.1.6. Save the calibration values into the calibration file.

4.2. Calibrate the data images from the experiment.

4.2.1. Open the diffraction images from the experiment.

4.2.2. Open the calibration file from the LaB_6 reference (saved in 4.1.6).

4.2.3. Open the reference Q ($=2\pi/d$) values of Al or Cu (current collectors for the electrodes) and use them as internal references.

4.2.4. Calibrate the pattern images by image fitting.

4.2.5. Integrate the image to Q vs. Intensity data (line scans).

4.2.6. Fit patterns using the desired fitting program (CelRef, Powdercell, RIQAS, GSAS, etc.).

4.3. Process electrochemical data using any convenient plotting program (Excel, Origin, KaleidaGraph, Igor, etc.).

4.4. For XAS data, use ARTEMIS/ATHENA in the IFEFFIT software package for analysis.

4.4.1. Calibrate data using the first peak in the derivative of the absorption spectra of the reference metals.

4.4.2. Merge like scans.

4.4.3. Subtract background and normalize data.

4.4.4. Use the AUTOBK function to isolate the EXAFS data.

4.4.5. Fourier transform the EXAFS data.

4.4.6. Use a least squares fit to the Fourier transformed spectra in R or k space to extract structural information.

Representative Results

Figure 2 shows a typical sequence used for an *in situ* experiment. After synthesis and characterization of active material powders, composite electrodes are prepared from slurries containing the active material, a binder such as polyvinylidene fluoride (PVDF) and conductive additives such as carbon black or graphite suspended in N-methylpyrrolidinone (NMP), cast onto either aluminum or copper foil current collectors. Aluminum is used for lithium ion battery cathodes and all sodium ion battery electrodes, and copper is used for lithium ion battery anodes. After the electrodes are dried, cut and weighed, cells are assembled in an inert atmosphere glovebox using microporous separators, the appropriate electrolytic solutions and negative electrodes consisting of either Li or Na foils. These components are then hermetically sealed in a protective pouch, made of polyester, which keeps out air and is reasonably x-ray transparent. Aluminum and nickel tabs are used to make electrical contacts to the positive and negative electrodes, respectively. The Al tabs are ultrasonically welded to the cathode current collectors, while the soft Li or Na metal used as the anode is simply pressed around the Ni tab to make contact. To maintain pressure, the pouch cell is compressed between two metal plates with 2 mm holes cut into them to allow the transmission of x-rays. Poor contact between cell components may result in high overpotentials and premature cutoff, particularly if voltage limits are not adjusted to accommodate the additional overpotential encountered in this configuration. Excessive pressure, on the other hand, may cause cell shorting and failure of the experiment. Better pressure control is achieved when components are first assembled into a coin cell with small holes drilled into the casings and spacers, which is then sealed into the protective pouch after tabs are attached. Wave washers and spacers are used to fill any extra volume in the device, maintain pressure, and ensure good contact among the components.

A small portable potentiostat/galvanostat and laptop computer are then used to perform the electrochemical experiment and collect data at the beam line. One charge-discharge cycle typically takes about 20 hours to complete. The cycle is usually performed galvanostatically (i.e., using constant current) between pre-selected voltage limits. The sample may either be kept stationary, rocked (left/right or up/down) or rotated around the beam axis in the beam line. Advantages to the last two are that results are obtained over a somewhat larger area of the electrode, effects of preferred orientation in powder-containing electrodes are minimized, and counting statistics are improved.

Transmission XRD ring patterns (see Figure 2, step 5) can be obtained in about 10 seconds, with a data readout time of about 1-2 minutes. Integration of calibrated image patterns yields line scans (intensity vs. Q). Beam line 11-3 at the Stanford Synchrotron Radiation Lightsource uses a single Si(311) monochromator, generating an incident wavelength of approximately 0.97 Å (12,735 eV), though energy fluctuations on the order of a few eVs (~0.01%) due primarily to diurnal cycling (daily temperature fluctuations) are often observed over the course of the lengthy charge and discharge measurements. Thus, image calibration for each scan is essential to de-convolute the diffraction pattern changes. Calibration is performed with The Area Diffraction Machine software developed in conjunction with the 11-3 beam line (http://code.google.com/p/areadiffractionmachine/).

Figure 3 shows *in situ* XRD data obtained on a Li/$Li_x[Ni_{0.45}Mn_{0.45}Co_{0.05}Al_{0.05}]O_2$ cell which underwent charge (in black) and discharge (in green), after calibration and conversion of the ring patterns to line scans. Peaks arising from cell components including the Al current collector, polyester pouch, and polypropylene separator are marked with red and blue dots (lithium metal is essentially transparent to x-rays, but additional peaks will arise if sodium metal anodes are used). Indexed reflections attributable to the $Li_x[Ni_{0.45}Mn_{0.45}Co_{0.05}Al_{0.05}]O_2$ active material are marked on the patterns. Because the unit cell parameters changed as a function of x (Li content), peaks due to this phase and the Al current collector overlapped in some of the patterns. The interference from cell components presented significant challenges both for perfect background subtraction and Rietveld refinement of the entire diffraction patterns. To circumvent this problem, backgrounds were manually subtracted, and a limited set of peaks that did not overlap with cell components were selected for the fitting. Unit cell parameters at various states-of-charge were subsequently calculated by a least-squares refinement using the available peak positions and the program CelRef (http://www.ccp14.ac.uk/tutorial/lmgp/celref.htm). The degree to which cell components interfere in patterns obtained from *in situ* experiments vary depending on the nature of the material under study, and these problems are not always encountered. In that case, any convenient refinement or fitting program may be used to analyze data (GSAS, PowderCell, RIQAS, FullProf, etc.).

Due to time constraints, it is sometimes preferable to perform synchrotron XRD experiments *ex situ.* It is obviously not practical to perform multiple cycles over a long time in the beam line, for example. Instead, electrodes can be removed from cycled cells, rinsed with solvent to remove residual electrolyte salt, dried, and covered with Kapton film to provide protection from air, for later examination. Additionally, it can be useful to study a few electrodes at different states-of-charge harvested from electrochemical cells, to give an idea of what to expect from a more involved *in situ* experiment performed later. These experiments are much simpler to carry out and much less time-consuming; several samples can usually be run in an hour. An additional benefit to the *ex situ* work is the absence of most interfering cell components, although signals from the current collector, binder and conductive additives are usually still observed and the Kapton itself contributes to the background. Caveats for *ex situ* work are that washing and long or improper storage may change or degrade the sample. In worst-case scenarios, the data obtained *ex situ* may not even provide relevant information because of these problems. If appropriate caution is maintained, however, *ex situ* work can still be of some value, although direct observation of processes using *in situ* configurations is clearly the most desirable option whenever time constraints allow.

Because XAS experiments are element-specific, interference from cell components other than the electrode material of interest are not as problematic as with XRD (assuming that cell hardware does not contain the metals of interest). Only one absorption edge (element) can be measured at a time, however. While switching to a new energy takes only seconds, tuning, changing gains and offsets on the ion chambers, changing reference foils, and purging with gas may take up to an additional ten minutes. Switching from one element to another during an *in situ* run may result in some loss of data. Meaningful EXAFS data can be difficult to obtain during *in situ* work, because the structural changes that are occurring often have similar time constants to that of the measurements themselves. Another consideration is that XAS beam lines are often heavily subscribed, meaning limited time for each user. For these reasons, it is generally more practical to carry out XAS experiments on *ex situ* samples rather than perform *in situ* work (although see reference 7 for an example of *in situ* work). Obtaining data on *ex situ* samples can take anywhere from a few minutes to one hour depending on how many elements are being studied and the facility at which the work is carried out. During each edge measurement, a similar metal foil (e.g., Ni, Mn, or Co) spectrum should be recorded for energy reference. This is carried out simultaneously with the sample measurement. In addition, the user may wish to record data on reference materials containing the metals of interest with known oxidation states, separately, particularly if unusual redox states are involved in the electrochemistry. For example, Li_3MnO_4 was used as a reference for a recent study of a series of lithium manganese oxynitride electrode materials to verify the presence of tetrahedrally coordinated Mn^{5+}.[8]

Most XAS experiments directed towards studying bulk processes in electrode materials are run in transmission mode, which is suitable when molar concentrations of the elements of interest are above about 5-10 % (http://xafstraining.ps.bnl.gov). Best results are obtained when the thickness of the sample, x, is adjusted so that $\mu x<3$ above the absorption edge. If the absorption coefficient (μ) is not known (e.g., for complex materials, which includes many battery electrode materials), it can be useful to start with a very small amount of powder sprinkled onto the sticky side of a piece of scotch tape. One or more additional pieces of powdered scotch tape can be attached to the original to increase the signal to the point where the optimum response is obtained (typically, corresponding to one absorption length). For materials where the absorption coefficient is known, the sample can be diluted with BN so that the correct absorption is obtained at a given thickness.

At SSRL, Ni, Mn, and Co K-edges can be studied at beam line 4.1, while Ti and S edges are investigated at beam line 4.3. Detuning the double crystal monochromator by about 30% eliminates higher order harmonics. Calibration is carried out using the first peak in the derivative of the absorption spectra of the reference metals. Duplicate scans can be run and merged after alignment to improve the quality of the data. Artemis/Athena from the software package IFEFFIT are used for analysis.[9] After merging like-scans, the background contribution is subtracted and the data is normalized. EXAFS data is isolated using the AUTOBK function, and is Fourier transformed. Least squares fitting to the Fourier transformed spectrum in R or k space is then used to extract structural information. An example of XAS data, taken at the Mn K edge, is shown in Figure 2, step 5 and the XANES and EXAFS regions are marked on the spectrum.

Tables and Figures:

Figure 1: Schematic of a Li ion battery with a graphite anode and layered metal oxide cathode undergoing discharge. Used with permission from reference 4.

Figure 2: Typical sequence of an *in situ* experiment. Steps include 1) preparation and characterization of the sample, 2) preparation of composite electrodes, 3) assembly of pouch cells, 4) set up of an *in situ* experiment in the beamline, and 5) data acquisition and analysis.

Figure 3: Line scans obtained by integrating image scans on a $Li/Li_x[Ni_{0.45}Mn_{0.45}Co_{0.05}Al_{0.05}]O_2$ cell undergoing charge (black) and discharge (green). Reflections attributed to the Al current collector and polymeric cell components (pouch and microporous separator) are marked with blue and red dots, respectively.

Table 1: Table of Materials.

Table 2: Table of Equipment.

Discussion

Analysis of XANES data indicates that as-made $LiNi_xCo_{1-2x}Mn_xO_2$ ($0.01 \leq x \leq 1$) compounds contains Ni^{2+}, Co^{3+}, and Mn^{4+}.[10] A recent *in situ* XAS study on $LiNi_{0.4}Co_{0.15}Al_{0.05}Mn_{0.4}O_2$ showed that Ni^{2+} was oxidized to Ni^{3+} and, ultimately, Ni^{4+} during delithiation, but that redox processes involving Co^{3+} contributed some capacity even at low states-of-charge, contrary to previous assumptions.[7] Another study involving the low cobalt compositions, $LiNi_{0.45}Co_{0.1-y}Al_yMn_{0.45}O_2$, also indicated that Co was electroactive at the early stages of delithiation.[11]

Synchrotron XRD[12] and XAS[11] studies of a series of NMCs with the composition $LiNi_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO_2$ ($0 \leq y \leq 0.1$) have yielded insights into the improved electrochemical performance of the Al-substituted variants. Analysis of high-resolution synchrotron XRD patterns obtained on the pristine powders indicated that the y=0.1 material exhibits a slight monoclinic distortion, not discernible in the conventional powder XRD patterns. To relieve strain in the transition metal planes, which consist of metal-containing edge-shared octahedra with different equilibrium M-O distances, local scale ordering occurs, resulting in the distortion. The strain-relieving distortion was further confirmed by close examination of the EXAFS data.[11] Electrochemical cycling induces additional strain, though the observed changes in the EXAFS data were smaller for electrodes containing Al. *In situ* XRD experiments on Li cells containing these NMC cathodes indicated that lattice changes during cell charge (delithiation) were smaller for the Al-substituted materials than for the unsubstituted baseline. Fewer structural changes upon prolonged cycling were also observed in the Al-containing electrodes.

Partial Al-substitution has also been proposed as a possible means to stabilize orthorhombic $LiMnO_2$ electrodes.[13] This material rapidly converts from the original zigzag layered structure to spinel upon electrochemical cycling, with a concomitant deterioration of the electrochemical properties. However, no stabilization effect was observed during *in situ* XRD experiments on an electrode substituted with 25% Al; in fact, reflections attributable to spinel formation were observed even during the initial cell charge.[14]

The degree of transition metal ordering in the high voltage spinel with the nominal composition $LiNi_{0.5}Mn_{1.5}O_4$ is expected to affect the voltage profile and other electrochemical characteristics of the material in operating cells.[15] In ordered materials (space group $P4_332$), the Ni and Mn occupy *4a* and *12d* octahedral sites, respectively, whereas in the disordered variants (space group Fd3_m) the transition metals are distributed randomly over octahedral *16d* sites. A comparison of synchrotron xrd patterns obtained on two samples with differing degrees of transition metal ordering in an *in situ* experiment revealed very different phase behavior during delithiation processes.[16] The disordered material exhibited a wide solid solution region during the initial delithiation, with two narrow two-phase regions observed at high states-of-charge. The solid solution region was much smaller for the ordered material, and the co-existence of three phases was observed at a composition of about x=0.3 in $Li_xNi_{0.5}Mn_{1.5}O_4$, flanked by two small two-phase regions. The dissimilarities in the phase behaviors, which are thought to be due to variations in lithium-vacancy ordering schemes, have been proposed as an explanation for rate capability differences observed between ordered and disordered $LiNi_{0.5}Mn_{1.5}O_4$. Contrary to expectations, however, the more ordered material in reference 16 performed better in this regard than the disordered sample. This was attributed to morphology effects; particles of the disordered sample consisted of plates with exposed (112) facets, whereas those of the ordered material were octahedral with (111) surface facets.

In addition to ordering and morphology effects, the physical and electrochemical characteristics of $LiNi_{0.5}Mn_{1.5}O_4$ are also dependent on impurity content and the amount of Mn^{3+} present. During the high temperature processing used during synthesis, a Ni-containing rock salt impurity is formed and some Mn^{4+} is reduced to Mn^{3+} in the main phase. It can be difficult to detect small amounts of the rock salt impurity because of peak overlap in the XRD patterns, or to determine its exact composition, which varies with the thermal treatment. Analysis of Ni and Mn K edge XANES data revealed the presence of a significant amount of rock salt impurity containing both Ni and Mn in a sample made at 1000ºC.[17]

The techniques described here were directed towards understanding bulk processes in electrodes undergoing charge and discharge. The assumption is that the structural changes observed using the very small spot size (e.g., 0.15 x 0.15 mm at beam line 11-3) for the experiment are typical of the electrode as a whole. This is generally true for well-made electrodes and cells, using the low current densities and relatively long charge-discharge times described above. *Ex situ* results have also generally been obtained on electrodes in cells subjected to normal operation, which have then undergone equilibration. In some circumstances, however, it can be instructive to obtain results under non-equilibrium conditions to gain understanding of failure modes of battery electrodes during operation at high current densities or under various abuse conditions. Non-uniform charge distributions may occur in these situations, particularly if electrodes or cells are unoptimized. The non-uniformity may result in local areas of overcharge or -discharge, causing structural degradation that ultimately results in reduced performance and safety of the device. A synchrotron x-ray microdiffraction technique has recently been used to map charge distribution in $LiFePO_4$ electrodes charged at high rates.[18] Although this was performed *ex situ*, the two-phase nature of the $LiFePO_4$ redox reaction essentially prevented relaxation of the charge distribution once the current was interrupted. For this experiment, partially charged electrodes were step-scanned using a monochromatic (6.02 keV) X-ray beam and a diffraction pattern was collected for each step. Scanning was carried out both perpendicular and parallel to the current collector on electrodes taken from partially charged coin cells and prismatic cells. In both cases, unequal distribution of charge was observed, with the surface of coin cell electrodes more highly charged than the active material close to the current collector, and the portion closest to the tab the most highly charged for the electrode taken from the prismatic cell.

These results illustrate the importance of good spatial as well as temporal resolution in synchrotron experiments directed towards a full understanding of battery operation. As the field advances, new techniques geared to imaging electrode materials in 3D are being developed. One such example is the combined use of full-field x-ray microscopy (TXM) with XANES to follow chemical and morphological changes in NiO electrodes as they underwent conversion to Ni and

Li_2O during cell discharge.[19] A particular challenge for these experiments, however, can be handling the large amount of data that is generated.

New high throughput inelastic X-ray scattering configurations have also been used recently to obtain finer detail on the functioning of battery materials. Examples include a combined soft XAS (Fe L-edge) and hard X-ray Raman scattering study of $LiFePO_4$ electrodes, done *ex situ*.[20] The latter combines the advantages of a hard x-ray technique (e.g., ability to probe bulk phenomena and, eventually, to perform experiments *in situ* under a variety of conditions) with the sensitivity associated with soft x-ray XAS, and can be used for low z elements such as C and O.[21] Nonresonant inelastic x-ray scattering (NIXS) has also been used to measure the Li and O K-edges of Li_2O_2 (the discharge product of lithium/air batteries with organic electrolytes), resulting in a better understanding of its structure.[22] The sensitivity of NIXS lends it particularly well for situations where poorly crystalline materials are encountered (such as in batteries undergoing discharge).

Disclosures

Authors have nothing to disclose.

Acknowledgments

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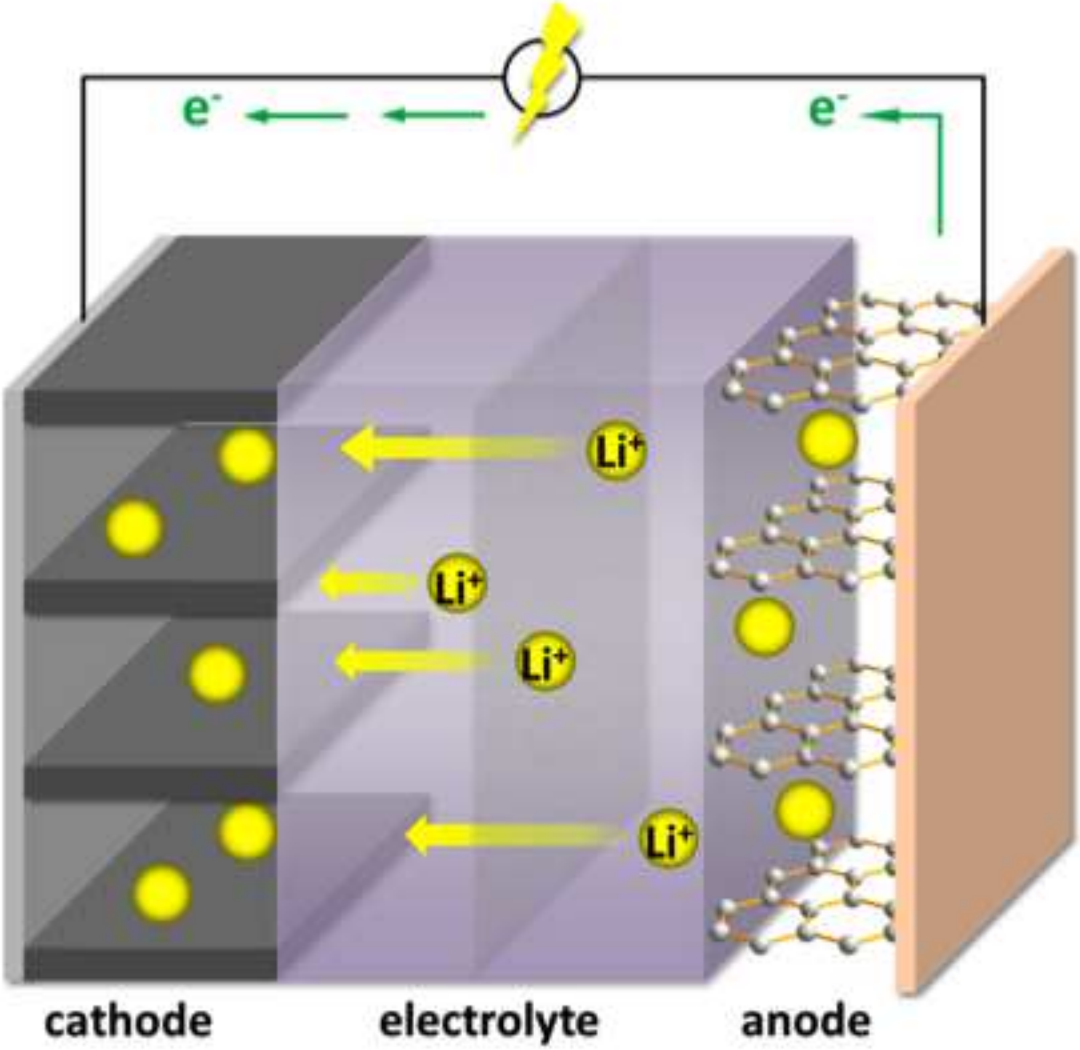
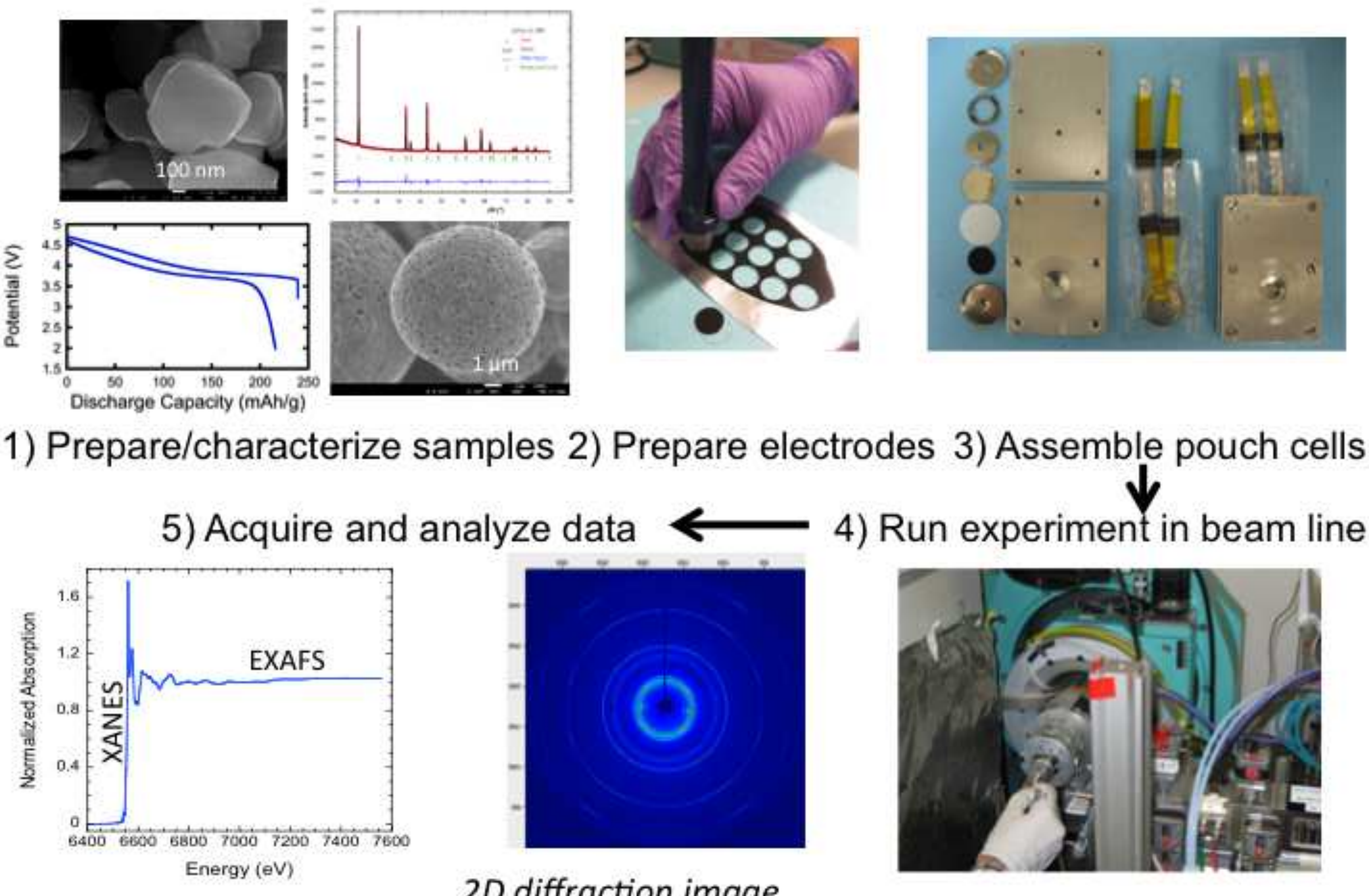


Figure 1.



Mn K-edge XAS data

2D diffraction image collected from area detector

Figure 2

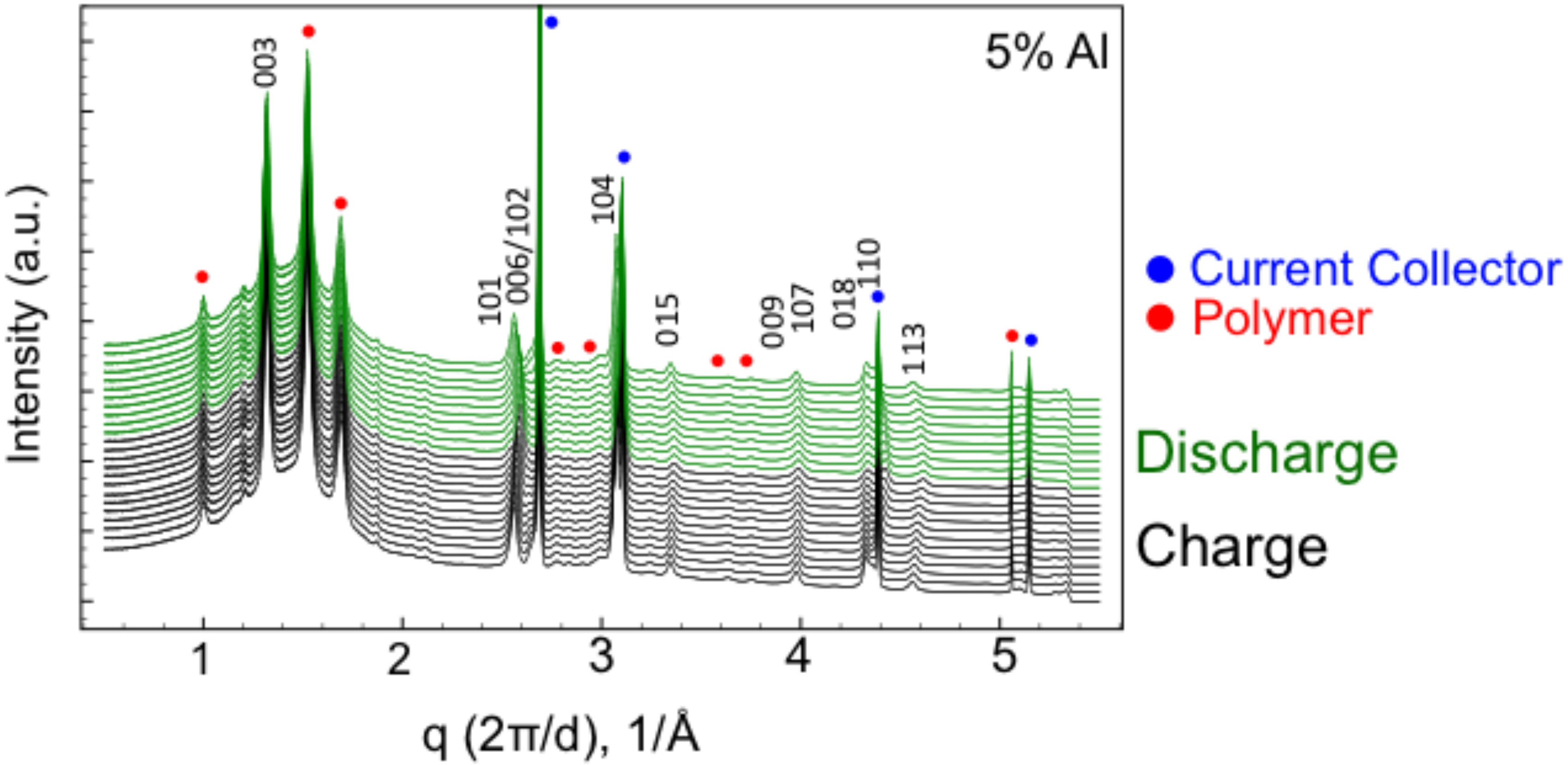

5% Al
003
101
006/102
104
015
009
107
018
110
113
● Current Collector
● Polymer
Discharge
Charge
Intensity (a.u.)
1
2
3
4
5
q (2π/d), 1/Å

Figure 3

*Table of Reagents/ Materials Used

Click here to download Table of Reagents/ Materials Used: JoVE_Materials_Table1.xlsx

Name of Reagent/Material	**Company**	**Catalog Number**
Electrode active materials	Various	
Synthetic flake graphite	Timcal (www.timcal.com)	SFG-6
Acetylene black	Denka (http://www.denka.co.jp/eng/index.html)	Denka Black
1-methyl-2-pyrrolidinone (NMP)	Sigma-Aldrich (www.sigmaaldrich.com)	328634
Al current collectors	Exopack (http://www.exopackadvancedcoatings.com)	z-flo 2650
	Alfa-Aesar (http://www.alfa.com)	10558
Cu current collectors	Pred Materials (www.predmaterials.com)	Electrodeposited Cu foil
Lithium foil	Rockwood Lithium (www.rockwoodlithium.com)	Contact vendor
	Sigma-Aldrich (www.sigmaaldrich.com)	320080

Sodium ingot	Sigma-Aldrich (www.sigmaaldrich.com)	282065
Electrolyte solutions	BASF (http://www.catalysts.basf.com/p02/USWeb-Internet/catalysts/en/content/microsites/catalysts/prods-inds/batt-mats/electrolytes)	Selectilyte P-Series contact vendor
Dimethyl carbonate (DMC)	Sigma-Aldrich (www.sigmaaldrich.com)	517127
Microporous separators	Celgard (http://www.celgard.com)	2400
Coin cell hardware (case, cap, gasket)	Pred Materials (www.predmaterials.com)	CR2016, CR2025, CR2320, CR2032
Wave washers	Pred Materials (www.predmaterials.com)	SUS316L
Spacers	Pred Materials (www.predmaterials.com)	SUS316L
Ni and Al pre-taped tabs	Pred Materials (www.predmaterials.com)	Contact vendor
Polyester pouches	VWR (https://us.vwr.com)	11214-301
	McMaster-Carr	

Kapton film	McMaster-Carr (www.mcmaster.com)	7648A735
Helium, Argon and 4-10% hydrogen in helium or argon	Air Products (http://www.airproducts.com/products/gases.aspx) or any other suitable gas supplier	contact vendor for desired compositions and purity levels Purity level needed depends on whether the glovebox is equipped with a water and oxygen removal system. Hydrogen mixtures needed to regenerate water/oxygen removal system, if present

Comments
Synthesized in-house or obtained from various suppliers
Conductive additive for electrodes
Conductive additive for electrodes
Used to make electrode slurries
Carbon-coated foils. Coated on one side.
0.025mm (0.001in) thick, 30x30cm (12x12in), 99.45% (metals basis), uncoated
For use with anode materials for Li ion batteries.
Anode for half cells. Available in different thicknesses and widths. Reactive and air sensitive. Store and handle in an inert atmosphere glovebox under He or Ar (reacts with N_2).

Anodes for half cells. Can be extruded into foils. Reactive and air sensitive. Store and handle in an inert atmosphere glovebox under He only.

Contact vendor for desired formulations.

Used to wash electrodes for *ex situ* experiments.

Polypropylene membranes

Match size to available crimping tool, Al-clad components also available.

Sizes subject to change. Inquire about custom orders.

Used to seal electrochemical cells for *in situ* work. Avoid heavy duty pouches because of strong signal interference.

Used to cover electrodes for *ex situ* experiments. 0.0025”

Used to cover electrodes for *ex situ* experiments, 0.0025 thick

Helium or argon used to fill glovebox where cell assembly is carried out and alkali metal is stored.

Do not use nitrogen because it reacts with lithium. Use only helium if sodium is being stored.

*Table of Reagents/ Materials Used

Name of Equipment	**Company**
Inert atmosphere glovebox	Vacuum Atmospheres (http://vac-atm.com) Mbraun (http://www.mbraunusa.com)
X-ray powder Diffractometer (XRD)	Panalytical (www.panalytical.com) Bruker (www.bruker.com)
Scanning Electron Microscope (SEM)	JEOL (http://www.jeolusa.com)
Pouch Sealer	VWR (https://us.vwr.com)
Manual crimping tool	Pred Materials (www.predmaterials.com)
Coin cell disassembling tool	Pred Materials (www.predmaterials.com)
Film casting knives	BYK Gardner (https://www.byk.com)
Doctor blades, Baker applicators	Pred Materials (www.predmaterials.com)
Automatic film applicator	BYK Gardner (https://www.byk.com) Pred Materials (www.predmaterials.com)
Potentiostat/Galvanostat	Bio-Logic Science Instruments (http://www.bio-logic.info) Gamry Instruments (www.gamry.com)
The Area Diffraction Machine	http://code.google.com/p/areadiffractionmachine/
IFEFFIT	http://cars9.uchicago.edu/ifeffit/
SIXPACK	http://home.comcast.net/~sam_webb/sixpack.html
CelRef	http://www.ccp14.ac.uk/tutorial/lmgp/celref.htm and http://www.ccp14.ac.uk/ccp/web-mirrors/lmgp-laugier-bochu/

Catalog Number

Custom order, contact vendors

X'Pert Powder
Bruker D2 Phaser

JSM7500F
contact vendor for options

11214-107

HSHCC-2016, 2025, 2032, 2320

Contact vendor

4301, 4302, 4303, 4304,4305,2325,
2326,2327,2328, 2329

Baker type applicator and doctor blade. Film casting knives also available.
2101, 2105, 2121, 2122
Contact vendor

VSP

Reference 3000

Free download

Free download

Free download

Free download

Comments

used during cell assembly and to store alkali metals and moisture sensitive components
various sizes (single, double) available, many options such as mini or heated antechambers
oxygen/water removal systems, shelving, electrical feedthroughs, etc.
X'Pert is a modular system. Many accessories available for specialized experiments.
Bruker D2 Phaser is compact and good for routine powder analyses.

High resolution field emission scanning electron microscope with numerous customizable opti
Low cost tabletop versions also available.

Used to seal pouches for *in situ* work

Used to seal coin cells. Match size to coin cell hardware

Used to take apart coin cells to recover electrodes for *ex situ* work. Needlenose pliers can also be used. Cover ends with Teflon tape to avoid shorting cells.

Used to cast electrodes films from slurries. Different sizes available, with either metric or English gradations. Bar film or Baker-type applicators and doctor blades are less versatile but lower cost options. Can be used by hand or with automatic film applicators.

Optional. Used with bar applicators, doctor blades, or film casting knives for automatic electrode film production. Films can also be made by hand but are less uniform.

Portable 5 channel computer-controlled potentiostat/galvanostat used to cycle cells for *in situ* experiments.

Portable single channel computer-controlled potentiostat/galvanostat used to cycle cells for *in situ* experiments.

Used for analysis of 2D diffraction data. Mac and Windows versions available.

Suite of interactive programs for XAS analysis, including Hephaestus, Athena, and Artemis. Available for Mac, Windows, and UNIX.

XAS analysis program that builds on IFEFFIT. Windows and Mac versions.

Graphical unit cell refinement. Windows only.

ions.

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Author(s): M Doeff G Chen J Cabana, T Richardson, A. Mehta, M. Shirpour, H. Duncan, C. Kim, K. Kam, T. Conry

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Article Title: Characterization of Electrode Materials for Lithium Ion and Sodium Ion Batteries Using Synchrotron Techniques

Signature: Marca M Doeff Date: 12/7/12

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April 5, 2013

Dear Dr. Kinahan,

Here is our revised manuscript. Note that the title has changed based on the request of one reviewer. It is now called "**Characterization of Electrode Materials for Lithium Ion and Sodium Ion Batteries using Synchrotron Radiation Techniques".** Although it is clear that the referees were somewhat unaware of the unusual format of the journal and the fact that filming is involved, we found many of their comments to be useful, and incorporated many of their suggested changes in the manuscript. We are particularly grateful to reviewers 2 and 3 for clarifications on fluorescence vs. transmission modes in XAS experiments. Based on their inputs, we have removed the discussion of fluorescence mode from the manuscript, as it is not really relevant to the experiments under discussion. Reviewers 2 and 3 also wanted more discussion of the pros and cons of *in situ* vs. *ex situ* experiments. We have now added a paragraph discussing the drawbacks of *ex situ* experiments. A list of the reviewer comments and our responses are appended to this letter. Changes to the manuscript are marked in red. We hope that the revised manuscript is now suitable for publication, and we look forward to scheduling the filming session.

Sincerely,

Marca M Doeff

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Response to Reviewers' comments:

Reviewer #1:
Manuscript Summary:
The submitted manuscript is a concise description of "Characterization of Electrode Materials for Lithium Ion and Sodium Ion Batteries using Synchrotron Techniques." The paper should be published in JoVE, but the know-how of the manufacture method of an in-situ cell should be explained in detail in the revised paper.

Major Concerns:
Authors should describe the procedure which makes an in-situ cell in more detail. In addition, they should explain the know-how of the manufacture method of an in-situ cell in detail in the revised paper.

Due to space constraints, more written specifics considering the construction of the *in situ* cell cannot be included in the manuscript. However, electrode and cell fabrication is included in the protocol and will be filmed, allowing readers and viewers of the final product to observe these procedures in detail.

Reviewer #2:

Editorial Comment: This reviewer has requested that a large deal of information be added to your manuscript. Please revise the manuscript according to these comments so that it relays your protocol - along with background information and representative results - as clearly, correctly and effectively as possible. JoVE publications generally have shorter introduction sections and focus primarily on the protocol being demonstrated. We do not expect a thorough discussion of all aspects of the field nor the intricacies of alternative methods.

Manuscript Summary:
In this manuscript is attempted a report about the required steps needed for the applicability of synchrotron radiation based XRD and XAS on battery materials. Authors provide a brief overview of the techniques but mainly a list of actions required (with bullets) in order to perform these experiment in a synchrotron radiation facility (e.g. preparing the samples, performing measurements, analyzing the data, etc); these are based on their research efforts performed at SSRL beamlines. Some indicative -but already published- results are reviewed and discussed for the purposes of this document.

Minor Concerns:
In title please change the "Synchrotron Techniques" to "Synchrotron Radiation Techniques"

Done.

in page 5 line 169-172: The authors mention that the XAS pre-edges arise from dipole forbidden transitions. This is mostly valid for octahedral geometries. For tetrahedral, these transitions are not totally dipole forbidden but mainly are there due to the orbitals hybridization induced by the ligands presence (for example, in 3d metals there is a strong 3d-4p mixing upon tetrahedral geometries; XAS mostly probes that 4p character, thus pre-edge is mostly a dipole allowed transition (1s->4p)). (see for instance F. de Groot et al, J. Phys.: Condens. Matter 21 (2009) 104207)

Statement has been modified and reference added.

in page 5, line 181: the "a complete picture" statement might be too strong.

Statement has been modified.

in page 5, line 152-160: the authors could also mention the recent development of high throughput inelastic x-ray scattering setups that allows XAS-like studies on low z elements like C,O, etc. by means of hard x-rays and thus can be suitable for in-situ battery related studies (for instance X. Liu et al., JACS 134, 13708 (2012); Sokaras et al., Rev. Sci. Instrum. 83, 043112 (2012); M. Chen et al, J. Phys. Chem. Lett. 2, 2483 (2011))

A paragraph summarizing these points and incorporating these references has been added to the end of the discussion section, where a brief description of where the field is going is included.

in page 11, line 365-366: Maybe they could discuss a bit on the influence of the electrode holes -required for transmission measurements- on the battery performance and then on how representative is the probing area (with the holes) compared to the pristine battery.

This is covered in the discussion section (p. 15) where we state that results are representative of batteries operating under normal, but not abuse, conditions.

in page 11, line 386: please quote the average energy fluctuation.

The issue is primarily temperature fluctuations over the course of the experiment. This is now clarified in the sentence.

in page 12, line 410: It is clear that from a practical point of view the ex-situ measurements are much easier to perform from various perspectives. However, what seems crucial to discuss is on whether is there a fundamental importance of doing the measurements in situ. I think authors should write a few sentences on this in-situ vs ex-situ (a paragraph or so).

We discuss the reason for doing in situ experiments briefly in the Introduction ("As a result, electrode structural changes can be observed as "snapshots in time" as the cell cycles, and much more information can be obtained than with conventional techniques.") We have also added a paragraph describing drawbacks of *ex situ* experiments in the Representative Results section.

in page 12, line 421-422: The authors could mention that this is the case when the element of interest is not present anywhere else along the battery (for example contacts or so). **A parenthetical comment has been added.**

in page 12, line 423-424: It looks very weird to read that it takes 10-20min to change the energy of the monochromator in order to study another element's edge. Usually this is a matter of seconds.
This statement has been clarified in the text. While changing energies is very fast, associated tasks such as tuning, changing reference foils, etc. can take some time, so that there will be a gap in the data collection.

in page 12, line 425-426: The statement for the EXAFS is valid for many beamlines; however, when using state-of-the-art high-throuput setups, it is straightforward to get great EXAFS data very fast (few minutes).
The statement has been modified.

in page 13, line 440-442: The Authors quote that fluorescence mode probes only the surface and that penetration depth of x-rays is sub-micron. This is not valid for x-ray energies along the K-edges of 3d metals that it is mainly discussed in this paper. Fluorescence comes from several um to tens of um (depending on the electrodes composition).

in page 13, line 445-447: "Some fluorescence detectors also have much higher...". I guess the authors consider "fluorescence detectors" the single photon counting solid state detectors (like silicon drift detectors) and as transmission detectors the "ionization chambers" or "photodiodes". In that case there cannot be attempted any special comparison on the 'sensitivity' among these two type of detectors since their functionality is different in a fundamental way. The former detectors have energy resolving capabilities, and in fact are spectrometers (since they can measure an energy spectrum of the emitted radiation) and the latter 'detectors' are overall dose counters (so they integrate an overall current). The limitation of measuring dilute samples in a "transmission mode" is the negligible absorption within the sample and not the detector as a hardware component per se.

in page 13, line 448-456: the way this paragraph is written indicates some kind of confusion between the fluorescence-mode XAS and the transmission-mode of XAS. The authors need to mention explicitly for which mode they intend to refer to. The so-called "saturation effects" are present when fluorescence mode of XAS is attempted on highly concentrated non-thin samples (e.g. in the case of a thick sample, the 3d metal of interest needs to be less than ~0.1% per weight in order not to have any significant influence from self-absorption -aka saturation- effects within the recorded XAS spectrum). On the other hand, the one absorption length rule is relevant for the transmission mode of XAS. In the transmission mode there are not "saturation" effects like in fluorescence mode; however the experimentalist needs to keep the sample in such thickness that would allow the ion-chamber/photodiode to have enough transmitted signal when the incident beam will get over the absorption edge (sample not to be too thick) but at the same time to have enough contrast (the sample not to be too dilute).

The discussion on fluorescence mode has been removed, based on the comments above. A lengthy explanation of fluorescence vs. transmission modes is beyond the scope of this paper, but we have now summarized why these experiments are usually done in transmission, as indicated by this referee. We have also modified the discussion on sample preparation/thickness using information obtained at http://xafstraining.ps.bnl.gov, which is now referenced in the text.

Additional Comments to Authors:
The authors are citing many of their works (if i counted correctly, the 12 out of the 18 references are co-authored by some of the authors of the present paper). On the one hand this shows that they have done some significant amount of work toward studying battery materials, but i am sure we would all agree that it is favorable to provide a broader range of citations, when possible.

We have added the references included in this referee's report (although we note that one that was suggested was co-authored by one of the authors of this manuscript). The point of this paper is, of course, to describe the synchrotron radiation experiments we are doing on battery materials, thus, citing our own work is inevitable.

The comments of this referee are comprehensive and insightful, and have helped us improve the paper. We appreciate the time s/he took in reviewing this paper.

Reviewer #3:
Manuscript Summary:
XAS and XRD can provide very useful information for a better correlation and understanding of material functionality and its physical and chemical properties. In particular, the in situ technique is of high interest, because it ensures that one can observe the real behavior of the material in operation. The manuscript describes the battery cell assembly for specific materials and gives a general idea how one can perform in situ and ex situ characterization by XRD and XAS based on synchrotron radiation. A detailed protocol how a beamtime at the SSRL synchrotron facility should be prepared is provided. The techniques of XRD and XAS are well described. In particular, the details about calibration and data evaluation should be helpful for new users. The strategies how to solve the main challenges of an in situ characterization based x-ray analytical techniques is quite general, somehow unspecific and of limited use for new users.

The manuscript is limited in scope due to length considerations. However, large parts of the protocol will be filmed and this should provide more information on the *in situ* techniques for the interested reader/viewer of the finished paper.

Major Concerns:
It is not clear for me how is addressed with this paper. Maybe scientists which are developing novel materials for Li ion batteries? On the one hand the authors provide a lot of details about the assembly of specific battery cells. These details are usually known by the material scientists. On the other hand important details about the in situ instrumentation are missing. One of the most important challenges is to design the in situ cell with x-ray transparent windows. Here, more details would be very helpful for the users. For example, what is a good thickness of the polyester foil for the x-ray windows, how thick the current collector foils can be etc. The

thickness of the complete cell limits strongly the elements (e.g. S and Ti) which can be accessed by XAS. It would be helpful for users to get some experienced data about material thicknesses and limitations.
In many cases the authors propose to perform ex situ experiments including the advice to wash the cathode and anode material. In general the proposal is right in view of learning as much as possible before starting the significantly more sophisticated in situ experiments. But the authors do not explain the drawbacks of ex situ experiments. In particular, there are many effects, such as self discharge and chemical reactions with ambient air, humidity and the washing solutions. These effects could cause strong changes in the material between the electrical characterization and the ex situ XRD and XAS experiments.

The paper/film is intended for those who wish to learn the experimental techniques involved in performing *in situ* synchrotron radiation experiments on batteries. It may include both beamline scientists new to the world of batteries, who would like to apply their expertise, and to materials scientists working in the field of batteries new to synchrotron radiation techniques. Thus, brief descriptions of both the materials science and the synchrotron radiation technique aspects are included in the text. The purpose of the journal is to record in detail the procedures involved in certain types of experiments. A unique feature of this journal is the filming of the experimental procedures, which allows direct observation by the viewer.

Two very detailed tables of materials and equipment have been included with the manuscript. For example, the table of materials includes suggested thicknesses for pouches and Kapton films used to cover samples or contain the coin cells, as well as for the current collectors. It also includes suggested vendors and catalog numbers. The referee may have missed these during the review of the manuscript (or perhaps did not receive them). The tables should be very helpful for those who want to replicate the experiments for their own research.

A few sentences have been added to the manuscript summarizing the drawbacks of *ex situ* experiments and emphasizing the benefits of *in situ* work, as suggested by this reviewer and reviewer #2.

Minor Concerns:
For the background of both techniques XRD and XAS some additional hand books should be cited.
In the paragraph at line 439, the authors state the XAS in fluorescence mode is more surface sensitive than in transmission mode. This is not true, because the energy of the exciting x-ray beam is usually above the absorption edge and the energy of the emitted fluorescence x-rays is below. Hence, the absorption of the emitted x-ray is less attenuated than the exciting beam. Both XAS in fluorescence and transmission mode suffer from saturations effects if the sample thickness is too high. In the extreme case of an unlimited thick sample one can still measure XAS spectra in fluorescence mode, with strong saturation, but not in transmission mode. I think, the reason to perform the XAS measurements in transmission mode is that the in situ cell can be also used for XRD and maybe the design of the cell is easier.

We have added an on-line reference (http://xafstraining.ps.bnl.gov), removed the discussion of fluorescence, and clarified the sample thickness issue in the revised manuscript.

Additional Comments to Authors:
I really appreciate you effort to introduce and advertise to analytical possibilities available at synchrotron facilities. Most of the material research seems still very empirical to me. A reliable material characterization would be indispensable to achieve a more systematic progress. In particular, the in situ capabilities at the synchrotron facilities are very promising.
An Ex situ characterization of the material is usually questionable, because of the potential impact of handling under ambient conditions and washing for example. This can change the materials properties and makes a reliable correlation of material properties and functionality difficult.
Unfortunately, I have the impression that your paper can be hardly understand by scientists from material research. For potential users additional information would be helpful. The part about the different material combinations for battery cells can be shortened. A deeper discussion about ex situ vs. in situ measurements

should be included. In addition, further details about the practical challenges for the in situ instrumentation and how one can solve them should be provided.

We have now included a paragraph outlining the drawbacks of *ex situ* experiments more explicitly, and emphasizing the advantages of *in situ* work. The description of battery materials (one paragraph in the Introduction) is necessary to provide the background and the rationale for doing synchrotron radiation experiments. This leads up to the Representative Results and Discussion section, in which specific examples from our previous work are used to illustrate the outcomes of the experiments. This format is required by the journal. The filming of the procedures will provide additional detail and is the main focus, with the written manuscript provided mainly as an aid to the viewer.

We thank this reviewer for helpful comments, particularly concerning fluorescence vs. transmission modes.

Editorial Comment: We understand that your protocol is focused on a specific set of experiments in order to fit the JoVE guidelines for video preparation and overall journal scope, and as such cannot encompass every aspect of this class of experiments in detail. However, please consider this reviewers comments and revise the protocol as you see fit to make it clearer and more useful to your targeted audience.