

Design of electrochemical cells for in-situ XAS experiments

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ABSTRACT

Understanding of the redox chemistry and changes in structure during the electrochemical cycling of the battery or fuel cell is critical in design of new advanced materials. As the user community gains the appreciation for the benefits of in-situ x-ray absorption spectroscopy (XAS) techniques more scientists desire to perform in-situ and operando experiments with battery materials. Often, deficiencies in overall experimental design cost valuable synchrotron experiment time and slow the turn-around time of insightful and useful results. While any particular element of the electrochemical cell (EC) system might be well understood, the success of in-situ/operando XAS experiments are determined by the overall design of the experiment and often relies on close collaboration between electrochemists and the synchrotron community. This presentation has resulted from multiple collaborations on in-situ XAS experiments and aims to summarize critical experiment design issues.

Keywords: in-situ characterization, electrochemical cell, x-ray absorption spectroscopy, EXAFS, transmission, fluorescence, synchrotron radiation

1 INTRODUCTION

The high demand for better performing battery electrodes and fuel cell catalysts has pushed the direction of experimental design for in situ electrochemical (EC) cells towards those experimental techniques which are not invasive, and allow data collection under battery/fuel cell operating conditions [1]. One of the most informative techniques available to researchers is x-ray absorption spectroscopy (XAS) [2, 3]. Measurement of the x-ray absorption coefficient across the absorption edge of a particular element permits element-specific observation of changes occurring within the electroactive material. XAS data allows an element-by-element reconstruction of the electronic configurations, oxidation states, and near-neighbor atom types and distances as the system undergoes electrochemical changes. Specifically x-ray absorption near edge structure (XANES) spectroscopy is sensitive to local electronic changes, i.e. changes in oxidation state, while

extended x-ray absorption fine structure (EXAFS) region of the spectra is responsive to changes in atomic structure around the absorbing atom (i.e. coordination number, atomic identity, and atomic distances). These techniques allow in-situ measurements on non-crystalline samples, making XAS a valuable resource for nanomaterials and electrochemical research.

Common design considerations regarding the transmission vs. fluorescence measurements, x-ray detectors, and data collection strategies must be considered within the scope of an in-situ EC cell experiment. The calculated absorption lengths of all materials including the electrodes, EC cell housing materials, and the active materials which intercept the incident beam must be addressed; else numerous artifacts can render an experiment virtually useless.

A cursory understanding of monochromatic x-rays, linearity of the detectors, beam alignment, sample uniformity, and overall incident beam flux, as it applies to the particular hosting beam line, should be laid as the starting foundation for any XAS EC in-situ experiment.

Coin cells with cathode and anode materials, lithography cells, flow cells with electroactive nanosuspensions, and pouch cells have all been attempted with differing degrees of success. A review of past results leading to changes in EC cell design philosophy will be compared to present results and pitfalls to avoid will be presented.

2 X-RAY BEAM PATH

Visually laying out the signal path as it originates from the source of the incident probing x-rays (synchrotron) to the data acquisition system can help in understanding multimodal in-situ XAS measurements (Figure 1). In a basic XAS transmission experiment the incident x-ray path first encounters a pair of white beam defining slits, a monochromator, a pair of post monochromator defining sample slits, an (I_0) ion chamber, the sample (e.g. EC cell), a (I_s) transmission ion chamber, a reference foil, and finally a (I_{ref}) reference ion chamber. If an EC cell is being employed as part of the experiment, all components of the cell which are in line with the synchrotron beam as well as the position of the cell with respect to the beam source need

to be considered in the total x-ray absorption with respect to the sample (e.g. electrode) [4].

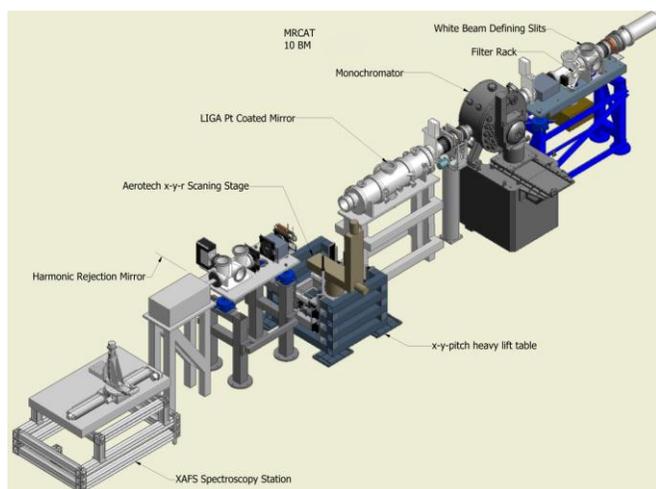


Figure 1. Layout of the MRCAT 10BM spectroscopy beamline.

3 IN-SITU XAS EXPERIMENT

The steps that one can follow when setting up an XAS experiment are (1) to calculate the proper gas mix to conduct the measurement; (2) physically move the x-ray optical components into the beam path, (3) load a reference, (4) calibrate the system to the reference, (5) check the linearity of the measurement, and (6) finally decide on the dwell times the monochromator and ion chambers will spend measuring the beam intensity at each point of the step scan, in each region of interest in the spectrum. In addition to in-situ XAS measurements ex-situ spectra of high quality standard materials of all possible valence states are necessary for data interpretation.

The edge energies for each element of interest should be checked against any known crystal glitches caused by the crystallographic cut of the specific monochromator's Bragg crystal. For example if Si (111) is used as the first Bragg crystal without a phi rotational motion one could expect ~ 7% variation in the incident x-ray beam uniformity at the Pb L3 edge (13035 eV) possibly resulting in XAS artifacts due to this glitch. The impact of this artifact on a measurement depends on the linearity between I_0 and I_t ion chambers. Keeping the same ionization gasses in I_0 and I_t can help improve linearity but potentially at the cost of increased measurement time.

Ability to see the finest XAS details is defined by the energy resolution, which is a function of the ratio between the sizes of white beam vertical slit and the monochromatic beam vertical slit. Higher energies are concentrated towards beam center, while the vertical outermost beam lobes contain a larger lower energy profile. Some beamlines offer optimized slit ratio settings unique to the specific operational energy ranges. Sizes of horizontal slits result in changes to beam intensity without changing the energy

profile. The vertical and horizontal slit sizes, the ion chambers' intensities, and amplifier settings at a particular energy should be noted as experimental parameters for future reference. The energy resolution should be considered based on pre-sample results in I_0 , I_t and I_{ref} that can be provided by beamline scientist.

The level of x-ray absorption, $\mu(E)$, will determine whether the data collection will be done in transmission or in fluorescence mode. Generally EXAFS requires $\mu(E)$ to be measured to 0.001. For transmission XAS measurement the signal should have an edge step height ($\ln(I_0/I_t)$) of 1, the sample should be uniform, free from pin holes, with the grain sizes of the same order, or smaller than the characteristic absorption length of the sample material. If the sample has a low concentration, or the sample is thick, measuring the fluorescence signal is the preferable method of data collection. Thick samples will experience self-absorption caused by an inordinate amount of absorber material diluting the XAS signal into oblivion. In this situation a fluorescence measurement should be conducted instead. It is a measurement of the emitted fluorescence lines of all the material in a sample's surface, including the inelastic and elastic peaks. Using an energy discrimination detector the fluorescence peaks need to be identified with respect to the known standard peak positions. Usually an EXAFS beamline will have a set protocol in setting up this type of measurement. Because of beam polarization in the synchrotron's horizontal plane the fluorescence detector placed at right angles to the incident beam, can suppress the elastic peaks in the data. The detector electronics can be optimized to completely suppress the scatter peak and other fluorescence lines in the sample which are of no interest, thus increasing the signal-to-noise ratio. Another way to suppress a scatter peak is to place a filter in front of the detector, whose K-edge is lower than the scatter peak energy but greater than the samples K_a line, thereby absorbing everything above the K_a fluorescence line. Artifacts caused from the re-radiation of the filter can be compensated by employing Soller slits whose focal point is determined from the sample to detector position, leaving all else to be absorbed by the slit assembly.

4 ELECTROCHEMICAL CELL DESIGN

An EC cell is a device capable of either deriving electrical energy from chemical reactions, or facilitating chemical reactions through the introduction of electrical energy. The EC cell for XAS experiment has to be designed with all the XAS experimental nuances in mind. Most of the times in-situ XAS experiments are conducted in a half cell mode, i.e. only one of the electrodes is of interest (sample) while the counter electrode is used to complete the circuit. Reference electrode can be used in some cases when precise control of the electrode potential is important. A simple description of an EC cell is of an assembly where by a volume of electrolyte is held in place between two electrically isolated conductive plates. The ions in the

electrolyte are subject to the electric field existing between the two electrodes, driving an ionic motion in the electrolyte and leading to the transport of an electrical current through the circuit.

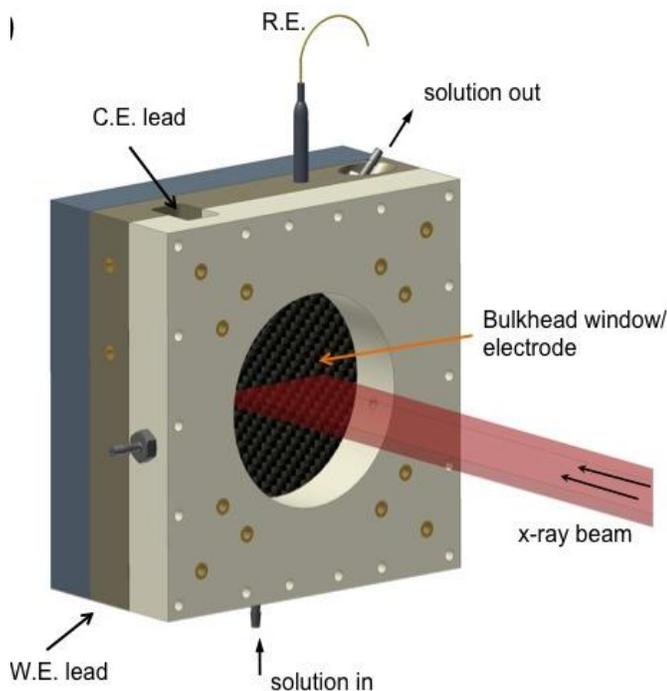


Figure 2. Example of Electrochemical cell for in-situ XAS experiment.

An example of EC cell which was specifically designed for an in-situ electrochemically assisted x-ray lithography experiment [5] is presented on Figure 2. Two graphite plates were sandwiched between three Teflon plates, each Teflon plate having a circular window bored out to allow the incident x-ray beam to pass. The graphite plates served as x-ray bulkhead windows for the cell, and as the working and counter electrodes of the three-electrode system with the working electrode always being the downstream face. A silver-silver chloride (Ag/AgCl) electrode was immersed into the cell from an orifice located at the top of the cell and used as a reference electrode. The x-ray absorption by each of the cell component in the beam path was calculated using the modeling programs (XOP 2.11[6] and Hephaestus [7]). Simultaneous collection of electrochemical and XAS data in the operating EC cell is successful when high quality of both signals can be obtained. This multimodal measurement requires the materials used in the EC cell to be transparent to the x-ray energy of interest while also inert to the reactions occurring in the cell. The choice of cell materials will depend on the sample (electrode) composition and energy the measurement is taken at. For example if the active material in the cell is LiNiCoO_2 , and the spectra at Ni-K edge (8333eV) are being measured the calculation of good sample thickness can be estimated as follows. For energies ~100-150 eV before and after the

edge mass of electrode material per unit area required for one absorption length can be calculated using Hephaestus software package [7]. In our example for energies of 8200 eV and 8466 eV samples of 7.429mg/cm^2 and 4.406mg/cm^2 are required respectively to achieve one absorption length. Taking the inverse and subtracting the higher energy mass absorption (μ^+) from the lower energy mass absorption (μ^-) leads to a $\Delta\mu = .09236$, the inverse leads to 10.827mg/cm^2 , which is the thickness (mass/area) of sample (M) required to produce a unit step height in transmission. The total absorption would be $(M \times \mu^+)$ plus the absorption of x-rays by all other cell components in a beam path. Transmission experiments are possible if the total absorption calculated this way is less than or equal to 3, which indicates that at least 5% of the beam goes through the EC cell, and into the transmission chamber. If this cannot be accomplished a fluorescence measurement of the sample electrode surface should be attempted instead, treating the entire EC cell as a thick sample.

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