

## Laboratory-Based X-Ray Absorption Spectroscopy as a New Research Tool for Battery-Relevant Materials and Beyond

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**Abstract:** X-ray absorption spectroscopy (XAS) is a powerful technique for investigating the local electronic and structural characteristics of a wide range of complex materials, including many compositions that are used in electrochemical energy storage and conversion applications. Recent advances in bench-scale instrumentation have brought XAS from synchrotron facilities to the local research laboratory, making this technique more accessible for everyday use. The Naval Research Laboratory (NRL) recently procured a commercially available XAS unit, which has since been used to analyze a large number of procured and NRL-developed materials. In this paper, we describe XAS investigations focused on the established battery cathode material, LiFePO<sub>4</sub>, in the form of powder-composite electrodes from a commercial vendor. We demonstrate that the laboratory-based XAS unit is capable of generating high-quality XANES data, even for transmission measurements through a fully packaged pouch-cell battery under electrochemically controlled state-of-charge. Shifts at the Fe K-edge are consistent with prior XANES analyses of LiFePO<sub>4</sub> collected at synchrotron-based spectrometers, showing that laboratory-based XAS is a viable alternative.

**Keywords:** X-ray absorption spectroscopy, XANES, EXAFS, lithium-ion batteries

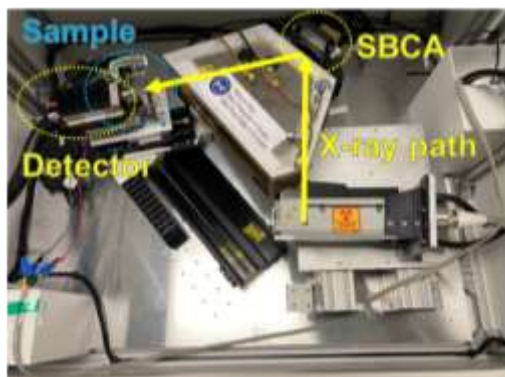
### Introduction

X-ray absorption spectroscopy provides fundamental insights on structure, mechanisms, and stability in such research fields as catalysis and energy storage.<sup>1,2</sup> A typical X-ray absorption spectrum contains element-specific information

in two distinct energy windows. In the vicinity of the absorption edge, X-ray Absorption Near-Edge Spectroscopy (XANES) yields information on elemental oxidation state and electronic structure. Beyond the absorption edge, Extended X-ray Absorption Fine Structure (EXAFS) data provide such structural information as coordination number, bond distances, and atomic arrangement. In contrast with X-ray diffraction, XAS can be used to analyze disordered materials, which are becoming increasingly relevant for energy science. While one turns to X-ray photoelectron spectroscopy to measure surface-sited element-specific information under ultrahigh vacuum, XAS probes the bulk material and can operate at ambient conditions or even in an in situ mode.

The collection of XAS data historically required the use of synchrotron-based photon sources to achieve necessary flux and energy specificity, limiting researcher access to this characterization tool. But now, laboratory-scale XAS units are available, enabled by contemporary advances in X-ray optics and design. The general layout of such an instrument (Figure 1) uses a polychromatic X-ray source that is first sent to a spherically bent crystal analyzer (SBCA). The now-monochromatic X-ray passes through the sample after which detectors collect signals in transmission mode (fluorescence detection is also possible). The X-ray source, SBCA, sample, and detector all lie upon a Rowland-circle geometry that allows such operation, a configuration based on designs from Seidler et al.<sup>3-5</sup>

The NRL Advanced Electrochemical Materials section recently installed a commercial XAS system that is capable of collecting measurements



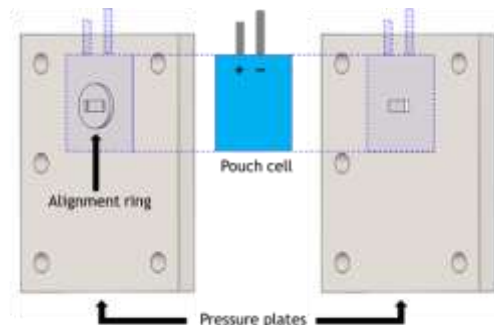
**Figure 1.** Interior configuration of a laboratory-scale X-ray absorption spectrometer.

spanning the energy range from 5–18 keV. This energy range includes K-edge excitations for the first-row transition metals, elements critical for materials used in electrochemical energy storage and catalysis.

Using this laboratory X-ray absorption spectrometer, we analyze battery-relevant materials in a variety of form factors, including pressed-powder pellets, thin films, and device-ready electrodes, the latter of which may also be interrogated in situ when incorporated into functional pouch cells. As a demonstration of these in situ XAS capabilities, we interrogate a  $\text{LiFePO}_4$  cathode in a packaged battery, using shifts in the Fe K-edge absorption to track changing Fe oxidation state as the cell is charged.

## Results and Discussion

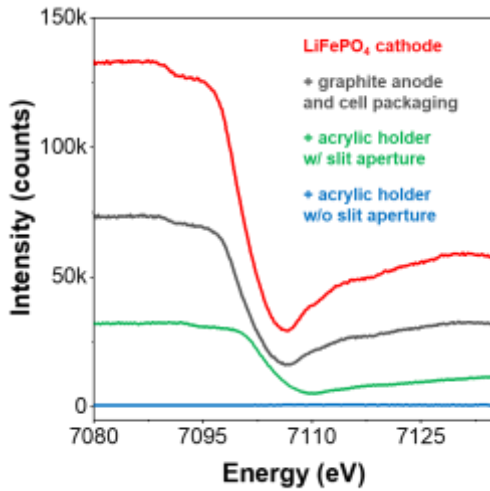
Lithium-ion battery pouch cells suitable for XAS measurements are constructed using powder-composite electrodes on metal foils:  $\text{LiFePO}_4$  on aluminum (sourced from Oak Ridge National Laboratory) as the cathode and graphite on copper (MTI Corp.) as the anode. Nickel tabs welded to the respective foils provide electrical contact to the outside of the cell. Electrodes ( $\sim 7 \text{ cm}^2$ ) are physically separated with a layer of Celgard 2500 soaked with electrolyte [1 M  $\text{LiPF}_6$  in ethylene carbonate:diethyl carbonate (1:1)]. Pouches are heat sealed under mild vacuum and then mounted between custom-designed acrylic plates (Figure 2) that provide pressure on the cell and maintain alignment within the X-ray beam path.



**Figure 2.** Schematic of a custom-made acrylic pouch cell holder for in situ electrochemical measurements.

Iron K-edge XANES measurements are collected using an in-lab X-ray absorption spectrometer (easyXAFS300) with a 1.2 kW X-ray tube operating at 30 kV and 12 mA. An SBCE of Si (110) is used to control X-ray energy at a step size of 0.2 eV and a dwell time of 10 s per point. To improve the signal-to-noise ratio, three consecutive scans are run at each state-of-charge (0, 25, 50, 75, and 100%). Spectra are analyzed using ATHENA software contained within the Demeter system for analyzing XAS data.<sup>6</sup>

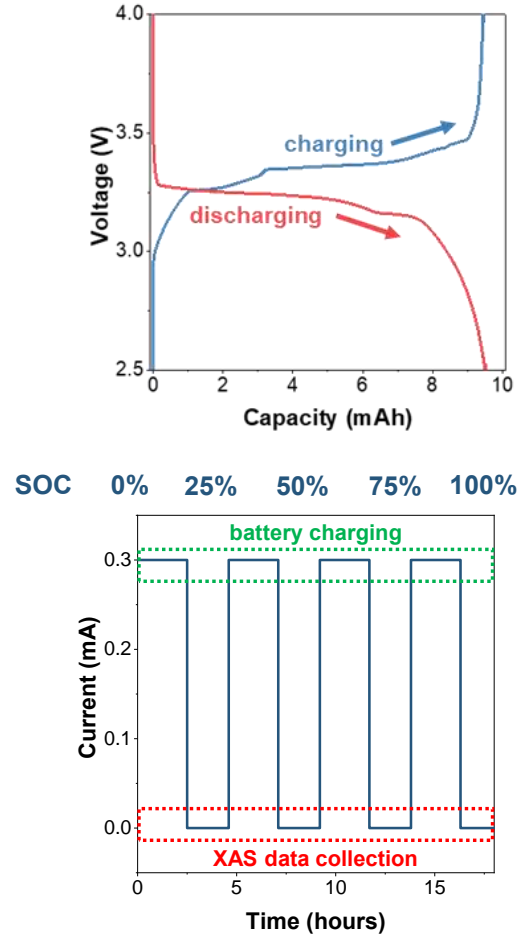
Because the photon flux of laboratory-based XAS is orders of magnitude lower than at a synchrotron, the total absorption of all sample components in the beam must be carefully considered. Prior to XAS analysis of the fully packaged pouch cell, we measured the X-ray transmission of the  $\text{LiFePO}_4$  cathode and then additional layers of the pouch cell and holder (Figure 3), expressed as intensity at the X-ray detector. Even transmitting X-rays through both electrodes and packaging material, detector counts are in the 60–80 kCount range. The thick acrylic used to construct the cell holder is a significant X-ray absorber, thus we cut slit-shaped apertures ( $5 \times 13 \text{ mm}$ ) to accommodate beam transmission. With the fully packaged cell plus cell holder, detector counts remain healthy at  $\sim 30\text{--}40 \text{ kCounts}$ , sufficient for recording high-resolution spectra.



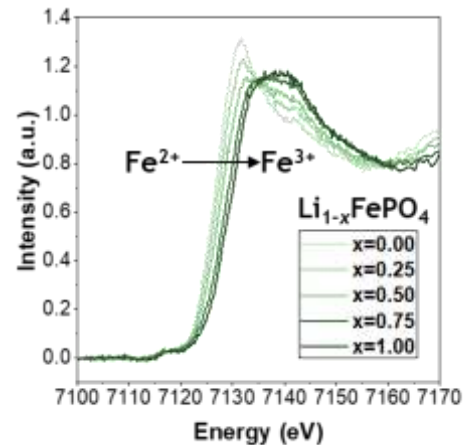
**Figure 3.** X-ray transmission through various combinations of pouch cell and holder components in the energy window coincident with the Fe K-edge absorption.

Prior to XAS measurements, cells are galvanically cycled three times at C/10 (300  $\mu$ A) from 2.5 to 4 V, ending in the discharged state. This step is performed to precondition the cell and ensure that the expected capacity (9.5 mAh) is achieved. The discharged cell is then charged in increments of 25% capacity at 300  $\mu$ A with each charge step followed by relaxation at open circuit for 2.5 h, during which time XAS data are collected (Figure 4).

Upon charging, iron sites in LiFePO<sub>4</sub> oxidize from Fe<sup>2+</sup> to Fe<sup>3+</sup>, accompanied by removal of Li<sup>+</sup> for charge compensation. Prior reports from synchrotron-based XANES measurements<sup>7,8</sup> show that oxidation of LiFePO<sub>4</sub> shifts the Fe K-edge positive and alters the shape of the white line. We observe similar results in Fe K-edge behavior at comparable energy resolution during in situ analysis of our pouch cells using the laboratory-based X-ray absorption spectrometer (Figure 5). The analysis of the extended fine structure is underway for comparison to DFT computation.



**Figure 4.** Electrochemical conditions for XAS data collection on a pouch cell: (top) Charge/discharge pre-conditioning; (bottom) charge profile and operation scheme.



**Figure 5.** Iron K-edge XANES of a lithium-ion battery pouch cell containing LiFePO<sub>4</sub> as a function of state of charge (SOC).

## Conclusion

In-lab X-ray absorption spectroscopy at the NRL enables facile, walk-up XANES and EXAFS measurements of a functional battery cell. We can now routinely observe the oxidation state of and local environment in energy-relevant materials without the need for synchrotron beam time and expense. We expect these new capabilities will expand fundamental understanding in such fields as electrochemical energy storage and catalysis.

## Acknowledgements

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## References

1. J. Singh, C. Lamberti, and J.A. van Bokhoven. Advanced X-Ray Absorption and Emission Spectroscopy: In Situ Catalytic Studies. *Chem. Soc. Rev.*, **2010**, *12*, 4754.
2. Q. Gu, J.A. Kimpton, H.E.A. Brand, Z. Wang, and S. Chou. Solving Key Challenges in Battery Research Using in situ Synchrotron and Neutron Techniques. *Adv. Energy Mater.*, **2017**, *7*, 1602831.
3. G.T. Seidler, D.R. Mortenson, A.J. Remesnik, J.I. Pacold, N.A. Ball, N. Barry, M. Styczinski, and O.R. Holden. A Laboratory-Based Hard X-Ray Monochromator for High-Resolution X-Ray Emission Spectroscopy and X-Ray Absorption Near Edge Structure Measurements. *Rev. Sci. Instrum.*, **2014**, *85*, 113906.
4. D.R. Mortenson, G.T. Seidler, A.S. Ditter, and P. Glatzel. Benchtop Nonresonant X-Ray Emission Spectroscopy: Coming Soon to Laboratories and XAS Beamlines Near You? *J. Phys.: Cong. Ser.*, **2016**, *712*, 012036.
5. E.P. Jahrman, W.M. Holden, A.S. Ditter, D.R. Mortenson, G.T. Seidler, T.T. Fister, S.A. Kozimor, L.F.J. Piper, J. Rana, N.C. Hyatt, and M.C. Stennett. An Improved Laboratory-Based X-Ray Absorption Fine Structure and X-Ray Emission Spectrometer for Analytical Applications in Materials Chemistry Research. *Rev. Sci. Instrum.*, **2019**, *90*, 024106.
6. B. Ravel and M. Newville. ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-Ray Absorption Spectroscopy Using IFEFFIT. *J. Synchrotron Rad.*, **2005**, *12*, 537.
7. C.T. Love, A. Korovina, C.J. Patridge, K.E. Swider-Lyons, M.E. Twigg, and D.E. Ramaker. Review of LiFePO<sub>4</sub> Phase Transition Mechanisms and New Observations from X-ray Absorption Spectroscopy. *J. Electrochem. Soc.*, **2013**, *160*, A3153.
8. S. Pongha, B. Seekoan, W. Limphirat, P. Kidhuthod, S. Srilomsak, Y.-M. Chiang, and N. Meethong. XANES Investigation of Dynamic Phase Transition in Olivine Cathode for Li-Ion Batteries. *Adv. Energy Mater.*, **2015**, *5*, 1500663.