

Rapid Characterization of Energy Materials using a Lab-Based XAS Spectrometer

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Developing the next generation of energy generation and energy storage materials requires rapid feedback from informative and accessible characterization tools. An excellent example of this is the use of X-ray absorption fine structure (XAFS) measurements to sample the state-of-charge and state-of-health of candidate Li-ion batteries. Here, concerted research efforts in the battery field have established XAFS as a powerful tool for identifying charge compensation mechanisms, tracking the utilization of active materials, monitoring oxidation state inhomogeneities, and quantifying reversible and irreversible bond length changes. Indeed XAFS, is often viewed as the premier technical capability for these purposes. However, the scientific impact of XAFS is necessarily constrained by the availability of instrumentation. In part, this is because XAFS studies are typically performed at synchrotron light sources. These facilities are the product of large financial investments and, thus, understandably finite resources. Consequently, access to synchrotron light sources is allocated according to infrequent and competitive proposal processes that select for projects of high societal impact that will push the forefront of science. This has enabled an extraordinarily large body of fantastic studies across a wide range of disciplines, but, out of necessity, has excluded many applications that are not amenable to this access model. In the area of energy materials discovery and development, such underserved applications include: rapid feedback for prototyping of new chemistries, especially in the areas of energy storage and catalysis where compositions, morphologies, and synthesis conditions are constantly refined to obtain optimal performance; prolonged studies of failure mechanisms such as those underlying battery fatigue; and end-of-line routine analytical characterizations for quality assurance and regulatory compliance testing.

Over the last half decade, many of the above authors have developed several classes of laboratory-based instruments to expand the accessibility of advanced x-ray spectroscopies. For the study of transition metal chemistry, we have constructed two Rowland circle spectrometers based upon related designs. The operating principles and capabilities of these spectrometers have been thoroughly documented in the literature. This was accomplished via a multitude of X-ray absorption near edge structure (XANES) measurements of materials ranging from 3d-transition metals to actinides, extended X-ray absorption fine structure (EXAFS) of model systems, and a large body of X-ray emission spectroscopy (XES) studies. The demonstrated performances recommend these tools to serve not as competitors, but as a crucial complement to current synchrotron-based research, particularly by providing regular, rapid answers to material research problems that do not require the full and exceptional range of capabilities found at a synchrotron light source facility.

This presentation will include a brief review of the present instrument design with an emphasis on practical performance metrics. The majority of discussion will then be dedicated to applications in energy materials. This will include two brief examples of representative results from supercapacitors and nanoparticle catalysts. Here, lab-based XAS was able to meet the needs of these materials researchers when the desired information was not available from other benchtop techniques and rapid feedback was required. Finally, the highlight of the talk will be a recent study in which an unmodified pouch cell was cycled at rates from C/5 to 3C. In this study, the evolving chemistry of the Ni-rich NMC cathode was measured via lab-based *operando* XANES measurements. At all charge rates, the Ni atoms exhibited continuous involvement in the charge compensation process. Indeed, the Ni K-edge showed a uniform, linear shift in edge position recommending Ni K-edge XANES in rapid, *in situ* state-of-charge analyses. Additional discussion will address the Mn and Co K-edge results as well as likely state-of-health signatures. Appropriate attention will be given to experimental design of lab-based XAS studies throughout the above discussions.