Tracking battery oxidation state changes with lab XANES

Application Note

By Dr. Srivatsan Seshadri, Dr. Ruimin Qiao, Sylvia Lewis | Sigray. Inc

Abstract

Initially developed in synchrotron facilities, XANES has demonstrated its powerful capability in analyzing battery materials, especially for determining the chemical states of the battery cathode materials. Sigray QuantumLeap is the first laboratory system that provides synchrotron-like XANES capabilities. In this application note, $LiFePO_4$ batteries were investigated using Sigray QuantumLeap™ to track chemical state changes during charge/discharge states with a ~0.5 eV energy resolution.

Introduction

Batteries are ubiquitous in modern world, which have been deployed in different aspects of our daily life, from various portable electronic devices to electric vehicles and large-scale stationary energy storage [1]. The core of any battery is a type of electrochemical reaction, involving changes of the chemical states of the electrode materials. Consequently, determining the influence of different material preparations, cell assemblies, and operation conditions on the chemical state of electrode material is critical to understand and optimize the battery design. X-ray absorption near edge spectroscopy (XANES) is a powerful technique used frequently for chemical state analysis. XANES measures the slight changes in the absorption characteristic of elements based on its chemical state.

A new laboratory approach

The Sigray QuantumLeap™ x-ray absorption spectroscopy (XAS) system is the first laboratory instrument with synchrotron-like XANES capabilities. The system provides a wide range of x-ray energies, ranging from 2.1-12 keV, for both modes of x-ray absorption spectroscopy: XANES (providing local information such as chemical state, atomic symmetry, etc.) and EXAFS (providing neighboring atomic information such as bond lengths, coordination number, etc.).

Unlike conventional lab or even synchrotron XAS, the QuantumLeap uses a patented single-acquisition approach rather than the time-consuming crystal stepping method that requires multiple acquisitions. Both high energy resolution (sub-eV) XANES and high throughput EXAFS are possible.

In this study, the energy resolving capability of QuantumLeap to differentiate the chemical states of Fe in $LiFePO_4$ batteries is demonstrated.

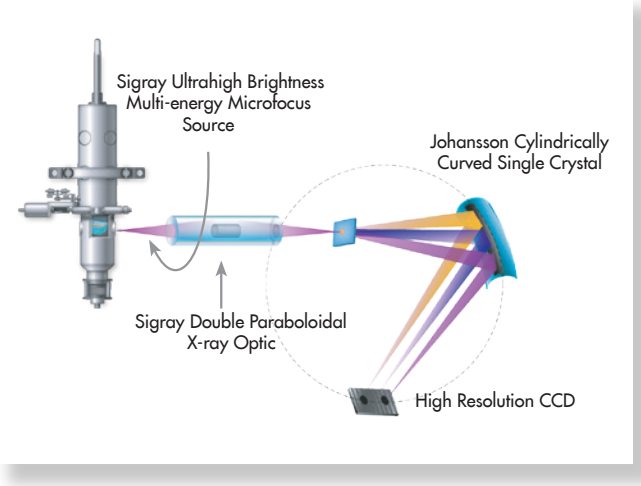

Figure 1: QuantumLeap's XANES off-Rowland geometry: Sample is placed within the Rowland circle to enable simultaneous detection of multiple wavelengths (vs. conventional energy scanning approach, which is lower throughput). High energy resolution of <0.5 eV is achieved by using Johanson crystals coupled with a high resolution CCD.

Experiment and results

Lithium Iron Phosphate battery

Lithium iron phosphate ($LiFePO_4$) batteries, which use $LiFePO_4$ in the cathode material, have been commercially mass-produced for applications in portable equipment, transportation vehicles, utility scale stationary electric energy storage and others. It has been presented as a low cost, low toxicity, and intrinsically safer cathode material [2].

In the present study, two $LiFePO_4$ cathodes were analyzed: the pristine marked as "NEW" and the cycled marked as "AGED." The cathodes were directly delayered from the current collector and placed on the sample stage. Sigray's patented multi-target microfocus source coupled to a high efficiency condenser lens was employed to focus the x-rays onto the sample. The transmitted x-rays were collected by a Johansson crystal spectrometer operated in an off-Rowland circle geometry for simultaneous acquisition of XANES data centered around the K-alpha absorption edge of Fe (7.11keV). The dispersed x-rays from the crystal were collected utilizing a high DQE 2D direct detection CCD. A data collection schematic is shown in Figure 1.

Quantum Design EUROPE
Quantum Design GmbH
Breitwieserweg 9
D-64319 Pfungstadt
Dr. Andreas Bergner: +49 6157 80710-12
bergner@qd-europe.com
Find your local contact at: www.qd-europe.com
SIGRAY

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The XANES spectra were collected at 0.5 eV pixel energy resolution. The evolving iron oxidation states were clearly captured by the changed absorption features, especially the energy shifts, shown on the XANES spectra, which is consistent with synchrotron data available in the literature [3]. By comparing samples in these two states, researchers are afforded unique insight into the long-term oxidation state evolution of these electrodes. X-ray radiation, non-destructive in nature, may thus be applied could conceivably be thus be used to track this evolution over time, examining the changing oxidation states throughout the lifetime of a long cycle-life $LiFePO_4$ battery.

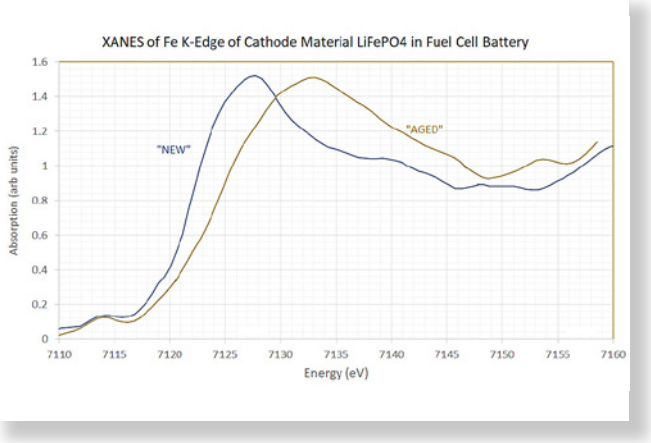

Figure 2: XANES spectra of $LiFePO_4$ cathodes at different charge/discharge states. QuantumLeap-210 scaled acquisition time and energy resolution for each cathode sample are 3 hours @ ~0.5 eV.

Summary

Sigray QuantumLeap has demonstrated synchrotron-like capabilities for analyzing chemical states of lithium iron phosphate battery electrode materials, with high throughput and energy resolution of <0.5 eV for XANES. The difference between pristine and aged batteries was identified through a shift in the absorption profile, which indicated a change in the oxidation state. Further studies employing this technique may track the evolution of a single electrode over time, providing precise tracking of the oxidation state evolution throughout the lifetime of a battery electrode.

References

1. US Department of Energy report: "Basic Research Needs for Electrical Energy Storage" 2007.
2. JB Goodenough, et al. "The Li-ion rechargeable battery: a perspective." Journal of The American Chemical Society Vol. 135, Issue 4 (2013): 1167-1176.
3. A Deb, et al. "Structural investigations of LiFePO4 electrodes and in situ studies by Fe x-ray absorption spectroscopy." Electrochimica Acta Vol. 50 (2005): 5200-5207.

Quantum Design EUROPE
Quantum Design GmbH
Breitwieserweg 9
D-64319 Pfungstadt
Dr. Andreas Bergner: +49 6157 80710-12
bergner@qd-europe.com
Find your local contact at: www.qd-europe.com
SIGRAY