Applications Note

QuantumLeap XAS

Analyses of Observed Speciation of Cobalt in NMC Cathodes Using Laboratory XAS

We report the X-ray Absorption Spectroscopy (XAS) investigation of four samples of NMC electrodes using QuantumLeap™ H2000. Co XANES shows three isosbestic points. Principal component analysis (PCA) and Iterative Target Transformation Factor Analysis (ITTFA) reconstructions of the experimental X-ray Absorption Near Edge Structure (XANES) indicate that two of the samples contain two unique species of Co. In the remaining samples, the speciation of Co can be described by the linear combinations of the two distinct species, further validating the synchrotron-like performance of QuantumLeap™.

This applications note discusses battery science enabled by Sigray QuantumLeap XAS.

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Analyses of Observed Speciation of Cobalt in NMC cathodes Using Laboratory X-ray Absorption Spectroscopy (XAS)

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Background: Continuing to meet the pace of global energy demand necessitates higher performance, lower cost, and environmentally-friendly energy storage technologies, including stationary energy storage solutions for power grids and electric vehicles. Lithium-ion batteries with high energy density are promising candidates, not only for electric vehicles but also for grid applications to efficiently store energy harvested from wind, solar, and other renewable sources. To achieve these goals, various chemistries are being explored to develop advanced materials for electrodes and electrolytes that can deliver higher capacity, energy density, operating voltages, structural stability, electron-transfer rates, safety, and lower cost.

X-ray absorption spectroscopy (XAS) provides a powerful element-specific probe to investigate the oxidation state, short-range structural and coordination environments, enabling scientists to understand the complex chemistries of these newly developed electrode materials as prepared and under real operating conditions. XAS is predominantly performed at synchrotron facilities because they provide high-brightness tunable energy X-ray beams [1,2]. However, limited beamtime availability restricts the use of synchrotrons as a routine technique for most research groups, particularly those in industry. Laboratory-based XAS instruments such as Sigray QuantumLeap enable academic and industrial researchers to perform routine measurements and analyses, enhancing research productivity and shortening the time required to develop novel high-efficiency electrode systems.

Novel Approach: Sigray QuantumLeap XAS

Sigray's QuantumLeapTM H200 is a laboratory XAS instrument that provides synchrotron-like capabilities and features:

- A patented ultrahigh brightness X-ray source
- Wide energy range coverage from 4.5 to 25 keV
- Cylindrically curved Johansson crystals
- A highly efficient data acquisition approach
- Both transmission and fluorescence mode measurement options which allow analyzing samples with concentrations as low as 0.1% wt
- Customizability to enable operando experiments under various environments

Method

Four NMC samples were analyzed on the QuantumLeap H2000 using a Ge(331) crystal. Co K-edge measurements were performed in fluorescence mode due to Co's low concentration (~3-5 wt.%) in the NMC electrodes. For all samples, a quick XANES scan ~300 eV from the Co-K edge was chosen. The results obtained were processed in the QuantumLeap GUI and then imported into the Athena program suite of the IFEFFIT package [3] for further analysis. The data from Athena were exported and then analyzed for the principal component analysis (PCA), least squares fitting, and iterative target transformation factor analysis (ITTFA).

Experiments and Results

Co-K edge XANES spectra for all four samples (numbered S1S1, S1S2, S1S3, and S1S4) were collected over 8 hours and are shown in Fig. 1. The XANES for the four samples clearly display three isosbestic points (Fig. 1A), indicating the presence of two distinct species of cobalt. Furthermore, since the S1S1 and S1S2 samples — shown in blue and red — represent the most reduced and oxidized species, respectively, we explore the possibility that the remaining two Co species in S1S3 and S1S4 could be linear combinations of these existing two species.

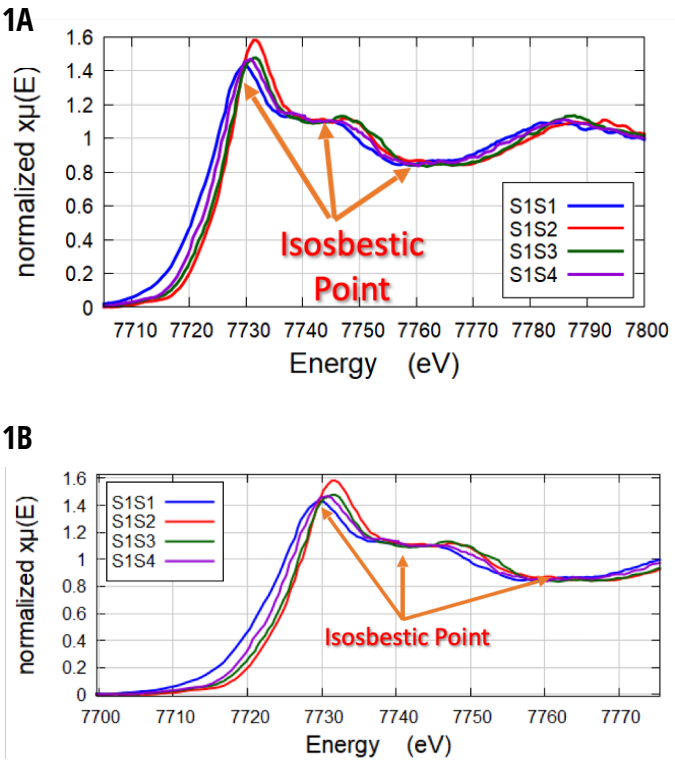

Figure 1: Co-K edge XANES of NMC electrodes prepared under different conditions of thermal treatment and coating conditions (1A). A zoomed view of the XANES region is bottom (1B).

To investigate this, we performed a least squares linear combination fit (LCF) with S1S1 and S1S2 as references for S1S3 and S1S4. As shown in Fig. 2, S1S3 (Fig. 2A) can be represented as a linear combination of 23.5% S1S1 and 76.4% S1S2, while S1S4 (Fig. 2B) is composed of 56.5% of S1S1 and 43.5% of S1S2.

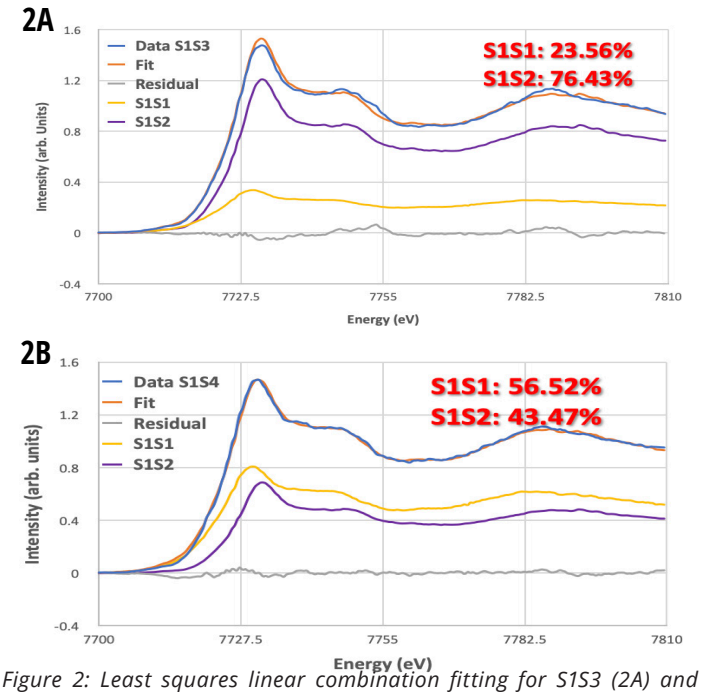

Figure 2: Least squares linear combination fitting for S1S3 (2A) and S1S4 (2B). For the fits, S1S1 and S1S2 XANES were used as principal components for the linear combination.

Principal component analysis (PCA) [4] of the Co XANES spectra was conducted over the energy range of 7673-7810 eV. The PCA cumulative variance plot (Fig. 3A) shows that with just two components, 99.98% (dashed red line) of the spectral variance from the four samples can be accounted for. Additionally, the PCA scree plot (Fig. 3B) confirms that there are only two unique cobalt components (red line) present in the samples, further validating the LCF analysis indicating that all observed electrode XANES spectra primarily consist of two principal cobalt components.

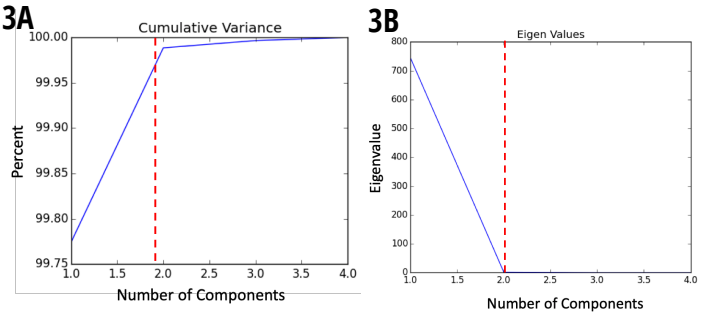

Figure 3: Cumulative variance of the PCA analysis (3A). Scree plot for the PCA analysis (3B). Both the Cumulative variance and the scree plot shows that there are 2 principal components of cobalt (red dash line) for all the NMC electrode samples studied here.

Iterative target transform factor analysis (ITTFA) [5] was then applied to align the components obtained from PCA with the real experimental XANES data. The ITTFA reconstructed XANES spectra for the unique cobalt species are shown in Fig. 4.

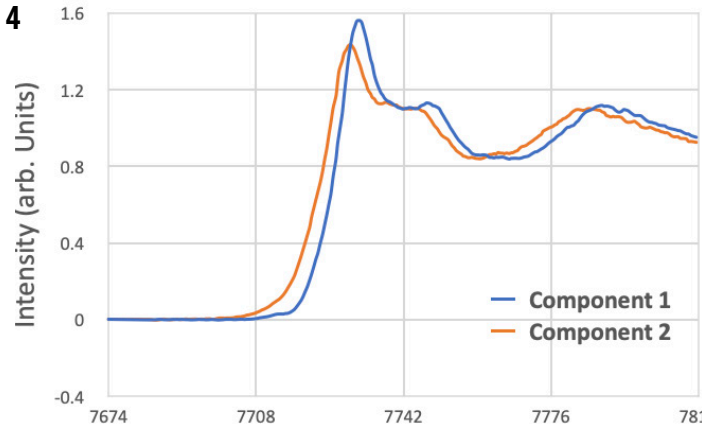

Figure 4: ITTFA reconstructed experimental two principal XANES components (component 1 in blue and component 2 in orange) of cobalt investigated in the series of NMC electrode samples.

The PCA components (components 1 and 2) derived from ITTFA (shown in Fig. 4) were used to perform a least squares linear combination fit to the experimental XANES of each NMC electrode sample, allowing for the determination of the fractional composition of each component. The fitting results using the PCA components are summarized in Table 1.

Sample	PCA Component 1 (in %)	PCA Component 2 (in %)
S1S1	0	99.95
S1S2	96.36	3.73
S1S3	74.60	25.16
S1S4	41.92	58.94

Table 1: Least squares linear combination fits using the PCA

Based on the PCA analysis and the ITTFA component fit results in Table 1, we find that S1S1 closely resembles PCA component 2 (with 99.95%), representing one of the unique Co species, while S1S2 resembles PCA component 1 (96.36%), Samples S1S3 and S1S4 are comfirmed to be linear combinations of S1S1 and S1S2. These PCA linear combinations for S1S3 and S1S4 are also consistent with the earlier linear combination least squares fitting shown in Fig. 2.

Summary

The investigation of the NMC electrode series using the Sigray QuantumLeap H2000 revealed the isosbestic points in the cobalt XANES. PCA analysis and ITTFA reconstruction confirmed the presence of two unique cobalt species within tNMC electrodes series studied. ITTFA's PCA component 1 corresponds closely to the XANES spectra of S1S2, while PCA component 2 aligns with spectra of S1S1, as further demostrated by the quantitative data presented in Table 1. The agreement between the linear combination fits for S1S1 and S1S2 and the PCA analysis strongly supports the conclusion that there are two unique cobalt species present in this series of NMC electrodes.

1. A. Deb, et al. X-ray absorption spectroscopy study of the LixFePO$_4$ cathode, J. Synchrotron Rad. 11 (2004) 497-504.
2. W.-S Yoon, et al. In Situ X-ray Absorption Spectroscopic Study on LiNi$_{0.5}$Mn$_{0.5}$O$_2$ Cathode, Chem. Mater. 15 (16) (2003).
3. B. Ravel and M. Newville, ATHENA, ARTEMIS, HEPHAESTUS, J. Synchrotron Rad. 12 (2005) 537–541.
4. I.T. Jolliffe and J. Cadima, Principal component analysis: a review. Phil. Trans. R. Soc. A. 374 (2016) 20150202.
5. A. Roßberg, T. Reich and G. Bernhard, Complexation of uranium(VI), Anal. Bioanal. Chem. 376 (5) (2003) 631–638.

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