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 show three isosbestic points. Principal component analysis (PCA) and Iterative Target Transform Factor Analysis (ITTFA) reconstruction of the experimental X-ray Absorption Near Edge Structure (XANES) show 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, validating QuantumLeap's synchrotron-like performance.

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 mobile energy storage solutions for electric vehicles. Lithium-ion batteries with a 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, different chemistries are being explored to develop new 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, allowing scientists to understand the complex chemistries at the atomic level of these newly developed electrode materials as prepared and under real operating conditions. XAS is predominantly performed at synchrotron facilities because they provide tunable energy X-ray beams of high brightness [1,2]. However, scarce beamtime availability limits the scope of their use as a routine technique for most research groups, particularly for researchers in industry. Laboratory-based XAS instruments such as Sigray QuantumLeap enable academic and industrial researchers to perform routine measurements and analyses to increase their research productivity and shorten the time scales involved to develop novel high efficiency electrode systems.

Novel Approach: Sigray QuantumLeap XAS

Sigray's QuantumLeap™ 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, and
- Customizability to enable *operando* experiments under various environments.

Method

Four NMC samples were acquired on QuantumLeap H2000 using a Ge(331) crystal. Co K-edge measurements were performed in the 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 to 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 at 8 hours and are shown in Fig. 1. We can clearly see that the XANES for the four samples show three isosbestic points (Fig. 1A). The three isosbestic points qualitatively indicate the presence of two distinct species of cobalt. Furthermore, since S1S1 and S1S2 samples shown in blue and red represent the most reduced and oxidized species, it allowed us to explore the possibility that the remaining two Co species in S1S3 and S1S4 are a linear combination of the existing two species.

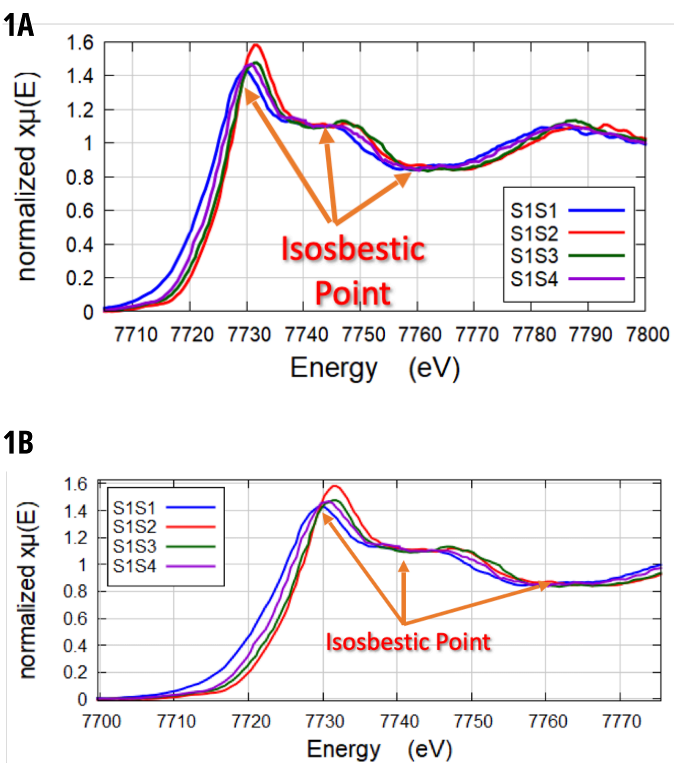

Figure 1: Co-K edge XANES of NMC electrodes prepared under different conditions of thermal treatment and coating conditions (1A). A zoomed view of the XANES region is bottom (1B).

To answer this, we performed a least squares linear combination fit (LCF) with S1S1 and S1S2 to S1S3 and S1S4 respectively. As shown in Fig. 2, S1S3 (2A) can be represented as a linear combination of 23.5% S1S1 and 76.4% S1S2, while S1S4 (2B) shows the linear combination of 56.5% of S1S1 and 43.5% of S1S2.

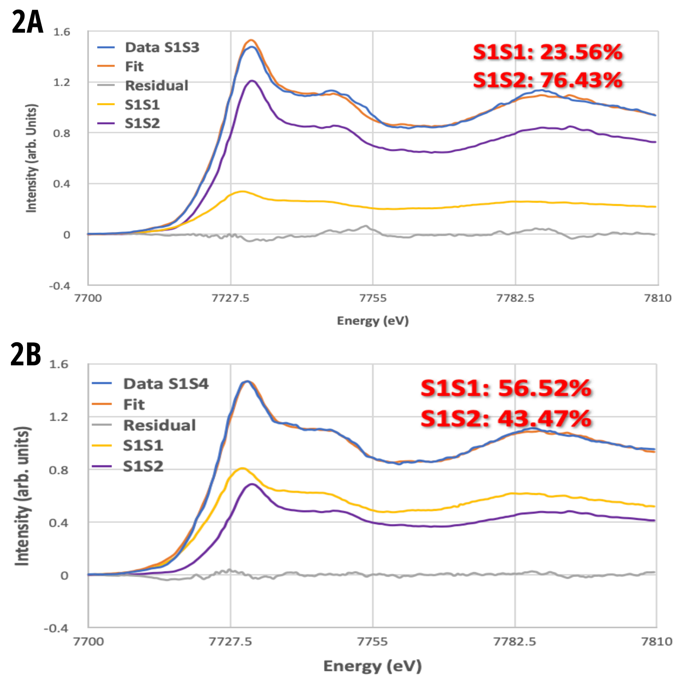

Figure 2: Least squares linear combination fitting for S1S3 (2A) and S1S4 (2B). For the fits, S1S1 and S1S2 XANES were used as principal components for the linear combination.

Principal component analysis (PCA) [4] of Co XANES was performed over the XANES energy range of 7673-7810 eV. The PCA cumulative variance, shown in Fig. 3A, shows that with only 2 components, 99.98% (dashed red line) of the spectra from 4 samples can be accounted for, while the PCA scree plot (Fig. 3B) also shows that there are only two unique components of cobalt (red line) present in the samples further validating the LCF analysis that there are mainly 2 principal cobalt components for all of the observed electrode XANES.

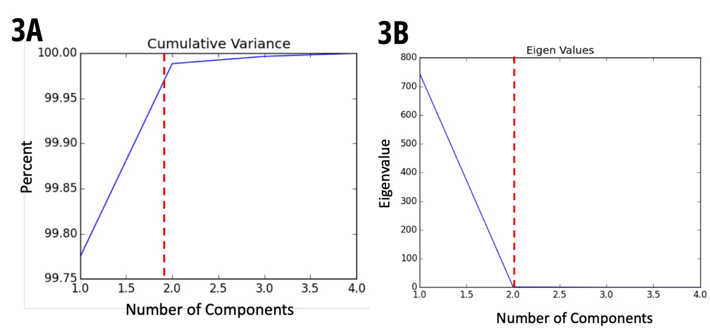

Figure 3: Cumulative variance of the PCA analysis (3A). Scree plot for the PCA analysis (3B). Both the Cumulative variance and the scree plot shows that there are 2 principal components of cobalt (red dash line) for all the NMC electrode samples studied here.

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

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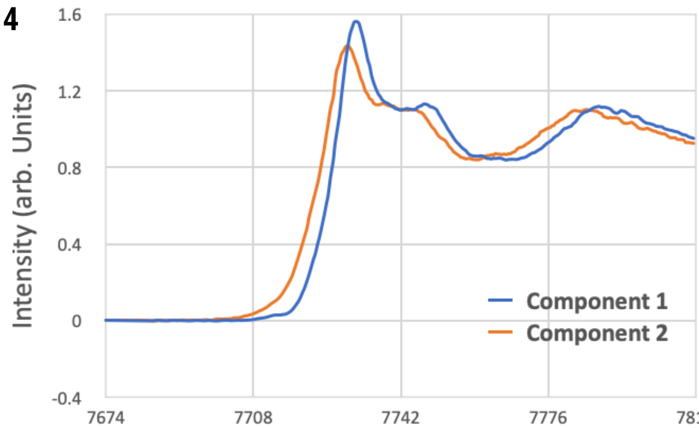
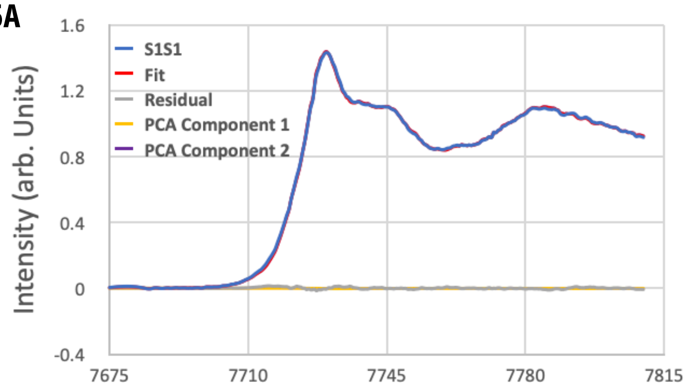


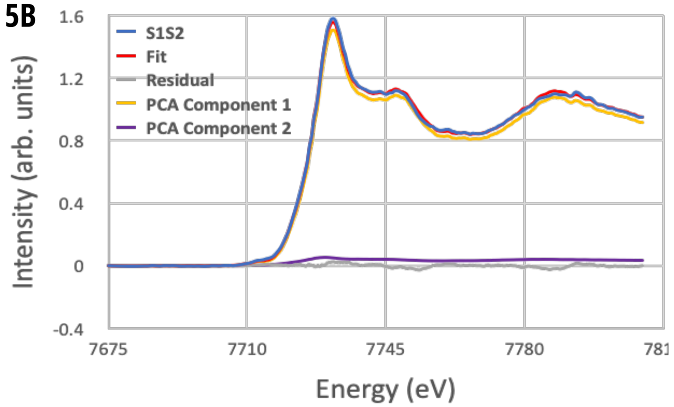
Figure 4: ITTFA reconstructed experimental two principal XANES components (component 1 in blue and component 2 in orange) of cobalt investigated in the series of NMC electrode samples.

The PCA components (components 1 and 2) that were obtained from ITTFA (shown in Fig. 4) were utilized to perform a least squares linear combination fit to the experimental XANES for each of the NMC electrode samples, from which the fractional composition of each component was determined. The results of the fit for each of the NMC electrodes as shown in Fig. 5. The fit results with the PCA components are shown in Table 1.

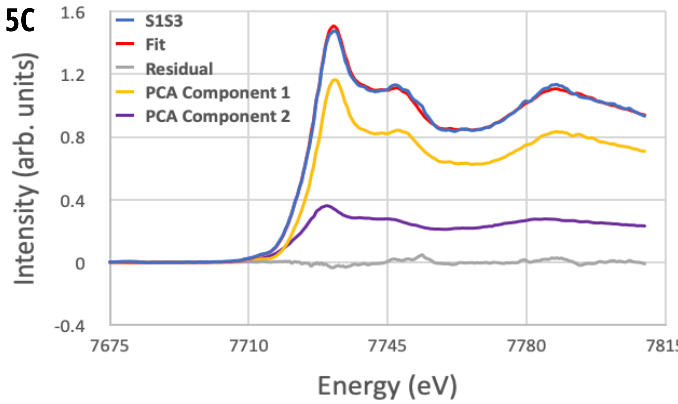
5A



5B



5C



5D

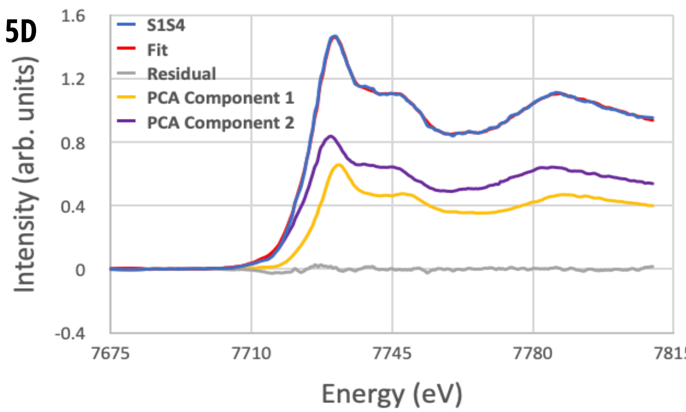


Figure 5: Least squares linear combination fit using the ITTFA PCA components 1 and 2 shown previously in Figure 4. Fit results of the sample are as follows: S1S1 in 5A, S1S2 in 5B, S1S3 in 5C, and S1S4 in 5D. Colors: The data is shown in blue, fit in red, residual (difference between the data and the fit) in gray. PCA component 1 is shown in yellow and PCA component 2 is shown in purple.

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 components

From the PCA analysis and the ITTFA component fit results in Table 1, we see that S1S1 resembles the PCA component 2 (with 99.95%) as one of the unique Co species and S1S2 resembles PCA component 1 (with 96.36%), while S1S3 and S1S4 are linear combinations of S1S1 and S1S2. These PCA linear combinations for S1S3 and S1S4 (Table 1) are also in good agreement with the results that were obtained earlier by the linear combination least squares fit shown in Fig. 2.

Summary

Investigation of the series of NMC electrodes using Sigray QuantumLeap H2000 shows the isosbestic points in the cobalt XANES. PCA analysis and the ITTFA reconstruction of the experimental XANES show that there are two unique species of cobalt in the series of NMC electrodes that were studied. The ITTFA PCA component 1 shows that it resembles the XANES spectra of S1S2 while the PCA component 2 resembles the XANES spectra of S1S1. This is also evident from the quantitative analysis shown in Table 1. Both linear combination fits of samples S1S1 and S1S2 and the PCA analysis are in agreement and show that there are two unique species of cobalt present in this series of NMC electrodes.

The above results demonstrate the synchrotron-like capabilities of laboratory-based QuantumLeap to produce the quality of data required for detailed and accurate analyses using PCA and ITTFA analysis (in this case, to understand the cobalt speciation in NMC electrodes).

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