Observing Lithium Ion Battery Bonds During Charge Cycling Using Laboratory XAS

X-ray Absorption Spectroscopy (XAS) analyses of results obtained with the QuantumLeap for low-Co (<3-5 wt%.) Li-ion NMC batteries is presented. High-quality EXAFS was obtained for Mn and Ni in transmission mode, while Co was obtained using fluorescence mode. Mn-O and Co-O bonds showed reversible/minimal changes, while Ni-O showed Jahn-Teller distortion, indicating different Ni oxidation states.

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

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Observation of Jahn-Teller Distortion Effect on Ni-O bonds in Lithium Based NMC batteries during cycling process using QuantumLeap

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Background: A sustainable future with renewable energy requires development of efficient energy storage systems with high-energy density that are both competitive and cost effective when compared with currently used energy sources like natural gas, coal, and oil. Lithium-ion batteries (LIBs) have attracted the technological market due to their promise of high energy density of ~800 Wh/kg. In LIBs, the intercalation of lithium ions (Li+) affects the atomic and electronic structure of the cathode material. This intercalation effect between the electrodes (cathode and anode) exploits diverse and complex chemistries that need to be understood at the atomic level to enable designing efficient electrode systems with excellent electrochemical behavior, energy density, and cycling behavior that correlates with better life cycles.

X-ray absorption spectroscopy (XAS), a powerful technique that provides element-specific short-range structural and coordination environments, allows scientists to investigate the influence of repeated cycling of the electrode on the oxidation state, coordination environment, and structural changes. To date, XAS is predominantly performed at synchrotron facilities because they provide tunable-energy x-ray beams with high brightness [1,2]. However, difficult accessibility, limited beamtime, and challenging logistic issues limit the scope of their use and preclude the possibility of using them for routine measurements. Laboratory-based XAS instruments, such as Sigray QuantumLeap, can enable academic and industrial researchers to perform routine measurements and analyses to shorten the time scales involved to developing novel high-efficiency electrode systems.

Novel Approach: Sigray QuantumLeap XAS

Sigray's QuantumLeap^{TM} is a laboratory x-ray absorption spectroscopy (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 allowing analyzing samples with concentrations as low as 0.1 wt%
- flexibility to enable *operando* experiments under various environments

Method

All data were acquired on the QuantumLeap using a Ge(331) crystal. Co K-edge measurements were made in fluorescence mode due to its low concentration (~3-5 wt.%), while the Mn and Ni edges were measured in transmission mode. For all measurements, a k-range of ~12 was chosen. Acquisition times were deliberately kept long (details given in the next section) to achieve very high Signal-to-Noise Ratios (SNR) for accurate analyses. However, the acquisition times can be reduced by >3X for quick measurements and qualitative analyses. The obtained results were processed in the QuantumLeap GUI and then imported into the Athena and Artemis program suite of the IFEFFIT package [3] for further analysis.

Experiments and Results

The Mn K-edge spectra for a fully charged and discharged electrode were collected over 12 hours (Figure 1). The weak pre-edge feature at ~6543 eV is clearly visible due to the high SNR in the data.

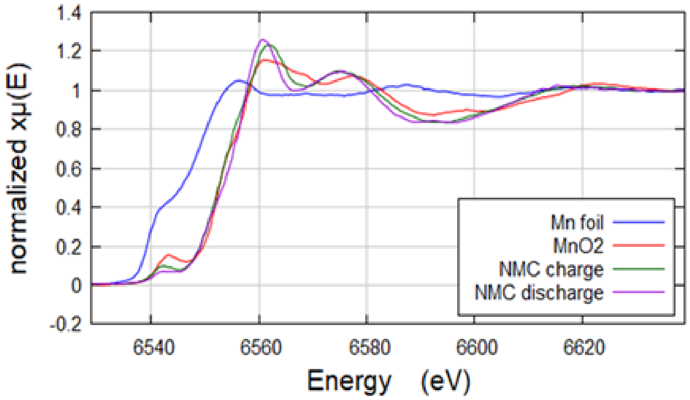

Figure 1: *Mn-K edge of NMC electrodes fully charged and discharged. Comparison of the MnO2 model and Mn foil oxidation states shows that Mn in NMC are in an oxidation state of ~4+. The absorption edge energy does not change much showing that Mn acts as a spectator during cycling.*

The weak pre-edge feature observed for both charged and discharged states is indicative of the retention of the octahedral coordination environment (MnO6), as opposed to the tetrahedral environment, which would result in a strong pre-edge intensity. The Mn-edge between the charged and discharged electrodes did not show any significant rigid shift in energy. This signifies that Mn almost acts as a spectator or is electrochemically inactive during the cycling process, while the small changes observed in the shape of the Mn-spectra suggest a possible change in the local structure around the Mn atom. XANES shows good agreement between the observed Mn-edge energy and the model compound (MnO2), suggesting that Mn is in a state of Mn4+ during cycling.

Figures 2 and 3 show the XAS data for the Co K-edge, measured in the fluorescence mode. The concentration of Co is around 3-5% by weight, and about 18 hours of acquisition were required to obtain high SNR EXAFS data up to k=11.

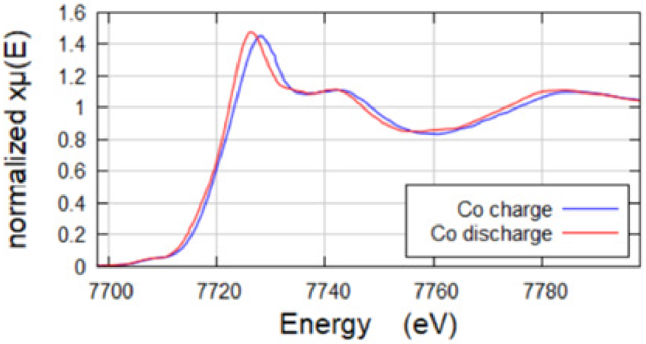

Figure 2: *Low concentration of Co ~3-5% by wt.% in NMC electrodes charged and discharged. Only about 100eV of the scan is shown.*

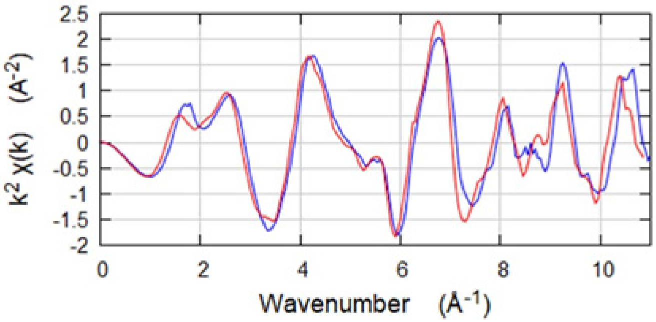

Figure 3: *EXAFS of low concentration of Co ~3-5% by wt.% in NMC electrodes charged (blue) and discharged (red).*

The Fourier transform (FT) magnitude for Mn and Co in NMC are shown in Figures 4 and 5, respectively.

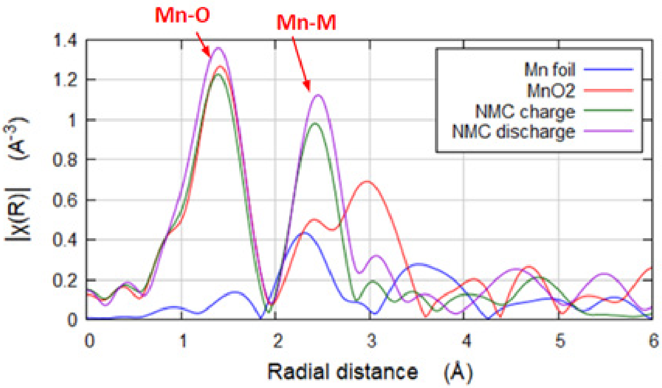

Figure 4: *Mn K-edge FT-EXAFS of NMC along with model systems showing the main peak at ~1.5 Å (uncorrected phase) corresponding to Mn-O bond and the second peak at ~2.3 Å corresponding to Mn-M bond*

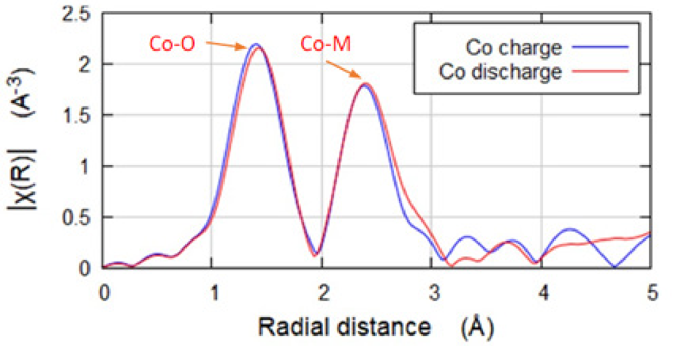

Figure 5: *FT-EXAFS of Figure 3, showing the comparison of the charged and discharged state of the NMC electrodes.*

In both figures 4 and 5, the first peak ~1.4 Å is attributed to the Mn-O/Co-O interactions, while the second peak at ~2.3 Å (non-phase shifted) is due to the M–M (metal-metal) interactions. For both Mn and Co, the first peak did not show any drastic shift between the charge and discharge states, which indicates reversible/minimal changes in the Mn-O/Co-O distances during cycling. However, as seen in Figure 6, the first peak attributed to the Ni-O shows a change, with the Ni-O bond distance increasing in the discharged sample (from 1.3 Å to 1.7 Å, non-phase shifted).

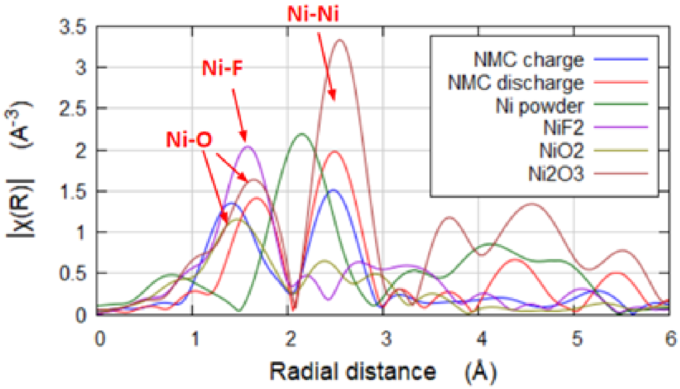

Figure 6: *FT-EXAFS of Ni in NMC, showing the comparison of the charged and discharged state of the NMC electrodes along with the model systems.*

This bond-length change beween charged and discharged states is consistent with the fact that, when charged, the nickel goes to the form of ~Ni4+, which is non-Jahn–Teller and does not undergo from Jahn–Teller distortion, resulting in a shorter Ni4+-O bond distance(~1.3 Å). On the contrary, in the discharged sample, there might be some presence of Ni in Ni3+ or a mixture of Ni3+/Ni2+ states. Since Ni3+ is Jahn–Teller active, the discharged sample shows a longer Ni3+-O bond distance of ~1.7 Å. The shorter Ni-O bond distance seen in Figure 6 for the charged sample can also be explained by the oxidation state picture, as Ni4+ in the charged sample has a shorter ionic-radii (0.46 Å) compared to the discharged sample with Ni2+/Ni3+ having a larger ionic-radii (0.69 Å/0.56 Å).

We can also see that the Fourier Transform (FT) *amplitude* of the first shell remains the same (Figure 6) for both charged and discharged samples, signifying that the local Ni-O coordination environment is preserved during cycling. However, the FT amplitude of the second peak (~2.3 Å) is not the same for charged and discharged states, indicating that the Ni-Ni coordination environment may have changed during cycling.

Summary

Studies of the current set of Li-ion NMC battery samples using the Sigray QuantumLeap was performed using both fluorescence (for Co) and transmission mode XAS (for Ni and Mn). Results show that Mn is electrochemically inactive and in octahedral coordination. The bond lengths of Mn-O and Co-O are shown to change minimally during the charge-discharge cycles. The Ni-O bond length changes due to Jahn-Teller distortion, indicating different Ni species between the charged/discharged samples. Local environment changes are not observed for Ni-O, but they are seen in for Ni-Ni. The above results demonstrate the synchrotron-like capabilities of a laboratory XAS tool in producing the quality of data required for detailed and accurate analyses to understand the NMC electrode's behavior under cycling conditions.

1. WS Yoon, CP Grey, M Balasubramanian, XQ Yang and J McBreen, Chemistry of Materials 15 (2003) p. 3161-3169.
2. J Timoshenko, D Lu, Y Lin, and AI Frenkel, The Journal of Physical Chemistry Letters 8 (2017) p. 5091-5098.
3. B Ravel and M Newville, ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEF-FIT, Journal of Synchrotron Radiation 12, 537–541 (2005).

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REV20250424