



Observing Lithium Ion Battery Bonds During Charge Cycling Using Laboratory XAS

X-ray Absorption Spectroscopy (XAS) analyses of measurement results obtained with QuantumLeap H2000 for low-Co (<3-5% wt.) Li-ion NMC batteries are presented. High quality EXAFS were obtained for Mn and Ni in transmission mode, while Co was obtained using fluorescence mode. Mn-O and Co-O indicated reversible/minimal changes, while Ni-O showed Jahn-Teller distortion that indicated different Ni oxidation states.

This applications note discusses battery science enabled by Sigray QuantumLeap XAS



5750 Imhoff Drive, Suite I
Concord, CA 94520 USA
P: +1-925-446-4183
www.sigray.com
info@sigray.com

Observation of Jahn-Teller Distortion Effect on Ni-O bonds in Lithium Based NMC batteries during cycling process using QuantumLeap H2000

Author: Dr. Aniruddha Deb, Dr. Srivatsan Seshadri | Sigray, Inc.

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 its promise of high energy density ~800 Wh/kg. In LIBs, the intercalation of Lithium ions (Li+) affects the atomic and the 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 the scientists to investigate the influence of repeated cycling of the electrode on the oxidation state, the coordination environment, and structural changes. To date, XAS is predominantly performed at synchrotron facilities because they provide tunable energy x-ray beams of 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 develop novel high efficiency electrode systems.

Novel Approach: Sigray QuantumLeap XAS

Sigray's QuantumLeap™ H200 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, and
- customizability to enable *operando* experiments under various environments.

Method

All data was acquired on QuantumLeap H2000 using a Ge(331) crystal. Co K-edge measurements were made in the fluorescence mode due to its low concentration (~3-5 wt.%), while the Mn and Ni edges were measured in the transmission mode. For all measurements, k-range of ~12 was chosen. Acquisition times were deliberately kept long (details given in the next section) to get very high Signal to Noise Ratios (SNR) for accurate analyses. However, the acquisition times can be reduced by >3X for quick measurements for qualitative analyses. The obtained results were processed in the QuantumLeap GUI and then imported to 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 in 12 hours (Figure 1). The weak pre-edge feature at ~6543 eV is clearly visible due to high SNR in the data.

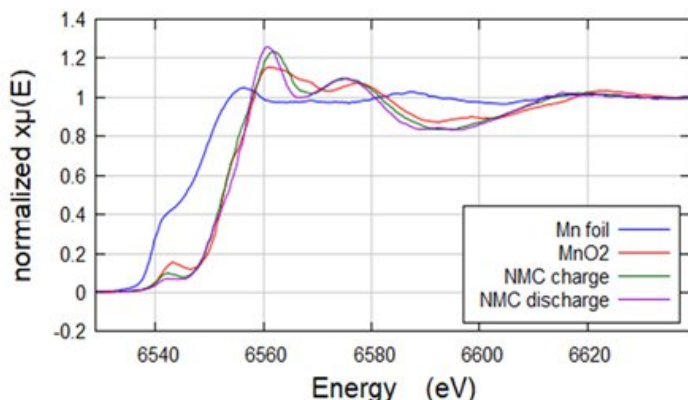


Figure 1: Mn-K edge of NMC electrodes fully charged and discharged. Comparison of the MnO₂ model and Mn foil oxidation states shows that Mn in NMC are in an oxidation state of ~4+. The absorption edge energy does not change much showing that Mn acts as a spectator during cycling.

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 the discharged electrode 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 that we see in the shape of the Mn-spectra show the possible change in the local structure around the Mn atom. The XANES shows good agreement between observed Mn-edge energy and the model compound (MnO₂) suggesting that the Mn is in a state of Mn⁴⁺ during cycling.

Figures 2 and 3 show the XAS data across 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 was required to obtain high SNR EXAFS data up to $k=11$.

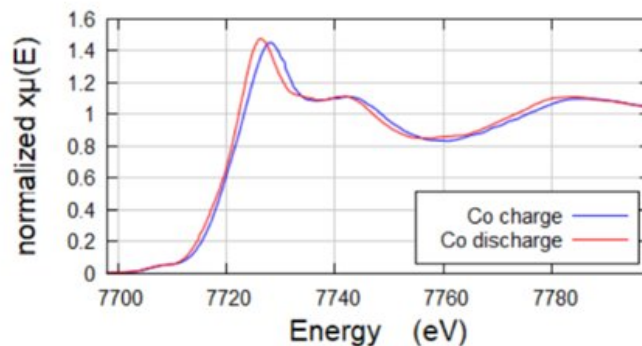


Figure 2: Low concentration of Co ~3-5% by wt.% in NMC electrodes charged and discharged. Only about 100eV of the scan is shown.

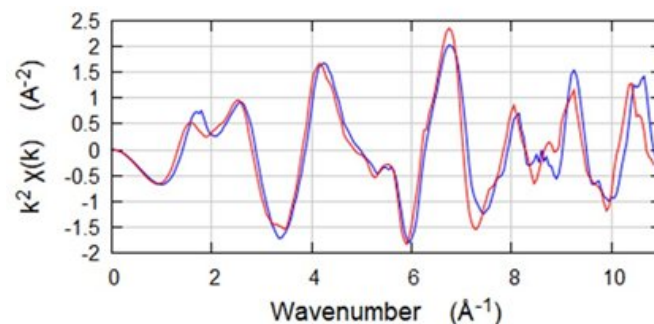


Figure 3: EXAFS of low concentration of Co ~3-5% by wt.% in NMC electrodes charged (blue) and discharged (red).

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

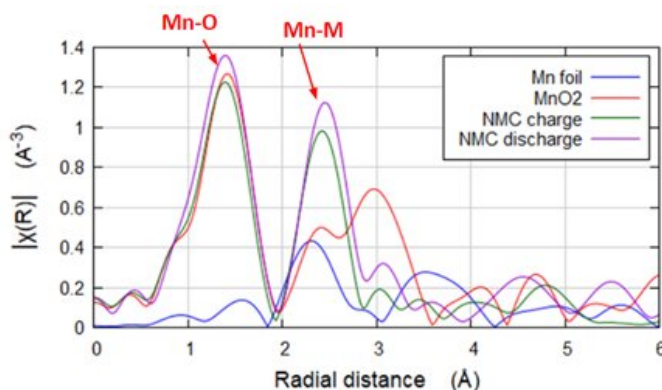


Figure 4: Mn K-edge FT-EXAFS of NMC along with model systems showing the main peak at ~1.5 Å (uncorrected phase) corresponding to Mn-O bond and the second peak at ~2.3 Å corresponding to Mn-M bond

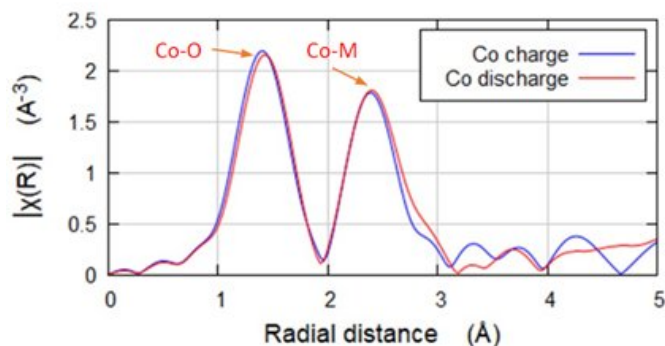


Figure 5: FT-EXAFS of Figure 3, showing the comparison of the charged and discharged state of the NMC electrodes.

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 ~ 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 charge and discharge state, which indicates reversible/minimal changes in the Mn-O/Co-O distances on cycling. But as seen on Figure 6, the first peak attributed to the Ni-O shows a change with the Ni-O bond distance increasing in the discharged sample (1.3 Å to 1.7 Å, non-phase shifted).

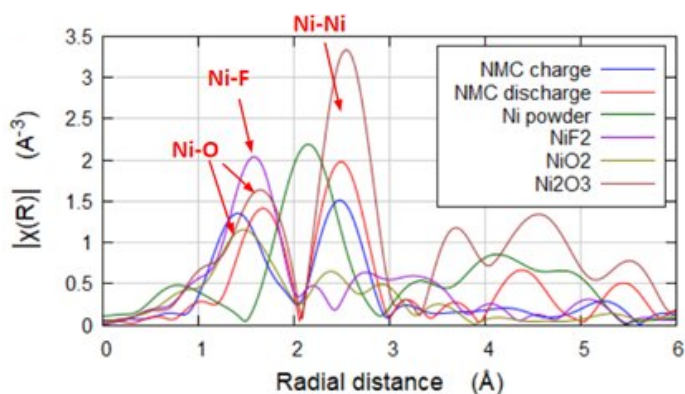


Figure 6: FT-EXAFS of Ni in NMC, showing the comparison of the charged and discharged state of the NMC electrodes along with the model systems.

This bond-length change between charged and discharged states is consistent with the fact that when charged, the nickel goes to the form of $\sim \text{Ni}^{4+}$ which is non-Jahn-Teller and does not suffer from Jahn-Teller distortion, and this results in a shorter bond distance of $\sim \text{Ni}^{4+}$ -O bond (~ 1.3 Å). On the contrary, in the discharged sample, there might be some presence of Ni in Ni^{3+} or a mixture of $\text{Ni}^{3+}/\text{Ni}^{2+}$ state. Since Ni^{3+} is Jahn-Teller active, the discharged sample shows a longer Ni^{3+} -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 from the oxidation state picture since Ni^{4+} in the charged sample has a shorter ionic radii (0.46 Å) compared to the discharged sample with $\text{Ni}^{2+}/\text{Ni}^{3+}$ with 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. But 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 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 in 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 seen for Ni-O, but they are seen in for Ni-Ni. The above results demonstrate the synchrotron-like capabilities of a laboratory XAS tool to produce the quality of data required for detailed and accurate analyses to understand NMC electrode's behavior under cycling conditions.

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