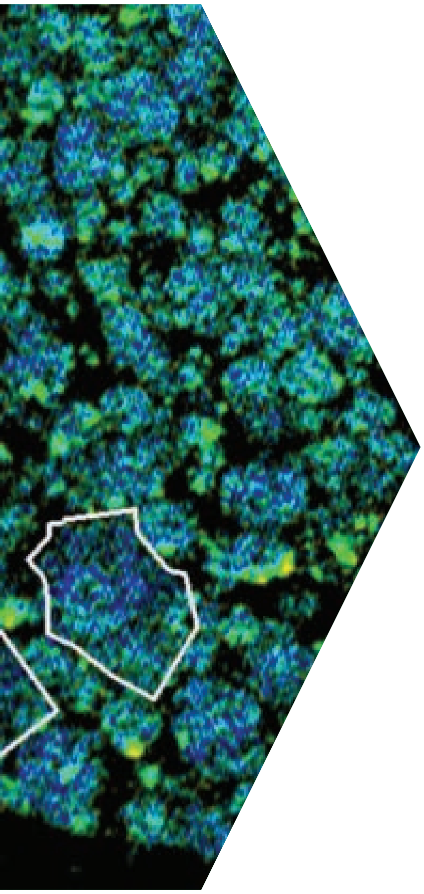

Li-Ion Battery Chemistry with Laboratory XAS

Initially developed in synchrotron facilities, XAS has demonstrated its powerful capability in analyzing battery materials, such as chemical states of transition metals in batteries. Sigray QuantumLeap is the first laboratory system that provides synchrotron-like XAS capabilities with sub-eV resolution and acquisition times within minutes. In this application note, lithium-ion batteries were investigated using Sigray QuantumLeap^{TM} to track chemical state changes.

This white paper will review battery applications of the QuantumLeap XAS

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

Lithium-Ion Battery Chemistry with Laboratory XAS

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

Background: Lithium-ion batteries (LIBs) are the dominant rechargeable battery technology, having an unmatched combination of high energy and power density [1]. Two primary types of chemistries are used in LIBs: lithium ferrum phosphate (LFP) and nickel maganese cobalt oxides (NMC). NMC is the newer of the two chemistries, providing faster charging rates and larger capacities but has a shorter lifetime [2-3]. Advances to the cycling performance of NMC batteries are an active area of research and include: increasing the ratio of Ni (the predominant electroactive transition metal) while still attaining electrochemical stability, adding coatings, applying heat treatments, and developing layers or gradients from the particle core to the surface [4]. Such changes have demonstrated increased battery lifetimes, but the chemical origins can be difficult to establish.

Oxidation state changes provides critical insight into the underlying chemical mechanisms behind successful modifications to Li-ion batteries. Such measurements typically require synchrotron X-ray Absorption Spectroscopy (XAS), a powerful approach for measuring bulk material chemistry, for determining oxidation state changes to the transition metals between and during charging cycles. However, a key bottleneck is that synchrotron XAS beamtime can be challenging to obtain and, even if granted, may only amount to a few days out of the year in which research can be done.

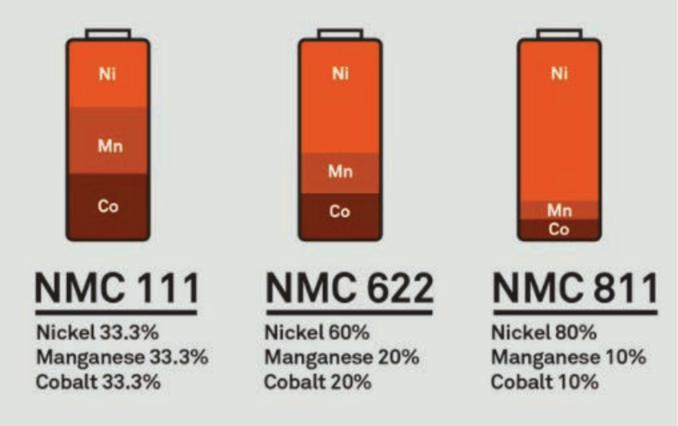

Figure 1: *Cathode compositions of different generations of NMC-type Li-Ion batteries: NMC111 (also called NMC333), NMC622, and NMC811. the battery industry has been improving NMCs by increasing the Ni content in each cathode generation.*

Novel Approach: Sigray QuantumLeap XAS

Sigray's QuantumLeap™ x-ray absorption spectroscopy (XAS) product line represents the first laboratory XAS instruments with synchrotron-like capabilities. The QuantumLeap product line features multiple patented technologies, including:

- ultrahigh brightness x-ray source technology,
- acquisition approach, and
- system design.

These patented innovations provide the throughput and energy resolution to enable 24-7 laboratory access to critical measurements of lithiation/oxidation states and bond lengths of a wide range of materials. Furthermore, Sigray's custom *in-situ* cells empower understanding of dynamic changes occuring *in-operando* or under conditions such as high temperature.

Experiments and Results

In this report, we applied the Sigray QuantumLeap™ to three NMC battery cathodes: NMC333, NMC622, and NMC811 (see Fig. 1). The nickel content of each cathode increases, with the first number of the three digits roughly corresponding to the percentage weight of Ni (e.g. 33% for NMC333 and 60% for NMC622).

From high resolution XANES (X-ray Absorption Near Edge Spectroscopy) measurements acquired on the QuantumLeap™, we were able to confirm expected oxidation states of Ni (increasing with increasing Ni content) and furthermore confirm that there were no changes to Co.

Method

Powdered samples were provided to Sigray ground to ~1 μm in diameter. The powder was then prepared in a straightforward manner by gently brushing the powder onto Scotch tape and stacking several layers of powdered tape together. Alternative approaches, such as pelletizing the powder with cellulose, can also be easily achieved using Sigray's established protocols.

Results were acquired on Sigray's QuantumLeap™-H2000 model, which provides energy resolution down to 0.7 eV. For the purposes of Ni and Co oxidation state discrimination, a pixel resolution of ~1.0 eV was selected and a Ge(400) crystal was employed. Each spectrum was acquired over 15 minutes.

Results and Discussion

The spectra acquired for the three samples (Figs. 2 and 3) demonstrate that Ni was primarily found in the Ni2+ state in NMC333 and that as Ni content increases, the Ni3+/Ni2+ ratio correspondingly increases. This observation can be confirmed with other similar studies [4]. Furthermore, the oxidation state of Co remains the same for all cathode types (Fig. 3), which is also expected [4].

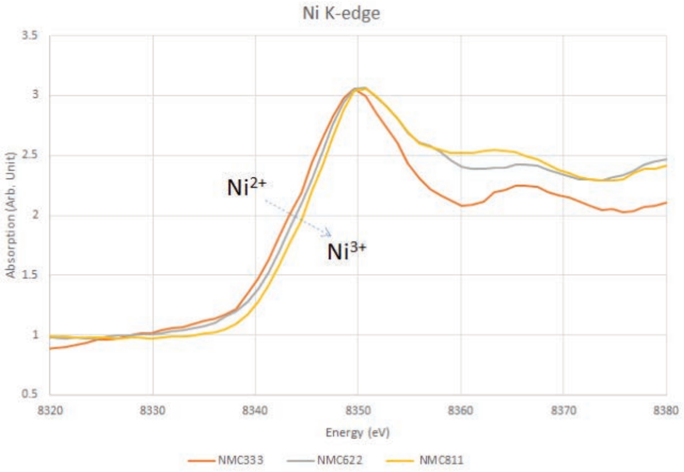

Figure 2: Nickel oxidation ratios shifts a smaller Ni3+/Ni2+ ratio in the NMC with lower Ni content (NMC333) to a large ratio for Ni-rich NMC (NMC811) material.

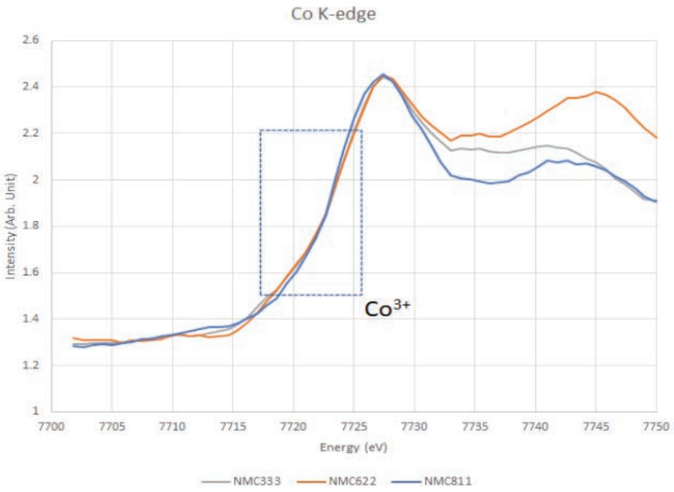

Figure 3: XANES measurement of the Co K-edge shows that Co oxidation state remains the same for all three NMC materials.

Summary

We have demonstrated that laboratory XAS through Sigray QuantumLeap^{TM} can provide excellent energy resolution to discriminate between minute changes in oxidation state ratios for battery materials. These changes can be used to predict electrochemical performance and to guide the development of future Li-ion battery materials and processes. Other potential applications includes *in-operando* studies of dynamic oxidation state shifts in batteries during charging/ discharging cycles, enabled using *in-situ* cells designed for the QuantumLeap^{TM}.

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4. JL White, et al. "Nickel and Cobalt Oxidation State Evolution at Ni-Rich NMC Cathode Surfaces During Treatment," 2020 J. Phys. Chem. C 124: 16508-16514.

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