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In situ soft XAS study on nickel-based layered cathode material at elevated temperatures: A novel approach to study thermal stability

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Tracking thermally induced reactions has always been challenging for electrode materials of electrochemical battery systems. Traditionally, a variety of calorimetric techniques and *in situ* XRD at elevated temperatures has been used to evaluate the thermal stability of electrode materials. These techniques are capable of providing variations in heat capacity, mass and average bulk composition of materials only. Herein, we report investigation of thermal characteristics of $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ by using *in situ* soft XAS measurements in combination with XRD. Fluorescence yield and partial electron yield measurements are used simultaneously to obtain element selective surface and bulk information. Fluorescence yield measurements reveal no energy change of the absorption peak and thus no valence state change in the bulk. However, electron yield measurements indicate that NiO-type rock salt structure is formed at the surface at temperatures above 200°C while no evidence for a surface reaction near Co sites in investigated temperature range is found. These results clearly show that *in situ* soft XAS can give a unique understanding of the role of each element in the structural transformation under thermal abuse offering a useful guidance in developing new battery system with improved safety performance.

Safety is an essential challenge for electrochemical battery technology. Current generation of high energy battery system is prone to thermal runaway reactions. For modern applications of battery system like electric vehicles, price of battery pack is heavily influenced by performance as well as its operating temperature profile. Therefore, it is important to evaluate the type of chemical reactions and structure changes which occur at high temperatures. Further, it is generally accepted that thermal runaway reactions are initiated at the surfaces of electrodes. Consequently, there have been several studies that involve tailoring the material surface composition by controlled synthesis or surface treatments, aimed at improving safety aspects of positive electrodes[1,2]. However, a fundamental understanding of the surface chemistry and structures when the electrodes are exposed to temperature excursions is still somewhat lacking. Undoubtedly, experiments that can monitor both the surface and bulk structures as a function of temperature can provide key information to help develop safer materials for battery applications. In prior publications, we have reported temperature dependent studies on the bulk structural changes of charged nickel based cathode materials, such as $Li_{1-x}NiO_2$, $Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$, $Li_{1-x}Ni_{0.5}Mn_{0.5}O_2$ and $Li_{1-x}Ni_{0.33}Co_{0.33}Mn_{0.33}O_2$ with and without the presence of electrolyte using synchrotron based X-ray diffraction[3–6]. Recently, Nam et al., Bak et al. and Wu et al. investigated the nickel based cathode materials using XRD, mass spectroscopy and TEM to determine the influence of high temperature on the cathode materials[7–9]. These techniques are useful in studying structural changes during the heating process but are not sufficient in elucidating each element's role on the structural stability, especially for simultaneously probing both the bulk and the surface of the electrodes. The partial electron yield (PEY) measurements in soft XAS give information about surface properties (up to ~5 nm), whereas the fluorescent yield (FY) measurements identify more or less bulk properties (up to ~300 nm) similar to XRD measurements[10]. Therefore, soft XAS is a very powerful tool to determine structural and valence state changes at elevated temperatures in an element specific manner with sensitivity to surface and the bulk structures. The fact that soft XAS measurements are element-specific and allow discrimination between surface and bulk, provides important complementary information that cannot be obtained by the sole use of XRD and/or TEM.

In this work, *in situ* temperature-dependent soft XAS measurements (both PEY and FY modes) in conjunction with *in situ* XRD studies have been applied to understand thermal degradation of the charged electrodes. Specifically, we have monitored the element selective structural changes of the charged cathode material at the surface and in the bulk at the same time during the heating process. The results of this study provide valuable guidance to design new electrode materials with enhanced thermal stability.

Results and Discussion

In situ XRD measurements were performed to monitor the bulk structural changes in charged $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode material during the heating process. The XRD patterns, measured with the temperature increased in a stepwise manner are shown in Figure 1. They reveal structure changes beginning at ~200°C. At lower temperature a diffraction pattern typical for layered structure with space group R-3m was obtained. At higher temperature above 200°C the layered structure gradually changed into the Fd-3m type spinel structure. This transformation is indicated by reflection (440) that emerges from the coalescence of reflections (108) and (110) of the layered structure. Moreover, the evolution of peak (220) is another indicator of the cubic spinel phase; this reflection is not expected in the rhombohedral structure[4]. Transition from a rhombohedral to a cubic unit cell involves cations reordering in the crystal structure, although transition metals might maintain their valence during this rearrangement. A closer look at the XRD patterns indicates continuous increase in intensity of the reflection (220) between 200–300°C, which suggests further rearrangements of cations. Substitution of Li^+ at 8a tetrahedral sites by transition metal from 16d octahedral positions decreases the intensity ratio (111)/(220)[11,12].

Schematic representation of *in situ* soft X-ray experimental setup is shown in Figure 2(a) and a photograph of the purpose-built heatable sample holder along with its schematic is presented in Figure 2(b). The soft X-rays enter the vacuum chamber and impinge the sample at an angle of 45°. The FY and PEY detectors were placed 90° out of the incoming X-rays. Inelastic and Compton scattered X-rays are reduced by placing the FY detector normal to the incident beam. The sample was mounted on the heatable sample holder, where a tantalum foil was used as a sample support and a resistance heater. The thermocouple used to register the sample temperature was welded directly on the tantalum foil of the sample support to get precise temperature readings. As alluded to earlier soft XAS experiments[13–15], it is possible to characterize surface and bulk properties of materials separately by detecting the electron and fluorescence yield simultaneously because of the smaller mean free path length of electrons as compared to the escape depth of photons. In comparison to total electron yield (TEY) mode, more of the Auger electrons and less of the inelastic secondary electrons are collected in PEY detection. This preferential collection renders higher surface sensitivity to the PEY mode. In addition, the measurements are intrinsically element-specific; specifically in the case of $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$, the unique electronic structure of nickel, cobalt and oxygen could be explicitly measured and evaluated. The Ni L-edge spectra are based on transitions starting at the $P_{1/2}$ and $P_{3/2}$ energy levels, where the strong peaks are due to transitions into 3d orbitals (e_g*). In a complex with octahedral coordination, 3d orbitals split into t_{2g} and e_g orbitals by crystal field effects. Since the bonding t_{2g} and e_g orbitals along with the non-bonding t_{2g}* orbitals are completely occupied, only transitions to the non-bonding e_g* orbitals and to empty orbitals above the d-orbitals are possible.

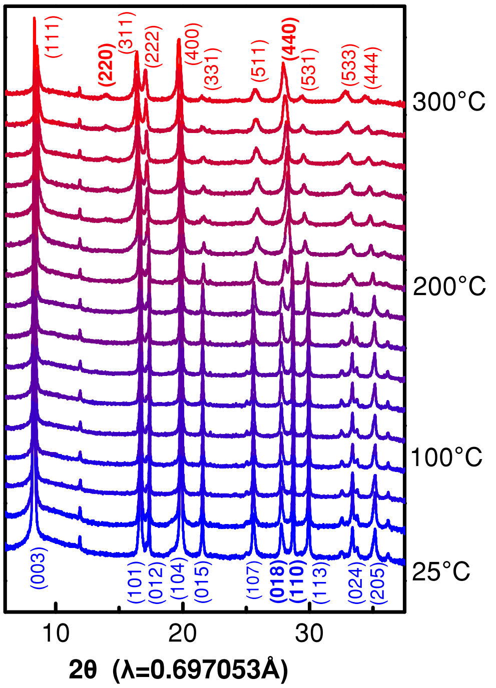

Figure 1 | *In situ* XRD patterns of $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode material when heated from 25°C to 300°C in the absence of electrolyte.

Normalized Ni L-edge spectra of $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode at different temperatures using FY mode are shown in Figure 3(a) and PEY mode spectra are shown in Figure 3(b). Due to spin-orbit interaction of the core hole the absorption spectrum is split into two well separated energy bands namely Ni $2p_{3/2}$ (L_3 edge) and Ni $2p_{1/2}$ (L_2 edge). In addition, these bands are expected to split due to 2p-3d interactions and crystal field effects, which should lead to a multiplet structure[16]. The pattern of these multiplets would offer information about the valence state, the spin state and the symmetry of the Ni coordination. The shape, energy position and other properties like the branching ratio contain information about the valence state and the spin state of the samples. Changes in energy position of the bands can indicate valence state changes during the heating process since energy position shifts about 1 eV per oxidation state change[17]. Ni L_3 and L_2 spectra obtained in the bulk sensitive fluorescent yield mode indicate no energy position changes. In fact the change to the Fd-3m structure does not involve a valence state change thus shift in energy position is not expected. However, the energy position of Ni L_3 and L_2 spectrum moves to lower energy levels in case of surface sensitive electron yield mode, where a rather strong shift takes place at ~200°C indicating the presence of NiO-type rock salt structure on the surface at this temperature.

The $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode material contained only 15% cobalt species but yet high quality L-edge spectra were obtained. Figure 3(c) and (d) illustrates normalized Co L-edge XAS spectra at different temperatures using FY and PEY mode respectively. In contrast to the Ni L-edge spectra, the electron yield spectra of the Co species do not show energy shifts. There are no visible changes in both the fluorescence yield and the electron yield spectra. It indicates that cobalt ions have superior thermal stability than the nickel ions. Partial substitution of nickel by cobalt in the cathode materials contribute to enhancement of the thermal stability. This finding is consistent with earlier XRD results, wherein a significant thermal stability improvement by Co doping has been seen, as the thermally induced structural changes in $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode occur at much higher temperature compared to $LiNiO_2$[4,18].

Normalized O K-edge XAS spectra of $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode material at different temperatures, using FY mode are shown

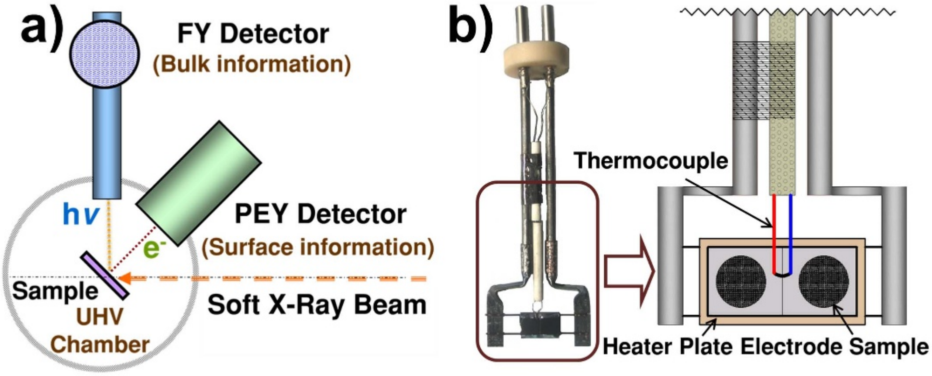

Figure 2 | Schematic diagram of (a) *in situ* soft XAS experimental setup and (b) sample heater with heating stage for *in situ* soft XAS experiment. W. Y. and S. M. created this figure.

in Figure 4(a) and PEY mode spectra are shown in Figure 4(b). The first single intense absorption peak at 528.5 eV corresponds to transition from oxygen 1s orbital to a hybridized state of metal 3d with O 2p orbitals[19–21]. The oxygen K-edge spectra contain information about the unoccupied d-p hybrid orbitals of the metal-oxygen bond. The broad peak above ~535 eV has been associated with transitions to hybridized states of O 2p - Ni 4sp and other empty orbitals in this energy region. Similar to the L-edge spectra, there is no significant change in the fluorescence yield spectra but the surface sensitive electron yield spectra show a remarkable decrease of the peak at 528.5 eV at temperature above 200°C. Also in contrast to the FY data, the PEY data show other distinct differences in spectral evolution. We point, in particular, to features at ~532 eV and ~534 eV in the PEY data. The distinct peak at ~534 eV is disappearing, whereas the peak at ~532 eV is growing with increasing temperature. Similar peaks, at the same energy positions, were observed in one of our previous soft XAS study on Li-ion deintercalation of $LiNiO_2$[22]. The features at ~532 eV and ~534 eV can be attributed to the presence of NiO and Li_2CO_3, respectively; this is evident from the spectra of the standards shown in Figure 4(b). On heating, features at ~534 eV diminish in intensity; this suggests that carbonate present on the surface is gradually decomposed and disintegrated. Conversely, the intensity of the ~532 eV peak increases with temperature, particularly above 200°C. Concomitantly, the

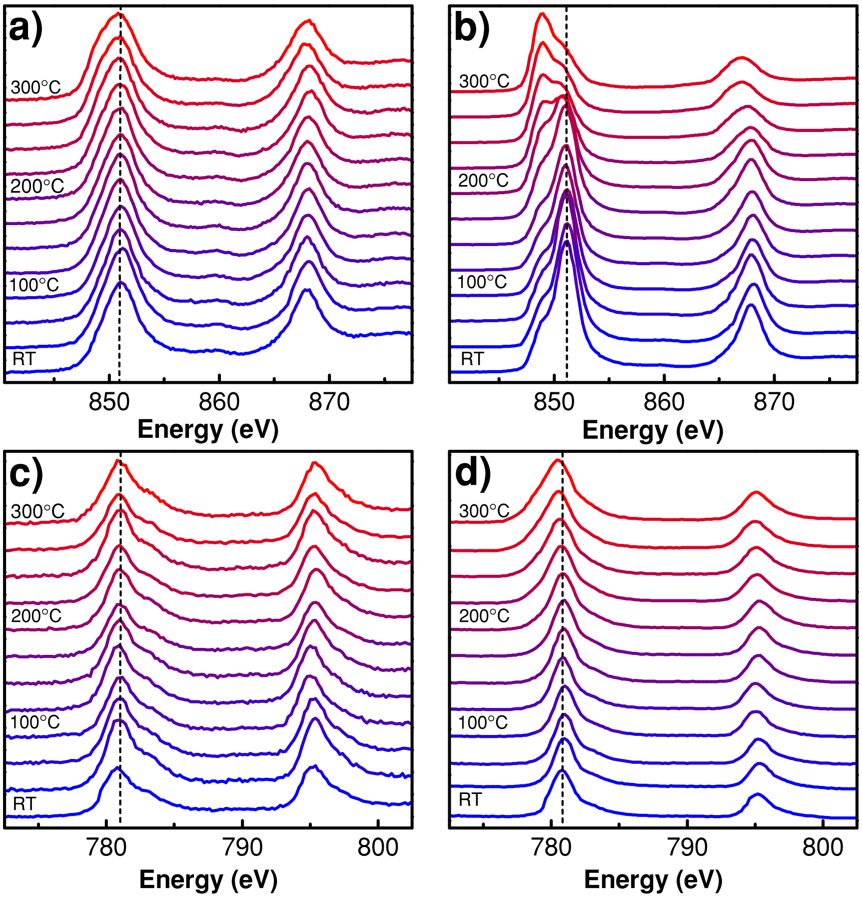

Figure 3 | Normalized XAS spectra of $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode material at different temperatures using (a) Ni L-edge FY mode, (b) Ni L-edge PEY mode, (c) Co L-edge FY mode and (d) Co L-edge PEY mode.

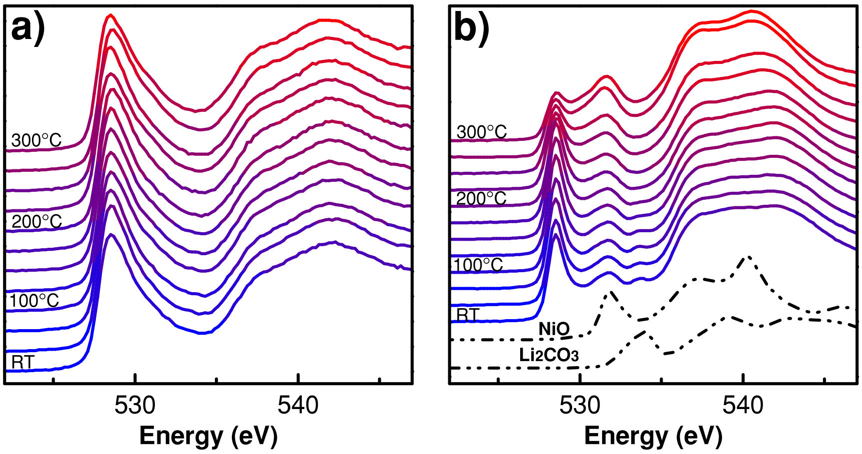

Figure 4 | Normalized O K-edge XAS spectra of $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode material at different temperatures using (a) FY mode and (b) PEY mode.

intensity of the 528.5 eV peak diminishes. These observations suggest the formation of reduced divalent nickel, similar to that seen in rock salt NiO. This finding is consistent with the Ni-L edge measurements (vide supra). The presence of NiO-type rock salt structure and its increasing formation at electrode surface with increasing temperature reveal nickel oxides have the tendency to release oxygen at higher temperature leaving the metal in a lower oxidation state. The oxygen K-edge spectra are in complete agreement with the data obtained from the Ni L-edge and point to the initiation of thermal reduction reactions specifically at Ni sites on the surface of the $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode material.

In summary, we successfully demonstrated the capability of *in situ* soft XAS techniques to investigate thermal behavior of cathode materials. In combination with *in situ* XRD and fluorescence yield soft XAS, comprehensive and element specific structural information of the bulk was obtained. These investigations clearly show that no valence state change takes place in the bulk even though the layered structure (R-3m) of the $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode material changes to spinel structure (Fd-3m) as indicated by the XRD measurements. The surface sensitive electron yield measurements allow the evaluation of the electronic structure of electrode material at the surface. It reveals that this electrode material loses oxygen at elevated temperatures leading to a lower valence state of Ni and formation of NiO-like rock salt structure. Interestingly, no evidence for a surface reaction near Co sites in the investigated temperature range was found. Therefore, it can be concluded that the Co species are more stable at elevated temperatures than the Ni species in $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$. These results indicate that soft XAS can be used as a powerful technique to study the thermal stability of electrode materials. In combination with *in situ* thermal XRD, soft XAS studies can provide valuable information for understanding the role of each element in the structural transformation under thermal abuse. Undoubtedly, the ability of soft XAS to decipher both the surface and bulk electronic structures with element specificity, makes it an invaluable addition to the arsenal of advanced diagnostic tools that help understand thermal behavior of battery electrodes.

Methods

The cathode material in this study was made of $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (84%) Fuji Chemical, carbon black (4%) Chevron, SFG-6 (4%) Timcal, and PVdF (8%) Kureha. The cathodes, coated on Al foil current collector, were incorporated into 2-electrode test cells. Each of these cells was made of a Li foil anode, a Celgard separator and 1.2 M $LiPF_6$ in a 3 : 7 EC:EMC solvent as electrolyte. The cell was charged at C/18 rate to a level corresponding to cathode composition of $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ and then transferred to the glove box for disassembly. The charged cathode material was scratched from the current collector and loaded into quartz capillaries of 0.3 mm diameter inside the glove box for the XRD measurements. The capillaries were sealed in a glove box before being mounted on the thermal stage of the diffractometer of beamline X7A at National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). A monochromatic beam of 0.697053 Å was selected using a channel-cut Ge(111) single crystal. Capillary sample was mounted on the second axis of the diffractometer inside the cryostat. Diffraction data were collected using a position sensitive detector (PSD) stepping in 0.25° intervals over the angular range 5–37.5° in 2θ. Sample temperature was increased up to 300°C and cryostat was rocked by 5° during data collection in order to obtain better powder averaging.

In parallel studies, soft XAS measurements were performed at beamline U7A at the NSLS. The estimated incident X-ray energy resolution was ~0.2 eV with beam size was 1 mm in diameter. The PEY data were recorded using a channel electron multiplier with a high pass filter entrance grid filter set to −150 V to enhance the surface sensitivity while the FY data were recorded using a windowless energy dispersive Si(Li) detector. A linear background fit to the pre-edge region was subtracted from the spectra. The O K-edge spectra were normalized between 585 and 630 eV. To eliminate the effects of incident beam intensity fluctuations and monochromator absorption features, the PEY and FY signals were normalized using the drain current of a gold mesh with 90% transmittance located along the path of the incident X-rays.

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Author contributions

W.Y. conceived, designed, and coordinated the study. W.Y., K.N., D.F., C.J., X.Y. and M.B. performed the experiment and acquired the data. W.Y., O.H., S.M., H.K., W.L., D.K. and M.B. processed the data and wrote the paper; all the authors participated in analysis of the experimental data and discussions of the results as well as preparing the paper.

Additional information

Competing financial interests: The authors declare no competing financial interests.

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