Spatially Resolved Ni L₃-, Co L₃-, Mn L₃-, and O K-edge Spectra Obtained from Pristine and Charged-State Li_{1.0}Ni_{0.88}Co_{0.08}Mn_{0.04}O₂ Cathode Materials Prepared by Focused-Ion-Beam Method

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ABSTRACT

Pristine and 4.35 V charged-state particles of the Li_{1.0}Ni_{0.88}Co_{0.08}Mn_{0.04}O₂ lithium-ion battery (LIB) cathode material were cross-sectioned by the focused-ion-beam method to allow the acquisition of spatially resolved Ni L₃-edge, Co L₃-edge, Mn L₃-edge, and O K-edge X-ray absorption spectra by scanning transmission X-ray microscopy with a spatial resolution of ~30 nm. The Co L₃-edge and the Mn L₃-edge spectra, respectively, displayed almost the same features throughout the particles for both the pristine-state and charged-state samples. The average oxidation states of the Co and Mn ions were estimated to be ~3+ and ~4+, respectively. The Ni L₃-edge and O K-edge spectra included different features, depending on the charge state and intra-particle location. The estimated average oxidation state of the Ni ions ranged from ~2.7+ to ~3.0+ for the pristine-state sample (space-averaged value: ~2.9+) and from ~2.7+ to ~3.5+ for the charged-state sample (space-averaged value: ~3.3+). A correlation was observed between the changes in the features of the O K-edge and Ni L₃-edge. These results would provide important implications for the development of high-performance LIBs.

Keywords: Li_xNi_{0.88}Co_{0.08}Mn_{0.04}O₂, Ni-Co-Mn-O, Scanning transmission X-ray microscopy, X-ray absorption, Transition-metal L₃ edge, Oxygen K edge, Spectro-nanoscopy, Oxidation-state change

1. Introduction

Cathode materials for lithium-ion battery (LIB) applications have become a subject of great interest and have been intensively studied to understand the changes in their physical and chemical properties during and after the charging and discharging processes. Among those changes are alterations in the crystal structure, local atomic structure, oxidation state, chemical state, and electronic structure [1–9]. Recently, spatially resolved local chemical-state investigations on a particle-by-particle basis have been performed, the results of which have provided information on the homogeneity of the charging and discharging behaviors inside individual particles as well as among particles [10–15]. For example, Chueh *et al.* reported that not all of the particles participated in the chemical reactions of a LiFePO₄-based LIB [10]; Lim *et al.* and Li *et al.*, meanwhile, found that charging and discharging kinetics occurred heterogeneously within individual LiFePO₄ particles [13–15]. These results highlight the validity of spatially resolved investigation of LIB particles by means of spectro-nanoscopy probes such as scanning transmission X-ray microscopy (STXM), and thus have attracted great attention and interest within the LIB research

community.

Li_xNi_{0.88}Co_{0.08}Mn_{0.04}O₂ (Ni-rich NCM) is considered to be a potential LiCoO₂ replacement for the realization of high-performance LIBs; the Mn ions therein are known to form a stable crystal structure, and the Ni ions are regarded as playing an active role in the electromotive force changes during the reaction processes. For a better understanding of the reaction processes and electromotive force changes, investigation of the oxidation-state and electronic-structure modifications undergone by the Ni, Co, Mn, and O ions is necessary. In this Ni-Co-Mn-O system, the valence and conduction band structures are dominated by the O 2p and transition metal (TM) 3d orbital structures [1,2]. The latter orbitals are partially occupied, and the absorption spectrum for the transition from the TM 2p to 3d orbitals shows a unique feature for each oxidation state [16,17]. Thus, the oxidation states of the Ni-Co-Mn-O elements can be estimated by measuring the TM L-edge absorption spectra. The O 2p orbitals hybridize with the TM 3d orbitals, and the degree of hybridization can be influenced by the oxidation states of the TM ions; thus, the O K-edge spectral features can be correlated with changes in the TM oxidation states. In the Ni-Co-Mn-O system, the O 2p orbitals are

able to undergo hybridization with all of the 3d orbitals of the Ni, Co, and Mn ions, leading to complicated O K-edge spectral features. One of the aims of the present study, therefore, is to try to understand the correlation between the O K-edge spectral changes and the spectral changes or oxidation-state changes of the TM ions, specifically, in the Ni-rich-NCM cathode material.

In this report, we provide spatially resolved TM L_3 -edge and O K-edge spectra and estimated average oxidation states for the TM ions in pristine- and charged-state Ni-rich-NCM cathode materials.

2. Experimental details

Pristine and charged $\text{Li}_{1.0}\text{Ni}_{0.88}\text{Co}_{0.08}\text{Mn}_{0.04}\text{O}_2$ cathode material samples were prepared by mixing co-precipitated $\text{Ni}_{0.88}\text{Co}_{0.08}\text{Mn}_{0.04}(\text{OH})_2$ powder with $\text{LiOH}\cdot\text{H}_2\text{O}$ and subsequent calcination of the mixture at 750°C for 24 h in O_2 . The washing process involved stirring $\text{Li}_{1.0}\text{Ni}_{0.88}\text{Co}_{0.08}\text{Mn}_{0.04}\text{O}_2$ powder in deionized water with a mechanical stirrer for 10 min, followed by filtration within 5 min. After washing and filtering, water was removed by evaporation in an air convection oven at 120°C overnight. Following drying, the powders underwent heat treatment at 720°C for 5 h in an O_2 gas flow. The electrochemical performance of the cathode materials was assessed in a CR2032 coin-type cell. The cell consisted of a $\text{Li}_{1.0}\text{Ni}_{0.88}\text{Co}_{0.08}\text{Mn}_{0.04}\text{O}_2$ cathode and a lithium metal anode separated by a porous ceramic-coated polyethylene film. The composite cathode was fabricated by spreading a slurry consisting of the active material (92 wt.%), Denka black (4 wt.%), and polyvinylidene difluoride (PVDF) (4 wt.%) in *N*-methyl-2-pyrrolidone (NMP) on aluminum foil, which was used as the current collector. The electrolyte solution consisted of LiPF_6 (1.0 M) dissolved in a mixture of fluoroethylene carbonate (FEC) and dimethyl carbonate (DMC). All cell fabrication, including the slurry casting and assembly of the coin cells, was conducted in a dry room. The cells were charged and discharged galvanostatically in the potential range of 2.8 V to 4.35 V at a rate of 0.1 C.

Pristine and 4.35 V charged-state particles were collected from the cathode composite. The particles resemble secondary particles of $\sim 15\ \mu\text{m}$ diameter. The samples for STXM measurement underwent focused ion beam (FIB) cross-sectioning (Helios Nanolab 450F1, FEI) to prepare thin ($\sim 100\ \text{nm}$) samples. The samples were attached to a transmission electron microscopy (TEM) grid and mounted on a holder for STXM measurement at the 10A1 beamline of PLS-II [18]. To acquire an STXM measurement, incident X-rays are focused onto a sample using a zone plate. The focused X-ray beam diameter at the sample position is $\sim 30\ \text{nm}$ (spatial resolution: $\sim 30\ \text{nm}$). By scanning the sample relative to the focused X-rays, the X-rays pass through the sample, and the X-ray intensity can be measured at each sample position using a photon counter (a photomultiplier tube coupled with a thin layer of phosphor powder). Thus, a spatially resolved absorbance-contrast image is obtained. When operated in image acquisition mode, the STXM instrument uses a PZT-driven stage for sample scanning. In this work, the data acquisition time per pixel was set at $\sim 1\ \text{ms}$, the scan range per image was $4\ \mu\text{m} \times 4\ \mu\text{m}$, and the pixel length was $20\ \text{nm}$. Spatially resolved O K-edge, Ni L_3 -edge, Mn L_3 -edge, and Co L_3 -edge spectra were determined from a stack of images obtained with different incident X-ray energies spanning each absorption-energy range. The energy-resolving power, $E/\Delta E$, of the STXM beamline is approximately 5,000 at 400 eV. The focused X-ray spot drifts slightly as the incident X-ray energy and focal length

change. This drift in the focal position is compensated by a stack image alignment software. For the data processing and stack image alignment, the aXis2000 software package was used [19]. Clipping during the stack alignment process, reduced the image size to $\sim 3.6\ \mu\text{m} \times 3.6\ \mu\text{m}$ after processing.

3. Results and discussion

Figure 1 shows images of the samples in pristine (a) and charged (b) states, both obtained at $h\nu = 529\ \text{eV}$. At this photon energy, the O ions strongly absorb X-rays because the energy matches the energy of the transition from the O 1s to the O 2p orbital hybridized with the TM 3d orbitals [see also the spectral details shown in Fig. 2(d)]. In the images, darker areas represent stronger absorbance. The scale bar in each image is $500\ \text{nm}$. Primary cathode particles are seen below the yellow-dashed line and marked as 'LIB' and the upper area marked 'No' is empty. The 'I₀' area is binder material for FIB preparation, and this contains no Ni, Mn, or Co content, nor has it any O K-edge spectral feature that affects the detailed spectral features in the 'LIB' area. The 'I₀' area was used for LIB spectral normalization. As shown in the images, each sample is comprised of submicron-sized primary particles. Within the primary particles, the inner areas appear darker than the outer or edge areas, implying that at this photon energy, the absorbance is strongest in the inner area. As will be shown later, the outer areas differ from the inner ones in terms of their Ni L_3 - and O K-edge spectral features, which is indicative of a reduction of Ni ions.

For both samples, photon-energy dependent image stacks were acquired at the TM L_3 - and O K-edges. From the stacks of images, the spatially averaged (Fig. 2) and spatially resolved (Fig. 3) L_3 - and O K-edge spectra were obtained. The spatially averaged spectrum at each absorption edge was obtained by averaging the spectra obtained over the entire LIB area. Figures 2(a)–(d) show the space-averaged spectra obtained at the Ni L_3 -, Co L_3 -, Mn L_3 -, and O K-edges, respectively. The space-averaged Co L_3 - and Mn L_3 -edge spectra display almost the same features for the pristine-state (red; 2-1) and charged-state (blue; 2-2) samples; however, clear differences between the two samples are seen in the Ni L_3 - and O K-edge spectra.

In the case of the Ni L_3 -edge shown in Fig. 2(a), the spectral differences between the two samples are indicated by blue arrows. These Ni L_3 -edge spectra include intense peaks at ~ 852.8 (red; 2-1)

Figure 1. STXM images of (a) pristine-state and (b) charged-state samples obtained at a photon energy of 529 eV. Each image size is $4\ \mu\text{m} \times 4\ \mu\text{m}$, and the pixel length is $20\ \text{nm}$. A $500\ \text{nm}$ scale bar is overlaid on each image. The sample area is indicated by the label 'LIB'.

Figure 2. Area-averaged (a) Ni L₃-edge, (b) Co L₃-edge, (c) Mn L₃-edge, and (d) O K-edge spectra obtained from pristine (red; 2-1) and charged (blue; 2-2) samples. The Ni L₃- and O K-edge spectra contain some key noticeable differences. On the right side of the panel (a), the results of curve fit for both samples are included.

and ~855 eV (blue; 2-2). According to a report by Yang *et al.*, the spectrum of Ni ions in the 2+ oxidation state [$3d^8 (t_{2g}^6 e_g^2)$] was dominated by the peak at low photon energy (~852.8 eV), and the spectrum of Ni ions in the 4+ oxidation state [$3d^6 (t_{2g}^6 e_g^0)$] was dominated by the peak at high photon energy (~855 eV) [20–22]. In their report, the Ni²⁺, Ni³⁺, and Ni⁴⁺ spectra, as well as the main peaks, were well resolved, and the energy separation between the main peaks of the 2+ and 4+ Ni ions was ~2.3 eV, while the energy separation between the 2+ and 3+ Ni ions was ~1.2 eV. Thus, we were able to estimate the average oxidation state of the Ni ions by comparing the measured spectral features with that of a linear combination of the Ni²⁺, Ni³⁺, and Ni⁴⁺ L₃-edge spectra from Ref. 21. The fitting results are shown on the right side of Fig. 2(a). As shown in the figures, the estimated average oxidation state is ~2.9+ for the pristine particles and ~3.3+ for the charged particles. The Ni²⁺:Ni³⁺:Ni⁴⁺ ion intensity ratios were found to be 0.32:0.48:0.20 and 0.16:0.41:0.44 for the pristine-state and charged-state samples, respectively. This observed increase in the average oxidation state of the Ni ions upon charging is consistent with previously published results [20,21].

In the case of the Co L₃-edge spectra (Fig. 2(b)), for both samples, similar features are seen: a strong peak appears at ~780.8 eV (middle bar) and a small peak appears at ~782.6 eV (right bar). The spectral shapes indicate that in both samples, the Co ions were in the ~3+ oxidation state [23], having an electronic configuration of $3d^6 (t_{2g}^6)$. When the oxidation state is lowered, new components appear

on the left side of the main peak. Previous reports have shown that when the average oxidation state of the Co ions is 8/3+, there exists a peak at the position marked on the spectrum by '+' having an intensity approximately half that of the main peak [24,25]. In this study, the negligible spectroscopic intensity was observed at the '+' position, by comparison to the main peak, and thus the oxidation state of the Co ions in the particles can be estimated as ~3+.

In the case of the Mn L₃-edges in Fig. 2(c), both spectra show similar features. An intense peak at ~643.5 eV (right bar) and a sharp peak at ~641 eV (left bar) are apparent. According to previous reports, if Mn ions are in the 2+ oxidation state, a strong peak appears at the position indicated by the left '+' mark in the spectrum (~640 eV), and if the 3+ oxidation state exists, a strong peak appears at the position of the right '+' mark (~642 eV) [26,27]. Alternatively, it has also been reported that when the Mn ions are in the 4+ oxidation state, the intensity of the 641 eV peak is ~two-fold that of the valley background around the right '+' position at 642 eV [26], or the intensity of the peak at 641 eV is slightly more intense than that of the valley background around the '+' position at 642 eV [27]. In light of these reports, we conclude that the measured data in Fig. 2(c) indicate that the average oxidation state of the Mn ions in both samples is 4+ [26], corresponding to an electronic configuration of $3d^3 (t_{2g}^3)$.

The O K-edge absorption corresponds to the transition from the O 1s to the O 2p orbitals, which are hybridized with the TM 4sp and TM 3d orbitals. The O 2p-TM 4sp hybridized-orbital spectral feature

Figure 3. Spatially resolved spectral features of the (a) Ni L_3 -edge, (b) O K-edge, (c) Co L_3 -edge, and (d) Mn L_3 -edge of the pristine (upper two rows) and charged-state (lower two rows) samples. In each row, the left image shows the locations at which the spectra were acquired (the location and spectrum are color-matched). A 500 nm scale bar is overlaid on each image. In each image, the intensity in the red-colored area was used for normalization. For clarity, some of the spectra have been shifted along the vertical axis.

occurs in the photon energy range of ~ 535 – 547 eV, and the O 2p–TM 3d hybridized feature appears in the photon energy range of ~ 527 – 534 eV, as indicated in Fig. 2(d). The O 2p–TM 3d hybridized feature at ~ 529 eV is strong for both the pristine and charged samples. It is apparent that the intensity of the peak at ~ 529 eV is stronger in the charged sample. Closer investigation (see also Fig. 5) reveals that the main peak of the charged sample occurs at slightly higher photon energy than that for the pristine sample. The intensity and peak-position differences for the samples can be explained in terms of changes in the average oxidation states of the Ni ions. By comparison with the report by G. Cherkashinin *et al.* [1], we conclude that the peak at approximately 529 eV, or that in the energy range of ~ 527 – 534 eV, could be assigned to the O 2p orbitals hybridized with the Ni 3d e_g , Mn 3d t_{2g} , Mn 3d e_g , and Co 3d e_g orbitals. This point is explained in more detail below, along with the discussion of Fig. 5.

From the stack of images obtained at each absorption edge, spatially resolved spectral features were extracted from the inner or edge areas of the particles. Fig. 3 shows spectral features thus obtained. In the figure, the spectra obtained from the pristine and charged samples are shown in the upper and lower two rows, respectively. In each row, the left image depicts the region of interest from which the spectra on the right are obtained. For the spectral normalization, the red colored area of the left image was used. Figures 3(b) and 3(c) show that, like the area-averaged cases (Figs. 2(b) and (2c)), the spatially resolved Co and Mn L_3 -edge spectral features are similar within the particles of both samples: each Co L_3 -edge spectrum displays the main peak at ~ 780.8 eV and a shoulder at ~ 782.6 eV, with negligible intensity at the ‘+’ position on the left of the main peak at ~ 780.8 eV (see Fig. 2(b)). Furthermore, each Mn L_3 -edge spectrum includes a peak at ~ 641 eV and an intense peak at ~ 643.5 eV, with negligible spectral intensities at the ‘+’ positions on the left of the ~ 641

eV peak (Fig. 2(c)) and between the main peaks. The spectral features imply that the average oxidation state of the Co ions is 3+ and that of the Mn ions is 4+, throughout the particles, in both samples.

By contrast, the Ni L_3 -edge spectra in Fig. 3(a) display clear differences, especially with respect to the intensity ratio of the peaks at 855 eV and 852.8 eV, depending on the location within the particles, and between the two samples. The average oxidation state of the Ni ions tends to be higher for the charged sample and inside the particles. Taking the spectral features of the 2+, 3+, and 4+ Ni ions reported by Qiao *et al.* [21] as references, the average oxidation states of the Ni ions of the pristine sample (upper two rows, Fig. 3(a)) in the present study are estimated to be as low as $\sim 2.7+$ in the edge areas and as high as $\sim 3.0+$ in the inner areas of the particles; when space averaged, the value is $\sim 2.9+$ (Fig. 2(a)). The average oxidation state of the charged sample (lower two rows, Fig. 3(a)) is estimated to be as low as $\sim 2.7+$ in the edge areas and as high as 3.5+ in the inner areas of the particles, and the space-averaged value is $\sim 3.3+$. It has been reported that the loss of oxygen ions in the edge areas results in the formation of NiO and a peak appearing at ~ 531.5 – 532 eV [8,22]. In our spectra, the intensity of the NiO peak at the O K-edge can be seen in some edge areas (the sky-blue spectrum in the second row and the yellow-red spectrum in the third row), but it is minor in most cases. The average oxidation state of the Ni ions was found to be lower in the edge area of the particles. This tendency might be explained by oxygen loss in the edge area [8,22] or may indicate that a higher concentration of Li ions remains on the particle surfaces. The fact that the Mn and Co ions have almost the same spectral features and average oxidation state in both the inner and outer areas implies that the Ni ions dominate the delithiation process. As shown in Fig. 3(d), the O K-edge spectra are also clearly different, depending on the samples and also on the location within each sample (compare the peak intensities corresponding to

Figure 4. (a) Ni L₃-edge spectra obtained from Ni ions with average oxidation states of 3.4+ (red) and 2.8+ (green). (b, c) RGB color maps obtained for the samples show the average oxidation state distribution, based on the spectra shown in (a); blue was used for the background. (b) The pristine sample is dominated by a lower average oxidation state, and (c) the charged-state sample is dominated by a higher average oxidation state. A 500 nm scale bar is overlaid on each image.

Figure 5. (a) O K-edge spectra obtained from pristine (red; 2-1) and charged (blue; 2-2) samples spanning the O 2p and TM 3d hybridization spectral region. The NiO spectral position is marked by an asterisk. (b) Difference spectrum, subtraction of '2-1' spectrum from '2-2' spectrum, highlighting the contributions of the Ni⁴⁺ and Ni²⁺ ions. The locations of the orbital states for the Ni⁴⁺ and Ni²⁺ ions are indicated by blue and red markers, respectively.

the O 2p-TM 3d and O 2p-TM 4sp hybridized orbitals). Later, in discussing Fig. 5, an attempt is made to correlate the feature changes in the O K-edge and Ni L₃-edge spectra.

Figures 2 and 3 demonstrate that the spectral features and, correspondingly, the average oxidation states of the Ni ions were not homogenous within the samples. The average oxidation state distribution for the Ni ions is plotted in Fig. 4. In Fig. 4(a), two representative spectral features are selected: a spectrum of highly oxidized Ni ions (~3.4+) from the charged sample, and a spectrum of Ni ions in a low oxidation state (~2.8+) from the pristine sample. From the stack of Ni

L₃-edge images, RGB color maps were obtained for the two spectra by using the Mantis program (<http://spectromicroscopy.com>). In these maps (Figs. 4(b) and 4(c)), the red color represents the 3.4+ average oxidation state, and the green color represents the 2.8+ average oxidation state; for the background, blue was used. Figures 4(b) and 4(c) show the RGB color maps for the pristine and the charged-state samples, respectively. It is clear that the pristine sample is dominated by Ni ions in lower average oxidation states, and that the charged-state sample is dominated by higher average oxidation states for the Ni ions. In the charged sample, the average oxidation state of the Ni ions is higher in the inner area of the larger primary particles.

The O K-edge spectral features plotted in Figs. 2(d) and 3(b) were generated from the O 2p orbitals hybridized with the 3d orbitals of the Ni²⁺, Ni³⁺, Ni⁴⁺, Co³⁺, and Mn⁴⁺ ions. It may be valuable to try to correlate the changes in these spectral features with those of the TM ions. The space-averaged O K-edge spectra of the pristine (red; 2-1) and charged (blue; 2-2) samples are reproduced in Fig. 5(a). Since the Ni³⁺ content is similar for these two samples, the subtraction of the spectrum of the charged-state sample from that of the pristine-state sample highlights the transitions involving the Ni²⁺ and Ni⁴⁺ ions. Fig. 5(b) shows such a subtracted spectrum. The expected spectral positions for the Ni⁴⁺ ions (blue) coexisting with the Mn⁴⁺ and Co³⁺ ions, and also for the Ni²⁺ ions (red) coexisting with the Mn⁴⁺ and Co³⁺ ions, are indicated, based on the report by Cherkashinin [1]. For the lower oxidation state, for example, the case of the Ni²⁺ ions relative to the Ni⁴⁺ ions, the effective increase in the electronic charge can result in the screening of the core holes, and it can be speculated that the transition energy will be shifted toward lower photon energies. This can result in an effective spectral shift toward lower photon energies for the pristine sample with respect to that for the charged-state sample, as observed in the figure. The above results indicate that as the sample becomes charged, the averaged oxidation state of its Ni ions increases, and the dominant spectral-feature change in the O K-edge is the increase in the peak intensity at ~529 eV (related to the Ni⁴⁺ e_g⁰ state) and a slight shift toward higher photon energies.

4. Conclusions

Pristine and charged-state Li_xNi_{0.88}Co_{0.08}Mn_{0.04}O₂ LIB cathode samples prepared by the FIB method were investigated by STXM with ~30 nm spatial resolution. The results produced diverse spatially resolved spectral features that were dependent on the location within the particle as well as whether the sample was pristine or charged. Although the spectral features of the Co L₃-edge and Mn L₃-edge and, correspondingly, the estimated average oxidation states (4+ for Mn and 3+ for Co), were almost the same throughout the samples, the Ni L₃-edge and O K-edge spectra showed clear differences depending on both the sample type and the location within the sample. This result indicated that the contribution of the Ni ions to the delithiation process was dominant. The average oxidation states of the Ni ions in the pristine and charged-state samples were estimated to be 2.9+ and 3.3+, respectively, when the entire particle area was averaged. The O K-edge spectral feature at ~529 eV increased in intensity as the average oxidation state of the Ni ions increased.

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