**Investigating the Reversibility of Structural Modifications of $\text{Li}_x\text{Ni}_y\text{Mn}_z\text{Co}_1$ -
 $_{y-z}\text{O}_2$ Cathode Materials during Initial Charge/Discharge, at Multiple
Length Scales**

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Abstract

In this work, we investigate the structural modifications occurring at the bulk, sub-surface, and surface scales of $\text{Li}_x\text{Ni}_y\text{Mn}_z\text{Co}_{1-y-z}\text{O}_2$ (NMC; $y, z = 0.8, 0.1$ and $0.4, 0.3$, respectively) cathode materials during the initial charge/discharge. Various analytical tools, such as X-ray diffraction, selected-area electron diffraction, electron energy-loss spectroscopy, and high-resolution electron microscopy, are used to examine the structural properties of the NMC cathode materials at the three different scales. Cut-off voltages of 4.3 and 4.8 V are applied during the electrochemical tests as the normal and extreme conditions, respectively. The high-Ni-content NMC cathode materials exhibit unusual behaviors, which is deviated from the general redox reactions during the charge or discharge. The transition metal (TM) ions in the high-Ni-content NMC cathode materials, which are mostly Ni ions, are reduced at 4.8 V, even though TMs are usually oxidized to maintain charge neutrality upon the removal of Li. It was found that any changes in the crystallographic and electronic structures are mostly reversible down to the sub-surface scale, despite the unexpected reduction of Ni ions. However, after the discharge, traces of the phase transitions remain at the edges of the NMC cathode materials at the scale of a few nanometers (i.e., surface scale). This study demonstrates that the structural modifications in NMC cathode materials are induced by charge as well as discharge at multiple scales. These changes are nearly reversible after the first cycle, except at the edges of the samples, which should be avoided because these highly localized changes can initiate battery degradation.

1 Introduction

2 Li-ion batteries (LIBs) have been applied to portable devices, such as laptops,
3 smartphones, and tablets. Beyond these small appliances, incorporating LIBs into large-scale
4 applications, such as electric vehicles¹ and smart grids², is a high-interest field of research.
5 Thus, both academia and industry have endeavored to improve the figure-of-merit of LIBs.
6 The realization of large-scale LIB systems requires a stringent set of criteria to be met,
7 including high energy and power densities, a high level of safety, low-cost fabrication, and a
8 long operational lifetime. Increasing the energy density of LIBs is currently the prime
9 concern because a high energy density results in longer operating times on a single charge.
10 Of the multiple parts that form a battery system, the cathode material has received particular
11 attention because it is a limiting factor on the capacity of LIBs.

12 To increase the capacity of cathode materials, a variety of lithium metal oxide
13 materials (LiMO_2 , where $M = \text{Co, Ni, Mn, etc.}$) with layered structures have been explored
14 after the successful commercialization of LiCoO_2 . Ni-based cathode materials have been
15 investigated in detail because of the potential for achieving high capacities. However, their
16 structural instability and safety issues are obstacles that have prevented the application of
17 batteries with Ni-based cathode materials to commercial appliances. Mn ions help to stabilize
18 the structure of LiMO_2 , but at a cost to the capacity. The addition of Co improves the rate
19 performance, but it is a toxic and high-cost element.³ In the literature, $\text{Li}_x\text{Ni}_y\text{Mn}_z\text{Co}_{1-y-z}\text{O}_2$
20 (NMC) cathode materials have been investigated to maximize the advantages of each
21 transition metal (TM), i.e., Ni, Mn, and Co, by balancing the composition of the TMs.
22 $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ are representative compositions of NMC
23 cathode materials that have been widely investigated.³⁻⁷ However, the growing demand for
24 high-capacity LIBs has encouraged the exploration of novel NMC compositions to improve
25 the energy density.

Ni-rich NMC materials have drawn much attention for achieving high capacities without compromising safety aspects.⁸⁻¹⁰ The primary concerns with such Ni-rich materials are the instability of the original structure and the following safety issues. Ni ions are continuously oxidized to maintain charge neutrality during the removal of Li. The highly oxidized Ni⁴⁺ ions are thermodynamically unfavorable; thus, Ni⁴⁺ tends to be reduced to more stable states. The unwanted reduction of Ni ions can lead to cation mixing between Ni²⁺ and Li⁺ ions because their ionic radii are comparable ($r_{Ni^{2+}} = 0.69 \text{ \AA}$, $r_{Li^+} = 0.76 \text{ \AA}$).¹¹ The movement of metal ions is highly associated with phase transitions, e.g., the original layered structure (space group = $R\bar{3}m$) to a disordered spinel structure (space group = $Fd\bar{3}m$), and then finally to the rock-salt structure (space group = $Fm\bar{3}m$); all of these structures share the same oxygen lattice but with different cation positions. The results of first-principle calculations have demonstrated that phase transitions are kinetically controlled processes;¹² therefore, the phase transitions can occur, even at room temperature, with a sufficient driving force for ionic movement. In a highly charged state, Li vacancies can facilitate phase transitions by providing sufficient empty space in the structure. These structural transitions are detrimental to cathode materials because they are accompanied by the release of O₂ gas, which can pose a considerable threat to safe operation by reacting with the flammable electrolytes inside the battery cell. In addition, the diffusion paths of the Li ions are blocked by cation mixing,¹³ resulting in the degradation of the battery performance.

In this study, we investigate the structural changes that occur in Li_xNi_yMn_zCo_{1-y-z}O₂ (y, z = 0.8, 0.1 and 0.4, 0.3, respectively) cathode materials during the initial charge/discharge at cut-off voltages of 4.3 and 4.8 V. The first electrochemical cycle only induces inceptive changes in the cathode material; thus, a careful analytical approach is required for such an investigation. While previous studies have focused on the average structural properties of cathode materials after severe electrochemical reactions,^{5,14,15} we

1 examine the structural modifications in the NMC materials at three different scales after the
2 initial charge/discharge. The thorough multiple-scale investigation reported in this paper
3 provides a comprehensive understanding of the nascent structural modifications induced by
4 the initial electrochemical cycle, which may initiate the degradation of the battery
5 performance. Bulk-scale analysis is conducted with X-ray diffraction (XRD), which indicates
6 that the bulk $R\bar{3}m$ layered structure is well maintained with only slight changes in the lattice
7 parameters. Changes to the crystallographic and electronic structures at the sub-surface scale
8 are explored with selected-area electron diffraction (SAED) and electron energy-loss (EEL)
9 spectroscopy, which is used to obtain spectra of the O K-edge and Ni, Mn, and Co $L_{2,3}$ edges.
10 In this study, the sub-surface areas are defined as the near-surface areas, which generally
11 span several tens of nanometers from the edges of the samples. These areas are investigated
12 as transient regions between the bulk of the sample and the surface. Several NMC particles
13 that cover each combination of cut-off voltage and composition are analyzed to trace the
14 changes in the crystallographic and electronic structures after the initial charge/discharge. In
15 most cases, the oxidation and reduction of Ni ions are the main mechanisms for relieving
16 charge imbalance during the delithiation and lithiation processes, respectively, but the high-
17 Ni-content NMC materials subjected to the higher cut-off voltage exhibits the opposite
18 behavior, i.e., the Ni ions are reduced during the delithiation process. Surprisingly, the
19 crystallographic and electronic structures are recovered at both the sub-surface and bulk
20 scales after the discharging process, despite the unexpected behavior of the Ni ions. However,
21 we find localized areas with spinel or rock-salt structures at the surface of the NMC materials
22 after the initial cycle, implying that the complete recovery from the structural changes is
23 difficult at the very edges of the samples. This work demonstrates that a single
24 electrochemical cycle can initiate surface degradation at the nanoscale, even though the

reduced Ni ions and resulting structural transitions induced by the initial charge can be retrieved in the sub-surface and bulk regions during the subsequent discharge.

Experimental Section

The NMC cathode materials ($\text{Li}_x\text{Ni}_y\text{Mn}_z\text{Co}_{1-y-z}\text{O}_2$; $y, z = 0.8, 0.1$ and $0.4, 0.3$, respectively; hereinafter referred to as NMC811 and NMC433, respectively; commercial products) were either electrochemically charged with a cut-off voltage of 4.3 V or 4.8 V, or charged and discharged (namely, discharged) over a voltage range of 2.0–4.3 V or 2.0–4.8 V. Both types of electrochemical experiments were performed at a rate of C/10 using a constant current. The actual compositions of the NMC cathode materials are given in our previous paper.¹⁶ The cathode part was prepared as a mixed slurry of 80 wt.% of the active NMC particles, 10 wt.% of the conducting agent (Denka Black), and 10 wt.% of a polyvinylidene fluoride (PVDF) binder in a N-methyl pyrrolidone (NMP) solvent. The mixed slurry was coated on the Al foil, which acted as a current collector. The cathode part was incorporated into 2032-type coin cells with Li metal for the anode, a Celgard separator, and an electrolyte of 1 M LiPF_6 dissolved in ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC) (volume ratio of 1:1:1). After reaching the designated potentials of 4.3 or 4.8 V (for the charged samples) and 2.0 V (for the discharged samples), the coin cells were disassembled and the cathode part was immersed in a pure DMC solution to remove any residual salts before the subsequent analysis of NMC cathode materials.

XRD patterns were obtained with a D-max 2500/PC X-ray diffractometer (Rigaku) using $\text{Cu K}\alpha$ radiation over a 2θ range of 10–70° at a scan rate of 2°/min. The XRD patterns were used to analyze the bulk structure of the NMC cathode materials in the mixed slurries.

For the transmission electron microscopy (TEM) observation, NMC particles were acquired by abrading the slurry coating on the Al foil. The particles were then sonicated in a

small vial of pure DMC to ensure an adequate dispersion of particles before dropping the solution onto a lacey-carbon TEM grid. The sample preparation and loading into the TEM sample holder were performed in a dry room or Ar-filled glove box to minimize the exposure of the sample to air and moisture. Bright-field (BF) images, selected-area electron diffraction (SAED) patterns, and high-resolution electron microscopy (HREM) images were obtained with a Tecnai G² F20 (FEI) TEM at an accelerating voltage of 120 kV. The electron energy-loss (EEL) spectra of the NMC materials were acquired with a Quantum 963 GIF system (Gatan). The spectra were obtained in the diffraction mode, with the selected-area (SA) aperture defining the area that was analyzed. The spectra were aligned with respect to the zero-loss peak position. The background of the spectra was subtracted by using the power-law method embedded within the Digital Micrograph (Gatan) software. The energy resolution, which was determined from the zero-loss peak, was approximately 1.0 eV.

Results and Discussion

Figure S1 of the Supporting Information shows the charge and discharge profiles of the NMC433 and NMC811 cathode materials at a rate of C/10 with cut-off voltages of 4.3 and 4.8 V, which are representative potentials for normal operation and extreme conditions, respectively. Table S1 summarizes the initial charge and discharge capacities of the NMC433 and NMC811 materials, with the results suggesting that a higher Ni content or higher cut-off voltage is favorable for delivering a higher energy density when using NMC-based cathode materials.

The structural changes induced in the bulk NMC-based cathode materials by the initial charge/discharge were analyzed with the XRD patterns presented in Figure 1(a). For both the NMC433 and NMC811, there is no evidence of new diffraction peaks or peak splitting in the XRD patterns, indicating that the core structure of the NMC materials is

maintained, i.e., an α -NaFeO₂ layered structure with a space group of $R\bar{3}m$, during the insertion and removal of Li ions. However, a shift in the positions of the diffraction peaks is noticeable, suggesting that the lattice parameters of the NMC materials have been modified. Figure 1(b) shows the changes in the lattice parameters and corresponding changes in the volume of the unit cell. During the charge, the a -axis of both of the NMC materials decreases as the voltage increases to 4.3 V and then it remains almost constant until 4.8 V is reached, while the c -axis increases as the voltage increases to 4.3 V but then decreases until 4.8 V is reached. The decrease in the a -axis originates from the decrease in the average metal-metal bond length because the effective ionic radii shrink when TMs are oxidized to fulfill the charge neutrality during charging.¹⁷ With the removal of Li ions, the c -axis is elongated at first because of the electrostatic repulsion between the TMO₂ layers along the c -axis of the unit cell. However, the c -axis decreases at high voltages. The average charge of the O ions is thought to be lowered by a low concentration of Li. Thus, the repulsion of the O layers also decreases, which results in a reduction of the c -axis.¹⁸ The changes in the lattice parameters of NMC materials during the initial charge are similar to that of other Ni-based layered-structure materials.^{4,15,19,20} After discharging to 2.0 V, the lattice parameters and unit cell volumes of both the NMC433 and NMC811 have mostly recovered. At the macroscopic bulk scale, the unit cells of the NMC433 and NMC811 are slightly deformed while maintaining their structure while charging. However, any deformation is recovered when the Li ions are re-inserted into the layered structure during the discharge.

Local areas, especially the surfaces of the electrode materials, are the reaction fronts of the electrochemically driven Li-ion movements. Thus, these areas are subjected to more severe reactions than the averaged areas. It has been reported that the gradient of the Li-ion concentration can induce local degradation during charge/discharge when compared to the bulk of the particles because of kinetic effects.²¹ Therefore, the crystal structures of the sub-

1 surface areas of the NMC particles were investigated at a smaller scale by obtaining SAED
2 patterns with TEM. The SAED patterns of the NMC433 and NMC811 are shown in Figure 2
3 alongside BF images, which show where the SAED patterns were acquired. A number of
4 particles were selected for the SAED acquisitions and the results are almost consistent. Thus,
5 only a representative set of results are presented in Figure 2. Additional examples are shown
6 in Figures S2 and S3 of the Supporting Information. Before charging NMC materials, the
7 surfaces of both the NMC433 and NMC811 have layered structures that are same to the bulk
8 materials. When charged to 4.3 V, the SAED pattern of the NMC433 is composed of spots
9 that only originate from the layered structure, which shows that the sub-surface structure of
10 the NMC433 has retained the original layered structure. However, a degree of surface
11 degradation has occurred at the sub-surface of the NMC811, as shown in the SAED pattern,
12 which is indexed as a mixture of the $2\bar{2}01$ zone-axis of the original layered structure and the
13 110 zone-axis of a spinel structure. The higher cut-off voltage of 4.8 V causes phase
14 transformations in both the NMC433 and NMC811. While the spots that originate from the
15 spinel structure are relatively dim in the SAED pattern of the NMC433 [Figure 2(d2)], there
16 are distinct diffraction spots that originate from the spinel structure in the SAED pattern of
17 the NMC811 [Figure 2(i2)]. This indicates that the phase transformation from the layered
18 structure to the spinel structure is more severe at the sub-surface of the high-Ni-content NMC
19 cathode materials. In addition, the morphology of the NMC-based cathode materials becomes
20 porous after being charged to 4.8 V. These crystallographic and morphological changes
21 indicate that the compositions of the TMs and the operating voltage have significant effects
22 on the stability of the crystallographic structure of the NMC materials even after the initial
23 charge. After being discharged to 2.0 V, the sub-surface structures of the NMC materials
24 have reverted to the original layered structure at the scale of several tens of nanometers,
25 regardless of the cut-off voltages and TM compositions, as confirmed by the SAED patterns

[Figures 2(c2), (e2), (h2), and (j2)].

NMC cathode materials can have three crystal structures, i.e., layered $R\bar{3}m$, disordered spinel, and rock-salt structures, and the material degradation occurs in a sequence.^{3,22,23} Each structure has a close-packed O lattice in common; thus, the phase transitions occur via the movements of the TM ions within the oxygen O framework. The relocation of the TM ions can lead to the modifications in the electronic configuration of each element. Therefore, to understand the structural modifications in detail, we exploited EEL spectroscopy to investigate the changes in the electronic structures of the elements in the NMC materials induced by the initial charge/discharge. Figures S4 and S5 of the Supporting Information exhibit the full EEL spectra containing the oxygen K-edge and Mn, Co, and Ni $L_{2,3}$ edges of the NMC433 and NMC811, respectively, after the charge/discharge at 4.3 and 4.8 V. Of these spectra, we present the EEL spectra of the O K-edge and Ni $L_{2,3}$ edges of the NMC433 at 4.3 V and NMC811 at 4.8 V in Figure 3. These spectra are representative of the extreme cases tested because the SAED patterns demonstrate that a high Ni content and high cut-off voltage play significant roles in the structural changes. In other words, the NMC433 at 4.3 V is an example of the mildest conditions tested, while the NMC811 at 4.8 V is the harshest conditions tested. In addition, the O K-edge shows highly noticeable changes during the phase transitions,^{24,25} and the Ni ions play a major role in charge compensation during the charge/discharge.⁴

The main features of the O K-edge in the EEL spectrum of a LiTMO_2 material with an $R\bar{3}m$ layered structure are two distinct peaks: a pre-edge peak and a subsequent main peak. The transition of electrons from the $1s$ core state to the unoccupied $2p$ states hybridized with the $3d$ states of the TMs forms the pre-edge peak.²⁶ The main peak is attributed to the transition of electrons from the $1s$ state to the hybridized states of the O $2p$ and metal $4sp$ states.²⁷ To compare the changes in the O K-edges that are induced by the electrochemical

reactions, we introduce an index, ΔE , which is the energy-loss difference between the main and pre-edge peaks at their highest intensities. The shifting of the pre-edge peak to a lower energy loss (higher ΔE) originates from the oxidation of the TM because the TM d -orbitals have higher binding energies and become closer to the ligand $1s$ -orbital during oxidation.²⁸ On the contrary, the pre-edge peak of the O K-edge moves to a higher energy loss (lower ΔE) when the TM ions bound to O are reduced.²⁷ Therefore, we can determine the changes in the valence of the TM ions bound to O with ΔE . Changes in the valence of the TM ions are also reflected in the $L_{2,3}$ edges of the given TM. The $L_{2,3}$ edges of TMs originates from the transition from the $2p$ states to the highly localized $3d$ states near the Fermi level. The splitting of the L edge stems from the degenerate $2p$ states being split into $2p_{1/2}$ and $2p_{3/2}$ levels because of spin-orbit coupling.²⁹ The white-line intensity ratio (L_3/L_2) implies the valence of the TM,³⁰ with the ratio decreasing during oxidation and increasing during reduction for the Mn,³⁰ Co,³¹ and Ni ions.³²

Figures 3(a) and (b) show changes in the O K-edge and Ni $L_{2,3}$ edges of the NMC433 at 4.3 V and NMC811 at 4.8 V, respectively, which are the two extreme cases of this study. The O K-edges are plotted on the x -axis of the ΔE based on the position of the main peak of a NiO reference. NiO has a rock-salt structure, which requires substantial modifications to be made to the chemical bonding between the O and TM ions, as well as the release of O_2 gas. Reversible structural changes are unlikely to occur in cathode materials with the layered structure once the rock-salt structure has been evolved. Therefore, the O K-edge of NiO is used as an indicator of irreversible structural modifications. The shape of the O K-edges of the NMC433 at 4.3 V and NMC811 at 4.8 V is roughly maintained during the charge/discharge. Our previous study demonstrated that the primary features of the O K-edge are maintained during the phase transition to the spinel structure, while significant changes occur in O K-edge with the phase transition to the rock-salt structure.²¹ Therefore, the O K-

edge indicates that the phase transition to the rock-salt structure barely occurs at the sub-surface scale during the initial cycle regardless of the TM composition or operating voltage, which corresponds well with the SAED patterns in Figure 2. However, the pre-edge peaks in the two cases move in opposite directions compared to the initial positions. In the case of the NMC433 charged to 4.3 V, the pre-edge peak of the O K-edge shifts to a lower energy loss; thus, ΔE becomes higher. However, the ΔE of the NMC811 charged to 4.8 V becomes lower as the pre-edge peak shifts to a higher energy loss. As the Li ions move in or out of the NMC materials, the valence of the Ni ions is modified to maintain charge neutrality inside the cathode materials, with the changes in the electronic configuration reflected in the Ni $L_{2,3}$ edges. For the NMC433 at 4.3 V, when the spectra are normalized to the intensity of the L_2 edge, the intensity of the L_3 edge decreases while charging, and then it increases while discharging. However, for the NMC811 at 4.8 V, the intensity of the L_3 edge increases during the charge but decreases during the discharge. In other words, the electronic structures of the NMC cathode materials are modified in different ways during charging at both extremes. However, it is noteworthy that despite the different trends in both cases, electronic structures return to their original states during the discharge. Theoretically, the threshold energy of an ionization edge is sensitive to the charge state and atomic bonding.³³ Thus, it can be a good indicator of any modifications made to the electronic structure. However, analyzing the chemical energy shift in the EEL spectra requires special attention because of the intrinsic energy-resolution of the electron beam (0.8–1.0 eV) and the possible instability of the high-voltage power supplies used with spectrometers and detectors.

Electrochemical reactions are kinetically limited. As a result, we have observed a localized phase transition to the disordered spinel structure in the sub-surface, even though the bulk structure is relatively unchanged during the initial charge. In addition to this microscopic inhomogeneity (within the particles), a macroscopic inhomogeneity (particle-to-

particle) is also expected. Thus, using EEL spectroscopy, we examine the electronic structure of several NMC particles that were subjected to various electrochemical-testing conditions. To compare the EEL spectra of the NMC materials intuitively, two indexes are used: ΔE for the O K-edge and the L_3/L_2 ratio for the TM $L_{2,3}$ edges. Figure 4 shows the changes in ΔE during the charge/discharge of the NMC433 and NMC811 at 4.3 and 4.8 V. In most cases, ΔE increases during the charging process and then decreases during the discharging process, suggesting that the TMs of the NMC cathode materials are oxidized when the Li ions are extracted and reduced when the Li ions return. The oxidation and reduction of the TMs during the charge and discharge processes, respectively, are the conventional mechanisms to maintain charge neutrality inside cathode materials. However, the behavior of ΔE is the opposite when charging the high-Ni-content NMC811 to 4.8 V, indicating that the TM ions are reduced during Li extraction. Despite the unusual behavior of the TM ions, ΔE recovers to its original value when discharged to 2.0 V.

Figure 5 shows the average and standard deviation of the L_3/L_2 intensity ratios acquired from several NMC particles tested at each condition, which were used to plot the graphs shown in Figure 4. By comparing the L_3/L_2 ratios determined for each TM in the charged or discharged NMC materials to that in the untested NMC particles, we can speculate which TM is the most responsible element for the changes in ΔE of the O K-edge, as well as the overall electronic structure of the NMC cathode materials during delithiation and lithiation. Figure 5 shows that the L_3/L_2 ratios of Mn and Co do not show considerable changes upon Li-ion uptake or removal in the NMC433 and NMC811 at either 4.3 or 4.8 V. However, the L_3/L_2 ratio of the Ni $L_{2,3}$ edges fluctuates as the Li ions are extracted or inserted, implying that the Ni ions are the most active TM participating in the charge-compensation during the electrochemical reactions. The abnormal response of the TM in NMC811 at 4.8 V is also reflected in the L_3/L_2 ratio, as shown in Figure 5(d). When charged to 4.8 V, the L_3/L_2

ratio of the Ni ions in the NMC811 increases, indicating the reduction of the Ni ions. To neutralize the charge imbalance during the Li removal and Ni reduction, certain elements in the NMC811 should be oxidized, or O₂ gas should be released. According to Figure 5(d), the changes in the L₃/L₂ ratios of Mn and Co in the NMC811 charged to 4.8 V are minor, implying that the Mn and Co ions are not oxidized to compensate for the charge imbalance. Thus, O is the only element left in the NMC materials. Even though the participation of O during the charging process in the NMC cathode materials has been reported elsewhere,^{7,14,28} the oxidation of O ions for charge compensation does not explain the reduction of the Ni ions. Therefore, we can assume that the O leaves the original structure. The BF image of the sub-surfaces of a NMC811 particle after being charged to 4.8 V [Figure 2(i1)] shows signs of porosity at the edges of the particle, and the porosity of the NMC811 particle is still present after being discharged [Figure 2(j1)]. Thus, the BF images indicate that O₂ gas has been released to relieve the charge imbalance, which is reflected in the morphological changes. Nevertheless, O₂ release is not the only mechanism for maintaining charge neutrality in the NMC811 because the crystal structure of the NMC811 returns to the original layered structure in the discharged state [Figure 2(j2)], which is unlikely to occur with only the loss of O₂. Sathiya *et al.*³⁴ reported interesting results regarding this peculiar phenomenon of the opposing evolution of TM ions in the case of Li₂Ru_{0.5}Sn_{0.5}O₃. They reported that Ru⁴⁺ ions were oxidized to Ru⁵⁺ ions when charged to 4.0 V, but the Ru⁶⁺ ions were reduced back to either Ru⁵⁺ or Ru⁴⁺ ions when charged to 4.6 V. They suggested that the sudden reduction of the Ru ions is induced by the formation of peroxo/superoxo-like species, such as Ru⁵⁺-(O₂)²⁻ or Ru⁴⁺-(O₂)⁻. In the case of the NMC cathode materials, there is insufficient evidence to confirm that the sudden reduction of the Ni ions in the NMC811 at a high voltage is caused by the formation of peroxo-like species. We expect that theoretical simulations will provide a deeper insight into this phenomenon.

We have investigated the reversibility of the structural changes in the NMC433 and NMC811 at the bulk scale with XRD and at the sub-surface scale with SAED and EELS during delithiation and lithiation at 4.3 and 4.8 V. Even though the unexpected behavior occurs in the NMC811 at a high operating voltage, we found that the crystallographic and electronic structural changes induced by the initial charge return to their original states when discharged, at least at the scale of several tens of nanometers. The structural changes during the Li uptake/removal in the NMC materials at 4.8 V were also examined at the nanoscale with high-resolution electron microscopy (HREM). Figure 6 shows the HREM images of the NMC433 and fast Fourier transforms (FFT) of the designated areas. The FFT results indicate that the edges of the NMC433 particles are more vulnerable to structural modifications than the bulk or sub-surface regions, and have structures that are not present in the SAED patterns [Figures 2(d2) and (e2)]. For example, the NMC433 particles have a rock-salt structure in the charged state and a spinel structure in the discharged state. More severe structural degradation at the edges is also shown in the HREM image of the NMC811 after being charged to 4.8 V, as shown in Figure 7(a). Figure 7(b) shows that the restoration of the original structure is not completed during the discharge; thus, the rock-salt structure is present at the surface. In addition, the surface porosity indicates that O₂ gas has released during the phase transformation when being charged to a high operating voltage, which occurs in order to maintain charge neutrality as the Ni ions are reduced. The release of O₂ gas from the structure can hinder the completion of the reverse phase transformation to the original structure. When the cut-off voltage is 4.3 V, even though the spinel and rock-salt structures are found at the surface of the NMC433 and NMC811 particles after being charged, the surface structures are almost recovered to the original layered R $\bar{3}$ m structure after discharging, as shown in Figure S6 of the Supporting Information. The HREM images in Figures 6 and 7 demonstrate that electrochemical reactions at 4.8 V induce severe structural

1 inhomogeneities at the surface of the NMC cathode materials. Furthermore, the recovery of
2 structural modifications at the surface of the NMC cathode materials is not complete at the
3 nanoscale when discharged, leaving highly localized regions with transformed structures.

4 5 **Conclusions**

6 In this study, we investigate the reversibility of the crystallographic and electronic
7 structural changes in NMC-based cathode materials during the initial charge/discharge at
8 multiple scales. The bulk NMC433 and NMC811 maintain their original layered $R\bar{3}m$
9 structure, but with some slight modifications to the lattice parameters, while nascent phase
10 transitions occur in the sub-surface areas during the charge. At the scale of several tens of
11 nanometers, any traces of phase transitions disappear during lithiation, implying that the
12 recovery of the original crystal structure is complete when discharged. Exploration of the
13 electronic structure of the NMC cathode materials at the same scale also demonstrates that
14 the changes to the valence of the TMs during the Li removal are retrieved when discharged.
15 Interestingly, the NMC811 exhibits an unexpected behavior. The Ni ions are initially
16 oxidized but then reduced at the higher potential. Even though different mechanisms govern
17 the charge compensation of NMC811 at the high cut-off voltage of 4.8 V, the valence of the
18 Ni ions still returns to its original value during the discharge. However, at the nanoscale,
19 structural inhomogeneities are induced by the initial charge, which are not entirely recovered
20 with discharging. After the first cycle, a few nanometers of the surface undergo an
21 irreversible phase transition and remain in this deformed structure. Even though it is a
22 negligible problem for the bulk battery performance after only one cycle, the gradual
23 accumulation of transformed structures may deteriorate the figure-of-merit of the battery cells
24 during long-term cycling. Therefore, surface engineering, which minimizes the structural
25 modifications that occur during charging and aids the complete recovery during discharging,

1 is highly recommended for retaining a high and long-term battery performance.

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10 **Supporting Information Available:** Charge/discharge profile of the NMC433 and NMC811
11 for cut-off voltages of 4.3 and 4.8 V, more examples of BF images and SAED patterns of the
12 charged/discharged NMC433 and NMC811, full EEL spectra of the NMC433 and NMC811
13 before and after the electrochemical tests, and HREM images of NMC433 and NMC811 at
14 4.3 V. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Figure Captions

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1 Table of Contents Graphic

2

3