Degradation of High-Nickel-Layered Oxide Cathodes from Surface to Bulk: A Comprehensive Structural, Chemical, and Electrical Analysis

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Multiple applications of lithium-ion batteries in energy storage systems and electric vehicles require highly stable electrode materials for long-term battery operation. Among the various cathode materials, high-Ni cathode materials enable a high energy density. However, cathode degradation accompanied by complex chemical and structural changes results in capacity and voltage fading in batteries. Cathode degradation remains poorly understood; the majority of studies have only explored the oxidation states of transition-metal ions in localized areas and have rarely evaluated chemical degradation in complete particles after prolonged cycling. This study systematically investigates the degradation of a high-Ni cathode by comparing the chemical, structural, and electrical changes in pristine and 500 times-cycled cathodes. Electron probe micro-analysis and X-ray energy dispersive spectroscopy reveal changes in the Ni:O ratio from 1:2 to 1:1 over a large area inside the secondary particle. Electron energy loss spectroscopy analysis related to structural changes is performed for the entire primary particle area to visualize the oxidation state of transition-metal ions in two dimensions. The results imply that the observed monotonic capacity fade without unusual changes is due to the continuous formation of the Ni$^{2+}$ phase from the surface to the bulk through chemical and structural degradation.

Li-ion batteries (LIBs) have been widely used not only in portable electronic devices, but also in large-scale energy storage systems.[1–4] With increasing demands for higher energy density and safety, extensive efforts have been made to achieve higher reversible capacity and output voltage and greater cycling stability in electrodes. Specifically, high-Ni-based layered oxide cathode materials, conventionally referred to as high-Ni NCM (Li[Ni$_{x}$Co$_{y}$Mn$_{z}$]O$_2$, $x > 0.8$), are considered the most promising cathode materials for electric vehicle applications because of their high specific capacities (more than 200 mAh g$^{-1}$ at high voltages of 4.3–4.6 V).[5,6] However, these materials have inherent problems due to their high Ni content.[7–11]

The electrochemical performance (e.g., cycle life) of a high-Ni NCM cathode is predominantly determined by the structural, mechanical, and surface stabilities of the cathode material. Specifically, the following problems are exacerbated as the Ni content increases, which can lead to performance deterioration: i) cation mixing between Li and Ni, which interferes with the mobility of Li ions,[12,13] ii) low thermal stability,[14,15] iii) crack formation during prolonged cycling,[16–18] iv) surface reactivity,[19] and v) oxygen release[20–23] and transition-metal (TM) dissolution.[23–26] Therefore, it is necessary to understand both the chemical state and structural changes of high-Ni NCM cathode materials to elucidate the degradation mechanism during cell cycling.

The chemical and structural changes in high-Ni NCM cathode materials have been intensively investigated with X-ray and electron beam-based analytical techniques. The chemical...
degradation of high-Ni NCM cathodes is generally attributed to surface reactions arising from the accumulation of a NiO-like rock-salt phase on the surface of the cathode material due to the reduction of reactive Ni\(^{2+}\) and oxygen release, which destabilizes the crystal structure. Previous studies have also reported on the origin of TM dissolution in high-Ni NCM particles in terms of structural stability, demonstrating that TM dissolution is a key degradation factor that preferentially occurs for particles with high surface area/volume ratios, i.e., severely cracked/broken particles.\(^{[27]}\)

The structural changes in LiNiO\(_2\) materials, similar to those in high-Ni NCM cathodes, represent a phase transformation from a layered structure (LiNiO\(_2\), \(R-3m\)) to a spinel structure (LiNi\(_2\)O\(_4\), \(Fd-3m\)) and, finally, to a rock-salt structure (NiO, \(Fm-3m\)) because of a collapse in the stoichiometry between Ni and O due to oxygen release and TM dissolution. Ryu et al. studied the capacity fading mechanism of NCM cathodes with Ni content and found that the anisotropic expansion of Li\([Ni_{1-x}Co_xMn_{1-y}]_2O_4\) (\(x > 0.8\)) is greater than that of Li\([Ni_{1-x}Co_xMn_{1-y}]_2O_4\) (\(x < 0.8\)); this anisotropic expansion eventually accelerates micro-cracking in the cathode particles.\(^{[5]}\) Thus, micro-cracks in the primary particles provide path ways for the electrolyte, leading to chemical degradation through electrolyte attack on the newly formed surface. Therefore, during repeated cycling, simultaneous chemical and structural changes in the cathode material adversely affect its stability.

Li et al. studied both the structural and chemical evolution of a high-Ni NCM cathode (LiNi\(_{0.8}Mn_{0.1}Co_{0.1}O_2\)) at the atomic level.\(^{[28]}\) They successfully observed the rearrangement of the atomic structure from a layered to spinel phase and, eventually, to a rock-salt phase, which included a disordered layered structure, during repeated cycling using transmission electron microscopy (TEM). In addition, electron energy loss spectroscopy (EELS) analysis has been employed to elucidate the chemical state changes in TMs.\(^{[29,30]}\) Although differences between TM oxidation states on the surface and in the bulk cathode have been used to illustrate the degradation mechanism, such information does not provide a full understanding of the degradation progress because of the lack of analytical data in the local area, whereas degradation occurs throughout the entire area of primary and secondary particles. Both the chemical and structural degradation of high-Ni NCM material begins from the surface in direct contact with the electrolyte before expanding into the bulk during continuous cycling.

Unfortunately, the degradation of layered cathode materials is complicated, such that their aging processes are even more complex. Capacity fading does not have a single cause, but rather originates from a variety of processes and their interactions. The majority of cathode material degradation is due to closely related chemical and structural changes, which cannot be interpreted independently. Therefore, enhancing high-Ni NCM cathode material performance should focus on a comprehensive understanding of chemical and physical changes.

The goal of this study is to understand the degradation of high-Ni NCM cathodes by comparing a pristine cathode and a cathode that has been cycled 500 times. Microstructural images of the chemical, crystal, and electronic structural changes are analyzed using electron microscopy-based analytical techniques. Specifically, the results of electron probe micro-analysis (EPMA), X-ray energy dispersive spectroscopy (XEDS), and EELS combined with TEM reveal changes in the Ni content, crystal structure, and oxidation state on the surface and bulk cathode, confirming localized degradation in the cathode. Our results clearly demonstrate that changes in the structure, chemical composition, and oxidation state of the TMs propagate from the surface to the bulk over prolonged cycling, leading to the degradation of high-Ni NCM cathodes. This study employs various analytical tools to indicate a new pathway for high-Ni NCM cathode degradation, especially at the primary particle level.

Electrochemical degradation was tested during long-term cycling, specifically by obtaining the charge/discharge voltage profiles corresponding to the differential capacity versus voltage (\(dQ/dV\)) plots, Coulombic efficiency (CE) with capacity retention, and direct-current internal resistance (DCIR). Figure 1a shows the charge/discharge voltage profiles of cylindrical-type full cells at the 2nd, 100th, 200th, 300th, 400th, and 500th cycles. The charge/discharge capacity decreases with cycling due to an increase in polarization. As shown in the charge/discharge curve (Figure 1a), the slope of the voltage versus specific capacity becomes steeper every 100 cycles. The voltage declines more rapidly and reaches the cut-off voltage at a lower capacity value with an increasing cycling number, resulting in accelerated capacity loss. This deterioration is mainly due to accumulated cell resistance with cycling. Furthermore, degradation of the cathode material is one of the main reasons for cell degradation, which can be electrochemically explained by the \(dQ/dV\) analysis. Figure 1b shows the \(dQ/dV\) curves at the 2nd, 100th, 200th, 300th, 400th, and 500th cycles. The peak intensity varies at \(\approx 3.5, 3.7, \) and \(4.2\) V, corresponding to the oxidation and reduction reaction peaks of cathode materials due to multiphase transitions, including the hexagonal (H1, H2, and H3) and monoclinic (M) phases.\(^{[31–33]}\) The pristine layered structure (H1) transitioned to the monoclinic (M) and two other hexagonal phases (H2 and H3), as shown in Figure 1b. Here, the H2 and H3 phases represent the reduced and increased d-spacing associated with the \(c\)-axis in the H1 phase, respectively. With increased cycling, the peak intensity appears to decrease due to the increasing irreversible phase transitions in the cathode materials. Finally, the degradation of the cell capacity during cycling is predominantly caused by increasing polarization and irreversible phase transitions. Specifically, \(dQ/dV\) peaks denoting the H2/H3 phase transition at \(\approx 4.2\) V disappear completely after 200 cycles. This irreversible phase transition and polarization influence the CE, such that the slope of CE decreases steeply after the 200th cycle, which is similar to the trend shown in Figure 1c. The discontinuity of CE every 100th cycle, as shown in Figure 1c, occurs when the electrochemical measurement is stopped and restarted for the measurement of DCIR. The average CE decreases from 99.74% at the beginning (0–100 cycles) to 99.52% at the end (400–500 cycles). As shown in Figure 1d, the DCIR, which is related to the internal resistance of the cell, was checked every 100 cycles up to 500 cycles. With increasing cycling, the DCIR gradually increases from 127 m\(\Omega\) for the uncycled cell to 275 m\(\Omega\) after 500 cycles, which is also confirmed by the increasing overpotential in the \(dQ/dV\) curves shown in Figure 1b. This finding indicates that electrochemical performance degradation accompanies changes in the structure and chemical composition of the cell.
The increase in the resistance of a full-cell can occur in both the anode and cathode materials. Among the various sources of increased resistance, previous studies have extensively reported on the chemical/structural degradation on the surface of the NCM particle in the cathode material and the formation of a solid electrolyte interface layer and the deposition of dissolute transition metals in the anode material. To verify the contributions from the anode and cathode to the electrochemical degradation of the full-cell, electrochemical impedance spectroscopy (EIS) measurements were performed separately for symmetric half-cells composed of the anode and cathode electrodes, which were disassembled from a 18650 cylindrical-type cell in pristine conditions and after 500 cycles. As shown in Figure S1 in the Supporting Information, the graphite anode does not exhibit significant resistance changes after 500 cycles, but a substantial resistance change occurs in the NCM cathode symmetric half-cell. Therefore, the degradation of NCM cathode materials rather than graphite anode materials is primarily responsible for the electrochemical performance degradation of full cells. Thus, in this study, we consider that capacity fading is predominantly due to the degradation of the NCM cathode. After the average impedance of the electrodes was confirmed by EIS measurements, we successfully visualized the spatial resistance difference in the cathode using electron beam-induced current (EBIC) analysis. A schematic view of the EBIC measurement process is provided in Figure S2 in the Supporting Information. The EBIC depends on the sum of all resistances along the shortest current path (including the contact resistance at the interfaces) and the electron beam absorbed current (EBAC) on the surface of the material. According to the EBIC images of the NCM cathode cross-section in Figure 2, the EBAC varies more with the material (i.e., NCM secondary particles, electrodes, or conductive binders) than with the total resistance of the shortest current path. If the resistance along the shortest current path is dominant, the difference in the EBIC between the primary particles should be quite large due to the existence of isolated primary particles generated by micro-cracking. However, there are no invisible or high-resistance NCM primary particles. In other words, although there is extensive cracking of primary particles, the primary particles are not electrically separated from each other and the contact resistance is not significant due to high electronic conductivity caused by the high Ni content.[14,34]

The EBIC images are colored according to the temperature contrast range, as shown in Figure 2c,d. However, it is difficult to observe any differences between Figure 2c,d. Hence, phase maps were reconstructed for improved visibility using a bivariate histogram analysis aided by the Digital Micrograph S/W (Gatan Ltd.) software, as shown in Figure S3 in the Supporting Information. In the bivariate histograms created using scanning electron microscopy (SEM)-back-scattered electron (BSE) and EBIC images, three primary areas of EBIC contrast are observed (Figure S3d,l, Supporting Information). The areas within the red dotted rectangles in Figure S3d,l in the Supporting Information correspond to artifacts from re-deposition on the surface during cross-sectional milling. Region of interest (ROI) 1 was reconstructed into a phase map to predominantly represent the Al current collector with low BSE contrast and high EBIC (low resistance), both in the pristine case and after 500 cycles. Similarly, the phase map of ROI 2 indicates NCM particles in Figure S3f,n in the Supporting Information. However, after 500 cycles, ROI 3, which has the lowest EBIC contrast (highest resistance), exhibits a greater concentration...
than the pristine case. The phase map reconstruction in this case represents the surface of the NCM secondary particles, whereas that in the pristine case corresponds to binder materials, as shown in Figure S3g,o in the Supporting Information and Figure 2e. In addition, the highest resistance area is clearer on most of the surfaces of the cracked secondary particles and small secondary particles when the phase maps from ROIs 1, 2, and 3 are combined into a single RGB mixed image (Figure 2f). Therefore, the EBIC results may indicate that increased internal resistance of the battery due to continuous long cycling is mainly attributable to the surface of the cathode particles or the new surface generated by crack formation.

The distributions of chemical compositions in the pristine cathode and cathode after 500 cycles were analyzed by cross-sectional EPMA (Figure S4, Supporting Information). To trace the changes in the chemical composition between the two cathodes, ternary composition diagrams of the TMs (Ni, Co, and Mn) were reconstructed from the EPMA results, as shown in Figure S4f,l in the Supporting Information. However, no significant compositional changes occur in the TMs (Ni, Co, and Mn) and the composition ratio is maintained despite the probable occurrence of TM dissolution. Previous studies have assumed that TM dissolution progresses at the same rate as the initial TM composition ratio.[27] Nevertheless, the ratio of

**Figure 2.** Electrical resistance characteristics according to the EBIC analysis. a,b) SEM-BSE images and corresponding c,d) EBIC images and e,f) RGB mixed phase maps. (a, c, e) and (b, d, f) correspond to the pristine electrode and that after 500 cycles, respectively. The dark spots at the surface of the NCM secondary particles in (a) are hydrocarbon contaminations formed by a long exposure to the atmosphere after cross-section polishing. All scale bars represent 20 μm.
Ni and O changes dramatically, with an increased proportion of Ni after 500 cycles, as shown in Figure 3a,b. Binary compositional diagrams of Ni and O were plotted using the quantitative EPMA results, as shown in Figure S4 in the Supporting Information. The colored contours indicate high concentrations for the Ni$_2$O composition results. However, quantifying the O content based on the EPMA and XEDS analyses is difficult because these approaches are not suitable for light elements, such as O, and exhibit large errors due to the assumptions, e.g., geometric factors, beam and sample angles, detector take-off angle, and sample composition. Therefore, in this study, we compared only the relative composition ratio distributions because all EPMA conditions were equal. In Figure 3a, the high Ni$_2$O ratio concentrations, as denoted by the colored contours, in the pristine case are distributed between the 1:1 and 1:2 composition guidelines. However, after 500 cycles, the oval shape of the colored contour elongates in the direction with a higher Ni content. Thus, the Ni:O ratio increases in certain NCM particles during long-term cycling. As the absolute amount of Ni decreases due to TM dissolution, the relative amount of O must be reduced even further for the relative amount of Ni to increase and the relative amount of O to decrease. Oxygen release phenomena$^{[23,35–37]}$ exist in NCM cathode systems and occur more frequently in high-Ni NCM cathodes.$^{[23]}$ To identify where the relative amount of Ni increases (O decreases), phase maps were reconstructed from the oval-shaped green and red areas at the Ni–O binary composition diagrams in Figure 3a,b. In the pristine case, the high Ni–O ratio concentrations, highlighted by the colored contours, occupy most of the area of the large and small NCM secondary particles. However, the high-Ni concentration distribution (beyond the 1:1 composition line) in red corresponds to a certain part of the surface of the NCM secondary particles. Previous studies have assumed that the destabilizing effect of a high-Ni content on the crystal structure and the chemical composition during the electrode manufacturing process are the causes of the formation of a Ni-rich area over part of the surface of the NCM secondary particles.$^{[14,22,38–42]}$ Detailed changes in the surface structure were examined in subsequent TEM analyses. However, for the cathode after 500 cycles, the equal area red oval in Figure 3b not only represents the surface, but also deep inside the NCM secondary particles, whereas the green area corresponds to the bulk of the NCM secondary particles, as in the pristine case. The depth of the Ni-rich area is estimated to extend more than 5 μm from the surface. The chemical compositional degradation toward the 1:1 Ni:O ratio appears to not only occur on the surface but also in the bulk interior of the NCM secondary particles.

To conduct an accurate analysis and visualize the chemical degradation of a single NCM secondary particle, chemical particle analysis was performed using the TEM-XEDS results shown in Figure 4 (see the Experimental Section). Inhomogeneous structural and chemical degradation occurs between high-Ni NCM secondary particles.$^{[27]}$ Therefore, to observe distinct structural and chemical changes, a single NCM secondary particle expected to undergo severe degradation (i.e., a severely broken particle) was selected as the TEM sample in the cross-section view of the focused ion beam. We note that most of the NCM secondary particles shown in Figure 4e are not uniformly degraded. As listed in Table S1 in the Supporting Information, the molar fractions of the TMs differ minimally between the pristine cathode and the cathode after 500 cycles, despite the fact that the atomic ratio between the TMs and O changes significantly from 1:2.0578 to 1:1.2052. Similar to the EMPA analysis, these findings can be explained by the fact that the absolute amounts of Ni, Co, and Mn decrease in proportion to the initial ratio of the molar fraction due to transition-metal
dissolution, with a decrease in the relative amount of O (TMs increase), i.e., oxygen evolution dominates over transition-metal dissolution phenomena. The detailed changes in Ni, Co, and Mn with O are shown using binary compositional distribution diagrams between the pristine case and that after 500 cycles in Figures S5 and S6 in the Supporting Information. After 500 cycles, all TMs increased relative to the chemical composition ratio in the pristine state. Therefore, we focused on the chemical degradation of Ni not only because we analyzed high-Ni cathode materials but also due to the similar chemical changes in all TMs. Figure 4a shows the Ni content histogram of the segmented particles determined using the particle image analyzer. The atomic percentage of Ni at half the number of accumulative particles for 500 cycles is 38.4 (±3.0) at%, whereas that in the pristine case is 29.2 (±3.5) at%. This difference can account for the fact that the Ni content distribution of the segmented particles shifts to a high Ni concentration after long-term cycling. To visualize the microstructural changes in the
Ni content distribution, sectionalized chemical composition maps of Ni were reconstructed for the pristine case and that after 500 cycles (Figure 4c,e, respectively). For the Ni content distribution, nearly all the segmented particles in the 500-cycle case exhibit an atomic percentage of more than 42.0 at% inside the NCM secondary particles. In contrast, in the pristine case, this percentage is less than 33.5 at%. Therefore, the chemical degradation of the NCM secondary particles causes the stoichiometry of Ni and O to change from 1:2 to 1:1 during long-term cycling not only on the surface but also inside the bulk cathode.

A substantial change in the ratio between the atomic percentages of Ni and O due to long-term cycling must involve a structural change in the layered structure. Thus, synchrotron X-ray high-resolution powder diffraction (HRPD) analysis was performed to identify the structural differences associated with the change in the Ni ratio. Synchrotron X-ray HRPD data in pristine conditions were indexed to a hexagonal LiNi_{0.87}Co_{0.09}Mn_{0.04}O_2 structure with a space group of R-3m, as illustrated in Figure S8 in the Supporting Information. After 500 cycles, the d-spacings of the c-axis-dependent (003) and (006) increased, whereas those of the a-axis-dependent (012) and (101) decreased. The lattice parameters of the a- and c-axes changed from 2.87402 and 14.20180 Å to 2.86241 and 14.28150 Å, respectively. The d-spacing changes due to long-term cycling are known to induce intergranular cracking that accompanies the anisotropic volume evolution of the primary cathode particles.[3,4,13,46] We conducted a Rietveld analysis to obtain a more thorough understanding of the structural changes between the pristine cathode and that after 500 cycles. This anisotropic volume expansion is direct evidence of structural degradation that leads to capacity fading due to intergranular cracking.

We confirmed that the chemical changes, such as those related to the Ni and O composition ratio, and structural changes, such as those related to the lattice parameters, are simultaneously accompanied by cathode degradation.

The Rietveld refinement results in the pristine case are summarized in Figure S9 and Table S2 in the Supporting Information, which show that the percentage of Li sites occupied by Ni ions is 1.85%. These results indicate that cation mixing is low only on the surface of up to ≈8 nm (Figure 5h). Cation mixing is not only observable from the surface to greater depths over a wide area but also partially observed in the bulk (Figure 5i). We note that the scale bars in Figure 5g,h are different from those in the other images.

To observe the microstructural degradation of the primary particles in more detail, we performed high-resolution scanning TEM and high-angle annular dark-field (HRSTEM-HAADF) analysis. As shown in Figure 5a,d,g, numerous defects were observed in the NCM primary particles after 500 cycles. These not only included nanosized voids but also intragranular cracking along the (001) plane due to anisotropic volume expansion of the NCM primary particles due to repeated charge/discharge processes during long-term cycling. These voids and micro-cracking have been frequently observed and reported.[37,46] The HRSTEM-HAADF images for the pristine case in Figure 5b,c show that the NCM particle has a layered structure (R-3m) both on the surface and in the bulk primary particles. For certain particles in the pristine case, we barely observed the cation mixing layer, with a thickness of ≈1–2 nm on the surface. However, after 500 cycles, as shown in Figure 5e, the cation mixing layer expands to more than 20 nm below the surface. Moreover, a phase transformation is observed from the layered structure to the cubic structure up to ≈3–7 nm below the surface. This layered structure is maintained in the center part of the primary particles at least 100 nm below the surface, where even cation mixing is not observed in Figure 5f. This cation mixing and the phase transformation from layered to cubic at the surface have been extensively studied, such that previous studies have documented that the formation of NiO (rock-salt-type cubic, Fm-3m) leads to capacity fading because NiO exhibits electronic and ionic insulation properties and interferes with the redox reaction, hindering the intercalation of Li.[39] Nonuniform structural degradation is observed between primary particles, as well as secondary particles. The selected area diffraction patterns (SADPs) in Figure S11 in the Supporting Information, which were taken in the e-beam direction parallel to the [100] zone axis at the center of the NCM primary particle, show that the crystal structure and orientation are off the [100] zone axis and distorted toward the surface. Thus, certain primary particles were subjected to severe structural deformation, followed by bending and the formation of a low-angle grain boundary or nano-cracking.[46,47] Figure S12 in the Supporting Information shows the STEM-HAADF images of the most severely deformed NCM primary particles after 500 cycles. The closer to the surface of a secondary NCM particle, the more structural distortion of the primary NCM particles is observed, including the observation of low-angle grain boundary, nano-cracking, and voids. For the severely deformed primary particle, such as that shown in Figure 5g, a thicker NiO layer forms on the surface of up to ≈8 nm (Figure 5b). Cation mixing is not only observable from the surface to greater depths over a wide area but also partially observed in the bulk (Figure 5i). We note that the scale bars in Figure 5g,h are different from those in the other images.

Although structural degradation in the bulk cathode can easily be observed by HRSTEM, analyzing changes across the entire area of primary particles (>150–500 nm) is difficult due to the limited field of view with HRSTEM (>50 nm). Therefore, to observe changes in structural degradation across the entire area of primary particles, STEM-EELS spectrum images were analyzed for phase identification according to the electronic structure. This approach is the best for examining the electronic structures of multiple phases in NCM particles because, similar
to near-edge X-ray absorption fine structure (NEXAFS), the electron loss near-edge structure (ELNES) can be measured as the sum of the spectra from all electronic structural phases in the sample. This approach also has good spatial resolution with less sensitivity to surface states than NEXAFS. Figure 6c–f shows the ELNES spectrum change in the Ni L₂,3 edge and the O K-edge of NCM primary particles in the pristine and 500-cycle samples, respectively. Line profiles were acquired in the directions of the red arrows shown in Figure 6a,b. As shown in Figure 6c,e, the Ni L₂,3 edge ELNES spectrum consists of two major peaks, which correspond to the transition from 2p₁/₂ orbitals (L₂ edge at 872 eV) and those from 2p₃/₂ (L₃ edge around 855 eV). Previous EELS studies of the electronic structure of LiNiO₂₃⁴,⁴⁰,⁴⁸ indicate that LiNiO₂ (Ni³⁺) has a broad peak at 855 eV, whereas NiO (Ni²⁺) and NiO₂ (Ni⁴⁺) have relatively sharp peaks at 854 and 857 eV, respectively. As shown in Figure 6c, a broad peak containing peaks at 853.5 and 855 eV is observed inside the pristine primary particles, which is likely attributable to certain NiO (Ni²⁺) and dominant LiNiO₂ (Ni³⁺) chemical structures. The peak at 853.5 eV appears sharper as it moves from inside the primary particle to the surface. In other words, the chemical structure of the NiO-like phase exists predominantly on the surface, which is consistent with the EPMA results. After degradation of the cathode by long-term cycling, the intensities of the peaks at 853.5 and 855 eV are nearly identical inside the primary particle. In addition, the 853.5 eV peak is relatively sharp, similar to that in the pristine case, when the EELS measurement point moves to the surface from the bulk. This characteristic may indicate that the NiO and LiNiO₂ phases inside the NCM cathode particle became mixed after degradation by electrochemical cycling. To visualize the microstructural distributions of Ni³⁺ and Ni²⁺ throughout the area of the NCM primary particles, the EELS spectrum images were reconstructed onto the energy dispersion map of the maximum intensity of Ni L₃ between 852.0 and 866.0 eV for both the pristine case and that after 500 cycles (Figure 6g,h, respectively). Thus, not only is Ni³⁺...
(855.0 eV) partly formed in the bulk, but Ni\(^{2+}\) (853.0–853.5 eV) is also partly formed from the surface to inside the bulk after 500 cycles, whereas Ni\(^{3+}\) is dominant throughout the area of primary particles in the pristine case. However, the energy dispersion map of maximum intensity merely shows where Ni\(^{2+}\) forms but does not quantify the amount of Ni\(^{2+}\) formation. In the ELNES analysis of Ni L\(_{2,3}\), another significant difference between Ni\(^{3+}\) and Ni\(^{2+}\) is the ratio between the intensities of Ni L\(_2\) and L\(_3\), \(I(L_2)/I(L_3)\).\(^{[49,50]}\) Specifically, the \(I(L_2)/I(L_3)\) ratio for Ni\(^{3+}\) is lower for Ni\(^{2+}\).\(^{[39,48,51]}\) The ELNES is the sum of the spectra from all electronic structural phases at the stationary e-beam position in the sample. Therefore, if the Ni\(^{2+}\) phase partly forms in the Ni\(^{3+}\) phase, then the \(I(L_2)/I(L_3)\) ratio will be lower. Moreover, the relative quantitative values depend on the amount of Ni\(^{2+}\) formation. For the LiNi\(_{0.6}\)Co\(_{0.2}\)Mn\(_{0.2}\)O\(_2\) particle cathode,\(^{[52,53]}\) the ratio between the intensities of the Mn L\(_2\) and L\(_3\) edges corresponds to the oxidation state of the Mn ions.\(^{[52,53]}\) The intensity ratio maps of Ni L\(_2\) and L\(_3\) are shown for the pristine case and the case after 500 cycles in Figure 6i,j, respectively. The majority of the primary particle area in the pristine case exhibits the Ni\(^{3+}\) phase with an intensity ratio of \(\approx 0.5\), whereas the surface has a ratio of \(\approx 0.4\), indicating that Ni\(^{2+}\) has partially formed. However, after 500 cycles, the intensity ratio is less than 0.5 in most of the primary particle area, except for a small area in the bulk center. The Ni\(^{2+}\) phase appears closer to the surface, such that there is a decrease in the intensity ratio. In other words, degradation of the Ni\(^{2+}\) phase on the surface is accelerated and propagated to the bulk. Furthermore, areas with high Ni\(^{2+}\) ratios are observable in the bulk, as well as on the surface. This region coincides with defects or cracked areas inside the bulk. These results clearly demonstrate the progression of the chemical and structural degradation of high-Ni NCM materials over long-term cycling at the primary particle level. Specifically, the 2D visualization of the difference in the Ni oxidation ratio in the primary particles clearly distinguishes the degree of local degradation in the primary particles. Consequently, the degradation of high-Ni NCM cathode materials should proceed in the following order: i) degradation begins at the surface of the particle; ii) intergranular cracking occurs between and inside the primary particles, where void generation is induced due to repetitive cycling; iii) electrolytes penetrate into the new surface created in (ii); and (v) degradation progresses within the particles via continuous reactions.
The electronic structure of O atoms was also measured with ELNES for the O K-edge. Previous studies have reported that the chemical shift in the O K-edge is not observed because there is not a substantial difference in the shape and peak positions of NiO and LiNiO₂,[48] which closely matches our experimental results. As shown in Figure 6k,l, the O K-edge (α-peak) does not experience any chemical shift in the primary particle area, either in the pristine case or after 500 cycles. In addition, the first peak (α-peak) of the O K-edge has a higher intensity for LiNiO₂ than for NiO due to the difference in Ni 3d corresponding to the contribution of the O 2p orbital.[54,55] Thus, as shown in Figure 6m,n, which depicts the intensity ratio maps of the α- and d-peaks at the O K-edge, we can obtain results similar to those of the ELNES Ni L₂,₃ analysis shown in Figure 6l]. This finding demonstrates that our analyses of the electronic structures of the Ni L₂,₃-edge and O K-edge in NiO and LiNiO₂ phases show similar distributions in the pristine case and after 500 cycles.

Figure 7. Schematic view of the microstructural degradation process observed in this study.
In this study, we successfully employed diverse analytical techniques at the nano- and microscales to reveal the degradation process associated with the high-Ni NCM cathode. Based on a comprehensive structural, chemical, and electrical analysis, we demonstrate that the degradation of high-Ni-layered cathodes in LIBs not only occurs on the surface but also extends into the bulk cathode during long-term cycling.

According to DCIR and EBIC measurements, capacity fading correlates with an increase in the internal resistance that occurred at the surface of the NCM particles. Microstructural visualization of chemical phase maps based on EPMAs and XEDS analyses show that the Ni:O ratio changed from 1:2 to 1:1, i.e., from the size of secondary NCM particles to that of primary particles (≈5–50 μm) due to chemical degradation (TM dissolution and oxygen evolution). These chemical changes indicate that a substantial area of secondary particles does not retain the original Ni–O bonding and that their own crystal structure (R-3m) will eventually collapse or change. Changes in the crystal structure were identified via synchrotron HRPD and high-resolution STEM analysis, which reveal the crystal structure evolution from a layered (hexagonal, R-3m) to rock salt (cubic, Fm-3m) phase not only on the surface but also in the bulk cathode. These results were also confirmed by EELS analysis over the entire primary particle area. Based on an analysis of the ELNES Ni L_{2,3} and K-edge, we find that the oxidation state of Ni was predominantly Ni^{2+} (LiNiO_2, R-3m) in the bulk and Ni^{4+} (NiO, Fm-3m) at the surface in the pristine case. However, after 500 cycles, Ni^{4+} and Ni^{2+} became mixed in the bulk, whereas Ni^{2+} was still dominant at the surface.

In summary, the high-Ni NCM cathode degradation process via long-term cycling is schematically illustrated in Figure 7. Secondary NCM particles, which consist of close-packed primary particles and certain defects, cause cracking between primary particles by repeated cycling, while newly exposed cracks between primary particles and certain defects cause continuous electrolyte penetration. As a result, degradation progresses from the newly exposed surface by cracking or defects in the primary particles and gradually propagates and accelerates into the primary particles. Finally, the degradation of the high-Ni NCM cathode, starting from the surface of primary particles, as well as the surface of the secondary particles, proceeds to particles spread over a wide area.

Overall, we suggest that the observed monotonic capacity fading without unusual changes was due to the continuous formation of the Ni^{2+} phase from the surface to the bulk due to chemical and structural degradation. We believe that our findings will help prevent the degradation of cathode materials in high-energy-density LIBs, as well as in all-solid-state batteries.

**Experimental Section**

**Materials Preparation and Cell Performance**: Cathode materials in the form of Li_{1-x}Ni_{x}Co_{0.5}Mn_{0.5}O_{2} (NCM) secondary particles, with a bimodal size distribution, were prepared via a co-precipitation method, as described previously. The composite cathode was synthesized as follows. First, the active materials, i.e., Denka Black and poly-(vinylidene difluoride), were mixed into a slurry in N-methyl-2-pyrrolidone. Next, the slurry was coated onto an Al foil (current collector), followed by vacuum-drying at 120 °C and roll-pressing. The electrochemical performance was tested with 18650 cylindrical-type full cells composed of the as-synthesized cathode material, graphite anode, 1.0 M LiPF_6 in fluoroethylene carbonate and dimethyl carbonate electrolyte, and a porous ceramic-coated polyethylene film. The fuel cell cycling tests were performed at up to 500 charge/discharge cycles between 2.8 and 4.3 V at a 1 C rate (200 mA g\(^{-1}\)).

During long-term cycling, the specific capacity and DCIR were measured every 100 cycles. To determine the resistance, a 1 A pulse current was applied to the cell in the discharge region and the terminal voltage was measured in regular 10 s intervals using Ohm’s law with a 50% state of charge. EIS measurements were performed separately for the half-cells with the cathode and anode, which were disassembled from a 18650 cylinder-type full cell in pristine conditions and after 500 cycles.

**Microstructural Characterization**: EPMAs (JXA 8530F, JEOL Ltd.) was used for the cross-sectional chemical analysis of the cathode. The cross-sectional EPMAs samples were prepared with a cross-section polisher (IB-19520CCP, JEOL Ltd.) cooled using liquid nitrogen to reduce surface damage from the high-energy Ar-ion beam.

TEM (Double Cs-corrected Titan G2 60–300, FEI) with a monochromator, XEDS (Super-X SDD EDX detector, Bruker), and EELS (Quantum 966 energy filter, Gatan Inc.) were employed to analyze the microstructure, as well as the corresponding chemical and electronic structures. In the EELS experiments, by activating a monochromator, an energy resolution of 0.13 eV, measured as the full-width at half-maximum of the zero-loss spectrum when using a dispersion of 0.01 eV, was achieved at an accelerating voltage of 300 kV. To minimize e-beam damage, the vertical binning of the EELS spectrum, which reveal the crystal structure evolution from a layered (hexagonal, R-3m) to rock salt (cubic, Fm-3m) phase not only on the surface but also in the bulk cathode. These results were also confirmed by EELS analysis over the entire primary particle area. Based on an analysis of the ELNES Ni L_{2,3} and O K-edge, we find that the oxidation state of Ni was predominantly Ni^{2+} (LiNiO_2, R-3m) in the bulk and Ni^{4+} (NiO, Fm-3m) at the surface in the pristine case. However, after 500 cycles, Ni^{4+} and Ni^{2+} became mixed in the bulk, whereas Ni^{2+} was still dominant at the surface.

In summary, the high-Ni NCM cathode degradation process via long-term cycling is schematically illustrated in Figure 7. Secondary NCM particles, which consist of close-packed primary particles and certain defects, cause cracking between primary particles by repeated cycling, while newly exposed cracks between primary particles and certain defects cause continuous electrolyte penetration. As a result, degradation progresses from the newly exposed surface by cracking or defects in the primary particles and gradually propagates and accelerates into the primary particles. Finally, the degradation of the high-Ni NCM cathode, starting from the surface of primary particles, as well as the surface of the secondary particles, proceeds to particles spread over a wide area.

Overall, we suggest that the observed monotonic capacity fading without unusual changes was due to the continuous formation of the Ni^{2+} phase from the surface to the bulk due to chemical and structural degradation. We believe that our findings will help prevent the degradation of cathode materials in high-energy-density LIBs, as well as in all-solid-state batteries.

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The post-processing of EELS spectrum images for reconstructing the dispersion maps of maximum intensity and intensity ratio maps were performed in the following sequence and are also illustrated in Figure S12 in the Supporting Information. First, the spectrum image was subtracted from the background spectrum for the core-loss EELS image using the power-law model. Second, the core-loss EELS image was extracted by dividing it into two energy windows, e.g., the Ni L_1 and L_2 edge signals; then, two spectrum images of the Ni L_1 and L_2 edge signals were reconstructed with the temDM script. Finally, the dispersion map of maximum intensity was directly reconstructed using the GMS function of the SI option. For the intensity ratio map of L_1 and L_2, after reconstructing the maximum intensity maps calculated by the spectrum image of the Ni L_1 and L_2 edge signals, the intensity ratio maps of Ni L_1 and L_2 were acquired using the maximum intensity maps of Ni L_1 and L_2 based on a simple math function from the GMS option.

Specifically, a particle image analyzer (ESPRIT Feature S/W, Bruker) was used to visualize the chemical composition distribution. Previous studies had described the method that used a particle image analyzer for sectional chemical composition map reconstruction from the XEDS spectrum map image. The TEM samples were prepared using a focused ion beam system (FIB, Helios Nanolab 450F1, FEI).

High-resolution synchrotron powder X-ray diffraction data (HRPD) for the electrodes were obtained with the 9B HRPD beamline of the PLS-II in South Korea. The XRD data were collected at room temperature from 2θ = 10°–120°, with a step size of 0.005°. Rietveld refinements of the recorded HRPD patterns were performed with FullProf to obtain the structural parameters of the pristine electrode structure, as well as that after 500 cycles. EBIC measurements were performed with a SmartEBIC system (Gatan Ltd.) in the SEM (Quanta 650, FEI). A beam current of 70 pA was used at an accelerated voltage of 10 kV. The probe size of the e-beam was less than 2 nm. Therefore, it was able to attain an image resolution of 7.3 nm per pixel. These images were taken at the same position in the cross-sectional EPMA samples.
Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Author Contributions

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