

A New Coating Method for Alleviating Surface Degradation of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ Cathode Material: Nanoscale Surface Treatment of Primary Particles

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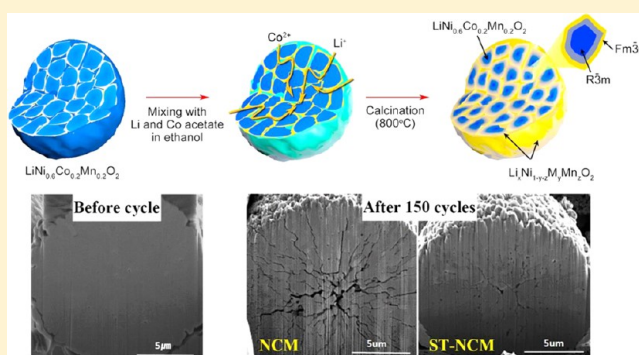
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Supporting Information

ABSTRACT: Structural degradation of Ni-rich cathode materials ($\text{LiNi}_x\text{M}_{1-x}\text{O}_2$; M = Mn, Co, and Al; $x > 0.5$) during cycling at both high voltage (>4.3 V) and high temperature (>50 °C) led to the continuous generation of microcracks in a secondary particle that consisted of aggregated micrometer-sized primary particles. These microcracks caused deterioration of the electrochemical properties by disconnecting the electrical pathway between the primary particles and creating thermal instability owing to oxygen evolution during phase transformation. Here, we report a new concept to overcome those problems of the Ni-rich cathode material via nanoscale surface treatment of the primary particles. The resultant primary particles' surfaces had a higher cobalt content and a cation-mixing phase ($Fm\bar{3}m$) with nanoscale thickness in the $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode, leading to mitigation of the microcracks by suppressing the structural change from a layered to rock-salt phase. Furthermore, the higher oxidation state of Mn^{4+} at the surface minimized the oxygen evolution at high temperatures. This approach resulted in improved structural and thermal stability in the severe cycling-test environment at 60 °C between 3.0 and 4.45 V and at elevated temperatures, showing a rate capability that was comparable to that of the pristine sample.

KEYWORDS: $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode, high voltage, thermal stability, primary particles, microcrack, structural degradation



Cathode materials for the next generation of lithium-ion batteries require higher energy density, longer cycle life, and better safety for applications in electric vehicles and stationary energy storage.¹ Nickel-rich systems ($\text{LiNi}_x\text{M}_{1-x}\text{O}_2$; M = Mn, Co, and Al; $x > 0.5$) are considered as promising candidates to meet such requirements, although their structural degradation and thermal instability pose challenging hurdles.^{2,3} These problems worsen with higher Ni content, higher temperature, and higher cutoff voltage (>4.4 V vs Li^+/Li).⁴ In general, Ni-rich cathode materials with a layered structure commonly undergo structural degradation from the layered phase ($R\bar{3}m$) to the spinel-like phase ($Fd\bar{3}m$) and rock-salt phase ($Fm\bar{3}m$) during cycling and at an elevated temperature.^{3–5} The structural change is caused by the migration of the transition metal (TM) ions into the lithium layer during charging and discharging.⁶ The TM ions' migration leads to the layered-to-spinel phase transformation, and the transformation is intensified by high-voltage and high-temperature cycling because of the increasing number of vacant Li sites during full delithiation and the diffusion of TM ions. These phase

transitions with TM-ion migration are accompanied by changes in the lattice constants and volume, which release oxygen from the lattice. Such results can lead to thermal and structural instability.⁷

The Ni-rich cathode materials, commonly prepared by a general coprecipitation method are composed of round-shape secondary particles in which many micrometer-sized primary particles (grains) are aggregated.⁸ Because all these primary particles have different crystallographic orientation and slip planes, anisotropic lattice volume expansion or contraction between the grains during lithium intercalation or deintercalation result in microcracks that act as new reaction sites with the electrolytes in turn leading to electrical disconnection between the grains.⁹ As a result, a new solid electrolyte interface (SEI) layer, comprising decomposition products of the electrolyte, is formed along the active surface of the primary

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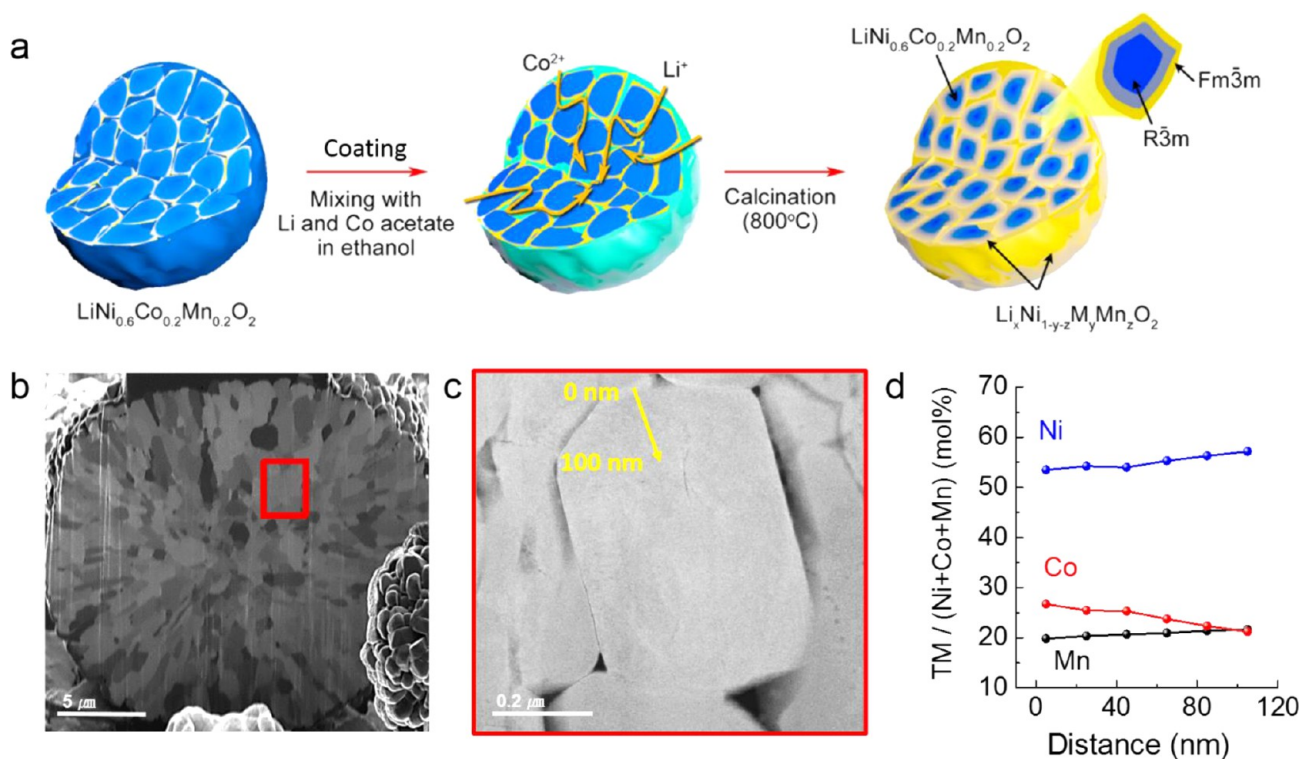


Figure 1. (a) Schematic diagram of the surface treatment on the primary particles. (b) Cross-sectional SEM image of the synthesized ST-NCM cathode material. (c) STEM image of the primary particle in the region indicated by a red rectangle in (b). (d) EDXS profile of the ST-NCM surface corresponding to the yellow arrow in (c).

particles (grains) developed by the microcracks. The SEI layers on the surface of the grains inhibit electron and lithium transport through the grain–electrolyte interface, thus diminishing the electrical performance.¹⁰ To resolve the structural and thermal instability of the Ni-rich cathode materials, many researchers have implemented surface modification such as surface coating (Al_2O_3 , AlPO_4 , ZrO_2)^{11–13} and developed core–shell structures.¹⁴ Although the structural degradation is intensified during cycling because of the microstructural evolution caused by the reaction between primary particles and the electrolyte inside the secondary particles,^{10,15–17} most researchers have focused on the surface modification of the secondary particles.^{11,14,18–22}

Herein, we propose the nanoscale surface treatment of primary particles of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode material using a mixed ethanol solution with dissolved lithium and cobalt precursors. This new approach resulted in improved structural and thermal stability under severe conditions such as high cutoff voltage (>4.4 V) and high temperature (>50 °C).

Results and Discussion. The schematic illustration in Figure 1a shows the surface treatment process for the primary particles of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM). A completely ionized solution consisting of lithium and cobalt ions could penetrate the core part of the particle along the grain boundaries because there were many empty microspaces between the primary particles. The cathode material was calcined at 800 °C for 4 h (denoted as ST-NCM), and the calcinated particles had a smooth surface, with no morphological changes when compared with the pristine sample (Supporting Information Figure S1). However, the Al_2O_3 -coated reference samples clearly showed that the coated nanoparticles were distributed throughout the surface of the secondary particles because Al-isopropoxide, which was used as a precursor, was precipitated

as $\text{Al}(\text{OH})_3$ nanoparticles in the isopropanol solvent (Supporting Information Figure S1). Figure 1b shows a cross-sectional scanning electron microscope (SEM) image of a NCM particle composed of the aggregated, fine, micrometer-sized primary particles. Scanning transmission electron microscope (STEM) image in Figure 1c shows many microvoids between the particles, enabling the surface treatment solution to penetrate the core. Energy-dispersive X-ray spectroscopy (EDXS) of the ST-NCM sample (along the yellow arrow in Figure 1c) confirmed the higher content of Co atoms than Mn and Ni atoms at a depth of ~60 nm into the interior (Figure 1d and Supporting Information Figure S2). The higher Co content in the Ni-based cathode materials led to better electrochemical performance.²³ In addition, the EDXS result of a randomly selected primary particle showed the same trend to Figure 1d (Supporting Information Figure S3).

Figure 2 presents more detailed structural and chemical information on a primary particle's surface, obtained by high-angle annular dark-field (HAADF)-STEM and electron energy-loss spectroscopy (EELS) analysis of the samples. Region 1 of the pristine $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM) sample exhibited an uneven NiO-like cation-mixing (CM) layer with a space group of $\text{Fm}\bar{3}\text{m}$ and thickness of 1–2 nm, as shown in Figure 2b (also refer to Rietveld refinement results in Supporting Information Figure S4 and Table S1). Here, bright spots of Li slabs resulted from Ni^{2+} migration from the original TM slabs to lithium slabs because Ni^{2+} , which has an ionic radius (0.69 Å) similar to that of Li^+ (0.76 Å), could easily move to Li sites. The layered phase with a space group of $\text{R}\bar{3}\text{m}$ was verified by the fast Fourier-transform (FFT) pattern (inset of Figure 2c). In the ST-NCM sample, region 1 consisted of the CM layer with a thickness of ~10 nm, as confirmed by the FFT pattern (inset of Figure 2e). In region 2, however, Figure 2f shows that only the layered

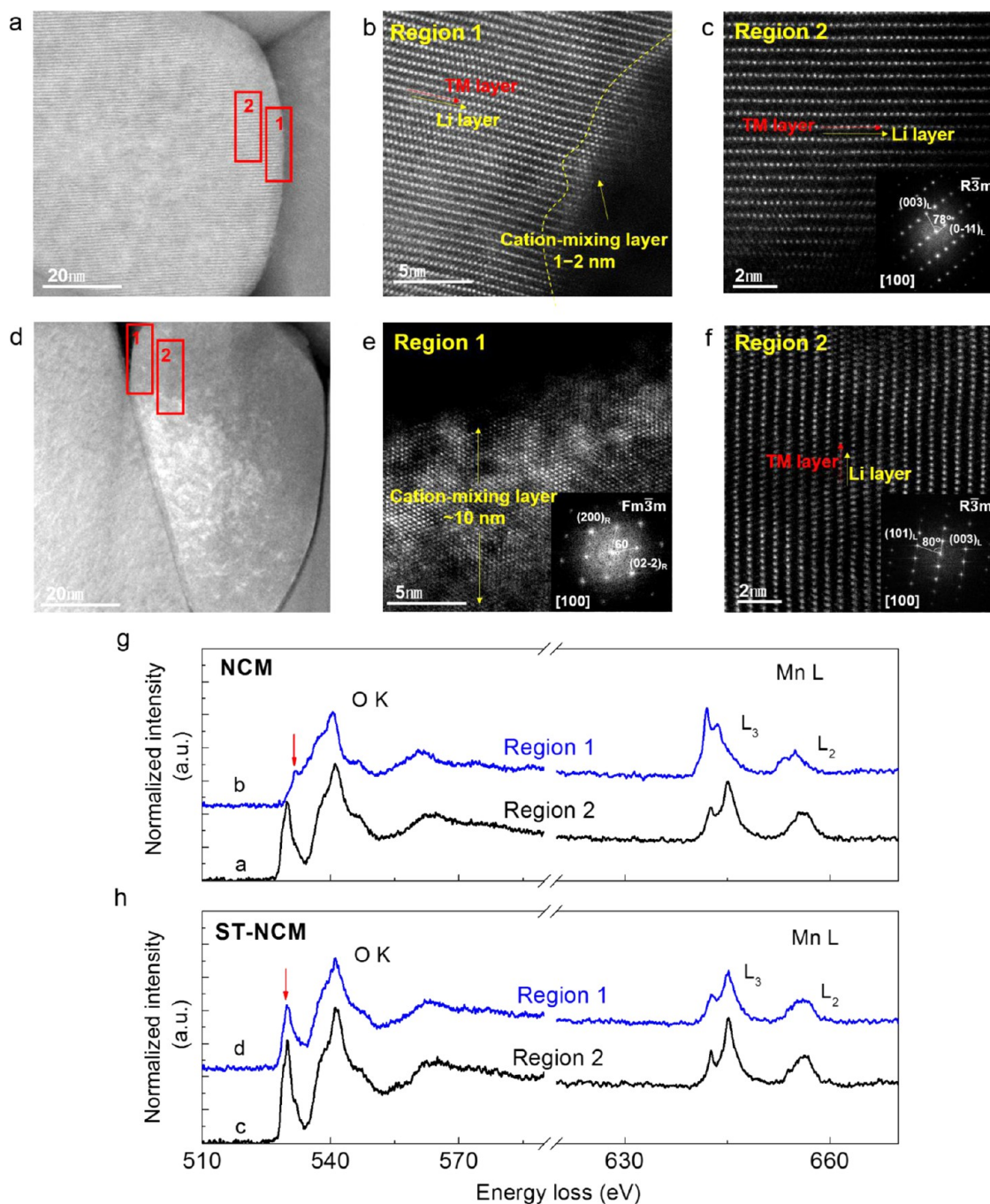


Figure 2. HADDF-STEM image of (a) $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM) on the surface of a primary particle (grain). Magnified STEM image of the NCM in (b) Region 1 and (c) Region 2 in (a). HAADF STEM image of (d) surface-treated $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (ST-NCM) on the surface of the primary particle (grain). Magnified STEM image of the ST-NCM in (e) Region 1 and (f) Region 2 in (d). The insets of STEM images show digitalized fast-Fourier-transformed (FFT) patterns. EELS spectra obtained on the surface of a primary particle in Regions 1 and 2 of (g) NCM and (h) ST-NCM.

(space group of $R\bar{3}m$) phase was observed, which is identical to the result for the pristine NCM sample. The NiO-like phase with a nanometer-range thickness has been reported to act as a pillar layer that suppresses the interslab collapse during cycling;²¹ therefore, particle pulverization is expected to be also reduced in our study.

More detailed observation on the surface chemical state of primary particles of the NCM and ST-NCM cathodes was carried out with EELS. The EELS profiles of the O K-edge and Mn $L_{2,3}$ -edges located around 530 and 640 eV, respectively, are

directly linked to the electronic structure of the materials (Figure 2g,h). The ratio of the integrated intensities of L_3 and L_2 , $I(L_3)/I(L_2)$, is correlated with the valence state of the transition metals, and increasing the $I(L_3)/I(L_2)$ ratio corresponds to decreasing the oxidation state of manganese ions.^{24,25} Table 1 summarizes the integrated $I(L_3)/I(L_2)$ ratio for the each region of the NCM and ST-NCM samples. Region 2 of the NCM sample had a $I(L_3)/I(L_2)$ ratio of 1.98, which is indicative of the dominance of Mn^{4+} . However, region 1 of the NCM sample had a $I(L_3)/I(L_2)$ ratio of 3.02, indicating a lower

Table 1. Information of the Integrated L_3/L_2 Ratio of the Mn L-Edge on the Region 1 and 2

	$I(L_3)/I(L_2)$ ratio	oxidation state of Mn
NCM (region 1)	3.02	$\sim 2.67^+$
NCM (region 2)	1.98	4^+
ST-NCM (region 1)	1.97	4^+
ST-NCM (region 2)	2.01	4^+

valence state of Mn $^{2.7+}$ than that in region 2. On the other hand, the ST-NCM sample had a quite similar ratio of ~ 2.0 , which is consistent with the presence of Mn $^{4+}$ between the two regions. The prepeak of the O K-edge near 530 eV, as indicated by the red arrow in Figure 2g,h, was reported to be the result of the transition from the O 1s state to the O 2p–TM 3d hybridized state.^{26,27} This peak became weaker and shifted to a higher energy as the oxidation state of Mn decreased because of the weakened hybridization of the O 2p–Mn 3d orbital owing to the 3d orbital of Mn with the filled e_g state.²⁵ In Figure 2g, the prepeak of the O K-edge weakened and shifted to a higher energy owing to the low oxidation state of Mn $^{3+}$ in region 1 of the NCM sample. However, the ST-NCM sample showed no difference between the prepeaks for both regions because of the

same oxidation state of Mn $^{4+}$. Consequently, we can recognize that the Mn ions in the NCM sample had mixed oxidation states of 3^+ and 4^+ on the surface of the primary particles. Generally, the oxidation states of Ni, Co, and Mn in $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ cathode materials are 2^+ , 3^+ , and 4^+ , respectively, with small concentrations of Ni $^{3+}$ and Mn $^{3+}$ ions.^{21,28} When Ni $^{3+}$ and Mn $^{3+}$ serve as the Jahn–Teller active ions, Jahn–Teller (J–T) distortions are allowed by breaking the symmetry of the cell.²⁹ In the case of the ST-NCM sample, the CM layer on the surface, which resulted from the migration of Ni $^{2+}$ ions from TM slabs to Li slabs, induced a higher Mn $^{4+}$ proportion to compensate the charge valence (Supporting Information Figure S5). The high average oxidation state of Mn $^{4+}$ in the ST-NCM sample could effectively diminish the J–T distortion.

The electrochemical properties of each sample were evaluated using coin-type 2032R lithium half-cells between 3.0 to 4.45 V at 60 °C. The first charge–discharge profiles of the NCM and ST-NCM samples at room temperature (RT, 25 °C) displayed no capacity decrease even after surface treatment with discharge capacities of 192 mAh g $^{-1}$ (Figure 3a). The ST-NCM sample also showed higher capacity retention of 80% after 150 cycles (from 195 to 156 mAh g $^{-1}$) than the NCM

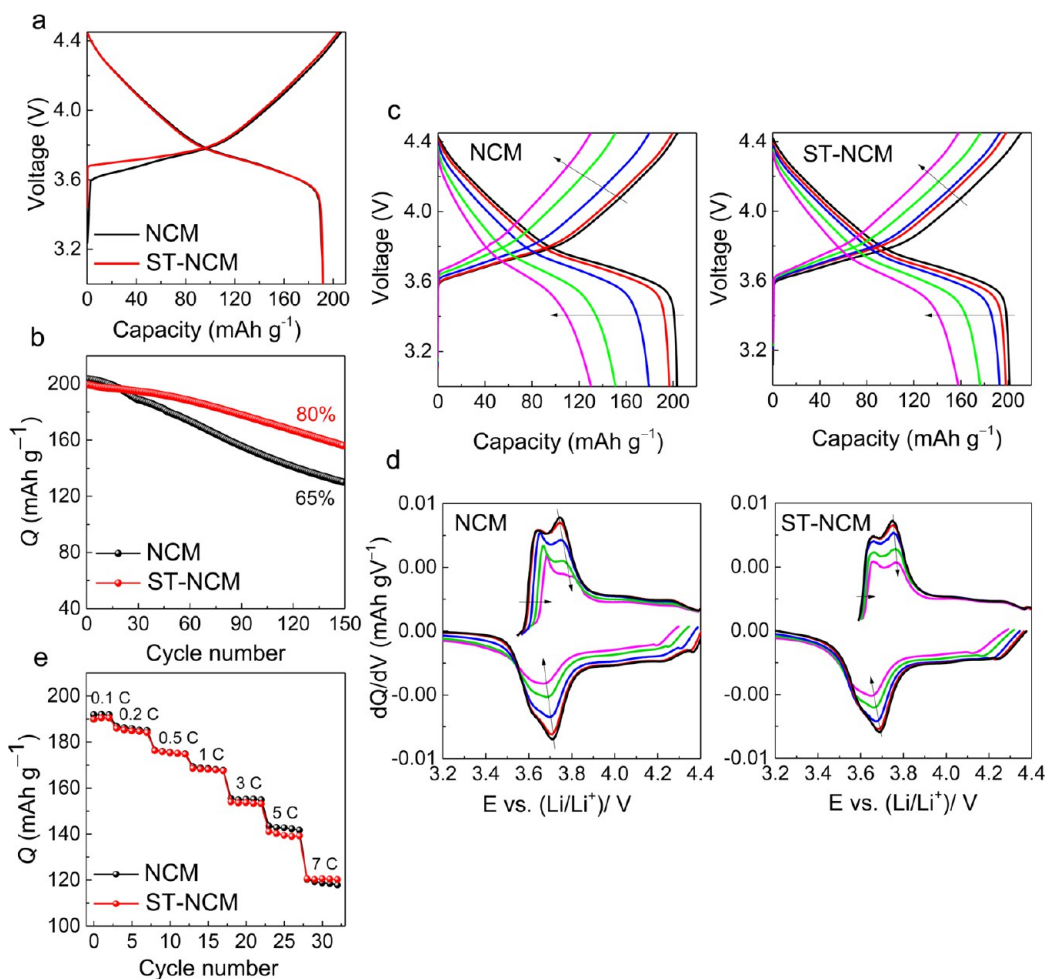


Figure 3. (a) First charge–discharge profiles of the NCM and ST-NCM samples at 0.1 C rate between 3.0 and 4.45 V at 25 °C. (b) Cycle performance of the NCM and ST-NCM samples between 3.0 and 4.45 V at 60 °C (charge rate: 0.5 C; discharge rate: 1 C, Q = discharge capacity). (c) Charge and discharge voltage profiles of the NCM and ST-NCM samples after the 10th, 20th, 50th, 100th, and 150th cycles at 60 °C (each cycle matched with black, red, blue, green, and pink color lines, respectively). (d) Differential curves of the NCM and ST-NCM samples corresponding to (c). (e) Rate capabilities of NCM and ST-NCM evaluated between 3.0 and 4.45 V at 25 °C. (Q = discharge capacity).

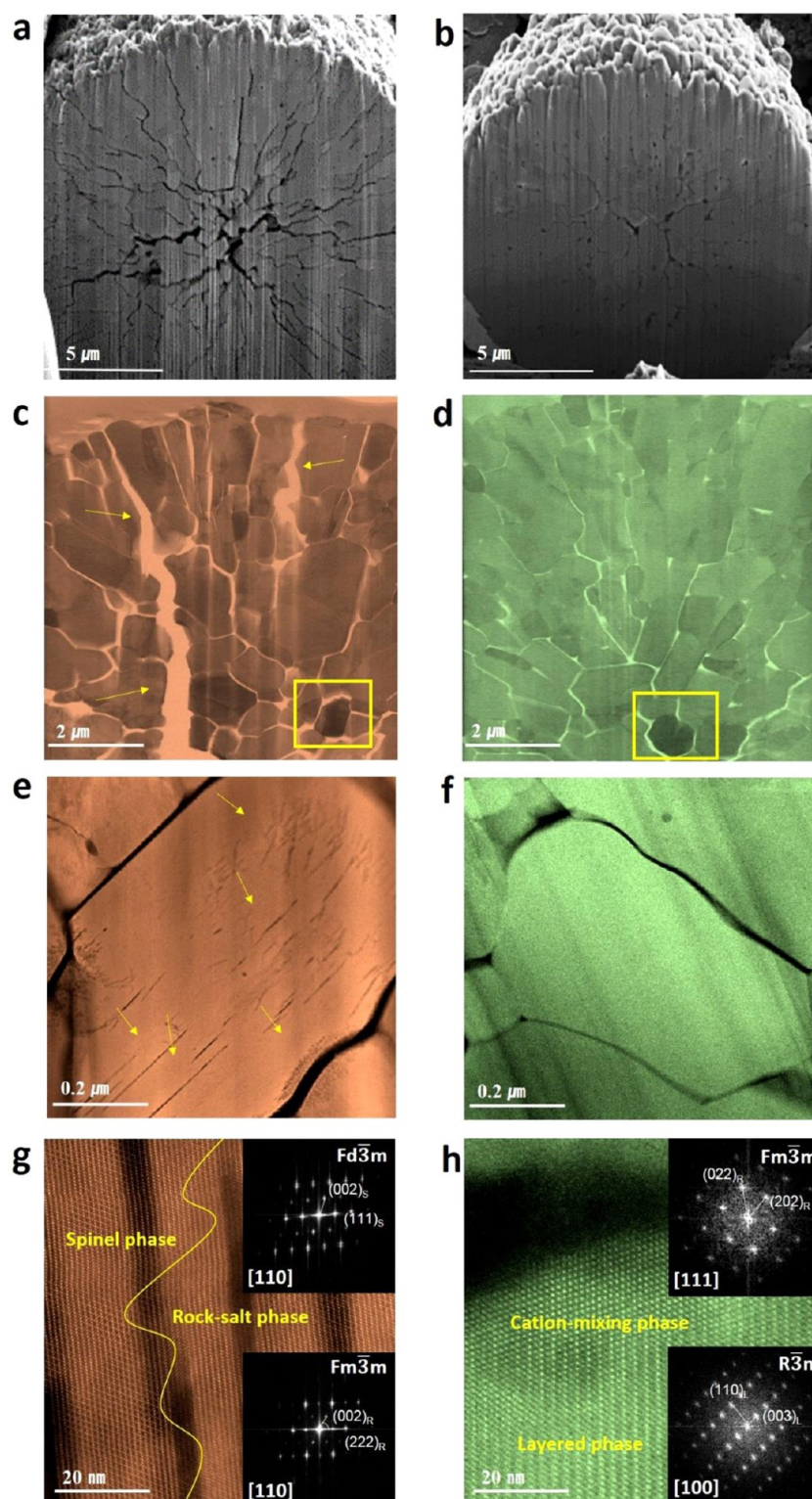


Figure 4. Particle morphology and fine structure of primary particles after 150 cycles between 3.0 and 4.45 V at 60 °C. Cross-sectional FIB-SEM images of the (a) NCM and (b) ST-NCM particles. HAADF-STEM images of (c) NCM and (d) ST-NCM particles. Magnified STEM images of (e) NCM and (f) ST-NCM particles in the regions indicated by the yellow frames in (c) and (d), respectively. High-magnification STEM images of (g) NCM and (h) ST-NCM particles in (e) and (f), respectively. The insets of (g) and (h) show the FFT patterns.

sample (65% retention from 198 to 130 mAh g⁻¹), as shown in Figure 3b. In addition, the ST-NCM sample exhibited better cycle performance than the Al₂O₃-coated sample (Supporting Information Figure S6c). The voltage profiles corresponding to Figure 3b indicate that the average working voltage of the

NCM sample became higher than that of the ST-NCM sample with increasing cycle number during charging (Figure 3c). Differential curves of the NCM and ST-NCM samples for 150 cycles at 60 °C revealed dominant double peaks at around 3.7 V, which are related to the phase transition from the

hexagonal (H1) phase to the monoclinic (M) phase in the charging process. As the number of cycles increased, the peak at 3.75 V of the ST-NCM sample maintained a similar intensity after 150 cycles, in contrast to the peak of the NCM sample (Figure 3d). The decreasing peak intensity of the NCM sample is associated with the irreversible phase transition from H1 to M that was caused by the J–T distortion of transition-metal ions such as Ni^{3+} and Mn^{3+} .³⁰ In this aspect, the J–T inactive Mn^{4+} ions in the CM layer, on the primary particles' surface of the ST-NCM sample, prevented the irreversible phase transition by suppressing the distortion. Despite the formation of the CM layer, the rate capability of the ST-NCM sample was quite similar to that of the NCM sample (Figure 3e). According to Ceder et al.,³¹ Li diffusion in a cation disordered rock-salt phase proceeds by Li ions hopping from one octahedral site to another via an intermediate tetrahedral site (o–t–o diffusion). Thus, the thin CM layer of the NiO-like phase on the surface of ST-NCM primary particles led to the favorable rate performance with no Li-diffusion limitation.

Figure 4a,b shows cross-sectional SEM images of the NCM and ST-NCM particles, respectively, after 150 cycles at 60 °C (also refer to Supporting Information Figure S7). The NCM sample had extensive microcracks along the grains, but those cracks were significantly diminished in the ST-NCM sample. Figure 4c–h shows HAADF-STEM images of the NCM and ST-NCM samples after 150 cycles. The secondary particles of the NCM sample had severe cleavages along the grain boundaries, as shown in Figure 4c. Furthermore, the primary particles of the NCM sample had many fractures (Figure 4e) in contrast to the ST-NCM sample (Figure 4f). Microcracks led to the penetration of the electrolyte along the grains and the reaction between the penetrating electrolyte and interior particles, accelerating structural degradation and side reactions.¹⁰ The magnified image of Figure 4e (Figure 4g) shows that along the cracks inside the particle of the NCM, the layered phase partially changed to the spinel-like phase and rock-salt phase after cycling, and the phases were identified by inserting FFT patterns (STEM images of the randomly selected NCM particles also exhibited a same trend, as shown in Supporting Information Figure S8). The phase transition in the NCM sample was deepened by the reaction between the grains and electrolyte, with many microcracks providing an increasing number of active sites. On the other hand, the ST-NCM sample displayed a similar phase on the surface of the grains without showing noticeable phase change compared to that before cycling (Figure 4h). Owing to the pillar effect, the migration of transition-metal ions to the lithium slab was contained, therefore the volume change (caused by phase transition) of the grains was effectively suppressed after 150 cycles. As a result, the ST-NCM sample exhibited improved electrochemical performance as it was relieved from the loss of electrical pathways.

The exothermic oxygen evolution with the structural change during heating in a fully charged state is a crucial problem for thermal stability in battery systems.³² To evaluate the thermal stability and safety of NCM and ST-NCM as cathode materials, differential scanning calorimetry (DSC) measurements were carried out on the NCM and ST-NCM electrodes soaking in the electrolyte after charging to 4.5 V; the DSC profiles are presented in Figure 5. The main peak temperature of 264 °C for the ST-NCM sample is higher than the NCM sample's peak temperature of 230 °C, indicating a significantly increased peak temperature of oxygen evolution from the lattice in ST-NCM.

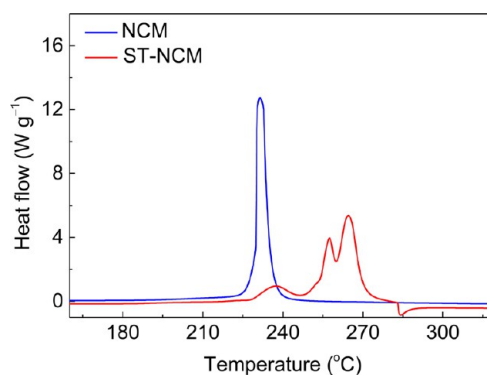


Figure 5. DSC profiles of NCM and ST-NCM after charging to 4.5 V.

Furthermore, the peak area indicative of the total generated heat (resulting from the oxygen evolution) in the ST-NCM sample was 696.8 J g^{-1} , which is lower than that in the NCM sample (910.9 J g^{-1}). A correlated study using X-ray absorption spectroscopy (XAS) was performed to understand the thermal decomposition mechanism with structural change in each sample. The XAS spectral measurement is a powerful method to identify fine structure information, such as electronic states and local environments for each transition-metal ion.

Figure 6 shows the temperature dependence of Ni, Co, and Mn K-edge X-ray absorption near edge structure (XANES) spectra for the fully charged NCM and ST-NCM materials at 4.5 V during heating at temperatures up to 450 °C. All TM K-edge XANES spectra showed characteristic peaks of a layered structure with $R\bar{3}m$ symmetry, including typical quadrupole-allowed $1s \rightarrow 3d$ (peak A) and dipole-allowed $1s \rightarrow 4p$ transitions with and without ligand-to-metal charge transfer (LMCT) (peaks B and C, respectively). Since the peak is associated with changes in the average oxidation state of the absorbing atoms, an *in situ* thermal XANES study can support the direct probing method for atomic-selective electronic structural characterization. The Ni and Co ions in both fully charged NCM and ST-NCM materials were oxidized to states of 4+, while the Mn ion remained in the initial 4+ state. As the temperature was increased beyond 300 °C, the overall absorption peak features for all the transition metals in the NCM sample abruptly shifted to the lower energy region and finally showed rock-salt like characteristics, which means that the transition-metal ions were effectively reduced to Mn^{2+} , Ni^{2+} , and Co^{2+} and the phase transition to divalent TM oxides occurred. On the other hand, the ST-NCM sample showed relatively smaller peak shifts to the lower energy region compared with those of the NCM sample. All TM K-edge XANES spectra gradually evolved to show typical spinel-like peak features with shoulder peaks B_1 and B_2 , not rock-salt-like features. At temperatures above 300 °C, the Mn and Co K-edge XANES spectra corresponded to the trivalent Mn^{3+} and Co^{3+} states, respectively, while the Ni K-edge XANES spectrum showed a clear Ni^{2+} peak feature.

Figure 7 shows the corresponding radial distribution functions (RDF) of Fourier-transformed (FT) transition-metal K-edge EXAFS spectra for the charged electrodes heated to 450 °C. Before heating, the fully charged NCM and ST-NCM samples displayed typical RDF features of the $R\bar{3}m$ layered structure with both six-coordinated TM–O and edge-shared TM–TM bonding pairs. Below ~250 °C, on the whole both the charged NCM and ST-NCM samples retained the layered structure, showing a constant RDF peak feature. Above

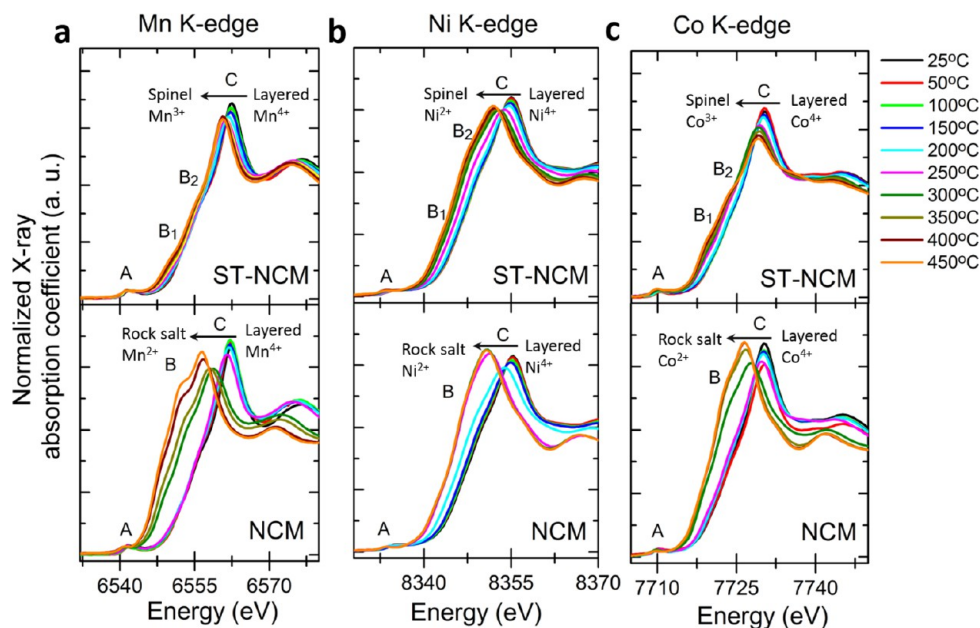


Figure 6. Normalized TM K-edge XANES spectra of the (a) Mn K-edge, (b) Ni K-edge, and (c) Co K-edge of NCM and ST-NCM as functions of heating temperature.

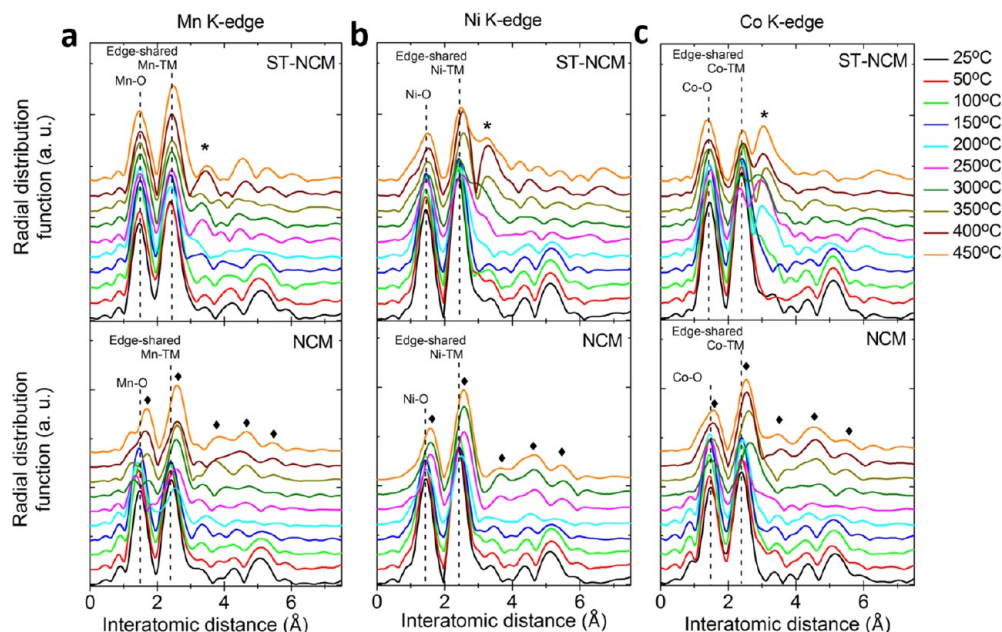


Figure 7. Radial distribution functions (RDF) for Fourier-transformed k^3 -weighted TM K-edge EXAFS spectra of the (a) Mn K-edge, (b) Ni K-edge, and (c) Co K-edge of NCM and ST-NCM as functions of heating temperature.

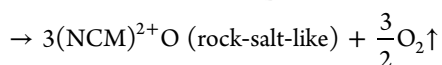
~250 °C, however, the RDFs of the two samples exhibited different spectral tendencies, reflecting the effect of surface treatment of primary particles with pillar layer on the thermal behavior. In the NCM sample, the RDF features of all TM elements abruptly changed to their cubic $Fm\bar{3}m$ rock-saltlike local structures (TM²⁺–O phase) and remained constant up to 450 °C. The cubic structural environment with divalent TM²⁺ ions led to the overall FT peak shift to higher r space region (marked with ◆), compared to those of the $R\bar{3}m$ layered structure. It should be noted that the edge-shared TM–TM in $Fm\bar{3}m$ symmetry can be differentiated from that in the $R\bar{3}m$ layered structure. On the other hand, the ST-NCM sample showed a rather different RDF dependence, compared with

NCM, on the same thermal conditions. Above ~250 °C, the RDFs for all of the TM ions developed features of the cubic $Fd\bar{3}m$ spinel-like phase with the coexistence of edge-shared and corner-shared octahedral sites. This means that the pillar layer on the surface of primary particle could lessen the thermal shock to the core-charged NCM material. Under the thermally mitigated environment, the Co and Ni ions in the layer would have the chance to easily migrate to the empty interstitial sites between the edge-shared octahedral slabs, instead of participating in the direct phase transition to cubic $Fm\bar{3}m$ rock salt. The atomic rearrangement resulted in a new generation of corner-shared TM–TM interactions (marked by * in Figure 7) and then the formation of short-range order of the spinel-like phase.

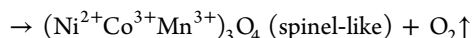
On the basis of the XANES result of the Ni^{2+} , Co^{3+} , and Mn^{3+} states at the higher temperatures, the locally thermal-driving phase was estimated to be a mix of the normal spinels of $\text{Ni}^{2+}\text{Co}^{3+}_2\text{O}_4$ and $\text{Ni}^{2+}\text{Mn}^{3+}_2\text{O}_4$.

As shown by the results, a thermally driven structural degradation mechanism can be suggested for the NCM and ST-NCM samples, based on the assumption that the atomic-selective thermal reductions of the TM elements during heating gave rise to the oxygen release from the lattice. The reaction can be classified as follows

NCM sample: $3(\text{NCM})^{4+}\text{O}_2$ (layered)



ST-NCM: $3(\text{NCM})^{4+}\text{O}_2$ (layered)



The structural change accompanied the oxygen evolution from the lattice, and the amount of the evolved oxygen for the structural transformation from the layered to rock-salt phase was higher than that for the transformation from the layered to spinel phase. This result is attained by the stabilized structure with pillars on the surface of grains. In addition, the stronger Mn–O bonding by Mn^{4+} in the ST-NCM primary particle's surface restrained the release of oxygen, and therefore the ST-NCM sample showed lower total generated heat in the highly delithiated state.

In conclusion, the $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode material with surface-treated primary particles (ST-NCM) was prepared using the solution with completely ionized lithium and cobalt sources. The ST-NCM primary particles' surface, which consisted of a cation-mixing layer as a pillar layer, effectively improved the structural stability and electrochemical performance by suppressing the microcracks in the particles and grains during cycling. Moreover, the ST-NCM evidently prevented the oxygen evolution from phase transition at elevated temperature by suppressing the structural degradation and stronger Mn–O bonding. This concept of coating for the primary particles can be applied as a new strategy for surface modification to realize improvements in both electrochemical properties and thermal stability.

Experimental Section. Preparation of Electrode Materials. The cathode materials of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ were synthesized by a coprecipitation method.³³ The ST-NCM sample was prepared from a fully ionized solution. First, 0.17 mol of CH_3COOLi and 0.2 mol of $(\text{CH}_3\text{COO})_2\text{Co}$ were completely dissolved in ethanol (50 g). Next, 100 g of the cathode powder synthesized as cathode material was added to the solution. The mixed solution was vigorously stirred at 70 °C until the solvent completely evaporated. Finally, it was calcinated at 800 °C for 4 h in air to remove the impurities after drying at 150 °C for 1 h.

Electrochemical Properties. The electrochemical properties were tested in a coin-type 2032R cell with a lithium–metal anode. Composite electrodes were prepared with 92% active material, 4% Super-P carbon black, and 4% poly(vinylidene fluoride) (PVDF) binder in *N*-methyl-2-pyrrolidinone and cast onto aluminum current collectors with active material loadings of 8–9 mg/cm². The electrolyte for the half-cells was 1.15 M LiPF_6 with ethylene carbonate–dimethylene carbonate–diethylene carbonate (30:40:30 vol %) (Panax Etec). The cycling

tests of the half-cell were performed between 3.0 and 4.45 V at a 0.5 C charge rate and a 1 C discharge rate at 60 °C.

Materials Characterization. Powder X-ray-diffraction (D/Max2000, Rigaku) measurements at $2\theta = 10\text{--}80^\circ$, using Cu K α radiation, were used to identify the phases. The morphology of the samples was observed using SEM. The cross-sectional TEM samples of particles were prepared by a focused ion beam (FIB) technique (FEI Helios Nano Lab 450). Additionally, the samples were thinned by a low-energy Ar-ion milling system (Fischione Model 1040 Nanomill). The HAADF-STEM images were taken using a probe-side aberration corrected TEM ((JEOL JEM-2100F). EELS spectra were recorded using an image-side aberration corrected TEM (FEI Titan³ G2 60–300) operated at an accelerating voltage of 80 kV. In situ transition metal (Ni, Co, Mn) K-edge XANES and extended EXAFS spectra were collected on BL10C beamline at the Pohang Accelerator Laboratory (PAL), Korea. The monochromatic X-ray beam can be obtained from high intense X-ray photons of multiple wiggler source using liquid-nitrogen cooled Si(111) double crystal monochromator (Bruker ASC). The transmitted XAFS spectra were collected using homemade heating stage in the temperature region from room temperature to 450 °C for ~4 h (i.e., heating rate = 2 °C/min). DSC samples of the cathodes were prepared by charging to 4.5 V at a 0.1 C rate and then the disassembled electrodes were prepared in the dry room. The disassembled electrodes were washed with dimethyl carbonate solvent several times, and fresh electrolytes were added after drying the electrode. The electrode transferred to aluminum pan and heated at a rate of 5 °C/min.

■ ASSOCIATED CONTENT

● Supporting Information

TEM images, Rietveld results, and battery cycling data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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