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Structural and Chemical Evolution of Li- and Mn-rich Layered Cathode Material

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ABSTRACT: Lithium (Li)- and manganese-rich (LMR) layered-structure materials are very promising cathodes for high energy density lithium-ion batteries. However, the voltage fading mechanism in these materials as well as its relationships to fundamental structural changes is far from being sufficiently understood. Here we report the detailed phase transformation pathway in the LMR cathode (Li[Li0.2Ni0.1Mn0.6]O2) during cycling for samples prepared by the hydrothermal assisted (HA) method. It is found that the transformation pathway of the LMR cathode is closely correlated to its initial structure and preparation conditions. The results reveal that the LMR cathode prepared by the HA approach experiences a phase transformation from the layered structure (initial C2/m phase transforms to R-3m phase after activation) to a LT-LiCoO2 type defect spinel-like structure (with the Fd-3m space group) and then to a disordered rock-salt structure (with the Fm-3m space group). The voltage fade can be well correlated with Li ion insertion into octahedral sites, rather than tetrahedral sites, in both defect spinel-like and disordered rock-salt structures. The reversible Li insertion/removal into/from the disordered rock-salt structure is ascribed to the Li excess environment that permits Li percolation in the disordered rock-salt structure despite the increased kinetic barrier. Meanwhile, because of the presence of a large quantity of oxygen vacancies, a significant decrease in the Mn valence is detected in the cycled particle, which is below that anticipated for a potentially damaging Jahn-Teller distortion (+3.5). Clarification of the phase transformation pathway, cation redistribution, oxygen vacancy and Mn valence change provides unique understanding of the voltage fade and capacity degradation mechanisms in the LMR cathode. The results also inspire us to further enhance the reversibility of the LMR cathode via improved surface structural stability.

INTRODUCTION

Lithium (Li) ion batteries (LIB) have been identified as one of the most promising systems for large-scale energy storage applications, including both electric grid and transportation systems such as pure electric vehicles (EV) and plug-in hybrid EVs.1-3 The cathode materials, such as conventional layered LiNi0.5Co0.2Mn0.3O2 (NCM) or LiMn2O4 spinel, used in the current LIB are still plagued with limited energy density and poor cycle life, as well as high cost and safety issues, impeding their large-scale applications in long-range EV and the electricity grid.4-6 Lithium- and manganese-rich (LMR) layered-structure cathode materials (generally designated as x Li2MnO3·(1-x) LiMO2 (M = Ni, Co, Mn etc.)7-9 have attracted significant attention and have been considered as one of the most appealing cathode candidates for the next generation LIB because of their high discharge capacity (≈250 mAh g−1), cost effectiveness and good thermal stability.10-14 However, significant technical barriers exist for LMR cathodes, including its poor rate capability and voltage fade, have to be overcome prior to its large-scale commercialization.15-18

The significant difference between the charge/discharge mechanisms of LMR cathodes and the conventional cathode materials such as layered NCM or LiMn2O4 spinel have been intensively investigated.19-24 The high discharge capacity of the LMR cathode can only be achieved by initially charging it to a high cutoff voltage, typically 4.6 - 4.8 V, to activate the Li2MO3 component via removal of Li ions concomitant with an irreversible loss of oxygen.20, 21 The extensive side reactions between the extracted oxygen species and the electrolyte give rise to continuous accumulation of a thick surface electrolyte interphase (SEI) layer on the electrode surface, resulting in rapid impedance rise and drastic capacity loss.25
During the initial activation process, a large amount of oxygen vacancies are formed at the end of the charge. As a result, the transition metal (TM) ions coordinated with reduced oxygen ions are destabilized and prone to migrate to the vacant octahedral sites in Li layers via the adjacent tetrahedral sites. This phase transformation initiates from the crystal surface, leading to the formation of a surface reconstruction layer and the gradual voltage fade during cycling.

The capacity retention of LMR cathodes can be significantly improved by stabilizing the electrode/electrolyte interface. Representative approaches include different kinds of surface modifications (surface coating or electrolyte additive), and/or improvement in the uniformity of the atomic scale elemental distribution in the prepared material. However, the voltage fade caused by the intrinsic structural instability of the LMR cathode still could not be completely solved. The crystal structure of the surface reconstruction phase is generally ascribed to a ‘spinel’ phase in the literature reports. However, the detailed structure of the ‘spinel’ phase has not been sufficiently understood and the pure LiMn$_2$O$_4$ type spinel structure has not been identified in LMR cathode by XRD or TEM. In this regard, a ‘spinel-like’ structure is a much better description than the ‘spinel’ phase. A more detailed understanding on the ‘spinel-like’ structure is important and will provide new perspectives for counteracting or eventually eliminating the voltage fade issue of LMR cathode materials.

Here, we used aberration-corrected scanning transmission electron microscopy (STEM) combined with electron energy loss spectroscopy (EELS) to probe the microstructural changes of the LMR cathode Li$_3$Ni$_{0.5}$Mn$_{0.5}$O$_2$ before and after cycling, to get insights into the surface reconstruction layer structure at atomic resolution. Aberration-corrected high angle annular dark field (HAADF) STEM imaging was used to identify the changes in stacking and ordering in the cycled particles while EELS chemical analysis revealed important chemistry changes. The results disclose that the layered structure of the LMR material transformed to a Li$_2$CoO$_2$ type defect spinel-like structure and then further converted to a disordered rock-salt structure. To the best of our knowledge, this is the first report clarifying the phase transformation pathway in LMR cathodes during cycling, which can be successfully correlated to the observed electrochemical performances of LMR cathode.

EXPERIMENTAL SECTION

Material synthesis. LMR cathode Li$_{3-x}$Ni$_{0.5}$Mn$_{0.5}$O$_2$ was synthesized using a hydrothermal (HA) assisted method, as reported previously, 5 mol% excessive Li source was added to compensate lithium loss during high temperature (900°C) calcination process and a quench process was applied to obtain the final Li$_{3-x}$Ni$_{0.5}$Mn$_{0.5}$O$_2$ material.

Characterizations. Chemical sensitive Z-contrast imaging and advanced EELS analysis in an aberration-corrected STEM were used to probe the microstructure at atomic scale of pristine and cycled nanoparticles. Exposure of the cycled materials to air may lead to the formation of additional lithium containing reaction products, such as LiOH, Li$_2$O, Li$_2$CO$_3$, etc. on the electrode surface. Therefore, a standard procedure has been established to minimize the effects of these reaction products. Sample preparation was carried out in an argon-filled glove box. The TEM sample was transferred to transmission electron microscope under Ar atmosphere and the turbo-pump of the microscope was pre-pumped to full speed. Once the sample was inserted into the microscope chamber, it was quickly pumped to high vacuum and thus the air exposure time was shorter than 10 seconds. Microstructures were investigated with a probe-aberration-corrected FEI Titan STEM and image-corrected FEI environmental transmission electron microscope (ETEM) operating at 300 kV. The STEM HAADF detector collects all the incoherently scattered electrons. The image intensity reflects the average atomic number of each atomic column (−Z^2 to Z^2), hence termed as Z-contrast imaging, which is chemically sensitive, enabling us to visually analyse the atomic structure. The HAADF Z-contrast images were taken at a magnification of ~5000 kX which produced a frame-size of 20 nm x 20 nm for 1024 x 1024 pixel frame. This means an equivalent electron-beam current-density of 25 A cm$^{-2}$ for an electron probe of 100 pA. For STEM imaging, our dwell time was in the range of 10 µs per pixel, a typical image of 1024 x 1024 pixel frame took only 10 seconds, which did not bring detectable damage to our samples. STEM images were acquired from several regions of the samples that were taken from the same set of electrochemical experiments. The results from different regions are very consistent; therefore, only representative data are demonstrated in this work. The EELS spectra were obtained with a Quantum model Gatan imaging filter with a collection semi-angle of about 100 mrad. All the EELS are collected with a dwell time of 0.5-1 second/spectrum. The EELS shown in this work is a sum of multiple spectra in a line scan. The EELS spectra of the O K edge are normalized to the middle peak of the oxygen K edge, while the Ni, Co, Mn L edges are normalized to the corresponding L$_2$ peaks for easy comparison.

Electrochemistry. The cathode electrodes were prepared by coating a slurry containing 80% active mass, 10% Super P (from Timcal), and 10% poly(vinylidene fluoride) (Kynar HSV900, Arkema Inc.) binder onto Al foil current collector. After drying, the electrodes were punched into disks with ø = 1.27 cm. A typical loading of the cathode electrode is about 4.5 mg. R2032 coin-type cells were assembled with the cathode electrodes, metallic Li foil as counter electrode, Celgard 2304 monolayer polyethylene membrane as separator and 1 M lithium hexafluorophosphate (LiPF$_6$) dissolved in ethyl carbonate and dimethyl carbonate (1:2 in volume) as electrolyte in an argon-filled MBraun glove box. The electrochemical performance tests were performed galvanostatically in the voltage range of 2.0 - 4.8 V on an Arbin BT-2000 battery tester. Unless specified otherwise, the cells were tested at room temperature (~25°C). Cycling performance was tested at C/5, C/3 and 1.0 C rates (1 C = 250 mA g$^{-1}$), respectively. The electrochemical impedance spectra (EIS) of the cell were measured at charged state of 4.3 V using a CHI 600D electrochemical station from frequency of 100 kHz to 10 mHz with a perturbation amplitude of ± 10 mV.

RESULTS AND DISCUSSION
Figure 1. Charge/discharge characteristics of LMR cathodes. (a) Cycling performance at different C rates in the voltage range of 2.0 – 4.8 V. (b) Charge/discharge profile evolution and (c) Corresponding dQ/dV curves of LMR cathode at different stage of cycling at C/10 rate. (d) A series of Nyquist plots for LMR cathode at different stage of cycling at C/10 rate.

The electrochemical properties of LMR cathodes Li[Li$_{0.2}$Ni$_{0.2}$Mn$_{0.6}$]O$_2$ are presented in Figure 1. Figure 1a shows the cycling performances of LMR cathode at different C rates. After activation of the Li$_2$MO$_3$ component, the LMR cathode material delivers a stable discharge capacity about 240 mAh g$^{-1}$ at C/10 rate. The cells cycled at C/3 and 1 C rates were subject to 3 formation cycles at C/10. The reversible capacities of LMR cathode decreased to 206 and 166 mA h g$^{-1}$ at C/3 and 1 C, respectively. Although the rate capability of LMR cathode is still unsatisfactory due to its intrinsically low electronic/ionic conductivity, it exhibits very decent capacity retention over 100 cycles at various C rates, especially at low current density of C/10. The charge/discharge profile evolution during cycling at C/10 is shown in Figure 1b. During the initial charge process, the sloped charge voltage region below 4.45 V is attributed to Li ion de-intercalation associated with the oxidation of Ni$^{2+}$ to Ni$^{3+}$ and then to Ni$^{4+}$. The subsequent voltage plateau between 4.45 to 4.6 V is ascribed to the removal of Li ions concomitant with an irreversible loss of oxygen from the Li$_2$MO$_3$ component (M is Mn(major)/Ni(minor)), according to differential electrochemical mass spectrometry results and in-situ X-ray diffraction investigations. Within the oxygen loss plateau, the Li$_2$MO$_3$ component (C2/m structure with monoclinic symmetry) is activated, and thus the material delivers high capacity during the subsequent discharge process.

One of the most significant technical challenges of the LMR cathode is the gradual voltage fade during cycling, as indicated by the black arrow in Figure 1b. Although the voltage fade can be partially attributed to the electrode polarization associated with the deterioration of electrode/electrolyte interface, the primary origin for the voltage fade is owing to the gradual intrinsic structural evolution from layered to ‘spinel-like’ phase during repeated cycling, as observed for other LMR cathode materials. With the extraction of oxygen at high voltage, TM ions with reduced oxygen coordinates are destabilized and migrate into the neighbouring Li layer via the adjacent tetrahedral sites. This process is energetically favourable and hence facilitates the formation of a ‘spinel-like’ phase. Consequently, evolution of voltage plateaus at ca. 3.0 V is observed after cycling, as reflected by the evolving redox reaction peaks in the ~3.0 V voltage region shown in the dQ/dV curves (Figure 1c). However, there is an apparent absence of a strong redox reaction peak at ~4.0 V that corresponds to the insertion/removal of Li ions into/from the tetrahedral sites (8a sites) of the evolving ‘spinel-like’ component. This discrepancy reveals the formation of a defect spinel structure in which the tetrahedral sites are not available for Li ion storage and only the octahedral sites are accessible for reversible Li ion insertion/de-insertion. The structure of the defect spinel phase will be discussed later in detail.

EIS measurements were carried out to study the impedance evolution of LMR cathode at different stage of cycling and the results are shown in Figure 1d. The impedance spectrum exhibits two depressed semicircles at high to medium frequency range and a sloped line at low frequency range.
Figure 2. Crystal structure and electronic structure of the pristine LMR cathode. (a) Aberration-corrected HAADF-STEM image. (b) High resolution Z-contrast image showing the mixed growth of different zone axes of the C2/m phase at particle surface region. (c) Higher magnification Z-contrast image showing the mixed [100] (cyan) and [1-10] zone (yellow) at inner bulk region. (d) Atomic model showing the atomic arrangement of the C2/m phase in [100] and [1-10] zone projections. (e) Intensity plot along the yellow dashed line (TM layer) shown in (b). (f) Intensity plot along the green dashed line (Li layer) shown in (b). (g) Detailed comparison of the O-K, Mn-L, and Ni-L edges at different depth of pristine material particle, as labelled with i, ii, iii in (a).

It is generally interpreted that high-frequency semicircle is related to the solid electrolyte interface (SEI) resistance while intermediate-frequency semicircle is due to the charge transfer resistance in the electrode/electrolyte interface and low-frequency tail is associated with the Li ion diffusion process in the solid electrode.\textsuperscript{39} Upon cycling, the SEI layer resistance remains relatively stable (inset in Figure 1d), indicating a stabilized SEI layer formed on the cathode particle surface. However, the charge transfer resistance increases dramatically after cycling, revealing a sluggish kinetics of charge transfer reactions between the surface reconstruction layer and the electrolyte.

Characterization of pristine material.

It has been reported that lithium-containing layered oxide cathode materials are sensitive to high-energy electrons.\textsuperscript{40} The electron-beam irradiation during STEM imaging may result in the formation of a thin surface reconstruction layer, because of the introduction of Li and O vacancies caused by the atomic displacement effect of the incident electron beam.\textsuperscript{40} The removal of Li and O ions from the structure near the surface creates an unstable environment, similar to that formed during electrochemical cycling, which result in TM-atoms migrating into Li vacancies, forming the defect spinel / disordered rock-salt structure. This phenomenon interrupts the observation of structural evolution induced by the electrochemical charge/discharge processes. In the present work, special cautions have been taken to avoid the structural changes induced by the electron-beam irradiation. First, we observed the sample particles at a low magnification less than 100 kX. Second, we used adjacent areas to optimize optical conditions, such as focus and astigmatism, at high magnification of ~5000 kX. Therefore, the STEM images presented in this work represent the real nature of the samples. The crystal structure of pristine LMR cathode Li[Ni\textsubscript{0.20}Li\textsubscript{0.20}Mn\textsubscript{0.60}]O\textsubscript{2} was initially investigated as a reference. The LMR cathode synthesized using a hydrothermal assisted method exhibits a much uniform distribution of cations in atomic level and forms a kind of solid solution dominated by Li\textsubscript{2}MO\textsubscript{3} type C2/m monoclinic structure, as reported previously.\textsuperscript{32} Figure 2a shows the HAADF STEM Z-contrast image of a pristine LMR cathode particle. Of note, the Li ion (2b, 2c, 4h sites)\textsuperscript{41} and oxygen (4i, 8j sites) are invisible in the high resolution Z-contrast images due to their low atomic number, while only the TM ions occupying the 4g site are visible in the high resolution Z-contrast images. Representative high resolution STEM images at particle surface region and the inner bulk region are demonstrated in Figure 2b, c. The atomic-scale image shows that the region labelled with cyan rectangle and yellow diamond (in Figure 2c) matches the atomic model of the Li\textsubscript{1.5}MO\textsubscript{3} type C2/m phase in the [100] zone axis projection and the [1-10] zone projection (Figure 2d). The plotted intensity profile in Figure 2e from the yellow dashed line indicated in Figure 2b shows that the nearest atomic column distance in the [1-10] projection is around 0.14 nm and the centres of the atomic dumbbells are around 0.42 nm apart.
The plotted intensity profile in Figure 2f from the green dashed line labelled in Figure 2b shows that the Li ion diffusion pathways are not blocked, so that the Li ions can be easily extracted out during charge process. An EELS line scan was performed along the direction indicated with red arrow in Figure 2a to study the uniformity of chemical species and the representative EELS spectra integrated from regions i, ii, iii are compared in Figure 2g. For the O K edge, the pre-edge peak at 525 - 532 eV is associated with the electron transition from O-1s core state to the unoccupied O-2p states that are hybridized with TM-3d states, while the main peak at 532 - 545 eV is attributed to the electron transition from O-1s core state to unoccupied O-2p states that are hybridized with TM-4sp states.42, 43 The O K edge spectra display identical pre-edge peaks. Meanwhile, the corresponding transition metal L-edge spectra show identical peak shapes and \( L_3/L_2 \) intensity ratio from surface to particle bulk.42, 44 These results reveal that the average valence states of TM ions remains the same from particle surface to bulk, which is in good agreement with the uniform cation distribution within the particle as we reported before.32

Characterization of cycled material.

After initial charge/discharge cycle at C/10 rate, there is about 20% residual Li$_2$MO$_3$ component remaining in the cycled particle based on the difference between practical charge capacity (302 mAh g$^{-1}$) and theoretical charge capacity (378 mAh g$^{-1}$ Li$^{+}$ per Li[Li$_{0.2}$Ni$_{0.2}$Mn$_{0.6}$]O$_2$ formula unit), which will be further activated during subsequent cycling. Most the C2/m Li$_2$MO$_3$ component with monoclinic symmetry is activated, leading to the formation of R-3m LiMO$_2$ type layered structure (Figure 3a, b). The bulk structure well matches the atomic model of the R-3m phase in the [100] zone projection and the nearest atomic column distance is around 0.28 nm (Figure 3c). A few atomic layers of TM ions have already been detected in the Li layer at the crystal edge, although this surface reconstruction layer is only about 2 nm. The intensity plot along the Li layer (Figure 3d) displays a low intensity in one octahedral site followed by a high intensity in the adjacent octahedral site. This means that the TM ions that have migrated to the Li layer do not continuously occupy the Li vacancies to reduce the repulsion between the neighboring TM ions. Such a cation arrangement is ascribed to the LT-LiCoO$_2$ type defect spinel structure viewed down the [011] zone axis (Figure 3e). At some particle surface where the 16c sites are still no occupied by alien TM ions, only defect spinel structure is found after first cycle, as shown in Figure S1 in the Supporting Information. This defect spinel structure will be further observed in the surface reconstruction layer of LMR material after more cycles.

After 10 cycles, more TM ions migrate into the Li layers and the reconstruction layer is clearly observed to thicken (ca. 4nm) on crystal edge region, as shown in Figure 4a. The contrast line profiles in Figure 4b, c acquired from the red/white dashed lines labelled in Figure 4a show that the Li ion diffusion pathways at the edge region are blocked by the TM ions migrated from the TM layers. From a structural point of view, in the R-3m structure, Li ions (3a sites) and TM ions (3b sites) order on alternate (111) planes of rocksalt structure because of the large difference in ionic radius and charge between Li$^+$ and Ni$^{2+}$/Mn$^{4+}$ ions.
Figure 4. Crystal structure of LMR material after 10 cycles at C/10 rate. (a) High resolution STEM image. (b) Intensity plot along the red dashed line (TM layer) shown in (a). (c) Intensity plot along the white dashed line (Li layer) shown in (a). (d) Enlarged STEM image showing the structure of defect spinel structure (LT-LiCoO$_2$ type structure) with empty 16c octahedral sites. (e) Enlarged STEM image showing the structure with filled octahedral sites (disordered rock-salt structure). (f) Fast Fourier transform (FFT) from the region indicated by yellow dashed rectangle in (a). (g) Atomic models explaining the structural evolution pathway based on the close observation from the structural changes in cycled materials.

Nevertheless, with the extensive removal of Li ions (creating a large number of Li vacancies in the Li layer) and loss of oxygen at high voltage, the migration of TM ions into the Li layer via the adjacent tetrahedral sites becomes energetically favourable at high voltages. This observation is in good agreement with previous reports for LMR cathode materials. The intensity profile in Figure 4c also discloses that there are a few intermediate atomic layers (near surface region with a depth of ca. 2 nm) where the Li sites are not successively occupied by the TM ions. The corresponding Z-contrast STEM image (Figure 4d) matches two different kinds of spinel structures with the same space group Fd-3m, the LiMn$_2$O$_4$ type spinel structure and the LT-LiCoO$_2$ type defect spinel structure viewed down from the [011] zone axis. In principle, formation of the LiMn$_2$O$_4$ type spinel structure involves migration of TM ions into Li sites and Li ions into tetrahedral sites followed by a distortion of oxygen lattices. However, the formation of ideal LiMn$_2$O$_4$ type spinel structure (with a Li ion at the 8a site, a TM ion at the 16d site, and O at the 32e site) is contradictory with the observed decrease in Li ion diffusion coefficients (Figure S2 in the Supporting Information) because the LiMn$_2$O$_4$ spinel structure has a much higher Li ion conductivity than the LMR layered structure due to the 3D Li ion diffusion pathways. The possibility of forming the LiMn$_2$O$_4$ type spinel structure can be further ruled out by the absence of the redox reaction peaks at ~ 4.0 V that corresponds to the insertion/removal of Li ions into/from its tetrahedral sites and the completely different charge/discharge voltage profiles between the spinel (two-phase reaction) and cycled LMR cathode (solid solution reaction) (Figure S3 in the Supporting Information). In contrast, there is no severe distortion of oxygen lattices required for the formation of the LT-LiCoO$_2$ type defect spinel structure, where the TM ions and Li ions occupy the 16d and 16c octahedral sites, respectively. In the LT-LiCoO$_2$ type defect spinel structure, only the 16c octahedral sites are available for reversible Li insertion/de-insertion, while the tetrahedral sites are electrochemically inactive, which not only explains the absence of 4 V voltage plateau after cycling but also accounts for the lowering of discharge voltage profiles (termed as voltage fade) as compared to the original layered structure.

At the outermost surface layers, some of the 16c octahedral sites of the LT-LiCoO$_2$ type structure are further occupied by the TM ions (Figure 4e), converting the defect spinel structure to a disordered rock-salt structure with Fm-3m space group, as confirmed by the Fast Fourier Transform shown in Figure 4f.
Figure 5. STEM image characterizing the LMR material after 100 cycles at C/10 rate. (a) High resolution Z-contrast image showing the [110] zone of Fm-3m disordered rock-salt structure. (b) Intensity plot along the red dashed line shown in (a). (c) Intensity plot along the green dashed line shown in (a). (d) Intensity plot along the yellow dashed line shown in (a). Possible environments for the Li ion diffusion in the Li transition metal oxides: (e) one adjacent octahedral transition metal (1-TM), (f) two adjacent octahedral transition metals (2-TM), or (g) no adjacent octahedral transition metal (0-TM).

Although the Z-contrast STEM image in Figure 4e also matches LiMn$_2$O$_4$ type spinel structure projected in the [111] zone axis, the possibility of the formation of LiMn$_2$O$_4$ type spinel structure has been excluded based on the above discussion. During further cycling, more of the TM ions will migrate to the Li layer, leading to the increased formation of the disordered rock-salt structure in the cycled material, which may eventually extend to the interior of the particle. Formation of defect spinel structure and disordered rock-salt structure has also been identified in other LMR particles after 10 cycles (Figure S4 in the Supporting Information). The above discussions are summarized with a schematic as shown in Figure 4g, describing how the layered crystal structure of the LMR cathode (R-3m structure activated from initial C2/m structure) transforms to a LT-LiCoO$_2$ type defect spinel structure followed by further conversion to a disordered rock-salt structure during extended cycling.

Further cycling to 100 cycles leads to the formation of a surface region with a thickness of ca. 10 nm that has been transformed to the disordered rock-salt structure (Figure 5). The image in Figure 5a reveals that the ions in the Li layer show almost equivalent intensity as compared to those in the TM layer, which makes it difficult to differentiate the Li layer and the TM layer. Other LMR cathode particles over the same period of cycling exhibit same trend of structural evolution, as substantiated by the Z-contrast images presented in Figure S5 in the Supporting Information. A question raised on these observations is whether the formation of the disordered rock-salt phase reduced the active Li ion sites in the material lattice. The answer is negative based on the good cycling performance in terms of capacity retention as achieved for this material during cycling (see Figure 1). The observation in Figure 5a can be explained with the following considerations: In the disordered rock-salt structure, the octahedral sites vacated by TM ions that migrate to Li layers are still accessible for reversible Li ion insertion/de-insertion during the long-term cycling. The intensity plots along different directions of atomic layers exhibit similar intensity (Figure 5b-d), further demonstrating the increased disordering of TM ion distribution in the rock-salt structure. The spinel and the disordered rock-salt structure (Fm-3m) have been identified in conventional layered structure NCM$_{44}$ and NCA$_{43}$ cathode material (typical Li$_{1.0}$TMO$_2$) when cycled with a high cutoff voltage of 4.7 V. However, conventional NMC or NCA cathode materials show fast capacity loss with 4.7 V as charge cutoff voltage, due to the formation of a surface reconstruction layer with the spinel and rock-salt structure. In addition, this capacity loss would be considerably accelerated when the material is cycled at lower current density, such as C/10 rate. In contrast, the LMR cathode exhibits good cycling stability in terms of capacity retention despite the high charge cutoff voltage of 4.8 V and the low C rate (C/10) (Figure 1). The primary difference between the conventional NMC cathode material and the LMR cathode material is the Li content in the crystal structure, which plays an important role in maintaining the electrochemical reversibility of the cathode material.
Li ion diffusion in stoichiometric layered Li metal oxides (ordered rock-salt structure) proceeds by hopping from one octahedral site to another octahedral site via an adjacent tetrahedral site (o-t-o diffusion). Basically, only the r-TM Li environment (Figure 5e) is active for Li ion diffusion in layered-structured cathode material.\(^{47, 48}\) Because of the formation of the disordered rock-salt structure in the cycled electrode, the migration of TM ions to the Li layer largely reduces the r-TM Li ion diffusion channels existing in the original layered structure, accompanied by an increase of 2-TM Li ion diffusion channels (Figure 5f). This can explain why the conventional NCM cathode shows fast capacity loss once the surface layered structure transforms to rock-salt structure.

As recently indicated by Ceder et al.,\(^{38}\) cation disordering (formation of the disordered rock-salt structure) does occur in some Li rich cathode material in which all the TM ions are electrochemically active. Excess Li in the cathode crystal structure is indispensable to reach the threshold (\(x = \sim 1.1 - 1.2\) in \(Li_x\text{TM}_{2-x}O_2\)) of a percolating network for Li ions in the disordered rock-salt structure, by increasing the r-TM and also the o-TM channels (Figure 5g). In the lithium-rich cathode Li[Li\(_{x}Ni_{1/3}\text{Mn}_{2/3}\)O\(_{2}\)] (Li/TM = 1.5), there is still excess Li ions in the crystal structure (Li\(_{x}\text{TM}_{2-x}O_2\)) (Li/TM = 1.25) during subsequent cycling assuming that the Li ions in the TM layer were irreversibly removed during initial activation process and most of the oxygen vacancies are preserved.\(^{49}\) The excess Li ions versus TM ions can reach the percolating threshold for Li ion diffusion despite the formation of the disordered rock-salt structure, hence enabling the sustainable operation of the material. To further substantiate this point, we investigated the performance of LMR cathodes (\(x Li_x\text{TM}_{2-x}O_2\)) with different Li content. As expected, the material with reduced excess Li content (decreased Li\(_{x}\text{TM}_{2-x}O_2\) component) exhibits faster capacity loss during cycling (Figure S6 in the Supporting Information), because the lower Li content could not satisfy the Li percolating in the disordered rock-salt structure evolved after cycling. As can be seen in Figure S2 in the Supporting Information, the lithium ion diffusion coefficients of the cycled sample (which exhibits a disordered rock-salt structure) decreases significantly during the Li ion extraction (early stage of charge) and Li ion insertion (early/ending stage of discharge). The result demonstrates an obvious increase of kinetic barrier for Li ion diffusion in the disordered rock-salt structure formed after cycling, which reveals that the LMR cathode undergoes significant power fade during cycling. From this point of view, a low current density such as C/10 rate is preferred for LMR cathode to ensure reversible/complete Li ion de/insertion and to achieve good capacity retention during cycling.

Another question of interest is whether Ni segregation occurs during the phase transformation. In this work, pristine material with homogeneous cation (Ni and Mn) distribution were used.\(^{33}\) To determine the local chemical evolution that is associated with the elemental redistribution
after 100 cycles, quantitative energy dispersive spectroscopy (EDS) mapping of Mn, Ni, O and C were performed on the cycled particle and the representative result is shown in Figure S7a-e in the Supporting Information. After cycling, a thin SEI layer with a thickness of 5 – 10 nm was uniformly formed on the particle surface, as shown by the carbon map (Figure S7e). The thin SEI layer accumulated on the cycled particle surface can be attributed to the stable surface structure associated with the reduced Ni segregation, which is in good agreement with the excellent cycling performance discussed above. However, the SEI layer formation gives rise to an increased kinetic barrier for Li ion transport, resulting in an increased power fade of the LMR cathode. The overlaid Mn/ Ni maps (Figure S7f) demonstrate that the Mn/ Ni elements are still homogeneously distributed throughout the particles, as reflected by the uniform Ni/Mn distribution in the EDS line scan result (Figure S7g). This is because the migration of TM ion to Li layer is perpendicular to the metal ion slabs, which does not result in any chemical gradient. The absence of any cation segregation after phase transformation is further confirmed by the EELS mapping as shown in Figure 6a-e, demonstrating that the TM ions are still uniformly distributed at surface regions, similar to that observed in pristine material.

The fine structures of EELS can provide useful information about the oxygen vacancy and valence states of the TM ions. To further investigate the electronic structure change in the disordered rock-salt phase, EELS acquired from different regions of the cycled particle are compared in detail, as presented in Figure 6f-h. Because the EELS were obtained at the discharge state, the oxidation state of Ni remains almost the same as Ni$^{2+}$ at the surface region and in the particle bulk. The oxygen electronic structure is quite different from bulk to surface in the cycled particle. The oxygen K-edge to Mn L-edge intensity ratio decreases considerably at the outmost crystal edge region as compared to the bulk region. This is due to the continuous loss of oxygen from the crystal surface for balancing the charge during initial activation of the Li$_2$MnO$_3$ component and during each charge to high voltage, leading to the formation of a great number of oxygen vacancies. The pre-peak of the O K-edge, which is sensitive to the oxidation states of TM ions, shows significant drop in intensity as compared to those of cycled bulk and pristine material. Meanwhile, the Mn $L_3/L_2$ intensity ratio in the cycled sample increases considerably at the oxygen deficient surface compared to the bulk region. Both of these electronic signatures reveal a valence state drop of Mn ions in the surface region.

The Mn $L_3/L_2$ intensity ratio has been found to follow a linear relationship with the Mn valence states, and thus can be used to quantitatively identify the Mn valence states. The Mn $L_3/L_2$ intensity ratio is determined to be 3.05 at the oxygen deficient surface (outmost 1 – 2 nm) and 2.52 at the inner cycled bulk (ca. 20 nm from surface), which are much higher than 2.10 for pristine material. Quantitative analysis indicates that Mn is $^{4+}$ (Mn$^{4+}$) before cycling, which however decreases considerably to $^{3.4+}$ (Mn$^{3.4+}$) in the cycled bulk. At the outmost surface region with considerable oxygen vacancies, the valence of Mn is determined to be as low as $^{2.7+}$ (Mn$^{2.7+}$), indicating a significant modification to the local stoichiometry and chemical bonding in the converted disordered rock-salt phase. Since the intercalation of Li ions into R-3m layered structure does not initiate the reduction of Mn, the lowering of Mn oxidation state in cycled bulk is triggered by the insertion of Li ions into the octahedral sites of the disordered rock-salt phase. Of note, the valence of Mn ions in the cycled particle, especially those at outmost surface, is below that expected for a damaging Jahn-Teller distortion (+3.5). The Mn$^{2+}$ at the surface region is unstable and tends to disproportionate to form soluble Mn$^{4+}$, leading to the loss of active material and gradual capacity fading.$^{54-55}$ The undesired phase transformation and unfavorable chemical evolution will eventually result in capacity fading of the LMR cathode material besides the significant voltage fade during cycling, as evidenced by the accelerated capacity/voltage fade at high temperature of 60°C (Figure S8 in the Supporting Information).

Finally, it is worth noting that the phase transformation pathway of the LMR cathode material during cycling is closely associated with the material composition, elemental distribution on the atomic level, and material synthesis method. Our previous investigations have demonstrated that the voltage and energy fade of LMR cathodes could be mitigated by improving the atomic level spatial uniformity of the chemical species. The findings reported in this work are based on the detailed observations on the material prepared by hydrothermal assisted method. In this case, the LMR (Li[Li$_{0.55}$Ni$_{0.35}$Mn$_{0.1}$]O$_2$) material shows uniform distribution of Ni/Mn at atomic level. The strong Ni-Mn interaction in this material stabilizes its crystal structure, thus leading to the good long-term cycling stability. For the materials prepared by co-precipitation method or sol-gel method, due to the existence of significant Ni segregation, the phase transformation pathway upon cycling can be quite different, which is not unexpected owing to the weakened Ni-Mn interactions, especially in the surface regions where the Ni segregation is significant. A systematic investigation recently performed by this group on the LMR material prepared by the co-precipitation method revealed that the material experienced a phase transformation from C2/m to M$_{0.3}$O$_{1.7}$-type spinel.$^{54}$ The M$_{0.3}$O$_{1.7}$-type spinel has been repeatedly identified as an intermediate phase between spinel and rock-salt phase in a heated overcharged Li$_{x}$Ni$_{0.55}$Co$_{0.35}$Mn$_{0.1}$O$_2$ sample.$^{55}$ The M$_{0.3}$O$_{1.7}$-type spinel has also been found in the delithiated Li$_{0.55}$Mn$_{0.35}$O$_2$ spinel electrode, which is considered to be closely related with the Mn dissolution during cycling.$^{57}$ Meanwhile, M$_{0.3}$O$_{1.7}$ (e.g. Mn$_{0.35}$O$_2$) is a kind of electrode material that is only active at a voltage below 2.0 V.$^{58}$ From this point of view, formation of a M$_{0.3}$O$_{1.7}$ phase is more undesired, directly leading to capacity degradation, as compared to the formation of disordered rock-salt structure, which is likely to be one of the main reasons for the resulting faster capacity degradation of materials prepared by co-precipitation than that prepared by hydrothermal assisted method.$^{32}$ These findings not only substantiate the importance of the homogeneous distribution of chemical species (Ni/Mn) in LMR cathodes but also suggest that enhancing the stability of the surface structures in the cycled electrode is the key to improving the
long-term cycle life of LMR cathode. Our results also shed light on the functioning mechanism of an additional surface coating, such as AlF₃ coating, which can prevent the electrode from etching by acidic species in the electrolyte, suppress the degradation of the surface reconstruction layer, thus improving the stability of the LMR cathodes.⁵⁹

CONCLUSIONS

In summary, in-depth characterization with STEM imaging and EELS chemical analysis reveal that the LMR cathode Li[Li₀.ₖ₁Ni₀.₄Mn₀.₃O₂] prepared by the HA approach experiences a phase transformation from a layered structure to a LT-LiCoO₂ type defect spinel-like structure (Fd-3m space group) and then to a disordered rock-salt structure (Fm-3m space group). The voltage fade can be correlated with Li ion insertion into the octahedral sites in the defect spinel-like structure and the disordered rock-salt structure. The reversible Li insertion/removal into/from the disordered rock-salt structure is ascribed to the Li excess environment that can satisfy the reversible Li percolation in the disordered rock-salt structure despite the increased kinetic barrier. There is no Ni/Mn cation segregation observed in the cycled particle, because the migration of TM ions to the Li layer occurs perpendicularly to the metal ion slabs. Meanwhile, owing to the formation of a great amount of oxygen vacancies, a significant decrease of Mn valence is detected in the cycled particle which is below that expected for a detrimental Jahn-Teller distortion (+3.5). These fundamental findings further substantiate the importance and fundamental functions of surface modifications in enhancing the surface structural stability of LMR cathode during cycling and thus improving the battery cycle life.

ASSOCIATED CONTENT

Supporting Information.

GITT result; supporting electrochemical data; Z-contrast images, intensity plots and EDX maps. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

J. Z. synthesized electrode materials and characterized their electrochemical properties. P.H. X. and M. G. performed microscopic analysis under the supervision of Nigel Browning and Chongmin Wang. J. Z., J. X., P. Y., C. M. W. and J.-G. Z wrote the manuscript through contributions of all authors.

Notes

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REFERENCES


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