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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.202005337

Link to VoR: https://doi.org/10.1002/anie.202005337
Size-Mediated Recurring Spinel Sub-nanodomains in Li and Mn-rich Layered Cathode Materials

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Abstract: Li and Mn-rich layered oxide (LMR-NMC) is one of the most promising cathode materials for Li-ion batteries with high theoretical energy density. Its practical application is, however, hampered by the capacity and voltage fade after long cycling. Herein, a finite difference method for near-edge structure (FDMNES) code was combined with in-situ X-ray absorption spectroscopy (XAS) and transmission electron microscopy/electron energy loss spectroscopy (TEM/EELS) to investigate the evolution of transition metals (TMs) in the fresh and heavily cycled electrode. Theoretical modeling reveals a recurring partially reversible LiMnO 2-like sub-nanodomain formation/dissolution process during each charge/discharge, which accumulates gradually and accounts for the Mn phase transition. From modeling of spectra and maps of the valence state over large regions of cathodes, it was found that the phase change is size-dependent. After pro-longed cycling, the TMs displayed different levels of inactivity.

Li and Mn-rich transition metal (TM) oxides, with a general chemical formula of xLi 2MnO 2(1-x)LiMeO 2 (Me = Mn, Ni, Co etc.) (LMR-NMC), have been regarded as some of the most promising cathode materials for the next generation high energy density lithium-ion batteries (LIBs). Different from conventional layered LiMeO 2, excess lithium ions reside in the TM layers, forming an inter-grow nLi 2MnO 2 crystal domain with LiMn 2 units in the parent LiMeO 2 structure. The combination of the C2/m Li 2MnO 3 and the R-3m LiMnO 2 crystal domains has allowed this material to deliver a capacity of over 250 mAh/g within a voltage window of 2.0 – 4.6 V (vs Li/Li + ), which represents the highest energy density reported so far in LiBs cathode materials.[5]

Currently, it is believed that the high capacity in LMR-NMC is achieved by sacrificing its structure integrity. This is a result of Mn migration into the Li layer after oxygen release, forming a spinel structure.[6] It severely block the Li-ion diffusion pathways, ending up with a very poor rate capability.[6] On the other hand, the agglomeration of the spinel phase leads to the decay of average voltage and results in the loss of energy density of the whole cell.[7] The migration of the TMs has also been studied by many researchers through microscopic characterization, each of the TMs tends to undergo different migration pathways and segregate from each other.[6b, 7] Despite the well-accepted phase transition mechanism, there still remain many unresolved questions in the LMR-NMC. First, even though the layer to spinel phase transition has been identified, more efforts are needed to investigate the incubation and reversibility of this process.[6] Second, how the TMs participate in the charge compensation of the charge/discharge process after the long-term cycling process is not clear. The fact that each of the TMs favors certain migration pathways could eventually lead to divergent electrochemical behaviors, hence it is of major significance to identify the evolution of each TM individually.[9] In order to deal with these questions, it is essential to utilize an approach that can probe the local information of the TMs with an in-situ manner. In-situ XRD, HRTEM, NMR and so forth have been reported, but they have certain limitations.[10] In-situ XRD only probes phases that are
large enough, hence the incubation period of the phase development cannot be evaluated. HRTEM tells local information down to atomic scale, but it is not element specific. An in-situ operation has been very challenging and electron beam hitting the sample, especially at an operating condition, may cause undesired impact that makes the result unreliable.[11] Most NMR probes the local environment of Li but cannot tell information about the environment of Mn/Co/Ni, not to mention that the material tends to lose Li upon cycling.[13]

X-ray absorption near edge spectroscopy (XANES) that enables the detection of core-electron excitation process of TMs has been widely used to probe the local structure of LIB materials in the range of sub-nanometers. TM K- and L-edge XANES, with its dipole selection rules, can provide abundant information on the electronic configuration and oxidation state of TM, therefore they are extensively used for understanding the structural changes of cathode materials.[18] In-situ XANES of the first and subsequent cycles of LMR-NMC have been studied, the charge compensation mechanism has been investigated in these reports using the XANES region, and the surrounding environment was evaluated based on the EXAFS results.[14] By collecting EXAFS and K-edge XANES, one gets not only 1st TM-coordination and 2nd TM-TM coordination in multiple species, hence phase speciation is not possible. Regarding this, it is of great interest to better utilize the XANES part and explore from different perspectives.[14, 15] There are two parallel approaches for XANES speciation. The first is based on the experimental data from model compound standards. This approach works well under the condition that model compounds in the standard system is correctly selected not only from speciation and crystallography perspectives, but also in the local structural environment for the corresponding interested element. Unfortunately, these prerequisites are not available for some XANES cases, including the research reported herein. Theoretical modeling based XANES approach is especially powerful when dealing with a system experiencing a dynamic course, e.g. the reduction reversible crystallization and dissolution process occurred during battery multiple charging and discharging process. Then the only option is to take a second approach, which is at least partially relying on XANES theoretical calculation to provide certain standard spectra for corresponding speciation, followed by linear combination fitting (LCF) analysis. Either finite difference method for near-edge structure (FDMNES) or FEFF has been used in this regard.[15] In this study, a FDMNES code was combined with in-situ XANES measurement and transmission electron microscopy and electron energy loss spectroscopy (TEM/EELS) mapping to track the evolution of TMs in both the first and 451th cycles. The development of the surrounding environment of Mn has been well reproduced with a partially reversible formation/dissolution of a LiMnO2-like nanodomain during the charging/discharging process. It accounts for the accumulation of the spinel phase after long term cycling. The phase accumulates predominantly in small particles and on the surface of large particles. This study offers new insights for the development of LMR-NMC cathode materials.

The chemical composition of the LMR-NMC was measured by inductively coupled plasma atomic optical emission spectrometry (ICP-OES). The relative ratio between Mn:Co:Ni was found to be 67:16:17, which is close to the theoretical ratio stoichiometry of 68:16:16 according to the chemical formula of Li10Mn5Co5Ni5O30. SEM images of the fresh electrode and the electrode after 450 cycles are presented in Figure S1, the original LMR-NMC particle diameter is around 100 nm (Figure S1a). The LMR-NMC material was cycled at C/2 rate (1C = 250 mAh/g) after an initial activation cycle at C/20. After cycling, although the size of the particles remains almost unchanged, the particles are covered by a dense film (Figure S1b). Chemical analysis of the O 1s XPS (Figure S1c-d) has revealed that the cycled sample has a large amount of C=O and C-O groups that belong to the solid electrolyte interphase (SEI).[18] The initial charge capacity was 303 mAh/g and the initial discharge capacity was 253 mAh/g, as shown in Figure 1a. The large irreversible capacity in this material due to the loss of active Li+ is detrimental for practical full cell configurations with limited Li amount. The capacity shows dramatic decay after long-term cycling, only 123 mAh/g discharge capacity was obtained in the 450th cycle. Figure 1b shows the charge/discharge curves of the 1st, 2nd, 50th, 100th, 250th and 450th cycles. In the initial charge process, the slope below 4.45 V has been ascribed to the de-intercalation of Li+ ions from the R-3m LiMnO2 phase.[19] Followed by this, a long plateau due to the release of oxygen from the edges of the LiO6 octahedra in the C2/m LiMnO2 emerged. The oxygen release promotes the electrochemical decomposition and structural deterioration.[17] The capacity drop during cycling was accompanied by a voltage drop as shown in the charge/discharge curves of the following cycles. The dQ/dV curves of the 1st and 450th cycles are illustrated in Figure 1c. All the capacity was delivered above 3.0 V in the first cycle, yet after 450 cycles, the capacity above 3.0 V became marginal. Such a voltage drop has been regarded as the biggest hindrance in the commercialization of LMR-NMC materials.[11] Notable studies have been carried out to understand this behavior, the majority of which believed that the voltage drop was closely associated with the irreversible phase transformation from layered to spinel and/or rock salt phases.[6d, 11, 18]

Atomic-resolution STEM images of the fresh LMR-NMC particle has been collected and shown in Figure 1d. The Li-TM-TM dumbbell structure can be clearly seen in the TM layers of the pristine LMR-NMC particle (Figure 1d, left panel). Note that the contrast of the HAADFSTEM image is proportional to the N-number of the elements present in the material. In this case, the bright atomic columns are the heavier TM atoms, and the lighter elements, Li and O, are not visible from the image. Regions A, B and C represent different stacking sequences of the TMs and Li atoms, which correspond to the projection of [110], [100] and [1-10] orientations of the C2/m monoclinic structure, such stacking faults have also been observed from previous studies.[2, 16] These monoclinic dumbbell features are still visible from the LMR-NMC cycled after 450 cycles (Figure 1d, right panel), the remaining layered phase has mostly transformed into a conventional NMC-type (R-3m) phase accompanied with the loss of TM layer Li. The alteration is also shown in the X-ray diffraction (XRD) patterns (Figure S2a-b), in the pristine LMR-NMC sample, the (003) peak at close position is ascribed to the diffraction from Li2O2.[20] In the meantime, spinel and rock salt phases were identified in the XRD and Raman spectra (Figure S2b-c).

Figure 1. (a) Cycling performance of the LMR-NMC. (b) Charge/discharge curves of the 1st, 2nd, 50th, 100th, 250th and 450th cycle. (c) dQ/dV curves of the initial cycle and the 450th cycle. (d) Aberration-corrected STEM image of the pristine LMR-NMC and LMR-NMC cycled for 450 times, scale bar: 2 nm.
The in-situ XANES measurement of the Mn K-edges of the first and 451st cycles are shown in Figure 2a-d. Figure 2a displays the Mn K-edge XANES of the charging process. Overall, four trends are observed. Trend α represents a development of the white-line which is in fact a multiple scattering since it appears significantly above the threshold; its intensity decreases and its position is drifting to the higher energy direction, indicating a shortening of the Mn-O distance on average since in multiple splitting theory, the position of the resonance above the threshold is inversely proportional to the square of the interatomic distance, thus the farther away the resonance from the threshold, the shorter the bond; while the trend β indicates progressive changing of edge jump line-shape from concave to convex (change of the densities of states of Mn p character in the conduction band). Trends A and B by showing in Figure 2b, the four XANES features show reverse changing trends with α shifting upward, Trend β shifting downward, and Trends A and B moving to lower intensity, revealing opposite Mn local structural adjustment trend between charging and discharging reaction.

During the 451st cycle, the evolution of Mn K-edge XANES spectra becomes subtle, especially for the changing extend between the starting and ending of the discharging process for trends A and B (Figure 2c), suggesting that certain reaction has brought to the end. Since these experimentally resolved XANES data trends were in step with the performance degradation of the cell throughout the charging and discharging process.

While tracing the local environment of Mn using XAS has been carried out in many previous in-situ XAS studies, it remains elusive as to how to correlate the Mn local structural environment and Mn speciation with the evolution of the cell performance. In this study, we attempt to address the Mn local environment by examining the line-shape of the edge jump using their first-derivative spectra of the Mn K edge XANES shown in Figure 2e-f. In the pristine LMR-NMC material, three characteristic peaks appear in the energy range of 6545-6560 eV at the beginning of the first cycle of charging with peak intensity for feature “e” being much more intense than the other two. However, upon charging, the intensity of peak “e” decreases significantly, eventually showing a flat triplet feature with roughly equal intensities at the end of this charging process. The trend is marked as γ in the figures, which is the angle between starting and ending point of the Mn K edge XANES (Figure 2f). Such an incomplete conversion trend implies that there was a partially reversible transition in the material. A complete set of the first derivative plots is shown in Figure S3, the γ trend is obvious in the beginning and becomes gradually weak when it reaches the end of charging/discharging. Further examining the first derivative peaks of the Mn K edges XANES of the 451st cycle (Figure 2f) shows that the angle changing of the γ trend becomes almost negligible compared to the first cycle, the first derivative spectra feature the triplet peak with almost equivalent intensity throughout the whole process. The sharp contrast between the initial cycle and the 451st cycle, along with the partially reversible γ trend in the first cycle imply that a second less active Mn domain/phase that features the triplet peaks with close intensities emerges when charging is started. During the discharging process, the above process was backward processed, but not complete. After extensive cycles, the accumulation of the related Mn domain becomes significant, and it is likely to be associated with the cell performance decay.

To address the structural and chemical significance of the experimentally revealed XANES features “A”, “B”, “α”, “β”, and the flat triplet feature “γ” characterized at the XANES edge jump of Mn K edge XANES (Fig. 2), XANES theoretical modeling was performed by using FDMNES code. A corresponding structure system was first developed, which is composed of Mn-centered and spherical particles or domains with domain radius progressively increased. FDMNES modeling was performed on each particle of the system to develop the corresponding theoretical XANES system. Then the best fit XANES was identified based on the comparison between experimental data vs. modeled XANES spectra.

At first, the Mn K-edge XANES of LiNi$_{0.5}$Mn$_{0.25}$Co$_{0.25}$O$_{2}$ was modeled using a hexagonal Li$_3$MnCoNiO$_6$ structure as shown in Figure S4, details of the modeling process can be found in the experimental section. By adjusting the size of the Mn-centered domain, a series of Mn K edge XANES of Li$_3$MnCoNiO$_6$ have been obtained. In order to validate the modeling result, the calculated XANES spectra have been paired with the experimentally collected Li$_3$Mn$_2$O$_8$ Mn K-edge XANES result using linear combination fitting (LCF). The LCF best fit has been achieved using a calculated XANES based on the domain radius of 5 Å (R5.5) as one of the standard spectra of LiNi$_{0.5}$Mn$_{0.25}$Co$_{0.25}$O$_2$ and experimental XANES model compound from Li$_3$Mn$_2$O$_8$ as second standard spectrum as shown in Figure S5. This approach gives an estimation that the LMR-NMC constitutes 75% Li$_3$Mn$_2$O$_8$ and 25% Li$_3$MnCoNiO$_6$. The nominal composition of this LMR-NMC is Li$_{(1.5-0.4x)_{0.5}}$Mn$_{0.13}$Co$_{0.13}$Ni$_{0.13}$O$_2$, which can also be written as the combination of 0.41Li$_3$Mn$_2$O$_8$+0.13Li$_3$MnCoNiO$_6$, with the actual percentage of the
Li$_2$MnO$_3$ phase being approximately 3 times that of Li$_2$MnCoNiO$_4$. The agreement between the XANES LCF analysis and the actual chemistry composition indicates that the theoretical modeling of the XANES spectra is a valid approach to evaluate the experimental data under favorable conditions.

A complete set of possible Mn-bearing phases were modeled, the results are shown in Supporting Table 1. Within these simulated Mn phases, LiMn$_2$O$_4$-like spinel phase uniquely display a triplet feature in the first derivative of the Mn K XANES edge jump with equivalent peak intensities throughout the triplet feature, which is shown in Figure 3a. With the increase of the Mn-centered domain size, this characteristic feature is observed at a radius of ~6 Å and is maintained beyond this limit, suggesting that overall a scale of nanometer in diameter is the critical size for the LiMn$_2$O$_4$-like domain to resolve the feature. The triplet peak feature of LiMn$_2$O$_4$ has also been observed in the experimentally obtained Mn K edge XANES from model compound LiMn$_2$O$_4$ shown in Figure S6, suggesting that the simulation is valid.

To analyze the aging process of the LMR-NMC material, the modeled Mn K edge XANES of LiMn$_2$O$_4$ phase with increasing domain radius has been shown in Figure 3b-d. The experimentally resolved four feature trends, i.e. α, β, A, and B, and have all been well resolved and reproduced throughout the simulated LiMn$_2$O$_4$ XANES system. Note that Trends A and B appear to be increasing in step as shown in Figure 3c-d. Peaks “A” and “B” are contributed by the backscattering from Mn local structural environment of different coordination shells. As shown in Figure 3c, R2.0 only the backscattering from the first shell octahedron coordination of Mn-O bonding is experienced by the center absorbing Mn, resulting the precursor of feature peak “A”. When the backscattering of the second shell Mn-Mn coordination (covered by cluster R3.0) joins the pre-edge feature effect, strong positive interference occurred between the signal from this shell Mn scattering related peak and that of the first shell Mn scattering with the intensity of “A” strangely enhanced. With the additional backscattering from atoms up to R3.5, the precursor of the feature “B” begins to grow at low energy side of the final feature “B” energy position. Induced by negative peak interference from these further scattering, the intensity of “A” is reduced. When the backscattering is extended to R4.6, the precursor of feature “B” is further enhanced in step with decrease in “A” from further negative peak interference; this effect further occurred to “A” up to cluster R5.0.

As shown in Figure 3d, the feature is experimentally at ~654Å. Since XAFS is a single electron process and XANES spectrum is analyzed under normalized scenario, the overall transition probability for features “A” and “B” is roughly constant throughout the progressively developed process. Therefore, evolution of “A” and “B” and their relative change is fingerprinted to development of the “B” phase, rather than “A” peak. The slight increase in “A” is induced at first by the progressive increase of “B” as background signal, and further induced by the progressive increase in the edge-jump signal as second part of the background signal. The major significance of the modeling from R5.0 to R6.8 is to address the dynamic development process in the domain size of the spinel structure from R5.0 to R6.8. Therefore, the herein reported systematic modeling result reveals that the progressive development process of “A” and “B” and their relative change is the fingerprint feature to address dynamic development process of the spinel type structure in the sample system. The modeling also indicates that the R5.0 cluster is a critical size. When the spinel structure is developed up to R5.0, “B” is well-resolved at ~654Å. With “B” further developed vs “A”, the size of the spinel structure is further developed beyond nano scale. This inconsistency in feature trends further correlates the experimental result (Figure 3a) to the domain size of LiMn$_2$O$_4$, revealing that the distribution of domain sizes in the actual material may vary largely, and the particle size effect directly impacts the XANES feature. The Trend A is mainly regulated by the change of LiMn$_2$O$_4$-type of small domains up to 5 Å in radius, while the Trend B is due to the change of larger domains with radius ≥5Å.

The well-resolved simulation result suggests that LiMn$_2$O$_4$-like domain is an ideal mathematical solution and poses a speculation that the experimentally obtained in situ Mn K edge XANES is indicative of the development of LiMn$_2$O$_4$ domains within the particle. The system under investigation has multiple coexisting Mn phases (Li$_2$MnO$_4$ and LiMnO$_2$), resulting in peak interference effect among backscattering from different scattering paths of a same Mn phases, and similar type of back scattering from domain size in the sample. The intensity of the first derivative XANES, and their relative change is finger print in this study in terms of Mn speciation and understanding of the dynamic process of battery performance. During charging, the sub-nanometer domain with LiMn$_2$O$_4$ type structure grows gradually. During discharging, the domain size decreases gradually yet cannot fully disappear at the end of discharge. Similar XANES features “A”, “B”, “α”, “β” are also observed in some other in-situ XAS studies of regular layered LiNiMnCoO$_{2-x}$($x ≈ 0.2$) since spinel LiMn$_2$O$_4$-type structure is involved in these materials as well.

As shown in Figure 3e, to form a spinel LiMn$_2$O$_4$-like phase, Mn needs to migrate into the octahedral site in the Li layer following a TM$_{oct}$-Li$_{oct}$-Li$_{oct}$-pathway. In the meantime, Li from the Li layer reversibly migrates into the adjacent tetrahedral site. Both reversible and irreversible migrations of Mn in LMR-NMC have been reported. The reversible migration is the process where the tetrahedral site in the Li layer is occupied at a meta-stable state and it is responsible for the voltage hysteresis, this is however not a spinel phase. The irreversible migration is arguably the process where Mn migrates through the meta-stable state to a cubic environment (i.e. the next octahedral site), this is when spinel phase forms. Previous ex-situ TEM studies have argued that there might be a partially reversible spinel phase formation during charging/discharging process, which supports the XANES observation and the corresponding XANES theoretical modeling of this work. At the end of each cycle, some Li$_2$MnO$_4$-like sub-nanodomains survive, which accumulate and become actual phases after long-term cycling, this has been verified by the XRD and Raman spectra of the sample after 450 cycles as shown in Figure S5a-c. Additionally, the Fourier transform spectra of Mn K edges EXAFS data of the fresh electrode, electrode after one cycle and electrode cycled for 450 times have been shown in Figure S2d. The intensity of the first Mn-O shell drops obviously after 450 cycles, it could be associated with both oxygen vacancies and less coordination number (i.e. tetrahedral instead of octahedral coordination, it is an evidence of spinel phase presence).
cycled for 450 times was collected and used to generate the Mn valence map using multiple linear least square method since there is a very clear shift in the Mn M and L edges from the surface of the particles compared to the bulk regions. As shown in Figure 4a-b, although Mn remains to be at tetravalent state in the bulk region of large LMR-NMC particles, there is a significant portion of active materials being reduced to lower oxidation state. Most of the near surface areas of the large particles and the entire small particles have been reduced. The significantly heavier reduction in small particles can be associated with more contact area with the electrolyte and shorter length for oxygen vacancy diffusion to the surface that exacerbates the oxygen release. Such heterogeneous valence reduction signifies the importance of material size homogenously and structural perfection. However, it is believed that in order to achieve high rate number of cycle, particle size is desired to be small for shorter Li-ion diffusion routes.

The observation of higher reduction in small particles implies that it is essential to balance the size distribution to achieve both short diffusion and low reduction simultaneously. Figure S9 shows a comparison of LMR-NMC performances with different particle sizes. Figure S9a-b show that the size of the small size (SS) LMR-NMC falls in the range of 100-200 nm and the large size (LS) LMR-NMC falls in the range of 1-2 μm. XRD patterns of these two samples (Figure S9c) show no difference in their phases. As shown in Figure S9d, the performance of SS-LMR-NMC is better than the large size LS-LMR-NMC in the beginning, this is because of shorter diffusion distance and hence higher capacity. After cycling for more than 60 cycles, the SS-LMR-NMC sample becomes unstable and the stability drops obviously. Comparing the corresponding dQ/dV curves of these two samples after 100 cycles (Figure S9e), the SS-LMR-NMC exhibited a transition to spinel structure (the discharge peak at <3.0 V is the evidence of such transition), which agrees with our observation that small particles suffer from more surface change. Within the first tens of cycles, the performance of LMR-NMC is mediated by the diffusion length, whereas after certain number of cycles, the performance starts to be dictated by the irreversible reduction.

The atomic-resolution STEM image acquired from a reduced small particle exhibits the MO-type rock-salt structure (Figure 4c), the corresponding Fourier transform diffractogram and atomic model are shown in Figure S10a-b. Surface reconstruction layers have also been discovered on the surface of large particles (Figure S10c-d). The results confirm that the reduced areas underwent structural transformation. In accordance, the core-loss EELS spectrum (Figure 4d-e) acquired from these Mn reduced region suggests that Co has also been reduced to lower oxidation state, as evidenced by the shift of the Co L edge towards lower energy range. In addition, as can be seen from Figure 4d, the Li K-edge from the bulk spectrum (red trace) decreases dramatically from the spectrum obtained in the reduced region (green trace), indicating a loss of Li in these areas. However, it is also noticed that the low-loss spectra from the TM reduced area varies among some regions, as shown in Figure S11. The peak located at ~61.5-62 eV, which is close to both Li K-edge and Co M\textsubscript{2,3} edge, is more intense at some regions than the one shown in Figure 4d (green trace). The variation in the Li K-edge intensity indicates that there are Li\textsuperscript{+} ions existing in some of the reduced regions, which may come from the electrolyte decomposition products, and/or Li-containing distorted phases, i.e. defect spinel phase. Nevertheless, most reduced regions suffer severe Li loss and structural transformation that is accompanied with the cation reduction.

The transformation to a spinel-like phase for Mn is accompanied by a reduction of its oxidation state. To further study the change of TM after prolonged cycles, the TM L\textsubscript{3,2} edges XANES were collected using soft X-ray under both total electron yield (TEY) and fluorescence yield (FLY), as shown in Figure S7. The TEY mode collects information up to a depth of 5 nm on the surface of the specimen and the FLY mode can penetrate to a depth of more than 100 nm into the bulk. After 450 cycles, both the Mn and Co were heavily reduced on the surface and moderately reduced in the bulk, whereas Ni remains to be divalent (Figures S7a-c). The reason why reduction is not observed only in Ni is because the Ni\textsuperscript{2+} cannot be further reduced. The reduction of TMs is also shown in the O K-edge XANES collected at FLY mode as shown in Figure S7d. The pre-edge corresponds to the excitation of O 1s electron to the hybridization of O 2p and TM 3d orbitals. The intensity drop indicates less electron vacancies to be filled by the core electron, which reveals reduced TMs and corroborates the TM L-edge XANES results.

The reason for the heavy reduction of Mn and Co can be ascribed to several possibilities. First, at fully charged state, these TMs are highly oxidizing, they tend to react with the electrolyte and end up being reduced and form species such as metal fluorides. Second, oxygen and Li loss from the structure can induce the TM reduction. Once the Mn\textsuperscript{4+} are reduced to Mn\textsuperscript{3+}, Jahn-Teller effect of the Mn\textsuperscript{3+} results in the formation of Mn\textsuperscript{2+}. Mn\textsuperscript{2+} ions are known to be prone to diffusion into the tetrahedral sites between two octahedral site and form a spinel phase, the LiMn\textsubscript{2}O\textsubscript{4}-like spinel structure simulated by FDMNES in the first cycle could gradually turn into a Mn\textsubscript{2}O\textsubscript{4}-like spinel structure accompanied with the loss of Li. To visualize the reduction of the TMs at a high spatial resolution, electron energy loss spectroscopy (EELS) data of the LMR-NMC...
These redox couples become inactive after long-term cycling due to the irreversible reduction of TMs, without the contribution from these redox couples, the average voltage of the whole process inevitably drops. In order to prevent the valence drop, most of the present studies aimed at either protecting the material surface from direct contact to the electrolyte or stabilizing the O²⁻ from loss should be continuously pursued. Fourth, the discrepancy between the actual capacity delivered during the 451st cycle and the weak redox activity of the TMs raises a speculation of surviving oxygen activity that needs to be further explored. The method developed in this study by combining FDMNES codes with in-situ XANES and TEM-EELS mapping will be highly valuable in the future quest for high performance electrode materials.

Acknowledgements

B.X., H.L. and N.C. contributed equally to this work. N.C. contributed to the modeling of this work. This research was supported by the Natural Science and Engineering Research Council of Canada (NSERC), the Canada Research Chair Program (CRC), General Motors R&D Center (GM), the Canada Foundation for Innovation (CFI), Canadian Light Source (CLS) at the University of Saskatchewan, the Canadian Centre for Electron Microscopy (CCEM) at McMaster University (a facility supported by the Canada Foundation for Innovation under the Major Science Initiative, NSERC and McMaster University), Beijing Natural Science Foundation (JQ19003) and the University of Western Ontario (UWO).

Declaration of Interests

The authors declare no competing interests.

Reference

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A finite difference method for near-edge structure (FDMNES) code was combined with in-situ XANES measurement and transmission electron microscopy and electron energy loss spectroscopy (TEM/EELS) mapping to track the evolution of transition metals in both the first and 451th cycles. The results reveal that the layer to spinel phase shows partial reversibility in each cycle at sub-nanometer scale depending on the particle size.