Li-rich Mn-Ni-Fe (MNF) oxide cathodes are emerging as a low-cost alternative to commercial Ni-Mn-Co (NMC) oxides with the cost of raw iron being three orders of magnitude lower than cobalt. MNF cathodes have demonstrated potential for high capacity and high discharge voltage cathodes, however, the capacity decay and instability of discharge voltage upon cycling still need to be resolved for their successful commercialization. Both phenomena are related to the changes in structure and, in this study, we utilize XRD and XAFS to investigate the structural changes correlated to electrochemical performance of Li1.2Mn0.56Ni0.16Fe0.08O2 cathode. This material, prepared by sol gel synthesis, showed initial discharge capacity of 226 mAh g\(^{-1}\) and 93% capacity retention after 100 cycles. Fitting of the XAFS results provided information on the changes in local environment of each transition metal atom. Such detailed information on atomic environment is reported for the first time and compared to prior studies of NMC cathodes. In the discharged state Mn atoms show a shift to lower oxidation state and an irreversible loss of oxygen near neighbors after cycling, while Ni and Fe show only minor changes in their environment. An observed 5.87% lattice expansion after cycling is suggested to contribute to voltage fade.

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Mn rich layered oxide cathodes stabilizes the layered structure and prevents the phase conversion to spinel upon cycling.\textsuperscript{28} Zhao et al.\textsuperscript{27} reported sol gel synthesis of Li1.16Mn0.50Ni0.16Fe0.16O2 using a citric, tartaric and adipic acid as chelating agents which exhibited 282, 289 and 289 mAh g\(^{-1}\) first discharge capacity with 71, 63 and 56\% retention after 50 cycles at 0.1 C rate. However, this material still exhibited significant voltage fading upon cycling. Liu et al.\textsuperscript{25} synthesized Li1.2Mn0.6-x/2Ni0.2-x/2FexO2 for x ≤ 0.1 cathodes and found that the sample with x = 0.03 exhibits 262 mAh g\(^{-1}\) first discharge capacity at 0.1 C rate with 91\% capacity retention after 80 cycles. Improvements in electrochemical performance of this cathode were correlated to a stabilized layered structure observed with high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) patterns.

Since both capacity and voltage fade are related to the changes in material crystal structure deeper understanding of the mechanism behind these phenomena is required. Thus, in this study we utilize synchrotron X-ray diffraction (SXRD) and X-ray absorption fine structure spectroscopy (XAFS) to investigate the structural changes correlated to electrochemical performance of a representative composition of nanoscale cobalt-free, lithium and manganese rich, layered MNF oxide cathode. The composition-performance trends of nanoscale cobalt-free, Li-rich oxide cathode, specifically Li1.2Mn0.5Ni0.2Fe0.1O2 material (abbreviated below as MNF521 for detailed investigation of structural and chemical changes) are examined. The XAFS data were collected in fluorescence mode using a 4 element Vortex detector (Hitachi) at the Mn, Ni and Fe K-edges and Fe K-edge with dk\(^{-1}\) weighting factor, and an R range of 4, 2 to 12 Å\(^{-1}\) for the Fe K-edge, 2 to 12 Å\(^{-1}\) for Mn and Ni K-edges, respectively, at the Advanced Photon Source, Argonne National Laboratory. The XAFS data were collected in fluorescence mode using a 4 element Vortex detector (Hitachi) at the Mn, Ni and Fe K-edges. Athena and Artemis software programs from the IFEFFIT suite\textsuperscript{36,37} were used for XAFS data analysis and fitting. The extended X-ray absorption fine structure (EXAFS) data were fitted in a k window of 2 to 10 Å\(^{-1}\) for the Fe K-edge, 2 to 12 Å\(^{-1}\) for Mn and Ni K-edges with dk = 4, k\(^{2}\) weighting factor, and an R range of 1 to 2 Å for all edges. The number of oxygen near-neighbors for each transition metal was fixed to 6 in pristine electrodes. The amplitude reduction factor obtained from the fit of pristine material was used to estimate the number of oxygen neighbors in cycled cathodes.

Synchrotron characterization of electrode materials.—After electrochemical tests, the coin cells were de-crimped inside the glove box and the electrodes were rinsed with dimethyl carbonate (DMC) solvent, and sealed inside Kapton tape for ex situ XAFS measurements. The XAFS and high resolution SXRD measurements (λ = 0.414534 Å) of pristine and cycled cathodes were taken at the 10 BM (Materials Research Collaborative Access Team, MRCAT) and 11 BM beamlines, respectively, of the Advanced Photon Source, at Argonne National Laboratory. The XAFS data were collected in fluorescence mode using a 4 element Vortex detector (Hitachi) at the Mn, Ni and Fe K-edges. Athena and Artemis software programs from the IFEFFIT suite\textsuperscript{36,37} were used for XAFS data analysis and fitting. The extended X-ray absorption fine structure (EXAFS) data were fitted in a k window of 2 to 10 Å\(^{-1}\) for the Fe K-edge, 2 to 12 Å\(^{-1}\) for Mn and Ni K-edges with dk = 4, k\(^{2}\) weighting factor, and an R range of 1 to 2 Å for all edges. The number of oxygen near-neighbors for each transition metal was fixed to 6 in pristine cathodes. The amplitude reduction factor obtained from the fit of pristine material was used to estimate the number of oxygen neighbors in cycled cathodes.

Experimental

Material synthesis.—The Li1.2Mn0.5Ni0.2Fe0.1O2 cathode material was prepared using a citric acid-assisted sol gel synthesis.\textsuperscript{33} The nitrates of transition metals and lithium (Mn(NO\(_3\))\(_2\)·4H\(_2\)O, Ni(NO\(_3\))\(_2\)·6H\(_2\)O, Fe(NO\(_3\))\(_3\)·9H\(_2\)O and LiNO\(_3\), reagent grade, Sigma Aldrich) were used as precursors. Stoichiometric ratios of metal salts were dissolved in a small amount of deionized water just sufficient to fully dissolve the salts. The citric acid chelating agent in a 1:1 molar ratio with all metal salts, was then added to the salt solution and the reaction mixture was heated to 70 °C with magnetic stirring until a transparent yellowish gel was formed (∼12 hours). The gel was then dried in the oven at 80 °C in air for 12 hours which resulted in formation of a dry yellowish foam product. The product was initially decomposed by annealing at 400 °C in a box furnace for 5 hours. The brown powder resulting from the low temperature annealing was partially decomposed by annealing at 400 °C in a tube furnace for 5 hours. The brown powder was then heated in a box furnace for 5 hours. The brown powder resulting from the low temperature annealing was finely ground and calcined for another 15 hours at 700 °C in a tube furnace with air flow to obtain the final product.

The XRD patterns of the product in the 20 range of 15−80° were collected at a scan rate of 0.01 degrees per 2 second using a Bruker D2 Phaser Diffractometer with Cu K\(_\alpha\) radiation (λ = 1.54056 Å) and a LynxEye detector with energy discriminator set to reject Mn and Fe fluorescence. The International Center for Diffraction Data (ICDD PDF4+2016) was used for background removal and phase identification. To obtain information on particle sizes and phase composition, XRD patterns were refined by the Rietveld method using GSAS\textsuperscript{38} and EXPGUI\textsuperscript{39} software packages. Scanning electron microscopy (SEM, Hitachi S-4700) was used to characterize size and morphology of the synthesized product. A droplet of dilute suspension of the product in alcohol was placed on a piece of silicon wafer and used for SEM imaging after solvent evaporation. Energy Dispersive Spectroscopy (EDS) analysis of the sample was conducted using a Phenom Pro-X (Nanoscience Instruments).

Preparation of solid casted electrodes.—The slurry for electrode depositions was prepared using 80:10:10 weight ratios of the active material (synthesized MNF521 powder), acetylene carbon black (50% compressed, Strem Chemicals) and polyvinylidene fluoride (PVDF) binder (Sigma Aldrich) respectively. The slurry was deposited on the aluminum current collector (0.018 mm thick) using a doctor blade at average loading of 1.3 mg cm\(^{-2}\). Standard CR2032 coin cells were used for electrochemical tests with Li foil (0.2 mm thick, Goodfellows) as the anode, Celgard 2325 polypropylene porous membrane as separator membrane and 1 M LiPF\(_6\) in 3:7 volume ratio of ethylene carbonate and ethyl methyl carbonate as electrolyte (Tomiyama Chemicals). The coin cells were assembled inside an argon atmosphere glove box, using an automated cell crimpler (MSK-1601, MTI Corporation).

The electrochemical performance of the cells was evaluated with galvanostatic cycling of the coin cells (battery cycler BST8-MA, MTI Corporation) and cyclic voltammetry (EZstat Pro potential-stat/galvanostat, NuVant Systems).

Synchrotron characterization of electrode materials.—After electrochemical tests, the coin cells were de-crimped inside the glove box and the electrodes were rinsed with dimethyl carbonate (DMC) solvent, and sealed inside Kapton tape for ex situ XAFS measurements. The XAFS and high resolution SXRD measurements (λ = 0.414534 Å) of pristine and cycled cathodes were taken at the 10 BM (Materials Research Collaborative Access Team, MRCAT) and 11 BM beamlines, respectively, of the Advanced Photon Source, at Argonne National Laboratory. The XAFS data were collected in fluorescence mode using a 4 element Vortex detector (Hitachi) at the Mn, Ni and Fe K-edges. Athena and Artemis software programs from the IFEFFIT suite\textsuperscript{36,37} were used for XAFS data analysis and fitting. The extended X-ray absorption fine structure (EXAFS) data were fitted in a k window of 2 to 10 Å\(^{-1}\) for the Fe K-edge, 2 to 12 Å\(^{-1}\) for Mn and Ni K-edges with dk = 4, k\(^{2}\) weighting factor, and an R range of 1 to 2 Å for all edges. The number of oxygen near-neighbors for each transition metal was fixed to 6 in pristine electrodes. The amplitude reduction factor obtained from the fit of pristine material was used to estimate the number of oxygen neighbors in cycled cathodes.

Results and Discussion

Material characterization.—The morphology and particle size of the synthesized material were evaluated with SEM (Figure 1). The particles in the synthesized product are polydisperse with sizes ranging from 10 to 200 nm. SEM images of these nanoparticles are shown in Figure 1. The particles are highly agglomerated and have a rough surface. The size distribution of the particles was determined using ImageJ software and the results are shown in Figure 2. The average particle size is around 50 nm, with a standard deviation of 15 nm. The SEM images also show that the particles are well dispersed and have a uniform distribution. The EDX analysis of the sample shows that the composition of the nanoparticles is close to the stoichiometry of Li1.2Mn0.5Ni0.2Fe0.1O2.
from 50 nm to 300 nm and irregular in shape. This is typical for products obtained through the sol-gel synthesis method, and could be better controlled through the amount of organic additives during the synthesis. Although control of the particle size was not the focus of this study, the particle size determines the electrode/electrolyte contact area, which on one hand could facilitate the charge/discharge process by reducing the average diffusion path for the Li-ion for full charge, but on the other hand may result in stronger negative contribution of solid electrolyte interface (CEI for cathode electrolyte interface), especially in the case of high voltage cathodes.

The XRD pattern of our product (Figure 2) is similar to that of Li and Mn rich layered composite oxide cathodes reported elsewhere. Due to the similarities of crystalline structures the strongest peaks in both rhombohedral LiMnO$_3$ and monoclinic Li$_2$MnO$_3$ phases are located at same 20 (∼18 and 44 degrees), which makes identification of phase fractions difficult. Pure Li$_2$MnO$_3$ monoclinic phase synthesized by the same sol-gel method is used for comparison with MNF521. The crystallite size from the monoclinic phase fitting is estimated to be 20 nm and 11 nm respectively. Similarly, the refinement that only considers monoclinic phase (Figure S3b) features small peaks between 20 to 25 degrees which are not resolved/present in the XRD pattern of MNF521. The crystallite size from the monoclinic phase fitting is estimated to be 20 nm and 13 nm along and perpendicular to the <001> direction. The latter indicates grain sizes are smaller than the average particle size from SEM imaging, suggesting random distribution of both phases within the cathode nanoparticles. Modeling with both of these structures simultaneously by fixing the fractional ratio of monoclinic to rhombohedral at to be the ratio of Mn$_3$Ni$_2$/Fe$_4$ as 5:3 (i.e. all the Mn is in the monoclinic Li$_2$MnO$_3$ phase) provides the best fit to the experimental data and is shown in Figure S3c (Supplementary Material).

**Electrochemical characterization.**—Cyclic voltammograms (CVs) were measured on pristine electrodes (Figure 3) to evaluate redox behavior of the synthesized cathode. The standard redox potential for Mn$^{3+}$/Mn$^{4+}$ is reported at 3.3 V followed by Ni$^{2+}$/Ni$^{3+}$ and Fe$^{3+}$/Fe$^{4+}$ at around 4.1 V, all vs. Li/Li$^+$. The relative potential of corresponding redox couples are provided (Supplementary Material, S4). CVs measured in the potential window between 1.5 V to 4.4 V show only one broad redox peak, likely corresponding to a combination of Ni$^{2+}$/Ni$^{3+}$ and Fe$^{3+}$/Fe$^{4+}$ conversions due to their close potentials and the mixed nature of Ni and Fe sites within our compound. No Mn$^{3+}$/Mn$^{4+}$ conversion was observed in this potential range (Figure 3). With the potential window extended to 4.9 V, the first oxidation peak at ∼4.1 V is followed by a second oxidation peak at ∼4.7 V, which is not reversible, and does not appear on subsequent CVs. In the following cycles, a reversible feature corresponding to Mn$^{3+}$/Mn$^{4+}$ appears at ∼3.3 V in addition to the Ni$^{2+}$/Ni$^{3+}$ and Fe$^{3+}$/Fe$^{4+}$ peaks observed on previous CVs. It was previously suggested that the irreversible peak at ∼4.7 V corresponds to the conversion of the Li$_2$MnO$_3$ monoclinic phase to layered LiMnO$_3$ (Eq. 2). After this transition the Mn$^{3+}$/Mn$^{4+}$ redox couple is enabled, as all three peaks from Mn, Fe, and Ni redox are observed in the stabilized CVs for the extended cycling window. Some studies also suggest that the peak at 4.7 V is related to decomposition of electrolyte, but this is not the case in this material because it only appears on the first CV, followed by appearance of the Mn$^{3+}$/Mn$^{4+}$ redox couple.

The coin cells were further cycled in galvanostatic mode in the potential window of 1.5 V–4.8 V vs. Li/Li$^+$ for over 100 cycles. Once the cell potential reached the limiting value of 4.8 V, it was held at that value in potentiostatic mode until the cell current decreased to one tenth of the initial current at that potential (designated as “galvanostatic-potentiostatic” charging hereafter). Characteristic charge/discharge curves are shown in Figure 4a. The first 3 cycles were measured at 0.1 C rate (25 mAg$^{-1}$,0.032 mAc$^{-1}$), assuming a theoretical capacity of 250 mAhg$^{-1}$ to “train” the electrode material and successive cycles were conducted at 0.3 C rate (83 mAg$^{-1}$,0.105 mAc$^{-1}$). The first experimental discharge capacity was measured as

![Figure 2. XRD pattern of as-synthesized Li$_2$MnO$_3$:Ni$_2$:Fe$_4$O$_2$ powder, compared to Li$_2$MnO$_3$ nanowater synthesized by the same method and standard XRD patterns of monoclinic Li$_2$MnO$_3$ and rhombohedral LiCoO$_2$ structures.](image-url)
Figure 4. (a) Evolution of charge/discharge curves during extended electrode cycling with cut-off voltage of 4.8 V; (b) specific charge and discharge capacity of Li1.2Mn0.5Ni0.2Fe0.1O2 cathode as a function of cycle number at different cut-off voltages.

A set of separate cells were cycled up to 4.4 V, 4.6 V and 4.8 V vs. Li/Li+ potential. As described above, the cells cycled to 4.6 V and 4.8 V were charged in galvanostatic-potentiostatic mode while the cells cycled to 4.4 V were only charged galvanostatically. The highest capacity of 226 mAhg\(^{-1}\) at 0.1 C and 194 mAhg\(^{-1}\) at 0.3 C with 93% capacity retention after 100 cycles was achieved at cut-off potential of 4.8 V, whereas when the charging voltage was limited to 4.6 V (below the Eq. 2 transition) a highest discharge capacity of 207 mAhg\(^{-1}\) at 0.1 C and 169 mAhg\(^{-1}\) at 0.3 C with 77% capacity retention was observed after 100 cycles. When the cell was charged to 4.4 V the highest discharge capacity of 131 mAhg\(^{-1}\) at 0.03 C rate, which is very close to the first discharge capacity, 226 mAhg\(^{-1}\), of the Li1.2Mn0.50Ni0.20Fe0.10O2 cathode measured at a faster 0.1 C rate. The capacity retention of Li1.2Mn0.55Ni0.15Co0.10O2 cathode at 0.03 C is 88% after 36 cycles, while the Li1.2Mn0.50Ni0.20Fe0.10O2 cathode showed 93% capacity retention even after 100 cycles at a 0.3 C rate.

Further, we have investigated the effect of the limiting charging potential on the long-term performance of the electrodes (Figure 4b).

The potentiostatic hold at the end charging eliminates kinetic limitations and enables completion of thermodynamically allowed processes. The effect of this potentiostatic hold was investigated by cycling a pristine coin cell up to 4.8 V without holding the potential for the first 28 cycles after which the charging mode was changed to galvanostatic-potentiostatic for the next 32 cycles (Figure 5). The maximum capacity without the potential hold at 4.8 V was 152 mAhg\(^{-1}\) whereas holding at 4.8 V resulted in 195 mAhg\(^{-1}\) at the same current density (0.3 C), i.e. ~30% of capacity was gained due to this cycling regime. The latter indicates significant impact of kinetic limitations in cathode charging.

Coulombic efficiency vs cycle number is also shown in Figure 5. When charging is conducted without holding at the cut off voltage in the first 28 cycles the average Coulombic efficiency is 96.0%, while charging mode with the potentiostatic treatment results in a Coulombic efficiency of 99.4%.

In addition to capacity fading, the discharge voltage also decays upon cycling as seen in Figure 4a. The decay of discharge voltage...
during cycling is examined by comparing the 1st and 100th discharge characteristic curves for cells cycled to 4.4, 4.6 and 4.8 V as shown in Figure 6a. The voltage fading is noticeably greater in cells cycled to 4.4 and 4.6 V, and less for the 4.8 V cut off voltage.

Quantitative evaluation of voltage fade was conducted for each case using the methodology reported for LiNi0.33Mn0.33Co0.33O2 and Li1.05Ni0.33Mn0.33Co0.33O2 cathodes. Average discharge voltage (Figure 6b) is calculated by dividing the area under the discharge curve by the respective discharge capacity. The cell cycled to 4.4 V shows rather gradual voltage decay throughout the 100 cycles from 2.9 V to 2.6 V. In the case of the cell cycled to 4.6 V the discharge voltage fades rapidly in first 30 cycles (from 3.0 V to 2.7 V) and continues slow decay to 2.6 V by the 100th cycle. The cell cycled to 4.8 V shows steady value of 2.9 V in first 10 cycles, followed by a significant voltage decay between 10th to 30th cycle to 2.8 V, and a slower voltage decay after the 30th cycle to 2.7 V. The average discharge voltage of the cells cycled to 4.8 V is always greater than the respective values for cells cycled to 4.4 and 4.6 V. The difference of discharge voltage from the 1st cycle to 100th cycle is a quantitative measure of voltage fade, showing 0.31, 0.47 and 0.29 V decrease in cells cycled to 4.4, 4.6 and 4.8 V respectively. Even though voltage fade is observed in all cases, charging of the MNF521 cathode to 4.8 V provides a significant improvement in reversible capacity, average cell voltage and voltage stability likely due to limited structural changes and engagement of both the rhombohedral and monoclinic phases.

Study of structural changes during cycling—Understanding the structural changes in correlation to electrochemical cycling is the key to understand the cathode performance and degradation mechanism. SXRD and XAFS were used to investigate structural changes in MNF521 cathode during cycling. The SXRD pattern of casted pristine cathode and the electrode in the discharged state after 100 cycles are compared in Figure S4 (Supplementary Material). Because of the significant contribution of aluminum foil current collector and carbon conductive filler, the intensity of the peaks from the MNF521 material is low, nonetheless some obvious changes in the electrode crystalline structure are observed. The intensity of all MNF521 peaks decrease and the peak positions are shifted to lower 2θ value indicating material amorphization and increase in lattice parameters after extended cycling. The splitting of the first XRD peak at 19 degrees (5 degrees for SXRD) in Li-rich composite oxide cathodes, was reported in the literature and correlated to the conversion of the layered phase to spinel.13,24 We were not able to detect any peak splitting in SXRD of the cycled sample but transformation to spinel phase cannot be fully excluded because of the low intensity of MNF521 peaks compared to the signal from the current collector. The intensity of the broad monoclinic peak decreased significantly, indicating Li2MnO3 conversion to LiMnO2.13 The GSAS fitting of the SXRD patterns with rhombohedral R-3m for MNF521 cathode and cubic Fm-3m for the aluminum current collector was used to align the entire SXRD pattern and enabled fitting the MNF521 phase. Carbon peaks are not included in the fit. The calculated lattice parameters of the pristine MNF521 cathode are a = 2.88 Å, c = 14.26 Å, (fit parameters χ² = 8.344, wRp = 0.105) consistent with the values from GSAS fit of the powder XRD from Cu Kα radiation. The calculated lattice parameters of the cycled cathode are a = 2.95 Å, c = 14.39 Å, (fit parameters χ² = 7.645, wRp = 0.095) indicating a 6.95 Å³ (5.87%) lattice volume expansion after 100 electrochemical cycles. The lattice volume expansion on cycling might have a direct impact on voltage fading through the lowering chemical potential of intercalated Li atoms in the cathode. Other factors might include the increased ohmic resistance, kinetic losses and parasitic interaction between electrode and electrolyte surfaces during cycling. The crystallite sizes remained roughly the same before and after cycling.

While XRD is a powerful technique for investigation of crystalline structures, it is insensitive to amorphous phases, which often are present in intercalation-based battery materials. X-ray absorption fine structure (XAFS) spectroscopy is an element-specific technique which allows the local electronic and atomic environment around only elements of interest to be probed. As XAFS measurements are not dependent on samples to have long range crystalline order, information on any and all crystalline and amorphous phases are accounted for, making it a critical technique for battery material characterization. XAFS spectra contain two main regions, X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) that are sensitive to local electronic information (i.e. oxidation state) and atomic structural information (coordination number, atomic
Figure 7. GSAS fits of ex situ SXRD (λ = 0.41453 Å) patterns of pristine and discharged state of cycled to 100 cycles MNF521 cathode. The peaks indicated by S and C are the peaks from MNF521 cathode and carbon respectively, other sharp peaks labeled A are from the aluminum foil current collector and the M peak is the monoclinic trace peak from the cathode.

Figure 8. |χ(R)| plots of MNF521 cathode at (a) Mn, (b) Ni and (c) Fe K-edges EXAFS spectra in pristine state and after 1st and 100th discharge.

The intensity and atomic distance) respectively. The EXAFS region can be modeled with theoretical structural models to extract details on the changes occurring at an atomic level during the electrode cycling.

The XAFS spectra at Mn (6539 eV), Ni (8333 eV) and Fe (7112 eV) K-edges were measured for the pristine electrode, and electrodes extracted from the cells after the 1st and 100th cycle in either fully charged or discharged state with galvanostatic-potentiostatic charging to 4.8 V (Figure 8). EXAFS spectra at the Mn K-edge (Figure 8a) show that the intensity of Mn-O peak decreases noticeably after the 1st cycle indicating oxygen loss in the Mn atom surroundings due to Li2MnO3 conversion to LiMnO2. This is consistent with previously reported Li2O2/Li2O extraction but for the first time it has been confirmed by XAFS. The position of the Mn-O peak (Figure 8a) does not change indicating constant Mn-O bond lengths. The intensity of the Mn-M peak also decreases during cycling, indicating the decrease in the number of transition metal neighbors around Mn atoms. Additionally, the position of the Mn-M peak shifts towards larger distances indicating the structural rearrangement. XANES spectra at the Mn, Ni, and Fe K-edges are presented in Figure S5 (Supplementary Material). The Mn K-edge spectra shift to lower energies during cycling indicating a lower average Mn oxidation state after the 1st discharge and after the 100th discharge. This result is consistent with Li2MnO3 phase activation which starts as Mn4+ in the pristine discharged state and is converted to Mn3+ (LiMnO2) in the discharged state as reported for Li-rich NMC.21 Interestingly, the first cycle does not provide complete conversion of the Mn environment, which likely takes few cycles. The details of the EXAFS first shell fits are presented in Supplementary Material, S7 and results (Table S2) are summarized in Figure 9. The Mn-O interatomic distance is the shortest in this cathode material and remained constant (1.90 ± 0.01 Å) in pristine, charged and discharged states. The Ni-O distance is the longest in the pristine material (2.06 ± 0.01 Å) and increases to 2.08 ± 0.01 Å in the 1st discharged state and remains at this value after 100 cycles. The Fe-O distance in the pristine cathode (2.00 ± 0.01 Å) decreases to 1.95 ± 0.01 Å in the 1st charged state and increases back to 2.00 ± 0.01 Å in the 1st discharged state. This is consistent with the higher oxidation state of iron atoms in the charged state, and thus stronger affinity to negatively charged oxygen atoms. The charging process is also accompanied by de-intercalation of lithium, however the sensitivity of the XAFS method to Li-ions is low due to their low atomic number compared to the other atoms in the material and their distances relative to the absorbing metal atom.

The number of metal-oxygen neighbors is another parameter that can help in understanding of the processes within the electrode. The number of Mn-O neighbors decreases from 6 in the pristine cathode down to 4.1 ± 0.5 after the 1st cycle and to 2.9 ± 0.5 after the 100th cycle. This gradual loss of oxygen in the first shell of the Mn atom correlates with the Li2MnO3 phase conversion and change in average Mn oxidation state observed in the XANES region. During Li2MnO3 activation Li2O2/Li2O is extracted from the transition metal layer (Figure 8b) creating oxygen vacancies and leading to significant

|Intensity (Counts/10^3)| θ | 5 | 10 | 15 | 20 |
|-----------------------|---|---|----|----|----|
|S | M | C |
|C | M | A |
|A | S |

|Pristine| Cycled|
|--------|-------|
|S | M | C |
|C | M | A |
|A | S |

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irreversible loss of oxygen from the local Mn environment converting to highly defective LiMnO$_{2-x}$. In contrast to the Mn-O trends, the number of Ni-O and Fe-O neighbors remain unchanged within the standard deviation after 100 cycles, suggesting that oxygen loss is predominantly occurs within the monoclinic phase.

The XAFS fitting results for the MNF521 cathode differ significantly from the previously reported in situ XAFS studies on Li$_{1.05}$Mn$_{0.44}$Ni$_{0.33}$Co$_{0.16}$O$_2$ cathode during first charge/discharge cycle and Li$_{1.20}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ cathode during first and second charge/discharge cycles with cut-off voltage of 4.6 V and 4.8 V respectively. Both of these studies reported that Ni$^{2+}$/Ni$^{3+}$ (per XANES shift) is the main redox reaction for electrochemical capacity. Very small shifts in the XANES region of Mn and Co edges are reported for Li$_{1.05}$Mn$_{0.44}$Ni$_{0.33}$Co$_{0.16}$O$_2$, indicating no redox participation of these elements. Reversible changes in the Co edge XANES and small changes at the Mn edge were reported for Li$_{1.20}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ cathode, indicating participation of Co$^{3+}$ but not Mn$^{4+}$. Only minimal changes in Mn-O and Co-O distances (less than 0.04 Å) but significant changes in Ni-O distances were observed. For Li$_{1.05}$Mn$_{0.44}$Ni$_{0.33}$Co$_{0.16}$O$_2$, the 2.05 Å Ni-O distance in the pristine material decreased to 1.89 Å in the first charged state and increased back to 2.04 Å after the 1st cycle. Similarly, for Li$_{1.20}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$, The Ni-O distance decreased from 2.04 Å to 1.90 Å in the first charged state and increased back to 2.04 Å after the first full cycle. Neither of these studies reported a significant change in Mn-O near neighbors in the first cycle, suggesting no Li$_2$MnO$_3$ phase conversion which is also consistent with low experimental discharge capacity (∼167 mAh$^{-1}$ for Li$_{1.05}$Mn$_{0.44}$Ni$_{0.33}$Co$_{0.16}$O$_2$ and ∼176 mAh$^{-1}$ for Li$_{1.20}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$). Therefore, XAFS results in this study suggest a different redox mechanism and a different activity of transition metals in Fe-substituted MNF cathodes vs. previously studied NMC cathodes.

Oxygen loss observed with EXAFS could be either (1) a local phenomenon of material amorphization, atomic re-arrangement and segregation of LiMnO$_2$ and Li$_2$O/Li$_2$O phases; (2) the loss of oxygen from the electrode as O$_2$ gas evolution (resulting in the shift of electrode elemental composition); or (3) oxygen participation in electrolyte decomposition and formation of cathode electrolyte interface (CEI), which would manifest as increased fraction of carbon, fluorine and phosphorus at the electrode surface.

To better understand the nature of the observed oxygen loss from Mn first shell environment the pristine electrode and the electrode after 100 cycles extracted from the cells and rinsed with DMC solvent were characterized with EDS mapping (Supplementary Material, S8). The EDS results show consistent fractions of all elements before and after the cycling, with no measurable reduction of oxygen content, thus excluding the O$_2$ evolution hypothesis. Lack of contribution of phosphorous, fluorine or increased contribution of carbon after cycling also eliminates the hypothesis regarding CEI formation, and confirms that the loss of oxygen observed with EXAFS is likely a local effect due to rearrangement of oxygen within the crystalline and amorphous phases of the electrode, specifically due to Li$_2$MnO$_3$ conversion to highly disordered LiMnO$_2$, and Li$_2$O/Li$_2$O, movement of oxygen ions to other sites and formation of oxygen vacancies around Mn atoms. It should be noted here that the ratio of elements in the cathode before and after 100 cycles does not change (Figure S7, Table S3), therefore dissolution of Mn species into electrolyte, commonly observed in LiMnO$_2$ cathodes can be excluded, as it would have resulted in decreased fraction of Mn atoms and increased fractions of Ni and Fe in the extracted solid electrode.

**Figure 9.** Summary of EXAFS first shell fitting results for ex situ MNF521 cathodes (a) interatomic distances for Mn-O, Ni-O and Fe-O and (b) number of near neighbors for Mn-O, Ni-O and Fe-O for pristine state, charged and discharged state after first and the 100th cycle.

**Conclusions**

We report on the detailed investigation of the mechanisms behind the reversible capacity and reduced voltage fading mechanisms in a promising composition of Li-rich Co-free nanoscale Li$_{3.2}$Mn$_{0.5}$Ni$_{0.2}$Fe$_{0.1}$O$_2$ cathode (MNF521) using advanced X-ray characterization tools and compare the results to the previous studies of NMC cathodes. The Li-rich MNF521 material shows up to 226 mAh/g capacity in the first cycle at 0.1 C and 93% capacity retention over 100 cycles at 0.3 C cycling rate and reduced voltage fade. The performance of the electrode material was investigated at different cut-off voltages (4.4, 4.6 and 4.8 V) and it was demonstrated that cycling to 4.8 V activates the Mn$^{3+}$/Mn$^{4+}$ redox couple through Li$_2$MnO$_3$ conversion to LiMnO$_2$, and improves the reversible capacity of the cathode material from 131 mAh g$^{-1}$ when cycled to 4.4 V to 226 mAh g$^{-1}$ for a charging limit of 4.8 V. In addition to improved capacity, cycling to the high voltage showed the smallest voltage fade over 100 cycles and highest average discharge voltage compared to the cells cycled to 4.4 and 4.6 V. The SXRD of pristine and cycled cathodes showed amorphization of the sample and 5.87% lattice expansion upon electrochemical cycling. The ex-situ XAFS study at Mn, Ni and Fe K-edges showed significant reduction of Mn-O first shell neighbors from 6.0 to 2.9 after 100 cycles, while the number of
Ni-O and Fe-O near neighbors remained nearly the same and only Ni-O interatomic distances increased slightly as a result of cycling. The dramatic decrease in Mn-O neighbors can be explained by the creation of oxygen vacancies correlated to the formation of highly defective, nonstoichiometric LiMnO$_2$ and Li$_2$O/Li$_2$O/Li$_2$O$_2$ extraction during Li$_x$MnO$_3$ activation. An EDS study of pristine and cycled electrodes showed no net loss of oxygen confirming that oxygen migration is local and doesn’t involve parasitic reactions with electrolyte or gas evolution. SXRD showed increase in the lattice parameter which per EXAFS results is related to the increase in M-M distances for all transition metals, while M-O distances mainly remained unchanged. It is suggested that oxygen atoms migrate away from Mn environment to form amorphous Li$_2$O$_2$ or to other metal sites. At the same time lattice expansion during battery cycling decreases the chemical potential of Li atoms in the cathode (the energy required to insert Li ion in the expanded lattice is lower compared to that in the pristine lattice) and hence reduces the discharge voltage. The results of this study show that performance of this material could be further improved if migration of oxygen atoms and lattice expansion could be further minimized through composition, particle morphology or better control of transition metal distribution within monoclinic and rhombohedral phases.

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