Utilizing Environmental Friendly Fe with Unique Electronic Structure as Substitution Element in Spinel Structured Cathode Material for Safer High Energy Lithium-ion Batteries

Enyuan Hu, Seong-Min Bak, Yijin Liu, Jue Liu, Xiqian Yu, Yong-Ning Zhou, Jigang Zhou, Peter Khalifah, Kingo Ariyoshi*, Kyung-Wan Nam*, Xiao-Qing Yang*

1. Introduction

Lithium Ion Battery (LIB) is one of the most important systems for energy storage application1-3. A key challenge that LIB faces is the safety issue4-6. When used as power sources, especially in vehicle applications, abusive condition can cause the so-called thermal runaway7, 8 for LIBs, in which the temperature grows out of control and leads to fire or even explosion. Many research results have been reported about the mechanism of this phenomenon9-11. It is well understood that the charged cathode releases oxygen at elevated temperature, facilitating the consequent oxidizing reactions. Since these reactions are significantly exothermic and considered as major factors for thermal runaway, mitigating
oxygen release has been proved to be an effective measure to minimize the risk of thermal runaway\textsuperscript{12, 13}. These studies show that although the oxygen release and structural changes of the cathode materials may have been investigated at higher temperature range and slower heating rates than the real batteries under thermal runaway conditions, the results obtained do have good co-relations with the practical situations and can serve as valuable guidance for developing safer materials.

Previously, oxygen release mechanism has been studied\textsuperscript{14} for the high voltage spinel\textsuperscript{15, 16} LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} (LNMO), a cathode with high energy density due to high operating voltage at around 4.7 V. When heated at fully charged state, the highly oxidized Ni\textsuperscript{4+} has the tendency to be reduced to lower valence states\textsuperscript{14, 17}, while at the same time, structural transition requires manganese to migrate from octahedral sites to tetrahedral sites which can only be realized after manganese is reduced from Mn\textsuperscript{4+} to Mn\textsuperscript{2+}. Both of these reductions will cause oxygen release and poor thermal stability problem for this material. Therefore, the solution we proposed to suppress the oxygen release is to lower nickel's concentration by introducing some more stable cations, which also has the tendency to migrate to tetrahedral sites from octahedral sites during heating without paying the price of reduction (Figure 1a). Indeed, Delmas et al\textsuperscript{18, 19} found that Al\textsuperscript{3+}, which doesn't need to be reduced to migrate, plays a positive role in improving the thermal stability of nickel-based layered material. Therefore, Al became a necessary component in the commercialized cathode material LiNi\textsubscript{0.8}Co\textsubscript{0.15}Al\textsubscript{0.05}O\textsubscript{2}. Here, we proposed to use transition metal cations as substitution candidates because they can be electrochemically active and therefore contribute to the capacity. In order to see the tendency of migration from octahedral sites to tetrahedral site, octahedral site stabilization energy (OSSE)\textsuperscript{20, 21} is plotted as a function of the electronic structure of 3d transition metal cations in Figure 1b. OSSE is used because it is the energy difference between an octahedron and a tetrahedron and therefore a good indicator of the tendency of migration. Generally speaking, higher OSSE corresponds to stronger tendency to migrate. Among cations with the greatest
migrating tendency (e.g., Ti$^{4+}$, V$^{5+}$, Cr$^{6+}$, Fe$^{3+}$, Zn$^{2+}$ etc.), Fe$^{3+}$ is considered as the most promising candidate with the following reasons. Firstly, Fe is environmentally benign and naturally abundant. Secondly, Fe$^{3+}$ is stable in air and therefore easy to be handled during synthesis process. Thirdly, Fe$^{3+}$/Fe$^{4+}$ electrochemically active redox couple can be utilized at the high voltage region (>4.7 V), as reported by Ohzuku$^{22, 23}$ and Manthiram$^{24}$. This means that Fe$^{3+}$ can potentially play the dual roles of both in keeping high energy density and in stabilizing the structure against oxygen release. Manthiram et al$^{24}$ has reported that low concentration Fe doping can improve the electrochemical performance of high voltage spinel and explained the mechanism behind the improvement. In this paper, we go beyond the low concentration doping level and use Fe to simultaneously substitute Ni and Mn to the greatest possible extent, aiming to obtain an optimized transition metal stoichiometry that delivers both excellent electrochemical performance and excellent thermal stability by suppressing oxygen release.

2. Results and Discussion

As explained previously, our design strategy lies in using cations with tendency of tetrahedral site migration without reduction like Mn$^{4+}$ to Mn$^{2+}$ as shown in Figure1a. According to crystal field theory$^{25}$, tendency of tetrahedral migration depends on the electronic structure of a transition metal cation which is specified by the number of valence electrons (3d electrons) and the spin state. In Figure 1b, such dependence is shown for all the 3d transition metal cations. Of those with strongest migrating tendency, high spin Fe$^{3+}$ is found to be particularly intriguing because it is electrochemically active in the high voltage region, easy for synthesis process and environmentally benign. Based on the big difference in tendency of migration between high and low spin Fe$^{3+}$, the high spin Fe$^{3+}$ substitution is more favorable than the low spin Fe$^{3+}$ substitution for stabilizing the structure and suppressing oxygen release during heating. The high or low spin state is determined by the ligand field splitting energy 10Dq. For Fe$^{3+}$, only when 10Dq is greater than 1.8 eV, the low spin state is
favored. Since the calculated L-edge x-ray absorption spectra are strongly related to the 10Dq value of the transition metal cation located in certain symmetry site, the 10Dq value of Fe\(^{3+}\) can be estimated by comparing the experimental Fe L-edge spectra with the calculate ones with different 10Dq values. From this value, the spin state of Fe\(^{3+}\) can be determined. We synthesized two Fe-substituted samples with the nominal composition LiNi\(_{0.5-x}\)Mn\(_{1.5-x}\)Fe\(_{2x}\)O\(_4\) (2x=0.2 and 2x=0.33, Fe simultaneously substitute Ni and Mn to minimize the presence of Mn\(^{3+}\), which is associated with the low voltage 4.0 V plateau and decreases the energy) and characterized them using soft x-ray absorption measurement at L-edge for Fe. In identifying its spin state, we calculated a series of Fe L-edge spectra using Oh (octahedral) symmetry and various ligand field splitting energy 10Dq values (Figure S1). The calculation was carried out by using CTM4XAS software\(^{26}\), which calculates 3d transition metal L-edge spectra using charge transfer multiplet theory\(^{27}\). Satisfaction simulation is achieved using 10Dq values in a range between 1.2 and 1.5 eV, which corresponds to the high spin state\(^{26}\) (Figure 1c). In contrast, spectrum calculated for low spin state (10Dq=2.7 eV) differs significantly from the experimental data. Therefore, it is confirmed that Fe does exist as high spin Fe\(^{3+}\) in LiNi\(_{0.5-x}\)Mn\(_{1.5-x}\)Fe\(_{2x}\)O\(_4\) samples with 2x=0.2 and 2x=0.33 and high migration tendency and good oxygen release suppressing effect are expected for such Fe\(^{3+}\) substitution.

Since Fe substitution is designed to improve the thermal stability while keep the high energy density of high voltage spinel, higher concentration of Fe is desirable, as long as the structural purity and electrochemical performance is not negatively impacted. LiNi\(_{0.5-x}\)Mn\(_{1.5-x}\)Fe\(_{2x}\)O\(_4\) samples with 2x=0, 0.2, 0.33, and 0.5 were synthesized and characterized by XRD (Figure 2a). It can be seen that the 2x=0 sample features a pure spinel phase, with all the major peaks indexed by the space group Fd\(\bar{3}\)m. The (220) peak, which is very sensitive to the transition metal cations at tetrahedral sites\(^{28}\), is almost invisible, suggesting that tetrahedral sites are almost exclusively occupied by lithium. Therefore, the structure can be described as lithium residing in tetrahedral 8a site, transition metal residing in octahedral 16d site and
oxygen in 32e site as shown in the crystal structure in Figure 2b. As the Fe concentration increases, some impurity phase starts to emerge and becomes significant in the 2x=0.5 sample. At the same time, the intensity of (220) peak increases and become clearly observable at 2x=0.5. Therefore, the solubility limit of Fe in the LiNi0.5-xMn1.5-xFe2xO4 is regarded at around 2x=0.33. This is supported by the linear relationship between lattice parameter and Fe concentration, following the Vegard's law29 as shown in Figure 2c.

In order to study the elemental distribution of the three transition metal elements cross the sample particles, we also performed nondestructive transmission X-ray microscopic (TXM) investigations. In Figure 3, the three dimensional tomographic results (collected at 8380 eV, above the k edges of all the three transition metal elements: Mn, Fe, and Ni) of a ~10-micron-sized particle (Figure 3a) and several selected slices through different depth (Figures 3c-3g) are shown. The three dimensional density distributions within this solid particle are homogeneous. By tuning the x-ray energy, we studied the energy dependency of each single voxels within this volume and quantitatively retrieved the elemental concentration as indicated in Figure 3b, in which the elemental concentration over the line path highlighted in Figure 3e is plotted. The relative concentration of Mn, Fe, and Ni, shown in Figure 3b is in good agreement with the expected elemental composition as designed. These results clearly demonstrated that the new material synthesized has a good degree of homogeneity in the structure and chemical distribution with designed composition.

To study the effect of Fe substitution on the structural evolution and oxygen release during heating the charged cathode, in situ XRD-Mass Spectroscopy (MS) experiments28 were carried out for the LiNi0.5-xMn1.5-xFe2xO4 (2x = 0, 0.2, 0.33) samples. It can be seen from Figure 4 that Fe substitution clearly improves the thermal stability of charged cathode by suppressing the oxygen release and maintaining the structure. Charged LiNi0.5Mn1.5O4 releases oxygen at around 250 °C and this threshold is pushed to around 380 °C for the 2x=0.2 sample. Further improvement is achieved in the 2x=0.33 sample which showed no
oxygen release up to 500 °C. Correlating with suppressed oxygen release is the integrity of the structure as seen in the right panel of Figure 4. To study the mechanism of such great improvement in the 2x=0.33 sample, *in situ* XRD-MS data is examined in details and compared with the case of 2x=0 in Figure 5. As shown in Figure 5a, the charged LiNi<sub>0.5</sub>Mn<sub>1.5</sub>Fe<sub>2x</sub>O<sub>4</sub> (2x = 0.33) which is in the λ-MnO<sub>2</sub> phase transforms into a Fe<sub>3</sub>O<sub>4</sub>-type spinel phase which has transition metals occupying tetrahedral sites but maintains the spinel framework (evidenced by the growing intensity of (220) peak and the fact that all the peaks in the final phase can be indexed by the Fd<sub>3</sub>̅m space group). In contrast, unsubstituted LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> decomposes into a mixture of NiMnO<sub>3</sub>, α-Mn<sub>2</sub>O<sub>3</sub> before transforming to the NiMn<sub>2</sub>O<sub>4</sub> phase as reported in detail in our previous publication, which is caused by the reduction of Ni and Mn and accompanied with oxygen release as shown in Figure 5b. The structural change comparison of these two samples is illustrated in Figure 5c. During heating, Fe ions migrate from octahedral to tetrahedral sites, as clearly indicated by the increasing intensity of (220) peak in Figure 5a (while Ni and Mn remain at octahedral sites as identified by *in situ* x-ray absorption experiment and shown in Figure S2, Supporting Information) for the charged LiNi<sub>0.5</sub>xMn<sub>1.5</sub>xFe<sub>2x</sub>O<sub>4</sub> (2x = 0.33) sample. SEM images (Figure S3, Supporting Information) indicate that the 2x=0.33 sample and the 2x=0 sample have similar morphologies and particle sizes, confirming the improvement is out of structural reasons.

Since our goal is to design cathode material with improved thermal stability while keeping the good electrochemical performance, it is important to make sure that the intrinsic good electrochemical performance of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> is not scarified by Fe substitution. Detailed electrochemical studies (Figure 6) were carried out for the 2x=0.33 sample as this material showed the greatest improvement in thermal stability. Upon Fe substitution, capacity (Figure 6a), cyclability and rate capability (Figure 6b) are well preserved. In fact, the 2x=0.33 sample showed even slightly better rate capability. It is also interesting to note that Fe substitution leads to a slopy discharging curve compared with the flat one for LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>.
In situ XRD (Figure S4, Supporting Information) results showed that the reaction proceeds in a solid-solution fashion for the Fe-substituted sample, compared with the two-phase reaction for LiNi_{0.5}Mn_{1.5}O_{4}. This phenomenon is also observed previously in Cr-doped LiNi_{0.5}Mn_{1.5}O_{4}. One possible explanation is that Fe substitution reduces the overall size differences among the cations (Ni^{2+}: 0.69 Å, Mn^{4+}: 0.53 Å, Fe^{3+}: 0.645 Å). Therefore, the overall strain is reduced in the system and the system is more tolerant to the variation of lithium concentration. In other words, the strain introduced by lithium extraction/insertion is no longer large enough to induce the phase separation. More accurate explanation may require detailed theoretical studies which will be planned for future studies.

The origin of undiminished capacity upon Fe substitution can be understood from the dQ/dV plot in Figure 6c. It can be seen that there are three redox couples in the Fe-substituted sample, corresponding to Ni^{2+}/Ni^{3+}, Ni^{3+}/Ni^{4+} and Fe^{3+}/Fe^{4+}. The third one is assigned to Fe^{3+}/Fe^{4+} on the basis of Fe K-edge x-ray absorption results shown in Figure 6d indicating the capacity lost due to reduced Ni content is compensated by the Fe^{3+}/Fe^{4+} contribution.

3. Conclusion

Taking the advantages of dual roles of Fe^{3+} in stabilizing the structure and contributing to the capacity, a series of Fe-substituted high voltage spinel with the stoichiometry LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_{4} were designed and synthesized. Spectroscopy studies confirmed that Fe exists as high spin Fe^{3+} in the LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_{4} (2x = 0.2, 0.33) samples with ligand field splitting energy 10Dq estimated to be around 1.5 eV. XRD results indicate that a generally pure normal spinel phase like the non-substituted LiNi_{0.5}Mn_{1.5}O_{4} is formed within the 2x≤0.33 limit. TXM results suggest that Ni, Mn and Fe are homogeneously distributed within the particle.

In situ XRD-MS studies show that Fe substitution significantly improves the thermal stability of high voltage spinel by suppressing the undesirable oxygen release during heating. When the charged LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_{4} (2x = 0.33) is heated, the spinel framework is
maintained without detectable oxygen release. In contrast, non-substituted LiNi$_{0.5}$Mn$_{1.5}$O$_4$ decomposes and releases fair amount of oxygen under the same condition. \textit{In situ} XRD and XAS studies at Fe K-edge during heating reveal that it is Fe that migrates from the octahedral site to tetrahedral site when the temperature is increased, stabilizing the structure at Fe$_3$O$_4$-type spinel phase.

Electrochemical tests show that Fe-substituted sample well preserved the good electrochemical performance of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ with improved rate capability. Fe substitution also changed the reaction mechanism from “two-phase” to “solid solution”. Fe K-edge x-ray absorption studies showed that Fe$^{3+}$/Fe$^{4+}$ is a reversible redox couple in the system, compensating the reduction of electrochemically active Ni content and leading to undiminished total capacity.

In summary, based on the fundamental understanding of the interplay between oxygen release and crystal structural change which is further related to the electronic structure of transition metal cations, we proposed using Fe as a major component for the high voltage spinel system in designing thermally stable and high-performance cathode. The synthesized LiNi$_{0.5-x}$Mn$_{1.5-x}$Fe$_{2x}$O$_4$ (2x = 0.33) material delivers both satisfactory thermal stability and competitive electrochemical performance. These results highlight the importance of fundamental studies in advancing the battery chemistry.

\textbf{Experimental Section}

See supporting information.

\textbf{Supporting Information}

Supporting Information is available from the Wiley Online Library or from the author.
Figure 1 (a) Illustration of the design strategy. $X^{n+}$ denotes a certain transition metal cation that readily migrates to tetrahedral site without reduction. (b) Tendency of migration (based on Octahedral Site Stabilization Energy) as a function of the electronic structure of 3d transition metal cations. Exchange energy is not considered in calculating the OSSE. (c) Experimental data of Fe L-edge x-ray absorption spectra for LiNi$_{0.5-x}$Mn$_{1.5-x}$Fe$_{2x}$O$_4$ ($2x = 0.2, 0.33$) compared with calculated spectra assuming high spin and low spin configurations.
Figure 2 (a) XRD patterns for LiNi$_{0.5-x}$Mn$_{1.5-x}$Fe$_{2x}$O$_4$ (2x = 0, 0.2, 0.33, 0.5) with the inset graphs showing the emergence of impurity phase as 2x exceeds a certain limit. A pure phase can be indexed by the Fd$ar{3}$m space group. (b) Illustration of the crystal structure of LiNi$_{0.5-x}$Mn$_{1.5-x}$Fe$_{2x}$O$_4$. (c) Variation of the lattice parameter as a function of the concentration of Fe. The linear relationship indicates that solid solution is formed in the LiNi$_{0.5-x}$Mn$_{1.5-x}$Fe$_{2x}$O$_4$ (2x = 0, 0.2, 0.33) series.
Figure 3 Rendering of the 3D structure of a selected LiNi$_{0.33}$Mn$_{1.34}$Fe$_{0.33}$O$_4$ particle is shown in panel (a) with the scale indicated in the axis and the color legend shown in the inset. Panels (c) through (g) are slices at different depth of the particle showing that it is a solid piece with no internal pores and the density distribution is relatively homogeneous. The elemental concentration over the line path indicated in panel (e) is plotted in panel (b) (the blue, green, and red curves represent the concentration of Mn, Ni, and Fe respectively), which is in good agreement with the elemental composition of the material. Panels (a) and (c) through (g) are reconstructed from nano-tomography data collected at 8380 eV (above the absorption k edges of all the three transition metal elements), while the data plotted in panel (b) is retrieved from the evaluation of the energy dependency of the absorption coefficient using a method known as Absorption Correlation Tomography$^{30}$. 
Figure 4 Effect of Fe substitution on the structural evolution and oxygen release during heating the charged samples of LiNi$_{0.5-x}$Mn$_{1.5-x}$Fe$_{2x}$O$_4$ (2x=0, 0.2, 0.33). The left panel is the *in situ* MS data for oxygen and the right three panels are the *in situ* XRD data for LiNi$_{0.5-x}$Mn$_{1.5-x}$Fe$_{2x}$O$_4$ (2x=0, 0.2, 0.33).
Figure 5 (a) *In situ* XRD-MS data of fully charged LiNi$_{0.5-x}$Mn$_{1.5-x}$Fe$_{2x}$O$_4$ ($2x = 0.33$) and (b) *In situ* XRD-MS data of fully charged LiNi$_{0.5-x}$Mn$_{1.5-x}$Fe$_{2x}$O$_4$ ($2x = 0$). (c) Illustration of effect of Fe substitution on structural evolution and oxygen release and Fe K-edge x-ray absorption spectroscopy results.
Figure 6 Electrochemical performance and XANES spectra. (a) Charge and discharge profiles together with capacity retention (inset graph) of LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_4 (2x = 0, 0.33). Cells were cycled at C/5 which corresponds to current density of 0.11 mA/cm². (b) Rate capability of LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_4 (2x = 0, 0.33). (c) dQ/dV plot of LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_4 (2x = 0, 0.33). (d) Fe K-edge XANES spectra of pristine, charged and discharged samples of LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_4 (2x = 0.33).


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Based on understanding the relationship between electronic structure of transition metal elements and the safety characteristics of cathode, a naturally abundant and environmentally-benign element—Fe is introduced into the LiNi_{0.5}Mn_{1.5}O_4 spinel. The LiNi_{0.33}Mn_{1.33}Fe_{0.33}O_4 material shows significant improvement in safety characteristics by inhibiting oxygen release upon heating, while maintaining the high energy density of LiNi_{0.5}Mn_{1.5}O_4.

**Keywords:** structure-property relationship, energy storage, lithium ion batteries, cathode, high voltage spinel

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**Utilizing High Spin Fe^{3+} in Spinel Structured Cathode Material for Safer High Energy Lithium-ion Batteries**

ToC figure
Supporting Information for

Utilizing High Spin Fe$^{3+}$ in Spinel Structured Cathode Material for Safer High Energy Lithium-ion Batteries

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Experiment Details

Synthesis of LiNi$_{0.5-x}$Mn$_{1.5-x}$Fe$_{2x}$O$_4$ ($0 \leq x \leq 1/6$) and cell test. LiNi$_{0.5-x}$Mn$_{1.5-x}$Fe$_{2x}$O$_4$ powders were synthesized by a solid-state reaction from stoichiometric amounts of Li$_2$CO$_3$, NiO, MnO$_2$ and Fe$_2$O$_3$ (Alfa Aesar). The mixtures of the samples were thoroughly ground using a vibratory ball mill, and then pressed into pellets. The pellets were heated at 1000 °C for 24 h with intermittent grinding. Then they were slowly cooled to room temperature at a cooling rate of 1° C/min. Cathode specimens were prepared by slurrying the active material with 10 wt% carbon black and 10 wt% poly-vinylidene fluoride in N-methylpyrrolidone solvent, and then coating the mixture on Al foil. After vacuum drying at 60 °C for 24 h, electrode disks were punched and weighed. The cathodes were incorporated into cells with a high-purity lithium metal foil anode and a Celgard separator. LiPF$_6$ (1 M) in ethylene carbonate and dimethyl carbonate with a volume ratio of 1:1 was used as the electrolyte. The 2032-type coin cells were assembled in an argon-filled glove box for electrochemical tests.

XRD Characterization. Powder diffraction data was collected at beamline X14A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory by a linear position sensitive silicon detector. The wavelength used was 0.7747 Å. To ease comparisons with other published results using conventional X-ray sources, we plotted the XRD patterns using converted 2θ angles corresponding to the Cu Kα ($\lambda = 1.54$ Å) radiation wavelength.

In situ time resolved XRD combined with mass spectroscopy during heating was conducted using the thermal stage at beamline X7B ($\lambda = 0.3196$ Å) of NSLS in the transmission mode, while the MS signals were simultaneously collected as the sample was heated from room
temperature to 500 °C at a rate of ~2.0 °C min⁻¹. Details of the preparation method were described in our previous publications¹. To ease comparisons with other published results using conventional X-ray sources, we also plotted the XRD patterns using converted 2θ angles corresponding to the Cu Kα (λ = 1.54 Å) radiation wavelength.

In situ high resolution XRD patterns of LiNi₁/₃Mn₄/₃Fe₁/₃O₄ during electrochemical cycling (Figure S4, Supporting Information) were collected at sector 11-BM of the Advanced Photon Source (APS) at Argonne National Laboratory. The wavelength of the X-ray beam used was 0.413326 Å. A pouch cell configuration was used for the in situ experiment.

**XAS characterization and data analysis.** Hard x-ray XAS experiments were carried out at beamline X18A of NSLS. Fe K-edge spectra were measured in a fluorescence mode with 4-element Si drift detector to efficiently filter out the contributions from more prevalent Mn by properly setting the energy window for Fe Kα peak. Ni and Mn K-edge spectra were measured in a conventional transmission mode. For in situ XAS during heating, the fully charged cathode electrodes were removed from the dissembled cell and washed by the DMC solvent, and then mounted on the sample holder of a specially designed heating cell and heated under the protection of He gas. Detailed description of experimental procedure can be seen in our previous publication¹. Soft x-ray XAS measurements were carried out at the SGM beamline of the Canadian Light Source. Powder samples were held onto the indium foil. X-ray Absorption Near Edge Structure (XANES) were measured in the surface sensitive total electron yield (TEY). Data were first normalized to the incident photon flux I₀ measured with a refreshed gold mesh prior to sample measurement and then further normalized to the edge jump between pre-edge platform and post-edge platform. XANES data were analyzed by ATHENA software package².

**Electron microscopy.** Scanning electron microscope (SEM) images (Figure S1, Supporting Information) were collected on a JEOL 7600 SEM operating at 5 kV in a low vacuum condition to minimize charging effects.
**Transmission X-ray Microscopy.** Non-destructive characterization of the three-dimensional structure of the cathode particles (with 3D spatial resolution down to ~30 nm and sensitivity to elemental compositions) was performed using the Transmission X-ray Microscopy (TXM) at beamline 6-2C of the Stanford Synchrotron Radiation Lightsource (SSRL) at the SLAC National Accelerator Laboratory. The sample was kept in Helium environment during the measurement to avoid oxidation and to reduce the heat load from the focused X-ray beam. Tomography were conducted at six selected X-ray energies (6510 eV, 6630 eV, 7080 eV, 7200 eV, 8300 eV, and 8380 eV) above and below the K edges of the three transition metal elements (Mn, Fe, and Ni). Projection images were collected over an angular range of 180 degrees with step size of 1 degree. The correlation of elemental concentrations was analyzed using the so-called Absorption Correlation Tomography\(^3\) and an in-house developed software package known as TXM W\(\text{i}\)\(\text{z}\)ard\(^4\).
Figure S1. Systematic variation of crystal field splitting energy $10D_q$ to simulate the experimental data (dotted) of Fe L-edge x-ray absorption spectrum of LiNi$_{0.5-x}$Mn$_{1.5-x}$Fe$_{2x}$O$_4$ ($2x = 0.33$) pristine sample. The most satisfactory simulation is achieved when $10D_q$ is between 1.2 eV and 1.5 eV.
Figure S2. *In situ* XANES spectra at the (a) Ni (b) Mn and (c) Fe K-edge for fully charged LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_{4} (2x = 0.33) during heating up to 475 °C. (d) Schematic of Fe migration to spinel tetrahedral site.

Figure S3. SEM images of (a) LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_{4} (2x = 0) and (b) LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_{4} (2x = 0.33) pristine samples.
Figure S4. *In situ* XRD of LiNi$_{0.5-x}$Mn$_{1.5-x}$Fe$_{2x}$O$_4$ (2x = 0.33) during charging and discharging.

**Additional References**


