SUPPORTING INFORMATION

Elucidating the Role of Fe Substitution on Structural and Redox Stability of Na₂Mn₃O₇

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Experimental Procedures

Materials Synthesis

 $Na_2Mn_3O_7$ was prepared by solid state method. Stoichiometric amounts of NaNO₃ (Thermo Scientific, 99%) with 5 mol% excess to compensate for loss during calcination and MnCO₃ (Sigma Aldrich, 99.9%) were mixed in a ball mill at 400 rpm for 4 hours. The precursor mixture was then heated at 550°C for 12 hours in a tube furnace with ambient atmosphere. The heating step was 5°C/min, and the sample was allowed to naturally cool to 150°C after calcination then quickly transferred to an Ar filled glovebox.

An overall composition of $Na_2Mn_{2.5}Fe_{0.5}O_z$, where the oxygen stoichiometry *z* will adjust to charge balance the cations during calcination (stoichiometry explained more in the caption of Table S3), was prepared by the same methods as $Na_2Mn_3O_7$ except using Fe₂O₃ (Sigma Aldrich) as an Fe source and mixing precursors by hand in a mortar and pestle for 30 minutes instead of using a ball mill.

Materials Characterization

Synchrotron powder X-ray diffraction ($\lambda = 0.7292$ Å) was used to determine the crystal structure and was conducted at Stanford Synchrotron Radiation Lightsource (SSRL) on Beamline 2-1. The chemical compositions were analyzed by ICP-OES (Agilent 5100 DVD Inductively Coupled Plasma-Optical Emission Spectrometer). SEM (Zeiss Merlin High-resolution SEM and Gemini 450 SEM) was conducted to study the particle morphologies. Scanning transmission electron microscopy (STEM) imaging, electron energy-loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDS) were performed on a probe corrected Thermo Fisher Scientific Themis Z G3 equipped with a Gatan Continuum EEL spectrometer and Super-X EDS detectors. The energy resolution of EEL spectra, as measured by the FWHM of the zero-loss peak, was 1.5 eV, and EEL Spectrum Images were collected with a 0.3 eV/channel dispersion, 0.02 s dwell time, and 0.33 nm pixel size. XAS was conducted at NSLS-II at Brookhaven National Laboratory (BNL) with hard XAS being done on Beamline 8-ID (ISS)¹ and soft XAS being done on Beamline 23-ID-2 (IOS). RIXS was performed at Lawrence Berkeley National Laboratory (LBNL) on Beamline 8.0.1.

Athena was used to process hard XAS data and conduct XANES analysis while Artemis was used for EXAFS analysis.²

Simulated electron diffraction was done with SingleCrystal (v4.1.9). Simulated X-ray diffraction was done with CrystalDiffract (v6.9.4) with a peak width of 0.17° and wavelength of 0.7292 Å to match the collected synchrotron XRD measurements.

XRD refinement was conducted with the GSAS-II software.³ The refinement procedure involved first refining the background, zero offset, and lattice parameters followed by the size and microstrain terms. This was followed by refining the atomic displacement parameters for all the elements.

Electrochemical Measurements

Electrochemical tests were performed in coin cells (CR2032), which were assembled in an Arfilled glovebox ($O_2 \le 1$ ppm, $H_2O \le 0.02$ ppm). Electrodes were prepared by coating slurry onto carbon coated Al foil current collectors. The slurry was composed of active material (AM) (80 wt%), carbon black conductive additive (10 wt%), and polyvinylidene fluoride (PVDF) binder (10 wt%) dispersed in N-Methyl-2-pyrrolidone (NMP) solvent. The electrode was coated inside the glovebox and dried overnight on a hotplate inside the glovebox. The electrode punches taken were 16 mm in diameter with mass loadings of ~2-4 mg AM/cm². Sodium metal foil was used as the counter electrode with glass fiber used as the separator. The electrolyte consisted of 1 M NaPF₆ in propylene carbonate (PC) with 4 vol% fluoroethylene carbonate (FEC) additive. Galvanostatic cycling and cyclic voltammetry were performed on a Bio-Logic BCS-800 in controlled temperature (~30°C).

Density Functional Theory Calculations

Ab initio calculations using density functional theory (DFT) were performed with the Vienna ab initio simulation package (VASP). The Perdew–Burke-Ernzerhof functional⁴ with additional Hubbard *U* parameter *PBE+U* was used. The *U* values were 3.9 and 5.3 eV for Mn and Fe, respectively.⁵ To find the density of states (DOS), first an ionic and electronic relaxation with a gamma-centered 4 x 4 x 4 k-mesh was used followed by an electronic relaxation with a 4 x 4 x 4 k-mesh. Finally, an electronic relaxation with an 8 x 8 x 8 k-mesh was run to obtain accurate DOS results.

Table S1. Atomic and lattice parameters of $Na_{2.25}Mn_{2.75}Fe_{0.25}O_7$ derived from Rietveld refinement from the structure for $Na_2Mn_3O_7$ ((ICSD #5665⁶). The refinement resulted in a weighted residual of 12.195%.

Space Group: P-1		a = 6.59(3) Å, b = 6.98(3) Å, c = 7.63(3) Å						
		$\alpha = 107.636^{\circ}, \beta = 107.203^{\circ}, \gamma = 111.254^{\circ}$						
Site	Wyck.	Atom	x	У	Z	Occ.	U _{iso}	
Na1	2i	Na	0.17578	0.67863	0.53723	1	0.01900	
Na2	2i	Na	0.37574	0.91493	0.14471	1	0.01900	
Mn1	2i	Mn	0.07066	0.10190	0.24004	1	0.00731	
Mn2	2i	Mn	0.37186	0.33732	0.06116	1	0.00089	
Mn3	2i	Mn	0.21239	0.19313	0.64724	1	0.02186	
01	2i	О	0.46268	0.39984	0.29807	1	0.00633	
O2	2i	О	0.29014	0.11531	0.79879	1	0.00633	
03	2i	О	0.01869	0.10903	0.05836	1	0.00633	
O4	2i	О	0.18001	0.34823	0.46586	1	0.00633	
05	2i	0	0.75959	0.50241	0.08697	1	0.00633	
O6	2i	0	0.10965	0.86103	0.41262	1	0.00633	
07	2i	Ο	0.45737	0.63163	0.44023	1	0.00633	



Figure S1. Synchrotron powder X-ray diffraction (XRD) of Na₂Mn₃O₇ (NMO) and Na_{2.25}Mn_{2.75}Fe_{0.25}O₇ (NMFO) over full scan range. The inset shows the NMO and NMFO patterns over the range where most characteristic peaks are found as well as simulated XRD patterns from reference compounds of NMO (ICSD Collection Code 5665 ⁶) and α -NaFeO₂ (ICSD Collection Code 187705 ⁷). Major characteristic peaks for NMO are labeled, and these correspond to the same peaks in NMFO. The peak labeled in NMFO at ~19° is the largest characteristic peak of the proposed α -NaFeO₂ impurity. The simulated XRD patterns are done with a mixture of 97 vol% NMO and 3 vol% α -NaFeO₂. NMFO is expected to have a similar XRD pattern as NMO since the structures are theoretically the same. In the NMFO pattern, there is a peak at ~19° that is not explained by NMO. This peak corresponds to the major peak in α -NaFeO₂, providing evidence that it is the impurity phase at about ~3 vol%. More evidence of α -NaFeO₂ being the impurity peak is provided throughout the rest of this paper. Since α -NaFeO₂ has a very small volume fraction in this measured sample, the rest of its peaks are drowned out by those from pure phase NMFO.



Figure S2. Synchrotron powder X-ray diffraction of Na₂Mn₃O₇ with Rietveld refined pattern. The refined parameters are listed in Table S2.

Table S2. Atomic and lattice parameters of $Na_2Mn_3O_7$ derived from Rietveld refinement from the structure for $Na_2Mn_3O_7$ ((ICSD #5665 ⁶). The refinement resulted in a weighted residual of 13.521%.

Space Group: P-1		a = 6.5292 Å, b = 6.94741 Å, c = 7.52888 Å						
		$\alpha = 109.019^{\circ}, \beta = 103.256^{\circ}, \gamma = 111.899^{\circ}$						
Site	Wyck.	Atom	x	У	Z	Occ.	U _{iso}	
Na1	2i	Na	0.2440	0.6985	0.5059	1	0.0025	
Na2	2i	Na	0.3264	0.8216	0.0803	1	0.0385	
Mn1	2i	Mn	0.0730	0.0737	0.2236	1	0.0025	
Mn2	2i	Mn	0.3632	0.3657	0.0860	1	0.0190	
Mn3	2i	Mn	0.2238	0.2250	0.6455	1	0.1599	
01	2i	О	0.3219	0.2521	0.2440	1	0.1226	
O2	2i	О	0.2204	0.0963	0.8129	1	0.2159	
03	2i	О	-0.0561	0.1535	0.0130	1	0.0063	
O4	2i	О	0.1647	0.3593	0.4647	1	0.0517	
05	2i	О	0.7065	0.4751	0.0881	1	0.0776	
O6	2i	Ο	0.1180	0.9254	0.4337	1	0.0158	
07	2i	О	0.4531	0.6368	0.2944	1	0.0063	



Figure S3. Identification of $[0\underline{1}2]$ zone axis in STEM image capturing ordered vacancies in Na_{2.25}Mn_{2.75}Fe_{0.25}O₇ (NMFO) (Figure 1e). (a) HAADF STEM image of NMFO viewing the $[0\overline{1}2]$ direction with Mn lattice (magenta color) from Na₂Mn₃O₇ (NMO) overlaid, showing the ordered vacancy. The alignment of the simulated lattice along the $[0\overline{1}2]$ zone axis indicates the correct identification of the zone axis. (b) FFT of STEM image in (a). (c) Simulated electron diffraction of NMFO along the $[0\overline{1}2]$ zone axis, which appears to be the same pattern seen in (b), offering further evidence of the correct identification of the zone axis.

Table S3. ICP-OES results for an overall composition of Na₂Mn_{2.5}Fe_{0.5}O_z where the oxygen stoichiometry z will adjust to charge balance the cations during calcination, which is done with ambient atmosphere. The measured composition is Na_{1.92}Mn_{2.52}Fe_{0.47}O_z, which is consistent with the stoichiometry of the precursors. We intentionally did not compensate Fe³⁺ substitution for Mn⁴⁺ with excess Na⁺ during synthesis (y = 2 instead of y = 2.5 in Na_vMn_{2.5}Fe_{0.5}O₇) to maintain our desired phase with ordered TM vacancies. Higher sodiation during synthesis leads to a driving force to form a P2 impurity phase without ordered TM vacancies, which can accommodate more Na⁺ (shown and discussed in Figure S4). Based on our abundant evidence of Fe³⁺ incorporating into the Na₂Mn₃O₇ lattice (Figures 1-2), which results in an improvement in specific capacity (Figure 6), we can conclude that in the majority pure phase ($Na_{2.25}Mn_{2.75}Fe_{0.25}O_7$), Fe^{3+} is charge compensated with excess Na⁺ also incorporating into the lattice. Maintaining the overall ratio between cations in Na₂Mn_{2.5}Fe_{0.5}O_z while achieving a majority Na_{2+x}Mn_{3-x}Fe_xO₇ phase and approximate oxidation states of Na⁺, Mn⁴⁺, and Fe³⁺ requires that not all Fe³⁺ ions are incorporated into the Na_{2+x}Mn_{3-x}Fe_xO₇ lattice and instead form impurity phases (e.g., lowly sodiated layered Fe oxides, other Fe oxides). Our XRD and EDX measurements (Figure 1) indicate that such sodiated Fe-rich oxide impurities do exist in the sample alongside the majority pure phase $(Na_{2.25}Mn_{2.75}Fe_{0.25}O_7).$

	Expected	ICP-OES	% Difference
Na:Mn	0.8	0.77	-3.75
Na:Fe	4	4.27	6.75



Figure S4. HAADF STEM image of $Na_2Mn_3O_7$ showing the ordered vacancies, which are represented by dark circles in the lattice due to the absence of matter in the atomic column. A few unit cells from the particle surface, the ordered vacancy phase transitions to a phase with no ordered vacancies. To maintain charge neutrality, the Mn must reduce compared to the ordered vacancy phase. This phenomenon is common for this lattice and is likely occurring for $Na_{2.25}Mn_{2.75}Fe_{0.25}O_7$ as well.



Figure S5. Effect of synthesis stoichiometry on phase purity shown through XRD measurements (PANalytical Empyrean, Mo source). We initially tried to synthesize $Na_{2.5}Mn_{2.5}Fe_{0.5}O_7$ (red line) to fully compensate Fe^{3+} substitution for Mn^{4+} with excess Na^+ . This led to major P2-type phase impurities (simulated P2 phase shown by the black line) and no ordered vacancies, which would form a small diffraction peak at ~7° (marked with a magenta rectangle on the plot). We found that by lowering the amount of Na used during synthesis ($Na_2Mn_{2.5}Fe_{0.5}O_7$), we could achieve our desired phase with ordered vacancies and only minor amounts of impurities, which are discussed more thoroughly earlier in this paper (Figure 1).



Figure S6. EDX elemental mapping of $Na_{2.25}Mn_{2.75}Fe_{0.25}O_7$ (NMFO). No impurity particles are observed.



Figure S7. Redox mechanisms investigated with soft XAS measurements of $Na_{2.25}Mn_{2.75}Fe_{0.25}O_7$ (NMFO) at different states of charge during the first cycle. (a) First cycle voltage profiles of $Na_2Mn_3O_7$ (NMO) and NMFO at C/20 over the voltage range 1.5-4.7 V. The high- and low-valent regime are colored yellow and purple, respectively. Mn (b) and Fe (c) L₃-edge iPFY measurements at different states of charge with reference measurements. Difference between the Mn (d) and Fe (e) L₃-edge iPFY measurements of $Na_{2.25}Mn_{2.75}Fe_{0.25}O_7$ at different states of charge during the first cycle with reference measurements. The consecutive spectra were subtracted from each other (e.g., 3.5 V subtracted from 4.23 V) to highlight changes in the spectra during charging. Nothing was subtracted from the spectra for the pristine state, which is the start of the charging cycle. The horizontal dotted lines in all plots are references that represent no change after subtraction.



Figure S8. First cycle electrochemical behavior in Na₂Mn₃O₇ (NMO) and Na_{2.25}Mn_{2.75}Fe_{0.25}O₇ (NMFO) at C/20 in the voltage window 1.5-4.7 V. Voltage profiles for NMO (top left) and NMFO (bottom left) with corresponding differential capacity to the right of each. The voltage range of 1.5-3.0 V is considered the "low-valent" regime because only low-valent redox reactions occur (e.g., Mn³⁺/Mn⁴⁺). The voltage range of 3.0-4.7 V is considered the "high-valent" regime since only high-valent (i.e., the over oxidation of transition metals or oxygen) redox reactions occur (e.g., O²⁻/O⁻). The high- and low-valent regime are colored yellow and purple, respectively. The voltage range 3.0-4.3 V is a relatively stable region for high-valent redox reactions because above this (4.3-4.7 V), liquid electrolytes are not stable, and high amounts of in-place TM migration can

lead to irreversible structural distortion. The plateau regions are highlighted in their corresponding differential capacity curves and labeled with their associated redox reaction. In the lower voltage regions below ~ 3 V, the cathode is sodiated more than it was initially desodiated, resulting in the material having a higher Na content than in its pristine state. This oversodiation corresponds to low-valent TM redox reactions (e.g., Mn^{3+}/Mn^{4+}). During the initial charge of NMFO, there is a notch in the voltage curve at ~ 3.3 V, which is characteristic of the voltage curve for α -NaFeO₂⁸, providing further evidence that it is the impurity.



Figure S9. Mn (a) and Fe (b) L₃-edge iPFY measurements of Na_{2.25}Mn_{2.75}Fe_{0.25}O₇ at different states of charge during the second cycle with reference measurements. The consecutive spectra were subtracted from each other (e.g., 3.5 V subtracted from 4.1 V) to highlight changes in the spectra during charging. Nothing was subtracted from the spectra for the pristine state and 1.5 V, which is the start of the charging cycle. The horizontal dotted lines in (a-b) are references that represent no change after subtraction. In (a), the disappearance of the "valley" in the spectra at ~642 eV is the clearest sign of a transition between Mn⁴⁺ and Mn³⁺. In (b), the disappearance of the "valley" in the spectra at ~711 eV is the clearest sign of a transition between Fe³⁺ and Fe²⁺ or Fe⁴⁺. At 1.5 V, the disappearance of this valley is assumed to correspond to partial Fe reduction from Fe³⁺ to Fe²⁺ while at 4.7 V, the disappearance of this valley is assumed to correspond to partial Fe reduction from Fe³⁺ to Fe³⁺ to Fe⁴⁺ since during charge Fe already oxidized from Fe²⁺ to Fe³⁺. Linear combination fitting was performed for Mn (c) and Fe (d) L₃-edge measurements as well. The references for different oxidation states of these transition metals, shown in the plots, are linearly combined to create an optimal model, shown as dashed red lines, for each scan. From this

fitting, the amount of each oxidation state can be estimated, so the average oxidation state of each transition metal can be estimated. This estimation for each transition metal at each voltage is plotted in (e) with the horizontal dashed lines representing the estimated oxidation state of the pristine material. For Mn, the oxidation state is theoretically Mn^{4+} , but the soft XAS scans show a slightly lower oxidation state for the pristine and charged samples. This is likely due to the fact that sXAS is sensitive to the material surface. These iPFY measurements probe to a depth of <200 nm, so the Mn reduction on the surface observed in EELS in Figure 2 is likely impacting these measurements. Fe, however, is at an Fe³⁺ state for the pristine sample as expected. The vertical dotted lines in (a-d) align with the resonances of the reference spectra.



Figure S10. Synchrotron powder X-ray diffraction of $Na_{2.25}Mn_{2.75}Fe_{0.25}O_7$ at different states of charge when cycling at C/20 in the voltage range 1.5-4.3 V vs. Na/Na⁺. Spectra marked "C" are charging from open circuit voltage or from 1.5 V if they are marked "2nd" for being in the second cycle. Spectra marked "D" are discharging from 4.3 V. The vertical dotted line at ~19° indicates the peak corresponding to the a-NaFeO₂ impurity. As the material is cycled, this peak fades, corresponding to the decomposition of this impurity phase. This peak reappears in the low-valent regime (pristine material or <3 V).



Figure S11. Local structure of Na_{2.25}Mn_{2.75}Fe_{0.25}O₇ (NMFO) at different states of charge during the second charging cycle investigated with extended x-ray absorption fine structure (EXAFS) measurements using the same Mn and Fe K-edge measurements shown in Figure 4. EXAFS spectra of Mn (a) and Fe (b) K-edge. The peaks corresponding to the bonds between TM-O and TM-TM are labeled with Fe having a secondary TM-TM bond distance, possibly from the α -NaFeO₂ impurity phase (Figure S12). Scattering distances of different EXAFS peaks for Mn (c) and Fe (d), which are not phase corrected. The right axis is the radial distance and the left axis is the percentage difference from the measurement from the pristine sample. The horizontal dashed line is the radial distance of the pristine sample. The peaks are very stable throughout charging with a maximum of ~1% change from the pristine state with the exception of the Fe TM-O bonds, which may vary from the pristine sample more due to the decomposition of the α -NaFeO₂ impurity phase and greater change in coordination. These results are consistent with EXAFS patterns of Na₂Mn₃O₇ found in the literature.^{9,10}



Figure S12. EXAFS investigation of secondary TM-TM bond in Fe for pristine $Na_{2.25}Mn_{2.75}Fe_{0.25}O_7$ (NMFO). Plotted in red is the simulated pattern for Fe-Fe scattering in the first shell for α -NaFeO₂, which has a peak corresponding to the secondary TM-TM peak in NMFO.



Figure S13. Determination of the voltage window for cycling over which the electrolyte is stable. A cyclic voltammetry measurement was done over the voltage range 0-4.7 V vs. Na/Na⁺ at a rate of 0.1 mV/s in a coin cell. The anode was Na metal, and stainless steel was the counter electrode. The electrolyte was 1M NaPF₆ in PC + 4 vol% FEC. These results show that the electrolyte significantly degraded above ~4.3 V due to side reactions. These reactions are avoided by using 4.3 V as the upper limit.



Figure S14. First cycle charge curves to 4.3 V at C/20 of Na₂Mn₃O₇ (NMO) and Na_{2+x}Mn_{3-x}Fe_xO₇ (NMFO) to estimate the value of *x*. The x axis is moles of Na⁺ ions deintercalated from the active material during this charging process. This was derived from the measured capacity using the common equation for theoretical capacity:

$$Moles of Na^{+} = \left(3,600\frac{A \cdot s}{Ah}\right) \left(\frac{1 \quad Ah}{1,000mAh}\right) \left(Measured \ Capacity \left[\frac{mAh}{g}\right]\right) \left(Molecular \ Weight \left[\frac{g}{mole \ of \ formula \ under a constraint of \ formula \ under a \ under a$$

where *F* is Faraday's constant and equal to 96,485 C/mol. Since the exact stoichiometry of the pure NMFO phase is not known, the molecular weight for NMO was used for both materials. It is assumed that any additional moles of Na⁺ removed from NMFO compared to NMO during charge is due to excess Na⁺ in the pure phase structure. The moles of Fe³⁺ ions in the pure phase NMFO structure would then be equal to moles of excess Na⁺ ions, which in this case is 0.23. This is the lower end of the estimate though, so we round up to approximately 0.25. There are two main reasons why rounding up is appropriate. First, in converting the number of moles of Na⁺ from capacity, the same molecular weight was used for NMO and NMFO, but in reality, the molecule weight for NMFO is slightly higher due to excess Na and Fe having larger mass than Mn. A formula of Na_{2.25}Mn_{2.75}Fe_{0.25}O₇ has a molecular weight of 328.76 g/mol, which is ~2% higher than the molecular weight of Na₂Mn₃O₇ (322.79 g/mol). Second, and more importantly, the measured

specific capacity of NMFO is normalized by the total mass of pure phase and impurities, which may have much lower or no electrochemical activity. This means that the measured specific capacity of NMFO is an underestimate for the pure phase, so the number of Na⁺ moles removed from the pure phase during charging is higher. This ultimately justifies $x \approx 0.25$ in Na_{2+x}Mn_{3-x}Fe_xO₇ as a reasonable estimate.



Figure S15. Electrochemical testing of $Na_2Mn_3O_7$ (NMO) and $Na_{2.25}Mn_{2.75}Fe_{0.25}O_7$ (NMFO) over the voltage range 1.5-4.3 V vs. Na/Na^+ at C/20. Select voltage profiles of (a) NMO and (c) NMFO and their associated differential capacity curves, (b) and (d), respectively.



Figure S16. Electrochemical testing of Na₂Mn₃O₇ (NMO) and Na_{2.25}Mn_{2.75}Fe_{0.25}O₇ (NMFO). (ac) Cycling over the voltage range 1.5-4.7 V vs. Na/Na⁺ at a C/20 rate. (d-f) Cycling over the voltage range 1.5-4.3 V vs. Na/Na⁺ at a C/10 rate. Select voltage profiles of (a, d) NMO and (b, e) NMFO. Cycling performance with (c) specific capacity and (f) specific capacity (left) and average discharge voltage (right) as a function of cycle. When cycling in the full accessible voltage range of 1.5-4.7 V at C/20 (a-c), the high voltage plateaus at ~4.2 V and ~4.5 V, which correspond to O²⁻ /O⁻ redox, quickly degrade with cycling and essentially disappear by 20 cycles. During the higher voltage O²⁻/O⁻ redox plateau, a significant amount of O²⁻ ions are oxidized, which could lead to a very strong driving force to form covalent bonds coupled with in-plane Mn migration.^{9,11,12} Further, the liquid electrolytes used are not stable past ~4.3 V (Figure S13), so their decomposition leads to irreversibilities. These two factors are illustrated in the capacity decay in (c) where initially NMFO has a higher specific capacity but decays more rapidly than NMO. The enhanced initial capacity of NMFO may be due to the fact that NMFO has a higher initial Na content than NMO. NMFO degrades quicker in this large voltage region likely because the upper limit of this voltage window corresponds to deep desodiation and is outside the stability window of available liquid electrolytes. A unique issue with Fe-based cathode materials for sodium-ion batteries is out-ofplane migration of Fe ions when enough Na vacancies are created during charging, which leads to poor cycle stability. This issue may become more significant at these extreme voltages for NMFO. A strategy to prevent this is incorporation of Li in the transition metal oxide (TMO) layer. Li will more readily migrate out of the plane to occupy a Na vacancy before Fe can, and then the Li⁺ ion will reversibly migrate back to its site in the TMO layer upon discharge.¹³ More cycling was conducted in the stable voltage range of 1.5-4.3 V at a higher C/10 rate (d-f). The O²⁻/O⁻ redox plateau for NMO initially contributes a specific capacity of ~40 mAh/g, but this decreases to ~10

mAh/g after 40 cycles and is completely gone by 60 cycles. (b) shows that the Fe substitution still initially decreases the capacity contribution of this plateau (~25 mAh/g), possibly shifting this capacity to Fe redox reactions and a more sloping voltage profile in this region. While the O^{2-}/O^{-} redox plateau at ~4.3 V is initially shorter in the Fe substituted system, it is stabilized throughout cycling, leading to a contribution of ~10 mAh/g remaining at cycle 60. This suggests that Fe introduces an increased energetic penalty for in-plane TM migration, leading to less structural deformation. This difference in capacity from O^{2-}/O^{-} redox is reflected by the average discharge voltage (f). The initially large contribution of the high-voltage O^{2-}/O^{-} redox plateau to the capacity of NMO leads to a superior average discharge voltage, but it begins to rapidly decrease after ~20 cycles. The average discharge voltage for NMFO, however, remains relatively steady, leading to it significantly outperforming NMO in this metric in later cycles. (f) also shows that NMFO shows superior specific capacity through 60 cycles. The specific capacity and average discharge voltages together lead to a better performance by NMFO at C/10, especially in later cycles.

Table S4. ICP-OES measurements of electrolyte for $Na_2Mn_3O_7$ (NMO) and $Na_{2.25}Mn_{2.75}Fe_{0.25}O_7$ (NMFO) after 12 cycles in the voltage range 1.5-4.3 V to investigate transition metal (TM) dissolution. The first cycle was conducted at a C/20 rate based on estimated capacity, and subsequent cycles used the first cycle discharge capacity to recalculate the C-rate. Subsequent cycles ran at C/10 with voltage holds. This accelerated the degradation process while ensuring full transition metal redox. The coin cells for this experiment had two Whatman Glass Fiber Class D separators. After cycling, these separators were extracted and soaked/sonicated in 5.25 mL of 3.5 vol% nitric acid in deionized water overnight. The remaining solution was passed through a 0.22 μ m filter and measured. The concentration in ppm was then normalized to the mass of the active material (AM) in the cell.

Material	Mn ppm/mg AM	Fe ppm/mg AM	TM ppm/mg AM	
NMO	49.91 ± 0.17	_	49.91 ± 0.17	
NMFO	2.65 ± 0.04	0.95 ± 0.01	3.6 ± 0.05	



Figure S17. Specific discharge capacity and average discharge voltage of $Na_2Mn_3O_7$ (NMO) and $Na_{2.25}Mn_{2.75}Fe_{0.25}O_7$ (NMFO) when cycling at C/20 (1.5-4.3 V) with specific capacity (left axis, filled points) and average discharge voltage (right axis, empty points) as a function of cycle.



Figure S18. Proportion of capacity from cationic and anionic redox for $Na_2Mn_3O_7$ (NMO) and $Na_{2.25}Mn_{2.75}Fe_{0.25}O_7$ (NMFO) when cycling at C/20 (1.5-4.3 V). Inset is zoomed to cycles 50-70.

Through our advanced X-ray characterization (i.e., soft and hard XAS and RIXS in Figures 4 and 5), we show that above 4.1 V, the capacity is coming almost entirely from oxygen redox reaction. Therefore, we can calculate the percentage of discharge capacity coming from oxygen redox as the percentage of discharge capacity occurring above 4.1 V with the remaining capacity originating from cationic redox. While NMO and NMFO's contribution from anionic redox degrades to a negligible amount after approximately the same number of cycles, the degradation compared to initial values was much more aggressive for NMO than NMFO.



Figure S19. Specific energy (with respect to cathode active material mass) as a function of cycle for $Na_2Mn_3O_7$ and $Na_{2.25}Mn_{2.75}Fe_{0.25}O_7$ cycled at C/20 over the voltage range 1.5-4.3 V vs. Na/Na^+ .



Figure S21. (a) Electrochemical impedance spectroscopy (EIS) of a pristine cell of $Na_2Mn_3O_7$ (NMO) and $Na_{2.25}Mn_{2.75}Fe_{0.25}O_7$ (NMFO). (b) The real component of impedance plotted against the reciprocal square root of frequency for data points taken at low frequencies (<~200 mHz) with

linear regression and labeled slopes. The method for calculating the Na diffusivity is adapted from Biswas et al.¹⁴ and is as follows:

The linear plots in (c) follow the equation

$$Re(Z) = R_{sol} + R_{ct} + \sigma\omega^{-\frac{1}{2}}$$
(1)

where Re(Z) is the real component of the impedance, R_{sol} is the resistance in the solid material, R_{ct} is the charge transfer resistance, σ is the slope of the real component of impedance plotted against the reciprocal square root of frequency, and ω is the frequency. R_{sol} and R_{ct} sum to the ohmic resistance in the setup. When fitting equation (1) to the low frequency data in (b), the slope σ can be derived. The apparent Na diffusivity is then estimated with the equation

$$D_{Na^{+}} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2}$$
(2)

where R is the universal gas constant, T is the temperature, A is surface area of the electrode, n is the number of electrons per charge transfer, F is the Faraday constant, C is the concentration of Na⁺ ions in the electrolyte, and σ is the slope obtained from equation (1).



Figure S22. Galvanostatic intermittent titration technique (GITT) measurements during the first cycle for (a) Na₂Mn₃O₇ (NMO) and (b) Na_{2.25}Mn_{2.75}Fe_{0.25}O₇ (NMFO). Gaps in pulses are due to temporary instrumental gaps in data collection but do not meaningfully impact results. (c) Calculated diffusivity from (a) and (b) as a function of voltage during charge and discharge. (d) Schematic illustration of experimental parameters and determination of ΔE_t and ΔE_s . GITT was performed over the voltage range 1.5-4.3 V at a C/20 current with a pulse time of 15 minutes and a relaxation time of 60 minutes. The method for calculating the Na diffusivity is adapted from Kim et al.¹⁵ and follows the equation

$$D_{Na^+} = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B A}\right)^2 \left(\frac{\Delta E_s}{\Delta E_t}\right)^2 \tag{3}$$

where τ is the duration of the current pulse, m_B is mass of the active material with no intercalant, V_M is the molar volume of the active material, M_B is the molar mass of the active material with no intercalant, A is the surface area of the electrode, and ΔE_s and ΔE_t are estimated from the GITT profile, as illustrated in (c).

References

- 1 D. Leshchev, M. Rakitin, B. Luvizotto, R. Kadyrov, B. Ravel, K. Attenkofer and E. Stavitski, *J Synchrotron Rad*, 2022, **29**, 1095–1106.
- 2 B. Ravel and M. Newville, J Synchrotron Rad, 2005, 12, 537–541.
- 3 R. B. Von Dreele, J Appl Cryst, 2014, 47, 1784–1789.
- 4 J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865–3868.
- 5 I. Abate, S. Y. Kim, C. D. Pemmaraju, M. F. Toney, W. Yang, T. P. Devereaux, W. C. Chueh and L. F. Nazar, *Angew. Chem.*, 2021, **133**, 10975–10982.
- 6 B. Song, M. Tang, E. Hu, O. J. Borkiewicz, K. M. Wiaderek, Y. Zhang, N. D. Phillip, X. Liu, Z. Shadike, C. Li, L. Song, Y.-Y. Hu, M. Chi, G. M. Veith, X.-Q. Yang, J. Liu, J. Nanda, K. Page and A. Huq, *Chem. Mater.*, 2019, **31**, 3756–3765.
- 7 N. Yabuuchi, H. Yoshida and S. Komaba, *Electrochemistry*, 2012, 80, 716–719.
- 8 M. Guaita, O. Oliveira, P. Catarini da Silva, L. Dall'Antonia and A. Urbano, *Green Materials*, 2022, **11**, 1–10.
- 9 I. I. Abate, C. D. Pemmaraju, S. Y. Kim, K. H. Hsu, S. Sainio, B. Moritz, J. Vinson, M. F. Toney, W. Yang, W. E. Gent, T. P. Devereaux, L. F. Nazar and W. C. Chueh, *Energy Environ. Sci.*, 2021, 14, 4858–4867.
- 10Y. Li, X. Wang, Y. Gao, Q. Zhang, G. Tan, Q. Kong, S. Bak, G. Lu, X.-Q. Yang, L. Gu, J. Lu, K. Amine, Z. Wang and L. Chen, *Advanced Energy Materials*, 2019, 9, 1803087.
- 11 W. E. Gent, I. I. Abate, W. Yang, L. F. Nazar and W. C. Chueh, Joule, 2020, 4, 1369–1397.
- 12R. A. House, U. Maitra, M. A. Pérez-Osorio, J. G. Lozano, L. Jin, J. W. Somerville, L. C. Duda, A. Nag, A. Walters, K.-J. Zhou, M. R. Roberts and P. G. Bruce, *Nature*, 2020, 577, 502–508.
- 13 Y. Niu, Z. Hu, H. Mao, L. Zhou, L. Wang, X. Lou, B. Zhang, D. Xiao, Y. Yang, F. Ding, X. Rong, J. Xu, W. Yin, N. Zhang, Z. Li, Y. Lu, B. Hu, J. Lu, J. Li and Y.-S. Hu, *Energy Environ. Sci.*, 2024, **17**, 7958–7968.
- 14I. Biswas, B. S. Kumar, A. Pradeep, A. Das, V. Srihari, H. K. Poswal and A. Mukhopadhyay, *Chem. Commun.*, 2023, **59**, 4332–4335.
- 15J. Kim, S. Park, S. Hwang and W.-S. Yoon, J. Electrochem. Sci. Technol, 2021, 13, 19–31.