Redox Chemistry and the Role of Trapped Molecular O₂ in Li-Rich Disordered Rocksalt Oxyfluoride Cathodes

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ABSTRACT: In the search for high energy density cathodes for next-generation lithium-ion batteries, the disordered rocksalt oxyfluorides are receiving significant attention due to their high capacity and lower voltage hysteresis compared with ordered Li-rich layered compounds. However, a deep understanding of these phenomena and their redox chemistry remains incomplete. Using the archetypal oxyfluoride, Li₅MnO₄F, we show that the oxygen redox process in such materials involves the formation of molecular O₂ trapped in the bulk structure of the charged cathode, which is reduced on discharge. The molecular O₂ is trapped rigidly within vacancy clusters and exhibits minimal mobility unlike free gaseous O₂, making it more characteristic of a solid-like environment. The Mn redox process occurs between octahedral Mn⁶⁺ and Mn⁴⁺ with no evidence of tetrahedral Mn⁵⁺ or Mn⁷⁺. We furthermore derive the relationship between local coordination environment and redox potential; this gives rise to the observed overlap in Mn and O redox couples and reveals that the onset potential of oxide ion oxidation is determined by the degree of ionicity around oxygen, which extends models based on linear Li−O−Li configurations. This study advances our fundamental understanding of redox mechanisms in disordered rocksalt oxyfluorides, highlighting their promise as high capacity cathodes.

INTRODUCTION

Advances in high energy density cathodes are crucial for the development of next-generation lithium-ion batteries for portable electronics and electric vehicles. Lithium-rich cathode materials are attracting considerable attention as they offer increased capacities by invoking redox chemistry on both the transition metal and oxide ions,¹⁻²⁶ rather than on only the transition metal as found in traditional oxide-based intercalation compounds.

Recently, there has been growing interest in disordered Li-rich intercalation materials, especially disordered rocksalt structures,²⁷⁻⁵² including early work on systems based on Li₃NbO₄ and Li₃VO₃F [refs²⁷⁻³⁰]. House et al.³⁶ presented for the first time an all-manganese oxyfluoride, Li₁₀Mn₀.₉₂O₂F₀.₉₉, with a disordered rocksalt structure, which exhibits a large capacity utilizing both Mn and O redox. This Li₅MnO₄F-based cathode has a discharge capacity of ~280 mA h g⁻¹ (corresponding to 960 W h kg⁻¹) after the initial charge, making it comparable to Li-rich layered oxides such as Li₅.₅₂(Nb₁₋₅₃Mn₀.₆₅Li₀.₃ₐ₃)O₃ and greater than conventional cathodes such as LiCoO₂ (170 mA h g⁻¹) and NMC-Li(Ni,Mn,Co)O₂ (200–220 mA h g⁻¹). Cathodes comprised of manganese (rather than cobalt or nickel) are also attractive due to its low cost, low toxicity, and high natural abundance.

Layered Li-rich cathode materials commonly undergo extensive structural rearrangement during the first charge/discharge cycle leading to a large voltage hysteresis and O₂ gas evolution at the surface; this involves a substantial loss of voltage and therefore energy density. In contrast, the disordered rocksalt Li₅MnO₄F does not exhibit such large first cycle voltage hysteresis (shown in Figure 1) and also shows minimal oxygen loss, which are major advantages of this system. These differences raise the important question: to what extent does the transition metal and oxygen redox chemistry in the ordered Li-rich layered compounds translate to disordered rocksalt systems?

In this work, combined operando X-ray absorption spectroscopy (XAS), high resolution resonant inelastic X-ray scattering (RIXS), and ab initio modeling techniques are used to elucidate and quantify the Mn and O redox chemistry as well as local structural changes upon delithiation. We show, for the first time, by experimental methods (O K-edge RIXS) and ab
initio modeling that Li removal from the rocksalt oxyfluoride is accompanied by the formation of molecular O₂ trapped inside the cathode particles. Ab initio molecular dynamics simulations show that the trapped O₂ exhibits substantially reduced freedom of mobility, making it more characteristic of a solid-like environment in line with recent solid state ¹⁷O NMR measurements for O₂ in the layered cathode Li₁.₂Ni₀.₁₃Co₀.₁₃Mn₀.₅₄O₂ [ref 26]. Previously the significance of the Li⁺−O−Li⁺ configurations in Li-rich oxides in pinning O₂p states at the top of the oxygen valence band and hence accessible for O-redox has been emphasized. Here, we show that the onset potential of oxygen oxidation varies with the number of coordinating Li⁺ ions and that, along with the strong modulation of Mn redox potential by its O/F anionic coordination environment, leads to overlap of the Mn and the O redox processes, i.e., transition metal and oxygen redox occur together in the disordered rocksalts.

RESULTS AND DISCUSSION

Disordered Rocksalt Structural Properties. Li₂MnO₂F was prepared by mechanochemical ball-milling, and the oxidation state of Mn was subsequently confirmed as +3.00(5) from iodometric titration. Li₂MnO₂F possesses a cubic rock-salt structure where each cation (Li⁺ or Mn³⁺) is octahedrally coordinated to six anions (O²⁻ or F⁻) and vice versa (illustrated in Figure 2). To investigate the possibility of local ordering, Mn K-edge extended X-ray absorption fine structure (EXAFS) and neutron pair distribution function (PDF) analysis were performed on pristine Li₂MnO₂F (the experimental methods are detailed in the Supporting Information (SI), Section S1).

The EXAFS technique is an element-specific probe of local coordination environment, in this case around Mn, giving a plot of the nearest-neighbor (NN) atoms as a function of distance from the central atom. As shown in Figure 2a, the first two peaks in the EXAFS spectrum for Li₂MnO₂F are a close match in shape and relative position to that of MnO, which has a well-defined cubic rocksalt structure. These peaks correspond to the first and second NN shells of atoms, anions and cations, respectively. Normalizing each spectrum by the first peak area, since O²⁻ and F⁻ are indistinguishable with EXAFS, permits direct comparison of the second peak area. Here, Mn is a much stronger scatterer of the photoelectron wave than Li, which is a very weak scatterer, so Mn dominates the second peak intensity. The difference in peak area between the two materials indicates a much lower amount of second NN Mn for Li₂MnO₂F than MnO, consistent with the presence of Li on the cation sites in the former. Measuring the peak intensity relative to a baseline of zero scattering from 12 Li and

Figure 1. Charge–discharge curves. Representative first cycle load curves for disordered rocksalt Li₂MnO₂F (blue) and layered Li₁.₂Ni₀.₁₃Co₀.₁₃Mn₀.₅₄O₂ (red) at a current rate of 20 mA g⁻¹. (Second cycle data are presented in Supporting Information, Figure S1).

Figure 2. Structure of Li₂MnO₂F. (a) Mn K-edge EXAFS for pristine Li₂MnO₂F compared with a MnO reference, each with cubic rocksalt crystal structure. The spectra are normalized to the area under the first peak corresponding to the occupancy of the first nearest neighbor anion site which is the same for both. A good fit of the EXAFS data can also be obtained with a rocksalt model with 4 × 2nd nearest neighbor Mn. (b) Neutron PDF data fitted to structural models of distortion-free random cubic rocksalt and the Monte Carlo derived model for pristine Li₂MnO₂F. Li, Mn, O, and F atoms are indicated by green, purple, red, and gray spheres, respectively. There is very good agreement between the models and the PDF data showing Li₂MnO₂F exhibits a close to completely disordered rocksalt structure. The slight asymmetry of the first peak at around 1.9 Å may indicate some element-specific preference for shorter bond length. Refined cell parameters a = 4.117 Å and a = 12.152 Å, b = c = 8.336 Å, and Uiso values 0.027 and 0.014, respectively.

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maximum scattering from 12 Mn (as in MnO), shows an average of 3.6 Mn as second NN for Li$_2$MnO$_2$F. This is in line with that expected from a completely random distribution of Li and Mn in a 2:1 ratio, i.e., four Mn. As further confirmation, a good fit was obtained of the EXAFS data using a rocksalt structure with six degenerate first NN O and four degenerate second NN Mn atoms, Figure 2a and Table S1.

PDF is another powerful tool for probing local structure, giving a superposed plot of all atom−atom pairs throughout the structure resolved as a function of increasing separation. Unlike EXAFS, neutron PDF can probe over much longer correlation lengths and is much more sensitive to Li, since neutrons are more strongly scattered by Li than X-rays. The fitted PDF data (Figure 2b), show that the local structure of Li$_2$MnO$_2$F can be well-described by a disordered rocksalt model indicating minimal short-range order. Together with the EXAFS data, the experimental evidence supports a close to completely disordered rocksalt structure for Li$_2$MnO$_2$F.

To obtain a computationally tractable structural model for Li$_2$MnO$_2$F capturing this disorder, a Monte Carlo random sampling approach was employed to generate a 3 × 2 × 2 unit cell which possessed a representative distribution of different sites (computational methods applied to battery cathode materials are well established$^{11,53,54}$ and detailed in the SI, Section S1). The validity of this Monte Carlo-derived model was checked by fitting to the neutron PDF data. The quality of the fit was even better than the distortion-free one showing it is a closer match to the experimentally observed structure. Furthermore, the calculated mean lattice parameter, 4.146 Å, compare well with the experimental value (a = b = c = 4.118 Å) from X-ray diffraction studies.$^{36}$ Our ab initio simulations confirm that the disordered rocksalt structure of Li$_2$MnO$_2$F does not exhibit the cooperative Jahn–Teller distortion usually associated with Mn$^{3+}$ in ordered structures, which often leads to poor cycling. The full structural data set for the pristine Li$_2$MnO$_2$F computational model is given in the SI, section S2.

Charge-compensation on Lithium Ion Extraction. To investigate the redox processes occurring over the first cycle in Li$_2$MnO$_2$F, operando Mn K-edge XANES was performed. Operando experiments allow the intercalation reaction in the cathode to be followed under operating conditions, eliminating the effect of any relaxation phenomena. As shown in Figure 3, a continuous shift in the Mn K-edge is observed during charge and discharge in line with the expected oxidation and reduction from Mn$^{3+}$ toward Mn$^{4+}$. Near the top of charge, around x ≈ 1.2 in Li$_x$MnO$_2$F, the changes become less pronounced as oxygen oxidation starts to dominate the redox process; this corresponds to a slight inflection in the electrochemical load curve. Note that previous operando electrochemical mass spectrometry studies$^{36}$ indicate that
there is negligible oxygen loss. Given that the edge continues to evolve and the voltage profile remains sloped throughout this region (Figure 1), there must be a significant degree of overlap between the Mn and O redox couples. Close analysis of the Mn K-edge pre-edge (Figure 3d), which is generally considered to be a better measure of oxidation state than the main edge, reveals a similar trend. The pre-edge shape (insets of Figure 3b,c) does not appear to change much, but there is evidence of a slight increase and decrease in intensity of the twin peaks. These peaks arise from the quadrupole-allowed transition from the Mn 1s to the Mn 3d states, which are subdivided by crystal field splitting, and are weak due to the centro-symmetry of octahedral coordination. The intensity gain can be attributed to a slight distortion of this centro-symmetry allowing mixing between the Mn 3d and 4p states. In contrast, pre-edge features for tetrahedral geometries tend to be of significantly larger intensity, often of comparable height to the main edge, reveals a similar trend.

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Interestingly, recent reports for the vanadium-based disordered rocksalt systems, Li$_{1.25}$Nb$_{0.25}$V$_{0.5}$O$_2$ and Li$_2$VO$_2$F, show XANES data indicating a strong increase in pre-edge intensity, characteristic of vanadium in a noncentrosymmetric coordination environment such as tetrahedral V$^{5+}$. Baur et al. recently confirmed the presence of tetrahedral vanadium by PDF in Li$_2$VO$_2$F, and Chang et al. report superoxide formation in this oxyfluoride from computational and EPR studies. We note that Lun et al. studied the Li–Mn–O–F chemical space to derive a capacity map of Li percolation and redox properties. In the context of Li-rich oxide structures, Hong et al. report oxidation beyond Mn in Li-rich Mn-oxides.

![Figure 4](https://dx.doi.org/10.1021/jacs.0c10270)

**Figure 4.** Manganese/oxygen redox activity and impact of local coordination environments in Li$_2$MnO$_2$F. (a) Relative contribution (%) of the Mn versus O redox processes to the overall redox activity at a given Li content (x). The data show significant overlap between Mn and O redox couples. (b) Oxidation potentials of Mn and O as a function of their coordination environment in Li$_2$MnO$_2$F; here, the Li content (x) is related to the experimentally measured voltage at that state of charge derived from Figure 1. 0Li$_3$Mn$_3$ is omitted for clarity as these O atoms did not show significant oxidation during Li extraction. (c) Change in the average oxidation state of octahedral Mn atoms in Li$_2$MnO$_2$F that are coordinated by three or more F atoms and those that are coordinated by fewer than three F atoms. (d) Change in the average oxidation state of O atoms with coordination environment in Li$_2$MnO$_2$F.
analyzed. As shown in Figure 3e,f, the first and second neighbor atoms to Mn do not change as a function of state of charge. This clearly shows Mn remains octahedrally coordinated throughout the charge/discharge cycle, with no evidence of tetrahedral Mn.

To complement our XANES and EXAFS work, we used DFT methods to examine local structures and to quantify the redox chemistry on lithium extraction from Li$_x$MnO$_2$F. As in previous studies,9,11 we stress that high level hybrid functionals were employed as they are found to be important in reproducing accurately the electronic structure of oxygen states (further details in the SI, S1 Methods). Figure 4a illustrates the overall contribution of Mn vs O redox as a function of Li content in Li$_x$MnO$_2$F derived from the ab initio calculations (Figure S2 shows the change in the average oxidation states of all the component elements of Li$_x$MnO$_2$F as Li is removed).

The results clearly show significant overlap between Mn and O redox couples with O redox activity starting from about x ≈ 1.5, well before all of the Mn has been oxidized and in accord with the XANES results; this is attributed to the disordered structure with a range of local ion environments (which we return to below). This behavior contrasts with the redox activity found in layered Li-rich ordered oxides (Figure 5) also show the strong hybridization between the Mn 3d and O 2p states, with the energy of the O-2p states raised in MnO$_2$F (Figure 5) also show the strong hybridization between the Mn 3d and O 2p states, with the energy of the O-2p states raised in MnO$_2$F (Figure 5) also show the strong hybridization between the Mn 3d and O 2p states, with the energy of the O-2p states raised.

Regarding charge compensation on Li extraction, Mn undergoes oxidation from Mn$^{3+}$ at x = 2.0 toward Mn$^{4+}$ at x = 0.75, with no evidence of any change to octahedral to tetrahedral coordination. Our DFT structural analysis also indicate that tetrahedral Mn$^{3+}$ is not formed during delithiation.

![Figure 5](https://example.com/figure5.png)

**Figure 5.** Projected density of states (pDOS) for Li$_x$MnO$_2$F. (a) Li$_2$MnO$_2$F, (b) Li$_{1.5}$MnO$_2$F, and (c) Li$_{0.75}$MnO$_2$F. The blue and red lines correspond to the Mn 3d and O 2p pDOS, respectively. For the charged structure, Li$_{0.75}$MnO$_2$F, the black bands represent the electron holes localized on molecular O$_2$. With respect to Li$_x$MnO$_2$F, the occupied states close to the Fermi level (which is set to zero) are composed of a mix of O 2p and Mn 3d states. For the charged structures, the energy of the O-2p states are raised, which promotes O redox activity.
Trapped Molecular O$_2$ in the Bulk Structure. Detailed analysis of the ab initio simulated structures of Li$_2$MnO$_2$F and Li$_{0.75}$MnO$_2$F, and the local environment of molecular O$_2$ in the bulk of Li$_{0.75}$MnO$_2$F, Li, Mn, O and F are indicated by green, purple, red, and gray, respectively. The weak Mn–O$_2$ and Li–O$_2$ interactions are indicated with dotted lines. (b) Ab initio molecular dynamics simulations of the molecular O$_2$ in the bulk cavity at 300 K showing the variation in O–O and Mn–O separations vs simulation time. The calculated O–O distances of the trapped molecular O$_2$, and the nearest-neighbor Mn–O$_2$ distances are shown in green and blue, respectively (derived at intervals of 1 ps). (c) Mean square displacements (MSDs) vs simulation time for molecular O$_2$ in the bulk cavity in comparison with free gaseous O$_2$ molecules in a very similar nanosized volume.

Figure 6. Structures and dynamics of molecular O$_2$ trapped in the bulk. (a) Calculated structures of Li$_2$MnO$_2$F and Li$_{0.75}$MnO$_2$F, and the local environment of molecular O$_2$ in the bulk of Li$_{0.75}$MnO$_2$F. Li, Mn, O and F are indicated by green, purple, red, and gray, respectively. The weak Mn–O$_2$ and Li–O$_2$ interactions are indicated with dotted lines. (b) Ab initio molecular dynamics simulations of the molecular O$_2$ in the bulk cavity at 300 K showing the variation in O–O and Mn–O separations vs simulation time. The calculated O–O distances of the trapped molecular O$_2$, and the nearest-neighbor Mn–O$_2$ distances are shown in green and blue, respectively (derived at intervals of 1 ps). (c) Mean square displacements (MSDs) vs simulation time for molecular O$_2$ in the bulk cavity in comparison with free gaseous O$_2$ molecules in a very similar nanosized volume.
which were directly compared with MSDs from simulations of free gaseous O2 molecules within a volume of the same size (Figure 6c).

Two key features emerge. First, the trapped O2 molecule has an O−O bond length that remains directly comparable to that of gaseous molecular O2 (1.21 Å) whereas the nearest-neighbor Mn−O distance (mean value of 2.33 Å) is always longer than the Mn−O bond (2.0 Å) in the solid lattice, again confirming weak O2 interactions with the host lattice. Even when the O2 molecule makes very close approach to its nearest-neighbor Mn atom, the O−O distance remains around 1.2 Å.

Second, the increase in the mean square displacement with time for free gaseous O2 (Figure 6c) clearly indicates significant molecular diffusion as expected, whereas this is not the case for the O2 in the solid particle. The results therefore indicate that while the O−O bond length might be similar between the two, the trapped molecular O2 is different from free, gaseous O2 in exhibiting substantially reduced freedom of mobility, making it more characteristic of a solid-like environment (Figure 6c); this result is in line with recent solid state 17O NMR measurements for O2 in Li1.2Ni0.13Mn0.54Co0.13O2.26 The rigid trapping of O2 within solid state 17O NMR measurements for O2 in rationalize how it could be reduced to O2 close proximity to cation centers in this cavity also helps to therefore indicate that while the O2 that formed in the fully charged samples is no longer present in the bulk material. The lack of O2 gas evolution at conditions, must be trapped within the bulk of the cathode as found from our ab initio simulations. The similarity of the peak spacing to that of gaseous molecular O2 suggests that there is minimal bonding interaction with the host lattice in agreement with the ab initio simulations, which would accord with the expectation for strong localization of electron density in the heavily hybridized O=O bond. However, as has been noted previously,65,66 the excitation energy at which these O-redox RIXS features appear is slightly higher relative to O2 in the gas phase by about 0.5 eV. This is consistent with the O2 molecules being trapped in a solid-like environment.

On discharge, the signal is no longer evident indicating that the O2 that formed in the fully charged samples is no longer present in the bulk material. The lack of O2 gas evolution at

Figure 7. High resolution RIXS data showing molecular O2 trapped in the bulk. (a) Ex situ high resolution O K-edge RIXS data collected at 531 eV excitation energy showing the presence of molecular O2 trapped in the bulk of the charged cathode particles (Li0.8MnO2F), which is reversibly reduced back to O2 on discharge. Both spectral features labeled are also observed in a reference spectrum of pure molecular O2.63 (b) The peak spacing of the vibrational progression decreases linearly with increasing energy loss (Birge–Sponer plot, upper panel) consistent with an anharmonically oscillating O2 diatomic. The initial peak spacing, equivalent to the fundamental vibration frequency (vf), is 0.192 eV (1550 cm−1) in charged Li2MnO2F corresponding closely to molecular O2 indicating negligible interaction with the cathode structure. A reference spectrum for Li2O2 is also included at 531 eV showing a fundamental vibrational frequency of 0.098 eV (790 cm−1) consistent with a peroxide O22− moiety.

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To probe experimentally the nature of oxidized oxygen in charged Li2MnO2F, O K-edge RIXS was performed at a higher resolution than previously achieved for this material.36 Previous RIXS data for charged electrodes revealed a more prominent elastic peak when exciting at −531 eV and a new energy loss feature, attributed to the formation of localized electron holes on oxygen. The new high-resolution data in Figure 7a show that the broad elastic peak can in fact be resolved into a progression of sharp peaks, as also observed for the layered O-redox material Li1.2Ni0.13Mn0.54Co0.13O2.26 This peak progression arises from the molecular vibrations of an O−O diatomic with well-defined frequency matching that of molecular O2 (1550 cm−1) and clearly distinguishable from superoxide O2− and peroxide O22− which have vibrational frequencies of around 1100 and 790 cm−1, respectively.62 The peak spacing decreases linearly with increasing energy loss (Birge–Sponer plot Figure 7b) consistent with an anharmonically oscillating diatomic. A reference RIXS spectrum for Li2O2 is also included showing a peak spacing consistent with peroxide O22− as expected, demonstrating the ability of RIXS to distinguish different O−O bond orders.

The other energy loss feature at 8 eV also belongs to molecular O2 and can be assigned to the filled π molecular orbitals. These results show that the localized electron hole states appearing at 531 eV reside on O2 molecules, which, since the RIXS experiment was performed under ultrahigh vacuum conditions, must be trapped within the bulk of the cathode as found from our ab initio simulations. The similarity of the peak spacing to that of gaseous molecular O2 suggests that there is minimal bonding interaction with the host lattice in agreement with the ab initio simulations, which would accord with the expectation for strong localization of electron density in the heavily hybridized O=O bond. However, as has been noted previously,65,66 the excitation energy at which these O-redox RIXS features appear is slightly higher relative to O2 in the gas phase by about 0.5 eV. This is consistent with the O2 molecules being trapped in a solid-like environment.
the surface during discharge from differential electrochemical mass spectrometry measurements, which, coupled with the disappearance of the O_2 signal from the RIXS data, indicates that the trapped O_2 is reduced back to O^{2-}. It is worth mentioning that O^{2-} ions and molecular O_2 are the most stable forms of oxygen.

To investigate the possibility of the RIXS features being beam-induced, we undertook low temperature measurements (20 K) to suppress sample heating by the beam. The data, Figure S5, show negligible difference between the spectra indicating no such effect. Taken together, the full outgassing of the electrode under UHV conditions and the reversible reduction of O_2 rule out O_2 being trapped anywhere other than in the particle bulk, where it can still be reversibly reincorporated back into the structure as O^{2-}. Overall, the reversible O-redox process involves O^{2-} being oxidized to form bulk molecular O_2 on charge, followed by its reduction on discharge to reform O^{2-}.

The observation of molecular O_2 in layered O-redox cathode materials and here, for the first time, in disordered rocksalts, suggests the two systems share the same O-redox mechanism, (i.e., 2O^{2-} ⇌ O_2 + 4e^{-}). However, Li_1.2Co0.13Ni0.13Mn0.54O_2 does not exhibit the commonly observed O-redox charging plateau at 4.6 V vs Li^+/Li, nor such large first cycle voltage hysteresis (Figure 1). Both phenomena have been recently linked with the irreversible loss of highly ordered honeycomb superstructures belonging to the layered cathodes. In Li_{1-x}Ni_{0.13}Mn_{0.87}O_2, all oxide ions in the honeycomb lattice will be coordinated by at least two transition metal (TM) ions (O(Li_n,TM_n)) which, during charge, are oxidized to O^{4+} at a high potential of 4.6 V. However, this honeycomb arrangement of O^{4+} is highly unstable. In-plane TM migration to form vacancy clusters occurs, causing some O to become coordinated by fewer than two TM ions which then dimerize to form stable O_2 molecules. On discharge, these vacancy clusters are repopulated by Li leading to O(Li_n,TM) and O(Li_{4-x}) configurations which remain in the structure explaining the lack of further voltage plateaus. In contrast, Li_1.2Ni_{0.13}Mn_{0.54}O_2 is already intrinsically ordered in the pristine state, possessing a range of coordination environments including some O(Li_n,Mn) and O(Li_{4-x}) regions. Therefore, O^{2-} redox can occur without such severe structural rearrangement and hence less pronounced voltage hysteresis. After the first cycle, the load curves for both compounds (Figure S2) exhibit a similar degree of voltage hysteresis in line with the presence of preformed sites for O_2 formation in both materials after discharging of the TM ions within the TM layer of Li_{1-x}Co_{0.13}Ni_{0.13}Mn_{0.54}O_2.

Our observations on Li_1.2Mn_{0.54}O_2 are unexpected in the context of previous work, which cannot be simply translated from ordered Li-rich layered compounds to disordered rocksalt oxyfluorides, and are important in future strategies to develop new high capacity cathodes.

■ CONCLUSION

The oxygen redox mechanism in the disordered rocksalt cathode, Li_{1-x}Mn_{0.54}O_2F, involves the formation of molecular O_2 trapped inside the bulk structure of the charged material, which is reversibly reduced to O^{2-} on discharge. Combined RIXS and ab initio simulation studies show that molecular O_2 is held within vacancy clusters in the structure.Bulk O_2 formation is triggered by driving the disordered rocksalt oxyfluoride structure to high degrees of Li deintercalation, such that the local coordination number decreases around oxidized O ions with local Li vacancies. The trapped molecular O_2 also exhibits minimal mobility unlike free gaseous O_2, making it more characteristic of a solid-like environment. This rigid trapping of O_2 within close proximity to cation centers also helps to rationalize how it could be reduced to O^{2-} with ease on discharge.

The Mn redox process occurs between 3+ and 4+, with no evidence of tetrahedral Mn^{3+} or Mn^{7+}. We show that the significant overlap between the Mn and O redox couples is determined by the different local coordination environments in the disordered oxyfluoride structure: more ionic Li-rich O environments (e.g., O(Li_{4-x}Mn)) are oxidized at lower voltages than the typically observed 4.6 V plateaus for layerd Li-rich oxides, whereas F-rich Mn coordination (e.g., Mn(F_2O_3)) increases the voltage for Mn oxidation, leading to the overlapping nature of the Mn and O redox processes.

Since Li_{1-x}Mn_{0.54}O_2F already possesses an intrinsically disordered structure, it avoids the extensive structural rearrangement observed in layered honeycomb cathodes resulting in reduced voltage hysteresis on the first charge/discharge cycle. This work advances our understanding of fundamental redox mechanisms in Li-rich disordered rocksalts and highlights their promise as more structurally stable oxygen-redox cathodes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://dx.doi.org/10.1021/jacs.0c10270.

Experimental and computational methods, EXAFS fitting, Buckingham potentials, DFT-computed structural data, change in oxidation states and magnetic moments, charge density of the O_2 and local environment, RIXS spectra collected at 20 and 300 K (Figures S1−S5 and Tables S1−S3) (PDF)

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REFERENCES
(1) Koga, H.; Crogueenec, L.; Ménétrier, M.; Douhil, K.; Belin, S.; Bourgeois, L.; Suard, E.; Weil, F.; Delmas, C. Reversible Oxygen Participation to the Redox Processes Revealed for Li10Mn5O16 CO11NiO4. J. Electrochem. Soc. 2013, 160, A786–A792.
(2) Sathiya, M.; Rousse, G.; Ramesha, K.; Laisa, C. P.; Vein, H.; Sougrati, M. T.; Doubler, M.-L.; Fox, D.; Gonbeau, D.; Walker, W.; Prakash, A. S.; Ben Hassine, M.; Dupont, L.; Tarascon, J.-M. Peroxo-like Dimers in High-Capacity Layered Oxides for Li-Ion Batteries. Nat. Commun. 2015, 6, 1516–1521.
(3) Oishi, M.; Yogi, C.; Watanabe, I.; Ohta, T.; Orikasa, Y.; Uchimoto, Y.; Ogumi, Z. Direct Observation of Reversible Charge Compensation by Oxygen Ion in Li-Rich Manganese Layered Oxide Positive Electrode Material, Li11Ni5Li0.5Co0.5Mn0.5O2. J. Power Sources 2015, 276, 89–94.
(4) Luo, K.; Roberts, M. R.; Guerrini, N.; Tapia-Ruiz, N.; Hao, R.; Massel, F.; Pickup, D. M.; Ramos, S.; Liu, Y.-S.; Guo, J.; Chadwick, A. V.; Duda, L. C.; Bruce, P. G. Charge Compensa tion in 3d-Transition-Metal-Oxide Inter Calation Cathodes through the Generation of Localized Electron Holes on Oxygen. Nat. Chem. 2016, 8, 684–691.
(5) Seo, D.-H.; Woo, J.; Urban, A.; Malik, R.; Kang, S.; Ceder, G. The Structural and Chemical Origin of the Oxygen Redox Activity in Layered and Cation-Disordered Li-Excess Cathode Materials. Nat. Chem. 2016, 8, 692–697.
(6) Du, K.; Zhu, J.; Hu, G.; Gao, H.; Li, Y.; Goodenough, J. B. Exploring Reversible Oxidation of Oxygen in a Manganese Oxide. Energy Environ. Sci. 2016, 9, 2575–2577.
(7) Gent, W. E.; Lim, K.; Liang, Y.; Li, Q.; Barnes, T.; Ahn, S.-J.; Stone, K. H.; McIntire, M.; Hong, J.; Song, J. H.; Li, Y.; Mehta, A.; Ermon, S.; TYlissczak, T.; Kilcoyne, D.; Vine, D.; Park, J.-H.; Doo, S.-K.; Toney, M. F.; Yang, W.; Prendergast, D.; Chueh, W. C. Coupling between Oxygen Redox and Cation Migration Explains Unusual Electrochemistry in Lithium-Rich Layered Oxides. Nat. Commun. 2017, 8, 2091.
(8) Prakash, A. S.; Ben Hassine, M.; Dupont, L.; Tarascon, J.-M. Fundamental Understanding and Practical Challenges of Anionic Redox Activity in Li-Ion Batteries. Nat. Energy 2018, 3, 373–386.
(9) Chen, H.; Islam, M. S.; Senyshyn, A.; Richter, C.; Yavuz, M.; Lee, M. H.; Jung, S. K.; Yang, W.; Seong, W. M.; Ku, K.; Tamwattana, O.; Park, S. K.; Hwang, I.; Kang, K. Voltage Decay and Minimization of Voltage Hysteresis in Oxygen-Redox Cathodes. Nat. Energy 2019, 4, 350–356.
(10) Luo, K.; Roberts, M. R.; Hao, R.; Guerrini, N.; Pickup, D. M.; McNally, D. E.; Lu, X.; Schmitt, T.; Robert, M. R., Edstrom, K.; Islam, M. S.; Bruce, P. G. Depth-Dependent Oxygen Redox Activity in Lithium-Rich Layered Oxide Cathodes. J. Mater. Chem. A 2019, 7, 25355–25368.
(11) Hua, W.; Wang, S.; Knapp, M.; Leake, S. J.; Senyshyn, A.; Richter, C.; Yavuz, M.; Binder, J. R.; Grey, C. P.; Ehrenberg, H.; Indris, S.; Schwarz, B. Structural Insights into the Formation and Voltage Degradation of Lithium- and Manganese-Rich Layered Oxides. Nat. Commun. 2019, 10, 5365.
(12) House, R. A.; Maitra, U.; Perez-Osorio, M. A.; Lozano, J. G.; Jin, L.; Somerville, J. W.; Duda, L. C.; Nag, A.; Walters, A.; Zhou, K.-J.; Roberts, M. R.; Bruce, P. G. Superstructure Control of First-Cycle Voltage Hysteresis in Oxygen-Redox Cathodes. Nature 2020, 577, 502–508.
(13) House, R. A.; Maitra, U.; Jin, L.; Lozano, J. G.; Somerville, J. W.; Rees, N. H.; Naylor, A. J.; Duda, L. C.; Massel, F.; Chadwick, A. V.; Ramos, S.; Pickup, D. M.; McNally, D. E.; Lu, X.; Schmitt, T.; Roberts, M. R.; Bruce, P. G. What Triggers Oxygen Loss in Oxygen Redox Cathode Materials? Chem. Mater. 2019, 31, 3293–3300.
(14) Eum, D.; Kim, B.; Kim, S. J.; Park, J.-H.; Woo, J.; Cho, S. P.; Yoon, G.; Lee, M. H.; Jung, S. K.; Yang, W.; Seong, W. M.; Ku, K.; Tamwattana, O.; Park, S. K.; Hwang, I.; Kang, K. Voltage Decay and Redox Asymmetry Mitigation by Reversible Cation Migration in Lithium-Rich Layered Oxide Electrodes. Nat. Mater. 2020, 19, 419–427.
(25) Gent, W. E.; Abate, I. I.; Yang, W.; Nazer, L. F.; Chueh, W. C. Design Rules for High-Valent Redox in Intercalation Electrodes. Joule. 2020, 4, 1369–1397.

(26) House, R. A.; Rees, G. J.; Perez-Osorio, M. A.; Marie, J.-J.; Boivin, E.; Robertson, A. W.; Nag, A.; Garcia-Fernandez, M.; Zhou, K.-J.; Bruce, P. G. First-cycle voltage hysteresis in Li-rich 3d cathodes associated with molecular O2 trapped in the bulk. Nature Energy. 2020, 5, 777–785.

(27) Yabuuchi, N.; Takeuchi, M.; Nakayama, M.; Shiba, H.; Ogawa, M.; Nakayama, K.; Ohta, T.; Endo, D.; Ozaki, T.; Inamasu, T.; Sato, K.; Komaba, S. High-Capacity Electrode Materials for Rechargeable Lithium Batteries: LiNbO4-Based System with Cation-Disordered Rocksalt Structure. Proc. Natl. Acad. Sci. U. S. A. 2015, 112, 7650–7655.

(28) Chen, R.; Ren, S.; Knapp, M.; Wang, D.; Witter, R.; Fichtner, M.; Hahn, H. Disordered Lithium-Rich Oxide Fluoride as a Stable Host for Enhanced Li+ Intercalation Storage. Adv. Energy Mater. 2015, 5, 1401814.

(29) Wang, R.; Li, X.; Liu, L.; Lee, J.; Seo, D.-H.; Bo, S.-H.; Urban, A.; Ceder, G. A Disordered Rock-Salt Li-Excess Cathode Material with High Capacity and Substantial Oxygen Redox Activity: Li12/13Nb12/13Mn0.5O4. Electrochem. Commun. 2015, 60, 70–73.

(30) Chen, R.; Ren, S.; Yavuz, M.; Guda, A. A.; Shapovalov, V.; Witter, R.; Fichtner, M.; Hahn, H. Li+ Intercalation in Isstructural Li1-xVO3 and Li1-xVO2F with Ox2− and Mixed Ox2-/F− Anions. Phys. Chem. Chem. Phys. 2015, 17, 17288–17295.

(31) Chen, R.; Maawad, E.; Knapp, M.; Ren, S.; Beran, P.; Witter, R.; Hempelmann, R. Lithiation-Driven Structural Transition of VO4 into Disordered Rock-Salt Li1-xVO4. RSC Adv. 2016, 6, 65112–65118.

(32) Yabuuchi, N.; Nakayama, M.; Takeuchi, M.; Komaba, S.; Hashimoto, Y.; Mukai, T.; Shiba, H.; Sato, K.; Kobayashi, Y.; Nakao, A.; Yonemura, M.; Yamanaka, K.; Mitsuhashi, K.; Ohta, T. Origin of Stabilization and Destabilization in Solid-State Redox Reaction of Oxygen Ions for Lithium-Ion Batteries. Nat. Commun. 2016, 7, 1–10.

(33) Freire, M.; Kosova, N. V.; Jordy, C.; Chateigner, D.; Lebedev, O. I.; Maignan, A.; Pralong, V.; A.; Kitchaev, D. A.; Ceder, G. A Disordered Rock-salt Li-Excess Cathode Material with High Capacity and Substantial Oxygen Redox Activity: Li12/13Nb12/13Mn0.5O4. Electrochem. Commun. 2015, 60, 70–73.

(34) Nakajima, M.; Yabuuchi, N. Lithium-Excess Cation-Disordered Rocksalt-Type Oxide with Nanoscale Phase Segregation: Li13/12Nb13/12Mn0.5O4. Chem. Mater. 2017, 29, 6927–6935.

(35) Lee, J.; Kitchaev, D. A.; Ceder, G. A.; Arcón, D.; Mägi, G.; Alwast, D.; Behm, R. J.; Fichtner, M.; Vegge, T.; Garcia Laffuma, J. M. Lithium Oxide Formation in Li1-xVO3 Cathode Material – a Combined Computational and Experimental Investigation of Anodic Redox Activity. J. Mater. Chem. A 2018, 6, 16551–16559.

(36) Crafton, M. J.; Yue, Y.; Huang, T.; Tong, W.; McCloskey, B. D. Anion Reactivity in Cation-Disordered Rocksalt Cathode Materials: The Influence of Fluorine Substitution. Adv. Energy Mater. 2020, 10, 2011500.

(37) Yue, Y.; Li, N.; Li, L.; Foley, E. E.; Fu, Y.; Battaglia, V. S.; Clément, R. J.; Wang, C.; Tong, W. Redox Behaviors in a Li-Excess Cation-Disordered Mn-Nb-O F Cathode Material. Chem. Mater. 2020, 32, 4490–4498.

(38) Euchner, H.; Chang, J. H.; Groß, A. On Stability and Kinetics of Li-Rich Transition Metal Oxides and Oxofluorides. J. Mater. Chem. A 2020, 8, 7956–7967.

(39) Liu, Y.; Ouyang, B.; Kwon, D.-H.; Hashimoto, Y.; Mukai, T.; Shiba, H.; Sato, K.; Kobayashi, Y.; Nakao, A.; Yonemura, M.; Yamanaka, K.; Mitsuhashi, K.; Ohta, T. Origin of Stabilization and Destabilization in Solid-State Redox Reaction of Oxygen Ions for Lithium-Ion Batteries. Nat. Commun. 2016, 7, 1–10.

(40) Chen, R.; Ren, S.; Maignan, A.; Pralong, V.; A.; Ceder, G. A Disordered Rock-Salt Li-Excess Cathode Material with High Capacity and Substantial Oxygen Redox Activity: Li12/13Nb12/13Mn0.5O4. Electrochem. Commun. 2015, 60, 70–73.

(41) Li, X.; Qiao, Y.; Guo, S.; Jiang, K.; Ishida, M.; Zhou, H. A New Type of Li-Rich Rock-Salt Oxide Li12/13Nb12/13Mn0.5O4 with Reversible Anionic Redox Chemistry. Adv. Energy Mater. 2019, 19, 1807825.

(42) Li, X.; Qiao, Y.; Guo, S.; Jiang, K.; Ishida, M.; Zhou, H. A New Type of Li-Rich Rock-Salt Oxide Li12/13Nb12/13Mn0.5O4 with Reversible Anionic Redox Chemistry. Adv. Energy Mater. 2019, 19, 1807825.

(43) Li, X.; Qiao, Y.; Guo, S.; Jiang, K.; Ishida, M.; Zhou, H. A New Type of Li-Rich Rock-Salt Oxide Li12/13Nb12/13Mn0.5O4 with Reversible Anionic Redox Chemistry. Adv. Energy Mater. 2019, 19, 1807825.

(44) Li, X.; Qiao, Y.; Guo, S.; Jiang, K.; Ishida, M.; Zhou, H. A New Type of Li-Rich Rock-Salt Oxide Li12/13Nb12/13Mn0.5O4 with Reversible Anionic Redox Chemistry. Adv. Energy Mater. 2019, 19, 1807825.

(45) Li, X.; Qiao, Y.; Guo, S.; Jiang, K.; Ishida, M.; Zhou, H. A New Type of Li-Rich Rock-Salt Oxide Li12/13Nb12/13Mn0.5O4 with Reversible Anionic Redox Chemistry. Adv. Energy Mater. 2019, 19, 1807825.

(46) Li, X.; Qiao, Y.; Guo, S.; Jiang, K.; Ishida, M.; Zhou, H. A New Type of Li-Rich Rock-Salt Oxide Li12/13Nb12/13Mn0.5O4 with Reversible Anionic Redox Chemistry. Adv. Energy Mater. 2019, 19, 1807825.

(47) Li, X.; Qiao, Y.; Guo, S.; Jiang, K.; Ishida, M.; Zhou, H. A New Type of Li-Rich Rock-Salt Oxide Li12/13Nb12/13Mn0.5O4 with Reversible Anionic Redox Chemistry. Adv. Energy Mater. 2019, 19, 1807825.

(48) Li, X.; Qiao, Y.; Guo, S.; Jiang, K.; Ishida, M.; Zhou, H. A New Type of Li-Rich Rock-Salt Oxide Li12/13Nb12/13Mn0.5O4 with Reversible Anionic Redox Chemistry. Adv. Energy Mater. 2019, 19, 1807825.

(49) Li, X.; Qiao, Y.; Guo, S.; Jiang, K.; Ishida, M.; Zhou, H. A New Type of Li-Rich Rock-Salt Oxide Li12/13Nb12/13Mn0.5O4 with Reversible Anionic Redox Chemistry. Adv. Energy Mater. 2019, 19, 1807825.

(50) Li, X.; Qiao, Y.; Guo, S.; Jiang, K.; Ishida, M.; Zhou, H. A New Type of Li-Rich Rock-Salt Oxide Li12/13Nb12/13Mn0.5O4 with Reversible Anionic Redox Chemistry. Adv. Energy Mater. 2019, 19, 1807825.

(51) Li, X.; Qiao, Y.; Guo, S.; Jiang, K.; Ishida, M.; Zhou, H. A New Type of Li-Rich Rock-Salt Oxide Li12/13Nb12/13Mn0.5O4 with Reversible Anionic Redox Chemistry. Adv. Energy Mater. 2019, 19, 1807825.

(52) Li, X.; Qiao, Y.; Guo, S.; Jiang, K.; Ishida, M.; Zhou, H. A New Type of Li-Rich Rock-Salt Oxide Li12/13Nb12/13Mn0.5O4 with Reversible Anionic Redox Chemistry. Adv. Energy Mater. 2019, 19, 1807825.
(58) Rana, J.; Papp, J. K.; Lebens-Higgins, Z.; Zuba, M.; Kaufman, L. A.; Goel, A.; Schmuck, R.; Winter, M.; Whittingham, M. S.; Yang, W.; McCloskey, B. D.; Piper, L. F. J. Quantifying the Capacity Contributions during Activation of Li$_2$MnO$_3$. ACS Energy Lett. 2020, 5, 634−641.

(59) Wang, X.; Huang, Y.; Ji, D.; Omenya, F.; Karki, K.; Sallis, S.; Piper, L. F. J.; Wiaderek, K. M.; Chapman, K. W.; Chernova, N. A.; Whittingham, M. S. Structure Evolution and Thermal Stability of High-Energy- Density Li-Ion Battery Cathode Li$_2$VO$_2$F. J. Electrochem. Soc. 2017, 164, A1552−A1558.

(60) Cambaz, M. A.; Vinayan, B. P.; Pervez, S. A.; Johnsen, R. E.; Geßwein, H.; Guda, A. A.; Rusalev, Y. V.; Kinyanjui, M. K.; Kaiser, U.; Fichtner, M. Suppressing Dissolution of Vanadium from Cation-Disordered Li$_{2-x}$VO$_2$F via a Concentrated Electrolyte Approach. Chem. Mater. 2019, 31, 7941−7950.

(61) Davies, D. W.; Morgan, B. J.; Scanlon, D. O.; Walsh, A. Low-Cost Descriptors of Electrostatic and Electronic Contributions to Anion Redox Activity in Batteries. IOPSciNotes 2020, 1, 024805.

(62) Radjenovic, P. M.; Hardwick, L. J. Evaluating Chemical Bonding in Dioxides for the Development of Metal−Oxygen Batteries: Vibrational Spectroscopic Trends of Dioxygenyls, Dioxygen, Superoxides and Peroxides. Phys. Chem. Chem. Phys. 2019, 21, 1552.

(63) Århammar, C.; Pietzsch, A.; Bock, N.; Holmström, E.; Araujo, C. M.; Gräsjo, J.; Zhao, S.; Green, S.; Peery, T.; Hennies, F.; Amerioun, S.; Föhlisch, A.; Schlappa, J.; Schmitt, T.; Strolov, V. N.; Niklasson, G. A.; Wallace, D. C.; Rubenson, J. E.; Johansson, B.; Ahuja, R. Unveiling the Complex Electronic Structure of Amorphous Metal Oxides. Proc. Natl. Acad. Sci. U. S. A. 2011, 108, 6355−6360.

(64) Zhuo, Z.; Liu, Y. S.; Guo, J.; Chuang, Y.; Pan, F.; Yang, W. Full Energy Range Resonant Inelastic X-Ray Scattering of O$_2$ and CO$_2$: Direct Comparison with Oxygen Redox State in Batteries. J. Phys. Chem. Lett. 2020, 11, 2618−2623.

(65) Meng, Y.; Eng, P. J.; Tse, J. S.; Shaw, D. M.; Hu, M. Y.; Shu, J.; Gramsch, S. A.; Kao, C.; Hemley, R. J.; Mao, H. K. Inelastic X-Ray Scattering of Dense Solid Oxygen: Evidence for Intermolecular Bonding. Proc. Natl. Acad. Sci. U. S. A. 2008, 105, 11640−11644.