The Impact of Oxygen Vacancies on Lithium Vacancy Formation and Diffusion in $\text{Li}_{2-x}\text{MnO}_{3-\delta}$

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Abstract

High-capacity battery cathode materials containing Li_2MnO_3 appear to be activated during the first electrochemical cycle through the generation of oxygen vacancies. These oxygen vacancies have been predicted to alter the atomistic scale structure of Li_2MnO_3 and thus impact the delithiation process. In order to understand the effects of these oxygen vacancies we computationally determine the location of lithium removal in $\text{Li}_2\text{MnO}_{3-\delta}$ ($\delta=0, 0.0625$ and 0.125) and study lithium diffusion in $\text{Li}_{2-x}\text{MnO}_{3-\delta}$. This study shows that it is energetically favorable for the lithium vacancies to form in the neighboring positions of the oxygen vacancies, suggesting that there is a strong interaction between the two vacancy types. This interaction also inhibits the diffusion of the lithium-ions, as seen in *ab-initio* molecular dynamics simulations where less hopping of lithium atoms is observed when oxygen vacancies are present. Additionally, the oxygen vacancy containing structures lead to an increase in the energy barrier for lithium hopping and the calculated diffusion coefficient decreases by ~ 5 orders of magnitude from the perfect crystal structure.

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1. Introduction

The layered excess lithium transition metal oxides of $x\text{Li}_2\text{MnO}_3-(1-x)\text{Li}(\text{Ni},\text{Co},\text{Mn})\text{O}_2$ have gained much attention due to their large reversible capacity (>200 mAh/g) (1) compared to other common cathode materials for lithium-ion batteries (LIBs) (2-5), such as LiCoO_2 (~ 160 mAh/g), LiFePO_4 (~ 160 mAh/g) and LiMn_2O_4 (~ 130 mAh/g). (6) This large reversible capacity is generally believed to come from the “activation” process of the Li_2MnO_3 component. This “activation” is observed at >4.4 V (1), which is necessary to access the Li in the Li_2MnO_3 phase. (7-9) While this material is promising, it suffers from problems such as structural instability, hysteresis, voltage decay (10-12), low rate capability (13), and poor life. These problems have prevented its practical applications.

Although there are still some arguments on whether $x\text{Li}_2\text{MnO}_3-(1-x)\text{Li}(\text{Ni},\text{Co},\text{Mn})\text{O}_2$ is mixed as a solid solution or segregated in separate domains (1, 14), it is unarguably important to understand how the Li in the Li_2MnO_3 component contributes to the observed high capacity. The Li_2MnO_3 phase was initially thought to be electrochemically inactive due to the high oxidation state (4+) of the Mn cation, thus inhibiting access to the Li cations. However, the Li_2MnO_3 component alone (15-24) and Li_2TMO_3 layered compounds (25), where TM is a combination of Mn and other transition metals or other transition metals, have been proven as high capacity cathodes as well. In them, an activation process is also necessary.

Several mechanisms have been suggested for the process of activating the Li_2MnO_3 component, such as oxidation of the O^{2-} to O^- ions (26, 27), the loss of oxygen (1, 17, 23, 27), the exchange of Li ions for H ions from the electrolyte (17), and possibly the oxidation of Mn^{4+} (15). Several studies have modeled the Li removal process in Li_2MnO_3 to mimic the activation process of $\text{Li}_2-x\text{MnO}_3$. (28-32). These studies detailed the sequence of Li being removed from either Li layer or

transition metal layer, and proved that it is energetically favorable to release O_2 after a large amount of Li being removed (such as $x > 1$ (28)). Thus, the oxygen loss contribution to the increase in capacity is still one of the most important and commonly accepted mechanisms, no matter whether the oxygen is lost from the bulk or the surface of the cathode. Lee and Persson (28) suggested that the oxygen diffusion barrier is too large for oxygen to be removed from the bulk and therefore it is removed from the surface. Oxygen vacancies can also be formed during material synthesis, as suggested by experiments (33) and modeling (34). Regardless, it is likely that oxygen vacancies facilitate the high capacity, such that the cathode material should be written as $Li_{2-x}MnO_{3-\delta}$ during electrochemical cycling, where δ denotes the oxygen nonstoichiometry. To improve the subsequent durability and performance of this material after the activation process, we must understand how oxygen vacancies in $Li_2MnO_{3-\delta}$ impact the delithiation process, structural change, and the rate performance of the $Li_{2-x}MnO_{3-\delta}$ phase.

It has been demonstrated that oxygen vacancies can change the transition metal diffusion. It is well established that degradation of the Li-excess layered $xLi_2MnO_3-(1-x)Li(Ni,Co,Mn)O_2$ phase is related to the transformation from layered to spinel (14, 35-38) which starts from Mn diffusion from the transition metal layer to the Li layer (39). Computational studies have shown that the oxygen vacancies decrease the energy barrier for the transition metal migration (40, 41). Because the spinel phase has lower energy and capacity than the layered phase, this is likely to be the fundamental reason for the voltage decay and hysteresis observed in this material. While various methods (1)(5) are pursued to prevent the phase transformation and maintain a layered structure, another technical challenge, its low intrinsic rate performance (13), is still unsolved.

It is not clear if oxygen vacancies will alter Li diffusion as well. Practically, $xLi_2MnO_3-(1-x)Li(Ni,Co,Mn)O_2$ also has the disadvantage of low intrinsic rate performance (13). Without the

proper kinetics, the high voltage and high capacity region cannot be accessed in practical applications. For example $x\text{Li}_2\text{MnO}_3-(1-x)\text{Li}(\text{Ni},\text{Co},\text{Mn})\text{O}_2$ exhibits very high resistance at low state of charge (SOC) (42), where the resistance increases rapidly and lowers the usable energy obtained with normal charge-discharge conditions in practical applications. This dramatic resistance increase occurs at lower SOC, when the $\text{Li}_{2-x}\text{MnO}_{3-\delta}$ participates in delithiation/lithiation. Galvanostatic intermittent titration technique with electrochemical impedance spectroscopy measurements (42) and direct observation on the reaction kinetics for each element (13) clearly suggested that the underlying high resistance is caused by the $\text{Li}_{2-x}\text{MnO}_{3-\delta}$ phase after the activation process. With the existing experimental evidences, it is still not possible to determine whether slow electron or slow Li ion transport is responsible for the high resistance. However, the computed band gap for Li_2MnO_3 is ~ 2.1 eV (29) (comparable to $\text{LiCoO}_2 \sim 2.7$ eV), thus the high resistance is more likely to be caused by slower Li-ion diffusion. Xiao et al. studied Li diffusion within Li_2MnO_3 using *ab-initio* molecular dynamics (AIMD) simulations, without considering any vacancies and at 3000 K, a temperature appeared to melt the lattice.(29) However, the oxygen and lithium vacancies may be strongly correlated, making a computational study of the kinetics of the $\text{Li}_{2-x}\text{MnO}_{3-\delta}$ component of great interest. Shi *et al.* have discovered that Li diffusion is strongly correlated with neighboring oxygen ions in Li_2CO_3 (43, 44), more specifically, lower oxygen coordination around the moving Li ions leads to higher diffusion energy barrier. This suggest that losing oxygen in $\text{Li}_{2-x}\text{MnO}_{3-\delta}$ may hinder Li diffusion and thus it is important to study Li diffusion kinetics with and without oxygen vacancies.

As discussed above, oxygen vacancies (although the actual amount may be unknown) generated during material synthesis and/or the “activation” process can have a profound impact on the durability and performance of $\text{Li}_2\text{MnO}_{3-\delta}$. Therefore, it is critical to understand the effect of

oxygen non-stoichiometry (δ) on the structural change and diffusion in $\text{Li}_{2-x}\text{MnO}_{3-\delta}$ and related compounds. Although the simultaneous removal of lithium and oxygen as Li_2O has been widely used to estimate δ , Meng et al. took this estimation further and compared it to a Rietveld refinement of the structure after cycling and suggested that δ was significantly less than the amount required to give the observed extra capacity, assuming oxygen vacancies were formed as Li_2O . (45). Experimentally, the investigations of oxygen non-stoichiometry in these materials have been limited by the lack of *in-situ* measurements of the non-stoichiometry as a function of the state of charge (i.e., Li content). Computationally, on the other hand, it is quite easy to control the oxygen non-stoichiometry, δ , and study of the effect of oxygen non-stoichiometry, δ , on Li vacancy formation and Li diffusion, providing the insight on the capacity and rate performance of this material.

Therefore, this study presented here is focused on using DFT calculations to analyze the formation of oxygen and lithium vacancies individually in section 3.1 and the effects of oxygen vacancies on the delithiation process of $\text{Li}_{2-x}\text{MnO}_{3-\delta}$ in section 3.2. Additionally, this study used AIMD to track Li diffusion in $\text{Li}_{2-x}\text{MnO}_{3-\delta}$ at 1500 K to avoid melting of the system and to analyze the effects of oxygen vacancies on Li diffusion in section 3.3. The energy barriers of lithium diffusion was additionally calculated to estimate the diffusion coefficients with and without oxygen vacancies in section 3.3. Section 3.4 contains open circuit voltage (OCV) calculation results and discussions on how V_{O} changes the subsequent capacity, voltage, and diffusion in $\text{Li}_{2-x}\text{MnO}_{3-\delta}$ and related compounds.

2. Computational Details

The Vienna *Ab initio* Simulation Package (VASP) (46-49) was used to perform plane wave density functional theory (DFT) calculations. Potentials constructed with the full potential projector augmented wave (PAW) method (50, 51) were used for the elemental constituents. The exchange-correlation part of the density functional was treated with the generalized gradient approximation (GGA) as parameterized by Perdew, Burke and Ernzerhof (52, 53) with a Hubbard U correction (so called GGA+U method). The U parameter was chosen to be 4.84 eV for Mn, a similar value to literature.(29-31) Valence electron configurations for the elemental constituents were as follows: Li-1s²2s¹, Mn-4s²3d⁵, and O-2s² 2p⁴. In all calculations, the electronic degrees of freedom were converged to 10⁻⁶ eV. During ionic position optimization, the Hellmann–Feynman force components on each atom were relaxed to 0.02 eVÅ⁻¹.

Prior to the vacancy calculations, the structure (lattice parameters and ionic positions) of the conventional cell of Li₂MnO₃ (C2/m) were optimized, as shown in Figure 1. For this purpose, a plane-wave basis cutoff energy of 550 eV and a **k**-points mesh of 3x3x3 for Brillouin zone sampling were found to be adequate to give an energy convergence of 0.2 meV/atom for the primitive cell. The minimized lattice parameters are listed in Table 1 and compared with literature values determined by calculation and experiments. Our calculated lattice parameters are only less than 2% different from the experimental values, likely to be due to the under binding of GGA, validating the parameters used in DFT calculations.

All reported vacancy calculations were performed on the 2x1x2 supercells (96 atoms for perfect Li₂MnO₃). From this starting structure Li₂MnO₃, one or two oxygen atoms were removed to form oxygen vacancy (V_O) containing structures as $\delta = 0.0625$ and 0.125 in Li₂MnO_{3- δ} , respectively. A continuous lithium vacancy (V_{Li}) generation simulation was designed to mimic the delithiation process at different oxygen vacancy concentrations. To be more general, we note

the simulation structure as $\text{Li}_{2-x}\text{MnO}_{3-\delta}$, where the lithium vacancy concentration x increases, as $x = 0, 0.0625, 0.1250, 0.1875$ and 0.2500 , while the oxygen vacancy concentration δ varies, as $\delta = 0, 0.0625$ and 0.1250 . At a given δ value, the continuous delithiation simulation was performed by generating various new configurations with one more Li vacancy added to the minimized structure for the previous x value, until a configuration with minimized energy is found. This process repeats itself to increase x values. Although, there are many possible configurations at a given x and δ combination, a general trend between Li vacancy formation energy and its distance from the oxygen vacancy was discovered. This relationship allows us to identify quickly the configurations with the lowest energy, instead of sampling all possible vacancy arrangements. In fact, calculations on a smaller $2 \times 1 \times 1$ supercell allowed sampling all possible lithium positions at each concentration, suggesting the same trend. More specific details of the sampling and the minimized configurations are discussed in sections 3.1 and 3.2. The configurations with the lowest energies at each x and δ in $\text{Li}_{2-x}\text{MnO}_{3-\delta}$ was taken as the minimized structure for further analysis and the energies were used to compute the formation energy. Assuming one more Li is removed from $E_{\text{Li}_{2-x_1}\text{MnO}_{3-\delta}}$ to form $E_{\text{Li}_{2-x_2}\text{MnO}_{3-\delta}}$, or in other words, the Li extraction from the structure with x_1 amount of lithium initially leads to the final structure with x_2 amount of lithium removed, the V_{Li} formation energy was calculated as

$$E_{f, \text{Li vacancy}} = E_{\text{Li}_{2-x_2}\text{MnO}_{3-\delta}} + E_{\text{Li,metal}} - E_{\text{Li}_{2-x_1}\text{MnO}_{3-\delta}} \quad (1)$$

To investigate the impact of oxygen vacancy on the diffusion of Li, *ab initio* molecular dynamics (AIMD) implemented in VASP were used. The AIMD simulations were performed on $2 \times 1 \times 2$ cells of approximately 96 atoms at 1500 K using the Nosé (54) thermostat. Systems of $\text{Li}_{2-x}\text{MnO}_{3-\delta}$ were analyzed for $x = 0.0625, 0.1250$ and $\delta = 0, 0.0625$. Diffusion was studied by tracking the displacement of the lithium and oxygen atoms from their initial positions.

Additionally, the climbing image nudged elastic band (cNEB) method implemented in VASP was used to calculate energy barriers for lithium diffusion.(55, 56)

3 Results and Discussion

3.1 Separate Oxygen Vacancy and Lithium vacancy formation

Before investigating the impact of oxygen vacancies on the formation of lithium vacancies, the location of the oxygen vacancies must be determined. The first V_O was determined by calculating the energy of two systems with either a V_O at the $8j$ or $4i$ position (unique Wyckoff positions for O) and comparing the system energies. It was found that the first V_O on the $8j$ site was more energetically favorable by 0.36 eV. However, this was unexpected at a first glance, since the bond length between the $8j$ oxygen ion and Mn was shorter than the bond length between the $4i$ oxygen ion and Mn. Therefore, we estimated the electrostatic energy ($E_{electrostatic}$) of both positions of oxygen using their nearest neighboring four Li and two Mn ions, their respective charges (q_{Li} , q_{Mn} , q_O) and the distance between the oxygen and the neighboring atom (r).

$$E_{electrostatic} = q_O \left(\sum \frac{q_{Li}}{r} + \sum \frac{q_{Mn}}{r} \right) \quad (2)$$

Thus, the oxygen ion at the $4i$ position had a more attractive electrostatic energy than the oxygen ion at the $8j$ position by 0.05 eV or 0.17 eV, when the classical or Bader point charges was used, respectively. Thus, it will be more energetically favorable to remove the oxygen at the $8j$ position. This observation is consistent with previous calculations done by Okamoto et al., showing that V_O at the $8j$ position is energetically more favorable than the $4i$ position by 0.4 eV.

The predicted V_O formation energy (on $8j$ site) is 2.1 eV. For the system with two V_O , or $\delta=0.1250$, the most energetically favorable position for the second V_O was in an $8j$ position 3.1 Å

from the first V_O . The energy of formation of the second vacancy was 0.05 eV smaller than the energy of formation of the first oxygen vacancy, and thus 0.05 eV smaller than the energy required to remove a second oxygen atom far from the initial V_O .

From the system with no V_O , a lithium atom from each unique Wyckoff position ($4h$, $2b$, and $2c$ shown in Figure 1) was removed. A DFT calculation was performed to relax the atomic positions and the system energies were compared. For the system without V_O the V_{Li} were formed in the $4h$ position, consistent with Okamoto.⁽³¹⁾ The V_{Li} at the $4h$ position was more favorable than the V_{Li} at the $2b$ position by 0.18 eV and 0.05 eV more favorable than the V_{Li} at the $2c$ position. Due to the small energy difference between these positions, it is likely that Li can sample all of these positions at room temperature.

3.2 Impact of Oxygen Vacancies on Lithium Vacancy Formation

For the systems with oxygen vacancies, lithium vacancies were introduced into the system one at a time. Preliminary simulations on a $2 \times 1 \times 1$ supercell suggested that lithium vacancies tend to form near oxygen vacancies. Therefore, the sampled structures include lithium atoms being removed from all possible positions near the V_O and a few more positions farther away to confirm the trend. The formation energy of the last generated V_{Li} according to Equation (1) are correlated with the distance between V_O and V_{Li} in Figure 2. For the system with one V_O the distance was defined using the optimized coordinates of the oxygen site in the perfect cell and the optimized coordinates of the Li atom in the oxygen vacancy containing structure prior to it being removed. When there are two oxygen vacancies, the center position of the two oxygen atoms in the perfect cell was used to compute the distance with the Li vacancy.

From Figure 2a it is apparent that the formation energy for V_{Li} in the first nearest neighbor sites is the lowest and the formation energy for the V_{Li} far away from the V_O appears to plateau at an energy which is much higher. However, when the third and fourth V_{Li} are formed, the formation energy difference between the V_{Li} far away or near the V_O diminishes, suggesting that the effect of the V_O becomes more delocalized as more lithium is removed. Additionally, the V_{Li} which formed in the second nearest neighbor positions, seen in Figure 2b at around 3.5 Å away from the V_O , have an energy higher than the energy at the plateau. This is thought to be because as the first Li nearest neighbors to the V_O repel each other and move farther away from the V_O , while the second nearest Li neighbors move slightly towards the V_O and towards the oxygen they share with the first nearest neighbor Li positions. This structural relaxation makes the second nearest Li neighbors to V_O more strongly bonded to oxygen, thus energetically less favorable to remove.

A similar analysis was performed for the starting system with two V_O from which lithium atoms were removed in Figure 2b. This analysis suggest that V_{Li} tended to form near the existing two V_O initially as the energetically favored V_{Li} formation energies mostly increased with distance between the V_O and V_{Li} and plateaued at large distances. This trend was consistent with the results on a smaller supercell. However, as the third and fourth V_{Li} are formed, the dependence of V_{Li} on its distance to the V_O s is diminishing, as the formation energy of V_{Li} near V_O is significantly closer to the formation energy of V_{Li} far away from V_O . The formation energy of V_{Li} are lower than those in Figure 2a with only one V_O , suggesting the two V_O have a synergistic effect on the V_{Li} formation.

The configurations with the lowest Li vacancy formation energies were plotted in Figure 3 with the V_{Li} colored yellow and labeled with the numbers indicating the order in which they are removed. It appeared that for the starting systems with V_O , the V_{Li} tended to cluster near the

present V_O . When there is only one oxygen vacancy, the first Li to be removed comes from the Li layer (site $4h$), and the second comes from the transition metal layer (site $2b$), and the third and fourth come from site $2c$ and $4h$ in the Li layer (Figure 3a). The two V_{Li} form a dumbbell structure around the oxygen vacancy, noted as $V_{Li}-V_O-V_{Li}$. When there are two oxygen vacancies, the first two Li atoms were removed from the Li metal layer and then transition metal layers, while the final configuration shows two $V_{Li}-V_O-V_{Li}$ dumbbell structures. These lithium sites closest to the V_O are the easiest to be removed during delithiation, but the last to be filled during lithiation due to the formation energy difference.

3.3 Impact of Oxygen Vacancies on Lithium Diffusion

AIMD simulations were performed on a few energetically favorable configurations of $Li_{2-x}MnO_{3-\delta}$, as determined by DFT calculations. These initial configurations are listed in Figure 4 and they either contained a single V_{Li} ($x=0.0625$ and $\delta=0$), a single V_{Li} and a single V_O ($x=0.0625$ and $\delta=0.0625$), or two V_{Li} and a single V_O ($x=0.125$ and $\delta=0.0625$). AIMD was performed at 1500K. Some literature have reported Li diffusion simulations at 3000K without any V_{Li} (29) nor V_O . However, we noticed that the lattice became disordered or melted at 3000K in AIMD. At 1500 K, most of the atoms are still vibrating around their lattice positions and hopping of atoms can be clearly tracked by analyzing the trajectory (the frequency of atomic structures writing is 0.02ps) during the 50ps of the AIMD simulations.

The system with one V_{Li} and no V_O showed significant displacement of the lithium atoms. The displacement of every lithium atom from its initial positions was tracked and only those which moved significantly are shown in, Figure 5a, while the displacement of others are almost zero indicating vibration and are not shown. Hopping of Li atoms at a step of $\sim 3\text{\AA}$ can be seen in Figure 5a. The trajectory also shows that the V_{Li} only moved on the Li layer. Each hopping

corresponds to one Li atom switching position with the Li vacancy. The V_{Li} position was determined by comparing the snapshots of the AIMD trajectory to the perfect crystal structure and defining the V_{Li} position as the position of the Li atom missing from the perfect crystal structure. To quantify the movement of V_{Li} , its position was tracked every five picoseconds and is shown in Figure 5b. One Li hopped away then back (the blue curve in Figure 5a). Other than that, the hopping events of Li and vacancy are well correlated. Multiple vacancy hopping events occurred during 50ps.

Figure 4b shows the minimum energy configuration for V_O and one V_{Li} was the configuration where they were in neighboring $8j$ and $4h$ Wyckoff positions, respectively. The AIMD results showed little movement of the V_{Li} in Figure 6a, and mainly vibrational movement of the V_{Li} , suggesting that it is unfavorable for Li atoms to be near the V_O and thus the V_{Li} and V_O vacancies cluster together. On the other hand, it also proved that this configuration is indeed an energetically favorable position for V_{Li} , and escaping from this position is energetically unfavorable. As V_{Li} and V_O tended to cluster in the most energetically favorable configurations, determined by DFT calculations, these vacancies tended to cluster together even at 1500K. This led to the V_O blocking diffusion of the lithium atoms. To further demonstrate this effect, a system was setup with the V_O and V_{Li} farther apart (Figure 4c). The displacement of the lithium atoms, Figure 6b, and oxygen atoms, Figure 6c, were then tracked. The lithium and oxygen atoms both moved such that the final positions of the lithium and oxygen vacancies were in neighboring layers, back to a clustered V_O - V_{Li} configuration.

The DFT optimized system with the V_{Li} - V_O - V_{Li} dumbbell structure (Figure 4d) was also investigated with AIMD. Initially, the V_O was located at the $8j$ position and the V_{Li} were at a $4h$ position in the lithium layer, and at a $2b$ position in the transition metal layer. No significant

movement, other than vibrations, of the O atoms was seen. However, there was some significant movement of Li atoms, shown in Figure 6d. The majority of the Li movement was the $2b$ V_{Li} in the transition metal layer moving to a lithium layer and then hopping within that layer. The only movement of the $4h$ V_{Li} that neighbored the $8j$ V_O was seen by one Li atom, which moved into that V_{Li} for a short time period, seen by the blue line in Figure 6d. This is an interesting observation, as it may suggest that one V_{Li} is much more tightly bounded to the V_O than the second one, and likely the rest of V_{Li} , since they are further away from the V_O . This is also consistent with the V_{Li} formation energy results, as the formation energy of V_{Li} increase with the x and the distance from the V_O . These AIMD results show that fewer or no hopping occurred after oxygen vacancy formation, suggesting oxygen vacancies hinder the diffusion of Li atoms.

Although multiple hopping events can be observed at 1500K with 50ps AIMD, this timescale is still too short to compute the diffusion coefficient with the mean displacement method. Therefore, we performed cNEB calculations to quantitatively compare the Li vacancy hopping barrier with and without oxygen vacancies. According to the sequences of Li to be removed from the structure with one V_O (Figure 3a), two diffusion paths were computed: Li and vacancy hopping between Wyckoff positions ($4h$, $2c$), within the Li layer, and ($2c$, $2b$), between the Li layer and the transition metal layer. These cNEB calculations were performed with and without a single V_O , Figure 7. The energy barrier for V_{Li} hopping between the $4h$ and $2c$ positions within the lithium layer was higher than the barrier along the hopping pathway between the $2c$ and $2b$ positions through the transition metal layer to the lithium layer. This observation is consistent with Xiao's DFT+U results.⁽²⁹⁾ Additionally, the energy barriers increased significantly due to the nearby V_O . For V_{Li} hopping between the $4h$ and $2c$ positions, the forward energy barrier increased from 0.78 eV to 1.01 eV and the reverse hopping energy barrier increased from 0.83

eV to 1.20 eV. For V_{Li} hopping between the $2c$ and $2b$ positions, the forward energy barrier increased from 0.55 eV to 0.91 eV and the reverse hopping energy barrier increased from 0.69 eV to 0.98 eV. To make comparisons with experimental measurements, the computed hopping barrier, E_A , and hopping distance, a , can be used to calculate diffusion coefficient with a standard random diffusion coefficient via,

$$D_{rw} = \nu a^2 \exp\left(-\frac{E_A}{k_B T}\right), \quad (3)$$

where k_B is the Boltzmann constant, T is the temperature, and ν is the vibrational frequency.

The value of ν in Eq. (3) was estimated as 10^{13} Hz, as commonly used in the literature. (57-62) As a comparison to the MD results, the number of hops expected in the 50 ps simulated time period was estimated by using the hopping frequency, $p = \nu \exp(-E_A/(k_B T))$. The MD results for the system with one Li vacancy and no oxygen vacancy ($x=0.0625$ and $\delta=0$) was used as a comparison for simplicity. Based on the E_A of Li hopping within the Li layer, because the AIMD simulation showed lithium diffusion on the lithium layer only, it was calculated that ~1 lithium atom should hop within 50 ps at the simulated 1500 K. This is consistent with the 4 lithium atoms hops observed in the AIMD simulation. This also supports the choice of vibrational frequency $\nu=10^{13}$ Hz for diffusion coefficient calculations. It is also estimated that it would require about 1100 ps for a hop to be observed at 1000 K and would be computationally too expensive for AIMD. Thus 1500 K was an appropriate temperature in terms of being high enough to see diffusion in a reasonable computation time and low enough to prevent the structure from melting or being significantly distorted.

D_{rw} was then calculated for both Li ion migrations ($4h \leftrightarrow 2c$ and $2c \leftrightarrow 2b$) according to Eq. (3).

The value of a was estimated to be 2.9 Å. The average value of E_A was chosen as an average of

the forward and reverse hopping barrier between the $4h$ and $2c$ positions, *about* 0.81 eV with no V_O and about 1.1 eV for the system with one V_O . At $T=300K$, the calculated D_{rw} is $2.5 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ for the system with no V_O and $2.2 \times 10^{-21} \text{ cm}^2 \text{ s}^{-1}$ with V_O , five orders of magnitude smaller. For the $2c \leftrightarrow 2b$ hopping, the average E_A values were again used, about 0.62 eV for the system without V_O and about 0.95 for the system with one V_O , and the value of a was estimated as 2.9 Å. The value of D_{rw} at $T=300K$ was calculated to be $3.3 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ without V_O and $1.01 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1}$ with V_O present, five orders of magnitude lower. Note we only used the diffusion barrier near the V_O to estimate the D_{rw} for the system with V_O , if the V_{Li} hopping occurs far away from the V_O , the effect of V_O will be reduced. Thus, this estimation represents the lower bound of D_{rw} in a V_O containing structure. The estimated D_{rw} for the system without oxygen vacancies is smaller compared to the estimated value of $4.78 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ determined for uncycled Li_2MnO_3 from muon-spin rotation and relaxation experiments (63, 64) but closer to $10^{-14} \sim 10^{-18} \text{ cm}^2 \text{ s}^{-1}$ obtained for $0.5\text{Li}_2\text{MnO}_3\text{-}0.5\text{LiMn}_{0.42}\text{Ni}_{0.42}\text{Co}_{0.16}\text{O}_2$ at higher activation voltage (in the activated Li_2MnO_3 phase). (42)

Using D_{rw} to interpret the computational results corresponds to a lower bound value, since it assumes oxygen vacancies impact all of the atomic jumps. While this permitted the approximate comparisons above, it is important to note that simple random walk statistics are not valid here (i.e. if the oxygen vacancies have the predicted effect on diffusion). Specifically, the oxygen vacancies should lead to correlation effects. In general, $D = f D_{rw}$, where the correlation factor, f , describes deviations from random walk behavior (65). Even a standard substitutional diffusion of a tracer atom based on random vacancy motion leads to $f = 0.56$ for the two dimensional hexagonal lattice considered below (65);, because of correlations between the motion of the tracer and a neighboring vacancy. When f is this large it is often neglected, however, in $\text{Li}_2\text{-}$

$x\text{MnO}_{3-\delta}$, the predicted changes in both the formation energy and the mobility of Li vacancies will potentially lead to much larger correlation effects. A full analysis of these effects in different crystallographic directions is beyond the scope of this paper. However, to demonstrate the implications of oxygen vacancies on Li diffusion, it is instructive to consider Li diffusion in the Li layers as a relatively simple example (i.e. a 2D problem). A simplified treatment can be obtained by defining only sites that are fully surrounded by occupied oxygen positions (A sites) and those that are adjacent to an oxygen vacancy (B sites). The Li diffusion coefficient in this plane can then be described as (65):

$$D = \frac{\overline{R_n^2}}{6t} = \frac{a^2}{6} \frac{n}{t} \quad (4)$$

$$\frac{n}{t} \cong 6 \omega_{AA} [V'_{Li}] (1 - \eta_o) f_c \left[\left(\frac{(1 - \eta_o)}{1 + \frac{\omega_{AB}}{\omega_{AA}} \frac{K_{VO} \eta_o}{(1 - \eta_o)}} + \frac{K_{VO} \eta_o}{\frac{\omega_{BA}}{\omega_{AA}} + \frac{\omega_{BB}}{\omega_{AA}} \frac{K_{VO} \eta_o}{(1 - \eta_o)}} \right) \right]^{-1} \quad (5)$$

$$K_{VO} = \exp \left[\frac{-(\Delta G_{VO}^o - \Delta G_{VL}^o)}{k_B T} \right] \quad (6)$$

where n is the total number of atomic jumps taken in time, t , $[V'_{Li}]$ is the mole fraction of Li vacancies, and η_o is the fraction of the Li sites that are adjacent to oxygen vacancies. In Eq. (5), the frequencies ω_{ij} refer to jumps between a Li atom in site i (A or B), to a vacant site j (A or B). The thermodynamic quantity K_{VO} , is based on the free energies of forming Li vacancies around fully occupied oxygen sites (ΔG_{VO}^o) and adjacent to a vacant oxygen site (ΔG_{VL}^o). A factor f_c is retained here to describe additional correlation effects that extend beyond the assumptions that lead to Eq. (5).

Two limiting cases of Eq. (5) are worth noting. In fully stoichiometric material, the limiting diffusion coefficient at $\eta_O = 0$ is $D(0) = a^2 \omega_{AA} [V'_{Li}] f_C$. With higher η_O , large ω_{AA} (compared to the other ω_{ij}), and the assumption that neighboring oxygen vacancies are not likely (i.e. such that the ω_{BB} term is negligible), Eqs. (4) and (5) can be used to obtain the following approximation for f :

$$f(\eta_O) = \frac{D(\eta_O)}{D(0)} \cong \frac{(1 - \eta_O) \omega_{BA}}{K_{VO} \eta_O \omega_{AA}} \quad (7)$$

This result provides a relatively simple demonstration of the expected impact of oxygen nonstoichiometry, δ , on the Li diffusivity. Note here that $\omega_{BA} / \omega_{AA}$ is the same ratio obtained by comparing D_{rw} values with and without oxygen vacancies, where the computational results predicted values of 10^{-5} or smaller. The remaining part of the right hand side of Eq. (7) is the ratio of Li vacancies on A and B sites. The DFT results in section 3.2 indicate that $K_{VO} > 1$. Thus with η_O values of several percent, the ratio $(1 - \eta_O) / K_{VO} \eta_O$ is expected to be on the order 10. While this increases the value of $f(\eta_O)$, the approximation in Eq. (7) still indicates that oxygen vacancies are expected to produce large decreases in the Li diffusivity. A more detailed kinetic Monte Carlo simulation will be used to further explore the Li diffusion as a function of x and δ value in $\text{Li}_{2-x}\text{MnO}_{3-\delta}$ in the near future.

3.4 Impact of Oxygen Vacancies on Voltage Curve and resistance

After understanding how Li was removed with respect to the oxygen vacancy concentration and locations and how oxygen vacancy impact Li diffusion, the DFT determined V_{Li} formation energies in the continuous Li removal simulation were used to calculate the OCV. For each x and δ value in $\text{Li}_{2-x}\text{MnO}_{3-\delta}$ a corresponding OCV was calculated using Equation 8. The V_{Li} formation energies were the lowest energy of formation calculated for each x and δ combination.

$$OCV = \frac{E_{f, Li\ vacancy}}{e} \quad (8)$$

These OCV values were then plotted against the calculated theoretical capacity and x values in Figure 8. This figure shows that an increasing amount of V_O allows for a higher capacity at the same cutoff voltages ($\sim 4.4V$ for example as a practical cutoff voltage to avoid oxidation of the electrolyte). The role of Li_2MnO_3 in cycling of excess lithium material $xLi_2MnO_3-(1-x)Li(Ni,Co,Mn)O_2$ can be understood as the following. During the activation process, Li_2MnO_3 loses x Li and δ O, becoming $Li_{2-x}MnO_{3-\delta}$. Considering V_O makes neighboring lithium atomic positions energetically less favorable, the Li atoms near V_O are the first to be removed. Comparing with the atomic configurations in Figure 3, it seems the $V_{Li}-V_O-V_{Li}$ dumbbell structures is favored, so this may be the structure after Li_2O release. However, as shown in the OCV curve, the values and the ratio of x and δ will be determined by the activation voltage. During re-lithiation process, if we consider the oxygen vacancy concentration will not change (although several experimental literature results suggest the change of δ), x amount of Li can be re-intercalated. Based on the formation energy, the sites next to V_O are the last to be filled. However, if the cutoff voltage is not low enough, less than x amount of Li will be re-intercalated, leaving some Li sites near the V_O empty. However due to the large hopping barrier of the Li next to the oxygen vacancy, the diffusion becomes sluggish at lower voltage (or lower state of charge) in the following cycles. Considering the AIMD results showing that one V_{Li} is much more tightly bounded to the V_O than the rest (Figure 6d on two V_{Li} and one V_O case), we can propose that although 2δ lithium capacity can be accessed in the Li_2MnO_3 component, only δ lithium capacity is kinetically accessible from Li_2MnO_3 . This, along with the irreversible structure change, might contribute to the irreversible capacity after the Li_2MnO_3 component is activated. Therefore, the oxygen vacancy amount needs to be well controlled during the activation process.

4. Conclusions

DFT calculations were combined with AIMD calculations to study the effect that oxygen vacancies have on the formation of lithium vacancies and the diffusion of lithium. The most energetically favorable locations of the V_{Li} in systems already containing V_O are in the neighboring positions of the V_O . A trend of increasing energy of formation of the V_{Li} with increasing distance from the V_O was also observed, suggesting that the V_{Li} closest to the V_O would be the first to be removed during the delithiation process and the last to be replaced during the relithiation process. Additionally, the first two V_{Li} generated in the system tended to form “dumbbell” structures around each V_O with one of the V_{Li} in the neighboring lithium layer and one in V_{Li} the neighboring transition metal layer.

During the AIMD simulations less Li atoms “hopped”, i.e. moved to neighboring positions, with oxygen vacancies present. In particular, it was observed that when one V_O and one V_{Li} were placed in their energetically most favorable positions only one V_{Li} “hopped” and only for less than 5 ps before hopping back to its original position. However, when a second V_{Li} was added in the most energetically favorable position, a significant amount of “hopping” of Li atoms was observed. This combined with the DFT results seems to suggest that while the ratio of V_{Li} which are energetically accessible in $Li_2MnO_{3-\delta}$ with to the amount of V_O created may be 2:1, it appears that only a 1:1 ratio may be kinetically accessible and this might contribute, along with structure change, to the irreversible capacity loss observed after the “activation” of the Li_2MnO_3 component. The effect of V_O on lithium diffusion was then quantitatively observed in the energy barrier for lithium migration increasing with V_O present and the diffusion coefficient decreasing by ~5 orders of magnitude with V_O present. Both the tendency of the V_{Li} to form near the V_O and the decrease in the lithium movement suggest a significant interaction between the V_{Li} and V_O .

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Table 1: Calculated Li_2MnO_3 lattice parameters compared to previously calculated parameters, by Koyama, et al.(30) and Okamoto,(31) and experimentally determined parameters by Strobel *et al.*(19)

Lattice Parameters	Calculated (Å)			Experimental (Å)
	Current calculation	Koyama et al.	Okamoto	Strobel, et al.
a	5.01	5.02	4.98	4.94
b	8.66	8.68	8.63	8.53
c	5.07	5.09	5.00	5.03

Figure 1: perfect Li_2MnO_3 unit cell projected along $[100]$ direction, serving as the starting structure for vacancy generations. The Wyckoff positions are depicted. (color online, black and white print)

Figure 2: Comparison of DFT calculated energy of formation for creating V_{Li} , one at a time from previously optimized structures containing (a) a single V_O and (c) two V_O . The solid and open symbols indicate the Li was removed from the Li layer or the transition metal layer, respectively. (b) & (d) show the number of Li atoms vs. the distances for (a) and (c), respectively. In (a) and (b), the distance is between the V_{Li} and the single V_O position; and in (c) and (d), the distance is between the V_{Li} and the center of the two V_O .

Figure 3: Relaxed atomic positions for systems with 4 V_{Li} and either (a) V_O or (b) two V_O . The yellow Li centered octahedral (or half octahedral due to oxygen vacancy) indicates where the removed Li atoms were located in the perfect crystal structure and the numbers indicate the sequences they were removed. (color online, black and white print)

Figure 4: Starting systems for ab-initio molecular dynamics calculations with (a) one V_{Li} , (b) one V_O and V_{Li} , (c) one V_O and V_{Li} farther apart, and (d) one V_O and two V_{Li} . (color online, black and white print)

Figure 5: Displacement of (a) lithium atoms and (b) the V_{Li} from their initial positions for a starting system with only one V_{Li} and no V_O (in Figure 4a) during a 50ps AIMD simulation. (color online, black and white print)

Figure 6: Displacement of lithium and oxygen atoms from their initial positions in the initial structures shown in Figure 4 for 50 ps AIMD simulations. (a): For the starting system with one V_{Li} and one V_O , in neighbor positions (shown in Figure 4b), the hopping of only one lithium atom was observed. (b) and (c): For a starting system with one V_{Li} and one V_O placed farther apart (shown in Figure 4c), displacements of both (b) lithium atoms and (c) oxygen atoms were observed. (d): For a starting system with two V_{Li} and one V_O (shown in Figure 4d), there was observed displacement of one of the two lithium atoms. (color online, black and white print)

Figure 7: Calculated energy barrier with no oxygen vacancies for (a) cross-layer hopping between the $4h$ and $2c$ positions, and (b) lithium-layer hopping between the $2c$ and $2b$ positions. The energy barrier was increased by the introduction of one oxygen vacancy in the system for both the hopping between (c) the $4h$ and $2c$ positions and (d) the $2c$ and $2b$ positions. To show the barrier, the reference energy was set zero for the equilibrium structure with the lowest energy for the four cases separately.

Figure 8: Calculated open circuit voltage curve for $0 \leq x \leq 0.25$ and varying δ in $\text{Li}_{2-x}\text{MnO}_{3-\delta}$.
(color online, black and white print)