CORRELATION OF POINT DEFECTS IN LITHIUM-RICH LAYERED CATHODE MATERIALS FOR LITHIUM-ION BATTERY APPLICATIONS

By

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ABSTRACT

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The limiting component of lithium-ion batteries continues to be the cathode component. Since the layered materials, such as $LiCoO_2$, have observed capacities of roughly half of their theoretical capacities, advances have been made in attempts to improve their stability and thus capacity. One such attempt is adding Li₂MnO₃, thus creating Li₂MnO₃-LiMO₂ materials, where M is typically a transition metal ion or combination of transition metals. These Li₂MnO₃ stabilized materials have been shown to be promising with >200mAh/g but still suffer from performance issues.

The Li₂MnO₃ component is observed to lose oxygen during the first charge cycle and thus creates Li_{2-X}MnO₃₋₆. These oxygen vacancies are related to some of the cathode performance issues. However, the amount of oxygen released and the role of the oxygen vacancies are still not very well understood. Therefore, this work takes an atomic level computational approach using density functional theory calculations to explore the impact of oxygen vacancies and the correlated effects on voltage, capacity, lithium diffusion, chemical strain, dopants and electrolyte decomposition. Despite the extensive computational work in the literature on lithium transition metal oxide cathode materials, little work has been devoted to the correlated effects of two vacancy types in these materials. Therefore, this work offers novel approaches to model both vacancy types and their impacts on each other.

First, it was found that the oxygen vacancies can decrease the formation energy of lithium vacancies. Less hopping of lithium atoms is observed and the energy barrier for lithium hopping is increased when oxygen vacancies are present. The calculated diffusion coefficient decreases by

~5 order of magnitude from the perfect crystal structure. This suggests oxygen vacancies cause an increased capacity but at the expense of decreased rate capability of these materials.

The chemical strain associated with both non-dilute lithium vacancies and dilute vacancies were analyzed with an anisotropic model. It was found that the oxygen vacancies and lithium vacancies are highly correlated causing the associated chemical expansion to not be a linear sum of the individual vacancy types. The predicted chemical strain due to a low energy V_{Li} - V_O - V_{Li} dumbbell structure can be correlated with the in situ experimentally measured stress.

To investigate if the amount of oxygen vacancies can be controlled, the effects of Si and Al dopants were also studied. The silicon was shown to decrease the oxygen vacancy formation energy in neighboring octahedral to the silicon, thus suggested to activate the manganese and increase the capacity of the materials, consistent with experimental observations.

Lastly, the impact of surface oxygen vacancies on adsorption and decomposition of an electrolyte component, ethylene carbonate (EC), on the Li₂MnO₃ surface was investigated. A two proton removal reaction from EC to Li₂MnO₃ (131) was discovered, suggesting some beneficial effect on the perfect Li₂MnO₃ surface. However, an EC appears to be repelled near a surface oxygen vacancy. The released oxygen can react with the EC molecule and trigger different decomposition reactions. Overall, the oxygen vacancies generated in the lithium-rich layered cathode materials are shown to have a very highly correlated impact on lithium, dopant and electrolyte-surface interactions which therefore can significantly impact battery performance and life.

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Chapter 1. Introduction

The work presented in this dissertation focuses on lithium-rich materials used for cathodes for lithium-ion batteries. Thus, Section 1.1 below will give an introduction into materials for lithium-ion batteries. Section 1.2 discusses computational methods which have been used to predict material properties for lithium-ion batteries. Then, Section 1.3 will discuss what was known in previous literature about the lithium-rich cathode materials and identify the key research problem to be investigated by this thesis. Lastly, an overview of the rest of the dissertation will be given in Section 1.4.

1.1 Introduction to Lithium-Ion Batteries

Rechargeable lithium-ion batteries are increasingly used in a wide variety of applications which include: mobile electronics, space power systems, aircraft power systems, plug-in hybrid electric vehicles (PHEV)/all-electric vehicles (EV), and smart grids due to their high gravimetric and volumetric energy densities compared to other current battery technologies, as shown below in Figure 1.1. Thus, the sales of lithium-ion batteries has been increasing over time, as shown in Figure 1.2.

The energy density of lithium-ion batteries is around 160 Whkg⁻¹ now and this is after it has been increasing by around 5Whkg⁻¹ each year during the past few. However, this energy density is much lower than the needs for electric vehicles (500-700 Whkg⁻¹), as shown in Figure 1.1. In addition, simultaneous improvements in energy density, rate capability, lifetime and safety are required. Therefore, much research is still needed in the area of materials for rechargeable lithium-ion batteries.



Figure 1.1 The theoretical and practical energy densities of different battery technologies. Republished with permission of RSC Publishing, from Electrical energy storage for transportation-approaching the limits of, and going beyond, lithium-ion batteries, Thackeray, M. M.; Wolverton,

C.; Isaacs, E. D., 5 (7) 2012;¹ permission conveyed through Copyright Clearance Center, Inc.



Figure 1.2 Sales (in cells) of lithium ion batteries. Reprinted by permission from RightsLink Permissions Springer Nature Customer Service Centre GmbH: Springer Nature Journal of Solid State Elecrochemistry (Lithium ion, lithium metal, and alternative rechargeable battery technologies: the odyssey for high energy density, Placke, T.; Kloepsch, R.; Duhnen, S.; Winter, M),² COPYRIGHT 2017.

Lithium-ion batteries contain three main components: cathode (the positive electrode), anode (the negative electrode) and electrolyte. When a lithium-ion battery is operated the Li⁺ ions are shuttled between the cathode and the anode through the electrolyte while electrons move through an external circuit during the discharge cycles in order to power a device. The Li⁺ ions move from the cathode to the anode during charging and back to the cathode during discharging. Figure 1.3 shows a schematic of the lithium-ion battery along with the direction of electron flow during both the charging and discharging cycles.



Figure 1.3 Schematic of a lithium-ion battery showing the flow of electrons and lithium ions during the charge and discharge cycle. Republished with permission of RSC Publishing, from Electrical energy storage for transportation-approaching the limits of, and going beyond, lithium-ion batteries, Thackeray, M. M.; Wolverton, C.; Isaacs, E. D., 5 (7) 2012;¹ permission conveyed through Copyright Clearance Center, Inc.

The design in which the anode, cathode, electrolyte and other lithium-ion battery components, including the separator and current collectors, are assembled together varies in size and shape according to the application for which it is being used. These cells can be cylindrical, coin, prismatic or pouch, all of which are shown schematically in Figure 1.4.



Figure 1.4 Batteries can be designed in different ways such as: (a) cylindrical, (b) coin, (c) prismatic or (d) the pouch cell. Reprinted by permission from RightsLink Permissions Springer Nature Customer Service Centre GmbH: Springer Nature, Nature³ (Issues and challenges facing rechargeable lithium batteries, Tarascon, J. M.; Armand, M.), COPYRIGHT 2001.

The electrolytes for lithium-ion batteries are typically liquids which should be good conductors of lithium ions while being electronic insulators. These liquids are usually composed of a lithium salt, commonly LiPF₆, dissolved in a mixture of organic solvents. The organic solvents are typically comprised of the high dielectric ingredients such as ethylene carbonate (EC), and low

viscosity ingredients, such as dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethylmethyl carbonate (EMC), and other additives. Solid electrolytes for lithium-ion batteries is currently an active area of research.⁴ Replacing the liquid electrolyte with a solid would improve the battery in terms of safety. However, most of the current solid electrolytes have ionic conductivities which are significantly smaller than those of liquid electrolytes.

Table 1.1 lists various positive electrode (cathode) and negative electrode (anode) materials, along with their electrochemical potential with respect to lithium-metal electrodes for lithium-ion batteries. The cell voltage of the lithium-ion battery refers to the difference in electrochemical potential between the positive and negative electrode materials. The energy of the battery is the capacity times the cell voltage. Two of the most common anode materials are graphite and silicon which are shown to have considerably high observed capacities and lower voltages. A significant concern with silicon is that it doesn't cycle well and undergoes a large volume change, about 300%. Other anode materials include metal oxides and tin. The cathode material is the focus of this research because it is the limiting component in terms of battery capacity. Common cathode materials include layered materials (such as LiCoO₂), spinel materials (such as LiMn₂O₄) and olivine materials (such as LiFePO₄). The cathode materials: LiCoO₂ (160 mAh/g), LiMn₂O₄ (130 mAh/g) and LiFePO₄ (160 mAh/g) have much lower observed capacities than graphite (330 mAh/g).⁵ From comparing the capacity of anode and cathode materials listed in Table 1.1, it is apparent that the cathode material is the limiting component in terms of battery capacity. Therefore, the cathode material is the focus of the research presented here.

Table 1.1 Table of various anode and cathode materials used for lithium-ion batteries. Republished with permission of CRC Press, from [Lithium-ion batteries : advanced materials and technologies, Daiwon Choi, Wei Wang and Zhenguo Yang, 2011]; permission conveyed through Copyright Clearance Center, Inc.⁵

Туре	Chemistry	Specific Capacity in mAh/g (theoretical/ observed)	Potential vs. Li⁺/Li	Note
Cathode	LiCoO ₂	273/160	3.9	First cathode, expensive
	LiNiO ₂	274/180	3.6	Cheaper than LiCoO ₂
	LiNi _x Co _y Mn _z O ₂	~270/150-180	3.8	Cheap and stable
	LiNi _x Co _y Al ₂ O ₂	~250/180	3.7	Stable
	LiMn ₂ O ₄	148/130	4.1	Unstable cycling
	LiMn _{1.5} Ni _{0.5} O ₄	146/130	4.7	High voltage, cheap
	$LiFePO_4$	170/160	3.45	Low voltage, safe, cheap
	LiMnPO ₄	171/80-150	4.1	Slow kinetics, cheap, high voltage
	$LiNiPO_4$	166/-	5.1	No suitable electrolyte
	$LiCoPO_4$	166/60-130	4.8	Expensive
	Li ₂ FeSiO ₄	165/160	2.8	Cheap, low voltage
	Li_2MnSiO_4	166/140	~4.0	Cheap
	$Li_3V_2(PO_4)_3$	131/130	4.1/3.6	Two voltage plateau
	$LiFeBO_3$	220/~150	2.7	Cheap, air sensitive
	LiMnBO ₃	222/-	3.7	Cheap, difficult to make active
	TiS ₂	239/200	2.0	Low voltage, Li metal anode
	VS_2	233/210	2.2	Low voltage, Li metal anode
Anode	Graphite	372/330	0.1-0.2	LiC4, vol. change: ~11%
	Soft Carbon	-/<700	<1	High capacity, sloping voltage profile
	Hard Carbon	-/600	<1	High capacity, sloping voltage profile
	$Li_4Ti_5O_{12}$	175/170	1.55	High voltage, no vol. change
	TiO ₂	168/168	1.85	Cheap, vol. change: ~4%
	(anatase/rutile)			
	SnO ₂	782/780	< 0.5	Large initial irreversible loss
	Sn	993/990	<0.5	Poor cycling, vol. change: 257%
	Si	4198/<3500	0.5–1	Poor cycling, vol. change: 297%
	Al	2235	<0.3	Poor cycling, vol. change: 238%
	Bi	385	< 0.8	Vol. change: 115%

Source: Ellis, B.L., Lee, K.T., and Nazar, L.F., Chem. Mater., 22, 3, 691–714, 2010; Armand, M. et al., Nat. Mater., 8, 2, 120–125, 2009; Nazri, G. and Pistoia, G., Lithium Batteries: Science and Technology, Springer, 2009. Three of the common and commercially used cathode materials have unique crystal structures of the forms: spinel (such as $LiMn_2O_4$), olivine (such as $LiFePO_4$) and layered (such as $LiCoO_2$). The spinel materials are of the form LiM_2O_4 and their crystal structure is illustrated below, Figure 1.5. The most common spinel material is $LiMn_2O_4$, in which the oxide ions are at a close-packed face centered cubic arrangement with lithium cations occupying 1/8 of the available tetrahedral sites and the manganese cations occupying $\frac{1}{2}$ of the octahedral sites. This material has a low theoretical capacity and also has issues with cyclability as it does not maintain its capacity as it is continued to cycle.



Figure 1.5 Crystal structure of spinel materials of the form LiM_2O_4 . Reprinted from Materials Science and Engineering: R: Reports, 73, Bo Xu, Danna Qian, Ziying Wang, Ying Shirley Meng, Recent progress in cathode materials research for advanced lithium ion batteries, Pages 51-65, Copyright 2012, with permission from Elsevier.⁶ Color scheme: lithium (red), M transition metal ions (blue).

Another common cathode material is LiFePO₄ which is an olivine material, structure shown in Figure 1.6. The lithium and iron are in $\frac{1}{2}$ of the available octahedral sites. The phosphorous ions occupy 1/8 of the tetrahedral sites. It has a hexagonal analog of the cubic spinel structure. It has several advantages such as being inexpensive and safe. However, this material has

a low theoretical capacity as compared to other materials, such as the layered materials and a relatively low voltage.



Figure 1.6 Crystal structure of LiMPO₄, olivine, materials. Reprinted from Materials Science and Engineering: R: Reports, 73, Bo Xu, Danna Qian, Ziying Wang, Ying Shirley Meng, Recent progress in cathode materials research for advanced lithium ion batteries, Pages 51-65, Copyright 2012, with permission from Elsevier.⁶ Color scheme: lithium (red), phosphorous (yellow), M transition metal (blue).

The first widely used lithium-ion battery cathode material was $LiCoO_2$. The structure of $LiCoO_2$, and more broadly $LiMO_2$, is referred to as layered. The structure of these layered materials are shown in Figure 1.7 and contain discrete layers of lithium, oxygen and the transition metal(s). In the layered $LiCoO_2$ structure, the oxygen ions are in a close-packed face centered cubic arrangement with the lithium and cobalt cations occupying the octahedral sites in an alternating manner between the close packed planes of oxygen ions. However, there are several problems with $LiCoO_2$, such as the high cost due to the cobalt and the instability upon cycling. This structural instability is largely why the observed capacity of $LiCoO_2$ is complicated and includes several different

phenomenon. One structural change is the dissolution of cobalt from the cathode into the electrolyte. This dissolution of cobalt allows for less lithium to be removed/replaced upon cycling. Additionally, there are further reactions between the $LiCoO_2$ surface and the electrolyte which causes the formation of a surface layer. After more than half of the lithium is deintercalated the material undergoes a phase change which also limits the observed capacity to about half of the theoretical capacity.⁷



Figure 1.7 Crystal structure of layered materials of the form LiMO₂. Reprinted from Materials Science and Engineering: R: Reports, 73, Bo Xu, Danna Qian, Ziying Wang, Ying Shirley Meng, Recent progress in cathode materials research for advanced lithium ion batteries, Pages 51-65, Copyright 2012, with permission from Elsevier.⁶ Color scheme: lithium (red), M transition metal (blue).

In an attempt to solve the structural stability problems associated with $LiCoO_2$, other layered materials of the form $LiMO_2$ have been studied, where M is most commonly another transition metal or combination of transition metals. $LiNiO_2$ results have shown a slight improvement compared to $LiCoO_2$ as it is less expensive and has a slightly higher observed capacity. However, the capacity still remains very low. $LiMnO_2$ was studied also and was promising due to its high theoretical capacity. However, it showed a significant drop in capacity immediately when it was cycled. Another common layered material mixes Ni, Mn and Co in the transition metal layer to form $LiCo_xMn_yNi_{1-x-y}O_2$. These materials have shown to be inexpensive and relatively stable. However, their capacity still remains low compared to typical anode materials.

Therefore, the problem of finding a cost effective and stable cathode material still persists with the layered materials. This has led to the study of Li₂MnO₃ stabilized (also known as lithiumrich) cathode materials, which will be described in further detail in Section 1.3. This evolution of improving the layered cathode materials beyond LiCoO₂ is summarized in Figure 1.8. First, replacing or partially replacing the cobalt was attempted and now adding the Li₂MnO₃ component to form Li[LiM]O₂, another way of writing xLi₂MnO₃-(1-x)LiMO₂, materials is being investigated.



Figure 1.8 The progression of LiCoO₂ materials as Co was replaced. Shown with Li(yellow), Ni (green), Mn(blue) and Co (purple). Republished with permission of Electrochemical Society, from Review-Li-Rich Layered Oxide Cathodes for Next Generation Li-Ion Batteries: Chances and Challenges, Patrick Roziera and Jean Marie Tarascon, 162, 2015]; permission conveyed through Copyright Clearance Center, Inc. ⁸

1.2 Motivation for Computational Analysis

Computational studies can be used to explore phenomenon that are not observable in experiments and to also make predictions for further experiments. There are many different computational methods which can be used to simulate varying length scales in lithium-ion batteries, as summarized by Shi et al. in Figure 1.9.⁹



Figure 1.9 Different levels of modeling techniques for materials. Used with permission from Chinese Physics B.⁹

At the lowest length scale, quantum mechanics methods, such as density functional theory (DFT), can be used to calculate the electronic structure of the material and predict material properties such as reaction energy, elastic constants, structural stability and dynamics of simple

lattice defects. Atomistic level simulations that represent the system energy as a function of atomic positions, allow for slightly larger scale simulations and include molecular dynamics simulations which enable the structural evolution to be studied. Above these two levels, the governing equations will be tailored to address specific material questions. For example, the microstructural simulations at the level of grains and grain boundaries can be described by continuum-level mechanics models with constitutive equations, so that the mechanical behavior (such as stress and strain) can be modeled. Or, the phase field model can be used to describe microstructural evolution based on governing thermodynamics equations, diffusion equations, and boundary evolution at the continuum level. Among these methods, quantum methods are the most accurate. It becomes more than a tool for explaining experiments but rather can be key to the prediction of material properties and ultimately structure and composition design.

First-principles methods have been used extensively in the literature to calculate properties of and simulate cathode materials for lithium-ion batteries.¹⁰ One of these first-principles methods is DFT calculations which allows for an approximate solution to the time independent Schroedinger's equation, Equation 1.1, and allows for the prediction of the electron density in and energy of crystal structures, especially with plane wave DFT.

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right)\Psi(\vec{r}) = E\Psi(\vec{r})$$
(1.1)

DFT calculations can be used to identify defects, simulate defect hopping and predict the diffusion barrier.¹¹ DFT can also be used to predict open circuit voltage (OCV)^{12, 13} and elastic properties of electrode materials.¹⁴

Being able to calculate the diffusion barrier in electrode materials for lithium-ion batteries allows for the study of how the lithium moves in and out of the material and can be used in other instances such as how the ionic movement can cause a phase change in the material. The calculation of the diffusion barrier frequently uses the nudged elastic band (NEB) method alongside the DFT calculations. An example of the use of using the NEB method and DFT to calculate the energy barrier for lithium diffusion is an Li_xTiS_2 study by Van der Ven et al. comparing two different migration pathways, shown in Figure 1.10.¹⁵ In this study, they found that lithium on the octahedral site prefers to go through the tetrahedral site when it moves to another octahedral site.



Figure 1.10 Comparison of two different migration pathways for lithium in Li_xTiS₂. Reprinted figure with permission from [Anton Van der Ven, John C. Thomas, Qingchuan Xu, Benjamin Swoboda and Dane Morgan, PHYSICAL REVIEW B, **78**, 104306 and 2008.] Copyright 2008 by the American Physical Society, https://doi.org/10.1103/PhysRevB.78.104306.¹⁵

Density functional theory (DFT) has long been used to predict the OCV of electrodes that store lithium via intercalation and alloying, through solid state reactions. The average OCV for a typical lithium reaction with host material M, such as:

$$Li_{x_1}M + (x_2 - x_1)Li \to Li_{x_2}M,$$
 (1.2)

with reference to the lithium-metal as 0V is defined as:

$$\langle OCV \rangle = = \frac{-\Delta G_r}{F\Delta x} = \frac{-(\Delta E_r - \Delta PV - T\Delta S_r)}{F\Delta x},$$
 (1.3)

Where ΔG_r is the Gibbs free energy of reaction (1.2), Δx is the lithiation amount/amount of charge transferred and F is Faraday's constant. In typical solid state lithiation reactions, the PV term and the $T\Delta S_r$ term in Equation 1.3 are often dropped, as they are much smaller than ΔE_r at room temperature for solids. Therefore, with lithium-metal as the reference electrode (0V), the equation simplifies to

$$\langle OCV \rangle = \frac{-[E(Li_{x2}M) - E(Li_{x1}M) - (x2 - x1)E(Li)]}{F(x2 - x1)}.$$
 (1.4)

All of the energy terms in Equation 1.4 can be directly computed with DFT.

The voltage for different battery materials is frequently calculated with DFT and some of the results are summarized in Figure 1.11 by Chevrier et al.¹⁶ As seen from Figure 1.11, a typical exchange correlation function used in DFT, such as the generalized gradient approximation (GGA) does not do well as far as calculating the intercalation potential due to the self-interaction of the d-electrons associated with the transition metals. As seen in Figure 1.11, Chevrier et al.¹⁶ compared conventional GGA, GGA+U, and the HSE06 hybrid functional approaches in terms of their accuracy by computing redox potentials, specifically looking at various cathode materials. In the GGA+U approach, U can be adjusted and is a parameter which accounts for on-site Coulomb and

exchange interactions, this is estimated with a Hartree-Fock approximation added to the DFT Hamiltonian. Chevrier et al.¹⁶ determined the most reliable results came from the hybrid functionals and avoided the necessity of finding the U parameter in the GGA+U method. However, due to the long computation time of the HSE06 hybrid functional approach, this work uses GGA+U for Li₂MnO₃ with a careful selection of the U parameter for Mn.



Figure 1.11 The relative error of the calculated potential for lithium intercalation for several cathode materials and GGA, GGA+U and HSE06. Reprinted figure with permission from [V. L. Chevrier, S. P. Ong, R. Armiento, M. K. Y. Chan, and G. Ceder, PHYSICAL REVIEW B, **82**, 075122, 2010.]¹⁶ Copyright 2010 by the American Physical Society, https://doi.org/10.1103/PhysRevB.82.075122.



Figure 1.12 Young's modulus calculations for several lithium-ion battery electrode materials. Figure from Qi, et al.¹⁴ and licensed under CC BY-NC-ND 4.0.

Elastic properties such as the elasticity tensor or Young's modulus can also be calculated for electrode materials in lithium-ion batteries. An example of this is shown in Figure 1.12 where Qi et al. shows calculations of Young's modulus for various lithium-ion electrode materials. These properties have been input to continuum diffusion-induced-stress models. These key elastic properties, along with their dependence on lithium concentration, are not reported in the literature, largely because many lithiated materials are air (oxygen, nitrogen, and moisture) sensitive, and obtaining them experimentally is difficult.

Another first-principles technique which has been used in the study of lithium-ion battery cathode materials is *ab-initio* molecular dynamics (AIMD) which uses first-principles to calculate the forces on the atoms and then simulates the motion of the atoms over time using Newton's second law of motion.

These methods are frequently used to simulate the lithium ion diffusion in cathode materials in lithium-ion batteries with just some lithium ions being removed (forming lithium vacancies). However, the material of interest in this study, Li_2MnO_3 , contains both lithium vacancies (V_{Li}) and oxygen vacancies (V_0) upon cycling. Therefore, this work uses previously developed computational methods and its novelty lies in developing new models in order to determine the correlated effects of the two vacancy types.

1.3 Li₂MnO₃ Stabilized Layered Materials

A material with a similar structure to the layered materials is Li₂MnO₃. The structure of layered materials, LiMO₂ where M is a single or combination of transition metals and possibly other dopants, and Li₂MnO₃ are very similar, shown in Figure 1.13. Both LiMO₂ and Li₂MnO₃ have oxygen, lithium and transition metal layers. The main difference is that Li₂MnO₃ contains excess lithium as compared to LiMO₂ because there is also lithium in the transition metal layers.



Figure 1.13 The crystal structures of LiMO₂, such as LiCoO₂, and Li₂MnO₃ for comparison.

The unit cell of Li₂MnO₃, shown in Figure 1.14, shows that there are two distinct oxygen sites, Wyckoff positions 8j and 4i, and three distinct lithium sites, Wyckoff positions 2c, 4h and 2b. The lattice parameters used in this study are shown in Table 1.2 and compared to other calculated and experimentally measured literature values.



Figure 1.14 Perfect Li₂MnO₃ unit cell projected along [100] direction, serving as the staring structure for vacancy generations. The Wyckoff positions are depicted. Figure from James, et al.¹⁷

Table 1.2 Calculated Li₂MnO₃ lattice parameters compared to previously calculated parameters, by Koyama, et al.¹⁸ and Okamoto,¹⁹ and experimentally determined parameters by Strobel *et al.*²⁰ Table adapted from James, et al.¹⁷

Lattice	Calculated (Å)			Experimental (Å)
Parameters	Current	Koyama et al.	Okamoto	Strobel, et al.
	calculation			
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

Since Li_2MnO_3 has lithium in the lithium layer and in the transition metal layer, it has a higher theoretical capacity than layered materials. However, Li_2MnO_3 is theoretically electrochemically inactive due to the high 4+ oxidation state of the manganese ion. The high manganese oxidation state inhibits the removal of lithium ions because the charge of losing lithium cannot be compensated by the oxidation of manganese. In the layered materials the loss of lithium is accompanied by the oxidation of M from 3+ charge state to 4+.

Therefore, Li₂MnO₃ was added to LiMO₂ materials for stabilization purposes and created materials of the form xLi₂MnO₃-(1-x)LiMO₂. Unexpectedly, these materials have very high capacities. As these materials are cycled it has been shown that there is an activation process during the first charging cycle which allows for higher capacity upon subsequent cycling. There are several possible mechanisms that could be occurring during the activation process which are outlined in Chapter 2. However, it is largely agreed that atleast part of the activation process which occurs above 4.4V includes the release of oxygen, creating oxygen vacancies within the Li₂MnO₃ material. This activation process is seen as the plateau around 4.5V in Figure 1.15 which then accounts for the increase in capacity from the first to the second cycle, again in Figure 1.15. The release of oxygen forms Li_{2-x}MnO_{3-δ}, which is electrochemically active and adds capacity to the material.



Figure 1.15 The first and second charge/discharge cycles for a half cell using $0.3Li_2MnO_3 \cdot 0.7LiMn_{0.5}Ni_{0.5}O_2$. Reprinted from Electrochemistry Communications, 8 (9), Thackeray, M.; Kang, S.-H.; Johnson, C.; Vaughey, J.; Hackney, S., Comments on the structural complexity of lithium-rich $Li_{1+x}M_{1-x}$ O₂ electrodes (M = Mn, Ni, Co) for lithium batteries, 1531-1538,²¹ Copyright 2006, with permission from Elsevier.

First-principles calculations could greatly help in the understanding of what is happening in $Li_{2-X}MnO_{3-\delta}$ on the atomic level. However, few simulation studies had been done on Li_2MnO_3 prior to this work with many more done in the past few years. ²²⁻²⁶ Additionally, prior to this work, no studies were done on the correlation of the oxygen and lithium vacancies.

Most Li₂MnO₃ computational work has been focused on the structural change and oxygen dimer formation due to lithium removal. Upon cycling, the Li₂MnO₃ containing materials have been experimentally shown to undergo a phase transformation from a layered structure to a spinel-like structure which is associated with the transition metal ions moving from the transition metal layer to the lithium layer. Thus many computational studies have focused on the energy barrier associated with the movement of manganese to the lithium layer in Li₂MnO₃.^{22, 23} Additionally, researchers have looked at the possibility of the oxygen forming oxygen dimers instead of oxygen being released.²⁷ Lee and Persson²³ suggested that the migration barrier for oxygen was too large for the oxygen ions to move through the material and thus oxygen vacancies must be formed only on the surface, which Shin and Persson later explored.²⁵ Xiao et al. studied the diffusion of lithium-ions in the material without oxygen vacancies and at very high temperatures which seem to melt the crystal and therefore not truly capture diffusion.²²

Therefore, since it is still unclear where oxygen vacancies are formed and more than plausible that they are forming in the bulk of the lattice to contribute to the high capacity, there is a large area that still remains unexplored. The impact of oxygen vacancies on capacity and rate capability are not understood and even the concentration of oxygen vacancies is unknown.

1.4 Overview of Dissertation

Cathode materials have a low capacity compared to anode materials and therefore limit the overall capacity of batteries. Materials which contain Li_2MnO_3 have been shown to have high capacities, atleast in part, due to the introduction of oxygen vacancies within the first cycle. Computational techniques have long been used to study materials for lithium-ion batteries. However, the amount of and role of oxygen vacancies is still unclear and largely unexplored by computational methods. Therefore, this work simulates $Li_{2-x}MnO_{3-\delta}$ using first-principle computational methods.

Specifically, it is found that the oxygen vacancies and the lithium vacancies formed upon cycling are correlated and this correlation is further studied. This work uses DFT calculations to calculate the effect of oxygen vacancies on the removal of lithium and the capacity of the material, in Chapter 2. Then, the diffusion of lithium is studied with AIMD and the migration barrier is calculated with the NEB method to determine the impacts of Vo on rate capability in Chapter 3. A method of calculating the chemical expansion due to oxygen and lithium vacancies and how they are correlated is discussed in Chapter 4. The aim of Chapter 4 is to further understand the chemical expansion induced by oxygen vacancies so that in the future these calculations can be combined with experimental in situ stress measurements in order to discern the amount of oxygen vacancies created upon activation of this material. Since Chapter 2 shows that the amount of oxygen vacancies influences the capacity and Chapter 3 shows the oxygen vacancies affect the rate capabilities of these materials, Chapter 5 looks at how dopant ions may influence the oxygen vacancy concentration within these materials and the activation of the manganese ions. Chapter 6 concludes with an analysis of how an electrolyte component, ethylene carbonate (EC), interacts with the Li₂MnO₃ surface with and without oxygen vacancies. Overall, these studies discuss the impact of the oxygen vacancies in Li₂MnO₃ and their coupled effects on capacity, Li diffusion, chemical strain, dopants, and electrolyte decomposition.

Chapter 2. Effect of Oxygen Vacancies on Lithium-Ion Battery Capacity

This chapter is adapted from James, et al.¹⁷ The layered lithium-rich transition metal oxides of xLi_2MnO_3 -(1-x)Li(Ni,Co,Mn)O₂ have gained much attention due to their large reversible capacity (>200 mAh/g) ²⁸ compared to other common cathode materials for lithium-ion batteries (LIBs) ⁶. ²⁹⁻³¹, such as LiCoO₂ (~160 mAh/g), LiFePO₄ (~160 mAh/g) and LiMn₂O₄ (~130 mAh/g).⁷ This large reversible capacity is generally believed to come from the "activation" process of the Li₂MnO₃ component. This "activation" is observed at >4.4 V ²⁸, which is necessary to access the Li in the Li₂MnO₃ phase.³²⁻³⁴ While this material is promising, it suffers from problems such as structural instability, hysteresis, voltage decay ³⁵⁻³⁷, low rate capability ³⁸, and poor life. These problems have prevented its practical applications.

Although there are still some arguments on whether $xLi_2MnO_3-(1-x)Li(Ni,Co,Mn)O_2$ is mixed as a solid solution or segregated in separate domains ^{28, 39}, it is unarguably important to understand how the Li in the Li₂MnO₃ component contributes to the observed high capacity. The Li₂MnO₃ phase was initially thought to be electrochemically inactive due to the high oxidation state (4+) of the manganese cation, thus inhibiting access to the lithium cations. However, the Li₂MnO₃ component alone ^{20, 40-48} and Li₂MO₃ layered compounds ⁴⁹, where M 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 O²⁻ to O⁻ ions ^{50, 51}, the loss of oxygen ^{28, 42, 47, 51}, the exchange of Li ions for H ions from the electrolyte ⁴², and possibly the oxidation of Mn^{4+ 40}. Several studies

have modeled the lithium removal process in Li₂MnO₃ to mimic the activation process of Li₂₋ _xMnO₃.^{18, 19, 22, 23, 52}. These studies detailed the sequence of lithium being removed from either lithium layer or transition metal layer, and proved that it is energetically favorable to release O₂ after a large amount of lithium being removed (such as $x>1^{23}$). 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 Persson²³ 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 ⁵³ and modeling ⁵⁴. Regardless, it is likely that oxygen vacancies facilitate the high capacity, such that the cathode material should be written as Li₂₋ _xMnO_{3- δ} 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 Li₂MnO_{3- δ} jmpact the delithiation process, structural change, and the rate performance of the Li_{2-x}MnO_{3- δ} phase.

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 Li₂MnO_{3- δ}. Therefore, it is critical to understand the effect of oxygen non-stoichiometry (δ) on the structural change and diffusion in Li_{2-x}MnO_{3- δ} and related compounds. Although the simultaneous removal of lithium and oxygen as Li₂O 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 Li₂O. ⁵⁵. 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., lithium 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 lithium vacancy formation and lithium 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 effects of oxygen vacancies on the formation of lithium vacancies and the effects of oxygen vacancies on the delithiation process of $Li_{2-x}MnO_{3-\delta}$ in section. The open circuit voltage (OCV) is also calculated and used to explore how oxygen vacancies (V₀) changes the subsequent capacity, voltage, and diffusion in $Li_{2-x}MnO_{3-\delta}$ and related compounds.

2.1 Computational Methods

The Vienna *Ab initio* Simulation Package (VASP) ⁵⁶⁻⁵⁹ was used to perform plane wave density functional theory (DFT) calculations. Potentials constructed with the full potential projector augmented wave (PAW) method ^{60, 61} 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 ^{62, 63} with a Hubbard U correction (so called GGA+U method). The U parameter was chosen to be 4.84eV for Mn, a similar value to literature.^{18, 19, 22} 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 Li_2MnO_3 (C2/m) were optimized. For this purpose, a plane-wave basis cutoff energy of 550 eV and a **k**-points mesh of $3x_3x_3$ 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 1.2 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). The first V₀ was determined by calculating the energy of two systems with either a V₀ at the 8*j* or 4*i* position (unique Wyckoff positions for O) and comparing the system energies. It was found that the first V₀ on the 8*j* site was more energetically favorable by 0.36 eV. However, this was unexpected at a first glance, since the bond length between the 8*j* oxygen ion and Mn was shorter than the bond length between the 4*i* 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_0) and the distance between the oxygen and the neighboring atom (*r*).

$$E_{electrostatic} = q_0 \left(\sum \frac{q_{Li}}{r} + \sum \frac{q_{Mn}}{r} \right)$$
(2.1)

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.,

although they showed that V_0 at the 8j position is energetically more favorable than the 4i position by 0.4 eV. The predicted V_0 formation energy (on 8j site) is 2.1 eV. For the system with two V_0 , or δ =0.1250, the most energetically favorable position for the second V_0 was in an 8j position 3.1 Å from the first V_0 . 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_0 .

From the system with no V₀, 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 V₀ the V_{Li} were formed in the 4h position, consistent with Okamoto.¹⁹ 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.

To determine where lithium would be removed during cycling one or two oxygen atoms were removed from the perfect structure to form oxygen vacancy (Vo) containing structures as δ = 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 Li_{2-x}MnO_{3- δ}, 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 δ = 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. The process of creating structures is described schematically in Figure 2.1.



Figure 2.1 A schematic showing the figure sampling, first oxygen vacancies were introduced and then lithium vacancies were created one at a time. Each row represents the sampled structures and the highlighted structure is the most energetically favorable.

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 2x1x1 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 Section 2.2. The configurations with the lowest energies at each *x* and δ in Li_{2-*x*}MnO_{3- δ} 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 $E_{Li_{2-x_1}MnO_{3-\delta}}$ to form $E_{Li_{2-x_2}MnO_{3-\delta}}$, 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:

$$E_{f, \ Li \ vacancy} = E_{Li_{2-x_{2}}MnO_{3-\delta}} + E_{Li,metal} - E_{Li_{2-x_{1}}MnO_{3-\delta}}.$$
(2.2)

The systems with oxygen and lithium vacancies in the most energetically favorable sites were used to calculate open circuit voltage (OCV) and to run calculations to analyze the Li diffusion. OCV was calculated, as shown in Equation 2.3, from the current energy of the system $(E_{Li_{2-x_{2}}MnO_{3-\delta}})$, the energy of the system with one less Li vacancy $(E_{Li_{2-x_{1}}MnO_{3-\delta}})$, the energy of the Li ion which was removed within pure Li metal $(E_{Li,metal})$ and the charge of an electron (e).

$$OCV = \frac{E_{Li_{2}-x_{2}}MnO_{3-\delta} + E_{Li,metal} - E_{Li_{2}-x_{1}}MnO_{3-\delta}}{e}$$
(2.3)

2.2 Increased Capacity with Oxygen Vacancies

To study the effect that oxygen vacancies had on the capacity of Li₂MnO₃ containing materials, oxygen vacancies were first added to the lattice and then Li vacancies were created one at a time each from the previously found most energetically favorable configuration.



Figure 2.2 The energy of formation of all the sampled V_{Li} sites for systems with the varying V_{Li} concentrations with (a) one V_0 or (c) two V_0 . The distribution of the lithium ions from the (b) V_0 and at an average distance from the (d) two V_0 . Figure from James, et al.¹⁷

Figure 2.2 shows the energy of formations of each sampled V_{Li} position for each X and δ concentration set which was sampled. In addition, the distribution of how far the lithium ions are from the oxygen vacancies is given as reference. It was predicted from calculations on a smaller cell that the lithium positions nearest the V₀ were less stable and therefore the nearest lithium sites to the V₀ were sampled along with an additional site further away as a reference and check. From

Figure 2.2, it was found that the trend of increasing vacancy formation energy at farther distances from the V_0 site was also true in this larger system size. In Figure 2.2 it is apparent that, for the most part, the energy of formation of V_{Li} increases as you move farther away from the V_0 and then plateaus.



Figure 2.3 Energetically most favorable configurations for the systems containing (a) one oxygen vacancy with the first two lithium vacancies and (b) two oxygen vacancies with the first four lithium vacancies. The dotted black lines encircle the V_{Li} - V_O - V_{Li} "dumbbells" seen in both energetically most favorable structures.

The most energetically favorable configurations for Li_{2-X}MnO_{3- δ} for the system with 1V₀ and 2V_{Li} (X=0.125, δ =0.0625) along with the system with 2V₀ and 4V_{Li} (X=0.25, δ =0.125) are shown in Figure 2.3. The most energetically favorable configurations showed that the initial V_{Li} added to the systems form V_{Li}-V₀-V_{Li} "dumbbells" before occupying other sites. This was seen in Figure 2.3(a) for the first two most energetically favorable V_{Li} positions when a single V₀ was initially in the system. This was also seen for the system with two V₀ initially in the system where the first 4 V_{Li} in the system formed two "dumbbells" with the V₀'s, Figure 2.3 (b). The OCV was calculated using Equation 2.3 for X=0.0625,0.125,0.1875,0.25 at V₀ concentrations of δ =0,0.0625,0.125. Each OCV value was calculated for the lowest energy configuration found for each X and δ combination. These values are plotted in Figure 2.4.



Figure 2.4 Calculated OCV curve for Li_{2-x}MnO_{3-δ}. Figure adapted from James, et al.¹⁷

Since 4.2V is a typical cutoff voltage for Lithium-ion batteries, the amount of capacity obtained below this voltage in Figure 2.4 would be the additional capacity added to this material when the Li_2MnO_3 material loses oxygen during the activation process. Looking at the available capacity at 4.2V or lower shows that with no V₀ the material does appear to be electrochemically inactive. However, a significant amount of capacity is added to the material once V₀ are formed.

2.3 Conclusions

The oxygen vacancies were shown to have a strong effect on where lithium vacancies form and their energy of formation. Thus, oxygen vacancies increase the capacity of the lithium-ion batteries. Interestingly, the first two lithium vacancies associated with each oxygen vacancy were found to form in neighboring positions to the oxygen vacancies, such that dumbbells were formed of V_{Li} - V_O - V_{Li} .

Chapter 3. Decreased Lithium Diffusion with Oxygen Vacancies

This chapter is adapted from James, et al.¹⁷ Chapter 2 illustrated how the oxygen vacancies impact the formation of lithium vacancies in and thus the capacity of the Li₂MnO₃ component of lithium-rich cathode materials. However, the impact of oxygen vacancies on the diffusion of lithium is an area that remains largely unexplored in the literature. It has been demonstrated that oxygen vacancies can change the transition metal diffusion. It is well established that degradation of the lithium-rich layered *x*Li₂MnO₃-(1-*x*)Li(Ni,Co,Mn)O₂ phase is related to the transformation from layered to spinel ^{39, 64-67} which starts from Mn diffusion from the transition metal layer to the Li layer ⁶⁸. Computational studies have shown that the oxygen vacancies decrease the energy barrier for the transition metal migration.^{69, 70} 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^{6, 28} are pursued to prevent the phase transformation and maintain a layered structure, another technical challenge, its low intrinsic rate performance,³⁸ is still unsolved.

It is not clear if oxygen vacancies will alter lithium diffusion as well. Practically, $xLi_2MnO_3-(1-x)Li(Ni,Co,Mn)O_2$ also has the disadvantage of low intrinsic rate performance.³⁸ Without the proper kinetics, the high voltage and high capacity region cannot be accessed in practical applications. For example $xLi_2MnO_3-(1-x)Li(Ni,Co,Mn)O_2$ exhibits very high resistance at low state of charge (SOC),⁷¹ 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 Li_{2-x}MnO_{3-δ} participates in delithiation/lithiation. Galvanostatic intermittent titration technique with electrochemical

impedance spectroscopy measurements⁷¹ and direct observation on the reaction kinetics for each element³⁸ clearly suggested that the underlying high resistance is caused by the Li_{2-x}MnO₃₋₆ 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 Li₂MnO₃ is ~2.1 eV²² (comparable to LiCoO₂ ~2.7 eV), thus the high resistance is more likely to be caused by slower lithium-ion diffusion. Xiao et al. studied Li diffusion within Li₂MnO₃ using *ab-initio* molecular dynamics (AIMD) simulations, without considering any vacancies and at 3000 K, a temperature appeared to melt the lattice.²² However, the oxygen and lithium vacancies may be strongly correlated, making a computational study of the kinetics of the Li_{2-x}MnO₃₋₆ component of great interest. Shi *et al.* have discovered that Li diffusion is strongly correlated with neighboring oxygen ions in Li₂CO₃ ^{72, 73}, more specifically, lower oxygen coordination around the moving Li ions leads to higher diffusion energy barrier. This suggest that losing oxygen in Li_{2-x}MnO₃₋₆ may hinder Li diffusion and thus it is important to study Li diffusion kinetics with and without oxygen vacancies.

3.1 Computational Methods

Diffusion was studied by using *ab-initio* molecular dynamics (AIMD) simulations, implemented in *VASP*, which uses first principles to calculate the forces between ions. The AIMD simulations were performed on $2 \times 1 \times 2$ cells of approximately 96 atoms at 1500 K using the Nosé⁷⁴ thermostat. To investigate the impact of oxygen vacancy on the diffusion of Li, *ab inito* molecular dynamics (AIMD) implemented in VASP were used. Systems of Li_{2-x}MnO_{3-δ} were analyzed with several different starting configurations for x = 0.0625, 0.1250 and $\delta = 0$, 0.0625, shown in Figure 3.1. The starting configurations included a lattice just a single V_{Li} and configurations with both V_{Li} and V_O near each other and far apart to examine the correlation between the vacancy types.



Figure 3.1 Initial positions for MD simulations with (a) one V_{Li} , (b) one V_{Li} - V_O in most energetically favorable positions, (c) one V_{Li} - V_O in not energetically minimized positions separate from each other and (d) V_{Li} - V_O - V_{Li} in energetically most favorable positions. Figure reprinted from James, et al.¹⁷

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 (E_A) for lithium diffusion.^{75, 76}

The lower bound of the diffusion coefficient was also estimated using the E_A for lithium hopping near a V_o site using the equation for the diffusion coefficient assuming random walk:

$$D_{rw} = \nu a^2 \exp\left(-\frac{E_A}{k_B T}\right) \tag{3.1}$$

The temperature, T, was assumed to be 300K and the vibrational frequency, v, was estimated as 10^{13} Hz. The hop distance, a, was varied to correspond to each hop. The values of E_A were estimated using the climbing image nudged elastic band method (cNEB)

3.2 Molecular Dynamics Simulations

Molecular dynamics simulations were run to determine the effects of oxygen vacancies on the diffusion of lithium ions. For comparison the first simulation cell only contained a single lithium vacancy. Figure 3.1(a). The motion of all lithium ions which moved further than vibrations around their site were tracked and their displacement is plotted in Figure 3.2 (a). Additionally, the movement of the vacancy was estimated based on the movement of the lithium ions and plotted in Figure 3.2 (b). From Figure 3.2 it was shown that there was a significant amount of lithium movement.



Figure 3.2 AIMD results for system with a single V_{Li} . The lithium ions which moved are shown in (a) with each color representing a different ions displacement from its original site over time. The displacement of the V_{Li} with respect to its original position is shown in (b). Figure reprinted from James, et al.¹⁷

The next simulation contained one V_{Li} and one V_0 in the configuration which was determined most optimal, as discussed in chapter 2 and shown in Figure 3.1 (b). Only one lithium ion was shown to move farther than just vibrating around its original site. This ion moved to the site which originally contained the V_{Li} but only for a few picoseconds before moving back to its original position, Figure 3.3. Therefore, it appears that the V_{Li} and V_0 appear to prefer to remain near each other in their most favorable position and that the barrier for oxygen or lithium ions to move into these sites must be high.



Figure 3.3 MD results from simulation with initial configuration shown in Figure 3.1 (b) with $1V_0$ and $1V_{Li}$ in their most favorable configurations in neighboring sites. The line shows the displacement of the one lithium ion which moved and its displacement over time. Figure from James, et al.¹⁷

To further explore the interaction between the V_{Li} and V_O and to test the favorability of the configuration where they are in their most energetically favorable position another simulation was run with the V_{Li} and V_O initially placed far away from each other, Figure 3.1 (c). In this simulation, movement of both lithium ions and oxygen ions were observed. The movement of two oxygen

ions was seen, Figure 3.4 (b), and they moved such that the V₀ moved across layers towards the V_{Li}. Additionally, significant movement of several lithium ions, Figure 3.4 (a), was observed as the V_{Li} moved to the favorable neighboring site of the oxygen ion. This unexpectedly large amount of movement of the ions showed that the configuration with V_{Li} and V₀ in neighboring positions is very favorable.



Figure 3.4 Ionic movement during MD simulation with 1VO and 1VLi placed away from each other in the initial configuration, shown in Figure 3.1(c). The displacement of all (a) lithium ions and (b) oxygen ions which moved significantly, beyond just vibrating around their equilibrium position, are shown. Figure from James, et al. ¹⁷

For the simulation with V_{Li} - V_O - V_{Li} in the most stable configuration, Figure 3.1(d), a lot of lithium displacement was observed, Figure 3.5. The V_{Li} position in the lithium layer stayed vacant for the

majority of the simulation. Only one lithium atom moved into this site and it was only for very short periods, shown by the blue line in Figure 3.5.



Figure 3.5 Lithium movement in system with two V_{Li} and a single V_0 initially in most energetically favorable positions. Only the displacement of the lithium ions which hopped are shown. Figure from James, et al.¹⁷

While the system with one V_0 and one V_{Li} appears very stable it was concluded that when the second V_{Li} was added the system is much less likely to stay in the most energetically favorable $V_{Li}-V_0-V_{Li}$ configuration. One of the V_{Li} in the $V_{Li}-V_0-V_{Li}$ seems significantly less strongly bonded and free to move. Therefore, it seems that while two V_{Li} may be able to be removed for every V_0 , it appears that only one of the V_{Li} can be replaced and thus add to the capacity of this material.

3.3 Estimation of Diffusion Coefficient

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 Vo, 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 V₀, Figure 3.6.



Figure 3.6 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. Adapted from James, et al.¹⁷

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.²² Additionally, the energy barriers increased significantly due to the nearby V₀. 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 diffusion coefficient was estimated using Equation 3.1.

The value of v in Equation 3.1 was estimated as 10^{13} Hz, as commonly used in the literature. ⁷⁷⁻⁸² As a comparison to the AIMD results, the number of hops expected in the 50 ps simulated time period was estimated by using the hopping frequency, $p = v \exp(-E_A/(k_BT))$. The MD results for the system with one Li vacancy and no oxygen vacancy (x=0.0625 and δ =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 v=10¹³ 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 V₀ and about 1.1 eV for the system with one V₀. At T=300K, the calculated D_{rw} is 2.5x10⁻¹⁶ cm²s⁻¹ for the system with no V₀ and 2.2x10⁻²¹ cm²s⁻¹ with V₀, 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 V₀ and about 0.95 for the system with one V₀, and the value of *a* was estimated as 2.9Å. The value of D_{rw} at *T*=300K was calculated to be $3.3 \times 10^{-13} \text{ cm}^2 \text{s}^{-1}$ without V₀ and $1.01 \times 10^{-18} \text{ cm}^2 \text{s}^{-1}$ ¹ with V₀ present, five orders of magnitude lower. Note we only used the diffusion barrier near the V₀ to estimate the D_{rw} for the system with V₀, if the V_{Li} hopping occurs far away from the V₀, the effect of V₀ will be reduced. Thus, this estimation represents the lower bound of D_{rw} in a V₀ 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 Li₂MnO₃ from muon-spin rotation and relaxation experiments ^{83, 84} but closer to $10^{-14} \sim 10^{-18} \text{ cm}^2 \text{s}^{-1}$ obtained for 0.5Li₂MnO₃-0.5LiMn_{0.42}Ni_{0.42}Co_{0.16}O₂ at higher activation voltage (in the activated Li₂MnO₃ phase). ⁷¹

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 ⁸⁵. 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 ⁸⁵:, because of correlations between the motion of the tracer and a neighboring vacancy. When f is this large it is often neglected, however, in Li_{2-x}MnO_{3- δ}, 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 ⁸⁵:

$$D = \frac{\overline{R_n^2}}{6t} = \frac{a^2 n}{6 t}$$
(3.2)

$$\frac{n}{t} \simeq 6 \,\omega_{AA} \left[V_{Li}' \right] (1 - \eta_0) f_C \left[\left(\frac{(1 - \eta_0)}{1 + \frac{\omega_{AB} \, K_{VO} \, \eta_0}{\omega_{AA} (1 - \eta_0)}} + \frac{K_{VO} \, \eta_0}{\frac{\omega_{BA}}{\omega_{AA}} + \frac{\omega_{BB} \, K_{VO} \, \eta_0}{\omega_{AA} (1 - \eta_0)}} \right) \right]^{-1}$$
(3.3)

$$K_{VO} = exp\left[\frac{-(\Delta G_{VO}^o - \Delta G_{VL}^o)}{k_B T}\right]$$
(3.4)

where *n* is the total number of atomic jumps taken in time, *t*, $[V'_{Li}]$ is the mole fraction of Li vacancies, and η_0 is the fraction of the Li sites that are adjacent to oxygen vacancies. In Equation 3.3, 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_{V0} , is based on the free energies of forming Li vacancies around fully occupied oxygen sites (ΔG_{VL}^o) and adjacent to a vacant oxygen site (ΔG_{V0}^o). A factor f_c is retained here to describe additional correlation effects that extend beyond the assumptions that lead to Equation 3.3.

Two limiting cases of Equation 3.2 are worth noting. In fully stoichiometric material, the limiting diffusion coefficient at $\eta_0 = 0$ is $D(0) = a^2 \omega_{AA} [V'_{Li}] f_C$. With higher η_0 , 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), Equations 3.2 and 3.3 can be used to obtain the following approximation for f:

$$f(\eta_0) = \frac{D(\eta_0)}{D(0)} \cong \frac{(1-\eta_0)\omega_{BA}}{K_{VO}\eta_0\omega_{AA}}$$
(3.5)

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. 3.5 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. 3.5 still indicates that oxygen vacancies are expected to produce large decreases in the Li diffusivity. A more detailed kinetic Monte Carlo simulation could be used to further explore the Li diffusion as a function of x and δ value in Li_{2-x}MnO_{3- δ}.

3.4 Conclusions

The molecular dynamics simulations and the calculation of the energy barrier of hopping both show that the diffusion of the lithium is clearly hindered by oxygen vacancies. Thus, while Chapter 2 showed the advantages of the oxygen vacancies in that they increase the capacity of the battery, there appears to be a limit to the amount of oxygen vacancies which should be added so that the rate capability is not greatly hindered. Chapter 5 will discuss adding dopants to Li_2MnO_3 and their impact on the quantity of oxygen vacancies.

Chapter 4. Correlated Chemical Expansion Due to Oxygen and Lithium Vacancies

The work in this chapter was adapted from Nation, et al.⁸⁶ and adapted and reproduced from James, et al.⁸⁷ with permission from Cambridge University Press. Chemical expansion (ϵ_c) is the change in dimensions of a material due to compositional changes. For an isotropic system, chemical expansion is a scalar computed using the initial lattice length (a_0) and the lattice length with the defects in the crystal (a):

$$\epsilon_c = \frac{a - a_0}{a_0} \tag{4.1}$$

Chemical expansion takes place in various electrochemical devices and impacts the durability of these devices. Most electrode materials used in lithium-ion batteries undergo volume changes which are associated with the changing lithium concentrations within the host electrode materials during the charging and discharging. Graphite, the most common anode material for lithium-ion batteries, undergoes an increase in volume by as much as 10% when the material is lithiated and lithium ions intercalate between the carbon sheets.⁸⁸ For the common cathode materials: LiCoO₂, LiMn₂O₄ and LiFePO₄ the volume typically changes by -2%, -7.3% and -6.5% to their fully delithiated states, respectively.⁸⁹ The volume expansion of these ceramic electrode materials beyond their elastic limitations and combined with the lithium diffusion-induced stresses can cause mechanical degradation and fracture. As a result, the battery can lose capacity and suffer from power fade.

However, the chemical strain can be taken advantage of in order to characterize the concentration of point defects in various materials.^{90, 91} Typically, the amount of expansion per defects is known as the chemical expansion coefficient (α_c) and is calculated from ϵ_c and the amount of vacancies per formula unit, δ or such:

$$\alpha_C = \frac{\epsilon_c}{\delta} \tag{4.2}$$

Furthermore, the elastic model, Equation 4.3, can be used to compute strain in a material from the stress response (σ_c) measured using the multi-beam optical stress sensor (MOSS) method and the elastic biaxial modulus \in of the measured electrode material. The MOSS method measures the stress in a thin film geometry (achieved by coating a thick substrate, with known properties, with a thin electrode film).^{92, 93}

$$\sigma_c = E\epsilon_c \tag{4.3}$$

While it is widely agreed that oxygen is lost from Li₂MnO₃ during the cycling of the material, the quantity of oxygen lost is unknown. A main reason the amount of oxygen lost is unknown is that it cannot be easily measured experimentally. One potential way to experimentally determine the oxygen loss quantity is to deconvolute the MOSS measured change in stress ($\Delta\sigma$) caused by both lithium and oxygen during the charge and discharge cycles:

$$\Delta \sigma = -\frac{M_f}{3V_m^0} \left[\int_{x_0}^x \overline{V_{Ll}} \, dx + \int_{\delta_0}^\delta \overline{V_O} \, d\delta \right]. \tag{4.4}$$

The values of x and δ are the lithium vacancy (V_{Li}) and oxygen vacancy (V₀) concentrations, respectively; V_m^0 is the original volume per formula unit and M_f is the effective modulus. The volume change associated with oxygen vacancies ($\overline{V_0}$) is defined as:

$$\overline{V_O} = \left(\frac{\partial V_O}{\partial N_O}\right)_{T,P,N_{Li},N_{Mn}} \tag{4.5}$$

and the volume change associated with lithium vacancies $(\overline{V_{Li}})$:

$$\overline{V_{L\iota}} = \left(\frac{\partial V_{Li}}{\partial N_{Li}}\right)_{T,P,N_O,N_{Mn}} \tag{4.6}$$

Then, accurately determining $\overline{V_0}$ and $\overline{V_{Ll}}$ via DFT calculations while measuring $\Delta \sigma$ allows for the number of oxygen vacancies formed to be solved for. However, in the case of Li_{2-X}MnO₃₋ δ the V₀ and V_{Li} exhibit correlated effects and therefore the volume change associated with each cannot just be analyzed separately.

Another challenge is how to calculate the chemical strain accurately using the DFT calculations. Equations 4.1 and 4.3 are for the case of an isotropic system and therefore we must modify our approach slightly for $Li_{2-X}MnO_{3-\delta}$ as both the elastic constants and the chemical expansion in $Li_{2-X}MnO_{3-\delta a}$ are anisotropic due to the layered crystal structure with low symmetry. In fact, anisotropic chemical expansion is even needed for cubic structures, such as CeO_2^{94} because the point defect is chemically anisotropic and causes anisotropic local deformation. However, anisotropic calculations are less common and our method will be described below. Overall, this chapter looks at the chemical expansion of V_0 and V_{Li} individually as well as a 1:1 and a 1:2 ratio of V_0 and V_{Li} .

4.1 Method of Calculating Anisotropic Chemical Expansion

This work looks at two methods of computing two types chemical expansion. The first method is straightforward and involves relaxing the volume of the single crystal of the electrode material with the vacancies introduced and calculating the lattice and volume change as compared to the perfect lattice volume. The lattice parameter tensor (h') of the structure which contains a large amount of V_{Li} can be modeled by the following equation, where the initial lattice parameters are the matrix h_0 and the chemical expansion matrix is $\varepsilon_{C,bulk Li}$:

$$\boldsymbol{h}' = \boldsymbol{h}_0 + \boldsymbol{\varepsilon}_{\boldsymbol{C},\boldsymbol{bulk}\,\boldsymbol{Li}}\boldsymbol{h}_0 \tag{4.7}$$

From Equation 3.6 and from the finding h' by relaxing the lattice parameters once the V_{Li} were added the values of $\varepsilon_{C,bulk Li}$ can be solved for:

$$\varepsilon_{C,bulk\,Li} = (h' - h_0) * (h_0)^{-1} \tag{4.8}$$

The first method was to model the chemical expansion due to the V_{Li} that were not directly correlated with the dilute V_0 and added to the high capacity of these materials. This method however was not used for the systems which contained oxygen vacancies since the oxygen vacancies are present in dilute concentrations and therefore their effect would not be accurately captured by this method. The results of this method are presented in Section 4.3.

The second method for calculating the chemical expansion coefficient tensor for dilute vacancies involved a derivation beginning with the total energy (ΔE_{total}) balance which accounts for the long (ΔE_{long}) and short range (ΔE_{short}) interactions of the vacancies:

$$\Delta E_{total} = \Delta E_{short} + \Delta E_{long} \tag{4.9}$$

This method is following the definition of Gillan⁹⁵ and is similar to that used by Er et al. for CeO_{2- δ}.⁹⁶ However, the model of Er et al. is for isotropic systems and therefore is modified in this work so that it shows the anisotropy of the chemical expansion. The main difference between this work and the derivation by Er et al. is that here the chemical expansion is solved for as a matrix (ϵ) instead of as single averaged value. In Equation 4.9, ΔE_{short} represented the local changes directly around the vacancy sites and was calculated using the unit cell volume and the elastic dipole tensor (**G**):

$$\Delta E_{short} = \frac{\delta}{V_{II}} G_{ij} \varepsilon_{ij} \tag{4.10}$$

The values of **G** were calculated from the equation for the energy of formation for a vacancy $(E_{f, vacancy})$:

$$E_{f, vacancy}(\varepsilon_{ij}) = E_{f, vacancy}(\varepsilon_{ij} = 0) + Gij\varepsilon_{ij}$$
(4.11)

From taking the derivative of Equation 4.11 with respect to chemical expansion the values of G are found to be:

$$G_{ij} = \frac{dE_{f, vacancy}(\varepsilon_{ij})}{d\varepsilon_{ij}}$$
(4.12)

The long range energy interactions were found from the following equation where C is the elastic stiffness tensor:

$$\Delta E_{long} = \frac{1}{2} C_{ijkl} \varepsilon_{ij} \varepsilon_{kl} \tag{4.13}$$

Returning to the total energy balance in Equation 4.9, the next step towards deriving the chemical expansion coefficient is to take the derivative of the entire equation with respect to ε_{ij} and set it to zero at equilibrium:

$$\frac{d\Delta \varepsilon_{total}}{d\varepsilon_{ij}} = 0 = \frac{\delta}{V_U} G_{ij} + C_{ijkl} \varepsilon_{C,ij}$$
(4.14)

Then, solving equation 4.14 yields the chemical expansion tensor equation which allows the computation of chemical expansion in all directions for an anisotropic material, in GPa:

$$\boldsymbol{\varepsilon}_{\boldsymbol{\mathcal{C}}} = \frac{-\delta\left(\boldsymbol{\mathcal{C}}^{-1}\boldsymbol{\mathcal{G}}\right)}{V_{U}} \tag{4.15}$$

The chemical expansion coefficient is the chemical expansion per concentration of defects and can also be solved for as a matrix:

$$\alpha_{C,dilute} = \frac{\varepsilon_C}{\delta} = \frac{-(C^{-1}G)}{V_U}$$
(4.16)

Equation 4.16 was again solved for V_O, V_{Li}, V_O-V_{Li} and V_{Li}-V_O-V_{Li} and the $\alpha_{C,dilute}$ values are shown in Table 4.4 which will be presented in Section 4.4. For this chapter all structural relaxations were again done in *VASP* in the same manner as is outlined in Section 2.1

4.2 DFT calculation of the Elastic Stiffness Tensor

The values of *C* can be computed from the following linear relationship between stress and strain:

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl} \tag{4.17}$$

The values of the elasticity tensor, C, were calculated by taking the first derivatives of the VASP computed stresses instead of taking the second derivatives with respect to strain of the total energies, according to the Le Page and Saxe et al.^{97, 98} least squares method, as implemented in MedeA. All of C tensor values were calculated at the same time instead of as independent sums. All computations were done with DFT at 0K, since there is likely to be very minimal temperature-related differences in the C tensor values. For this work, the component values of C are solved for Li₂MnO₃ both manually and directly using the software package MedeA.

A strain of ±0.2% was used to calculate the values of C. For all other calculations strains of ±1% and ±2% was used. The computed least squares residual was used to assess accuracy and was found to be $\leq 1.0\%$ for all calculations. The C values calculated via MedeA for Li₂MnO₃ are below, in GPa:

$$\boldsymbol{C}_{Li_2MnO_3} = \begin{bmatrix} 269 & 48 & 35 & 0 & 0 & 0 \\ & 274 & 34 & 0 & 0 & 0 \\ & & 220 & 0 & 0 & 0 \\ & & & 79 & 0 & 0 \\ & & & & 81 & 0 \\ & & & & & 105 \end{bmatrix}$$

The LiCoO₂ \boldsymbol{C} values were calculated by Qi et al., in GPa:¹⁴

$$\boldsymbol{C}_{LiCoO_2} = \begin{bmatrix} 422 & 106 & 62 & 0 & 0 & 0 \\ & 422 & 163 & 0 & 0 & 0 \\ & & 239 & 0 & 0 & 0 \\ & & & 68 & 0 & 0 \\ & & & & 68 & 0 \\ & & & & & 168 - 0 \end{bmatrix}$$

There are logical similarities and differences between $C_{Li_2MnO_3}$ and C_{LiCoO_2} . The fact that Li_2MnO_3 has lower C_{ij} values in the xx and yy directions than $LiCoO_2$ is likely due to the added lithium within the transition metal layer. Whereas the only slightly lower C_{ij} value in the zz

direction also makes sense because the structure of Li_2MnO_3 and $LiCoO_2$ are very similar in the z direction.

This paragraph is adapted and reprinted from Qi, et al.¹⁴ which is licensed under CC BY-NC-ND 4.0. Deposited electrode thin films are typically polycrystalline and are also often modeled as isotropic elastic materials; therefore, the averaged bulk (*B*), shear (*G*), and Young's (*E*) moduli and Poisson's ratio (v) can be calculated by inputting the experimental or theoretical C_{ij} into Reuss's lower bound, Voigt's upper bound, and Hill's homogenization schemes.⁹⁹ All of these models use the assumption of a polycrystalline structure. The Voigt scheme assumes there is a uniform strain on each grain and therefore is an upper bound on elastic. The Reuss scheme, on the other hand is a lower bound because it uses the assumption of a constant state of stress in the crystallites or grains, which therefore preserves equilibrium. Taking an average of the Voigt and Reuss values is the Hill scheme.¹⁰⁰ The averaged bulk modulus (*B*) and shear modulus (*G*) were computed first and are listed in Table 4.1.

For an isotropic system, the following equations are used to calculate the Young's modulus (E) and Poisson's ratio (v): ⁹⁹

$$E = 9BG/(G+3B)$$
 (4.18)

$$v = (3B - 2G)/(6B + 2G) \tag{4.19}$$

	Voigt	Reuss	Hill
Bulk Modulus, B	111	109	110
Shear Modulus, G	96	94	95
Young's Modulus, E	224	219	221

Table 4.1 The bulk modulus, shear modulus and Young's modulus as determined by the Voigt, Reuss and Hill schemes, all are in GPa.

4.3 Chemical Expansion of Non-Dilute Concentrations of Lithium Vacancies

For the non-dilute concentrations of lithium vacancies, which contribute to the high capacities of the Li_2MnO_3 containing materials, a more direct approach was taken. A few structures were generated at several Li vacancy concentrations, and each has several conjurations containing lithium vacancies at random and their atomic positions and cell volume were relaxed. The system that had the lowest V_{Li} formation energy was used for each lithium vacancy concentration. The systems which were analyzed and the associated V_{Li} formation energies are shown in Figure 4.1 (a).



Figure 4.1 The (a) energy of formation for various configurations was calculated and these configurations were used to analyze the (b) strain in the axes and the (c) overall volume change.

The red line in Figure 4.1 (a) connects the lowest energy structures which were evaluated. One of the structures at X=0.875 is significantly, 45 meV/formula unit, lower in energy than the second lowest energy structure at this concentration. This lowest energy structure at X=0.875 is so low in energy because a lithium ion migrated to a tetrahedral site from the octahedral site. This could be showing the system undergoing a structural change and the movement of lithium ions from octahedral sites to tetrahedral sites would be interesting to further study. However, for this work only the systems with all lithium ions still in the octahedral sites were considered.

The lowest energy configurations determined by Xiao et al. are also shown in Figure 4.1 for comparison. The lowest energy configurations determined by this study were used to analyze the anisotropic chemical expansion by looking at the chemical expansion in all three lattice parameters, as shown in Figure 4.1 (b). However, the chemical expansion in the three directions did not show linear trends which could be modeled. Therefore, the overall volume change was studied, Figure 4.1 (c). The volume change shows a clearer trend of chemical expansion up to a current concentration (about X=0.875), followed by contraction of the lattice. These results could potentially be combined with experimental stress measurements in order to determine the amount of vacancies in the system. The general trend of the c-lattice parameter first increasing before decreasing as the lithium concentration decreases was also observed in LiCoO₂ by Van der Ven et al.¹⁰¹

4.4 Chemical Expansion due to Dilute Vacancies

In order to explore the chemical expansion due to the dilute oxygen vacancies and oxygen-lithium vacancy pairs, the systems with V_0 , V_0 - V_{Li} and V_{Li} - V_0 - V_{Li} were explored. These point-defect structures will create large short-range/local lattice distortion, which is then balanced by the long range elastic deformation, as shown in Equation 4.9.

The chemical expansion and the local bond length changes were calculated for the energetically most stable configurations with a single V_0 or single set of V_0 and V_{Li} . These configurations are shown in Figure 4.2 along with the bonds we analyzed and numbered for clarity. In order to analyze the short range effects of the vacancies, the bonds which are numerically labeled in Figure 4.2 were measured and summarized in Table 4.2.



Figure 4.2 Configurations for systems with (a) VO, (b) VLi-VO and (c) V¬Li-VO-VLi which are energetically most stable and were used for chemical expansion calculations. The bonds that are numbered in the schematic to the right of each configuration are the local bonds to the vacancies which were monitored and summarized in Table 4.2.

	Perfect	Vo		V _O -V _L	i	V _{Li} - V _O	- V _{Li}
Bond #	Bond Length (Å)	Bond Length (Å)	%	Bond Length (Å)	%	Bond Length (Å)	%
1	2.08	2.27	9.13	2.26	8.65	-	-
2	1.94	2.03	4.64	2.08	7.22	2.11	3.94
3	1.93	2.00	3.63	2.03	5.18	2.1	5.00
4	2.13	2.42	13.62	2.41	13.15	2.39	-1.24
5	2.18	2.45	12.39	2.43	11.47	2.42	-1.22
6	2.06	2.27	10.19	-	-	-	-
7	2.18	2.20	0.92	2.27	4.13	2.25	2.27
8	2.13	2.08	-2.35	2.2	3.29	2.19	5.29
9	2.13	1.92	-9.86	2.17	1.88	2.17	13.02
10	2.18	2.22	1.83	2.24	2.75	2.24	0.90
11	2.06	2.07	0.49	2.11	2.43	2.11	1.93
12	2.08	1.90	-8.65	1.92	-7.69	2.13	12.11
13	2.10	2.04	-2.86	2.06	-1.90	2.16	5.88
14	2.08	2.02	-2.88	2.01	-3.37	2.13	5.45
15	2.08	2.08	0.00	2.07	-0.48	2.15	3.37
16	2.10	2.12	0.95	2.11	0.48	2.17	2.36

Table 4.2 A summary of the relaxed bond lengths and the percent difference between these bond lengths and the perfect bond lengths for systems with V_0 , V_{Li} , V_0 - V_{Li} and V_{Li} - V_0 - V_{Li} .

Figure 4.2 and Table 4.2 collectively show that after the addition of the first V_0 the directly connected bonds increased quite significantly in length. On the other hand, the bonds between the lithium ions and the other oxygen ions they were connected to either increased a smaller amount or decreased in length. When the first V_{Li} was added in order to create the V_0 - V_{Li} pair, all of the neighboring oxygen ions to the V_{Li} moved away from the V_{Li} . When the second V_{Li} was added in order to form the V_{Li} - V_0 - V_{Li} dumbbell structure the same trend was seen. The oxygen ions near the V_{Li} moved away from the V_{Li} . This increase in the lengths between the first nearest neighbor ions and the site where the vacancies are created is expected and likely due to the loss of the shielding effect when the vacancy is first formed. Another interesting observation is that with the

 V_{Li} - V_O - V_{Li} set of vacancies the first nearest neighbor lithium ions which remain in the system have moved closer to the V_O while the nearest two manganese ions are further away from the V_O than they were initially.



Figure 4.3 The calculated energy of formation of a vacancy or vacancy set plotted against the applied strain for (a) VO, (b) VLi, (c) VO-VLi and (d) VLi-VO-VLi. Figure (a) and (b) are adapted and reprinted with permission from Cambridge University Press from James, et al. ⁸⁷

The long range chemical strain was calculated following the procedure listed in Section 4.2. First, the elastic dipole tensor, G values, were obtained by fitting the formation energy to the applied strain along each deformation direction. Thus Equation 4.11 was solved for by plotting the $E_{f, vacancy}$ against ε_{ij} and finding the slope, shown in figure 4.2. These G values are summarized in Table 4.3.

$G_{ij}(V_0) [eV]$	$G_{ij}(V_{Li}) [eV]$
$\begin{bmatrix} -5.30 & 0.52 & 0.66 \\ 0.52 & -5.58 & -0.63 \\ 0.66 & -0.63 & -1.44 \end{bmatrix}$	$\begin{bmatrix} -0.98 & 0.00 & 0.68 \\ 0.00 & -0.61 & 0.00 \\ 0.68 & 0.00 & -0.34 \end{bmatrix}$
$G_{ij}(V_0 - V_{Li}) [eV]$	$G_{ij}(V_{Li} - V_O - V_{Li}) [eV]$
$\begin{bmatrix} -4.52 & 0.44 & 1.20 \\ 0.44 & -3.49 & -1.56 \\ 1.20 & -1.56 & -2.61 \end{bmatrix}$	$\begin{bmatrix} -4.47 & -0.64 & 1.43 \\ -0.64 & -1.30 & -1.42 \\ 1.43 & -1.42 & -1.49 \end{bmatrix}$

Table 4.3 Calculated **G** matrices for V_O , V_{Li} , V_O-V_{Li} and $V_{Li}-V_O-V_{Li}$. Portion of table reprinted with permission from Cambridge University Press from James, et al.⁸⁷

Using Equation 4.15 the chemical expansion in each direction was calculated for V_0 , V_{Li} , V_0-V_{Li} and $V_{Li}-V_0-V_{Li}$. The chemical expansion for the V_0 and V_{Li} alone at dilute concentrations were compared to the chemical expansion observed with the V_0-V_{Li} pair, Figure 4.3, and the $V_{Li}-V_0-V_{Li}$ set, Figure 4.4. The chemical expansion was calculated for a single defect or defect set and then extrapolated to other dilute concentrations, plotted in Figure 4.4 and Figure 4.5, using the chemical expansion coefficients which are calculated and shown in Table 4.4.
Table 4.4 Computed values of the chemical expansion coefficient tensor for V_0 , V_{Li} , V_0 - V_{Li} and V_{Li} - V_0 - V_{Li} . Portion of table reprinted with permission from Cambridge University Press from James, et al.⁸⁷

$\alpha_{C,ij}(V_0)$	$\alpha_{C,ij}(V_{Li})$		
$\begin{bmatrix} 0.051 & -0.014 & -0.028 \\ -0.014 & 0.053 & 0.024 \\ -0.028 & 0.024 & 0.004 \end{bmatrix}$	$\begin{bmatrix} 0.010 & 0.000 & -0.026 \\ 0.000 & 0.005 & 0.000 \\ -0.026 & 0.000 & 0.003 \end{bmatrix}$		
$\alpha_{C,ij}(V_{\rm O}-V_{\rm Li})$	$\alpha_{C,ij} ((V_{Li} - V_O - V_{Li}))$		
$\begin{bmatrix} 0.044 & -0.010 & -0.049 \\ -0.010 & 0.028 & 0.061 \\ -0.049 & 0.061 & 0.026 \end{bmatrix}$	$\begin{bmatrix} 0.050 & 0.022 & -0.057 \\ 0.022 & 0.004 & 0.058 \\ -0.057 & 0.058 & 0.013 \end{bmatrix}$		

The chemical expansion was compared for the three directions which were largest in magnitude, xx, yy and zz. The chemical expansion for the various vacancy types were compared to determine if the chemical expansion of multiple vacancies was equal to the linear sum of the chemical expansion of the individual vacancy types. Figure 4.4 shows the chemical expansion for only V_0 and only V_{Li} and how they compare to $Li_{2-x}MnO_{3-x}$ both in the actual system and if the chemical expansion of V_{Li} and V_0 is summed together. It is clearly shown that the chemical expansion due to V_0 and V_{Li} . Therefore showing that the V_0 and V_{Li} interact and have correlated effects.



Figure 4.4 The chemical expansion for the actual chemical expansion in $Li_{2-X}MnO_{3-\delta}$ (solid purple lines) is compared to the chemical expansion for the linear sum of V_{Li} (red lines) and V_O (blue lines) and shown by the purple dotted lines. The chemical expansion is shown in the (a) xx direction (b) yy direction and (c) zz direction. Adapted from James, et al.⁸⁷ and reprinted with permission from Cambridge University Press.



Figure 4.5 The chemical expansion for the V_{Li} - V_O - V_{Li} dumbbell is plotted in the solid purple lines and compared to the dotted purple lines which represent the linear sum of the V_O chemical expansion (blue lines) and twice the chemical expansion of the V_{Li} (red lines). The chemical expansion is plotted for the (a) xx direction, (b) yy direction and (c) zz direction.

The chemical expansion of V_0 and V_{Li} in a 1:2 ratio was studied in a similar way to the vacancies in a 1:1: ratio. The chemical expansion due to V_0 only, V_{Li} only and $Li_{2-2X}MnO_{3-X}$ are plotted in Figure 4.5 along with the linear sum of V_0 and V_{Li} in a 1:2 ratio. It was again shown that the actual chemical expansion is significantly different than the linear sum of the chemical expansion due to the individual vacancies separately.

Figures 4.4 and 4.5 also both show that the chemical expansion in the xx and yy directions are significantly greater in magnitude than the chemical expansion in the zz direction.

The DFT prediction shows that oxygen vacancy generation causes volume expansion in the electrode materials, this will induce a compressive stress in the electrode thin film, since the substrate constrains the in-plane expansion of the active electrode material during electrochemical cycling. Therefore, the DFT predicted chemical strain contribution due to the creation of oxygen vacancies in Li₂MnO₃ was compared to MOSS measured stress and experimental strain values associated with the irreversible first delithiation expansion in the lithium-rich samples.



Figure 4.6. (a) Experimental results of stress and voltage for a Li/ $Li_{1.2}Mn_{0.55}Ni_{0.125}Co_{0.125}O_2$ cell during the initial two cycles. (b) Comparison of oxygen vacancy concentration calculated from capacity and strain. Figure (a) reprinted from and figure (b) adapted from Nation, et al.⁸⁶

Table 4.5 Estimated oxygen vacancy concentrations from capacity compared to estimation from strain. Table adapted from Nation, et al.⁸⁶

Sample	δ capacity	δ_{max} Strain
1	0.30	0.15
2	0.43	0.30
3	0.46	0.51
4	0.44	0.09
5	0.11	0.08

Fig 4.6(a) shows a typical measured stresses (with respect to the initial stress state of the pristine film), correspond to lithiation and delithiation induced structural and chemical changes. The voltage profiles (blue curves) and average in-plane stress (orange curves) response of the first two cycles in a rewriting $Li_{1.2}Mn_{0.55}Ni_{0.125}Co_{0.125}O_2$ film. The stress response during electrochemical cycling is mostly reversible beginning in the second cycle, where delithiation induces a tensile stress (volume contraction), and lithiation involves a compressive stress (volume expansion). The stress response during the first delithiation is initially tensile but reverses around 4 V and becomes compressive, which is attributed to oxygen vacancy generation. More discussions related to the experiments can be found in Nation et al.⁸⁶

Traditionally, a vacancy concentration is estimated using the first charge capacity during the "activation" process. To estimate the number of oxygen vacancies created during the first charge, it was assumed that 60% of the material was Li₂MnO₃ by rewriting Li_{1.2}Mn_{0.55}Ni_{0.125}Co_{0.125}O₂ as 0.6 Li₂MnO₃ - 0.4 LiMn_{.375}Ni_{.3125}Co_{.3125}O₂. This is not a comment as to whether this material is a solid solution or a two-phase system, but rather an approximate exploration of a potential explanation for the compressive drop behavior. This breakdown made it

possible to estimate the lithium vacancy concentrations that were created in the Li₂MnO₃ phase using the measured capacity as

$$x_{Li} = \frac{C_{1st \ charge} - (0.4C_{NMC})}{0.6C_{Li2Mn03}} \tag{4.20}$$

Where $C_{1st \ charge}$ is the first charge capacity of Li_{1.2}Mn_{0.55}Ni_{0.125}Co_{0.125}O₂, C_{NMC} is the theoretical capacity of LiMn_{.375}Ni_{.3125}Co_{.3125}O₂ and $C_{Li2MnO3}$ is the theoretical capacity of Li₂MnO₃. It is assumed that during the activation process, oxygen and lithium are removed in a 1:2 ratio. This gives an upper limit value on the oxygen non-stoichiometry, since it assumes that all of the lithium removed along the plateau is accompanied by oxygen loss. Thus, it is defined as

$$\delta_{cap} = \frac{x_{Li}}{2} \tag{4.21}$$

in Fig 4.6(b).

We then compared the strain-based estimated oxygen vacancy concentration with δ_{cap} estimated using the first charge capacity during the "activation" process. To estimate the oxygen vacancy concentration using DFT predicted chemical strain, the strain associated with the measured stress is first estimated. The elastic constants are assumed to be isotropic and independent of lithium content, with a biaxial modulus of 135 GPa based on DFT predictions in Section 4.3 and experimentally derived values¹⁰² of oxide cathodes. With this rudimentary analysis and elastic deformation relationships (Hooke's law), the average measured irreversible stress during the first delithiation cycled corresponds to an expansion strain of 0.1%.

A vacancy concentration estimated using the compressive strain during the activation process can also be compared to the capacity based estimation described above. The chemical expansion coefficient tensor provides a strain per amount of oxygen non-stoichiometry, δ . Using

the strain per δ and the strain from experimental observations, the oxygen vacancy concentration can be inferred by Equation (4.2).

An average strain-predicted vacancy concentration is estimated using the trace of the chemical expansion coefficient tensor of the Li-O-Li vacancy dumbbell structure, assuming Li:O ration is 1:2. These are indicated by the solid diamond symbols in Figure 4.6(b). An upper bound for the strain prediction of the oxygen vacancy concentration is also calculated using the minimum normal chemical expansion coefficient. There are indicated by the solid square symbols in Figure 4.6(b). Assuming that dilute approximations are valid and that the compressive drop effect is entirely due to oxygen removal, a measured strain of 0.13% corresponds to an average oxygen vacancy creation of δ =0.06 in in Li_{2-x}MnO_{3- δ} using the trace of the chemical expansion coefficient tensor and a maximum vacancy creation of δ =0.29 using the minimum normal chemical expansion

Based on the analysis described above (i.e., using the capacity to calculate the oxygen vacancy levels), comparisons with the estimates of oxygen vacancies based on the measured stress were carried out for five samples. These results are tabulated in Table 4.5 and plotted in Fig. 4.6(b). Most of the strain-derived values are below this equal trend line, which is consistent with idea that the values estimated from the capacity, which assume all Li removal is accompanied by oxygen loss, provide an upper bound on oxygen loss. This seems to be consistent with other estimations of δ based on Rietveld refinement of the structure after cycling, which also suggested that δ was significantly less than the amount required to give the observed extra capacity, assuming oxygen vacancies were formed as Li₂O.⁵⁵ There are several possible explanations for the observation that the capacity-derived oxygen vacancy estimate usually overestimates the vacancies using the strain estimation method. As already noted, it is possible that the actual oxygen loss is less than the

assumed 1:2 ratio here, or more Li are lost in addition to the $V_{Li} - V_O - V_{Li}$ dumbbell structure generation. The additional Li loss will likely cause the volume to decrease, countering the compression due to oxygen loss. Also, edge relaxations along the crack faces in these films tend to decrease the stresses. Other possible factors include oxygen participation in the redox reactions,¹⁰³ the impact of non-dilute vacancies (i.e., correlation effects), or a lower elastic modulus in the delithiated state, as the modulus of a layered compound can be four times higher in the lithiated state than when fully delithiated.¹⁴ Furthermore, oxygen mobility is low,²³ but measurements on thin films are likely more sensitive to oxygen loss than measurements in particles.

In spite of the possible discrepancies that are cited above, the DFT predicted chemical strains can account for the observed stress, and on average accounts for 65% and 13% of the stress using the max and trace chemical expansion coefficients, respectively. These findings support the hypothesis that oxygen loss during the first charge cycle leads to significant irreversible compressive stress during the first charge cycle.

4.5 Conclusions

The chemical expansion was analyzed for both large amounts of lithium removal and dilute vacancy concentrations. The analysis for the large quantities of lithium removal showed that the volume of the material first increased and then decreased with the extraction of lithium. The chemical expansion associated with the dilute oxygen and lithium vacancies was shown to be highly correlated as opposed to a linear sum of the individual vacancies.

Chapter 5. Controlling Oxygen Vacancy Concentration with Dopants

This Chapter is adapted and reprinted from Nation, et al.¹⁰⁴ with permission from Cambridge University Press. Chapters 2-4 showed that V_0 and V_{Li} are much correlated. Chapter 2 showed that V_0 can increase the capacity of the cathode material by activating the manganese ions. The V_0 were also shown, in Chapter 3, to have a negative impact on battery performance by decreasing the diffusion coefficient of the lithium ions. It appears that there might be an ideal amount of oxygen vacancies that increase the capacity without significantly hindering diffusion. This chapter focuses on the addition of dopant ions in the material and specifically how they affect the formation of V_0 .

Through the collaborations with experimentalists, several redox active dopants, such as Si, Sn and Al, have been tried. Interestingly, only Si has shown improved discharge capacity. Figure 5.1 shows experimentally that the high-energy NMC (HENMC), referred to here as lithium-rich, materials exhibit a higher discharge capacity when doped with silicon. The charge curve also exhibited a slight shift (higher capacity at the same voltage) with Si doping. Since silicon is not a redox active element, it seems that it should not affect the capacity of Li₂MnO₃ when added in dilute concentrations. Therefore, section 5.2 first explores the effect of the silicon dopant both locally and on its effect on the energy of formation of lithium ions. Silicon is likely to subsite the manganese, since Si forms a Li₂MO₃ phase¹⁰⁵ that is structurally compatible with the layered oxide. Additionally, Si (4⁺) has the same valence state as manganese, and therefore should not change the valence of the other ions in the pristine material. Si has been successful incorporated into LiNi_xMn_yCo_(1-x-y)O₂ and was shown to increase the capacity and decrease electrochemical impedance.¹⁰⁶



Figure 5.1 Charge and discharge curves for the first cycle of $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ (control) and $Li[Li_{0.2}Mn_{0.49}Si_{0.05}Ni_{0.13}Co_{0.13}]O_2$ (HENMC-Si_{0.05}). Figure adapted from Nation, et al.¹⁰⁴ and reprinted with permission from Cambridge University Press.

Aluminum was also studied as a dopant ion for comparison with Si. In experiments, the ionic size is often used as a guideline for dopant selection. In the layered compounds, the ionic size of Li is about 0.76 Å, much larger than the transition metal ions, $Co^{3+}=0.545$ Å, Mn^{3+} (high spin) = 0.65 Å, Mn^{4+} (high spin) = 0.53 Å. Since the ionic size for $Al^{3+}=0.535$ Å is larger than $Si^{4+}=0.40$ Å, it may be more compatible with the transition metal layer. Section 5.2 shows how it affects the material differently because it has a different oxidation state (3⁺) than the manganese it replaces.

Both aluminum and silicon were added in dilute concentrations, replacing one of the 48 manganese ions in the 96 atom Li₂MnO₃ cells. With one Si or Al substitution of Mn, the concentration is Li₂Mn_{0.94}Si_{0.06}O₃ and Li₂Mn_{0.94}Al_{0.06}O₃. The aluminum or silicon ions were added at the octahedral site of the manganese ion they replaced, as shown in Figure 5.2. In a perfect Li₂MnO₃ lattice, the Mn is in the center of an oxygen-octahedral site. However, Si generally prefers

tetrahedral coordination (e.g., in SiO₂ and Li₄SiO₄), therefore its energy at a tetrahedral site is also computed. This tetrahedral site substitution quickly relaxed back to the octahedral site upon ionic relaxtion, which confirms that the octahedral Mn-site substitution is preferred. All structures went through ionic relaxation with either fixed volume or fully relaxed volume using *VASP* using the same parameters as outlined in section 2.1. The valence electron configurations for the additional elemental constituents were as follows: Si-3s²3p², Al-3s²3p¹. For structures with fully relaxed volume, all cell parameters were fully relaxed to keep the stress below 100MPa.

Figure 5.2 Simulation cells used for the Li_2MnO_3 systems with an (a) aluminum dopant atom and (b) a silicon dopant atom.

5.1 Silicon Dopant

The fully relaxed structures of Li_2MnO_3 with and without silicon dopant at the manganese octahedral site were compared. Figure 5.3 shows the relaxed octahedral structures, with fixed volume, and the bond lengths with the neighboring oxygen ions for the manganese in the perfect system and the silicon with only a single manganese replaced with silicon. By comparing bond lengths it is clear that the silicon brings the neighboring oxygen ions closer. This is consistent with the smaller Si⁴⁺ ionic radii than Mn^{4+.}

Figure 5.3 The (a) Mn-O bond lengths for the perfect crystal structure and (b) Si-O bond lengths for the structure with one silicon dopant. Volume was fixed. Figure adapted from Nation, et al.¹⁰⁴ and reprinted with permission from Cambridge University Press.

Table 5.1 compares the lattice parameters change when the volume was fully relaxed and contained Si dopants with experiments. Experimentally, a control sample with Li_{1.2}Mn_{0.54-} _xNi_{0.13}Co_{0.13}O₂ stoichiometry, and Si doped samples with concentrations, two Li[Li_{0.2}Mn_{0.52}Si_{0.02}Ni_{0.13}Co_{0.13}]O₂ (HENMC-Si_{0.02}) and Li[Li_{0.2}Mn_{0.49}Si_{0.05}Ni_{0.13}Co_{0.13}]O₂ (HENMC-Si_{0.05}), were synthesized. The lattice parameters of these structures were determined using X-ray powder diffraction measurements while all X-ray patterns were matched to the α -NaFeO₂ type layered structure ($R\overline{3}m$ space group). More experimental details can be found in the work by Nation et al.¹⁰⁴ The Li₂MnO₃ crystal structure C2/m has a different symmetry with α-NaFeO₂ type layered structure. To facilitate comparison with experiments, the lattice parameters of the 2x1x2 super cell of Li₂MnO₃ were converted to the α -NaFeO₂ structure.

$$a(in \alpha - \text{NaFeO}_2) = \frac{1}{3}b(in \text{Li}_2\text{MnO}_3)$$
(5.1)

$$c(in \alpha - \text{NaFeO}_2) = \frac{3}{2}c(in \text{Li}_2 \text{MnO}_3) \times \sin(\beta)$$
(5.2)

The increased Experimental data shows that the *a* and *c* parameters increase by ~0.05%-0.15% as the Si doping level increases and the c/a ratio also increases with the doping level. This effect on lattice parameters was also observed in Si-doped LiNi_xMn_yCo_{1-x-y}O₂.¹⁰⁶ However, the DFT

predicted lattice parameters show that the lattices reduces the increasing Si doping. This seems to contradict lattice parameters observed with Si doping. However, Si incorporation can also impact lithium and oxygen vacancy generation, due to defect coupling.

Table 5.1. DFT predicted crystallographic parameters in comparison with as-synthesized HE-NMC samples.¹⁰⁴ Volume was allowed to relax. Table adapted from Nation, et al.¹⁰⁴ and reprinted with permission from Cambridge University Press.

	Sample	a (Å)	c (Å)	c/a	Vol (Å ³) /
					f.u. of
					LiMO ₂
	Control	2.8502	14.2234	4.9903	33.3552
Experiment	HENMC-Si _{0.02}	2.8515	14.2313	4.9908	33.4042
	HENMC-Si _{0.05}	2.8524	14.2448	4.9940	33.4570
DET	Li ₂ MnO ₃	2.8840	14.3509	4.9760	34.5237
calculations	$Li_2Mn_{0.94}Si_{0.06}O_3$	2.8765	14.3423	4.9860	34.3232
	Li ₂ Mn _{0.94} Si _{0.06} O _{2.94}	2.8865	14.3402	4.9680	34.5587

Oxygen vacancies are widely believed to play a role in HE-NMC activation. Thus, the impact of Si doping on all possible oxygen vacancy sites was evaluated. The energy of formation of all possible oxygen vacancies in the system was calculated at a fixed volume and the formation energy is plotted as the oxygen vacancy distance to the Si dopant, as shown in Figure 5.4.

Figure 5.4 Oxygen vacancy formation energy compared to distance from silicon dopant. Volume was fixed at all points.

Figure 5.5 The supercell with a single silicon dopant and a V_0 in the most favorable position. Volume was fixed for these calculations. Figure adapted from Nation, et al.¹⁰⁴ and reprinted with permission from Cambridge University Press.

Figure 5.4 shows that the energy of formation for V_0 was decreased by 0.05eV with a silicon dopant ion as compared to the perfect system, 2.09eV to 2.04eV. Additionally, the energy of formation of V_0 didn't appear to change greatly with respect to distance from the silicon ion. However, there was a small decrease in formation energy for V_0 around 6Å from the silicon ion.

The location of the oxygen ion with the lowest energy of formation at a fixed volume is shown schematically in Figure 5.5.

The most favorable oxygen vacancy position (the lowest formation energy) was located within the octahedral of a lithium which shared a corner with the silicon octahedral. The oxygen vacancy is in another transition metal layer, connecting to the Si via Si-O-Li-O bonding. This could be a reason why the silicon ions cause the Li_2MnO_3 to have a higher capacity even though the silicon is not redox active. The V₀ formed away from the silicon might activate neighboring manganese ions allowing lithium to be removed. In this environment, the oxygen vacancy formation energy is sensitive to the dopant and the strain in the lattice. For example, with a constant volume approach, the oxygen vacancy formation energy is reduced from 2.09eV to 2.04eV (i.e., by 0.05 eV due to Si doping). Without the Si dopant, just expanding the volume by 1%, the vacancy formation energy is reduced from 2.09 to 2.03 eV, as shown in Figure 4.3 for G calculation, due to the volume expansion induced by oxygen vacancy generation.

Si dopants may slightly increase the oxygen vacancy concentration as it lowers the oxygen vacancy formation energy, To further investigate this the system with a silicon dopant and the most favorable V_0 was volumetrically relaxed and shown to expand by 0.84 Å³. With the volume of the cells relaxed the energy of formation of V_0 was 2.03 eV for the perfect system and 2.06 eV for the system with the silicon dopant. This resulting super cell with one Si dopant and one oxygen vacancy (Li₂Mn_{0.94}Si_{0.06}O_{3-0.06}) has a larger volume than the perfect Li₂MnO₃, as shown in Table 5.1. Based on this result, increased oxygen vacancy concentrations in the Si-doped HE-NMC is a likely cause of the increased lattice parameter observed in the experiments.

Oxygen vacancies will also reduce the lithium vacancy formation energy. This should then increase the Li storage capacity at a given cutoff voltage, which provides a possible explanation for the observed impact of Si doping on HE-NMC capacity. In Figure 5.1, the shift in the charge curve means to obtain the amount of charge capacity, the Si-doped samples require less activation energy, as the length of the activation plateau is 13 mAh/g shorter; in the following discharge cycle, the Si-doped samples show ~10% increased capacity.

Note these initial DFT calculations do not address the impact of Si doping on the other degradation mechanisms such as transition metal diffusion into the Li-layer, phase transformation, and electrolyte degradation. Additional experiments and modeling are needed to investigate these possibilities.

5.2 Aluminum Dopant

The addition of an aluminum ion at a manganese octahedral site was also calculated for comparison and the change in the bond lengths with the neighboring oxygen ions in the oxygen octahedral were calculated at fixed volume and compared to those with manganese in the perfect cell, Figure 5.6.

Figure 5.6 Bond lengths of manganese/aluminum with their neighboring oxygen ions. Volume was fixed during calculation. Portion of figure with manganese was adapted from Nation, et al.¹⁰⁴ and reprinted with permission from Cambridge University Press.

As seen in figure 5.6, the bond lengths did not change significantly but became more even, when the volume was fixed. This is also consistent with the similar ionic size of $Al^{3+} = 0.535$ Å with $Mn^{4+}(high spin) = 0.53$ Å.

Figure 5.7 Calculated formation energy for V_0 as compared to their distance from the aluminum dopant ion. Volume was fixed during calculations.

The impact of Al doping on all possible oxygen vacancy sites was evaluated. As shown in Figure 5.7, the V₀ formation energy was significantly decreased (from 2.09 eV to 0.89 eV) for the oxygen ions directly neighboring the aluminum dopant. This is very different from what is in Si dopant. This is mainly because the charge on Al is ³⁺. Therefore the neighboring oxygen gets one electron less than that from Mn^{4+} , thus becomes less stable that that in the bulk of Li₂MnO₃. This can be represented by the following defect reaction:

$$O_o + 2Mn_{Mn} = V_o^{-} + 2Al'_{Mn} + \frac{1}{2}O_2(g)$$
(5.3)

It shows substituting Mn^{4+} with Al^{3+} will increase the oxygen vacancy concentration. Therefore, due to the change in the charge of aluminum as compared to manganese, the formation energy of V_0 changed significantly.

However, it is expected that this oxygen vacancy generation will not affect the capacity of the Li₂MnO₃. In Si doped Li₂MnO₃, the V₀ formed away from the silicon is in a Mn-O octahedral. So oxygen vacancy generation will likely activate the neighboring manganese ions (changing it from Mn⁴⁺ to Mn³⁺), which in turn allowing the lithium to be removed. However, in Al doped structure, the oxygen loss is next to the Al and it is compensated by the difference in oxidation state of aluminum compared to manganese. So this oxygen vacancy loss will not cause any valence change on Mn and therefore will not activate the material to deliver more Li capacity. This has been observed by experiments.¹⁰⁴

5.3 Conclusions

In Chapters 2 and 3 it was shown that the oxygen vacancies could increase the capacity of Li₂MnO₃ and also decrease the rate capability. This chapter showed that adding dopant ions can change the energy of formation of the oxygen vacancies and thus potentially help to tune the amount of oxygen vacancies in the system. Silicon, specifically, was shown to decrease the energy of formation of an oxygen vacancy in a neighboring octahedral of the silicon dopant which could potentially activate a manganese ion.

Chapter 6. Interactions between Li2MnO3 Surface and Ethylene Carbonate

The previous chapters have illustrated how oxygen vacancies impact some key performance criteria of lithium-ion batteries and how oxygen vacancy concentrations may be altered by dopants. The oxygen vacancies can be generated inside of particle¹⁰⁷ and surfaces²³. Specifically, Lee et al. argued V_o can only be created on the surface of Li₂MnO₃ because of the large energy barrier O ion to hopping.²³ Nevertheless, oxygen vacancy should be easier to form on the surface than in the bulk. Recently, Jung et al. suggested that the oxygen release may accelerate the degradation of the electrolyte.¹⁰⁸ Therefore, this chapter focus on the interaction of electrolyte with the Li₂MnO₃ surface with and without the oxygen vacancies on the surface.

Another often observed degradation mechanism in Mn containing cathode materials is the disproportionation of Mn³⁺ into Mn⁴⁺/Mn²⁺ and the dissolution of Mn²⁺ from the oxide surface. Many papers reported that ppm levels of dissolved Mn ions diffuse to the anode surface, deposit on the solid electrolyte interface (SEI) on the anode, cause degradation of the passivating SEI layer and result in capacity loss. Previous Mn dissolution studies are largely focused on spinel LiMn₂O₄. Computational studies have been done on this material to illustrate the dissolution process in order to help the design of electrolyte additives and coatings. This problem has been computationally studied in the spinel cathode material Li₂MnO₄^{109,110,111} Side reactions at the surface of the LiMn₂O₄/electrolyte interface have been observed that degrade the electrode surface and ethylene carbonate (EC) (a key component in common electrolytes) when the voltage is high. Materials containing Li₂MnO₃ are frequently cycled to ~4.4V or higher on the first cycle and thus it is of interest to study the interactions between EC and the Li₂MnO₃ surface.

Jung et al. investigated the reaction between oxygen and EC in the context of LiMO₂ materials and proposed that two O₂ molecules reacted with EC to form 2 CO₂, CO and H₂O.¹⁰⁸ However, the reaction between EC and the Li₂MnO₃ surface, with and without V₀ remains largely unexplored. Additionally, there is little research done on the Li₂MnO₃ surface itself. Shin et al. calculated the Wulff structure and studied many surfaces, proposing that the (001), (110) and (100) facets are dominate.²⁵ However, that study did not look at the (131) surface and the (131) surface appears to be the most similar to the stable (104) LiCoO₂ surface. The work presented here, therefore, creates and analyzes the (131) Li₂MnO₃ surface and investigates the interaction between the surface and EC, both with and without the presence of V₀.

6.1 Computational Method

The calculations were done using a Li_2MnO_3 slab in *VASP*. Most computational details are the same as listed in Section 2.1. The valence electron configurations for the additional elemental constituents were as follows: C-2s²2p², H-1s¹. Slab model were constructed to compute surface energies. The slab models contained a vacuum space that was >15Å thick above the Li_2MnO_3 surface. A k-points mesh of 3x3x1 was used for all the slab models.

The surface energy for two stoichiometric surfaces, namely (131), and (101) and one nonstoichiometric (001) surface were calculated via the slab models. For stoichiometric surfaces, the surface energy (γ) was computed using its relation to the slab energy (E_{slab}), the number of layers (N), the bulk energy per layer (E_b) and the surface area of the slab (A):

$$E_{slab} = NE_b + 2A\gamma \tag{6.1}$$

In order to solve for γ from Equation 6.1, the E_{slab} was plotted against N and the y-intercept of the linear fit of this plot was divided by 2A.

After determining the surface orientation with the lowest surface energy, possible vacancy generation site was determined by computing the surface oxygen vacancy formation energy on all possible site.

Then the adoption energy of EC molecule on the surface were computed via

$$E_{adsorption} = E_{total} - E_{slab} - E_{adsorbate}, \tag{6.2}$$

where E_{total} , E_{slab} and $E_{adsorbate}$ are the total energy of the optimized slab with the molecule (EC) adsorbed on the Li₂MnO₃ surface, the clean Li₂MnO₃ surface and the single molecule (EC). Various EC adsorption configurations were tested in order to identify the lowest energy configuration. Here a more negative adsorption energy indicates a stronger adsorption.

6.2 Ethylene Carbonate Adsorbed on Li₂MnO₃ Surface

First, the surface energy for Li_2MnO_3 (001), (131) and (101) orientations were computed and compared. Each layer in the (131) and (101) slabs contains stoichiometric lithium, manganese and oxygen as in the bulk Li_2MnO_3 . The (001) surface is lithium-terminated and nonstoichiometric. It is also important to note that one of the most favorable surface of the layered $LiCoO_2$ is (104).¹¹² As Li_2MnO_3 is usually added to the layered materials, it is likely that Li_2MnO_3 surface will take the most comparable structure with the (104) $LiCoO_2$ surface. Due to the different symmetry of LiCoO₂ and Li₂MnO₃, (131) Li₂MnO₃ surface is the most compatible structure of the (104) LiCoO₂ surface.

Following Equation 6.1, Figure 6.1 plots the the E_{slab} as a function of the number of layers N for the two stoichiometric surface models, (131) and (101). The resulting values of γ are shown in Table 6.1.

Table 6.1 The surface energy values for the (101), (131) and (001) Li_2MnO_3 surfaces.

	Surface Energy, γ
Surface	(J/m²)
(101)	1.72
(131)	0.88
(001)	0.94

The surface energies of lithium-terminated (100) slab structures was determined according to:

$$\gamma = \frac{1}{2A} (E_{slab} - n_{formula} * \mu_{bulk} - \Sigma n_{Li} \mu_{Li}, \tag{6.3}$$

where A is the surface area, E_{slab} is the total energy of the slab, $n_{formula}$ is the integer number of stoichiometric formula units in the slab, μ_{bulk} is the energy of one formula unit of corresponding bulk structure, n_{Li} is the number of excel Li in the slab and μ_{Li} is the chemical potential of Li (-1.9 eV/atom). The γ value for the (001) surface however was not solved for using several different numbers of layers, due to computational complexity only a slab with 5 layers was computed and used to calculate γ directly.

Figure 6.1 Plots of E_{Slab} vs the number of layers (N) for the (a) (101) and (b) (131) Li_2MnO_3 surfaces.

The Li_2MnO_3 (131) surface was chosen for the following surface studies because it was the lowest energy surface analyzed plus two additional reasons. First, it is most similar to the most stable $LiCoO_2$ surface, (104). Additionally, it contains lithium, manganese and oxygen ions which is helpful in determining how EC will adsorb.

Figure 6.2 shows both the Li_2MnO_3 (131) and $LiCoO_2$ (104) surfaces. It is clear that the Li_2MnO_3 (131) surface is the Li_2MnO_3 surface most similar to the $LiCoO_2$ (104) surface. The transition metal and lithium layers of these materials are evident in both the Li_2MnO_3 (131) surface and $LiCoO_2$ (104) surface. Also, the each of the transition metal ions have four nearest oxygen neighbors within the same layer, one oxygen nearest neighbor below and one oxygen nearest neighbor above in both surfaces.

Figure 6.2 Comparison of the similar structure of (a) Li_2MnO_3 (131) and (b) $LiCoO_2$ (104) surfaces. Green atoms are lithium, red are oxygen, purple are manganese and blue are cobalt.

Figure 6.3 Fully atomically relaxed structures with EC (a) parallel to the surface, (b) horizontal on the surface and (c) vertically placed on the surface. White atoms are hydrogen, bronze are carbon, red are oxygen, green are lithium and purple are manganese.

To determine how the EC molecule would interact with the Li₂MnO₃ (131) surface, three possible EC adsorption configurations were fully relaxed and their energies were compared. The first configuration of EC is referred to here as parallel to the surface, as shown in Figure 6.3 (a). The second configuration is referred to as horizontal here because EC is not flat on the surface but on its side, as shown in Figure 6.3 (b). Lastly, a vertical configuration of EC was also analyzed, as shown in Figure 6.3 (c). For each of the three EC configurations shown in Figure 6.3, the adsorption energy was calculated using Equation 6.2. The adsorption energies were -0.66 eV, -

0.30 eV and -0.12 eV for the parallel EC, horizontal EC and vertical EC, respectively. This suggests that the EC molecule prefers to interact with the surface as the configuration with the EC most flat on the surface was the energetically most stable one. Typically when the adsorption energy is less than -0.4eV (or -40kJ/mol), the adsorption is considered a chemical adsorption. Therefore the parallel adopted configuration (Figure 6.3(a)) will be further investigated for different EC decomposition pathways.

6.3 Decomposition of Ethylene Carbonate on Surface

Two different EC decompositions were looked at which were found to be favorable on LiMn₂O₄ (Leung).¹⁰⁹ The first was the breaking of one of the C-O bonds within the EC molecule, Figure 6.3 (a) and (b). For this configuration the bond between the ketone carbon and an oxygen with the ring was broken, similar to what was done by Leung, Figure 6.4 (c).¹⁰⁹ The broken molecule was placed such that the oxygen in the broken bond was placed near a surface manganese ion and the carbon from the broken bond was near a surface oxygen ion. This configuration was 0.10eV higher in energy than the parallel adsorption configuration.

Figure 6.4 The decomposition of EC via breaking one of the C-O bonds in the ring on (a) Li_2MnO_3 . A more zoomed in image of the EC is shown in (b). The (c) EC decomposition in a similar manner on $LiMn_2O_4$ is shown for comparison, figure (c) was adapted with permission from Leung.¹⁰⁹ Copyright 2012 American Chemical Society.

Another decomposition of the EC which was studied was the loss of a single hydrogen to the Li₂MnO₃ (131) surface. However, as the DFT atomic minimization was performed the system relaxed to a state where two hydrogen atoms left EC and were on the surface. The system with a single hydrogen on the surface is 0.95 eV higher in energy than the intact EC adsorbed parallel to the surface. The system with two hydrogen on the surface forming two –OH bonds, however, is 1.20eV lower in energy that the system with the intact EC adsorbed. The systems with the possible decompositions of EC are summarized in Figure 6.5 and compared to the intact EC configuration.

Figure 6.5 The intact EC are plotted along with the different possible decomposition configurations studied and their corresponding energies with respect to the EC adsorbed state. Color scheme: carbon (brown); oxygen (red); hydrogen (white); manganese (purple); lithium (green).

The chemically adsorbed EC seems to be energetically favorable to loss two H atoms to the O on the Li₂MnO₃ (131) surface. It suggested a new EC decomposition reaction as:

$$\underbrace{\bigcirc}_{O} \\ (EC) \\ \bullet \\ (EC) \\ \bullet \\ (VC) \\ (VC) \\ \bullet \\ (VC) \\ (VC$$

The resulted product is a vinylene carbonate, (VC), that is physically adsorbed on the Li₂MnO₃ (131) surface indicated by the large distance of over 3 Å to the surface. This reaction was considered as a proton abstraction reaction by Borodin et al.^{113.} They found that it was favorable for two protons to be removed at once for the EC/NMO[100] system and also they found a favorable reaction for the loss of a single proton on DMC/NMO[100], EC/NMO[111], and EC/NMO[111], where NMO refers to delithiated spinel-structured LiNi_{0.5}Mn_{1.5}O₄ cathode materials. Based on the energetics shown in Figure 6.5, the one proton abstraction reaction seems to be an energy barrier of 0.95eV for the two proton abstraction reaction. The physical adsorption of VC also means it will return to the electrolyte easily. VC is known to be a common electrolyte additive that is beneficial to SEI stability.¹¹⁴ Therefore this decomposition mechanism may be beneficial as well.

6.4 The Effect of Oxygen Vacancies on the EC Interaction with the Li₂MnO_{3-δ} (131) Surface

In order to further study the impact of the oxygen vacancies, the location and impact of surface oxygen vacancies were explored on $Li_2MnO_{3-\delta}$ (131) surface. There were found to be 12 possible oxygen sites on the surface and amongst them were three categories in as far as nearest neighbors, this is summarized below in Table 6.2 along with the system energies and V_o formation

energies. One of these categories had three in-plane lithium neighbors, one in plane manganese neighbor and one lithium neighbor below it. Another set of oxygen sites had two lithium in plane neighbors, two manganese in plane neighbors and one lithium neighbor below. The last category had 3 lithium in plane neighbors, 1 manganese in plane neighbor and one manganese neighbor below it. Within these categories were other assumed configurational differences because there were surface V₀ with the same configuration of lithium and manganese neighbors but different formation energies. The V₀ which was determined most favorable had a formation energy of 0.85eV, 3 lithium in-plane neighbors, one manganese in plane neighbor and a single lithium neighbor below it. Note this formation energy is much lower than that in the bulk (2.09eV), therefore it confirms that the oxygen vacancy formation will likely start from the Li₂MnO₃ (131) surface.

Energy		Li in	Mn in	Li	Mn
(eV)	Ef (eV)	Plane	Plane	below	below
-710.90	0.85	3	1	1	
-710.55	1.20	3	1	1	
-710.90	0.85	3	1	1	
-710.55	1.20	3	1	1	
-710.19	1.56	2	2	1	
-710.18	1.57	2	2	1	
-710.19	1.56	2	2	1	
-710.18	1.57	2	2	1	
-710.02	1.72	3	1		1
-709.87	1.88	3	1		1
-710.02	1.73	3	1		1
-709.87	1.88	3	1		1

Table 6.2 The total system energy, energy of formation of a V_0 for each oxygen site on the Li₂MnO₃ (131) surface. Additionally, the number of Li and Mn neighbors, both in plane and in other planes, are listed.

The adsorption of EC on the surface with the most favorable V₀ present was investigated. The EC was added both tilted and completely vertical with the ketone oxygen in the V₀ site. After full structure relaxation, the EC in the completely vertical position is more favorable by 0.02eV. Additionally, both molecules appeared to move so the EC oxygen was not in the V₀ site on the Li₂MnO₃ (131) surface. This suggests that the EC molecule does not interact as much with the surface near a V₀. Therefore it can be considered that EC will prefer to be absorbed at the oxygen free Li₂MnO₃ (131) surface, as discussed in Section 6.3. However, will the oxygen release have an impact on electrolyte decomposition?

Figure 6.6 An EC molecule on the (131) Li_2MnO_3 surface containing a single V₀ on the top, surface, layer and the EC (a) tilted or (b) completely vertical.

Therefore, the interactions and possible reaction pathways between an oxygen atom released from the surface with the EC molecule were also investigated. The EC molecule and the oxygen atom were placed together in a 20Åx20Åx20Å cube. First all atomic positions except the extra oxygen atom and one of the carbon atoms it was closest to in the EC ring were relaxed. Then all the atoms in the EC plus the extra oxygen atom were relaxed. The initial and relaxed configurations are shown below in Figure 6.7. The total energies of the systems shown in Figure 6.7 are summarized in Table 6.3 and the difference between the energy of configuration 1 and each configuration is summarized in Table 6.4.

Figure 6.7 Configurations of EC molecule plus an extra oxygen before and after the atomic positions were minimized using DFT.

Table 6.3 Total energies for each configuration both while the C-O distance was constrained and when all the atoms were allowed to relax.

	Total Energy (eV)				
	1	2	3	4	5
Fixed C-O position	-63.55	-63.77	-66.12	-63.64	-67.88
All Atoms Relaxed	-63.72	-63.80	-68.55	-67.80	-67.94

Table 6.4 The difference between the energy of configuration 1 and the other configurations summarized for both while the C-O bond distance was fixed and when all atomic positions were minimized.

	Difference in Energy from Configuration 1 (eV)				
	1	2	3	4	5
Fixed C-O position	0.00	-0.22	-2.57	-0.09	-4.33
All Atoms Relaxed	0.00	-0.09	-4.84	-4.08	-4.22

From Table 6.4 it appears that the completely relaxed structure of EC and the oxygen where the oxygen bonds with the EC ring between a hydrogen and carbon atom is the most favorable structure. The -OH group on the EC molecule may not be stable, so continuous reaction with O atoms will lead to further decomposition of EC to CO₂, CO and H₂O, as suggested by Jung et al.¹⁰⁸ Further calculations are needed to clarify this.

6.5 Conclusions

Li₂MnO₃ (131) is the most stable surface for Li₂MnO₃. The (131) Li₂MnO₃ contains lithium, manganese and oxygen on the surface. This is the surface which is most similar to the stable (104) LiCoO₂ as the lithium and transition metals have four in plane oxygen neighbors with one oxygen neighbor in the layer below and one oxygen neighbor in the layer above.

EC chemically adsorbed on the Li_2MnO_3 (131) surface. An EC to VC reaction after two proton abstraction reaction from EC is found on Li_2MnO_3 (131) surface. We believe this reaction is beneficial to the life of the lithium-ion battery, as VC tends to form more stable SEI.

However, the oxygen vacancy on the surface did not promote EC adsorption. Therefore it will not facilitate this EC deprotonation reaction. At the same time, due to the oxygen loss, the Mn will be subject to Mn dissolution more easily and triggers more SEI related degradation mechanisms that are beyond the scope of this thesis.

Chapter 7. Conclusions and Proposed Work

7.1 Conclusions

Li₂MnO₃ stabilized materials, or lithium-rich materials, have the potential to be high capacity materials for lithium-ion batteries. These materials are activated during the first charging cycle, at least in part, with the release of oxygen. However, prior to this work, little was known about the impact of the created oxygen vacancies in the Li₂MnO₃ component.

This work found that there is a clear correlation between oxygen vacancies and lithium vacancies. The formation of oxygen vacancies causes the neighboring lithium sites to be unfavorable. This impacts the performance of the battery in two ways. First, it causes a lower formation energy for lithium vacancies near the oxygen sites which increases the capacity of the material. Additionally, the migration barrier for lithium to hop into the sites near the oxygen vacancies increase, causing the battery to have a lower rate capability.

The chemical expansion corresponding to the creation of oxygen vacancies and lithium vacancies was also explored. The oxygen vacancies and lithium vacancies were observed to also be correlated in terms of chemical expansion. The chemical expansion associated with multiple vacancies was not a linear sum of the individual vacancy types which shows that the two vacancy types have a correlated impact.

Oxygen vacancies were also found to be affected by dopants. In particular, silicon was shown to decrease the energy of formation for oxygen vacancies in neighboring octahedral to the silicon dopants. This is important because it shows that the amount of oxygen vacancies might be tunable. Additionally, the oxygen vacancies that are now more favorable to form could activate manganese ions and add capacity to the material. Lastly, the interactions between the Li₂MnO₃ (131) surface and an electrolyte component, ethylene carbonate (EC), were explored. The Li2MnO3 was shown to be similar to stable LiCoO₂ (104) surface in that the transition metals in both surfaces had four planar oxygen neighbors. An energetically favorable decomposition reaction of the loss of two hydrogen atoms from the EC to the Li₂MnO₃ surface was found forming vinylene carbonate (VC). Additionally, interaction between EC an oxygen ions, which could potentially be lost from the surface was explored. The oxygen vacancies clearly impact electrochemical properties and decomposition of the electrolyte. Additionally, dopant ions have an impact on the formation of oxygen vacancies.

7.2 Proposed Future Work

The role of oxygen vacancies can still be more deeply explored in Li_{2-x}MnO₃₋₆. Further combined experimental and theoretical studies to determine the amount of oxygen vacancies in experimental Li₂MnO₃ containing electrodes would be of interest. In particular, an unanswered question is if there is an optimal amount of oxygen vacancies that would increase electrochemical properties, such as capacity, of the material without significant negative impact of other electrochemical properties, such as rate capability. The amount of oxygen vacancies might be tunable via the addition of dopants to Li₂MnO₃ and should be further investigated by looking at dopants beyond silicon and aluminum. Lastly, more research could be done on the Li₂MnO₃ surface to see how the EC which is interacting with an oxygen ion lost from the surface may decompose on the surfac

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