INTERFACIAL REACTIVITY STUDIES OF ELECTROCHEMICAL ENERGY STORAGE MATERIALS FROM FIRST PRINCIPLES

A Dissertation

Submitted to the Faculty

of

Purdue University

by

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In Partial Fulfillment of the

Requirements for the Degree

of

Doctor of Philosophy

December 2019

Purdue University

West Lafayette, Indiana

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Dedicated to my wife, Michelle, and to my parents, Scott and Lori.

ACKNOWLEDGMENTS

First, I want to express gratitude toward my advisor, Prof. Jeffrey Greeley, for his support and guidance throughout graduate school. I have learned a lot from working with him and hope to emulate his technical expertise and scientific creativity in the future. I also appreciate his willingness to let me explore new ideas independently in order to foster my own creativity in research, while continuing to challenging me and keeping the vision for my graduate studies focused. I am also thankful for the scientific mentorship of Dr. Larry Curtiss throughout my time researching in his group at Argonne National Laboratory, in addition to our work together in continuing collaborations. Thank you also to the other members of my dissertation committee, Prof. Vilas Pol, Prof. Jeffrey Miller, and Prof. Edwin García, for promoting stimulating scientific discussions in my qualifying and prelim exams, and for directing me toward interesting new research avenues throughout my graduate studies.

I am thankful to have worked with, and to have learned from, the current and former members of the Greeley research group, including: Dr. Handan Yildirim, Dr. Zhenhua Zeng, Dr. Jeff Lowe, Dr. Tej Choksi, Dr. Hee-Joon Chun, Dr. Paulami Majumdar, Joseph Kubal, Dr. Brandon Bukowski, Pushkar Ghanekar, Ranga Rohit Seemakurthi, Siddharth Desphande, Yinan Xu, Ankita Morankar, Kaustubh Sawant, and Tristan Maxson. I especially want to acknowledge Dr. Handan Yildirim and Siddharth Deshpande for their direct contributions and collaborations on the energy storage projects within the group. I also want to thank the other members of the Molecular Materials group at Argonne for their guidance, collaborations, and good company throughout my tenure at ANL: Dr. Márton Vörös, Dr. Hakim Iddir, Dr. Juan Garcia, Dr. Peter Zapol, Prof. Badri Narayanan, Dr. Rajeev Assary, Dr. Lei Cheng, Dr. Stefan Vajda, Dr. Avik Halder, Dr. Ahn Ngo, Dr. Mingxia Zhou, Dr. Jason Howard, and Barbara Hall.

Much of the work in this thesis is collaborative in nature and therefore would not have been possible without the contributions of many excellent experimental and computational researchers outside of the Greeley and Curtiss research groups. These include: Dr. Jeff Elam, Dr. Lin Chen, Prof. Matthias Young, Dr. Donghyeon Kang, Dr. Anil Mane, Dr. Maria Chan, Prof. Kendra Letchworth-Weaver, Dr. Chris Johnson, Dr. Wesley Dose, Dr. Paul Fenter, Dr. Tim Fister, Dr. Jae Jin Kim, Prof. Andrew Gewirth, Dr. Kimberly Bassett, Kenneth Madsen, Prof. Chris Wolverton, Shane Patel, Prof. Michael Bedzyk, Dr. Guena Evmenenko, Prof. Vinayak Dravid, Dr. Fernando Castro, Prof. Mark Hersam, Dr. Kan-Sheng Chen, Prof. Amin Salehi-Khojin, and Leily Majidi. This is likely not an exhaustive list, and I apologize for any omissions, but the co-authors of publications associated with this work are also listed at the header of their corresponding chapters. I also want to thank the other members of the Purdue Catalysis Center (research groups of Profs. Fabio Ribeiro, Nick Delgass, Raj Gounder, Jeffrey Miller, Peilin Liao, and Christina Li) for many stimulating discussions in our weekly seminars.

This research was funded by the Center for Electrochemical Energy Science, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. Additional funding from the DOE SCGSR Fellowship is appreciated as well, for supporting my research at Argonne National Laboratory. In general, the commitment of the Department of Energy toward funding basic energy research is greatly appreciated. I also want to acknowledge computing resources from Purdue University (RCAC), Argonne National Laboratory (Center for Nanoscale Materials and the Laboratory Computing Resource Center) and Lawrence Berkeley National Laboratory (NERSC).

I am grateful for the friends I have made throughout graduate school, of which there are too many that have touched my life in some way to list. However, a special shoutout to The Boyz is warranted: Jason Bates, Phil Kester, Adam Wingate, and Mr. Manager himself, Dr. Scott McClary. Shred til yer dead.

Finally, I would like to thank my family, including: my parents Scott and Lori Warburton, my in-laws Mike and Donna Rasicci, my grandparents, siblings, brotherand sister-in-laws, and many aunts, uncles, and cousins, who have been supportive throughout my growing up and throughout my education and career. Thank you to my four-legged companion, Louie, for sitting around my shoulders throughout a good portion of my writing this dissertation. Lastly, of course, thank you to my wife, Michelle Warburton, for her enduring love and support.

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ABSTRACT

Warburton, Robert E. Ph.D., Purdue University, December 2019. Interfacial Reactivity Studies of Electrochemical Energy Storage Materials from First Principles. Major Professor: Jeffrey P. Greeley.

Since their commercialization in the early 1990's, rechargeable lithium ion batteries (LIBs) have become ever-present in consumer electronics, and the share of electric vehicles within the transportation sector has become much more significant. *Ab initio* modeling techniques - namely density functional theory (DFT) - have played a signifcant role in describing the atomic scale nature of Li⁺ insertion and removal chemistry in LIB electrode materials, and have been pivotal in accelerating the design of energy dense battery materials based on their bulk properties. Despite these advances, there remains a knowledge gap with respect to understanding the many complex reactions that occur at the surfaces and interfaces of rechargeable battery materials. This work considers several case studies of surface and interfacial reactions in energy storage materials, using DFT modeling techniques to develop strategies that can rationally control the interfacial chemistry for optimal electrochemical performance.

The first portion of this thesis aims to understand the role of interfacial modification strategies toward mitigating Mn dissolution from the spinel LiMn_2O_4 (LMO) surface. First, a thermodynamic characterization of LMO surface structures is performed in order to develop models of LMO substrates for subsequent computational surface science studies. A subset of these surface models are then used analyze interfacial degradation processes through delithiation-driven stress buildup and crack formation, as well as reaction mechanisms for ethylene carbonate and hydrofluoric acid to form surface Mn^{2+} ions that are susceptible to dissolution. Surface passivation mechanisms using protective oxide and metallic coatings are then analyzed, which elucidate an electronic structure-based descriptor for structure-sensitive atomic layer growth mechanisms and describe the changes in lithiation reactions of coated electrodes through electronic band alignment at the solid-solid interface. These studies of protective coatings describe previously overlooked physics at the electrode-coating interface that can aid in further development of coated electrode materials. Using the LMO substrate models, a thermodynamic framework for evaluating the solubility limits and surface segregation tendencies of cationic dopants is described in the context of stabilizing LMO surfaces against Mn loss.

Next, solid-solid interfacial models are developed to evaluate the role of nanostructure in catalyzing the lithiation of NiO to form reduced Ni and Li_2O as concurrent discharge products. Applying a Ni/NiO multilayer morphology, interfacial energies are evaluated using DFT and implemented into a classical nucleation model at a heterogeneous interface. These calculations, alongside *operando* X-ray scattering measurements, are used to explain atomic scale mechanisms that reduce voltage hysteresis in metal oxide LIB conversion chemistry.

The structure between a Li metal anode and the lithium lanthanum titanate solid electrolyte are subsequently analyzed as a model system to understand potential interfacial stabilization mechanisms in solid-state batteries. This analysis combines bulk, surface, and interfacial thermodynamics with *ab initio* molecular dynamics simulations to monitor the evolution of the interfacial structure over short time scales, which provides insights into the onset of degradation mechanisms. It is shown that the reductive instability of Ti^{4+} is the primary driving force for interfacial decomposition reactions, and that a lanthanum oxide interlayer coating is expected to stabilize the interface based on both thermodynamic and electronic band alignment arguments.

In the last part of this thesis, charge transfer kinetics are studied for several applications using constrained DFT (cDFT) to account for electronic coupling and reorganization energies between donor and acceptor states. Charge hopping mechanisms to and from dichalcogenide-based electrocatalysts during O_2 and CO_2 reduction/evolution reactions in Li- O_2 and Li- CO_2 battery systems are first evaluated.

Then, the role of the spatial separation Li^+ vacancies and interstitials on hole and electron polaron hopping in the prototypical Li_xCoO_2 cathode is analyzed. The results demonstrate that Marcus rate theories using cDFT-derived parameters can reproduce experimentally observed anisotropies in electronic conductivity, whereas conventional transition state theory analyses of polaron hopping do not. Overall, this proof-of-concept study provides a framework to understand how charged species are transported in battery electrodes and are dependent on charge compensating defects.

Finally, the key insights from these studies are discussed in the context of future directions related to the understanding and design of materials for electrochemical energy conversion and storage.

1. INTRODUCTION

1.1 Electrochemical Energy Storage

Atmospheric CO_2 levels have been rising exponentially since the industrial revolution, and in recent years have exceeded 400 parts per million [1]. As a consequence, climate change poses great ecological challenges that will translate further into global economic and developmental challenges, necessitating drastically reduced consumption of fossil fuels and a transition to more sustainable sources of energy [2]. Although fossil energy resources continue to make up a majority of the domestic energy profile of the United States, there has been increased adaptation of renewable energy sources in recent years [3]. In practice, further transition from fossil fuels to widespread adoption of renewable energy technologies will require large scale infrastructural transformations related to both the grid and transportation sectors of the energy economy [4, 5]. However, given these trends, many opportunities lie ahead for technological developments toward methods of energy production with reduced or zero net greenhouse gas emissions [6, 7]

Many of the potential environmentally friendly technological approaches have solutions rooted in, or related to, electrochemistry vis-á-vis electrochemical energy conversion and storage [8]. Since wind and solar renewable energy sources are intermittent, electrochemical energy conversion and storage technologies are promising avenues to convert energy into liquid fuels or to be stored in batteries. For example, there is great interest in using hydrogen for fuel cell technology [9], wherein the electrochemical oxygen reduction reaction at the fuel cell cathode [10, 11, 12] produces energy that can power vehicles with only water as the exhaust byproduct. Although most production of the hydrogen energy carrier in fuel cells occurs through natural gas steam reforming which releases greenhouse gases, there is much work being done to develop (photo)electrochemical cells that can perform water splitting (hydrogen evolution) reactions [13, 14] to generate hydrogen with zero net emissions. Moreover, there are considerable research efforts to use electrochemical reactions to generate liquid fuel production, with CO_2 electroreduction [15] to methanol [16] as perhaps the most well-documented example.

Additionally, electrochemical energy storage in rechargeable batteries have found widespread application in the consumer electronics and transportation sectors of the economy [17], and these technologies are likely to find further use in the grid storage applications in the years to come [18]. This dissertation will focus in particular on addressing knowledge gaps related to electrochemical energy storage in rechargeable batteries, where the specific scientific challenges to be addressed will be motivated in further detail throughout this Introduction and in the the subsequent chapters. While the studies in this work are limited in scope to rechargeable batteries, the insights demonstrated herein are also likely to be transferable to the aforementioned electrochemical reactions, among others. Through these scientific investigations, many of the key insights related to the modeling and simulation of electrochemical interfaces are likely to prove useful toward the understanding and design of efficient electrochemical devices for sustainable energy conversion and storage applications.

1.2 Lithium Ion Batteries

Since their commercialization by the Sony Corporation in 1991 [19], rechargeable lithium ion batteries (LIBs) have been ubiquitous in consumer electronics and have increasingly been adapted for transportation applications in electric vehicles in recent years [17]. In recognition of the essential role that LIB technology plays in modern life with respect to consumer electronics, in addition to their potential to combat climate change through decreased dependency on the internal combustion engine with electrified transportation, the 2019 Nobel Prize in Chemistry was recently awarded to three pioneers in the field for their early development of lithium ion batteries [20]. In 1976, Stan Whittingham first demonstrated that lithium ions could react with TiS₂ dichalcogenides in a 2 V electrochemical cell with a lithium metal anode [21]. A few years later in 1980, John Goodenough and co-workers discovered the lithium cobalt oxide cathode material, $\text{Li}_x \text{CoO}_2$, which pushed the cell voltage to ~4 V, dramatically increasing its energy density [22]. Akira Yoshino later developed the first commercially viable lithium ion battery in 1987, by implementing a carbon anode that could insert lithium ions, rather than use a lithium metal anode, dramatically improving upon safety issues associated with previous prototypes [23].



Figure 1.1.: Schematic of a lithium ion battery during charge and discharge. The two electrodes (anode and cathode) are separated by an ionically conducting, electrically insulating electrolyte. During discharge $(Li^+ + e^-)$ pairs are transferred from the anode to the cathode, and the reverse reaction occurs upon charge. Adapted from Ref. [17].

In terms of their operation and performance, LIBs (as well as other rechargeable battery chemistries) consist of three main components: two electrodes (anode and cathode) and an electrolyte; see Figure 1.1. As shown in Figure 1.1, lithium ion and electron pairs ($\text{Li}^+ + \text{e}^-$) are transferred from the anode to the cathode during discharge of the battery, which generates energy. Upon charge, the reverse reaction occurs, and the ions and electrons are transferred back to the cathode. The driving force for lithium-coupled electron transfer is predicated on the electrochemical equilibrium criterion of the electrochemical potential equivalency of the working ion, Li, between the cathode (c) and anode (a) [24, 25]:

$$\mu_{Li}^c - z_{Li} F \phi_c = \mu_{Li}^a - z_{Li} F \phi_a \tag{1.1}$$

where μ_{Li}^i is the chemical potential of Li in electrode *i*, ϕ_i is the voltage (or potential) of electrode *i*, *F* is the Faraday constant, and z_{Li} is the valence of Li ions. Of course, in a LIB the working Li ion will have a valence of one (Li⁺, $z_{Li} = 1$), so $z_{Li}F = e$, the elementary charge of an electron. As such, the effective cell voltage between the cathode and anode is

$$\Delta \phi = \phi_c - \phi_a = -\frac{\mu_{Li}^c - \mu_{Li}^a}{e} \tag{1.2}$$

This relationship is convenient for *ab initio* thermodynamic analyses using theoretical simulation techniques, and has analogies to aqueous electrochemical systems through the computational hydrogen electrode approach popularized by Nørskov and co-workers for the study of fuel cell and electrolyzer catalysis [11]. The electrostatic potentials of the electrodes, in turn, can also be related to the Fermi energy (E_f) of each electrode at a given state of charge, which corresponds to the chemical potential of the electrons.

Given the principles that underpin the operating voltage of a lithium ion cell, this also imposes certain design constraints toward the development of high performance electrolyte compounds. At the most fundamental level, the electrolyte must be electronically insulating [27] to ensure that charge (electrons) are passed through the external circuit and to prevent safety issues associated with a short circuit cell [28]. Further, the electrolyte must remain oxidatively (at high voltage limit against the cathode) and reductively (at low voltage limit against the anode) stable. This can



Figure 1.2.: Electronic energy levels of battery electrodes and electrolyte compatibility requirements for a stable voltage window. The ϕ_i correspond to the work functions of the electrodes, or the chemical potential of electrons, and $\Delta \phi$ is the cell voltage. IP_{elec} is the ionization potential of the electrolyte molecule and E_g is the HOMO-LUMO gap. The figure on the right demonstrates drawbacks to higher voltage cells, which push the oxidative and reductive stability limits of typical molecules used as electrolytes. Adapted from Ref. [26].

be understood at a basic level through vacuum alignment of the electrode potentials (ϕ_i) and the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) of the electrolyte molecule.¹ As described by Goodenough [26, 29] and shown in Figure 1.2 this outlines, in general, whether the voltage window set by the anode and cathode is "stable" when paired with a given electrolyte. In the left panel of Figure 1.2 a stable voltage window is shown, wherein the electrolyte is both oxidatively and reductively stable since the HOMO is lower in energy than ϕ_c and the LUMO is higher in energy than ϕ_a . In contrast, an unstable voltage window (shown in the right panel of Figure 1.2) is one wherein either the HOMO is higher

¹A molecular orbital-based framework for the electrolyte is presented here since most electrolytes used in LIBs are liquid-phase organic compounds. For solid-state electrolytes, as will be discussed in detail in Chapter 10, the HOMO and LUMO would instead correspond to the valence band maximum (VBM) and conduction band minimum (CBM), respectively.

in energy than ϕ_c (electrolyte oxidation would tend to be thermodynamically favored at the cathode) and/or the LUMO is lower in energy than ϕ_a (electrolyte reduction is favored at the anode). While this schematic - in dealing with bulk properties of the anode, cathode, and electrolyte materials - is quite simplistic, it can still provide important insights into boundary conditions for the design of safe battery systems with high energy density. There are certainly complexities associated with a bulk-like analysis of side reactions in LIBs, since these processes occur at electrode/electrolyte interfaces, which will be discussed further in Section 1.4, as well as many of the following chapters of this dissertation.

1.3 Lithium Ion Battery Electrode Materials

In terms of LIB chemistry, most electrode materials are based on Li⁺ intercalation into a host electrode material, as illustrated by the schematic in Figure 1.3a. For intercalation reactions, the maximum charge (or capacity) that an electrode can hold is set by the solubility limit of Li⁺ ions in the host material (or rather, the density of interstitial sites available for lithiation and delithiation reactions).

As mentioned in the previous section, graphite is the most commonly used anode material in LIBs [23]. Carbon-based materials such as graphite can intercalate ~1 Li^+ ion per 6 carbon atoms (theoretical capacity of 372 mAh g⁻¹) and lithiate between 0.1-0.2 V vs. Li/Li⁺ [32, 33, 34]. Since the voltage of graphite is quite low, this is also often in the range of the reduction potentials of molecules in the liquid electrolyte [26]. As a consequence, this leads to the facile formation of a solid electrolyte interphase (SEI) [35, 36] comprised of a mixture of solids such as Li₂CO₃ [37] and LiF [38], which are associated with decomposed electrolyte molecules. However, the SEI also serves as a protective passivation layer and Li ions are still able to diffuse through the SEI between the electrolyte and the anode. In recent years, there has also been interest in silicon anodes, which offer an exceptional increase in theoretical capacity over graphite (~3579 mAh g⁻¹) given its ability to insert up to 3.75 Li⁺ ions per silicon atom through an alloying reaction [39, 40]. A > 300% volume expansion



Figure 1.3.: a) Schematic of a lithium ion intercalation reaction, where Li⁺ ions are inserted and removed from interstitial sites of the electrode host material; reproduced from Ref. [30]. b) Common crystal structures of lithium ion cathode materials, where Li⁺ are shown in green and the polyhedrons represent the localize metal-oxygen and polyanion geometries; reproduced from [31].

limits the practical use of pure silicon anodes [39], although research into the optimization of silicon-carbon composite anodes has lead to capacity increases compared to the graphite baseline, while limiting volume expansion problem associated with the silicon component [41, 42]. Lithium metal is the theoretically optimal anode material, offering the highest potential energy density through a 0 V vs. Li/Li⁺ redox potential (by definition) and a maximum possible specific capacity of 3860 mAh g⁻¹ through the absence of a secondary host material. However, safety issues limit its usage including dendrite growth through the uneven deposition of lithium, having the potential to short circuit the cell [23, 28]. Solid-state electrolytes are being actively considered to enable the usage of lithium metal anodes [43], although there are many scientific challenges to this implementation as will be touched on in Chapter 10.

Figure 1.3b shows the three most common types of LIB cathode materials: layered $LiCoO_2$ [22], spinel $LiMn_2O_4$ (LMO) [44, 45], and olivine $LiFePO_4$ (LFP) [46, 47]. The crystal structures of these cathodes suggest different mechanisms for Li⁺ conductivity in the bulk lattice (diffusion is in 1D, 2D, and 3D for LFP, LCO, and LMO, respectively) and there are tradeoffs between the materials in terms of voltage and practical specific capacities (LCO: ~ 4.2 V vs. Li/Li⁺, 140 mAh g⁻¹; LMO: ~ 4.1 V vs. Li/Li⁺, 120 mAh g⁻¹; LFP: ~ 3.45 V vs. Li/Li⁺, 160 mAh g⁻¹) [31]. These figures of merit can be further tuned through further alloying. For example, introduction of electrochemically inert Al³⁺ into LCO (NCA cathodes) enhances electrochemical stability [48], Ni and Mn introduction into LCO increase the capacity (NMC) [49], and Mn introduction into LFP increases the voltage (LMFP) [46]. Despite improvements by some metrics, the drawbacks to these alloying strategies include that NCA has decreased capacity (since Al^{3+} ions are electrochemically inactive), NMC is more reactive with the electrolyte, and LMFP has decreased rate capability [50]. Ni^{2+} can be also alloyed with Mn in spinel LMO, which can push the cathode above 4.5 V vs. Li/Li⁺, enabling very high voltage LIBs; however, this exceeds the stable voltage window (oxidation potential) of most commonly used liquid electrolytes [26, 51].

In addition to intercalation reactions, whose capacities are limited by the starting material volume and availability of interstitial sites, conversion reactions present an opportunity for higher capacity electrode materials [52]. As depicted in Figure 1.4, a conversion reaction involves the direct reaction of Li⁺ ions with the chalcogen ion in a metal oxide, fluoride, phosphide, or nitride. In oxides [53], the most common class of conversion electrode materials, Li⁺ reacts with oxygen ions to form Li₂O while electrons reduce the transition metal ions to metallic particles. Because these reactions are not limited by the volume of the electrode, they have the potential for extremely high capacities (> 500 mAh g⁻¹) [54]. There are many issues related to

the reversibility of conversion reactions, however, due in part to large volume changes and significant voltage hysteresis from interfacial thermodynamics [52, 53].



Lithium Ion Conversion Reactions:

Figure 1.4.: Schematic of a lithium ion converison reaction, where Li^+ react with the chalcogen ion (X) in a metal oxide, fluoride, phosphide, or nitride, to form reduced metal nanoparticles in a matrix of lithium oxide; reproduced from Ref. [30]

Theoretical calculations have proven quite useful toward an understanding the performance of battery electrodes and for designing materials with enhanced energy storage capabilities. Using the principles outlined above, first principles calculations have been able to describe reaction voltages [55, 56, 57, 40, 58] and phase stability [59, 58] of electrode materials. Calculations have also been used to describe surface structure [60, 59, 61, 62, 63, 64] and surface lithiation reactions [65], and can provide insights into rate capability through evaluation of ionic [66, 67, 58, 68, 69] and electronic [70, 50, 71, 72] conductivities of known or candidate electrode materials. High-throughput calculation efforts, such as the Materials Project [73], have also enabled rapid screening of promising battery materials based on their bulk properties.

1.4 Interfacial Reactivity

In the previous section, the reactivity of the electrolyte with the anode and cathode were discussed in terms of electrode potential alignment with the HOMO and LUMO levels of the electrolyte. On the cathode side, while electrolyte oxidation is known to be facile at the interface with high voltage LNMO spinels [74], reactions between lower voltage cathodes and the electrolyte can occur as well. As mentioned previously in the context of Figure 1.2, the experimentally observable voltage of a cathode (from electrochemical characterization) come largely from the bulk properties, whereas interactions with the electrolyte occur at the surface. These reactions can be quite complex and in general are not understood in a totally comprehensive manner. Complications may arise from the fact that most cathode materials are semiconductors with anisotropic ionization potentials depending on the surface facet that may vary from bulk properties [75], which has been should to lead to structuresensitive SEI growth [76].

This work will largely focus on using computational techniques to understand and control interfacial reactivity in LIB systems. Mechanisms for undesired side reactions and potential methods to mitigate them will be explored through the theoretical modeling of surface-functionalized electrode materials. There will also be several analyses of solid-solid interfacial chemistry presented in the context of nanostructured electrodes for lithium ion conversion reactions and the interface between solid electrolytes and lithium metal.

1.5 "Beyond Lithium Ion" Battery Chemistries

There is also great interest in so-called "beyond lithium ion" battery systems, which encompasses a broad class of chemistries. This includes monovalent sodium [77] and potassium [78] ion batteries, as well as multivalent magnesium, calcium, and aluminum ion batteries [79]. These chemistries, are analogous to LIBs in that they are largely predicated on intercalation reactions. The potential benefits include that some of these working ions are more earth abundant than lithium (Na, K, Mg, Ca) and that multivalent chemistries offer the potential for increased capacities since more than one electron is transferred per ion. However, these ions are all bigger than lithium, presenting conductivity issues. Reversible intercalation of multivalent ions has proven especially difficult, though there is much ongoing work to address these challenges.

Bearing some similarily to the aforementioned LIB conversion reaction chemistry, there is much work being done on lithium sulfur [80] and lithium oxygen (or lithium air) [81] battery chemistry. These systems, using sulfur and oxygen as the cathode have the potential for exceptionally high energy densities based on the formation of Li_2S and Li_2O_2 discharge products. While the majority of this work will focus on lithium ion chemistry, charge transfer studies are performed on metal dichalcogenide electrocatalysts for Li-O₂ batteries in Chapter 13. Motivated by both the presence of CO_2 in a real "air" cathode for Li-O₂ chemistry as well as energy storage applications of CO_2 storage, there has also been recent work toward the reversible electrochemical reduction of CO_2 with Li⁺ to form Li₂CO₃ in a Li-CO₂ battery system [82]. An electrocatalytic study of Li-CO₂ battery chemistry will be discussed in Chapter 14, applying similar methods to that of the analysis of the Li-O₂ system.

1.6 Theoretical and Computational Methods

Similar to the applications-oriented Introduction presented previously in Sections 1.1-1.5, this section is meant to be a broad overview of the theoretical and computational techniques applied across the different studies presented herein. Within the individual chapters, a more focused and system-specific subset of these methods will be presented. This discussion should serve as a general introduction to the relevant *ab initio*, thermodynamic, and kinetic theories, whereas certain Chapters may assume a certain level of background knowledge in these approaches.

1.6.1 Density Functional Theory

The computational approaches applied in this work are based on approximations to the Schrödinger wave equation of quantum mechanics [83, 84, 85]:
$$H\Psi = E\Psi \tag{1.3}$$

where H is a Hamiltonian operator, Ψ is the wave function, and E is the energy.

The discussion herein, going from the Schrödinger wave equation to a computationally tractable form of the Hamiltonian that can be solved using a model basis for the wave function is largely guided by selections from the texts in Refs. [86, 87]. First, without any initial approximations or simplifications, the total Hamiltonian for a system with N electrons, K nuclei of charges Z_n is given by the following:

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{n=1}^{K} \frac{P_n^2}{2M_n} + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{i,j=1;i\neq j}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{1}{4\pi\epsilon_0} \sum_{n=1}^{K} \sum_{i=1}^{N} \frac{Z_n e^2}{|\mathbf{r}_i - \mathbf{R}_n|} + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{n,n'=1;n\neq n'}^{K} \frac{Z_n Z_{n'} e^2}{|\mathbf{R}_n - \mathbf{R}_{n'}|}$$
(1.4)

where the terms in equation 1.4 (from left to right) are the kinetic energy of the electrons, kinetic energy of the nuclei, Coulomb repulsion between electrons, Coulomb attraction between electrons and nuclei, and Coulomb repulsion between the nuclei. The dimensionality of this operator becomes very large, very quickly, before N can reach double digits, making the resulting Schrödinger equation impossible to solve for most systems of interest. Therefore, certain approximations must be made.

First, the Born-Oppenheimer approximation [88] states that since the motion of nuclei is much slower than that of electrons, these interactions are effectively decoupled, simplifying the electronic Hamiltonian.

$$H_{BO} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{i,j=1;i\neq j}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{1}{4\pi\epsilon_0} \sum_{n=1}^{K} \sum_{i=1}^{N} \frac{Z_n e^2}{|\mathbf{r}_i - \mathbf{R}_n|}$$
(1.5)

However, the second term in equation 1.5 is still computationally intractable, given its high dimensionality. In general, this term can be modeled approximately using an uncorrelated effective potential dependent on the positions of the nuclei, \mathbf{R}_i , such that:

$$H = \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} + V(\mathbf{r}_i) \right]$$
(1.6)

This effective potential $(V(\mathbf{r}_i))$ takes many forms in different quantum mechanical approximations such as the Hartree and Hartree Fock exchange potentials, but in general will be dependent on models for Ψ . The atomic wave functions ψ_i are generally modeled through a combination of elementary functions called basis functions, the sum of which is referred to as a basis set, which will be discussed briefly following the introduction of the Kohn-Sham equations.

The quantum mechanical modeling in this dissertation is primarily performed using an approximation called density functional theory, or DFT. The pioneering development of DFT is described in seminal works by Walter Kohn, Pierre Hohenberg, and Lu Jeu Sham, namely the Hohenberg-Kohn theorem [89] which led to the construction of the Kohn-Sham equations [90] that form the theoretical basis of modern DFT electronic structure codes. In brief, the Hohenberg-Kohn theorem shows that the ground state properties can be represented accurately by a functional of the electron density. This drastically reduces the dimensionality of the Hamiltonian, given that $V(\mathbf{r}_i)$ can be described simply in terms of electron density, $n(\mathbf{r})$, rather than on the basis of the individual electron orbitals. The general independent single particle DFT Hamiltonian, in three-dimensions and atomic units is given by:

$$H_{DFT} = -\frac{1}{2}\nabla^2 - \sum_{n} \frac{Z_n}{|\mathbf{r} - \mathbf{R}_n|} + \int d^3 r' n(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} + V_{ex}[n](\mathbf{r})$$
(1.7)

The $V_{xc}[n](\mathbf{r})$ is the exchange correlation potential that depends on the electron density. While Kohn-Sham DFT demonstrated that there is a form of V_{xc} that accurately reproduces the exact ground state properties, the exact functional form is unknown. Much of the method development work within DFT involves improved or adapted forms of V_{xc} , which tend to fall within the following approximations. The local density approximation, where V_{ex} depends only on the density, i.e. $V_{xc} = V_{xc}[n(\mathbf{r})]$. The generalized gradient approximation (GGA) [91, 92] accounts for inhomogenaeities in the system through consideration of local perturbations in electron density by incorporating the gradient into the exchange and correlation, $V_{xc} = V_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r})]$. GGA-type exchange correlation functionals tend to be the work horse of modern applications in DFT calculations of solids. However, meta-GGAs, which also incorporate the Lagrangian of electron density, i.e. $V_{ex} = V_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r})]$, are gaining traction as computational power improves over time. Clearly, as the functional form of the exchange correlation potential becomes more complex and presumably more accurate, the computational expense of the corresponding calculation increases as well. In addition to LDA, GGA, and meta-GGA functionals, hybrid functionals such as PBE0 [93], HSE06 [94], among others [95] incorporate mixing with the so-called exact exchange afforded by quantum chemical Hartree Fock calculations.

The eigenvalue solutions, ϵ_k , to the set of DFT eigenvalue problems in equation 1.7 correspond to the electronic energy levels in the system,² factoring into the total DFT energy.

$$E = \sum_{k=1}^{N} \epsilon_k - \frac{1}{2} \int d^3 r d^3 r' n(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}') + E_{xc}[n] - \int d^3 r V_{xc}[n](\mathbf{r}) n(\mathbf{r})$$
(1.8)

As implied from previous discussion, the electron densities in DFT are determined from the expectation value of the model wave functions, which are expanded in series of basis functions, called a basis set. In molecular systems, the basis functions typically adopt Slater [97] or Gaussian [98] type orbitals, e.g. Pople basis sets [99]. For extended systems, i.e. solids, it becomes mathematically convenient to represent the atomic basis functions (ϕ_k) through an expansion of sines and cosines in reciprocal space within periodic boundary conditions:

²Koopmans' theorem [96] states that the ionization potential is equal to the negative of the HOMO energy, CBM, or E_f (the latter only in the case of a metallic system). Similar ideas were presented in the discussion of the Goodenough diagram (Figure 1.2) and the relative electronic band levels of battery electrodes and this therefore allows for analogous parameters to be evaluated computationally through DFT. The absolute numerical values of these eigenvalues will vary based on the approximate form of the exchange-correlation functional and as such, generally only relative values in the orbital levels and total energies are compared.

$$\phi_k(\mathbf{r}) = e^{i\mathbf{G}\cdot\mathbf{r}} \tag{1.9}$$

where \mathbf{G} is the wave vector [100]; the exponential functional satisfies the periodicity of the lattice, according to Bloch's theorem [101], and the total wave function is comprised of an expansion of this basis set:

$$\psi = \sum_{\mathbf{G}}^{G_{max}} c_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$$
(1.10)

that is truncated by a user-specified cutoff associated with the maximum frequency (or kinetic energy) of the wave vector, called the energy cutoff, $E_{cut} = \frac{\hbar^2}{2m} G_{max}^2$.

Overall, these theoretical approaches allow for wave function optimization of extended systems, which can determine the ground state charge densities and energies of the systems of interest.

1.6.2 Hubbard U Correction

As mentioned in Section 1.6.1, GGA exchange-correlation functionals have seen widespread use in DFT modeling of solids. While GGA functionals perform quite well for systems with highly delocalized electron densities, such as metals, they often fail to describe the material properties of systems with more localized, molecule-like, bonding environments, such as transition metal oxides. More specifically, the electrons in 3d transition metal oxides, as well as f electrons in rare-earths, are strongly correlated with on-site Coulombic repulsions and often have crystal field splittings that would be inconsistent with a Hund's rule-like filling of these orbitals. GGA and LDA exchange-correlation functionals fail to reproduce these complex physics. As discussed previously, hybrid functionals can be used to address some of these issues through introduction of Hartree-Fock exchange and correlation mixing; however, these calculations are very expensive and therefore infeasible for large-scale production run DFT calculations. As such, DFT with a Hubbard U correction (DFT+U) [102, 103, 104] has been routinely employed in computational studies of battery materials, the cathodes of which are most often lithium 3d transition metal oxides.

The GGA+U energy depends on the electron density (ρ) as discussed in Section 1.6.1, but also on the occupation matrix of the set of orbitals to which the U correction is applied (\hat{n}). The GGA+U total energy expression can be represented by the following:

$$E_{GGA+U}[\rho, \hat{n}] = E_{GGA}[\rho] + E_{Hub}[\hat{n}] - E_{dc}[\hat{n}]$$
(1.11)

where the U correction term $E_U[\hat{n}]$ is represented by the latter two terms in equation 1.11:

$$E_U[\hat{n}] = E_{Hub}[\hat{n}] - E_{dc}[\hat{n}]$$
(1.12)

There are various representations of the E_{dc} term that have been implemented [103, 104, 105], though the commonly employed the spherically averaged E_{dc} term as presented by Dudarev [106] is as follows:

$$E_{dc}[\hat{n}] = \frac{U - J}{2} \operatorname{Tr} \hat{n} (\operatorname{Tr} \hat{n} - 1) = \frac{U_{eff}}{2} \operatorname{Tr} \hat{n} (\operatorname{Tr} \hat{n} - 1)$$
(1.13)

$$E_U(\hat{n}) = \frac{U - J}{2} \operatorname{Tr}(\hat{n}(1 - \hat{n})) = \frac{U_{eff}}{2} \operatorname{Tr}(\hat{n}(1 - \hat{n}))$$
(1.14)

where U and J are the Coulomb and exchange, terms, respectively. As shown in equations 1.13 and 1.14, these parameters are often lumped into an effective U-value, $U_{eff} = U - J.$

Overall, DFT+U approaches have been shown to give more accurate voltage predictions of Li⁺ insertion reactions in battery materials [107, 108, 109], as well as more accurate thermochemistry predictions for 3d transition metal oxides in general [110, 109]. The selection of a proper U-value is not trivial, and often depends on the application. Chapter 2 will further discuss an example of DFT+U calibration for surface models based on redox thermochemistry, similar to the approach in Ref. [110].

1.6.3 Bulk, Surface, and Interfacial Thermodynamics

Ensuring that DFT calculations are being performed using realistic atomic-scale models requires thermodynamic characterization of equilibrium surface and interfacial structures under physically meaningful conditions. This involves determining reference states that are consistent with the phase stability of the compound of interest. For example, the free energy per atom of a multicomponent compound, α is the sum-product of the component (*i*) mole fractions and their chemical potentials (μ_i).

$$g_{\alpha}^{bulk} = \sum_{i} x_i \mu_i \tag{1.15}$$

The free energy of formation (Δg_{α}) of this compound is taken as the difference between its free energy and the component chemical potential references under standard conditions (μ_i^0) :

$$\Delta g_{\alpha} = \sum_{i} x_i (\mu_i - \mu_i^0) \tag{1.16}$$

The compound α is thermodynamically stable if, for its composition the second derivative of its Δg_{α} is positive in all dimensions of phase space (convex).

$$\left(\frac{\partial^2 \Delta g}{\partial x_i^2}\right) > 0 \tag{1.17}$$

for all *i*. It is relatively straightforward to show that for the composition of the compound α in cases where this stability criterion is not satisfied, that the system free energy is minimized by decomposing into two or more neighboring compounds in phase space that do satisfy the criteria of a convex energy surface at that point. This convex energy surface is commonly referred to as the convex hull and can be solved for numerically [111] to determine a set of thermodynamically stable phases given thermodynamic inputs.

However, chemical conditions are likely to modulate the values of the system μ_i which, in turn, determine which compounds are stable at those conditions. These chemical potential tuning knobs could be adjusted by pressure, temperature, activity coefficients in solution, and (for the case of i = Li as discussed in Section 1.3) voltage in an electrochemical system.

Therefore, the phase stability of α must also be linked with a physically meaningful range of μ_i for appropriate chemical reference states. This can be determined by first identifying phases on the convex hull to which α is a nearest neighbor (close in composition) and solving for the two-phase equilibrium criteria of component chemical potential equivalency. For equilibrium between α and the stable phase β ,

$$\mu_i^{\alpha} = \mu_i^{\beta} \tag{1.18}$$

for all *i*. This enables the determination of stability conditions in terms of chemical potentials that can be correlated to some of the aforementioned experimental conditions and can aid in determining driving forces for defect formation and other chemical reactions, as well as surface and interfacial energies.

In the periodic DFT calculations of this work, surfaces are represented by pseudotwo-dimensional "slabs" with two identical interfaces separated by a vacuum layer in one direction. Therefore the total internal energy of the system is the following, following Euler integration of the fundamental equation.

$$E_{slab} = TS_{slab} + 2\gamma A + \sum_{i} \mu_i N_i \tag{1.19}$$

The surface energy, defined as the grand potential $(\Omega = G - \sum_{i} \mu_i N_i)$ over area:

$$\Omega = E_{slab} - TS - \sum_{i} \mu_i N_i = G_{slab} - \sum_{i} \mu_i N_i$$
(1.20)

$$\gamma = \frac{1}{2A} [G_{slab} - \sum_{i} \mu_i N_i] \tag{1.21}$$

The entropy contributions from solids are usually small and generally cancel out between solid phases, so $G_{slab} \sim E_{slab}$ and $\mu_i^0 \sim E_i^{per\,atom}$ for a solid-state *i* reference under this approximation. This approach is used for surface energy calculations in Chapters 2 and 10.

Similarly to quantify an interfacial energy (γ_{int}) between two solids α and β , the reference state is the two bulk free energies in addition to any excess components.

$$\gamma_{int} = \left[G_{interfacial\ model} - \left(N_{atoms}^{\alpha}g_{\alpha}^{bulk} + N_{atoms}^{\beta}g_{\beta}^{bulk} + \sum_{i}N_{i}^{excess}\mu_{i}\right)\right]$$
(1.22)

In principle, an extensive strain energy that converges with thickness should be added to this expression to account for lattice mismatch between the two phases. However, we assume that in our work these contributions are relatively small due to application of a lattice matching code to minimize strain between the two phases [112, 113, 114, 115]. This approach for interfacial energies is used in Chapters 11 and 12 and 10.

1.6.4 Charge Transfer Kinetics and Constrained Density Functional Theory

Charge transfer processes are ubiquitous in electrochemical systems and the kinetics of such ion-coupled electron transfer processes are typically modeled using Butler-Volmer electrode kinetics [24, 25]. However, recent work has shown that even in relatively conventional LIB systems that current-overpotential relations do not necessarily obey Butler-Volmer theory [116] and suggests that more sophisticated rate theories might instead need to be applied to model charge transfer kinetics to the study of the non-equilibrium thermodynamics of LIB systems [117].

For reactions involving charge transfer, the Born-Oppenheimer approximation might not hold across the potential energy surface between the initial and final states. Figure 1.5 demonstrates a model charge transfer reaction, $\mathcal{D} + \mathcal{A} \rightarrow \mathcal{D}^+ + \mathcal{A}^-$. For an adiabatic (Born-Oppenheimer) charge transfer process the potential energy surface is smooth at the point of charge transfer, but for a non-adiabatic charge transfer reaction there is a cusp at the transition state (see the intersection of the blue and red parabolas, also referred to as diabats, in Figure 1.5) associated with an abrupt transition from the initial (blue diabat) to the final (red diabat) charge state along



Figure 1.5.: Marcus parabola construction and geometric description of parameters involved in non-adiabatic rate theories for a given model charge transfer reaction, $\mathcal{D} + \mathcal{A} \rightarrow \mathcal{D}^+ + \mathcal{A}^-$.

the reaction coordinate. Whether an electron transfer process is adabatic or nonadiabatic will depend on the magnitude of the electronic coupling (H_{ab} , as labeled in Figure 1.5) where in the case of adiabatic electron transfer H_{ab} is large and for non-adiabatic electron transfer H_{ab} is small.

For adiabatic electron transfer, where Born-Oppenheimer holds and H_{ab} is large (strong coupling), the charge transfer kinetics can be modeled using transition state theory. However, as becomes H_{ab} small (weaker coupling), alternate non-adiabatic rate theories must be considered. The most well known of these theories is the Marcus rate theory [118], which accurately models electron transfer kinetics in the limit where $H_{ab} \rightarrow 0$. Some of the key relevant parameters in this rate expression are labeled in Figure 1.5, which is often referred to as a Marcus parabola construction. As they are labeled on Figure 1.5, the driving forces (ΔG) and reorganization energies (λ)³ can

³As equation 1.24 shows, the reorganization energy refers to the energy released from geometric relaxation following charge transfer. This is often split up into two terms: the inner sphere reorganization (λ_{inner}) and the outer sphere reorganization (λ_{outer}). λ_{inner} refers to relaxation of the individual \mathcal{D} and \mathcal{A} species that are directly involved in the charge transfer reaction in terms of their

be represented in terms of the electronic energies of the donor (\mathcal{D}) and acceptor (\mathcal{A}) in the x electronic state and y atomic configuration, \mathcal{D}_x^y and \mathcal{A}_x^y .

$$\Delta G = (\mathcal{D}_f^f + \mathcal{A}_f^f) - (\mathcal{D}_i^i + \mathcal{A}_i^i)$$
(1.23)

$$\lambda = (\mathcal{D}_i^f + \mathcal{A}_i^f) - (\mathcal{D}_f^f + \mathcal{A}_f^f)$$
(1.24)

Given the definitions of ΔG and λ the activation energy (E_{act}) can be derived in terms of these two energetic quantities.

$$E_{act} = \frac{(\Delta G + \lambda)^2}{4\lambda^2} \tag{1.25}$$

In addition to E_{act} and λ defined above in equations 1.23-1.25, the electronic coupling (H_{ab}) between the two electronic states a and b assocated with the charge transfer process is defined as the off-diagonal Hamiltonian element associated with this two-state configuration interaction.

$$H_{ab}[\rho_a, \rho_b] = \langle \psi(\rho_a) | H | \psi(\rho_b) \rangle \tag{1.26}$$

These parameters factor into the overall Marcus theory rate expression.

$$k_{CT}^{Marcus} = |H_{ab}|^2 \sqrt{\frac{\pi}{\hbar^2 k_B T \lambda}} \exp(-\frac{E_{act}}{k_B T})$$
(1.27)

As mentioned above, however, Marcus theory is valid as $H_{ab} \rightarrow 0$ and transition state theory is only valid when H_{ab} is large. Instead the Landau-Zener rate equation [120, 121] captures kinetics in intermediate regimes and converges to the Marcus and transition state theory expressions in the limits of small and large H_{ab} , respectively.

bond lengths/angles, whereas λ_{outer} instead refers to the reorganization of solvent molecules around the species in response to the modified charge distribution. While the work described herein does not explicitly deal with the latter, there are empirical models such as the Marcus two-sphere model [118, 119] that can be used.

$$k_{CT}^{LZ} = \left(\frac{2P_{LZ}}{1+P_{LZ}}\right)\nu\exp\left[-\frac{1}{k_BT}\left(E_{act} - |H_{ab}| - \frac{\lambda}{2} + \sqrt{\frac{\lambda^2}{4}} + |H_{ab}|\right)\right]$$
(1.28)

where P_{LZ} is the Landau-Zener charge transmission probability and is calculated from H_{ab} and λ .

$$P_{LZ} = 1 - \exp\left(-\frac{|H_{ab}|^2}{\hbar\nu}\sqrt{\frac{\pi}{k_B T \lambda}}\right) \tag{1.29}$$

In actuality, this expression for P_{LZ} is in a simplified form considering the fact that this parameter depends on the velocity of the diabatic potential energy surfaces at the crossing point [120]. Here, we generally assume that ν is ~ 10¹³ s⁻¹, on the order of typical molecular attempt frequencies, or to be representative of typical phonon vibrational frequencies in the solid state.

These rate expressions enable calculation of charge transfer kinetics in both adiabatic and non-adiabatic regimes. As discussed in Section 1.6.1, however, DFT is a ground-state theory and the properties needed to evaluate non-adiabatic Marcus and Landau-Zener rate expressions depend on information regarding the total energies, wave functions, and charge densities of excited electronic states (e.g. H_{ab} , λ). To address this, Van Voorhis and co-workers have developed a method known as constrained density functional theory (cDFT) [122, 123] that can constrain charge to specific \mathcal{D} and \mathcal{A} sites, enabling the calculation of such properties. In recent years, cDFT has also been implemented into several different electronic structure codes [122, 123, 124, 125, 126, 127].

The basic working principle of cDFT is the addition of a constraining potential (V) as a Lagrange multiplier in the total energy expression, which is otherwise described by DFT methodology.

$$F_i[\rho_i(\mathbf{r})] = \langle \Psi_i | H + V_i w_i | \Psi_i \rangle = E_i^{DFT}[\rho_i(\mathbf{r})] + V(\int_{\Omega} w(\mathbf{r})\rho(\mathbf{r})d^3r - N_0)$$
(1.30)

Within DFT-based methods, where the actual wave functions of each diabat (ψ_i) are assumed to be represented accurately by the Kohn-Sham single particle wave functions (Φ_i) such that equation 1.30 becomes

$$F_i[\rho_i(\mathbf{r})] = \langle \Phi_i | H + V_i w_i | \Phi_i \rangle = E_i^{DFT}[\rho_i(\mathbf{r})] + V(\int_{\Omega} w(\mathbf{r})\rho(\mathbf{r})d^3r - N_0)$$
(1.31)

In equations 1.30 and 1.31, $w_i(\mathbf{r})$ is a weight function based on the real-space charge partitioning between the \mathcal{D} and \mathcal{A} ; most cDFT codes apply Hirshfeld charge partitioning schemes [128] in this step, although other atomic charge partitioning routines can certainly be applied in principle [123].

$$w_i(\mathbf{r}) = \frac{\sum_{i}^{\mathcal{D}} \rho_i(\mathbf{r}) - \sum_{i}^{\mathcal{A}} \rho_i(\mathbf{r})}{\rho(\mathbf{r})}$$
(1.32)

Through this type of calculation, for example, λ can be determined enforcing charge separation associated with an excited state at a fixed geometry, i.e. $\mathcal{D}_i^f + \mathcal{A}_i^f$ in the limit where the charge separation converges to the input constraint.

As discussed in Section 1.6.1 and as indicated from equations 1.30 and 1.31, the DFT energies are determined from the solution to the Kohn-Sham eigenvalue problem based on the model Hamiltonian, such that the Kohn-Sham orbitals reproduce the charge density. However, constrained cDFT involves a configuration interaction term into the Hamiltonian between diabatic states a and b, where the electronic coupling (H_{ab}) between the two diabatic states is defined by the off-diagonal Hamiltonian elements (where $H_{ab} = H_{ba}$).

$$H_{ab} = \langle \Phi_a | H | \Phi_b \rangle \tag{1.33}$$

$$H_{ba} = \langle \Phi_b | H | \Phi_a \rangle \tag{1.34}$$

Wu and Van Voorhis [129] showed that a more convenient representation of equations 1.33 and 1.34 enables a relatively simple derivation of the electron coupling elements using cDFT. This is done by introducing the constraining portion of the cDFT Hamiltonian corresponding to the Lagrange multiplier portion of the cDFT energy, in order to split the bra-ket representation of the H_{ab} and H_{ba} into two terms.

$$H_{ab} = \langle \Phi_a | H + V_a w_a - V_a w_a | \Phi_b \rangle \tag{1.35}$$

$$H_{ab} = \langle \Phi_a | H + V_a w_a | \Phi_b \rangle - \langle \Phi_a | V_a w_a | \Phi_b \rangle$$
(1.36)

As shown in equations 1.30 and 1.31, the first term corresponds to the cDFT energy, along with a remaining overlap term between the a and b diabatic wave functions:

$$H_{ab} = F_a \left\langle \Phi_a | \Phi_b \right\rangle - \left\langle \Phi_a | V_a w_a | \Phi_b \right\rangle \tag{1.37}$$

where $\langle \Phi_a | \Phi_b \rangle$ is the Slater overlap [97, 85] between the two diabats, S_{ab} . Since $H_{ab} = H_{ba}$ by definition, cDFT codes will take an average of these two quantities in order to numerically evaluate H_{ab} , followed by a Löwdin orthoganalization [130] step to return H_{ab} onto the basis of the Φ_a and Φ_b Kohn-Sham single particle wave functions.

$$H'_{ab} = \frac{F_a + F_b}{2} - \langle \Phi_a | V_a w_a + V_b w_a | \Phi_b \rangle$$
(1.38)

$$|H_{ab}| = \begin{bmatrix} 1 & S_{ab} \\ S_{ba} & 1 \end{bmatrix}^{-\frac{1}{2}} \begin{bmatrix} E_a^{ks} & H_{ab}' \\ H_{ab}' & E_b^{ks} \end{bmatrix} \begin{bmatrix} 1 & S_{ab} \\ S_{ba} & 1 \end{bmatrix}^{-\frac{1}{2}}$$
(1.39)

Overall, this section describes the framework needed to evaluate the relavent parameters involved in charge transfer reactions, which will be applied later on to the studies in Chapters 13-15.

1.7 Overview of the Dissertation

The motivations described in this Introduction is meant to broadly relate scientific challenges addressed in the subsequent studies of this dissertation. The chapters corresponding to each of these particular studies will begin with a more detailed introductory section specific to the scientific questions addressed therein. Each chapter will apply a subset of the theoretical and computational methods as described in Section 1.6. With few exceptions, most of these modeling and simulation results are complemented by results from experimental collaborators, the contributions of whom are mentioned within the relevant chapters. The content of this work is organized as follows.

The first part (Chapters 2-9) focuses on understanding and controlling the interfacial reactivity of a particular lithium ion intercalation cathode material, $LiMn_2O_4$ (LMO). Following an initial thermodynamic characterization of equilibrium LMO surface structures (Chapter 2), degradation mechanisms related to stress-strain relationships (Chapter 3) as well as electrolyte decomposition and Mn dissolution (Chapter 4) are presented; thereafter interfacial modification strategies related to the deposition of protective coatings (Chapters 5-8) and cationic surface doping (Chapter 9) are described.

In Chapter 10, the solid/solid interfaces in solid-state batteries are explored, with a focus on strategies to understand and modify the interfacial reactivity of a lithium lanthanum titanate solid electrolyte materials with a lithium metal anode.

Next, Chapters 11 and 12 describe the nickel oxide conversion reaction chemistry in nanostructured electrode materials, using a combination of DFT calculations with classical nucleation theory modeling alongside *operando* X-ray scattering measurements during the lithiation of nickel oxide thin film electrodes.

Chapters 13-15 are focused on charge transfer kinetics in rechargeable electrochemical energy storage systems, with a particular focus on applications of nonadiabatic rate theory treatments. Chapters 13 and 14 concern the "beyond lithium ion" chemistries of lithium-oxygen (or lithium-air) and lithium-CO₂ battery chemistry, respectively, and the role of charge transfer to/from nanostructured transition metal dichalocgenide electrocatalysts in the formation and decomposition of solid discharge products during charge and discharge. These techniques are later applied to study charge transfer in covalent systems in order to provide a baseline proofof-concept study for Li-coupled electron transfer in intercalation-based cathode materials, applying studies of electron and hole transport in the prototypical Li_xCoO_2 cathode as a model system (Chapter 15).

Lastly, concluding remarks and future perspectives are discussed briefly in Chapter 16.

2. THERMODYNAMIC STABILITY OF LOW- AND HIGH-INDEX SPINEL LIMN₂O₄ SURFACE TERMINATIONS

This chapter is reproduced with the permission of the American Chemical Society from: Robert E. Warburton, Hakim Iddir, Larry A. Curtiss, and Jeffrey Greeley; Thermodynamic Stability of Low- and High-Index Spinel LiMn_2O_4 Surface Terminations. ACS Applied Materials & Interfaces **2016**, 8(17), 11108-11121.

Density functional theory calculations are performed within the generalized gradient approximation (GGA+U) to determine stable terminations of both low- and high-index spinel $LiMn_2O_4$ (LMO) surfaces. A grand canonical thermodynamic approach is employed, permitting a direct comparison of off-stoichiometric surfaces with previously reported stoichiometric surface terminations at various environmental conditions. Within this formalism, we have identified trends in the structure of the lowindex surfaces as a function of the Li and O chemical potentials. The results suggest that, under a range of chemical potentials for which bulk LMO is stable, Li/O and Li-rich (111) surface terminations are favored, neither of which adopts an inverse spinel structure in the subsurface region. This thermodynamic analysis is extended to identify stable structures for certain high-index surfaces, including (311), (331), (511), and (531), which constitute simple models for steps or defects that may be present on real LMO particles. The low- and high-index results are combined to determine the relative stability of each surface facet under a range of environmental conditions. The relative surface energies are further employed to predict LMO particle shapes through a Wulff construction approach, which suggests that LMO particles will adopt either an octahedron or a truncated octahedron shape at conditions in which LMO is thermodynamically stable. These results are in agreement with the experimental observations of LMO particle shapes.

2.1 Introduction

Spinel $LiMn_2O_4$ (LMO) has attracted considerable interest as an inexpensive, nontoxic, and earth-abundant alternative to LiCoO₂ cathode materials in Li-ion batteries. Its thermal stability, high operating voltage (4.1 V vs Li/Li⁺), and excellent rate capability give LMO the potential for widespread applications in Li-ion systems for grid energy storage and electric vehicles [131, 44, 132, 133]. However, LMO experiences instabilities after extensive cycling, due to reduced crystallinity and structural integrity [134, 135], increased Mn^{3+} cation concentration from Li intercalation at 3 V, leading to the formation of a Jahn Teller-distorted tetragonal $Li_2Mn_2O_4$ phase at the surface [136, 137], and a Mn^{3+} disproportionation reaction, due to the presence of HF in the electrolyte at elevated temperatures [131, 133], which leads to dissolution of Mn^{2+} [138, 139]. Strategies that have been considered to suppress Mn^{2+} dissolution include cation doping [140] and the application of protective surface coatings [141, 142]. Experimental work has also recently identified a strong sensitivity of LMO capacity retention to the local surface structure. It has been proposed that nanoparticles dominated by the (111) surface are more resistant to Mn^{3+} disproportionation, whereas the (001) and (110) facets are more susceptible to dissolution [143].

As a prelude to understanding these instabilities at the atomic scale, the surface structure of LMO must be rigorously described. Some insight into the features of single-crystal facets that are relevant to surface degradation processes can be obtained from experimental studies that have demonstrated that LMO particle morphologies are sensitive to synthesis conditions [143, 144, 145, 146, 147, 148]. The particles often adopt octahedral shapes as they approach equilibrium, suggesting that the (111) surface is generally the most stable. For example, Tang et al. determined that molten salt synthesis produces platelet LMO crystals, dominated by the (001) surface, which evolve towards more octahedral morphologies with increased reaction time and temperature [145]. This suggested equilibrium morphology of LMO particles is consistent with observations of other spinel crystals [149]. Depending on the synthesis and treatment conditions, however, different morphologies may be observed [143, 150, 151, 152]. Furthermore, the (311), (331), (511), and (531) high-index facets have been identified by high-resolution transmission electron microscopy (HRTEM) diffraction patterns of LMO nanoparticles [143] and polycrystalline LMO [153, 154]. Features of these high-index facets may also be present as edges on LMO particles or as metastable defects on low-index terraces.

Although particle studies have been invaluable in suggesting what facets of LMO are stable in given environments, they do not provide direct resolution of the atomic structure of the surfaces under electrochemically relevant conditions. Theoretical methods, however, are well suited to providing such information, and the atomic structure of the low-index surfaces of LMO has been the subject of several first principles studies [142, 62, 64, 155]. Ouyang et al. performed surface energy calculations for LMO with analysis constrained to the (001) surface [142]. Benedek and Thackeray, in turn, carried out first-principles calculations on stoichiometric terminations of the low-index surfaces of LMO, applying ferromagnetic (FM) ordering for the electronic ground state [62]. Through the use of *ab initio* molecular dynamics (AIMD) simulations, these authors determined that the polar Tasker III-type (111) surface [156, 157] may reconstruct, reducing the strong local dipole at the surface. In spite of this possible stabilization mechanism for the (111) surface, the authors found the (001) surface to be the most stable. This result, however, is in tension with the experimental results, mentioned above, that indicate that LMO nanoparticles tend to adopt an octahedral shape, dominated by the (111) surface [144, 145, 146, 147, 151, 152]. Motivated by these considerations, Karim et al. [64] performed additional calculations on stoichiometric terminations of low-index surfaces, applying antiferromagnetic (AFM) ordering along the [110] direction. By coupling these calculations with a proposed reconstruction of LMO(111) to an inverse spinel phase via exchange of undercoordinated surface Mn cations with subsurface Li cations, the researchers predicted an octahedral nanoparticle shape that is dominated by the low energy (111) facet.

The theoretical studies described above have provided important insights into the thermodynamics of the (001), (110), and (111) surfaces of LMO. However, these efforts have been limited to a canonical approach, wherein the stoichiometric composition of the bulk LMO is preserved on the surfaces. The resulting surface models require the introduction of defect features on the corresponding low-index facets, possibly altering the surface energetics in a complex manner. A comprehensive analysis of both stoichiometric and off-stoichiometric surface terminations, therefore, is desirable to permit conclusions of maximum possible generality to be drawn regarding the surface structure of LMO. Such analyses may be performed using grand canonical thermodynamic formalisms, which have been applied to binary [158, 159] and ternary[61] oxide systems for many applications, including materials for Li-ion batteries and heterogeneous catalysis. Very recently, Kim et al. have used such approaches to perform an environment-dependent analysis of LMO surfaces [155]. The authors identified Li-terminated stoichiometric and off-stoichiometric surfaces of LMO(001)and LMO(111) to be thermodynamically favorable. For the (111) surface, the inverse spinel reconstruction mechanism proposed by Karim et al. was also considered [64]. This grand canonical approach led to a proposed trend in equilibrium particle morphology, wherein the truncated octahedral nanoparticles adopt a more octahedral shape [the (111) surface is dominant] under Li-deficient and oxidizing conditions, while the particles are expected to exhibit more cubic properties [the (001) surface is dominant] under Li-rich and reducing conditions. In general, these truncated octahedral morphologies are indeed seen experimentally, although various other (111) to (001) surface area ratios have also been observed [144, 145, 146, 147, 151].

Although the above analyses have made significant contributions to understanding the thermodynamics of LMO surfaces, the studied structures represent a small fraction of the many possible surface terminations, and there is a need to explore alternative structures both to predict equilibrium LMO particle geometries under different electrochemical conditions and to ultimately illuminate the mechanisms by which Mn loss from these surfaces occurs. To provide additional insight into the overall trends in

the LMO surface structure and stability, we employ first principles calculations, along with a grand canonical thermodynamic analysis, to an extensive set of candidate surface structures. The approach constrains the limits of component chemical potentials to conditions in which bulk LMO is thermodynamically stable. Both stoichiometric and off-stoichiometric terminations of low-index surfaces are modeled, considering several structures for each surface facet. Additionally, selected terminations of highindex surfaces, which could be interesting model systems for stepped and defected features, including edges, on LMO particles, are analyzed. The density of such features on the surface of LMO particles is likely to increase over time as LMO is cycled [143], and surface degradation processes, such as Mn^{2+} dissolution, begin to influence the structure of the electrode/electrolyte interface. These findings lead to detailed predictions of the LMO surface structure and stoichiometry as well as to trends in particle morphologies under different environmental conditions. The detailed atomistic understanding of LMO surface structures that emerges from the analysis will serve as a foundation for future modeling efforts to describe chemical and physical processes occurring at the interfaces of these oxide materials with electrolytes.

2.2 Methods

2.2.1 Electronic Structure Calculations

Spin-polarized density functional theory (DFT) calculations are performed using the Vienna *Ab initio* Simulation Package (VASP 5.3.3) [160, 161] at a planewave energy cutoff of 520 eV. Projector augmented wave pseudopotentials are used to model the core electrons [162], with the 1s and 3p electrons treated as valence for Li and Mn, respectively. The generalized gradient approximation (GGA) of Perdew-BurkeErnzerhof (PBE) is selected as the exchange correlation functional [163]. Bulk LMO calculations employ a 4 x 4 x 4 Γ -centered k-point mesh, where we find total energies that differ by less than 0.1 meV per formula unit compared to denser k-point grids. The k points used for the surface slabs are dependent on the lattice vectors of the surface and are chosen such that the total energies vary by less than 1 meV per atom; the specific values are included in Appendix A. Gaussian smearing with a width of 0.05 eV is used for slab calculations. For surface calculations, symmetric slabs are constructed in order to effectively eliminate the presence of any net slab dipole moment and to facilitate determination of the excess interfacial free energy contributions for each slab termination. All atoms in the slab calculations are subject to full ionic relaxation and are converged to an energy tolerance of 1 meV per unit cell and to a force criterion of $0.02 \text{ eV} \text{ Å}^{-1}$.

The rotationally invariant, spherically averaged, DFT+U method is used to treat the incorrect localization of d electrons in semiconductors by DFT [102, 103, 104, 106]. A U value of 3.5 eV applied to the 3d electrons of Mn gives excellent agreement with experimental formation enthalpies, ΔH_f , for the following manganese oxides: LMO, MnO, MnO₂, Mn₃O₄, Mn₂O₃, and LiMnO₂. This value for the U parameter agrees well with the recently reported value of 3.9 eV, which was, in turn, fit to formation energies for manganese oxides with an average Mn oxidation state of 3.5 + |110|. In this scheme, the standard enthalpy of O_2 is fit to minimize the mean absolute error (MAE) in ΔH_f for the following set of non-transition metal oxides: Al₂O₃, CaO, Li₂O, MgO, Na₂O, BaO, Na₂O, and SrO. Fitting to experimental ΔH_f values in the JANAF Thermochemical Tables [164] leads to an O_2 energy correction of 1.27 eV with respect to PBE. The bulk Mn reference is also fit at different values of U to minimize the MAEs of the aforementioned class of manganese oxides. The chosen U value leads to a MAE of 1.71% for calculated ΔH_f values. Furthermore, the calculated ΔH_f at 298 K for LMO is 14.63 eV per formula unit (expt. $\Delta H_f = 14.31$ eV per formula unit [165], corresponding to an error of less than 2.22% with respect to the experimental results.

The magnetic ordering of bulk LMO has been treated with different approaches in previous theoretical work [62, 64, 166]. Ouyang et al. [166] and Karim et al. [64] reported that LMO is in its lowest energy state when Mn atoms are AFM [$\uparrow \downarrow \downarrow$] along the [110] direction, in agreement with experimental observations of low temperature magnetic ordering for LMO.[167] It has been suggested that FM ordering, as employed by Benedek et al. [62], gives a higher energy bulk structure because of constraint of the bulk structure to the cubic $Fd\bar{3}m$ space group, which prohibits the well-known Jahn-Teller distortion of Mn³⁺ cations that is observed at low temperatures [167]. However, breaking cell symmetry within the DFT+U framework with FM ordering allows for proper electron localization on Mn³⁺ and Mn⁴⁺ cations, leading to the Jahn-Teller distortion seen from AFM calculations and suggesting that energy differences between these approaches should not be too large. Indeed, we find that the total energies between FM, AFM (110)[$\uparrow\uparrow\downarrow\downarrow$], and AFM (110)[$\uparrow\downarrow\downarrow\downarrow$] vary by less than 50 meV per formula unit, consistent with recent work by Kim et al. [155]. We have also found that surface energies are relatively insensitive to alternate magnetic ordering at the surface. Further details may be found in Appendix A. For the results presented within the present work, FM ordering is used for all slab calculations.

Finally, AIMD [168] simulations are performed within the canonical ensemble (NVT) in VASP to sample alternate configurations that may form from the reconstruction of Tasker III-type surfaces. These calculations are used as a simple tool to sample different minimum energy states on the potential energy surface and are not intended to be rigorous statistical treatments. The AIMD simulations use a minimal $1 \ge 1 \ge 1 \ k$ -point mesh and are equilibrated with a Nosé thermostat with 1 ps timestep at 300 K [169]. A Verlet algorithm is used to integrate Newton's equations of motion over a time step of 0.5 fs. The Climbing Image Nudged Elastic Band (CINEB) method is used to identify the activation barriers and minimum energy paths for transition states in the proposed reconstruction mechanisms [170].

2.2.2 Surface Energy Calculations

The surface energy can be considered to be an excess free energy per unit area, with respect to the bulk, as a result of cleavage of a pristine crystal. Thus, one can calculate the surface energy, γ , by

$$\gamma = \frac{1}{2A} \left[E_{slab} - \sum_{i} N_i \mu_i^{bulk} \right]$$
(2.1)

where A, E_{slab} , N_i , and μ_i^{bulk} are the slab surface energy, the DFT energy of the slab, the number of atoms of species *i*, and the chemical potential of species *i* in the slab, respectively. The factor of 2 is included in the denominator of equation 2.1 to account for the generation of two surfaces, given that the system is periodic in the direction orthogonal to the cleavage plane. All calculations correspond to symmetric slabs in which each interface has identical surface structure and energy. Details of the chemical potential determinations are discussed in Section 2.3.1.

2.3 Results and Discussion

2.3.1 LMO Bulk

At room temperature, LMO adopts a cubic $(Fd\bar{3}m)$ spinel structure with experimental lattice parameters of a = 8.20 Å, b = 8.25 Å, and c = 8.28 Å[171]. From the DFT+U calculations with FM ordering, lattice parameters of a = 8.21 Å, b =8.21 Å, and c = 8.79 Å are found, where the elongation of the cell in the [001] direction is due to the Jahn-Teller distortion of Mn³⁺ cations (see also discussion in Section 2.2.1. These bulk electronic structure properties are analogous to the results of previous work using AFM ordering[142, 166] and hybrid functionals [72].

To evaluate the chemical potential limits consistent with the thermodynamic stability of bulk LMO, we consider its equilibrium with other Li-, Mn-, and O-containing compounds. DFT-calculated ΔG_f values for the lithium manganese oxides, on a per atom basis, are used to construct a ternary phase diagram in Li-Mn-O phase space. These free energies, together with the phase diagram module in the Open Quantum Materials Database [172], are used to construct the phase diagram in Figure 2.1a. The phase diagram is generated using the QuickHull algorithm[111] to construct the convex hull, based on the fundamental criterion that a state is thermodynamically stable if



Figure 2.1.: Bulk thermodynamic stability of LMO. (a) Ternary phase diagram indicating the stable compounds bounding bulk LMO. (b) Bulk stability region of LMO and its equilibrium with other LiMnO compounds at the limits of its stability.

$$\left(\frac{\partial^2 G_f}{\partial x_i^2}\right) > 0 \tag{2.2}$$

The compounds represented with black dots in Figure 2.1a represent the stable compounds in the given phase space. The gray lines connecting these nodes are equilibrium tie lines at the base of the convex hull; hence, all lines drawn from LMO on the phase diagram connect to compounds with which LMO may be in equilibrium at the limits of its stability. The stable phase region of bulk LMO is therefore bounded by its equilibrium with the following species: MnO_2 , Mn_2O_3 , Mn_3O_4 , $LiMnO_2$, Li_2MnO_3 , and O. Moreover, the bulk LMO structure imposes certain physical constraints on the chemical potentials. First, the component chemical potentials must sum to the bulk free energy per formula unit, g_{bulk} :

$$g_{bulk} = \sum_{i} x_i \mu_i^{bulk} \tag{2.3}$$

where x_i are the number of atoms of species *i* per formula unit of bulk. This constraint immediately reduces the surface energy equation in equation 2.1 to an expression with only two adjustable parameters for a ternary compound such as LMO.

In this work, $\Delta \mu_i$ is defined to be the difference between the chemical potential of component *i* and its reference chemical potential at 0 K. The reference chemical potential for Mn is assumed to be approximately equal to the fitted value for enthalpy at 298 K. The chemical potential for O₂ at 1 atm is extrapolated to 0 K using the fitted enthalpy value at 298 K and the standard gas phase entropy according to the NIST Chemistry Webbook [173]. At equilibrium for two or more compounds, *a* and *b*, the chemical potential of each component, *i*, must be equivalent between the compounds in equilibrium:

$$\Delta \mu_i^a = \Delta \mu_i^b \tag{2.4}$$

By additional constraint of $\Delta \mu_{Mn}$ by the free energy of bulk LMO in equation 2.3, equilibrium lines can be plotted for the equilibrium between LMO and the six compounds bounding its bulk stability region. The intersection of these equilibrium lines represents the bulk LMO stability region plotted in Figure 2.1b, providing appropriate limits on the component chemical potentials to be considered in the grand canonical surface stability analysis.

2.3.2 Low-Index Surfaces

In this section, we consider the stability of stoichiometric and off-stoichiometric slabs of the (001), (110), and (111) surfaces of LMO. For completeness, we present the results for selected structures that have been previously studied within both canonical [62, 64] and grand canonical [155] thermodynamic formalisms. We also consider multiple additional surface stoichiometries that, as we will demonstrate, provide useful additional insight into LMO surface thermodynamics for the range of chemical potentials over which bulk LMO is stable. The results are presented in the form of phase diagrams that indicate the most stable surface structure for a given set of applied chemical potential conditions. An extensive table of surface energies for all considered surface structures is also given in Appendix A; this description includes the surface energies at the intersection of the ternary phase equilibrium lines in Figure 2.1b.

For each of the low-index surface facets of LMO, multiple strategies are employed to generate a comprehensive set of surface structures. First, multiple offstoichiometric terraces are straightforwardly generated by cleaving the corresponding slabs along planes with differing surface stoichiometries. Second, surface terminations exposing undercoordinated Mn ions are partially saturated with O ions. In general, we find that this strategy provides favorable coordination for Mn, while at the same time negating some of the strong positive charge density at the surface induced by a layer of unsaturated Mn cations. This result is consistent with earlier reports [64] that demonstrate that surface terminations exposing undercoordinated Mn are inherently unstable. However, as we discuss further below, this O saturation strategy may, in a limited number of cases, induce a strong dipole at the interface, making the surface less stable. Finally, various types of excess surface stoichiometries are also considered. For example, removal of Li atoms may, in some cases, be thermodynamically favorable for $\Delta \mu_{Li}$ values associated with Li-deficient conditions. O vacancy formation, leading to local surface Mn reduction, is also evaluated for selected surface structures and may be favorable under highly reducing chemical potential conditions.

2.3.2.1 (001) Surface

The (001) surface consists of alternating layers of Li_x and $\text{Mn}_{2x}\text{O}_{4x}$ formula units. This repeating structure suggests natural surface terminations at planes corresponding to either of these stoichiometries, and the surface structure may be further modified via the strategies mentioned above. The terminations associated with the Li_x and $\text{Mn}_{2x}\text{O}_{4x}$ layers are denoted as the Li and Mn/O terminations. Adding additional O atoms to the surface or near-surface Mn atoms of the Li and Mn/O terminations



Figure 2.2.: (001) surface terminations and surface phase diagram. Low energy surface terminations are shown for the (001) surface in $\Delta \mu_{Li}$ - $\Delta \mu_O$ phase space. The phase diagram indicates the most stable surface structure at the corresponding chemical potential. Li and O refer to the difference in the chemical potential with respect to bulk Li metal and gas phase O₂, respectively, at 0 K and 1 bar. The LMO bulk stability region is outlined by the black polygon in the figure. Section 2.3.1 may be referred to for details regarding the bulk stability region and the chemical potential references. Structures of different surface terminations are pictured below the phase diagram with the [001] vector oriented upward. Li, Mn, and O atoms are denoted by green, purple, and red, respectively. The total cell stoichiometry, as well as the excess Li (ξ_{Li}) and O (ξ_O) per surface in the unit cell, is given with respect to the bulk stoichiometry.

generates the Li/O and O-rich terminations. The two base surface terminations (Li and Mn/O) can additionally be modified to generate slabs that are stoichiometric with respect to bulk LMO (Li-stoich and Mn/O-stoich), as has been described previously [62, 64]. Finally, more highly reduced surface configurations, with additional O vacancies introduced into each of the above structures, are also considered (see the discussion below). The phase diagram in Figure 2.2 indicates which of the surface terminations are most thermodynamically favorable under different conditions. As mentioned previously, the $\Delta \mu_{Li}$ and $\Delta \mu_O$ values are representative of the departure of the component chemical potentials from the bulk (Li) or gas phase (O) reference states at 0 K and 1 atm. Thus, a value of $\Delta \mu_i$ approaching zero corresponds to conditions that are extremely rich in component *i*, whereas large negative values of $\Delta \mu_i$ correspond to conditions deficient in component *i*. The value of $\Delta \mu_{Mn}$ is constrained by the free energy of bulk LMO, as indicated in equation 2.3. Appendix A contains a short discussion of the relationship between $\Delta \mu_{Li}$ and the voltage in an electrochemical cell.

For the (001) surface, the Mn/O termination is most stable under Li-deficient conditions, whereas the Li termination is most stable at Li-rich conditions. The surface energy of the Li-stoich termination, which represents the partially formed Lix layer, is most stable at intermediate values of $\Delta \mu_{Li}$. These results are fully consistent with the intuitive notion that the Mn/O termination will gradually become saturated with the subsequent Li layer as the Li chemical potential increases. The Li-stoich and Li terminations have been previously calculated to be stable [64, 155], but the present calculations indicate that the Mn/O termination will dominate the (001) family of facets on LMO nanoparticles under Li-lean and oxidizing conditions.

In addition to the structures described above, we have considered the possibility that additional O vacancies might form in any of these surface configurations. Indeed, O loss is expected to occur upon cycling in the delithiated λ -MnO₂ state [174], and first principles calculations have demonstrated that vacancy formation energies for faceted β -MnO₂ are quite low (0.95 to 1.5 eV at 0 K) with respect to other metal oxides [175]. However, we find, for the (001) surface, that O vacancy formation energies are 1.96 and 3.07 eV atom¹ at 0 K ($\Delta\mu_O = 0$) for the (001) Mn/O and (001) Li surface terminations, respectively (because the Li-stoich termination contains features of both the Mn/O and Li surface terminations, we expect that the latter O vacancy energetics will be very similar to those of analogous sites on the Li-stoich surface). These energies are sufficiently high that the resulting surface structures do not become thermodynamically favorable with respect to the defect-free Mn/O and Li phases within the chemical potential window where bulk LMO is stable. Thus, these reduced (001) surface structures are only likely to be thermodynamically favored under conditions where bulk LMO is metastable. Further details regarding the vacancy formation energies for the (001) surface are included in Appendix A.

Some insight into the oxidation states of the near-surface Mn ions, which, as mentioned above, may be related to the dissolution of Mn ions into solution, can be estimated through Bader charge analysis [176, 177, 178]. As a simple example, we show, in Figure 2.3, the calculated oxidation states for surface Mn for the (001) Li surface, both with and without additional O vacancies (similar analyses for other LMO surfaces are provided in Appendix A). The surface without vacancies (Figure 2.3a) contains some ions in an approximately 3+ oxidation state. Because this particular oxidation state has been associated with disproportionation and subsequent Mn dissolution, these results are consistent with the general intuition that the (001) surface is susceptible to corrosion and Mn dissolution [143]. Further, if additional metastable vacancies could be introduced, the surface Mn ions would be further reduced to less than a 2+ oxidation state (Figure 2.3b), which might significantly accelerate dissolution. We caution, however, that such arguments are largely heuristic, and detailed mechanistic relationships between the oxidation state of surface Mn ions and the susceptibility of the surface to Mn dissolution remain to be developed. It is worth noting that, although Bader charge analyses provide only an approximate estimate of the Mn oxidation states, the results are consistent with projected density of states (PDOS) analysis. The PDOS of the pristine (001) Li surface, plotted in Figure 3c, shows good agreement with previous theoretical work for Mn^{3+} at the surface of LMO(001) [142, 179]. The e_q bands for Mn³⁺ are partially occupied, dividing these states above and below the Fermi energy, E_f . The charge compensation that occurs as a result of O vacancy formation leads to full electronic occupation of the spin-up states in the



Figure 2.3.: Influence of the O vacancies on the electronic structure of the (001) Li surface. Predicted oxidation states for Mn on (a) a clean (001) Li-terminated surface without O vacancies and (b) a (001) Li-terminated surface with an O vacancy present. The site of the most stable O vacancy is denoted by the empty circle with the black border. Each of the oxidation states refers to either a surface or a subsurface Mn atom. Bader charges are calibrated by linear regression of Bader charges on bulk manganese oxides. O vacancy formation leads to the local reduction of Mn on the surface. The PDOS is given for Mn atoms for (c) a clean (001) Li-terminated surface without O vacancy present. The Fermi energy, E_f , is denoted by the dotted line. The PDOS represents only spin-up states in the Mn 3d bands. All spin-down states are unoccupied because of the FM ordering of the surface and lie at energies above the Fermi energy. The PDOS is calculated for the Mn atoms outlined in blue in parts a and b.

 e_g band, as seen by a further shift of Mn 3d states below the Fermi level in Figure 2.3d.

Finally, results for additional, higher energy, (001) surface structures, which do not appear on the phase diagram, are also briefly presented in Appendix A. An analysis of the phase stability of the (100) and (010) surfaces, which are structurally distinct from (001) due to the Jahn-Teller distortion of bulk LMO, is also presented in Appendix A. The surface energies of each termination of these surfaces are very similar to the energies of the corresponding (001) terminations, leading to almost identical phase diagrams.

2.3.2.2 (110) Surface

Figure 2.4 includes some of the considered surface terminations for the (110) surface. The surface may be cleaved along the Mn_xO_{2x} and $Li_xMn_xO_{2x}$ layers, which comprise the stoichiometric repeat units along the [110] Miller direction. Again, modification of these Mn/O and Li/Mn/O surface terminations allows for the construction of stoichiometric slabs (Mn/O-stoich and Li/Mn/O-stoich, respectively). Passivation of surface or near-surface Mn atoms on Mn/O and Li/Mn/O with O is likewise considered, yielding the Li/O and O-rich surface terminations. While only the structures appearing on the phase diagram are shown in Figure 2.4, all (110) surface terminations included in this analysis may be found in Appendix A. According to the surface phase diagram, the Li/O termination is the most stable configuration of the (110) surface under oxidizing conditions. This is likely because the Li/Mn/O termination contains undercoordinated Mn atoms at the surface, and the saturation of these surface Mn atoms with O (Li/O termination) satisfies the MnO_6 polyhedra, leading to enhanced stability. While the O-rich termination represents a similar saturation effect for the Mn/O surface, this configuration adds a strong surface dipole to the already negatively charged Mn_xO_{2x} layer at the surface, rendering this surface less stable. Interestingly, O defect formation energies on the (110) Li/O surface are only 0.96 eV atom⁻¹, which is significantly less than defect formation energies on both



Figure 2.4.: (110) surface terminations and corresponding surface phase diagram. Low energy surface structures for the (110) surface in $\Delta \mu_{Li}$ - $\Delta \mu_O$ phase space are shown. Stoichiometries of the relevant surface structures, as well as the excess Li and O in each slab, are included. Figure 2.2 may be referenced for further information regarding notation and the phase diagram details. The atomic structures for surface terminations containing one (Li/O-1Ovac) or two (Li/O-2Ovac) O vacancies are annotated with \bigotimes at the site of the vacancy. The Li/O-2Ovac termination contains a second O vacancy at the surface, leading to depletion of half of the O atoms in this layer. The analogous structure in which all O atoms in this layer are removed corresponds to the Li/Mn/O termination (see Appendix A).

the (001) and (111) surfaces. This suggests that the (110) surface is quite reducible, to the extent that this defected surface structure (Li/O-1Ovac) becomes the most thermodynamically favorable surface phase under reducing environments where $\Delta \mu_O$ is less than 0.96 eV. Furthermore, the formation of a second O vacancy per unit cell (Li/O-2Ovac) becomes the most thermodynamically stable surface structure when $\Delta \mu_O$ is less than 1.30 eV. The formation of such defects may have implications for Mn³⁺ disproportionation from the resulting undercoordinated Mn. Further surface Mn reduction through O vacancy formation beyond the Li/O-2Ovac structure is not calculated to be thermodynamically stable within the chemical potential range in Figure 2.4. As with the (001), (100), and (010) surfaces, we find that the energetics of the (011) and (101) surfaces are very similar to those of the (110) surface. The surface phase diagrams for the (011) and (101) surfaces are included in Appendix A.

2.3.2.3 (111) Surface

The stoichiometric repeat units of the (111) surface of LMO consist of the following layering sequences: O_{4x} , Mn_{3x} , O_{4x} , Li_x , Mn_x , and Li_x . Thus, each layer of the (111) surface contains a single, distinct, chemical species. These structural features correspond to layers of nonzero charge density and dipole moment, characteristic of Tasker III-type polar oxide surfaces [156, 157]. As previous surface thermodynamic studies on LMO [64] and other polar oxides [159] indicate, reconstruction of the surface may reduce the net dipole at the surface and thus provide thermodynamic stabilization. To ensure convergence of the reconstructed surfaces with respect to the slab thickness, we add an additional bulk layer to the slabs, which converges all surface energies to within 0.05 J m².

The reconstructed surfaces considered, along with their unreconstructed parent surfaces, are depicted in Figure 2.5. We have considered the reconstruction mechanism proposed by Karim et al. [64], where an undercoordinated Mn cation at the surface exchanges positions with a monovalent Li cation in the subsurface region, leading to formation of an inverse spinel phase near the surface. This reconstruc-



Figure 2.5.: LMO (111) surface reconstructions. The left panel represents unreconstructed (111) surface terminations, and the right panel includes the reconstructed surface analogues. The Mn/O-stoich and Li/Mn/O surfaces reconstruct via surface Mn cation exchange with subsurface Li to form an inverse spinel surface phase, as in Karim et al. [64]. Reconstruction of the Mn/O surface occurs via Li diffusion through the Mn_{3x} and O_{4x} layers and is identified from AIMD simulations.

tion of the Mn/O-stoich (reconstructs to Li-stoich) and Li/Mn/O (reconstructs to Li/Mn/O-stoich) terminations has been demonstrated to be thermodynamically favorable in previous work [64, 155], leading to significant reductions in the calculated surface energies. Analogous (111) surface reconstructions are also considered for other surface terminations, as well as for several subsurface inverse spinel reconstructions, in the present work (see Appendix A for structural and energetic details). Additional O vacancy formation processes are considered, in selected cases, on thermodynamically stable surfaces. In general, the calculations suggest that the inverse spinel reconstruction is favorable when resulting in increased Mn coordination at the surface or in the near-surface region. The inverse spinel structural features in the subsurface do not appear to be thermodynamically favorable, however, if there is no increase in coordination for the Mn cation involved in the reconstruction process. This result may be understood on the basis of the resulting Mn coordination number. With respect to bulk LMO, a fully coordinated Mn cation will form a MnO_6 polyhedron. While reconstruction of the Li/Mn/O, Mn/O-stoich, and Li terminations increases the coordination number of the surface Mn from 3 to 4, the subsurface Mn is still undercoordinated with respect to bulk LMO.

Finally, we describe a reconstructed surface identified through additional AIMD calculations at 300 K. AIMD suggests that the Mn/O termination may undergo reconstruction in which Li cations in the Li_x layer closest to the surface may diffuse through the vacant sites in the Mn_{3x} layer to align in- plane with the O₄x layer at the interface. This process introduces vacancies between the Mn_x and O_{4x} layers. Such a reconstruction negates the strong dipole moment at the surface of the Mn/O termination induced by the negative charge density from the O_{4x} layer at the surface/vacuum interface. NEB calculations confirm that the kinetic barrier associated with this Li diffusion mechanism to form the Mn/O-rec termination is very low, 0.04 eV, so reconstruction will be facile at ambient conditions. Reconstruction of the (111) Mn/O termination to the Mn/O-rec structure also reduces the work function of the surface from 7.98 to 6.68 eV ($\Delta \phi_{rec} = -1.30$ eV), confirming a reduction in the polarity of the surface, as has been demonstrated for other O-terminated polar oxide surfaces in previous theoretical work [159].

The most stable surface terminations of the (111) surface are depicted in Figure 2.6, together with the corresponding phase diagram. All terminations considered for the (111) surface (including other surface reconstructions) are included in Appendix A. The Li/O and Li-rich surface terminations bear some similarity to the Mn/O-rec termination, described above, which was identified by AIMD. The additional Li_x layer in the Li/O termination is located at nearly the same atomic coordinates as the final state of Li atoms in the Mn/O-rec termination following their diffusion through the Mn_{3x} and O_{4x} lattices. The additional Li provides the same dipole stabilization



Figure 2.6.: (111) surface terminations and surface phase diagram. Low energy surface structures are shown for the (111) surface in $\Delta \mu_{Li} - \Delta \mu_O$ phase space. Stoichiometries of the relevant surface structures, as well as the excess Li and O in each slab, are included. Figure 2.2 may be referenced for further information regarding notation and the phase diagram details. The Li/O surface termination, which is predicted to be the most stable phase within the majority of the bulk stability region, is generated by cleavage of the LMO bulk along the [111] direction with no reconstruction. The Mn/O-rec, Li-stoich, and Li/Mn/O-rec surfaces are reconstructed structures. Figure 2.5 may be referenced for details regarding the schemes used to generate these structures. The Li-rich structure is identical to the surface of the Li/Mn/O-rec termination but with the introduction of Li over-stoichiometry at the surface, rather than reconstruction in the subsurface layer. Further discussion may be found in Section 2.3.1
effect as that discussed above but without the introduction of the subsurface vacancy that is found in the (111) Mn/O-rec surface. The Li-rich surface termination is a variation of the previously reported Li-stoich and Li/Mn/O-rec structures [64, 155] that adopt inverse spinel surface configurations. The surface structure of the Li-rich configuration is identical to that of the Li/Mn/O-rec termination, but the Li-rich termination preserves the identity and position of the subsurface atoms from the bulk spinel structure.

Previously, Karim et al. determined that the lowest energy surface involves a Li/Mn exchange to an inverse spinel surface phase (either the Li-stoich or Li/Mn/O structures) [64]. We calculate, however, that the Li-stoich termination is not the most stable surface phase within any portion of the chemical potential space where bulk LMO is stable. Rather, we find that the Li/O termination is the most stable (111) surface within a majority of the bulk stability region of LMO. The Li/O termination does have some features that are similar to the Li-stoich and Li/Mn/O surfaces, including full saturation of the Mn_{3x} layer with the subsequent O_{4x} layer and the presence of monovalent Li cations at the surface. The Li cations reduce the strong surface dipole moment that would otherwise be present in the absence of the Li_x layer (a Tasker III-type polar surface, such as the Mn/O termination). However, in contrast to the Li-stoich and Li/Mn/O terminations, the Li/O termination preserves a subsurface structure that is identical to that of bulk LMO. The Li-rich surface phase, which also has the same subsurface structure as bulk LMO, becomes thermodynamically favorable at higher Li chemical potentials. These findings suggest that the reconstructed inverse spinel surface structures (Li/Mn/O and Li-stoich) introduced in previous work [64, 155] are not, in fact, the most stable structure of LMO(111) under conditions where bulk LMO is stable.

We note that, under Li-deficient and highly oxidizing conditions, the Li/O and Mn/O-rec surface terminations have comparable surface energies. Thus, features of the Mn/O-rec surface termination might appear as weakly metastable states at Li chemical potentials near the leftmost part of the bulk stability region, and indeed we

demonstrate that Li point defects in the near-surface region may be stable at relatively low surface coverages within the stable LMO chemical potential space (further details are included in Appendix A). Finally, we have also considered O vacancy formation energies on the Li/O and Li-rich surface terminations, which are calculated to be 1.76 and 2.22 eV atom⁻¹, respectively. However, because the $\Delta \mu_O$ values of 1.76 and 2.22 eV are well beyond the bulk stability region of LMO, these features will not appear on the phase diagram within the stable chemical potential space for bulk LMO.

In this section, we have identified stable, environment-dependent low-index surface terminations for the (001), (110), and (111) surfaces. Certain surface terminations have been analyzed in previous computational work [62, 64, 155], and we have identified additional structures that are thermodynamically preferred under chemical potential ranges in which bulk LMO is stable. In particular, we propose an alternate stable structure for the (111) surface, which has previously been the source of much debate in the literature [62, 64, 155]. The Li/O termination of the (111) surface (Figure 2.6) does not require the Li/Mn reconstruction to the inverse spinel surface structure but rather reduces the dipole of the $Mn_{3x}O_{4x}$ layers with an additional Li_x layer at the interface. Calculations for additional reconstructed surfaces suggest that the bulk modification induced by the inverse spinel surface phases does not, in general, result in the most thermodynamically stable phases. In addition, the possibility of O vacancy formation on different stable surface terminations has been considered. The low O defect formation energies on the (110) surface may be indicative of facile reduction under certain conditions. From the stable surface structures that we have identified, this highlights the probability of reduced Mn at the surface along the (001)and (110) surface planes (see Appendix A). The reduced nature of the Mn cations on these surfaces may provide some atomistic insight toward the enhanced Mn^{3+} disproportionation along these planes identified in experimental work [143, 76]. A comparison of the relative stabilities of the (001), (110), and (111) surface facets, together with considered high-index surfaces, will be discussed in Section 2.3.4.



Figure 2.7.: (311) surface terminations and surface phase diagram. Low energy surface structures are shown for the (311) surface in $\Delta \mu_{Li} - \Delta \mu_O$ phase space. Stoichiometries of the relevant surface structures, as well as the excess Li and O in each slab, are included. The excess Li and O are determined on the basis of the interfaces in the 1 x 1 unit cell used for the Li/Mn/O and Mn/O surface termination calculations. The Li-stoich termination requires a 2 x 1 unit cell and, by definition, has no excess elemental composition with respect to the bulk LMO stoichiometry. The atomic structure for the Li/Mn/O-1Ovac termination is annotated with \bigotimes at the site of the O vacancy. Figure 2.2 may be referenced for further information regarding notation and the phase diagram details.

2.3.3 High-Index Surfaces

High-index LMO surfaces may provide useful models of LMO particle edges, as well as of more general stepped or kinked surface features. Consideration of such surfaces is motivated, in part, by their observation in HRTEM images of polycrystalline LMO [154]. In addition, TEM images have provided experimental evidence for the presence of the (311) surface appearing as an edge between the (001), (110), and (111) facets of LMO nanoparticles [143]. Below, we analyze the (311), (331), (511), and (531) terminations, employing strategies to generate surface configurations similar to those developed above for the low-index surfaces. The atomic structures for the stable surface terminations that appear on the phase diagrams are included in the main text, while additional surface terminations that have been considered for each surface facet are described in Appendix A.

2.3.3.1 (311) Surface

Low energy surface terminations of the (311) surface are included in Figure 2.7, along with the corresponding surface phase diagram. The results demonstrate that the Li/ Mn/O termination is the most stable structure for the (311) surface facet under oxidizing conditions within the LMO bulk stability region. The additional O, compared to the Li/Mn termination, stabilizes an otherwise undercoordinated surface Mn atom. The negative charge density at the surface induced by this O atom is likely transferred from the in-plane Li at the surface, reducing the polarity of this structure. Additional saturation of surface Mn (Li/O and O-rich terminations) is not found to give a thermodynamically stable surface, except under highly oxidizing conditions ($\Delta\mu_O < 0$) that are well outside of the calculated bulk stability region. Under more reducing conditions, the stability of Li-stoich termination is enhanced. This surface structure is constructed by removing an LiMnO₄ unit from each side of a 2 x 1 supercell slab with the Li/Mn/O termination. Although the loss of O contributes to the stability of the Li-stoich surface under more reducing conditions, the Li- stoich surface is not a low energy surface termination within the chemical potential ranges associated with the stability of bulk LMO. However, we find that the Li/Mn/O termination has an O vacancy formation energy of 0.59 eV, such that the defected structure (Li/Mn/O-1Ovac) becomes the thermodynamically stable phase for $\Delta \mu_O$ values of less than 0.59 eV (see Appendix A for additional details). Subsequent reduction of the surface through the formation of additional O vacancies is not calculated to be stable within the LMO bulk stability region. The phase diagrams for the (131) and (113) surfaces are included in Appendix A. The features of these phase diagrams are comparable to the results for the (311) surface.

2.3.3.2 (331) Surface

As shown in Figure 2.8, the Li/O-terminated surface is calculated to be the most stable (331) surface termination under oxidizing conditions. The stoichiometry near the surface of this termination is heterogeneous in Li, Mn, and O, leading to a relatively balanced layer charge density. However, O vacancy formation on the Li/O surface termination is likely to be facile under the most relevant conditions, with a formation energy of 0.16 eV. This leads to the Li/O-10vac surface termination becoming the most thermodynamically stable (331) surface phase for $\Delta \mu_O$ values of less than 0.16 eV. This result suggests that vacancy formation on the Li/O surface termination will be spontaneous, except under very oxidizing conditions. Moreover, for $\Delta \mu_O$ values of less than 0.98 eV, further surface reduction via O vacancy formation is calculated to be thermodynamically favorable, making a more O-deficient phase (Li/O-2Ovac) the low energy surface.

A stoichiometric (331) surface is constructed by removing three Mn atoms from each side of a Li/Mn-1-terminated slab in a 2 x 1 supercell. This surface structure bears some similarity to the Li/O termination but with additional Mn present, consistent with a shift to higher Mn chemical potentials under these conditions. This surface, however, is calculated to be a metastable structure for the range of chemical potentials where bulk LMO is stable. Under the most reducing conditions, the lowest



Figure 2.8.: (331) surface terminations and surface phase diagram. Low energy surface structures are shown for the (331) surface in $\Delta \mu_{Li} - \Delta \mu_O$ phase space. Figure 2.2 may be referenced for further information regarding notation and the phase diagram details. The atomic structures for surface terminations containing one (Li/O-1Ovac) or two (Li/O-2Ovac) O vacancies are annotated with \bigotimes at the site of the vacancy.

energy terminations for the (331) surface become the Li/Mn-2 and Li/Mn/O-2 terminations. While these surface terminations are calculated to be the low energy (331) surface phases under Li-deficient and reducing conditions, these regions of the phase diagram correspond to ranges of chemical potentials where bulk LMO is thermodynamically metastable. We find similar trends considering analogous terminations for the (133) and (313) surfaces, whose phase diagrams are included in Appendix A.

2.3.3.3 (511) Surface

Surface terminations and the associated phase diagram for the (511) surface are provided in Figure 2.9. Under Li-deficient and oxidizing conditions, the Li/Mn/O termination is calculated to be the most stable surface structure. We note, however, that under these conditions the Mn/O surface termination has similar energetics [the difference in the surface energies is between 0.04 and 0.14 J m⁻² for the (511), (115), and (151) facets at chemical potentials along the equilibrium line between bulk LMO and MnO_2]. As conditions shift to more Li-rich conditions, it becomes more thermodynamically favorable for additional Li atoms to be present at the surface, as in the Li termination. O vacancy formation energies on the Li/Mn/O and Li surface terminations are 0.83 and 0.81 eV, respectively, on the (511) surface. The energetics for vacancy formation on these two surface terminations are quite similar, as is the case for the (115) and (151) surface facets (see Appendix A). A stoichiometric surface termination, constructed by removing an Mn_3O_8 unit from each side of a 2 x 1 supercell of the Li/Mn/O-terminated slab, does not become the low energy surface phase at any point within the LMO bulk stability region. These results are consistent with results for the (115) and (151) surfaces, whose phase diagrams are included in Appendix A.



Figure 2.9.: (511) surface terminations and surface phase diagram. Low energy surface structures are shown for the (511) surface in $\Delta \mu_{Li} - \Delta \mu_O$ phase space. The atomic structures for surface terminations containing O vacancies (Li/Mn/O-1Ovac and Li-1Ovac) are annotated with \bigotimes at the site of the vacancy. Figure 2.2 may be referenced for further details regarding notation and the phase diagram details.



Figure 2.10.: (531) surface terminations and surface phase diagrams. Low energy surface structures are shown for the (531) surface in $\Delta \mu_{Li} - \Delta \mu_O$ phase space. The atomic structures for surface terminations containing O vacancies (Mn/O-1Ovac, Mn/O-2Ovac, and Li-1Ovac) are annotated with \bigotimes at the site of the vacancy. Figure 2.2 may be referenced for further details regarding notation and the phase diagram details.

2.3.3.4 (531) Surface

For the (531) surface, the phase diagram in Figure 2.10 indicates that there exist two distinct stability regions associated with the Mn/O and Li terminations of the (531) surface. Under Li-deficient conditions, the Mn/O termination is lowest in energy. Although this surface is similar in stoichiometry to the Li/Mn/O surface, the extra Li present is not sufficiently close to the surface to provide any surface charge density stabilization, as seen for other high-index surfaces. Instead, the Li termination is most stable under Li-rich conditions, containing two extra Li atoms at the surface compared to the Mn/O termination. Each of these surface terminations have modest O vacancy formation energies of 0.94 and 1.23 eV, for the Mn/O (reduces to Mn/O-1Ovac) and Li (reduces to Li-1Ovac) terminations, respectively. Furthermore, the Mn/O termination may become further reduced (Mn/O-2Ovac) for $\Delta \mu_{O}$ values of less than 0.97 eV. The reduction of the Mn/O termination, however, is not calculated to occur within the range of component chemical potentials where bulk LMO is stable, suggesting that the Mn/O-1Ovac and Mn/O-2Ovac terminations are metastable (see also Appendix A). The phase diagrams for the (135), (153), (315), (351), and (513) surfaces follow similar behavior and are also plotted in Appendix A.

2.3.4 Relative Surface Stability and Predicted LMO Particle Shapes

In Figure 2.11, we plot surface energies for the various surface facets as a function of the Li and O chemical potentials. Only the most stable surface terminations for a given surface facet under each set of chemical potential conditions are shown. Figures 2.2, 2.4, and 2.6-2.10 may be referenced to identify the relevant surface structures under each set of conditions. From these data, the predicted particle shape, found by minimizing the excess interfacial free energy of a nanoparticle based on the calculated surface energies at each set of conditions, is determined (Figure 2.12). The Wulffmaker software [180] is used to calculate the normalized surface area of each facet.



Figure 2.11.: Surface energies of the most stable surface terminations for the lowand high-index surface facets considered in this work. Each phase diagram is plotted for a fixed value of $\Delta \mu_{Li}$, whereas $\Delta \mu_O$ is considered as a tunable parameter. The pink shaded regions denote the ranges of chemical potentials where bulk LMO is thermodynamically stable.



Figure 2.12.: Cumulative nanoparticle surface area plot. On the basis of calculated surface energies, the excess interfacial free energy of a hypothetical LMO nanoparticle is minimized by adjusting the relative surface areas of each surface on the nanoparticle. The shaded regions correspond to the relative contribution of each surface facet to the nanoparticle morphology under a given set of conditions. The black-outlined polygon in each figure corresponds to the range of chemical potentials where bulk LMO is calculated to be thermodynamically stable.

The results suggest that, under more Li-rich ($\Delta \mu_{Li}$ approaching the chemical potential of bulk Li) and reducing conditions ($\Delta \mu_O$ approaching highly negative values), nanoparticles are likely to exhibit more cubic morphologies, exposing a greater surface area of (001) planes with respect to (111). These results are consistent with the very recent work from Kim et al. [155], despite the differences in surface terminations for the (001) and (111) surfaces under various conditions. In general, the results suggest that the equilibrium shape of LMO particles tends to be either an octahedron or a truncated octahedron, depending on the environmental conditions. Additionally, the phase diagrams in Figure 2.12 indicate that the (511) family of surface facets have relatively low surface energies (consistently less than 1 J m⁻²) and thus may be reasonable model systems for features of LMO nanoparticle edges.

2.4 Conclusions

Low energy surface structures for the (001), (110), and (111) surfaces of spinel LMO are identified using a combination of DFT calculations and a grand canonical thermodynamic formalism. The excess Li content at the interface, which depends directly on the system Li chemical potential, is found to be an important descriptor for the (001) surface structures. The Li/O termination of the (110) surface, not previously identified in the literature, has been identified as the low energy surface termination for this facet under oxidizing conditions. It is also suggested, however, that LMO (110) is susceptible to reduction of surface Mn through O vacancy formation. An extensive discussion of low energy structures for the (111) surface is further presented, and several Li-rich surface phases are identified that have lower calculated surface energies than the inverse spinel phases discussed in previous work [64, 155]. Finally, stable high-index surface terminations are described that could serve as appropriate models for steps and other defects that may appear on low-index terraces of large LMO nanoparticles.

The relative energetics of all surface structures are combined to provide predictions for LMO particle shapes. On the basis of the low surface energies of the (001) and (111) facets, we suggest that the LMO equilibrium particle shape is either an octahedron or a truncated octahedron, depending upon conditions, in excellent agreement with the experimental results. These results provide a comprehensive catalog of structures likely to be present under realistic electrochemical conditions, together with insight into the molecular origins of their stability, and serve as a starting point for future studies of interfacial chemistry and cycling to enhance the stability of LMO cathodes.

Supporting Information for this chapter is included in Appendix A.

3. ORIENTED LIMN₂O₄ PARTICLE FRACTURE FROM DELITHIATION-DRIVEN SURFACE STRESS

This chapter is reproduced from a manuscript that is being prepared for publication: Robert E. Warburton, Fernando C. Castro, Siddharth Deshpande, Kenneth E. Madsen, Kimberly L. Bassett, Andrew A. Gewirth, Vinayak P. Dravid, Jeffrey P. Greeley; Oriented LiMn₂O₄ Particle Fracture from Delithiation Driven Surface Stress.

The insertion and removal of Li⁺ ions into Li-ion battery electrodes can lead to severe mechanical fatigue due to the repeated expansion and compression of the host lattice during electrochemical cycling. In particular, the lithium manganese oxide spinel (LiMn₂O₄, LMO) experiences a significant surface stress contribution to electrode chemo-mechanics upon delithiation that is asynchronous with the potentials where bulk phase transitions occur. In this work, we further probe the stress evolution and resulting mechanical fracture from LMO delithation using an integrated approach consisting of cyclic voltammetry, electron microscopy, and density functional theory (DFT) calculations. High-rate electrochemical cycling was used to exacerbate the mechanical deficiencies of the LMO electrode and shows that delithiation and lithiation kinetics are slower following cycling due to mechanical degradation, which is confirmed through identification of significant fracturing in LMO using scanning electron microscopy. DFT calculations are used to model the mechanical response of LMO surfaces to electrochemical delithiation and suggest that particle fracture is unlikely in the [001] direction, due to tensile stresses from delithiation near the (001)surface. In fact, transmission electron microscopy and electron backscatter diffraction of the as-cycled LMO particles indicate that particle fracture instead tends to preferentially occur along {111} planes. This joint computational and experimental analysis informs a further understanding of the chemo-mechanical response of the LMO electrode to electrochemical delithiation, as well how surface stresses may lead to particle fracture in Li-ion battery electrodes.

3.1 Introduction

Li-ion batteries are necessary to power consumer electronics and are enabling widespread use of electric vehicles [17]. However, improvements in energy density and long-term cycling performance are necessary for Li-ion batteries to be a competitive solution in the transportation sector. Spinel lithium manganese oxide (LiMn₂O₄, LMO) is of great interest as a Li-ion battery cathode because of its high voltage, high thermal stability, and low cost compared to cobalt-containing cathode materials [31, 181]. Despite these advantages, chemical and structural instabilities limit the electrochemical performance of LMO. For instance, manganese ion dissolution into the electrolyte [182, 183, 184] typically occurs alongside irreversible formation of a static Jahn-Teller-distorted tetragonal phase during cycling (below 3 V vs. Li/Li⁺) [136]. Additionally, there is a 7.7% volume expansion and contraction for each charge and discharge cycle between LMO and λ -MnO₂ [45, 132].

The significant volume change between the charged and discharged states of LMO, particularly as it relates to interface coherency, or the lattice mismatch, between Li⁺rich and Li⁺-deficient domains in the electrode [185, 186], can lead to substantial mechanical degradation and particle fracture [184, 187, 188, 189, 190]. As a result, the concentration of defects and reactive surface area of the electrode may increase, accelerating capacity fade and delamination from the current collector. Therefore, further understanding the relationship between stress, strain, and particle fracture is necessary for improving intercalation electrode design toward reduced mechanical degradation.

Electrochemical stiffness analysis is an approach to determine the stress-strain relationship of electrodes by comparing the rate of change of electrode stress relative to that of electrode strain [191]. This comparison offers a strategy for analyzing the different mechanical changes taking place on an electrode and their relative importance. In-situ electrochemical stiffness measurements have recently shown that LMO cathodes have distinct stress-strain relationships during lithiation and delithiation [192]. During delithiation, an increase in the electrochemical stiffness prior to the low-voltage oxidation peak, suggests a surface stress-dominated process prior to or just as the first delithiation phase transition to $Li_{0.5}Mn_2O_4$ ($L_{0.5}MO$) begins. In the same voltage range during lithiation, however, this feature of the electrochemical stiffness does not appear is not offset from the reduction potential, but instead occurs at the same potential as the bulk phase transition. This suggests that an expansion of the bulk lattice constant (or strain) is the dominant chemo-mechanical process upon lithiation, in contrast to the surface-stress driven mechanisms for delithiation. Additional works have also suggested that surface stress-driven mechanical degradation of electrodes is more pronounced upon delithiation in comparison to lithiation [193, 194, 195]. While increased surface stress may be indicative of a fundamental driving force for mechanical degradation of LMO, especially at higher scan rates, an atomic scale understanding of such mechanisms and their consequences remains unclear.

Density functional theory (DFT) calculations have recently described the physics of adsorption-driven surface stress changes in electrocatalytic systems [196, 197], and such approaches may also aid in understanding analogous lithiation- or delithationdriven surface stress changes. In combination with theoretical studies, materials characterization and structural analysis of LMO particles may provide additional insights toward the surface stresses responsible for particle fracture. In particular, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) can provide morphology and defect orientation information through direct visualization of individual LMO particles. Previous reports have used SEM and TEM to examine phase transformations, particle fracture, and mechanical properties in LMO systems [184, 136, 198, 199], but detailed analysis of the crystallographic orientation of fracturing in individual particles of LMO has not been presented in the literature, nor understood in combination with DFT calculations of stress evolution in the particles. In this work, we examine delithiation-induced surface stress on LMO and its role in mechanisms of electrode particle fracture. DFT calculations are used to calculate stress tensor components in response to Li⁺ removal from the (111) and (001) facets, which dominate the LMO particle surface area [200]. Cyclic voltammetry (CV) scans are performed at variable scan rates, and SEM subsequently confirms LMO particle fracture. Electron backscatter diffraction (EBSD) and TEM are used to provide additional information regarding the orientation of cracks formed during high-rate electrochemical cycling. This combined experimental and theoretical approach provides a deeper understanding of mechanical degradation in LMO and could inform rational strategies to enhance mechanical integrity upon electrochemical cycling.

3.2 Methods

3.2.1 Electrode Fabrication

All chemicals were used as received. Electrodes were fabricated from an aqueous slurry of 8:1:1 wt% LiMn₂O₄ (Electrochemical Grade, Sigma-Aldrich, St. Louis, Mo), conductive carbon (Super P Li, Timcal), and carboxymethylcellulose sodium salt (Aldrich). LMO and conductive carbon were ground in a mortar and pestle until uniform in color, added to an aqueous solution of carboxymethylcellulose (2.9 wt%), and mixed by sonication until homogenous. The resulting slurry was cast on an aluminum foil current collector (MiniBin, Sigma-Aldrich) with a doctor blade to a thickness of ca. 100 μ m, dried in air overnight, then dried under vacuum at 80°C for 12 hours. Typical mass loadings for the 0.5 inch diameter electrodes were ca. 1.1 mg cm⁻².

3.2.2 Electrochemical Measurements

Electrochemical measurements were conducted in CR2032 coin cells (MTI corporation, Richmond, CA). Battery stacks were composed of a 0.5 in. diameter lithium (0.75 mm thickness, 99.9%, Sigma-Aldrich) counter/reference electrode, a glass-fiber

paper separator (Whatman, GF/C) onto which an electrolyte solution (1 M LiPF₆ in 50:50 ethylene carbonate (EC): ethyl methyl carbonate (EMC), Battery Grade, Aldrich) was added dropwise until the separator was saturated (ca. 5 drops), a LMO working electrode, a stainless-steel separator, and a wave spring. The cell was sealed and unsealed using a hydraulic coin cell crimper (MTI corporation, Richmond, CA).

Cyclic voltammetry (CV) was performed with a CH Instruments electrochemical workstation (Model 6002E, Austin, TX). To induce material degradation, the cells were cycled between 3.5 and 4.5 V vs Li/Li⁺ for 5 cycles per scan rate for the following rates: 0.5, 1, 2, 5, 10, 0.5 mV s⁻¹. The final scan rate was returned to 0.5 mV s⁻¹ to evaluate changes in cycling behavior following high-rate electrochemical cycling.

3.2.3 Microscopy

Cycled cathodes were removed from their coin cells, rinsed thoroughly with EMC (Sigma-Aldrich), and dried under vacuum at 80°C for 12 hours to remove residual electrolyte. The disassembled LMO electrode was attached to a stub with carbon tape to prepare for cross-section sample preparation. Initial SEM imaging was done using a FEI Helios 600 FIB SEM. This instrument was also used to prepare cross-section samples of the cracked LMO particles. A FEI Quanta 650 SEM operating at 30 kV was used for additional imaging and for TKD analysis with an Oxford AZtec EBSD system. The pixel size for the TKD orientation maps is 5 nm². TEM analysis of the FIB cross-section was done after TKD, using a JEOL 2100 TEM with 200 kV accelerating voltage.

3.2.4 Density Functional Theory Calculations

Periodic, spin-polarized density functional theory (DFT) calculations were performed using the Vienna Ab initio Software Package [160, 168, 161]. The effective core states were treated using the projector augmented wave method [201, 162], with the 3p and 1s electrons of Mn and Li, respectively, treated as valence and expanded in a plane-wave basis set. A kinetic energy cutoff of 520 eV was used in all calculations, with total energies converged to 0.10 meV per unit cell with a force criterion of 20 meV Å⁻¹ for geometry relaxations. The generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE) was used as the exchange and correlation functional [163]. The DFT+U method [102, 103, 104] was used to correct for over-delocalization in the highly correlated Mn 3*d* states using a Hubbard *U*-value 3.5 eV, which reproduces bulk thermochemistry of Mn oxides of variable oxidation states with sufficient accuracy [200, 110, 202, 203].

3.2.5 Thermodynamic and Surface Stress Calculations

The computational studies in this work focus on identifying the chemo-mechanical behavior around the low-voltage α -peak, representing the equilibrium between the LiMn₂O₄ (LMO) and Li_{0.5}Mn₂O₄ (L_{0.5}MO) phases [204]. DFT calculations were performed to identify the appropriate near-surface LMO and L_{0.5}MO models and determine the corresponding stress tensor to understand the mechanical response to (de)lithiation. We applied a sequential (de)lithiation procedure to identify the most stable Li configurations of LMO and L_{0.5}MO surfaces. As done in previous surface (de)lithiation studies [205, 65, 206], we fixed part of the slab to represent the bulk of LMO and L_{0.5}MO (see Appendix B, Figure B.8). Thus, we limited our (de)lithiation studies to (de)intercalation sites within the range of atoms that are subject to ionic relaxation. For delithiation of the LMO surfaces, we begin with a lithiated surface configuration and evaluate the most stable Li configurations for each delithiated stoichiometry.

The free energy of reaction for delithiation $(\Delta G_{Li_xMO \to Li_yMO})$ between LMO slabs with lithium contents of Li_xMO and Li_yMO is calculated as a function of the cell voltage (U), where U modulates the electrochemical potential of lithium with respect to the metallic lithium reference electrode $(g_{Li}^{bulk} - eU)$. As represented by the electrochemical potential expression, U is the voltage with respect to the reversible Li/Li⁺ electrode, by definition [11]. The $\Delta G_{Li_xMO \to Li_yMO}$ can therefore be represented by the following expression.

$$\Delta G_{Li_x MO \to Li_y MO} = [G_{Li_y MO} + (y - x)(g_{Li}^{bulk} - eU)] - G_{Li_x MO}$$
(3.1)

In these calculations, we assumed that the free energies are accurately represented by the DFT total energies for the slabs and metallic lithium reference and that entropic corrections to the free energy are systematic and self-correcting for the solid-state materials of interest at room temperature.

As in recent work from our group [196, 197], we determined the differential surface stress at each stage of delithiation, we calculated the stress tensor using DFT and apply the surface stress theorem of Nielsen and Martin [207]. In general, the differential surface stress ($\Delta \sigma$) between a delithiated LMO surface and its fully lithiated reference is determined by the following expression.

$$\Delta \sigma = \frac{c}{2} \left[\left(\tau_{xx}^{delithiated} - \tau_{xx}^{lithiated} \right) + \left(\tau_{yy}^{delithiated} - \tau_{yy}^{lithiated} \right) \right]$$
(3.2)

In equation 3.2, τ_{xx} and τ_{yy} are x and y diagonal components of the stress tensor, where z corresponds to the direction of the interface (towards vacuum), and c is the length of the calculation cell in the z-direction.

3.3 Results

3.3.1 High-Rate Electrochemical Cycling

Cyclic voltammetry (CV) scans were performed on LMO at scan rates of 0.5, 1, 2, 5, 10, and 0.5 mV s⁻¹ for five cycles each. Figure 3.1a shows the CV scans for the third of five cycles at each scan rate. The two electrochemical couples indicate the two stage removal of Li⁺ from tetrahedral sites, in which LMO passes through the intermediate $L_{0.5}MO$ phase prior to fully delithiated λ -MnO₂ [45, 132, 44]. Figure 3.1b shows the 0.5 mV s⁻¹ CV scans before and after the increasing scan rate experiment. Between the pre- and post-cycling 0.5 mV s⁻¹ CV scans, the peak splitting



Figure 3.1.: LMO cyclic voltammetry. (a) Cyclic voltammetry between 3.5 and 4.5 V vs. Li/Li^+ at scan rates ranging between 0.5 to 10 mV s⁻¹. The data presented is from the third of five cycles at each scan rate. (b) Cyclic voltammetry at 0.5 mV s⁻¹ before and after high-rate cycling. The dashed lines are drawn between analogous charge and discharge peaks to represent changes in kinetic resistance. The arrows show the direction of capacity and voltage evolution after extended cycling.

between charge and discharge increases by 41 mV and 33 mV for the lower and higher potential electrochemical couples, respectively, which indicates increased kinetic resistance in the cell [208]. This is shown in Figure 3.1b by the dashed lines between each peak during charge and discharge which indicates a larger peak splitting postcycling. Based on the integrated current in Figure 3.1b, the total charge decreases by ca. 3.5% (shown by arrows in Figure 3.1b), which suggests a loss of active material available for lithiation and delithiation. Together, the increased peak splitting and decreased charge after cycling show a decrease in electrode performance possibly due to film formation by electrolyte decomposition products, loss of Mn, or mechanical degradation such as particle cracking [136, 209, 210, 211, 212].

After electrochemical cycling, the cell was disassembled, the LMO electrode was washed with ethyl methyl carbonate, and imaged using SEM to identify morphological changes or cracking in the electrode particles. Figure 3.2a shows a representative LMO particle post-cycling, which contains several cracks (highlighted with yellow arrows). The particle is also covered with the conductive carbon additive. Figure B.1



Figure 3.2.: Imaging of LMO particle cracking. (a) SEM image of LMO particle after extended electrochemical cycling. Multiple cracks can be seen in the particle, as indicated by yellow arrows. (b) SEM image of FIB cross-section of LMO particle area outlined by the yellow dashed box in (a).

in Appendix B further highlights the prominence of cracking in LMO particles, which was frequently observed after high-rate cycling. Moreover, we also observe multiple parallel cracks on the same particle (as indicated by the yellow arrows in Figure 3.2a), suggesting a common crystallographic orientation for particle fracture. In order to examine the extent of cracking into the particle interior, cross-section samples were cut from the boxed area on the cracked LMO particle in Figure 3.2a using a focused ion beam (FIB) technique. The cross-section sample was cut out from the boxed area in Figure 3.2a. Figure 3.2b shows an SEM image of the cross-section sample prepared from the cracked LMO particle. The surface-level cracks from the LMO are visible at the top of the cross-section sample. These cracks are faceted and extend over 1 μ m deep into the particle. Several smaller and thinner cracks were seen in the middle of the cross-section, indicating that the LMO particle interior had additional fracturing and cracking that is not evident from surface imaging.

3.3.2 Density Functional Theory Calculations

To further understand the origins of particle fracture, DFT calculations are performed to evaluate the stress response of LMO surfaces as a function of Li^+ content. Starting with the Li/O-terminated (111) and Li-terminated (001) surfaces [200], we sequentially remove Li⁺ from the near-surface region in order to calculate the associated reaction thermochemistry and surface stress response. For the purpose of estimating the differential stress response of each surface, we assume that the most thermodynamically stable Li⁺ configuration is the most relevant phase for determining the concentration- and voltage-dependent surface stress.

Figures 3.3a and 3.3d show the most stable Li⁺ configuration at a given stoichiometry for LMO(111) and LMO(001), respectively, where we evaluate Li^+ removal from different layers (labeled L#, where L1 is the surface layer). Similar to our recent work [213], the stoichiometric notation used is normalized by the relative Li⁺ content in the near-surface delithiation region with respect to the Mn_2O_4 stoichiometry (described in Section 3.2.4). We note that the LMO(111) surface is oxygen-rich and as such the x = 1.5 in Li_xMn₂O₄ stoichiometry of the fully lithiated state in Figure 3.3a does not imply that the average Mn oxidation state in this model is 3.25+. As discussed in our previous work [200], the oxygen-termination of surface Mn on LMO(111) makes it thermodynamically unfavorable to remove Li⁺ from the top-most layer (L1) since this Li⁺ is necessary to stabilize the negative charge density at the surface. As shown in Figure 3.3a, the most stable configuration contains Li⁺ in the surface layer (L1) through deep stages of delithiation (x = 0.25). In the case of LMO(001), following the half-removal (x = 0.875 in Figure 3.3d) and full-removal (x = 0.75 in Figure 3.3d) from the top-most layer (L1), Li⁺ removal again proceeds from the sub-surface (L4) beginning with the x = 0.50 phase. The voltage-dependent thermodynamics of the stable LMO(111) and LMO(001) phases in Figures 3.3a and 3.3d, as well as their corresponding metastable Li⁺ configurations, are presented in Appendix B, Figures B.2 and B.3. Using equation 3.1 (in Section 3.2.5), we calculate a wider range of surface concentrations that are thermodynamically accessible prior to the point of the $LMO/L_{0.5}MO$ phase equilibrium (calculated to be 3.84 V vs. Li/Li⁺ at the DFT+U level of theory) for LMO(001) as compared to LMO(111). More specifically, the 1.50 $\leq x \leq 1.25$ and $1 \leq x \leq 0.5$ phases of LMO(111) and LMO(001), respectively, are calculated to be accessible under the relevant range of potentials. More lithium-deficient surface phases are calculated to be metastable, where there exists a stronger thermodynamic driving force for the $LMO/L_{0.5}MO$ bulk phase transition to occur instead. Using these results as a guide, we next consider the evolution of surface stress in the context of these thermodynamically relevant surface phases.

Figures 3.3b, 3.3c, 3.3e, and 3.3f show the differential surface stress ($\Delta \sigma$) determined from the DFT-calculated stress tensor incorporated into the surface stress expression in equation 3.2 (in Section 3.2.5). Figures 3.3b and 3.3e show the calculated $\Delta \sigma$ as a function of Li⁺ content (corresponding directly to the phases shown in Figures 3.3a and 3.3d), whereas Figures 3.3c and 3.3f incorporate thermodynamics of these different near-surface phases to illustrate voltage-dependent mechanical response of each surface to delithiation. The filled circles in Figures 3.3b and 3.3e represent the low-energy Li⁺ configurations and the hollow circles denote the metastable Li⁺ configurations. In each of these figures, the yellow-shaded region corresponds to conditions where Li⁺ removal and the chemo-mechanical response is a surface dominated process, i.e. these phases are thermodynamically stable at voltages below the $LMO/L_{0.5}MO$ bulk equilibrium potential. In contrast, the blue-shaded region corresponds to bulk dominated delithiation and chemo-mechanics due to the driving forces for the $LMO/L_{0.5}MO$ bulk phase transition for voltages above the equilibrium potential. Although the blue-shaded region represents surface phases where the LMO bulk is unstable, we present these corresponding stresses as well since these could correspond to kinetically trapped surface phases prior to the bulk phase transition to $L_{0.5}$ MO. As shown in Figures 3.3b and 3.3c, the tensile stress moderately increases (positive $\Delta \sigma$) by 0.31 N m⁻¹ for LMO(111) prior to the predicted bulk phase transition at 3.84 V vs. Li/Li⁺ (denoted by the dashed line). Although the stress becomes more compressive for $x \leq 1$, we emphasize that the delithiated phases of LMO(111) for $x \leq 1$ are not thermodynamically favorable at these potentials (as indicated by the blue-shaded bulk dominated region of the plot). Instead, the bulk will transition to $L_{0.5}MO$, retaining a finite concentration of Li⁺ at the surface to reduce the surface dipole and to ensure the Mn ions are not oxidized beyond Mn^{4+} . Figure 3.3e shows



Figure 3.3.: Surface stress evolution upon delithiation of LMO surfaces. (a,d) Lowenergy structures of the (a) LMO(111) and (d) LMO(001) surfaces at different Li⁺ contents. (b,e) Differential surface stresses of (b) LMO(111) and (e) LMO(001) as a function of Li⁺ content for various Li⁺ configurations. The filled circles in (b) and (e) represent the most energetically stable structures for a given stoichiometry, as shown in (a) and (d) for LMO(111) and LMO(001), respectively. The unfilled circles in (b) and (e) denote metastable lithium configurations. The stoichiometries correspond to only near-surface Li⁺ content, which is normalized to the Mn₂O₄ stoichiometry withing the delithiation region as defined for the slab model. (c,f) Differential surface stresses of (c) LMO(111) and (f) LMO(001) as a function of the cell voltage, determined from thermodynamic calculations presented in Appendix B, Figures B.2 and B.3. (Caption continued on the following page.)

Figure 3.3.: (continued) The dashed lines correspond to the calculated equilibrium potential of 3.84 V vs. Li/Li⁺ between LMO and $L_{0.5}MO$ at the DFT+U level of theory. The yellow-shaded regions of (b,c,e,f) correspond to surface dominated mechanics from near-surface delithiation, as determined by the stable surface phases that occur below the equilibrium potential. The blue-shaded regions correspond to surface phases that are thermodynamically inaccessible since they become stable only at voltages above the equilibrium potential, where it is more thermodynamically favorable for the bulk phase transition to proceed. The stresses corresponding to these surface phases are unlikely to be relevant, since the chemo-mechanical response at higher potentials is instead likely to be coincident with the LMO/L_{0.5}MO phase transition.

that the calculated stress for x = 0.50 phase of the LMO(001) surface increases to 1.75 N m⁻¹, which corresponds to a differential tensile stress more than five times larger than that which was calculated upon delithiation of the LMO(111) surface. Moreover, the x = 0.5 phase is thermodynamically stable below the LMO/L_{0.5}MO equilibrium potential (as indicated by the yellow-shaded, surface dominated region of Figures 3.3e,f), suggesting that delithiation of the (001) surface is likely the major contributor to the previously reported tensile stress increases prior to the LMO/Li_{0.5}MO phase transition [192, 214, 215].

Recent experiments suggest that the dominating driving forces of LMO chemomechanical changes are different for delithiation and lithiation. Upon delithiation, surface stress is dominant prior to the LMO/L_{0.5}MO phase transition upon delithiation, whereas during lithiation, the L_{0.5}MO/LMO bulk phase transition occurs simultaneously with the observed stress-dominated chemo-mechanical changes [192]. While we observe a significant buildup of surface stress for LMO(001), we also consider the process of lithiation of this surface with a fixed L_{0.5}MO bulk. Figure B.4 in Appendix B shows that there is a limited range of stable surface Li⁺ configurations for L_{0.5}MO, suggesting that surface stress is not likely to be influenced by near-surface lithiation, in contrast with the increase in surface stress observed upon delithiation of LMO. These findings are in agreement with the chemo-mechanical measurements of the



Surface stresses and crack formation at LMO surfaces. Figure 3.4.: (a)Schematic showing the mechanical response induced by a Li⁺-deficient near-surface $(Li_{1-x}Mn_2O_4, in yellow)$ that is constrained in the plane of the surface by the fixed lattice constant of the fully lithiated bulk ($LiMn_2O_4$, in blue). When Li^+ is removed, Mn ions are oxidized and there is a driving force for Mn-O bonds to shorten (shown by the blue arrows). This effect, in combination with the fixed lattice constant of the bulk region limiting the extent to which Mn-O bonds can shorten leads to tensile stress in the near-surface (shown by the orange arrows). (b,c) Diagram of the response of (b) LMO(001) and (c) LMO(111) surfaces to delithiation concerning the opposing forces of Mn-O bond compression upon Li⁺ removal and a constrained bulk. The in-plane Mn-O bond modes are antiparallel to the tension imposed by the bulk, which contributes to increased stress buildup for LMO(001). All Mn-O bonds are partially oriented toward the [111] surface normal for LMO(111), which is why stress buildup upon delithation is less severe in comparison to LMO(001).

delithiation- and lithiation-dependent stress-strain relationship in LMO by Çapraz et al [192].

Given that surface stress appears to be most relevant upon delithiation of the LMO(001) surface, we consider the structural effects of delithiation in order to rationalize the structure-specificity of LMO chemo-mechanics. Based on the surface stress theorem of Nielsen and Martin (equation 3.2) [207], an increase in the tensile stress is defined by normal stress tensor components with orientation in the plane of a given surface. Figure 3.4a shows how tensile stress is induced upon delithiation of the near-surface of the electrode (shaded in yellow), while the bulk (shaded in blue) maintains its full Li⁺ content. Delithiation promotes strain-driven Mn-O bond compression due to Mn oxidation and the smaller ionic radius of Mn⁴⁺ compared to Mn^{3+} (shown by the blue arrows in Figure 3.4a), but the fixed lattice constant of LMO in the bulk prevents these surface bonds from fully contracting to their equilibrium bond lengths. These opposing forces acting on near-surface Mn-O bonds result in increased tensile stress (shown by the orange arrows in Figure 3.4a). Figures 3.4b and 3.4c show that these effects are most pronounced for LMO(001), since four of the six Mn-O bond compression modes (for a fully coordinated Mn ion) are parallel to the (001) surface plane and antiparallel to the tension imposed by the LMO bulk, leading to maximal tensile stress on these Mn-O bonds (Figure 3.4c). On the other hand, Mn-O bonds near the LMO (111) surface are allowed more flexibility to compress due to partial orientation toward the surface normal, where these bonds are free to relax (Figure 3.4b). We emphasize that the tensile stress buildup upon delithiation near the LMO(001) surface corresponds to tension in the (001) plane, not in the direction of the [001] surface normal. Thus, if LMO(001) is the major contributor to observed stress increases, the overall magnitude of the stress will not be oriented in the [001] direction, i.e. stress-induced fractures are unlikely to occur along the {001} planes.

3.3.3 EBSD Analysis of LMO Particle Cracking

In order to determine the crystallographic orientation of the cracks in LMO particles we perform EBSD analysis, which determines the local crystallographic orientation of a bulk material. The spatial map of local crystallographic orientations from EBSD in combination with cracks observed through microscopy (SEM, TEM) can posit the propagation direction of the observed cracks. However, EBSD analysis requires stringent surface preparation of the materials of interest, as significant surface roughness or deformation results in poor signal-to-noise diffraction data. EBSD analysis of the as-is particles after cycling is therefore not possible due to the particle roughness and carbonaceous material at the surface. Thus, the aforementioned FIB cross-section of post-cycling LMO enables EBSD analysis since the sample surface is thinner and smoother. In fact, the samples thin (100 nm) geometry makes it possible to use an advanced EBSD variant known as transmission Kikuchi diffraction (TKD), which provides the same crystallographic information with significantly improved spatial resolution [216]. TEM images can provide additional information regarding crystalline defects and the orientation of cracks in the material [198, 217].



Figure 3.5.: TKD analysis of cracking in LMO particle after extended cycling. (a) SEM image of cross-section. The white boxed area indicates the mapping region. The sample orientation axes are also shown. (b) Inverse pole figures (IPFs) for the entire mapping region indicated in (a) in the x, y, and z sample directions. (c) TKD map of the region highlighted in (a), with IPF-x coloring. (d)TKD map of the same region, with IPF-y coloring. The IPF color key is shown to the right of the map in (c,d). The weaker orientation signal seen in (b) is marked with an asterisk (*) and corresponds to the area in (c,d) also marked by an asterisk. The pixel size of the maps shown in (c,d) is 5 nm².

Figure 3.5 shows the TKD analysis of the cracked region of the LMO particle seen in Figure 3.2. The mapped area was indexed to the spinel LiMn_2O_4 structure, since cycling finished in the fully lithiated state, and shown by the TKD phase map in Figure B.5. The uncolored pixels in Figure 3.5c,d indicate an area where there was no indexed diffraction pattern. An orientation map was collected from the boxed region shown in Figure 3.5a. Figure 3.5b shows the inverse pole figures (IPF) from the mapped region, where the IFPs project the crystallographic orientation of the sample along the different sample directions onto a heatmap for visualization. In Figure 3.5b, the 'x' direction corresponds to the sample direction perpendicular to the crack direction, while the 'y' sample direction lies parallel to the crack direction. The IPFs in Figure 3.5b show that the $\langle 111 \rangle$ orientation is approximately parallel to the 'x' direction of the sample, indicated by the intense contour feature in the [111] corner of the IPF. Likewise, the 'z' sample direction, which lies normal to the surface of the cross-section, is approximately parallel to the $\langle 111 \rangle$ direction. The sample 'y' direction, which corresponds to the crack direction in the cross-section, shows a small deviation away from the $\langle 111 \rangle$ direction towards the $\langle 111 \rangle$ direction. Overall, these TKD results suggest that the particle fracture and crack propagation happened primarily along the $\langle 111 \rangle$ crystallographic direction of the particle.

The crystallographic orientation of each direction in the particle is also shown through TKD mapping. Figures 3.5c,d show these TKD maps with IPF coloring corresponding to the 'x' and 'y' directions, respectively. The left and middle regions in the map are deeply blue colored in both Figure 3.5c and 3.5d, indicating a strong $\langle 111 \rangle$ orientation character of the 'x' and 'y' direction in those regions. Figure 3.5c shows a more homogeneous coloration than Figure 3.5d, reflecting the more homogeneous distribution of $\langle 111 \rangle$ orientation in the 'x' sample direction. The right-most region of both maps shows different coloration. This region is responsible for the weaker features appearing in the IPFs of the 'x' and 'y' sample directions. These regions are marked with an asterisk (*) in Figures 3.5b-d. However, this difference in orientation is likely due to sample bending observed in this region during TKD analysis, resulting in some change in orientation of the sample with respect to the detector. This sample bending also resulted in some widening of the crack in that region, that can be seen when comparing the images from Figure 3.2b and 3.5a.

3.3.4 TEM Analysis of LMO Particle Cracking

Figure 3.6 shows TEM verification of the crystallographic direction of the LMO cracks, using the same sample used for TKD analysis. The overall FIB cross-section sample is shown in Figure 3.6a, with the area that was mapped with TKD boxed in white. Higher magnification imaging of the cracked region is necessary to identify the orientation of the LMO lattice planes in the sample. Figure 3.6b shows high-resolution TEM (HRTEM) images of the region outlined by a black box in Figure 3.6a, which also corresponds to the left-most region in Figure 3.5. This region shows that the crack has split into multiple faceted directions.

A higher-magnification HRTEM image of this cracked region is shown in Figure 6c. LMO lattice planes are clearly seen in two directions parallel to the cracks. These lattice planes have a spacing of ~0.47 nm, suggesting that they are LMO $\langle 111 \rangle$ -type crystalline lattice planes [218]. The fast Fourier transform (FFT) of this region (Figure 3.6c inset) was indexed to the LMO [110] zone axis, which confirms that the lattice planes are $\langle 111 \rangle$ -type. This result is consistent with selected-area electron diffraction analysis of the region, which is shown in Figure B.6. Furthermore, both results are consistent with the TKD analysis shown in Figure 3.5. The (-111) and (1-11) planes identified via FFT, which lie parallel to the crack, are highlighted in Figure 3.6c.

Figures 3.6b and 3.6c also show some line defects in the cracked region. These line defects, marked with white arrows in Figure 3.6c, also lie along the LMO $\langle 111 \rangle$ planes. Their defect density appears to increase closer to the cracked region. These defects are stacking faults, which are common along the $\langle 111 \rangle$ planes of spinel structures due to the fact that these planes provide the lowest energy barriers for slip to occur [219, 149]. The stacking fault formation is likely related to the overall crystalline fracture that occurred in this region of the particle, and their presence has been previously observed and reported in the literature [198].



Figure 3.6.: HRTEM analysis of area used for TKD analysis. (a) Low-magnification TEM image of FIB cross-section sample. The white box indicates the region used for TKD analysis in Figure 3.5 and the black boxed area shows the region imaged in (b). (b) HRTEM image of cracked region. The boxed area shows the region imaged in (c). (c) HRTEM image of the LMO lattice near the particle crack. White lines highlight the (-111) and (1-11) lattice planes in the sample. White arrows show the location of stacking faults in the crack region. The inset shows the FFT of the entire region imaged in (c).

Overall, the TKD and TEM analysis of the sample both indicate that crack formation and propagation happen primarily along the $\langle 111 \rangle$ planes. This might be expected due to the $\langle 111 \rangle$ planes being the primary slip planes in the spinel crystal structure [219]. Moreover, LMO(111) is the lowest energy facet of LMO [200] suggesting that particle cleavage or fracture will be most thermodynamically favorable along this plane. However, we also note that the TKD suggests some $\langle 110 \rangle$ -type orientation distribution to the crack propagation direction in addition to $\langle 111 \rangle$. The absence of $\langle 001 \rangle$ -type orientations of the cracks is supported by the DFT analysis of the system, which suggests that fracture is unlikely to occur along (001) planes due to the orientation of Mn-O bonds in the [001] directions and their relation to delithiation-induced tensile stress. Additional analysis of cracking in a different LMO particle gave similar results, with a strong $\langle 111 \rangle$ orientation in the 'x' sample direction and 'y' sample direction with an orientation distribution between (110) and (111) orientations, as shown in Figure B.7. Instead, the high stress buildup upon delithiation of the LMO(001) surface may lead to cracking preferentially along the (111) planes in order to relieve the tension near the surface.

3.4 Conclusions

In this work, we have analyzed the chemo-mechanical response of LMO cathode surfaces to electrochemical delithiation. Increases in surface stress during delithiation may lead to particle fracture, which presents additional issues including delamination from the conductive support, defect generation, higher surface area for reactivity with the electrolyte, and accelerated Mn ion dissolution into the electrolyte. DFT calculations provide an atomistic understanding of stress buildup at the LMO surfaces during delithiation. We have demonstrated that delithiation of the LMO(001)near-surface likely contributes to the stress buildup preceding the $LMO/L_{0.5}MO$ lowvoltage phase transition. These changes in stress along the LMO(001) surface are due to the orientation of Mn-O bonds in the surface plane and require tensile stress to keep bonds between Mn^{4+} and O^{2-} ions elongated beyond their equilibrium lengths. We conclude from analysis of theoretical calculations that cracks due to tensile stress buildup are not likely to orient preferentially in the [001] direction since the stress buildup instead involves stresses acting in the plane of the (001) surface. Instead, we suggest that favorable decohesion along (111) planes, also the primarily slip planes in spinels, may be a driving force for crack propagation in the electrode. EBSD and TEM have been performed on FIB cuts of the cycled LMO to further understand the orientation dependence of cracks in the material. The EBSD and TEM analysis suggests that cracks preferentially propagate along $\langle 111 \rangle$ planes, with additional $\langle 110 \rangle$ character in some instances. These studies of the chemo-mechanical response of LMO can provide a basis for understanding and controlling surface stress-driven mechanical degradation mechanisms in Li-ion battery electrode materials.

R.E.W., S.D., and J.P.G. performed the DFT calculations. F.C.C. and V.P.D. performed the microscopy analysis. K.E.M., K.L.B., and A.A.G. performed the electrochemical cycling experiments.

4. MECHANISMS FOR MN(II) FORMATION AT DEFECT SITES ON LIMN₂O₄ SPINEL CATHODES

This chapter is excerpted from a manuscript being prepared for publication: Robert E. Warburton, Badri Narayanan, Márton Vörös, Hakim Iddir, Larry A. Curtiss, Jeffrey P. Greeley; Mechanisms for Mn(II) formation at defect sites on $LiMn_2O_4$ spinel cathodes. In Preparation

4.1 Introduction

Mn ion dissolution is one of the key impediments to high capacity retention in lithium ion battery cells based on spinel LiMn_2O_4 cathodes [132, 220, 221, 222]. Following dissolution from the LMO surface into the electrolyte, Mn ions can deposit within the solid electrolyte interface (SEI) on the counterelectrode leading to kinetic issues with respect to impedance [139] or by transition metal reduction and catalyzed SEI layer growth [223, 224]. Many strategies have been implemented to suppress Mn dissolution from LMO surfaces [133], including cationic doping [140] and deposition of protective surface coatings [225, 213, 226, 227]. In order to further rationally tailor LMO interfaces for enhanced stability, however, a further understanding of the mechanisms involved in Mn dissolution must be further understood.

It is widely assumed that Mn dissolution is preceded, or is concomitant, with charge transfer, motivated by the Hunter disproportionation [228] mechanism (2 Mn³⁺ \rightarrow Mn⁴⁺ + Mn²⁺) wherein Mn⁴⁺ ions remain on the LMO electrode and Mn²⁺ ions dissolve into the electrolyte. However, there remains debate in the literature regarding the charge state of dissolving Mn ions. Recent electron paramagnetic resonance and X-ray absorption near edge structure experiments suggesting primarily Mn³⁺ in solution [229, 230], in tension with computational results suggesting Mn^{2+} complexes are involved in dissolution [231, 232, 233] and is the most stable charge state in solution. As such, there is a particular need for further atomistic insights into the fundamental surface chemistry mechanisms involved in dissolution, and in particular pathways in which Mn^{2+} ions may form on the surface. We have previously used first principles calculations to thermodynamically characterize various LMO surface facets and terminations. In particular, we identified the LMO(511) surface as a relatively stable model for step or defect models on LMO electrode particles, and one in which redox chemistry is quite thermodynamically facile through the formation of oxygen vacancies [200]. As an analogue to the proposed redox chemistry involved in Mn dissolution mechanisms, these surface models are a suitable template for further examining mechanisms in which Mn^{2+} may form at the surface of LMO cathodes.

In the present work, we investigate formation of Mn^{2+} on LMO(511) surfaces using first principles density functional theory with on-site Hubbard corrections (DFT+U). We focus our efforts on direct Mn^{2+} formation via surface Hunter charge disproportionation mechanisms, as well as chemical mechanisms involving hydrofluoric acid (HF) electrolyte impurities and oxidation of ethylene carbonate (EC) electrolyte molecules.

4.2 Results

We first consider mechanisms for direct formation of Mn^{2+} species at LMO steps through defect generation, as well as direct charge disproportionation. Previously, we evaluated the thermodynamic stability of high-index LMO surfaces as model defect sites, and found that LMO(511) steps were only modestly metastable relative to the low-index (001) and (111) surfaces. In general, we also calculated lower oxygen vacancy formation energies on high-index surfaces, in which donation of the excess electrons from displaced O^{2-} anions leads to a reduction in the oxidation state of Mn ions at the step edge [200]. Figure 4.1a shows the structural models of LMO(511) steps with different numbers of oxygen vacancies formed on the Mn ion at the step edge


Figure 4.1.: Chemical Mn^{2+} formation and $2 Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+}$ charge disproportionation at LMO(511) steps in vacuum. (a) Structural models for Li-terminated LMO(511) steps with oxygen vacancy formation on the edge Mn ion (marked by *). (b) Phase diagram for oxygen vacancy formation and corresponding magnetic moments of the edge Mn ions (marked by * in Fig. 4.1a). (c) Structural models for Mn ion migration from O_h sites to T_d sites (migrating Mn ion marked by *) and (d) minimum energy path from nudged elastic band calculation with the corresponding magnetic moments of each image along the reaction coordinate for the migrating ion (diamond shape) and a neighboring Mn ion along the (001) plane (square shape). (e) Structural models and the procedure to induce the Mn³⁺ disproportionation reaction at an LMO(511) step. Divalent and tetravalent dopants are introduced to distort the lattice and constrain charge distribution. (f) Magnetic moments of edge (replaced by Ca²⁺ dopants and marked by a diamond) and basal plane (replaced by Si⁴⁺ dopants and marked by a square) Mn ions during each stage of the reaction coordinate in (e).

(edge Mn is marked by *). Figure 4.1b shows the grand canonical thermodynamics associated with the different oxygen vacancy concentrations, as well as the associated magnetic moments calculated for these Mn ions at the step edge. Since Mn ions in LMO are high-spin, a higher magnetic moment corresponds to greater occupation of local Mn 3d electronic states and a lower projected oxidation state. What these results show is that the formation of two additional oxygen vacancies may lead to Mn species that are highly undercoordinated (only three bonds to oxygen compared to six in the bulk) and have magnetism close to those observed for Mn^{2+} .

We also consider defects involving Mn migration to T_d sites, which is associated with Mn^{2+} in LMO [234] and corresponds to the coordination environment of Mn^{2+} ions in bulk oxides such as Mn_3O_4 . Figure 4.1c shows a pathway for Mn migration from the more stable O_h sites to a subsurface T_d site, reminiscent of the previously reported inverse spinel, or Mn_3O_4 -like near-surface phases [234, 64, 235], as well as T_d Mn resulting from cation migration in layered LiMnO₂ cathodes [236]. In order to accompany the Mn ion at this T_d site, the Li⁺ ion that occupies this site is removed in the model to facilitate analysis of diffusion kinetics. The mobile Mn ion, which corresponds to the ion represented in Figures 4.1a,b is marked with *. Figure 4.1d shows the energetics (in filled black circles) and Mn ion magnetic moments of different configurations along the minimum energy path. The mobile Mn ion and the adjacent Mn ion along the low-index [001] plane are shown in blue diamonds and blue squares, respectively. The oxidation state ranges correspond to those previously presented by Chan et al. [237] and are also in line with the calibrations reported by Leung [231]. The results show that while diffusion to the T_d site is only modestly endothermic (by 0.22 eV), there is a large kinetic barrier or 2.37 eV that is unlikely to be surmounted at room temperature or even at 55 °C. Moreover, while the magnetic moment analysis suggests that diffusion to the T_d site leads to charge disproportionation, Mn^{2+} is being formed in the sub-surface and is therefore less likely to be relevant toward Mn dissolution reaction mechanisms.

The final defect we consider is that of direct charge transfer between two Mn ions associated with the Hunter disproportionation mechanism. Figure 4.1e outlines the procedure applied to analyze these direct charge disproportionation mechanisms, in order to identify final states where an electron is trapped on the edge Mn ion while simultaneously forcing a hole to localize on a Mn ion away from the step edge. Following identification of each electronic state, charge transfer rates can in principle be evaluated using either adiabatic (transition state theory) [70, 50, 238, 71] or non-adiabatic (Marcus or Landau-Zener rate theory [239, 240, 241, 126, 242, 243] approaches. Figure 4.1f shows the corresponding magnetic moment of the edge and

basal plane Mn ions (marked by a diamond and square, respectively) at each step in the charge localization procedure. First, the edge Mn ion is replaced by Ca^{2+} and the Mn ion on the basal plane is replaced by Si^{4+} (state (2) in Figure 4.1e). These ions are chosen to be substituted based on their relatively inflexible oxidation states. Following the geometry optimization of (2), the Si⁴⁺ ion is replaced by Mn (state (3)) in Figure 4.1e) and relaxes with a magnetic moment of ca. 3.1 μ_B , consistent with an oxidation state of Mn^{4+} as shown by the blue-shaded region in Figure 4.1f. A single point calculation (fixed geometry evaluation of system charge density and wave function) following the re-introduction of Mn for the Ca^{2+} ion at the edge (state (4) in Figure 4.1e) leads to an electronic state consistent with Mn^{2+}/Mn^{4+} charge disproportionation based on the magnetic moments (Figure 4.1f). However, we were unable to relax the surface in such a way that could trap a metastable structure that maintains the Mn^{2+}/Mn^{4+} electronic state. Instead, upon relaxing the surface (state (5) in Figure 4.1e) both Mn ions have a magnetic moment of ca. 3.8 μ_B , consistent with the Mn³⁺ oxidation state as shown by the red-shaded region in Figure 4.1f. Following the work of Deskins and Dupuis on charge localization TiO_2 [244, 245, 246], we have also enforced separate DFT+U treatments on each Mn ion as an intermediate step in this procedure and have obtained similar results.

To summarize the results in Figure 4.1, we have identified structures consistent with a Mn^{2+}/Mn^{4+} electronic structure at high-index LMO(511) stepped surfaces. However, with the exception of oxygen vacancy formation we find that these tend to be either metastable or kinetically inaccessible. From these analyses, we suggest that direct charge disproportionation or surface reconstruction to form Mn^{2+} is highly unlikely, unless assisted by chemical reactions with the electrolyte compounds that could generate defects susceptible to dissolution on the LMO surface.

To probe the potential influence of electrolyte compounds, we consider reactions with HF, which has been widely cited to accelerate Mn dissolution [231, 232, 247, 248, 249, 250]. Tebbe et al. have studied HF reaction with LiCoO₂ surfaces and found that in the presence of surface hydroxyls, LiCoO₂ surfaces are highly reactive toward HF



Figure 4.2.: HF reaction with LMO. (a) Structures for intermediate states upon reaction of two HF molecules with an LMO(511) step containing a single vacancy and two hydroxyls. (left to right) Starting structure with two hydroxyls (OH^{*}), dissociative adsorption of HF leading to F-substitution for O and dehydration of an OH^{*}, dissociative adsorption of a second HF filling the vacancy site with a F⁻ anion and formation of a second OH^{*}. (b) Magnetic moments (for the Mn ions marked by the corresponding shapes in (a)) and energies corresponding structures in (a).

and also lead to H_2O formation and release from LiCoO₂ surfaces [251]. Figure 4.2a shows the intermediates for the reaction of two HF molecules with the LMO(511) step edge. We consider initially the step edge with a single vacancy and two hydroxyls (left panel, Figure 4.2a) to allow for two subsequent dehydration reactions. The top and bottom panels of Figure 4.2b show the magnetic moments of Mn ions participating in the reaction (symbols correspond to labels in Figure 4.2a) and the corresponding reaction thermochemistry, respectively. During HF dissociative adsorption, the F⁻ ions fills an oxygen vacancy while a new vacancy is formed due to reaction of the proton in HF with a hydroxyl group to form H₂O (center panel, Figure 4.2a). H₂O desorption and release into the electrolyte may react with LiPF₆ electrolyte salts to catalyze HF formation. The second HF molecule, however, does not lead to dehydration since oxygen vacancies are not as easily formed on low-index planes in comparison to the LMO steps [200]. Instead, dissociative adsorption HF is thermodynamically favorable, wherein the F⁻ fills the vacancy present on the step edge and the proton is transferred to the oxygen anion on the basal plane, re-forming a second hydroxyl group along the [001] plane. This results in the edge Mn ion five-fold coordinated to the following: one O²⁻ anion, two F⁻ anions, and two -OH groups (right panel, Figure 4.2a). As shown by the top panel in Figure 4.2b, the formation of this complex corresponds to reduction to Mn²⁺ on the step edge. Despite the presence of a reduced Mn²⁺-containing complex, Mn leaching from the lattice is highly endothermic in vacuum. We suggest that further complexation with the electrolyte may assist in the dissolution of this complex into the electrolyte, given previous evidence that Mn-F complexes are relevant dissolving species [231, 232, 247, 248, 249, 250].

Leung recently showed that where F^- incorporation occurs on (001) surfaces, it also leads to Mn^{2+} formation, albeit with a high barrier for dissolution calculated from thermodynamic integration [231]. Benedek similarly showed that the strong binding of an Mn-F complex weakens its adhesion to the LMO lattice, which results in Mn^{2+} formation and may facilitate dissolution [232]. F^- incorporation into the bulk lattice of Li-Mn oxides, also can increase the Mn^{2+} content of the material due to both the iconicity and lengths of the Mn-F bond [252, 253, 254]. Based on our results, $F^$ incorporation at stepped and defect sites on the surfaces of LMO particles is likely to be facile and to occur alongside dehydration. Such reactions are less likely at pristine terraces, although such mechanisms may certainly become relevant as these surface features are degraded following extensive cycling and further reaction with the electrolyte.

Building off the calculated reactivity of the (511) surface toward HF, we also consider the reaction of an EC solvent molecule on these surfaces. EC decomposition has been studied computationally on low-index surfaces of LMO [210, 212], the high-



Figure 4.3.: EC reaction with LMO. (a) Schematic of ethylene carbonate (EC) oxidation on a LMO surface involving (top left) the separated EC molecule and the surface, (top right) adsorption of EC through the carboxyl group, (bottom left) ring opening of adsorbed EC, and (bottom right) hydrogen extraction from EC to oxygen sites on the LMO surface. (b) Top view of the LMO(511) step representing an intersection between low-index (001) and (111) surfaces. Following EC adsorption near the oxygen vacancy $(V_{O}^{"})$, ring opening may occur over either a single Mn ion (marked (1)) or the vacant O_h 16c site which connects a neighboring Mn ion along the step edge (marked (2)). (c) EC decomposition reaction showing various thermodynamically favorable pathways through ring-opening on sites (1) and (2), denoted in different shades of red and blue, respectively. (d) Structures, relative energies, and magnetic moments of edge Mn ions for different configurations of EC decomposition following H abstraction, with view from the step edge with the [001] direction oriented upwards. (d) Diffusion of Mn from the configuration in (c) with high Mn spin of 4.57 μ_B in bulk 16d sites to defective 16c octahedral sites from with decomposed EC (filled black circles) and without on a clean (511) step with one vacancy (hollow circle). The minimum energy path is represented by the black line connecting the initial and final states, and polyhedra surrounding the diffusing Mn ion is highlighted in orange in each of the insets.

voltage LiNi_{0.5}Mn_{1.5}O₄ spinel [255], as well as LiCoO₂ [256] and other layered cathodes [257, 258, 259]. Furthermore, charge transfer from hydrogen abstraction during EC decomposition scales with the surface O 2p band center [258, 259] and is therefore related to surface oxygen vacancy formation energies [260], the latter of which we have recently shown to undergird the structure-sensitive reactivity of high-index LMO surfaces toward ALD precursors [261]. Figure 4.3a shows a schematic of the steps involved in EC decomposition, where (from top left to bottom right) and EC molecule approaches the LMO surface (*) and then adsorbs (EC*), whereupon the LMO surface catalyzes EC ring opening $(EC_{ring opened}^*)$, followed by hydrogen abstraction from $EC_{ring opened}^*$ to the LMO surface $(EC_{H abs}^*)$. Figure 4.3b shows two potential sites for ring opening of the adsorbed EC^{*}, either over a single Mn ion ((1), marked in red) or over the vacant 16c site along the step edge (2), marked in blue). We consider both of these ring opening pathways as well as the subsequent hydrogen abstraction steps, the thermodynamics of which are shown in Figure 4.3c. Figure 4.3d shows the final structures of EC_{Habs}^* on the step edge (with the border colors corresponding to the data series shown in Figure 4.3c) along with their relative energies and the magnetic moments of the edge Mn ion.

We note that, in general, Mn^{3+} remains the dominant electronic state on the edge along the EC decomposition reaction coordinate (we refer the reader to Figures 4.1d,f and 4.2b for the relevant oxidation states for magnetic moments). However, in cases where ring opening occurs over the edge Mn ion (pathway ①) and hydrogen abstraction occurs in the direction of the (111) plane we find that Mn adopts a divalent oxidation state (top middle structure of Figure 4.3d with the magnetic moment underlined) and is only modestly metastable (by 0.31 eV) with respect to H abstraction farther away from the ring opened EC on the surface (top left structure of Figure 4.3d). While it remains unclear from this structure at the LMO step edge how divalent Mn would directly participate in dissolution reactions, we find that Mn²⁺ formed as a result of electrolyte oxidation has greater mobility within the LMO lattice. Figure 4.3e shows that in the presence of EC_{H ads}* on the step edge, diffusion

to defect 16c O_h sites is downhill by 0.14 eV, in contrast to a thermodynamic penalty of 2.59 eV incurred for diffusion to the defect site on the bare step without EC_{Hads}^* present. Moreover, the kinetic barrier for this Mn diffusion process is only 0.80 eV, wherein one might expect such events to happen on the time-scale of seconds at elevated cycling temperatures of 55 °C. Thus, interactions between the electrode and electrolyte could catalyze the formation of high energy defect sites and increase the mobility of Mn ions within the LMO lattice, both of which may make certain Mn²⁺ ions more susceptible to dissolution.

4.3 Conclusions

We have performed first principles DFT+U calculations to analyze mechanisms for Mn^{2+} ion formation at stepped LMO(511) surfaces. We have shown that redox occurs on edge Mn ions through oxygen vacancies on otherwise defect-free step edges. Mn ion migration to subsurface T_d sites involves Hunter charge disproportionation, although we calculate these processes to be kinetically infeasible. We extended these analyses to the direct charge transfer between two surface Mn³⁺ ions and identified lattice distortions consistent with disproportionation, although we were unable to trap these bipolaron defects to a local geometric minimum in the metastable electronic state. We have shown instead that reduction of Mn ions to Mn^{2+} may occur due to chemical reactions between solvent compounds and the LMO electrode. Accompanied by dehydration reactions, Mn^{2+} may form following dissociative HF adsorption and F^- incorporation into the LMO lattice. Reduction to Mn^{2+} may also occur in certain cases at LMO steps following EC ring opening and H abstraction to lattice oxygens. In this case of EC decomposition, we also find that these Mn^{2+} ions have significantly reduced diffusion barriers to defect sites in the lattice. The increased mobility of Mn ions in LMO induced by reactions with the electrolyte as well as increased defect concentrations may further reduce the stability of electrode-electrolyte interfaces, having consequences in terms on Mn ion dissolution. Despite this, the direct connection between Mn^{2+} formation and dissolution remains somewhat unclear. We suggest that disproportionation (or charge transfer more generally) may be a necessary, though insufficient criterion, for Mn dissolution to occur based the resulting instabilities of Mn^{2+} ions near defect sites. Future work will need to build off these mechanistic findings to provide further insights towards their dynamic roles in dissolution mechanisms.

4.4 Methods

Spin polarized density functional theory calculations were performed using the VASP code [160, 168, 161]. The generalized gradient approximation of Perdew, Burke, and Ernzerhof [163] was applied as the exchange correlation functional, with a Hubbard U [102, 103, 104] correction of 3.5 eV [200, 202, 110] applied to Mn 3d valence states. The effective cores were modeled using projector augmented wave [201, 162] pseudopotentials and the valence states were expanded in a plane wave basis set with a kinetic energy cutoff of 520 eV. We applied Γ -centered k-point sampling with Brillouin zone sampling density analogous to our previous work [261], which used similar supercell models for LMO(511).

5. MECHANISM FOR AL_2O_3 ATOMIC LAYER DEPOSITION ON LIMN₂O₄ FROM *IN SITU* MEASUREMENTS AND *AB INITIO* CALCULATIONS

This chapter is reproduced with the permission of Elsevier from: Lin Chen, Robert E. Warburton, Kan-Sheng Chen, Joseph A. Liberia, Christopher Johnson, Zhenzhen Yang, Mark C. Hersam, Jeffrey P. Greeley, and Jeffrey W. Elam; Mechanism for Al_2O_3 Atomic Layer Deposition on $LiMn_2O_4$ from *In Situ* Measurements and *Ab Initio* Calculations. *Chem* **2018**, 4(10), 2418-2435.

Here, we elucidate the mechanism for Al_2O_3 atomic layer deposition (ALD) on LiMn₂O₄ (LMO) cathodes for lithium-ion batteries by using *in situ* and *ex situ* experimental characterization coupled with density functional theory (DFT) calculations. We demonstrate that not only does Al_2O_3 coat the LMO, but the Al heteroatom of the trimethylaluminum (TMA) precursor also dopes to interstitial sites on the LMO surface, thereby reducing the oxidation state of near-surface Mn ions. DFT calculations further suggest facile transfer of methyl groups from the TMA precursor to oxygen atoms on the LMO surface, which blocks adsorption sites for subsequent TMA adsorption. These predictions are supported by quartz crystal microbalance experiments demonstrating inhibited growth below ten ALD Al_2O_3 cycles, suggesting that sub-monolayer coverages of alumina are present on the LMO surface in the early stages of film growth. In comparison with fully conformal films, these sub-monolayer coatings show enhanced electrochemical capacity when cycled in coin cells.

5.1 Introduction

Rechargeable lithium-ion batteries (LIBs) have enabled the rapid growth and development of portable electronics, electric vehicles, and large-scale energy storage because of their high energy density [30, 47, 262, 263]. LIBs also have great potential to stabilize renewable, yet intermittent, energy sources such as solar energy and wind power [264, 265]. With increased demand for renewable energy and sustainable development, however, current commercial battery systems experience shortcomings with respect to capacity retention. Such non-idealities are exacerbated over time, leading to significant deviations from theoretical energy densities and limiting the practical operating lifetime of battery systems.

The lithium manganate spinel $(LiMn_2O_4 [LMO])$ has been widely studied as a LIB cathode because of its low cost and low toxicity, as well as its thermal stability [266, 267]. Nevertheless, performance is limited by a Jahn-Teller distorted tetragonal phase transition at 3 V [268] and by Mn dissolution accelerated by the attack of HF present in the electrolyte [269] during cycling. Substitutional doping for Mn [270, 271] and application of protective coatings [272, 273] have been shown to enhance the cycling performance of LMO. A number of metal dopant ions have been investigated to stabilize the crystalline phase and restrain Jahn-Teller distortion, such as Ni [274, 275, 276], Cr [277], Co [278], and Mo [279]. Substitutional Al doping in Mn also effectively retains the capacity performance of LMO. It has been proposed that Al reduces the fraction of Mn^{3+} that can participate in the disproportionation reaction that leads to dissolution [280, 281]. Yang et al. examined Al-doped LMO nanorods and measured a 5% higher capacity retention compared with undoped LMO, and the performance increased further at higher cycling temperatures [282]. Similarly, Xiao et al. found improved electrochemical stability by using substitutional Al-doping values as low as 2% [283]. Another strategy to improve the stability of LMO cathodes is to passivate the surface with metal oxide coatings [272] to reduce Mn dissolution. In practice, thin Al_2O_3 coatings prepared by atomic layer deposition (ALD), a self-limiting technique for conformal and sub-nanometer-scale thin films [284], demonstrated improved capacity. In previous work, it was speculated that the coating isolates LMO from contact with electrolyte and reduces HF attack [272, 285]. Although coated electrodes demonstrate enhanced performance compared with uncoated LMO, they still exhibit capacity fade, especially at elevated temperatures. Hence, despite the observed electrochemical performance of ALD-coated LMO electrodes, there is much to be understood regarding the growth mechanism, the nature of the deposited material, and how the coating affects electrochemical behavior. For instance, ALD Al_2O_3 films are most commonly grown using trimethylaluminum (Al(CH₃)₃, TMA) and H₂O. The nature of the TMA reaction on LMO surfaces, which contain an ensemble of potential reaction sites that include vacant 16c octahedral sites [132], and the resulting consequences for film growth and electrochemical performance remain poorly understood.

With these questions in mind, we sought an improved molecular-level picture of the ALD coating process and its impact on LMO battery performance. In situ Fourier transform infrared spectroscopy (FTIR), quadrupole mass spectrometry (QMS), and quartz crystal microbalance (QCM) measurements are used in concert with density functional theory (DFT) calculations to elucidate the mechanisms for ALD Al_2O_3 film growth on LMO. The results illustrate that Al_2O_3 does not merely form a uniform coating on LMO, but may dope Al³⁺ ions into LMO via highly stable octahedral coordination to oxygen at the 16c site on the spinel surface. Moreover, rapid demethylation of TMA leads to site blocking and sluggish film growth in early ALD cycles, leading to unique electrochemical performance for sub-monolayer, versus continuous, alumina coatings on the surface. Coupled with systematic cycling experiments and electrochemical impedance spectroscopy (EIS), we also find that the improved capacity may be a consequence of synergetic contributions from Al doping and the Al_2O_3 coating. These insights should be applicable to more energy-dense cathode materials (e.g., $\text{LiNi}_x \text{Mn}_y \text{Co}_{1-x-y} O_2$, $\text{LiNi}_x \text{Mn}_{2x} O_4$) that also experience transition metal dissolution.



Figure 5.1.: In situ QMS measurements of Al_2O_3 ALD and schematic for TMA reaction on LMO. (A) Reaction products during the first ten ALD Al_2O_3 cycles. (B) The total amount of CH_4 and C_2H_6 during the first ten ALD Al_2O_3 cycles. (C) During initial Al_2O_3 ALD cycles, TMA reacts with MnO bonds on LMO, reducing surface Mn ions and generating C_2H_6 . (D) After several Al_2O_3 ALD cycles, LMO is covered by Al_2O_3 so that TMA reacts with -OH groups and CH_4 is the only gaseous product.

5.2 Results

5.2.1 Nucleation of ALD Al_2O_3 on LMO

The reaction mechanism of Al_2O_3 ALD on LMO surfaces was explored with in situ QMS. Figure 5.1A shows the gaseous reaction products produced during the first ten ALD Al_2O_3 cycles. Upon the first TMA pulse, CH_4 (m/e = 16) and C_2H_6 (m/e =30) signals are observed. Contrary to the CH_4 signal, however, C_2H_6 is observed only

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during TMA exposures, whereas CH_4 is produced during both the TMA and H_2O exposures. Moreover, the C_2H_6 signals decrease with increasing ALD cycles. C_2H_6 is rarely seen during Al_2O_3 ALD using TMA, but small quantities were previously observed for TMA reaction on platinum and palladium noble metal surfaces, which are both well-known catalysts for C-C bond chemistry [286]. Evidently, different reactions occur for TMA on LMO surfaces than for TMA on Al_2O_3 surfaces, where CH_4 is the only gaseous product [286]. As is discussed further in Section 5.2.3, this may be a direct consequence of significantly stronger binding between the resulting methylaluminum (Al(CH_3), MA) to three oxygen atoms at the LMO surface, relative to the binding energy of TMA. The release of CH_4 is attributed to the reaction of TMA with surface hydroxyl groups. We note, however, that relatively little CH_4 is produced during the initial Al₂O₃ ALD cycles on LMO, which is practically hydroxylfree (see discussion of FTIR difference spectra and DFT-calculated phase diagram in Appendix C, Figure C.13), whereas the CH_4 signal is enhanced in later ALD cycles as TMA is able to react with Al_2O_3 hydroxyl groups. In the Section 5.2.2 of this work, this observation is further supported by *in situ* QCM measurements, which show that a larger fraction of the TMA methyl groups remains on the surface after TMA exposures in the initial cycles than in the later cycles of Al_2O_3 ALD on LMO.

Overall, the C_2H_6 signals diminish and the CH_4 signals increase with increasing Al_2O_3 ALD cycles. We attribute this to the gradual conversion of the LMO surface to an Al_2O_3 surface. Beginning with the second ALD cycle, the C_2H_6 signals increase initially during ten microdoses that comprise a single TMA exposure. This effect is most clearly seen in Figure C.1A of Appendix C, and arises because the TMA microdoses are insufficient to saturate all of the reactive sites in the powder bed. During the initial TMA microdoses, the TMA reacts on the outer surfaces of the powder bed that have already converted to Al_2O_3 , so CH_4 is the only product. During the later microdoses, the TMA diffuses deeper into the powder where it encounters fresh LMO, forming C_2H_6 . In each of the TMA and H_2O exposures, the CH_4 signals are largest during the first microdose and decrease to a steady-state value. The

cracking patterns for both TMA and H₂O contain a peak at m/e = 16, so the nonzero steady-state signals in Figures 5.1A and C.1A (Appendix C) result from the ALD precursors and not the reaction products. Figure 5.1B shows the total C₂H₆ and CH₄ signals from each Al₂O₃ ALD cycle versus the number of cycles. In this plot, we have subtracted the background signals observed in an empty reactor (Appendix C, Figure C.1B). Figure 5.1B illustrates the trend of increasing CH₄ and decreasing C₂H₆ formation with ALD cycle number.

Based on the QMS results, we propose the reaction scheme in Figures 5.1C and 5.1D. During the initial ALD cycles, TMA reacts with bridge-bonded oxygen on the LMO surface and loses its methyl groups either through C_2H_6 formation or demethylation to the LMO (Figure 5.1C). This yields a complex between Al and existing MnO bonds, accompanied by Mn reduction-oxidation (redox) to account for charge compensation where applicable. After multiple ALD cycles, the Al₂O₃ forms a continuous film over the LMO, so that TMA reacts with surface hydroxyls (OH) on Al₂O₃, and CH₄ is the only by-product (Figure 5.1D).

As suggested by the schematic in Figure 5.1C, TMA reacts with Mn-O bonds on a dehydroxylated LMO surface, as informed by *in situ* FTIR absorption spectroscopy measurements. For these measurements, the LMO nanopowder was pressed into a metal grid to provide a high surface area substrate with a large infrared absorption [287, 288]. The grid was preheated at 400 °C to remove residual water from the LMO surface. The FTIR results are presented in Figures 5.2A and 5.2B as difference spectra to highlight the spectral changes produced by each precursor exposure. A spectrum was recorded after each precursor exposure, and the difference spectrum was obtained by subtracting the previous spectrum. Therefore, positive absorbance features imply the formation of new surface species, while negative signals indicate the removal or consumption of existing surface species.

The red curves in Figures 5.2A and 5.2B show difference spectra recorded during in situ FTIR measurements of the first TMA exposure on LMO at 150 °C in the low-frequency (Figure 5.2A) and high-frequency (Figure 5.2B) regions. During the



Figure 5.2.: In situ FTIR and Ex Situ XPS Measurements of Al_2O_3 ALD on LMO. (A and B) Difference spectra in the low-frequency region (A) and high-frequency region (B) for the first TMA-H₂O cycle on LMO at 150 °C after preheating at 400 °C for 1 hr. (C) XPS of uncoated LMO deposited by sputtering on AAO substrate. (D) (D) XPS of LMO on AAO substrate after one ALD Al_2O_3 cycle (designated as 1 x Al_2O_3 LMO hereafter). (E) XPS of 3 x Al_2O_3 LMO on AAO substrate.

first TMA exposure on LMO, positive absorbances appear at 1,215 cm⁻¹ that can be attributed to symmetric CH₃ deformation [289], while the absorbances at 796 and 712 cm⁻¹ (Figure 5.2A) are ascribed to Al-O stretching [290, 291]. This confirms the formation of CH₃ species and Al-O after the TMA exposure. Negative absorbances emerge at 630 and 505 cm⁻¹, which we attribute to the asymmetric and symmetric stretches, respectively, of Mn-O bonds in LMO [292]. This implies that TMA has reacted with Mn-O bonds (further discussion provided in Section 5.2.3). It is worth mentioning that the negative absorbance from Mn-O bonds may be due to bond elongation associated with a reduction of the Mn oxidation state on the LMO surface. This possibility will be evaluated later by X-ray photoelectron spectroscopy (XPS). In the high-frequency range (Figure 5.2B), there is an increase in the C-H stretching region $(2,750-3,000 \text{ cm}^{-1})$ from the formation of surface methyl groups, but no changes in the O-H stretch region from 3,750 to 3,100 cm⁻¹ as one would expect for TMA reacting with surface hydroxyl groups. This behavior is surprising given that most metal oxide surfaces show obvious OH consumption in FTIR upon exposure to TMA. These results indicate that the LMO surface has little or no hydroxyl coverage. A similar conclusion was reached in a recent XPS study of Li-metal-oxide surfaces [293]. This peculiarity of LMO likely explains the unusual observation of C₂H₆ as a gaseous reaction product in Figure 5.1. These FTIR measurements were repeated on an LMO sample heated to 200 °C prior to Al₂O₃ ALD (Appendix C, Figures C.2A and C.2B) and the results were very similar to those in Figures 5.2A and 5.2B. The only exception was that the TMA exposure caused a slight decrease in the OH stretching region. However, the magnitude of this change was only 10% of that on an Al₂O₃ surface, suggesting that the OH concentration on LMO preheated to 200 °C is quite low.

The subsequent H_2O exposure yields a negative absorbance change at 1,215 cm⁻¹ (Figure 5.2A, blue trace) corresponding to the removal of CH₃ groups. This result is consistent with the CH₄ gaseous product observed by QMS during the H₂O exposures in Figure 5.1. In contrast, the Mn-O region remains relatively flat, indicating that Mn-O bonds are neither formed nor consumed during the H₂O exposure. In the high-frequency range (Figure 5.2B, blue trace), the H₂O exposure causes a decrease in the C-H stretching region from CH₃ consumption, and an increase in the OH region from Al-OH species. Additional FTIR spectra were recorded after each TMA and H₂O exposure for six ALD cycles on the 400 °C treated LMO (Appendix C, Figures C.3A-C.3F) and on the 200 °C treated LMO (Appendix C, Figures S for only two or three cycles, after which the TMA reacts exclusively with surface Al-OH. In addition, the Al-O stretching features continue to appear with each TMA exposure, consistent with the continuous growth of ALD Al₂O₃ on the LMO. The continuous

 Al_2O_3 growth is most easily seen in Figures C.3G and C.4G in Appendix C, showing the FTIR spectra recorded after each Al_2O_3 cycle referenced to the bare LMO.

On the basis of *in situ* QMS and *in situ* FTIR analyses, it becomes clear that the Al heteroatoms from TMA significantly alter the nature of the MnO bonds through the formation of stable Al-O-Mn complexes at the LMO surface. In Section 5.2.3 we describe this phenomenon further, and consider the possibility of Al doping to interstitial sites in the LMO lattice. This strong interaction between Al and lattice oxygen atoms of LMO is suspected to be a driving force for C_2H_6 formation. Moreover, the Mn-O peak consumption in the FTIR (Figure 5.2A) may be associated with MnO bond elongation from Jahn-Teller distortion accompanying reduction to the Mn³⁺ oxidation state, owing to the partial e_g band occupation. The corresponding redox process, as suggested earlier, may occur to charge compensate the proposed reaction sequences.

To probe directly the redox processes hypothesized in Figure 5.1, we performed ex situ XPS measurements on LMO surfaces before and after Al_2O_3 ALD. Figure 5.2C shows a high-resolution XPS scan of the Mn $2p_{3/2}$ peak for the as-deposited LMO film, before ALD. This spectrum is fit very well using peaks at 641.4 and 642.8 eV that we attribute to Mn^{3+} and Mn^{4+} [294, 295], respectively. Integration of the peak intensities yields Mn^{3+} and Mn^{4+} atomic percentages of 52.6% and 47.4%, respectively, indicating that the surface of the LMO sample is slightly off-stoichiometric. After one ALD Al_2O_3 cycle (1 x Al_2O_3 LMO; Figure 5.2D), the Mn³⁺ percentage increases to 59.3%, 6.7% higher than the uncoated LMO. There may be several explanations for the reduction in Mn oxidation state. First, Al³⁺-containing species, either bound to the surface or doped to 16c interstitials, can only be charge-compensated with respect to TMA if there exists a Mn ion that is able to accept additional electrons. Since there is a significant amount of Mn^{4+} in the sample (which is nearly stoichiometric), this likely occurs by reducing a near-surface Mn^{4+} ion to Mn^{3+} . As discussed in Section 5.2.3, reduction can also occur via CH_3 bound through oxygen on the LMO surface, although these effects cannot be explicitly probed here given that the XPS is performed *ex situ* after the H₂O pulse. Second, on the basis of DFT calculations of AlO_xH_y adsorbate thermodynamics on the LMO surface (Appendix C, Figure C.19), the limited reactivity of surface Al compounds reduces the extent to which Mn ions in LMO are oxidized during the H₂O pulse (Appendix C, Table C.2), consistent with the *ex situ* XPS observations. We note, however, that the Mn³⁺ ratio does not continuously increase in subsequent ALD cycles, with XPS of 3 x Al₂O₃ LMO (C, Figure C.2E) demonstrating a Mn³⁺ atomic ratio of 59.8%, a minimal change in comparison with the large increase observed for 1 x Al₂O₃ LMO. This change is consistent with the FTIR measurements that showed Mn-O consumption only during the first two or three cycles. Once the Al₂O₃ coating covers the LMO surface, it will inhibit direct contact between TMA and LMO, and the Mn oxidation state will no longer change appreciably. Duplicate XPS measurements at different sample locations yielded consistent results (Appendix C, Figure C.5).

5.2.2 Growth of ALD Al_2O_3 on LMO

We performed *in situ* QCM measurements to probe the growth of ALD Al₂O₃ on LMO, *i.e.*, the mass changes on the LMO surface at each step in the ALD process. For these measurements, LMO thin films were sputtered onto a gold-coated QCM sensor (inset of Figure 5.3A). The sputtered LMO films were continuous and nanocrystalline based on atomic force microscopy (AFM) and scanning electron microscopy (SEM) measurements (Appendix C, Figures C.6A-C.6D). Figure 5.3A shows the QCM mass signal versus time during the Al₂O₃ ALD where the individual TMA and H₂O exposures are indicated at the bottom of the graph. It is evident that each Al₂O₃ ALD cycle yields a stepwise mass increase, and that the size of these steps increases during the initial ten or so cycles. These data suggest that Al₂O₃ ALD is inhibited on the LMO surface, requiring approximately ten ALD cycles to form a continuous coating. These changes are more evident in Figure 5.3B, which shows the mass change for each ALD cycle converted to thickness changes assuming a density [296] for ALD Al₂O₃ of 2.9 g cm⁻³. The first Al₂O₃ ALD cycle yields only ~0.2 Å far below steady-state



Figure 5.3.: In situ QCM measurements of Al_2O_3 ALD on LMO. (A) Mass gain of ALD Al_2O_3 on LMO for the first 20 cycles. Inset shows bare QCM sensor (left) and QCM sensor with sputtered LMO film (right). (B) Growth per cycle of ALD Al_2O_3 on LMO. (C) Ratio of mass gain from TMA exposure over the total mass gain for each cycle.

value for Al_2O_3 ALD of ~1.3 Å per cycle [296]. The Al_2O_3 growth per cycle increases steadily over approximately ten ALD cycles to achieve the steady-state value. The overshoot in Figure 5.3B between ~10 and 20 ALD cycles is indicative of island coalescence [288]. A duplicate set of measurements on a different LMO-coated sensor yielded similar results (Appendix C, Figure C.7).

The shape of the QCM steps during Al_2O_3 ALD can be used to infer a growth mechanism. In particular, the ratio, R, of the mass gain after the TMA exposure to the mass gain in one full ALD cycle can be related to the relative number of CH₃ groups lost during the TMA and H₂O half-reactions [297]. This method requires assumptions about the precise surface species after each half reaction, so rather than attempting to extract the number of CH₃ groups, we instead plot R versus the number of ALD cycles (Figure 5.3C) and note that R changes for the first ~15 cycles. Moreover, the final steady-state value of $R \sim 0.9$ is the expected value for Al₂O₃ ALD on oxide surfaces [297]. The significantly higher initial R value of 0.98 indicates that the surface species produced by TMA and H₂O on the LMO surface are different from those on Al₂O₃.

In the Introduction to this chapter (Section 5.1), we described two explanations that have been proposed in the literature for the increased capacity retention of LMO with Al_2O_3 : (1) substitutional doping of the LMO lattice reduces the number of Mn^{3+} species that can undergo disproportionation and dissolution, and (2) the formation of a continuous coating prevents direct contact between the liquid electrolyte and the LMO surface. On the basis of our *in situ* and *ex situ* investigations, we conclude that neither scenario accurately describes the early stages of Al₂O₃ ALD on LMO. During the initial one to three cycles, Al bonds to near-surface oxygen by consuming Mn-O bonds, accompanied by surface methylation and C_2H_6 formation. Moreover, less mass is added during the water cycle than in conventional Al_2O_3 ALD (*i.e.*, the R value is smaller), presumably because Al is highly coordinated to the surface oxygen of LMO and/or the Al acts as a surface dopant by occupying octahedral interstitial sites. This Al adsorption is accompanied by a net reduction in the average Mn oxidation state for the first two or three ALD cycles. In other words, there is an *increase* in the concentration of Mn^{3+} on the surface - the opposite outcome compared with that of previous reports [281, 283, 290], where the average oxidation state of Mn increased. Beyond the third cycle, Al₂O₃ ALD proceeds with minimal changes to the Mn-O binding and Mn electronic structure, although the film growth rate does not achieve steady state until 10-15 ALD cycles. A possible explanation for this inhibited growth is that the high coordination of Al to LMO surface oxygens, accompanied by methyl decomposition to the surface, reduces the number of sites available for TMA to adsorb. This would require a greater number of ALD Al_2O_3 cycles to form a fully conformal coating than predicted based on the steady-state growth per cycle.



Figure 5.4.: FETEM images of $10 \ge Al_2O_3$ on LMO recorded at two different regions showing amorphous ALD Al_2O_3 coating at perimeter of LMO particle. (A) Low resolution. (B) High resolution.

High-resolution field emission transmission electron microscopy (HRTEM) was used to examine the Al₂O₃ deposited on LMO. ALD Al₂O₃ is amorphous [296], and the elements have low Z, so it was not possible to identify the ALD Al₂O₃ by TEM in the early region of growth (one to three cycles). However, TEM images of the 10 x Al₂O₃-coated LMO (Figure 2.4 and Figure C.9 in Appendix C) clearly show a thin, amorphous film on the edges of the LMO particles. The thickness estimated from the TEM images is 2 ± 1 nm, which is within experimental error of the expected 1 nm thickness. This finding supports the model derived from the in situ QCM and QMS measurements where the ALD Al₂O₃ forms a continuous coating after approximately ten ALD cycles such that the growth achieves a steady state. Scanning EM images of the bare and ALD Al₂O₃ coated LMO are shown in Appendix C, Figure C.8.

5.2.3 DFT Calculations

To further elucidate the mechanisms of Al_2O_3 ALD on LMO, we analyzed the reaction between TMA and LMO by DFT calculation by using the previously determined, thermodynamically stable Li/O-terminated LMO(111) surface [200] as the model substrate. C-H deformation modes in FTIR (Figure 5.2A) suggest surface-bound CH₃, as was previously shown on metal and oxide substrates [298, 299, 300, 301]. Demethylated surface intermediates may therefore include $Al(CH_3)_3^*$ (TMA*), $Al(CH_3)_2^*$ (DMA*), $AlCH_3^*$ (MA*), and Al^* via the decomposition reactions outlined in equations 5.1-5.4:

$$TMA(g) + * \to TMA^* \tag{5.1}$$

$$TMA^* + * \to DMA^* + CH_3^* \tag{5.2}$$

$$DMA^* + * \to MA^* + CH_3^* \tag{5.3}$$

$$MA^* + * \to Al^* + CH_3^* \tag{5.4}$$

Thermodynamics for intermediates in equations 5.1-5.4 are shown in Figure 5.5A, with coadsorbed CH_3^* fragments assumed to be widely separated from one another (closer proximity of the methyl groups does not change any trends). Adsorption configurations are considered at the lattice oxygen top, two-fold, and three-fold sites, as labeled in Figure 5.5C. The overall reaction thermochemistry of TMA decomposition is quite exothermic, downhill by -6.44 eV. This is more exothermic than TMA reaction with Al_2O_3 , measured by calorimetry to be -3.56 eV per TMA [302], and is driven by the associated Mn redox chemistry. TMA adsorbs on lattice oxygens, since stable (111) surface terminations [200, 62, 64, 155, 234] have Mn cations in the subsurface. Favorable electrostatics between a partial negative charge on methyl groups and Li⁺ cations lead to slight stabilization, by 0.1 eV, at O_b sites (see inset in Figure 5.5A). Whereas intact $-CH_3$ groups on TMA are electron accepting (Lewis acid), the decomposed CH_3^* fragments thermodynamically favor binding to lattice oxygen atoms, adopting electron donating (Lewis base) behavior; the corresponding $O-CH_3$ stretches, calculated to occur at 967 $\rm cm^{-1}$, are likely obscured by the O-Al peaks in Figure 5.2 (low-frequency O-CH₃ modes are also calculated below 500 $\rm cm^{-1}$ where



Figure 5.5.: TMA decomposition thermodynamics on Li/O-terminated LMO(111) surface. (A) Free-energy diagram for TMA decomposition through demethylation on the LMO surface. Insets contain corresponding low-energy structural configurations for Al(CH₃)_x* on the surface, along with adsorbed CH₃* fragments widely separated from one another (coadsorption thermodynamics are included in Appendix C, Figures C.15-C.18). (B) Side view of the Li/O-terminated (111) surface. (C) Oxygen top, two-fold, and three-fold adsorption sites on the (111) surface. (D) Alternative angle of low-energy configuration of Al* species, involving occupation of interstitial 16c sites (3f-c), with octahedral coordination to lattice oxygen atoms.

changes in Mn-O bonds are observed in the FTIR). The shift in donor and acceptor behavior of $-CH_3$ is enabled by the amphoteric nature of the protecting group. The corresponding acid-base chemistry yields two electrons promoted to Mn 3*d* states, reducing two Mn⁴⁺ions to Mn³⁺. Moreover, additional bonds formed to surface oxygens either elongate Mn-O bonds (from ~1.9 to ~2.2 Å) from the formation of a Jahn-Teller distorted Mn³⁺ ion or lead to Mn-O bond breaking (bond lengths > 2.4 Å). The negative FTIR absorbance changes corresponding to Mn-O consumption (Figure 5.2A), coupled with the measured Mn redox (discussed above), are likely indicative



Figure 5.6.: DFT-calculated pathways for alkane by-product formation during TMA pulse. (A) Reaction between adsorbed TMA^{*} and surface hydroxyl group, H^{*}, to form gas-phase CH₄. (B) Concerted reaction between methyl groups on adsorbed TMA^{*} to form C_2H_6 , leaving behind MA^{*} on the surface.

of these structural details. Analogous chemistry is observed for explicit inclusion of coadsorbates in the model, as shown in Appendix C, Figures C.15-C.18.

We next apply DFT calculations to establish potential mechanisms for observed alkane by-products and to highlight trends in CH_4 and C_2H_6 QMS signal intensity. As demonstrated in Figure 5.6A, TMA* may react with surface hydroxyl groups to form gas-phase CH_4 , in this example, with a barrier of only 0.16 eV. Although FTIR (Figure 5.2B and Figures C.2-C.4 in Appendix C) and DFT (Appendix C, Figure C.13) suggest low hydroxyl coverage under ALD pretreatment conditions, we note that additional hydroxyls may also form during the TMA pulse through further decomposition of CH_3^* groups on the surface (Appendix C, Figure C.14), which may lead to the modest CH_4 production seen in the QMS measurements during TMA exposures for initial ALD cycles. Reaction between CH_3^* groups adsorbed on LMO surface oxygens and hydroxyls to form CH_4 is more unlikely, however, with reaction thermochemistry endothermic by 0.93 eV. C_2H_6 , on the other hand, may form through an intramolecular reaction between CH_3 groups on adsorbed TMA* with a very low barrier of 0.21 eV (Figure 5.6B), analogous to metal-catalyzed alkane metathesis reactions in the literature [303]. The driving force for a low C_2H_6 formation barrier may also be attributed, in part, to the strong binding of the MA* species that remains on the surface (Figure 5.5A). C_2H_6 is thus competitive with Al-C bond cleavage and subsequent deposition of CH₃ fragments on lattice oxygen sites, especially as sites become blocked by CH₃* in early ALD cycles. Decreased C_2H_6 formation in subsequent ALD cycles is likely accounted for by increased rate of CH₄ formation on Al-OH* hydroxyls.

5.2.4 Electrochemical Behavior of ALD Al_2O_3 on LMO

The surface chemistry for Al₂O₃ ALD on LMO leads to an unexpected surface configuration during the first one to three cycles where the LMO is sparsely coated with Al at interstitial O_h 16c sites, and Mn is reduced in the near-surface region. After 10-15 cycles, the Al_2O_3 forms a continuous film that completely coats the LMO surface. Here, we probe the LMO electrochemical behavior in these two regimes of the Al_2O_3 growth using LMO powders coated with one, two, four, six, and ten Al₂O₃ ALD cycles. Coin cells were prepared using the uncoated and coated LMO powders and cycled against Li and graphite anodes to study the effect of the ALD Al_2O_3 on electrochemical cycling. The LMO powders were preheated before ALD and testing since untreated LMO yielded fast capacity degradation, likely attributable to reactions between physisorbed water and the electrolyte. Figure 5.7A shows the charge-discharge measurements taken at 0.5 C and room temperature (RT), and the corresponding voltage-capacity curves are shown in Figure 5.7B. These results are summarized in Figure 5.7C, which presents data for each of the cathodes at the 100^{th} cycle and plots the discharge capacity (red) and capacity retention relative to the first cycle (blue).

Figure 5.7C reveals that $1 \ge Al_2O_3$ LMO and $2 \ge Al_2O_3$ LMO demonstrate higher specific capacities than the uncoated LMO. The initial capacity for $1 \ge Al_2O_3$ LMO is 118 mAh g⁻¹, whereas the uncoated capacity is only 110 mAh g⁻¹, indicating a



Figure 5.7.: Electrochemical measurements of coin cells prepared with uncoated and ALD Al₂O₃-coated LMO powders. (A) Specific capacity versus charge-discharge cycle number measured with a 0.5 C rate at room temperature (RT). (B) Voltage versus capacity profiles for all samples recorded during the first cycle. (C and D) Discharge capacity and capacity retention of LMO/Li half cells upon the 100th cycle tested at 0.5 C at RT (C) and 55 °C (D). (E) Charge-transfer resistance (R_{ct}) versus the number of ALD Al₂O₃ cycles on LMO extracted from EIS measurements on half cells before cycling.

7% increase. This behavior is quite reproducible (Appendix C, Figures C.10A and C.10B). The higher capacity for the 1 x Al_2O_3 LMO than for the bare LMO persisted with different charging rates (Figure 5.7D and Appendix C, Figure C.12A), different temperatures (Appendix C, Figures C.10E and C.12B), different LMO suppliers (C, Figures C.11 and C.12), and full cells (Appendix C, Figures C.10C and C.10D). The magnitude of the capacity enhancement for the 1 x Al_2O_3 LMO compared with the bare LMO was in the range of 5%-10% for the half cells but as high as 20% for the full cells. In all cases studied, the capacity dropped precipitously for the 10 x Al_2O_3 LMO compared with the bare LMO. The average capacity drop is 40%, and ranges from 17% to 75% depending on the conditions.

EIS is often used to evaluate Li-ion diffusion kinetics in oxide electrodes [304]. Appendix C, Figure C.10F shows EIS data for all samples before cycling and the equivalent circuit used to model the data, with fitting parameters provided in Appendix C, Table C.1. We find that the charge-transfer resistance, R_{ct} , increases with increasing ALD Al_2O_3 cycles on LMO (Figure 5.7E), consistent with the expectation that thicker Al_2O_3 coatings are more insulating. We speculate that during the early one or two ALD cycles, the sub-monolayer Al_2O_3 deposit stabilizes the LMO surface against dissolution and this offsets the increase in R_{ct} so that the capacity increases. XPS revealed that some Mn is converted from Mn⁴⁺ to Mn³⁺ during the initial one or two ALD cycles. Although an increase in Mn^{3+} should in principle increase the number of ions that would undergo the Mn^{3+} disproportionation reaction [228], these Mn ions are localized in the subsurface, which may isolate the Mn from the electrolyte. In other words, the initial one or two ALD cycles may passivate surface defects susceptible to dissolution in the uncoated sample. FTIR showed that TMA begins to react with Al-OH hydroxyl groups at the third ALD cycle, indicating a transition from surface passivation of Mn to the nucleation and growth of a continuous Al_2O_3 film. In addition, the R_{ct} continues to increase so that the lithiation and delithiation of LMO become impeded and the overall performance deteriorates. It is puzzling that the thicker ALD Al_2O_3 coatings did not consistently increase the capacity retention (Figures 5.7C, 5.7D, and Appendix C, Figures C.10B-C.10D), given that thicker and more continuous coatings should suppress Mn dissolution, which is thought to be the primary mechanism for capacity loss in LMO. Although there is not a firm consensus in the literature, similar behavior has been observed previously, suggesting that ALD Al_2O_3 may not be stable on LMO during cycling [272, 285].

5.3 Conclusions

In situ and ex situ experimental techniques, along with DFT calculations, are used to elucidate the mechanisms for ALD Al_2O_3 growth on and stabilization of LMO surfaces. Experimental signatures are observed for surface decomposition of CH_3 fragments (FTIR, QCM, and XPS), as well as C_2H_6 and CH_4 formation (QMS), which appear to be in direct competition for the first few TMA/H_2O cycles, where sub-monolayer coverages are observed. This is accompanied by the Al heteroatom bridging several oxygen atoms at the LMO surface, in some cases doping to the LMO surface via a favorable octahedral coordination at 16c interstitial sites. The facile demethylation of the precursor at the surface, however, may also impede Li transport in cases where the diffusion channels are blocked by the interstitial Al dopant. We find that in early cycles, ALD leads to a reduction in the average Mn oxidation state, with a higher ratio of Mn^{3+} observed because of Al doping and high coordination to surface oxygen. This is predicted to reduce the amount of oxidation of Al-containing adsorbates during the H_2O pulse, consistent with the relatively low mass gain during the H₂O pulse observed from QCM measurements in early ALD cycles. The increased Mn^{3+} ratio is proposed to enhance Li diffusion, leading to higher capacities. Moreover, the improved capacity with one or two ALD cycles may also be attributed to the stabilization of defects present in the uncoated sample. which may be particularly susceptible to dissolution. Further ALD cycles decrease performance, primarily because of an increase in the charge-transfer resistance. These findings offer key insights regarding the unique chemistry that occurs at the onset of protective thin film growth on Li battery materials. These mechanistic insights provide a viable avenue to further understand, and to rationally tune, the interfacial stability and electrochemical performance of other electrode materials through the application of novel coating chemistries.

5.4 Experimental Procedures

5.4.1 ALD Al_2O_3 on LMO Powders

ALD was performed in a custom viscous flow stainless tube reactor system28 with ultrahigh-purity Ar (UHP, 99.999%) carrier gas at a flow rate of 216 sccm and a pressure of about 1 Torr. Al₂O₃ ALD was conducted with alternating exposures to TMA and water. The ALD timing sequences are expressed as t1-t2-t3-t4, corresponding to the TMA exposure time, the TMA purge time, the H₂O dose time, and the H₂O purge time, respectively, in seconds. Commercial LMO powder (200 mg; MTI) confined in a powder coating tray was loaded into the ALD reactor. The powders were heated overnight at 200 °C for the removal of water residue from the surface. After heating, the LMO powders were coated at 200 °C with the timing sequence 60-120-60-180. Different numbers of ALD Al₂O₃ cycles, varying from one to ten cycles with the nominal Al₂O₃ thicknesses of 1.3 to 13 Å, were performed.

5.4.2 In Situ QMS Measurements

The goal of these experiments was to record the gaseous reaction products from Al_2O_3 ALD on the LMO powder to explore whether the surface chemistry for the TMA and H₂O reactions on LMO are different from the corresponding reactions on Al_2O_3 . The ALD tube reactor has an internal surface area of $\sim 1 \text{ m}^2$. Considering that TMA and H₂O will react on all exposed surfaces, the QMS signals will be the sum of the signals from reactions on the LMO and reactions on the reactor tube. To account for this, the specific surface area of powder should be ~ 10 -fold that of the reactor tube; moreover, a background measurement was performed with no LMO powder, and the recorded background signals were subtracted from the signals measured with the

LMO installed. The LMO powder from MTI has a modest specific surface area of only $\sim 1 \text{ m}^2 \text{ g}^{-1}$. To increase the surface area, we mechanically milled the LMO powder for different periods and performed Brunauer-Emmett-Teller (BET) measurements to determine the surface area of the ball-milled powders. A surface area of 13 m² g⁻¹ was achieved after 25 hr (see Appendix C, Figure C.1C).

One-gram ball-milled powder with specific surface area of 13 m² g⁻¹ was loaded into the reactor. The QMS (Stanford Research Systems, Model RGA300) is located in the downstream region of the tube reactor in a differentially pumped chamber separated from the reactor tube by a 35 mm orifice. This configuration yields a pressure of $\sim 10^{-6}$ Torr in the QMS chamber when the reactor tube pressure is ~ 1 Torr. The gas-phase products generated in the ALD process can pass through the orifice and be detected by the QMS, which is interfaced to the PC for data recording. More details about the QMS measurements are given in Appendix C.

5.4.3 In Situ FTIR Measurements

The *in situ* FTIR measurements of the Al_2O_3 ALD on LMO were performed in transmission mode with a Nicolet 6700 FTIR spectrometer (Thermo Scientific). The *in situ* FTIR measurements used a small, dedicated reactor equipped with gate valves that were closed during the precursor exposures to prevent growth on the infrared (IR)-transparent CsI windows. Substrates for FTIR measurements were prepared by pressing LMO powder into a stainless-steel grid [287, 305]. The grids were fabricated by photochemical machining (Fotofab) and were 50 mm thick with 50 mm bars and 200 mm square openings. The powder-filled grid was mounted into a stage that could be heated to 500 °C. This stage was then loaded into the FTIR reactor such that the IR beam passed through the center of the grid. During *in situ* FTIR measurements, the substrate temperature was maintained at 200 °C by the heated stage.

5.4.4 In Situ QCM Measurements

In situ QCM was performed for studying the growth chemistry of Al_2O_3 on the LMO surface, so this required LMO-coated QCM sensors. Before the measurement, ~10 nm LMO thin films were deposited onto QCM crystals by sputtering. These modified crystals were installed in the QCM holder (Maxtek BSH-150 bakeable sensor head) and placed in the ALD reactor at 200 °C until the QCM signals stabilized before the TMA and H₂O pulses began.

5.4.5 Ex Situ Characterizations

For the SEM measurements, pristine and Al_2O_3 -coated LMO particles were attached onto carbon tapes on Al substrates. The powders were coated with a thin gold layer to improve the image quality. FESEM (JEOL 7500 model) was performed in the Center for Nanoscale Materials (CNM) at Argonne. For TEM characterization, 10 cycled (10x) Al₂O₃-coated LMO was put onto TEM grids. TEM and high-resolution TEM (HRTEM) were performed with a JEOL 2100 at the CNM. As for XPS characterization, considering that XPS is highly surface sensitive and probes only the first few nanometers of a sample, we prepared a substrate composed of an ultrathin, sputtered LMO coating on an anodic aluminum oxide (AAO; Whatman) membrane. The AAO membrane has a high surface area and was used to boost the XPS Mn signals. Approximately 10 nm LMO thin films were obtained by sputtering. One cycle and three cycles of ALD Al_2O_3 were deposited on the substrates and then transferred to XPS chamber. The XPS was carried out in ultrahigh vacuum in a Thermo Scientific ESCALAB 250Xi with a nominal spot size of 400 mm. Two spots for as-deposited LMO, 1 x Al_2O_3 LMO, and 3 x Al_2O_3 LMO samples were analyzed for ensuring repeatability.

5.4.6 Electronic Structure Calculations

The Vienna *ab initio* Software Package (VASP) [160] was used for performing spinpolarized DFT calculations. A plane wave basis set with a 520 eV kinetic energy cutoff was applied. Core electronic states were treated with the projector augmented wave pseudopotentials [162] with small core potentials for Li and Mn, including the 1s and 3p states as valence electrons, respectively. The generalized gradient approximation of Perdew-Burke-Ernzerhof was chosen as the exchange-correlation functional [163]. A Hubbard U value of 3.5 eV added to Mn 3d states through the implementation of Dudarev et al. [106] accurately reproduced bulk thermochemistry of Mn oxides with Mn^{4+} , Mn^{3+} , and Mn^{2+} transition-metal cations [200]. Because demethylation steps also involve Mn redox, as discussed in the main text, we assumed that the DFT + Umethods were also sufficiently accurate for estimating accessible kinetic barriers for these processes and that quantitative discrepancies resulting from the level of theory chosen would not significantly influence the predicted trends. Thermodynamics of surface species were calculated on the thermodynamically stable Li/O-terminated LMO(111) surface [200], and hydrogen passivation of oxygen atoms was used for minimizing contributions from dangling bonds. Ferromagnetic ordering was applied in all cases. A $2 \ge 2 \ge 1$ Γ -centered k-point scheme was used for sampling the Brillouin zone. Gaussian smearing of the electronic states was applied with a Fermi temperature of 0.05 and 0.01 eV for solid-state and gas-phase calculations, respectively. Dipole corrections were included within a 20 Å vacuum layer and were included explicitly in the calculated total energies. Convergence to an energy tolerance of 0.1 meV per unit cell and to a force criterion of 20 meV $Å^{-1}$ was imposed. Transition-state calculations were performed according to the climbing image nudged elastic band (NEB) method [170], and initial guesses were made according to the Image Dependent Pair Potential method of Jónsson and co-workers [306]. The dimer method was used to refine transition states, where a saddle point was confirmed by the presence of a single imaginary frequency. NEB calculations were modified according to the procedure in Getsoian et al. [307] for diabatic potential energy surfaces. Further details are provided in Appendix C. Similar to previous work [286, 298], 473 K translational entropy corrections to gas-phase TMA, CH_4 , C_2H_6 , and H_2O were 0.84, 0.75, 0.79, and 0.76 eV, respectively.

5.4.7 Electrochemistry Tests

The cathode laminates were prepared from a mixture of 85% LiMn2O4 powders (mass ratio) with or without ALD Al_2O_3 , 10% carbon black, and 5% polyvinylidene diffuoride binder. 1-Methyl-2-pyrrolidinone was used as the solvent to make the mixture a slurry, which was then cast on an aluminum foil. After drying in an oven inside an Ar-filled glovebox at 100 °C for 8 hr, the laminates were then punched into 1.0 $\rm cm^2$ disk electrodes. 2032-type coin cells were assembled in the glovebox with Celgard 2325 as the separator. The electrolyte was 1.2 M LiPF_6 in 3:7 EC-EMC solution. For cycling in half cells where Li metal was employed as the anode, all cathodes were measured between 3.5 and 4.3 V at RT or 55 °C with either an Arbin 2043 battery tester or a LAND battery tester. Other parameters, including different current rates (0.5 and 1.0 C), were systematically investigated. For electrochemical tests on full cells, graphite with a mass loading of 2 mg $\rm cm^{-2}$ was cast onto a Cu foil. The electrode process was the same as above. To form a solid electrolyte interphase, we first assembled the graphite electrodes with Li metal as the anode. After five cycles at 0.5 C, the coin cells were disassembled, and the graphite electrodes were harvested and used as the anode to pair with LMO. LMO cathodes with and without ALD Al_2O_3 coatings were used, and the resulting cells were cycled at 0.5 C. The capacity was calculated on the basis of the mass of $LiMn_2O_4$ as the active material. AC impedance spectroscopy of coin cells was performed with a Solartron Analyzer using a 5 mV stimulating wave with a frequency ranging from 100 kHz to 20 mHz.

Supporting Information for this chapter is included in Appendix C.

L.C. fabricated the batteries with different thickness of ALD coatings and measured the cell performance; R.E.W. completed the DFT calculations; K.-S.C. performed AFM and ex situ XPS; Z.Y. conducted the EIS and BET experiments. L.C., J.W.E., R.E.W., and J.P.G. wrote the associated publication; and all authors participated in the analysis of the experimental data and discussions of the results, as well as preparation of the associated publication.

6. DESCRIPTOR-BASED ANALYSIS OF ATOMIC LAYER DEPOSITION ON SPINEL LIMN₂O₄ LITHIUM ION BATTERY CATHODES

This chapter is reproduced from a manuscript that has been submitted for publication: Robert E. Warburton, Matthias J. Young, Steven Letourneau, Jeffrey W. Elam, Jeffrey Greeley; Descriptor-Based Analysis of Atomic Layer Deposition on Spinel Li Mn_2O_4 Lithium Ion Battery Cathodes. *Submitted* **2019**

Protective coatings have been shown to effectively suppress Mn ion dissolution from the spinel $LiMn_2O_4$ lithium ion battery cathode by stabilizing the surface against undesired side reactions with the electrolyte. In spite of extensive study, however, there remains a lack of atomic-scale understanding of how such coatings are deposited, and no molecular-level descriptor to predict trends in deposition mechanisms has been identified. We have recently shown that Al₂O₃ coatings grown by atomic layer deposition (ALD) with alternating trimethylaluminum (TMA) and water exposures exhibit sub-monolayer growth due to precursor decomposition on the LMO surface during early ALD pulses. In the present work, we elucidate the underlying mechanisms of this Al_2O_3 ALD process using density functional theory (DFT) calculations and Xray photoelectron spectroscopy (XPS) experiments, and we introduce a generalized descriptor-based framework to understand the resulting trends across a spectrum of surface structures and functionalities. We demonstrate that all decomposition products, including CH_3 -aluminum adducts and dissociated CH_3 groups, are Lewis bases and are coordinated to oxygen atoms on the LMO surface, leading to charge transfer to Lewis acidic Mn 3d states. Inert-transfer XPS supports these theoretical predictions, showing an increase in near-surface Mn³⁺ content following TMA exposure, as well as shifts in C 1s spectra consistent with C-O bond formation. We extend the DFT studies to various low- and high-index LMO surface facets, as a proxy for tuning
the Lewis acid-base interactions between surface-bound CH_3^* and near-surface Mn ions. The thermochemistry for TMA reactions on these chemically distinct LMO surfaces demonstrates that ALD is structure-sensitive and that there is higher reactivity for TMA decomposition and Al_2O_3 nucleation near LMO steps and defects. Motivated by the Lewis basic character of the decomposition products, we introduce the oxygen vacancy formation energy as a descriptor for decomposition energetics, and we demonstrate that all energetics are correlated to this quantity through the number of electrons that are transferred along the reaction coordinate. Based on these findings, we hypothesize that improved electrochemical cycling with only 1-2 ALD cycles may be due to selective passivation of defect sites on the LMO surface that are more susceptible to Mn dissolution, and we suggest that similar descriptor-based analyses could be useful for the study of other ALD coatings on oxide substrates.

6.1 Introduction

Lithium manganate spinel (LiMn₂O₄, or LMO) is an attractive Li-ion battery (LIB) cathode material with high rate capability and thermal stability [44, 132]. In spite of these promising features, however, LMO has several shortcomings that limit its electrochemical performance. These challenges include chemo-mechanical degradation upon cycling [188, 192], Li intercalation below 3 V vs. Li/Li⁺ to form the Jahn-Teller distorted Li₂Mn₂O₄ tetragonal phase [136, 137], and dissolution of surface Mn ions into the electrolyte [209, 138, 133]. The problem of Mn dissolution, in particular, leads to significant capacity fade through sluggish anodic (de)lithiation kinetics following Mn deposition onto the counterelectrode [308, 309, 310, 311, 139]. It has been suggested that Mn dissolution from LMO is preceded by the Mn³⁺ disproportionation mechanism of Hunter [228], where Mn²⁺ ions dissolve into the electrolyte: 2 Mn³⁺ \rightarrow Mn⁴⁺ (insoluble) + Mn²⁺ (soluble). The presence of acid is proposed to accelerate Mn dissolution [228, 249], which becomes particularly relevant at elevated temperatures (~55°C) where decomposition of LiPF₆ in the presence of trace water impurities leads to increased concentrations of HF in the electrolyte [138, 312]. Although recent electron paramagnetic resonance (EPR) and X-ray absorption near edge structure (XANES) experiments suggest that Mn^{3+} may actually be the dominant species in solution [229, 230], theoretical calculations provide evidence that dissolving Mn ions are divalent [233, 231, 232], suggesting that dissolution may in fact be facilitated by interfacial charge transfer that produces soluble, low-valence Mn ions.

To alleviate problems stemming from Mn dissolution, fundamental studies are needed to understand and control the reactivity of the interface between LMO cathodes and the electrolyte. In addition, the problem of transition metal dissolution is relevant to other classes of cathode materials [313], and insights from model studies on LMO may therefore be relevant to efforts to stabilize these other electrodes. Currently, the most successful and widely used strategies to suppress Mn dissolution from LMO are substitutional doping and the deposition of protective coatings. Monovalent [209, 314], divalent [315], and trivalent [316] cationic doping of LMO has been suggested to reduce the amount of Mn^{3+} ions available to undergo disproportionation. Moreover, selective doping of the LMO near-surface with Ti⁴⁺ has been demonstrated to reduce Mn dissolution and enhance cycling performance [140]. Protective oxide [226, 272, 317, 318, 319, 320] and fluoride [321, 322, 323] coatings have also demonstrated enhanced capacity retention for LMO and other cathode materials. Protective coatings provide a physical barrier between Mn ions and the electrolyte [154, 324, 325], and computational studies have also shown that passivation of the LMO surface increases the oxidation state of surface Mn ions from Mn^{3+} to Mn^{4+} [142, 179, 326]. In addition, high-throughput computational screening efforts have recently identified other promising coating chemistries based on bulk properties, such as lithiation and HF scavenging thermodynamics [327, 328].

A variety of experimental strategies have been explored to deposit coatings on LIB electrodes, including electroless deposition [227, 213], sonochemical methods [317], colloidal suspensions [329], and atomic layer deposition (ALD) [284]. In particular, thin film growth by ALD allows for uniform film growth of the target coating chemistry [330, 331]. Consequently, ALD-grown surface coatings allow for a precise study

of the structural and chemical factors that may dictate electrochemical performance. For example, experimental work has shown that six ALD cycles deposited on LMO appear to provide optimal thickness for Al_2O_3 , ZnO, and ZrO₂ films, suggesting that films of this thickness (~1 nm) sufficiently mitigate Mn^{2+} dissolution, while allowing for efficient Li⁺ transport at the interface [154, 324]. We have recently shown that film growth by ALD Al_2O_3 on LMO is non-uniform, with only a partial sub-monolayer coating formed on the cathode surface for up to ten ALD cycles. Electrochemical performance is enhanced with only 1-2 ALD cycles, whereas further ALD cycles significantly increase impedance, indicative of sluggish Li⁺ diffusion kinetics [225].

In spite of the enhanced cycling performance of surface-modified LMO electrodes, there remains a compelling need to elucidate the atomic-scale details of how coatings are deposited and, more generally, to identify descriptors that describe trends in this process over larger structural and chemical spaces of oxide substrates. To address this imperative, in the present work, we employ first principles density functional theory (DFT) calculations and inert-transfer X-ray photoelectron spectroscopy (XPS) to understand the mechanisms of ALD Al_2O_3 film growth on LMO cathodes and to identify descriptors to predict reactivity as a function of the local oxide surface structure. We consider ALD Al_2O_3 growth through alternating exposures of trimethylaluminum (Al(CH_3)₃, TMA) and water (H₂O). The TMA/H₂O system has been extensively studied for applications in batteries [226, 319, 324, 142, 251], catalysis [286, 298, 299, 300, 301], and semiconductors [332, 333, 334, 335, 336, 337, 338], including several computational studies on the subject [225, 251, 286, 298, 336, 337, 338]. In our previous work, we demonstrated that decomposition of methyl groups $(-CH_3)$ from TMA to the oxygen atoms on the Li/O-terminated LMO(111) surface is facile, blocking adsorption sites for TMA in early ALD Al_2O_3 cycles [225]. Here, we provide a comprehensive analysis of the acid-base chemistry associated with these reactions, and we discuss how ALD mechanisms on highly reducible oxides, such as LMO, can be fundamentally different from those on more widely studied irreducible oxides such as Al_2O_3 . We further demonstrate how the underlying acid-base chemistry of ALD reactions on LMO leads to variations in surface reactivity between low-index terrace and high-index step models of the LMO surface. Although (111) is the dominant facet of LMO [200, 144, 145, 146, 147, 151], polycrystallinity and defect sites have been shown to influence ALD mechanisms on different materials [339, 340]. We provide an electronic structure basis to describe the reactivity of the TMA precursor at the onset of protective film growth at specific sites on the LMO, and motivated by the unusual acid-base chemistry of TMA decomposition, we introduce compact descriptors that can be used to efficiently predict trends in the thermochemistry of these growth and deposition processes. These findings reveal details related to electrode/coating interface formation at different stages in the ALD process that can be applied to rationally tune the interfacial reactivity of LIB electrode materials, in addition to providing a broader understanding of ALD surface chemistry on oxide and semiconductor substrates.

6.2 Methods

6.2.1 First Principles Calculations

Self-consistent, spin-polarized density functional theory calculations were performed using the Vienna Ab initio Simulation Package (VASP) [160, 168, 161]. The core states were treated using the projector augmented wave (PAW) method [201, 162], with 1s and 3p core electrons for Li and Mn, respectively, included as valence states in the small-core pseudopotentials. The Kohn-Sham valence states were expanded using a planewave basis set with a kinetic energy cutoff of 520 eV. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was applied as the exchange-correlation functional [163]. The rotationally invariant, spherically averaged, DFT+U method [102, 103, 104, 106] was used to correct for electron overdelocalization in the highly correlated Mn 3d states. A Hubbard U value of 3.5 eV was added to the Mn 3d electronic states and has been previously shown to accurate reproduce bulk thermochemistry of Mn oxides with Mn^{2+} , Mn^{3+} , and Mn^{4+} , as well as mixed-valence oxidation states [200, 110, 202, 203].

We applied ferromagnetic (FM) ordering of Mn ions for LMO, which was previously shown to give similar results surface thermodynamics to antiferromagnetic (AFM) ordering [200, 155]. We allowed for full relaxation of the Jahn-Teller distorted Mn^{3+} ions, leading to localization of Mn^{3+} and Mn^{4+} ions and lattice parameters of a = 8.21 Å, b = 8.21 Å, and c = 8.79 Å in the LMO bulk. Mechanistic analyses were performed on low-index (111) and (001) surfaces and on the (511) stepped surface. The (111) Li/O, (111) Li-rich, (001) Mn/O, (001) Li, (511) Li/Mn/O and (511) Li/Mn/O-1Ovac terminations, previously demonstrated to be thermodynamically stable off-stoichiometric surface terminations [200], were considered. To reduce spurious interactions with dangling bonds through the vacuum layer, oxygen atoms were passivated with hydrogen at the bottom end of the slabs, which were initially subject to full ionic relaxation. Following this initial relaxation, some layers at the bottom of the slab were fixed for adsorption calculations to reduce computational expense (see Appendix D, Figure D.1). Dipole corrections were added normal to the surface within a 20 Å vacuum layer. A Γ -centered k-point scheme was used to sample the Brillouin zone, with densities of $2 \ge 2 \ge 1$ for (111) and (001) low-index surfaces and $1 \ge 2 \ge 1$ for the (511) stepped surfaces, respectively. Convergence to an energy tolerance of 0.10 meV per unit cell and a force criterion of 20 meV $Å^{-1}$ was imposed. Gaussian smearing of the electronic states was applied, with Fermi temperatures of 0.05 eV and 0.01 eV for condensed and gas phase calculations, respectively. For density of states (DOS) calculations, k-point densities were doubled with respect to standard geometry relaxations and tetrahedron smearing with Blöchl corrections. Site-projected densities of states (PDOS) were evaluated by projecting on individual atoms, according to the default Wigner Seitz radius indicated in the PAW potentials. Free energies were determined using translational entropy corrections of 0.84 eV and 0.75 eV for gas phase TMA and CH₄, as established in previous work [225, 286, 298].

Transition state (TS) searches were performed using the Nudged Elastic Band (NEB) method [170, 341] as implemented in VASP, with initial geometry estimates along the band aided by the Image Dependent Pair Potential pre-optimization tool developed by Jónsson and co-workers [306]. The demethylation of TMA generally proceeds with decomposition of methyl $(-CH_3)$ groups to lattice oxygen atoms on LMO, resulting in a net charge transfer of two electrons due to the underlying Lewis acid-base chemistry of the reaction (discussed further in Section 6.3.2). Due to the magnetic ordering of Mn ions, this results in a changing spin state between initial and final states along the demethylation reaction coordinate. In such cases, we estimated the kinetic barriers following the general approach outlined previously in the literature [342, 307, 343]. Briefly, an adiabatic NEB run was performed, without implementation of the climbing image algorithm [170], converging forces on each free atom to 100 meV $Å^{-1}$. Subsequently, two sets of single point calculations were performed for each geometry along the band at each spin state (corresponding to the initial and final spin states along the NEB). The minimum energy path (MEP) was then constructed by evaluation of two intersecting diabatic (constant spin) potential energy surfaces (PES), where the probability of a spin-crossing event (P_{LZ}) was estimated by the Landau-Zener approach [120]. We treated the breakdown of Born-Oppenheimer electron/nuclear dynamics in this case, with the coupling between the two diabatic reaction coordinates assumed to be controlled by spin-orbit coupling. The energy at the point of intersection of the two adiabatic reaction coordinates, minus the spin-orbit coupling energy (H_{SO}) , was used to connect the two diabats to estimate the adiabatic MEP. In this work, transition states typically involve the formation of Mn^{3+} cations, so H_{SO} was estimated using the literature value [344] of the coupling constant (ζ) for Mn³⁺ of 355 cm⁻¹ along with the changes in angular momentum of the Mn 3d states:

$$H_{SO} = \zeta [J(J+1) - L(L+1) - S(S+1)]$$
(6.1)

In equation 6.1, L is the angular quantum number (L = 2 for d electrons), S is the spin quantum number ($S = +\frac{1}{2}$), and J is the sum of S and L. P_{LZ} is calculated using H_{SO} and the two calculated diabatic PES curves.

$$P_{LZ} = \frac{\int_0^\infty [1 - \exp(-\frac{4\pi^2 H_{SO}^2}{h\nu |\nabla E_{hs} - \nabla E_{ls}|})] \exp(-\frac{\nu^2}{2k_B T}) d\nu}{\int_0^\infty \exp(-\frac{\nu^2}{2k_B T}) d\nu}$$
(6.2)

In equation 6.2, h is Planck's constant, ν is the velocity of the nuclei, and $|\nabla E_{hs} - \nabla E_{ls}|$ is the magnitude of the difference in energy gradients for the high-spin (hs) and low-spin (ls) PESs. The gradients were calculated with respect to a reaction coordinate (ρ) defined by the mass-weighted mean squared displacement of the N free atoms for n images in the NEB calculation:

$$\rho_n = \sum_{i=0}^{n+1} \sqrt{\sum_{j=0}^{N+1} m_j dx_j^2}$$
(6.3)

The tangent estimation scheme by Henkelmen and Jónsson [341] was modified using the mass-weighted reaction coordinate in equation 6.3 to fit the spline for each MEP. The rate constant of a demethylation step could thus be estimated using a transition state theory formalism, which additionally incorporates P_{LZ} :

$$k \sim \frac{k_B T}{h} P_{LZ} \exp(-\frac{E_A}{k_B T}) \tag{6.4}$$

The rate expression in equation 6.4 was used to assess whether a reaction is likely. Under ALD conditions (200°C) and given the availability of sites on the LMO surface, a reaction barrier of less than ~1.39 eV would proceed at a rate of ~1 min⁻¹, which is the approximate time scale of typical ALD pulses.

6.2.2 LMO Sample Preparation

LMO pellets were prepared by pressing $\sim 100 \text{ mg}$ of LMO powder (MTI, $\leq 25 \text{ ppb}$ metal impurity) onto a 50 μ m thick stainless steel mesh with 50 μ m bars and 200 μ m square openings (Fotofab Inc.) under 30 tons of force to provide a pellet on a support

mesh for handling. LMO pellets were baked out at 50°C in a vacuum oven overnight, then loaded via an antechamber into an argon-filled glovebox (~0.2ppm O₂, < 0.5 ppm H₂O). The LMO pellets were annealed for >1 hour at 500°C on a hotplate in the glovebox to remove any surface carbonates before use. Three LMO pellets were prepared for this study: one with no ALD treatment, one with just TMA exposure, and one with both TMA exposure followed by H₂O exposure.

6.2.3 Atomic Layer Deposition

ALD-treated LMO pellets were transferred into a custom ALD reactor connected directly to the argon-filled glovebox used for sample preparation. ALD was carried out at 200°C under 1.4 Torr (90 sccm) of continuous argon purge. LMO pellets were held in the reactor for > 15 minutes prior to the initiation of ALD doses to allow for the samples to reach reaction temperature. The LMO pellet with one ALD cycle was loaded into the ALD reactor first and coated with one ALD cycle consisting of 30 s TMA exposure at ~1 Torr partial pressure, 120 s argon purge, 30 s H₂O exposure at ~1 Torr partial pressure, and 30 s argon purge. These long exposures were used to ensure complete reaction on the surface of the LMO. This first LMO pellet was removed from the ALD reactor and a second LMO pellet was loaded. The second LMO pellet was exposed to a 30 s TMA dose, then removed from the reactor after 5 s of argon purge.

6.2.4 X-ray Photoelectron Spectroscopy (XPS) Measurements

In order to minimize exposure to oxygen and water, all three LMO pellets (no ALD treatment, TMA exposure, and TMA/H_2O exposure) were loaded into a vacuum-transfer module (Thermo Fisher Scientific) within the glovebox environment immediately after removing the LMO pellet which was exposed to a TMA dose from the ALD reactor. The vacuum-transfer module was sealed under vacuum and then immediately loaded into the XPS chamber for analysis. XPS was performed using a K-Alpha X-ray

Photoelectron Spectrometer (Thermo Fisher Scientific) equipped with a monochromated, micro-focused Al-K α X-ray source at 1486.6 eV. XPS spectra were obtained using a pass energy of 50 eV and a step size of 0.1 eV. Avantage Surface Analysis (Thermo Fisher Scientific version 5.986) was used for data collection and analysis.

6.3 Results

To elucidate the fundamental chemical mechanisms of Al_2O_3 atomic layer deposition on LMO, we begin by analyzing reaction of the TMA precursor with the Li/Oterminated LMO(111) surface. We have previously demonstrated that this surface is expected to be thermodynamically stable under typical lithium ion battery conditions [200], and the detailed chemistry described for this termination provides a foundation for subsequent generalization of the reactivity trends to different structural features on LMO particles and for identification of appropriate reactivity descriptors.

6.3.1 TMA Decomposition Thermodynamics on the LMO(111) Surface

We begin by briefly reviewing the thermodynamics of TMA decomposition on the (111) surface, some of which was described in our previous work [225]. Initial TMA adsorption to oxygen sites on the Li/O-terminated LMO(111) surface is exothermic by 0.13 eV (Figure 6.1a). Subsequent demethylation steps involve formation of dimethylaluminum [Al(CH₃)₂, DMA*], methylaluminum [Al(CH₃), MA*], and aluminum (Al*), with CH₃* products adsorbing on lattice oxygen sites (Figure 6.1b - * indicates surface-bound species). As TMA* sequentially loses its CH₃ groups, the Al* heteroatoms in the DMA*, MA*, and Al* intermediates increase their coordination to surface oxygen atoms to maintain a tetrahedral coordination. After complete demethylation (Al* + CH₃*), the Al* heteroatom is preferentially located at vacant octahedral 16c sites on the surface (Figure 6.1b). This structure is indicative of near-surface aluminate formation, potentially blocking the 16c sites needed for Li⁺ diffusion through LMO.



Figure 6.1.: Reaction thermodynamics for TMA adsorption and demethylation on the Li/O-terminated LMO(111) surface. (a) Free energies of intermediates along the reaction coordinate with CH_3^* adsorbates at infinite separation. The inset shows different adsorption sites, where, in addition to oxygen top sites (O_a and O_b), the 2*f*- and 3*f*-prefixes denoting sites where the adsorbate is two-fold and three-fold coordinated to oxygen atoms, respectively. (b) Legend for atomic species and converged geometries of intermediates in (a). The image in the bottom right (Al^{*}) demonstrates adsorption of the heteroatoms of the fully decomposed TMA precursor to octahedral 16c sites, reminiscent of near-surface aluminate alloy formation. Adapted with permission from ref. [225], with permission from Elsevier.

6.3.2 Effect of Spin Crossing on TMA Decomposition Kinetics

Although results described in the previous section demonstrate that the thermodynamics of TMA decomposition are highly exothermic, the kinetics of these reactions may ultimately determine whether they are feasible. The approach outlined in the Section 6.2.1 is used to estimate kinetic barriers, including treatment of the changes in spin states that are typically observed along the demethylation reaction coordinates. An example of this general process is shown in Figure 6.2c for the decomposition of MA^{*} to Al^{*} + CH₃^{*}. The intersection of two diabatic reaction paths, starting from the reactant (MA^{*}) in a low-spin state, and ending up at the product (Al^{*} + CH_3^*) in a high-spin state (2 μ_B higher than the initial state), is shown. The transition from a low- to high-spin state is associated with the charge transfer to Mn e_q electronic states, as is shown in Figures 6.2a-b. The spin-coupled (adiabatic) MEP is constructed using the intersection of the two diabatic curves, with an energy gain of $H_{SO} = 88$ meV. Barrier estimates for other demethylation steps along the reaction coordinate for (111)Li/O, as well as other low- and high-index LMO surface terminations, are included in Table 6.1 and will be discussed later in this work. In general, we find that spin crossing probabilities (P_{LZ}) are nearly unity in all cases, due to the relatively strong coupling between electronic states and the high mass of the $-CH_3$ species being transferred near the spin transition. As a comparison, many spin-forbidden reactions often involve much lighter species such as single hydrogen atoms [342].

6.3.3 Lewis Acid-Base Chemistry of TMA Decomposition

We note that CH_3 ligands transition from electron accepting (Lewis acid) when bound to $Al(CH_3)_x$ to electron donating (Lewis base) when bound to oxygen on the LMO surface. The net result is that each demethylation step involves transfer of two electrons to Mn 3*d* states. This effect is observed in Figure 6.2a-b, where calculation of the Mn projected density of states (PDOS) identifies the reduction of two near-



Figure 6.2.: Electron transfer during TMA demethylation on LMO shown through changes in the Mn 3*d* projected density of states (PDOS) for (a) the initial (MA^{*}) and (b) final (Al^{*} + CH₃^{*}) states along the reaction coordinate, and (c) the kinetic barrier for the corresponding step.

surface Mn ions from Mn^{4+} to Mn^{3+} upon decomposition of MA^* to $Al^* + CH_3^*$. In Figure 6.2a-b, Mn^{4+} has a fully unoccupied e_q band (above E_f), whereas the e_q band is partially occupied for Mn^{3+} , with degeneracy broken about E_f , indicative of the well-documented Jahn-Teller distortion of Mn^{3+} ions [345, 346]. Similar analyses of DFT+U calculations of LMO surfaces have been used to distinguish between Mn^{3+} and Mn^{4+} electronic states previously in the literature [142, 179]. Analogous surface chemistry and electronic structure signatures are observed for the other demethylation steps along the reaction coordinate. While the DFT+U level of theory underestimates band gaps of LMO and different MnO_2 polymorphs and shifts the relative energy levels of the t_2g and e_g states compared to more accurate hybrid or GW treatments [347, 348, 75], we stress that the thermodynamics of surface redox reactions are treated with sufficient accuracy for a Hubbard U correction that is benchmarked against bulk redox thermochemistry [200, 110]. Moreover, DFT+U properly localizes electrons on Mn^{4+} and Mn^{3+} ions in the ground state and qualitatively captures the crystal field splitting of e_g states of high-spin Mn³⁺ ions, whereas more delocalized GGA calculations without Hubbard corrections will not.

While Lewis basic behavior is observed for CH_3^* adsorbates on LMO(111), $-CH_3$ ligands are amphoteric and can, in theory, also adopt Lewis acidic behavior if bound

to undercoordinated Mn ions on the LMO surface. For example, it has been reported that different electron accepting/donating behavior may be predicted for open-shell adsorbates on oxides, in comparison to cases where a charge-neutralizing coadsorbate is explicitly included in the calculation cell. In cases with explicit inclusion of two amphoteric coadsorbates, cooperative Lewis acid-base pair interactions may also be thermodynamically favorable [349, 350]. In light of these considerations, we consider additional TMA decomposition pathways where CH_3^* may behave as either a Lewis base (e⁻ donating, bound to O sites) or a Lewis acid (e⁻ accepting, bound to Mn sites). Since Mn ions are in the subsurface for stable (111) surface terminations, we consider the Mn/O-terminated [200] LMO(001) surface to enable comparison of CH_3^* binding energies at Mn and O sites. The surface layer of Mn ions on LMO(001) are undercoordinated (five-coordinate to oxygen in comparison to six-coordinate in the bulk), so additional bonds may be formed with adsorbates. For simplicity, we evaluate the coadsorption energies of CH_3^* and H^* (or dissociative adsorption energy of CH_4) at different sites on the LMO(001) Mn/O surface corresponding to different Lewis acid or base characteristics of the adsorbates (Figure 6.3a). We note that this analysis resembles the cooperative Lewis acid-base pair coadsorbate effect highlighted in work by Chrétien and Metiu on $La_2O_3(0001)$ [350].

DFT calculations performed for $CH_3^*-H^*$ pairs, at Mn and the two distinct O sites, on the Mn/O-terminated LMO(001) surface (inset, Figure 6.3b) suggest that the formation of Lewis acid-base pairs between coadsorbates on the LMO surface is unlikely. Instead, based on the CH₄ dissociative adsorption free energies plotted in Figure 6.3b, the formation of Lewis base-base adsorbate pairs is most thermodynamically favorable. In this case, two Mn⁴⁺ ions behave as Lewis acid adducts to the Lewis base adsorbates (Figure 6.3c). While the surface layer contains Mn³⁺, higher valence Mn⁴⁺ ions in the nearest sub-surface layer are able to accept the electrons from surface species, accompanied by changes in near-surface Mn-O bond lengths commensurate with the appropriate oxidation states. While Lewis acid-base pair formation between CH₃* and H* was reported on La₂O₃ (0001), analogous calculations





Figure 6.3.: Lewis acid-base chemistry of $-CH_3$ groups adsorbed on the LMO surface. (a) Configurations of Lewis acid-acid, base-base, and acid-base pairs between CH_3^* and H^* adsorbates. The electron donor/acceptor behavior may vary with inclusion of coadsorbates. (b) Adsorption free energies for different CH_3^*/H^* configurations on the Mn/O-terminated LMO(001) surface. Adsorption sites are labeled on the figure in the insert, with Lewis acidic and basic adsorbate configurations indicated by red and blue font, respectively. (c) Schematic of Lewis acid-base chemistry (adsorbate electron accepting and donating behavior) in the context of TMA demethylation on LMO. Upon demethylation, the $-CH_3$ fragments undergo a change in their donor/acceptor behavior and prefer binding to oxygen atoms on LMO. In this case, two Mn⁴⁺ ions behave as the Lewis acidic adduct (electron acceptor) to each of the Lewis basic adsorbates. The overall reaction leads LMO to gain two electrons (localized in Mn 3d orbitals) per demethylation event.

on rutile $TiO_2(110)$ revealed that base-base pairs are thermodynamically favorable when the transition metal in the oxide is more Lewis acidic than either coadsorbate [350]. In the present work, this suggests the Lewis acidity of Mn ions in LMO leads to decomposition of the CH₃ groups from TMA to oxygen sites on the surface, where the CH₃* adsorbates are electron donors to the LMO surface.

In the context of ALD, the Lewis acid-base chemistry observed for CH_3^* and Mn suggests a unique mechanism for the reaction of the TMA precursor on LMO, in comparison to literature reports for ALD on irreducible oxide substrates, such as Al_2O_3 , ZnO, or ZrO_2 . For example, on hydroxyl-free Al₂O₃(0001), DFT calculations by Elliott and Greer determined that decomposed CH_3 groups are most stable when adsorbed at Al sites on the surface [333]. For TMA reaction on Al_2O_3 , $Al(CH_3)_{x-1}^*$ and CH_3^* form Lewis acid-base adsorbate pairs on the surface, with $Al(CH_3)_{x-1}^*$ bound to oxygen and CH_3^* bound to Al. On LMO, however, $Al(CH_3)_{x-1}^*$ and CH_3^* both bind through oxygen and form Lewis base-base pairs on the surface following each demethylation step, as depicted in Figure 6.3c. Rather than coadsorbate Lewis acidbase interactions, the near-surface Mn ions instead act as the Lewis acidic electron acceptor from the Lewis basic surface adsorbates. As discussed above, this mechanistic picture is consistent with the promotion of two electrons per demethylation step to Mn 3d electronic states, as shown in the PDOS analysis of the near-surface Mn in Figure 6.2a-b. The transfer of two electrons further suggests that TMA decomposition energetics might be correlated with other acid-base surface chemistries, such as oxygen vacancy formation, that also involve electron transfer (see discussion in Section 6.3.5).

In order to experimentally evaluate the chemical environment of Mn on the surface of LMO in the presence of CH₃ ligands, we performed inert-transfer XPS (K-alpha system, Thermo Fisher Scientific) on an LMO pellet after exposure to TMA, as described in Section 6.2.4. LMO pellets were also prepared with no ALD treatment and one full TMA/H₂O ALD cycle for comparison. All three samples were transferred under inert environment into the XPS. The Mn-3s splitting is evaluated for all three samples to measure changes in the average oxidation state of Mn (Figure 6.4) [351]. The uncoated (bare) LMO pellet exhibits a Mn-3s splitting of 5.09 eV (Figure 6.4a), which corresponds to an average Mn oxidation state of ~ 3.3 , close to the expected value of 3.5 for equal portions of Mn⁴⁺ and Mn³⁺ present in stoichiometric LiMn₂O₄ (see correlations in Figure 6.4b). Our XPS measurements indicate 11% carbon on



Figure 6.4.: Inert transfer X-ray photoelectron spectroscopy of Mn 3s peaks for bare uncoated LMO, LMO exposed to a single TMA pulse, and LMO exposed to a full ALD Al₂O₃ cycle of TMA and H₂O along with (b) apparent average oxidation states of these samples based on known Mn 3s splitting of various manganese oxides [351].

the bare LMO substrate, which may suggest some residual surface carbonate which could contribute to the lower-than-expected Mn oxidation state. Following exposure to TMA, we observe an increase in Al (4 % overall) and an increase in C to 15% overall, suggesting the formation of surface Al* and CH_3^* species. The measured Mn-3s splitting also increases to 5.29 eV, indicating electron transfer to (reduction of) surface Mn atoms upon TMA exposure. This is consistent with the electronic structure changes predicted by DFT (Figure 6.2a-b), which suggest that surface Al* and CH_3^* groups act as Lewis bases upon TMA exposure (Figure 6.3) and donate electron density to surface Mn.

Following H₂O exposure, the Al concentration remains constant, and the carbon concentration decreases to 11%, suggesting that CH_3^* groups are removed. However, the Mn-3s splitting in Figure 6.4a increases further to 5.41 eV upon H₂O exposure, corresponding to a decrease in the average Mn oxidation state from ~3 to ~2.8 according to the calibration in Figure 6.4b. This would seem to indicate further electron transfer (reduction) to surface Mn upon H₂O exposure. Replacement of electron donating CH_3^* groups with electron withdrawing OH* groups upon H₂O exposure is seemingly inconsistent with further electron transfer to surface Mn. We



Figure 6.5.: Inert transfer X-ray photoelectron spectroscopy of C 1s peaks for bare uncoated LMO, LMO exposed to a single TMA pulse, and LMO exposed to a full ALD Al_2O_3 cycle of TMA and H_2O .

suggest instead that the decrease in the average oxidation state of Mn measured by XPS following the H₂O exposure may be due to a change in the sampling depth of the XPS measurement. Specifically, after the H₂O exposure, Al₂O₃ forms on the surface of LMO and reduces the amount of electrons which escape from the bulk LMO during XPS measurement such that a larger fraction of surface Mn is represented in the XPS measurement. Near-surface Mn is expected to be in a more reduced form than Mn in the bulk LMO due to the Lewis basicity of surface AlO_xH_y, such that a more surface-sensitive XPS measurement would lead to a measurement of lower average oxidation state. This conclusion is supported by the attenuation of the Mn-3s signal in Figure 6.4, where the peak at a binding energy of ~83.5 eV has a height above the background of 9310 counts s⁻¹ for the bare sample, 8860 counts s⁻¹ for the TMA-exposed sample (4.8% attenuation), and 6450 counts s⁻¹ for the TMA/H₂O-exposed sample (30.8% attenuation).

Examination of the C 1s peak following TMA exposure in Figure 6.5 further supports the conclusions that the CH_3^* is bound to surface oxygen as a Lewis base. The C 1s spectra were obtained from the same samples used in Figure 6.4 and measured under the same conditions. The main C 1s peak for the bare LMO sample has a fitted peak center at 284.9 eV. Upon TMA exposure, we observe an increase in intensity of this peak, which arises from the appearance of a broad feature with a fitted peak center at a higher binding energy of 285.7 eV, evident in Figure 6.5 as an apparent peak shift to higher binding energy upon TMA exposure. When CH₃ is bound to more electronegative oxygen in methoxy groups, the C 1s peak is observed at a higher binding energy of 285.9-286.5 eV [352]. Conversely, in methalocene complexes, when carbon is in the presence of electropositive metals (e.g. Mn, Fe, Co), the C 1s peak is observed at a lower binding energy of 284.6-284.8 eV [353]. The observed shift in C 1s to higher binding energy in Figure 6.5 is therefore consistent with CH₃* acting as a Lewis base bound to electronegative surface oxygen upon TMA exposure. The changes observed in the C 1s peak upon TMA exposure are reversed upon H₂O exposure, suggesting that the CH₃* is removed from the surface, and providing further support that the increase in C 1s signal upon TMA exposure arises from CH₃*.

6.3.4 Structure-Sensitivity of TMA Decomposition During ALD

In order to probe the structure-sensitivity of TMA reaction at chemically distinct film nucleation sites on LMO electrode particles, and to establish more general descriptors for TMA ALD chemistry on reducible oxide surfaces, we consider the Lewis acidity (reducibility) of Mn ions present at various crystalline facets and terminations of LMO. Building upon the fundamental chemical details of TMA reactions on LMO outlined above, we analyze the mechanistic details on different LMO surface facets and terminations (Figure 6.6a). The DFT-calculated free energies for different intermediates along the TMA decomposition reaction coordinate are plotted for different surface terminations in Figure 6.6b. The notation for different surface terminations in Figure 6.6a corresponds to that in Ref. [200]. Further details on the slab models are included in Appendix D, Figure 6.1. The results of these calculations show that full demethylation of TMA* to Al* + 3 CH₃* is thermodynamically favorable on all surface terminations studied, although the degree of exothermicity is highly variant



Figure 6.6.: Reaction of TMA precursor on different LMO surface facets and terminations. (a) Low-index (001) and (111) terraces, as well as high-index stepped (511) surface terminations, considered in this work. LMO(511) Li/Mn/O-1Ovac includes an oxygen vacancy on the step edge. Notation refers to that used in Ref. [200]. (b) Free energy diagrams for different LMO surface facets and terminations.

(with a range greater than 6.5 eV) depending on the surface termination. This result suggests that, while TMA is likely to react with most features on the TMA surface, there also exists a thermodynamic driving force for this reaction to proceed at certain sites on LMO particles. In particular, TMA decomposition reactions appear to be most exothermic on the high-index (511) stepped surfaces over low-index (001) and (111) terraces.

Kinetic barriers for demethylation are also calculated for the different surface terminations, with the lowest barriers for each step included in Table 6.1, and barriers for additional pathways included in Appendix D, Figures D.2-D.7. The considered kinetic pathways also include reactions that initiate via metastable configurations of the reactants, which may be populated under non-equilibrium conditions. For instance, decomposition of MA* to Al* + CH_3 * from the most stable 3f-d adsorption site on the Li/O-terminated LMO(111) surface requires a high kinetic barrier of 2.54 eV to form Al* + CH_3 *, suggesting this process is unlikely to proceed (Appendix D, Figure D.2h). However, MA* is metastable by 1.14 eV at 3f-c sites with respect to DMA*,

	$\mathrm{TMA}^* \rightarrow$	$\mathrm{DMA}^* \rightarrow$	$MA^* \rightarrow$
	$DMA^* + CH_3^*$	$MA^* + CH_3^*$	$Al^* + CH_3^*$
(111) Li/O	0.73^{+}	0.27	1.02^{+}
(111) Li-rich	1.95	0.78	1.83
$(001) {\rm Mn/O}$	0.00^{\diamond}	1.10	0.51^{+}
(001) Li	0.38^{\diamond}	1.50	1.00
(511) Li/Mn/O	0.09	0.28	0.66
(511) Li/Mn/O-1Ovac	0.12	0.55	0.55

Table 6.1.: Lowest demethylation barriers (in eV) calculated for different surface terminations.[‡]

[‡] Structural details for these, as well as additional demethylation pathways, are included in Appendix D, Figures D.2-D.7.

[◦] The calculated barriers for the TMA^{*} → DMA^{*} are for dissociation of -CH₃ groups to Mn atoms on the (001) surfaces. As mentioned in the text, -CH₃ groups are more stable when bound to O, and we calculate that diffusion from Mn to O sites on the (001) surfaces is facile (see Appendix D, Figures D.5d and D.8).

⁺ These represent barriers from metastable configurations of the initial state, as mentioned in the main text. Corresponding structures, as well as other calculated intrinsic barriers for alternate pathways may be referenced in Appendix D, Figures D.2-D.8.

and may decompose to $Al^* + CH_3^*$ with a much lower intrinsic kinetic barrier of 1.02 eV (shown in Figure 6.2c and Appendix D, Figure D.2i). While demethylation to lattice oxygen atoms is, in general, kinetically facile at ALD-relevant temperatures (intrinsic barriers less than 1.39 eV based on approximations discussed in Section 6.2.1), some demethylation steps may have high activation barriers on more lithium rich surfaces, such as the (001) Li and (111) Li-rich terminations. We attribute the larger barriers on these surfaces to Coulombic repulsion between the adsorbates and extra Li ions at the surface (see Appendix D). In these select cases, reaction thermodynamics for individual demethylation steps are also less exothermic in comparison to the other surface terminations considered. We note, however, that demethylation may also occur through other mechanisms, such as methyl recombination, to form ethane or reaction with trace surface hydroxyls to form methane [225].

6.3.5 Descriptors for ALD Thermochemistry on LMO

The trends in Figure 6.6 suggest that the TMA reaction is most exothermic at steps and defect sites on LMO, since demethylation is most exothermic on (511) surfaces in comparison to the low-index (001) and (111) facets. As described earlier in the present work, the decomposition of CH_3^* to surface oxygen atoms is also associated with redox, where near-surface Mn ions accept electrons from, and are therefore reduced by, Lewis basic CH_3^* on the surface. In addition, in our previous work, we showed that near-surface Mn ions on stepped surfaces are also more reducible through formation of oxygen vacancies $V_{O}^{::}$ [200], suggesting that the electron accepting behavior of high-index stepped surfaces may underpin the thermochemical trends of these two analogous redox reactions. Thus, V_O° may be considered as a potential descriptor for the reaction thermodynamics of TMA at different LMO surfaces. We therefore propose that the reducibility of the surfaces where the TMA demethylation reaction is most facile is directly related to the Lewis acid-base chemistry involving CH_3^* adsorbates as electron donors and near-surface Mn ions as electron acceptors. This underlying acid-base chemistry, involving reduction of near-surface Mn ions. further points to the physical basis of $V_O^{\cdot \cdot}$ as a chemical descriptor for these reactions.

The free energies for all steps along the demethylation reaction coordinate are therefore considered as a function of the calculated $V_{O}^{"}$ formation energies ($\Delta E_{V_{O}^{"}}$)65 for each corresponding surface termination. As shown in Figure 6.7a, each of the demethylated intermediates exhibit linear free energy relationships with $\Delta E_{V_{O}^{"}}$. The exception to these relationships is the adsorption free energy of TMA*, which lacks dependence on $\Delta E_{V_{O}^{"}}$) since TMA is a closed-shell molecule in the gas phase and therefore does not induce any net charge transfer to LMO upon adsorption. As demethylation proceeds, however, two electrons are transferred to Mn 3*d* states as CH₃ is transferred to the LMO surface (see schematic in Figure 6.3c). The slopes of the free energy relationships in Figure 6.7a gradually increase along the reaction coordinate (from TMA* to Al* + 3 CH₃*) and are related to the total number of



Figure 6.7.: Relationship between surface reducibility and the TMA decomposition free energy surfaces presented in Figure 6.6b. (a) Linear free energy relationships between decomposed TMA compounds on LMO versus the oxygen vacancy formation energies ($\Delta E_{V_{O}}$) calculated in Ref. [200] on each surface termination, which are labeled accordingly on the plot. (b) Relationship between linear regression slopes in (a) and the number of electrons added to Mn 3*d* states for the corresponding step along the reaction coordinate. The slope of 0.53 (approximately $\frac{1}{2}$) corresponds to the two electrons (in slope denominator) transferred from the Al(CH₃)_x* adsorbate to LMO for each demethylation step in the pathway.

electrons that have been transferred to LMO with respect to the clean LMO surface and gas phase TMA reference. These correlations, shown in Figure 6.7b, are related by a factor of approximately $\frac{1}{2}$, corresponding to the two electrons that localize on Mn per $V_O^{::}$ formed on the LMO surface. Based on these findings, the free energy of an intermediate, *i*, along the TMA decomposition reaction coordinate (ΔG_i) may be expressed as a simplified function of the $V_O^{::}$ descriptor:

$$\Delta G_i = \Delta n_{electrons,\,i}^{Mn\,3d} \frac{\Delta E_{V_O^{..}}}{2} + \beta_i \tag{6.5}$$

In equation 6.5, $\Delta n_{electrons,i}^{Mn\,3d}$ is the number of electrons transferred to Mn 3d states for intermediate i with respect to the LMO surface and gas phase TMA reference state, and β_i is a constant specific to each intermediate, *i*. Correspondingly, differentiation of equation 6.5 leads to the relationship observed in Figure 6.7b.

$$\frac{\partial \Delta G_i}{\partial \Delta E_{V_{\alpha}^{\circ}}} = \frac{1}{2} \Delta n_{electrons,i}^{Mn\,3d} \tag{6.6}$$



Figure 6.8.: Differences in TMA reaction and Al_2O_3 ALD film growth between early and later ALD pulses. The silver polyhedra indicate the position of the Al^{3+} ion coordinated to lattice oxygen atoms. During initial ALD pulses (left), structure sensitivity dominates, passivating most defects on the surface, which are likely more susceptible to Mn loss. In later cycles (right), film nucleation to terraces, including Al^{3+} occupation of the 16c diffusion channels leading to kinetic limitations to electrochemical performance.

The findings imply an inherent dependence of the reactivity of the ALD precursor on different surface features of LMO particles, with a preference for sites on the surface that are more reducible (electron accepting). The results suggest that such mechanisms and descriptors are likely to be relevant toward a broader understanding of ALD surface chemistry involving different precursor and substrate chemistries. The DFT-calculated $\Delta E_{V_{O}}$ for a given surface termination is representative of a local, near-surface, electronic structure descriptor for the reactivity of the TMA molecule near these features. Similar electronic structure descriptors, based on the O 2*p* band center, have been developed recently for ethylene carbonate reaction energies at Li-ion battery electrode surfaces [258]. The structure-sensitivity arguments may therefore also be relevant for electrode-electrolyte interfacial reactions involving electron transfer, such as hydrogen abstraction during the decomposition of ethylene carbonate [210, 212, 256, 257]. The lower $\Delta E_{V_{O}}$ on LMO(511) stepped surfaces suggests a strong thermodynamic driving force for TMA to selectively decompose near steps and defects on LMO particles, which, due to their reducible nature, may also be more susceptible to Mn charge disproportionation and dissolution. This result is particularly relevant during early ALD pulses, wherein Al_2O_3 films deposit on LMO with sub-monolayer coverages [225]. As summarized in Figure 6.8, the findings suggest that the structure-sensitivity of the first TMA half-cycle is likely to passivate most defect sites on the surface at the onset of film growth, while forming a partial film on low-index terraces of electrode particles. This may explain modest enhancement in electrochemical cycling performance with only \sim 1-2 ALD cycles [225], where we hypothesize that the sites on the surface most susceptible to Mn loss are protected by the partially formed Al_2O_3 coating. In later ALD cycles, film growth extends to low-index terraces where dissolution is less facile. Precursor decomposition on terraces may lead to Al^{3+} occupation of 16c sites, as shown in Figure 6.1b, which are the Li⁺ diffusion channels in LMO. In turn, full TMA decomposition on terrace sites is likely to lead to severe kinetic limitations during electrochemical cycling.

6.4 Conclusions

We have described mechanisms for the onset of ALD Al_2O_3 growth on LMO through theoretical calculations and experimental characterization. We find that it is thermodynamically favorable for TMA, a common ALD precursor, to lose its -CH₃ groups to oxygen atoms on the LMO surface. The amphoteric nature of the -CH₃ ligand enables electron transfer from the adsorbate to LMO, reducing near-surface Mn^{4+} ions to Mn^{3+} . The DFT-predicted Lewis acid-base chemistry is supported by inert-transfer XPS experiments which show a reduction in the oxidation states of surface Mn ions upon TMA exposure and a shift in the C 1*s* peaks, consistent with -CH₃ binding to electronegative oxygen sites on the LMO surface. The strong adsorption of CH₃* to oxygen sites on the LMO surface partially blocks TMA adsorption, leading to formation of a sub-monolayer Al₂O₃ coating in early ALD pulses

[225]. The mechanisms outlined in the present work suggest that the onset of film growth, in addition to being highly non-uniform, is also structure-sensitive, with the TMA precursor reacting most favorably on more reducible surface features of LMO particles. Due to their near-surface electronic structure and propensity to participate in redox reactions, these sites on the LMO surface are also those which are most likely to undergo Mn disproportionation and dissolution. These mechanistic interpretations help explain trends suggesting optimal electrochemical performance with only 1-2 ALD cycles, corresponding to a sub-monolayer coating that selectively stabilizes surface defect sites. Informed by the fundamental chemistry of TMA reaction with the LMO surface, we have identified oxygen vacancy formation energies as a comprehensive and quantitative descriptor for the relative Lewis acid-base behavior between the ALD precursor and the substrate, which enables efficient analysis and prediction of ALD reaction thermochemistry. We anticipate that this molecular-level descriptor, and the fundamental surface chemistry that it represents, is transferrable to the study of ALD film growth on battery electrodes using different precursors, and that such insights may be used to rationally tailor growth of protective coatings and their interfacial structures with the electrode substrate. Beyond ALD for energy storage applications, we expect that such descriptor-based analyses can also be applied more broadly to further understand thin film growth at the atomic scale within semiconductor surface science research.

Supporting Information for this chapter is included in Appendix D.

R.E.W. and J.G. performed the DFT analysis and wrote the associated section of the manuscript. M.J.Y., S.L., and J.W.E. performed the experimental studies and wrote the associated sections of the manuscript.

7. HIGH RATE SPINEL LIMN₂O₄ (LMO) FOLLOWING CARBONATE REMOVAL AND FORMATION OF LI-RICH INTERFACE BY ALD TREATMENT

This chapter is reproduced with the permission of the American Chemical Society from: Matthias J. Young, Steven Letourneau, Robert E. Warburton, Wesley M. Dose, Christopher Johnson, Jeffrey Greeley, Jeffrey W. Elam; High Rate Spinel LiMn₂O₄ (LMO) Following Carbonate Removal and Formation of Li-rich Interface by ALD Treatment. *The Journal of Physical Chemistry C* **2019**, *123*, 23783-23790.

Recent work has identified enhanced charge storage capacity in the spinel lithium manganese oxide ($LiMn_2O_4$;LMO) lithium ion battery cathode upon a single atomic layer deposition (ALD) cycle comprised of one chemical exposure of trimethylaluminum (TMA) and one exposure of water (H_2O) . Here, we report further study of the rate capability following one TMA/H_2O exposure and identify enhanced rate capability versus pristing LMO. To understand this effect, we experimentally probe the surface composition of LMO with TMA/H₂O treatment using X-ray photoelectron spectroscopy (XPS) measurements with inert-transfer. This includes a study of the LMO surface properties following TMA exposure before exposure to H_2O . We identify the removal of a surface carbonate layer from LMO upon TMA exposure, and the formation of a Li-rich aluminum oxide surface layer upon subsequent H_2O exposure. We also observe a previously undescribed phenomenon of Li ions depleting from the LMO surface upon TMA exposure and returning upon H_2O exposure. These effects are connected with the enhanced rate capability of ALD-coated LMO and are related to a range of emerging studies on carbonate surface layers in battery cathodes, as well as the use of ALD to stabilize battery interfaces.

7.1 Introduction

Spinel lithium manganese oxide (LiMn₂O₄; LMO) is one of the first cathode materials discovered for lithium-ion batteries [44] and has been widely studied over the last 40 years [221]. The three-dimensional lithium diffusion channels in LMO provide faster charging rates than other cathode materials [313, 354], and Mn is considered more environmentally friendly than other transition metals commonly used in battery cathodes. However, LMO suffers from poor cycle stability [209], which has been correlated with the dissolution of manganese into the electrolyte [355]. Once in solution, manganese has been found to migrate to the counter electrode (anode) and lead to high charge-transfer resistance [139]. Manganese dissolution has been hypothesized to proceed via disproportionation [228] exacerbated by electrolyte decomposition at the LMO surface [247], attack by hydrofluoric acid [249], and other surface-based mechanisms [62, 233, 348, 75]. While the mechanism for manganese dissolution is debated [221], the LMO-electrolyte interfacial properties are expected to control the dissolution process, and surface modification has been widely pursued to stabilize LMO.

LMO cycling stability has been improved using thin-film coatings deposited using a variety of techniques. Broadly, sol-gel synthesis [356, 329], precipitation [357], electroless deposition [227], chemical vapor deposition [179], and atomic layer deposition (ALD) [358, 225, 140, 359] have been studied with recent examples of coatings including gold [227], graphene [179], and metal oxide [225, 359]. Of the various available coating techniques, ALD is an ideal chemical approach for modifying LMO surfaces as it provides conformal, uniform coatings with atomic-scale control of the thickness and composition [360, 361, 362]. Recent work from our groups employed *in situ* measurements and *ab initio* modeling to study the nucleation and growth of ALD aluminum oxide (Al₂O₃) on LMO to understand the impact of Al₂O₃ on LMO performance [225]. In this prior work, six ALD cycles of trimethylaluminum (TMA) and water (H₂O) provided enhanced stability with a ~90% capacity retention at 100 charge-discharge cycles but at the cost of a ~20% reduction in the initial capacity. Interestingly, in this previous work, we observed a ~10% higher charge capacity with one ALD cycle of TMA/H₂O on LMO than was observed for pristine LMO. We expect that this enhanced capacity may arise from the formation of either a surface layer with enhanced lithium-ion mobility, which improves rate capability, or of a redoxactive surface layer, which adds capacity to the LMO. In both of these scenarios, the interfacial structure is expected to drive enhanced performance. Here, we perform additional electrochemical characterization, in-depth X-ray photoelectron spectroscopy (XPS) characterization, and Hubbard-corrected density functional theory (DFT + U) modeling to reveal the impact of one TMA/H₂O ALD cycle on the interfacial properties and charging performance of LMO in an effort to understand the capacity enhancement observed in this prior study.

7.2 Results and Discussion

In the first part of this work, we study the rate performance of LMO with and without one cycle of ALD Al₂O₃ to identify whether we observe either enhanced rate capability or added capacity in LMO coated with one ALD cycle of Al₂O₃ at different charge rates. Figure 7.1 presents a comparison of cycling data for the uncoated (bare) LMO composite electrode and LMO composite electrode coated with one cycle of TMA/H₂O. In Figure 7.1a, the first-cycle charge and discharge curves at a charge rate of 0.1C are compared. Examination of the first charge/discharge profiles is helpful in understanding the formation of the solid electrolyte interphase (SEI) layer and can provide insight into differences in surface composition and reactivity. In Figure 7.1a, we observe that on the first charge cycle bare LMO exhibits a peak in potential at a charging potential of ~4.1 V (and a capacity of ~40 mAh/g). Such a feature was observed on the first charge cycle in four bare LMO cells we tested. The feature varied in intensity among the replicates, where the trace in Figure 7.1a represents the most prominent feature we observed. We also found evidence of this feature in data for the first charge cycle of LMO presented in prior work [174, 363]. As discussed in detail below, this feature suggests a temporary degradation process or barrier to charge transport in line with a surface carbonate layer present on LMO. This feature was not observed for the TMA/H₂O-treated LMO; however, an analogous peak in potential was observed below 10 mAh/g, which could arise from a surface barrier layer introduced by the ALD coating. We also observe that the overall charge capacity of the bare LMO was 130 mAh/g - 5 mAh/g larger than the 125 mAh/g capacity observed for the TMA/H₂O-treated LMO. These data may suggest that the TMA/H₂O contributed to passivating or stabilizing the surface of the LMO, reducing SEI formation.



Figure 7.1.: Effect of 1 cycle of TMA/H_2O exposure on electrochemical cycling of LMO composite cathodes including (a) 1^{st} cycle charge and discharge at 0.1C and (b) rate capability between 0.1C and 2C. The multiple traces in (b) reflect duplicate measurements.

The first charge/discharge cycling data in Figure 7.1a also suggest that the ALD treatment may decrease the realizable capacity of the LMO at low charge rates. During the first charge in Figure 7.1a, the second plateau at 4.15 V was not as pronounced for the LMO treated with TMA/H_2O than that for the bare LMO, and on discharge, the corresponding first plateau had less capacity for the TMA/H_2O -treated LMO than that for the bare LMO. These observations suggest that this charging process did not go to completion in the presence of the ALD surface layer. Also, the LMO treated with TMA/H_2O exhibited a lower total discharge capacity than the

bare LMO (115 vs. 121 mAh/g, respectively). These data suggest that the ALD treatment may limit the realizable capacity of the LMO, which is at odds with the prior observation that one ALD cycle leads to an enhanced capacity over no ALD treatment. Below, we elucidate the reasons for the deviation between these results and our prior conclusions.

In Figure 7.1b, these same coin cells were cycled at increasingly higher charge/ discharge rates. At charge rates ≤ 0.5 C, the trend observed in Figure 7.1a holds, that the capacity is significantly higher for the bare LMO than that for the LMO treated with TMA/H₂O. However, at a rate of 1C, the capacities for the bare LMO and the LMO treated with TMA/H₂O are roughly equivalent. At a charge rate of 2C, the capacity of the LMO treated with TMA/H₂O is 68 mAh/g, substantially higher than the capacity of 22 mAh/g measured for the bare LMO at 2C. These data suggest a surprising result, that the LMO treated with TMA/H₂O yields a lower maximum capacity but provides substantially improved rate capability, with a 3-fold capacity enhancement at 2C.

These data shed new light on our prior result, which showed that one ALD cycle led to a higher LMO capacity at 1C [225]. Specifically, these data suggest that the capacity enhancement observed in our prior work may arise from enhanced rate capability following the ALD treatment, not from added capacity. Enhanced rate capability in battery cathode materials following ALD treatment with ALD Al_2O_3 is also reflected in prior studies, including Ni-Mn-Co (NMC)-based cathodes [361] and $LiCoO_2$ cathodes [364]. This higher rate capability has been hypothesized to originate from facile Li transport in the ALD-deposited layers [364]. However, thicker ALD films yield lower discharge capacity and rate capability [225], with the effect limited to thin ALD films deposited using fewer than five ALD cycles. This suggests that the LMO surface chemistry is the key to understanding the origins of this enhanced rate capability.

In Figure 7.2 and Table 7.1, we examine the effect of pretreatment temperature and TMA exposure on the LMO surface composition. Following TMA exposures, the



Figure 7.2.: XPS spectra in the C 1s region for LMO collected following inert transfer after (a) 266°C pre-anneal in argon with varying TMA exposure times and (b) 500°C pre-anneal in argon with TMA and H_2O exposures. The inset in (a) depicts a scheme of the etching from TMA exposure.

LMO samples were immediately loaded into the XPS using an inert transfer module to limit exposure to H₂O, O₂, CO₂, etc. and preserve unreacted surface ligands. During the ALD, the LMO samples are heated to >200 °C, and so, the control sample of bare LMO in Figure 7.2a was also heated to >200 °C. Surprisingly, the surface composition for bare LMO measured by XPS did not match our expectations for ideal LiMn₂O₄. The XPS data indicated a surface rich in lithium (22.4%), carbon (25.0%), and oxygen (39.8%), with little Mn (12.8%). In Figure 7.2a, we observe a strong carbonate peak in the C 1s XPS region at a binding energy of ~288 eV, which, coupled with the surface composition rich in Li, C, and O, would suggest the presence of Li₂CO₃. The observation of a Li₂CO₃ surface layer on LMO here complements other recent work, which has highlighted the importance of a Li₂CO₃ surface layer in the electrochemical performance/stability of other cathode materials including Ni-rich LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ [365, 366, 367, 368] and LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ [369].

We observe that the XPS carbonate feature for the LMO sample in Figure 7.2a decreases with increasing TMA exposure, suggesting that TMA exposure is removing

	Li %	Al $\%$	C%	O%	Mn $\%$
ideal $LiMn_2O_4$	14.3	0.0	0.0	57.1	28.6
bare LMO (266 $^{\circ}$ C)	22.4	0.0	25.0	39.8	12.8
5 s TMA	10.0	6.3	26.5	45.1	12.2
120 s TMA	0.0	10.6	30.3	47.3	11.8
bare LMO (500 $^{\circ}$ C)	10.7	0.6	11.5	45.8	31.5
15 s TMA	1.4	4.6	14.5	52.5	27.0
TMA/H_2O full cycle	14.1	4.2	12.4	51.2	18.7

Table 7.1.: Effect of Pretreatment Temperature and TMA Exposure on LMO Surface Composition

carbonate from the LMO surface. This may proceed, for example, by the reduction of Li₂CO₃ to release CO₂ according to Li₂CO₃ + Al(CH₃)₃ \rightarrow 2LiCH₃ + CO₂(g) + $AlOCH_3$, as depicted in the inset of Figure 7.2a. In this potential reaction mechanism, the unstable $LiCH_3$ species is expected to react with surface hydroxyls to produce $LiCH_3 + -OH \rightarrow -OLi + CH_4$. The -CH₃ carbanion (in $LiCH_3$ or $Al(CH_3)_3$) is also expected to react with $-CH_3$ carbocation surface groups according to $LiCH_3$ + $-OCH_3 \rightarrow -OLi + C_2H_6$, returning Li⁺ to the bulk LMO and yielding ethane as a byproduct. This reaction pathway helps to explain the ethane observed by mass spectrometry during TMA exposure to LMO, as reported in our prior work [225]. For the XPS data reported here, we do not observe a decrease in the percentage of surface C or O by XPS; however, these species percentages are offset by the removal of Li, which constitutes >20% of the starting film and is reduced to 0% after a 120 s TMA exposure. Additionally, upon TMA exposure, the carbonate feature at a binding energy of ~ 288 eV in the C 1s XPS in Figure 7.2b also decreases, providing further support that TMA exposure is removing surface carbonate from LMO. We note that using a 500 °C preanneal substantially reduces the amount of surface carbonate (Figure 7.2b), as discussed below, but this carbonate is still removed by the subsequent TMA exposure. In our prior work [225], we employed Fourier transform infrared (FTIR) spectroscopy during TMA exposure to LMO and observed the removal of unknown features at 1420-1510 cm⁻¹, as well as 1091 and 1320 cm⁻¹. Considering the XPS data presented here, we recognize that these FTIR features can be attributed to Li_2CO_3 [370, 371, 372] and ROCO₂Li [372, 373] and that these FTIR data support the indications from XPS that TMA exposure removes carbonate from the surface of LMO.



Figure 7.3.: DFT+U calculations of Gibbs Free Energy of formation for surface complexation of CO₂ onto (a) (111), (b) (001), and (c) (511) LMO surface facets, along with (d) the free energy of TMA surface complexation on these LMO surface facets with CO₂ displacement.

In Figure 7.3, DFT + U calculations of single-molecule CO₂ adsorption on LMO surfaces provide insight into the removal of a surface carbonate by TMA exposure. Our calculations here are on the stable (001), (111), and (511) surfaces of LMO [200] and indicate that CO₂ adsorption onto the (001) LMO surface is favorable at room temperature (Figure 7.3a-c). However, the adsorption and decomposition of TMA are predicted to be more thermodynamically favorable (Figure 7.3d), where $-CH_3$ groups easily decompose and migrate to oxygen atoms on the LMO surface [225, 374], displacing CO₂. These models are based on single-molecule CO₂ adsorption and are expected to hold under small fractional surface coverages of CO₂ on LMO. While we expect the formation of lithium carbonate on the surface of LMO, these calculations provide a fundamental basis for understanding the initiation of lithium carbonate formation and removal by TMA.

The removal of surface carbonate during TMA exposure helps to explain the difference in first-cycle charging behavior we observed in Figure 7.1a. The electrochemical oxidation of a surface carbonate is expected to proceed by $2Li_2CO_3 \rightarrow 4Li^+ + 2CO_2$ + O₂ + 4e⁻, giving rise to additional features in the initial charging curve, as observed at ~ 3.7 V in the LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ cathode [365, 366, 368]. We attribute this reaction to the irreversible feature we observe at 4 V and $\sim 40 \text{ mAh/g}$ in Figure 7.1a. The release of CO_2 and O_2 during electrochemical operation is undesirable as it leads to cell pressurization, could damage ionic and/or electronic pathways, and may upset the conductive network in the electrodes; therefore, the removal of the Li_2CO_3 prior to electrochemical cycling is preferred. Furthermore, the transport of lithium through any remaining surface carbonate is also expected to be slow - the extrapolated room-temperature ionic conductivity of lithium carbonate has been measured to be $\sim 10^{-9}$ S/cm [375], and molecular dynamics simulations predict the diffusion coefficient of Li⁺ in lithium carbonate to be on the order of 10^{-12} cm²/s [376]. We note that while the lithium-ionic conductivity of ALD-grown Al_2O_3 is also very low [359], a single ALD Al_2O_3 cycle is insufficient to form a continuous coating on the LMO surface. Therefore, the removal of a surface carbonate upon TMA exposure is expected to increase the rate capability of LMO, as observed in Figure 7.1b. In general, the removal of surface carbonates by TMA is expected to influence the composition and structure of the electrode-electrolyte interface for any battery material and will likely prove important for understanding the impact of ALD on the performance of other battery electrodes.

While the removal of a surface carbonate by TMA is a key point in understanding the effect of TMA on the performance of LMO, we are also interested in understanding the surface chemistry effects of TMA on LMO without surface carbonates. In an effort to remove the surface carbonate and study TMA reaction on pristine LMO, we heated the LMO to 500 °C under argon atmosphere in Figure 7.2b and observed a sharp decrease in the overall C 1s signal for the bare LMO by XPS, as well as a marked drop in the carbonate feature of the bare LMO versus the bare LMO in Figure 7.2a, which was exposed to a 266 °C Ar preanneal. While changes in the O 1s peak might be expected to reflect the removal of carbonate at elevated temperatures, these changes were obfuscated by O present in the underlying LMO. The C/Mn ratios for LMO following 266 and 500 °C preannealing are 1.95 and 0.36, respectively, reflecting an 82% decrease in surface carbon by preannealing at 500 °C in argon. This is consistent with FTIR investigations in our prior study, where the intensity of features related to carbonate was diminished upon heating at 400 °C in argon [225]. This is also in agreement with prior studies, in which surface carbonates have been removed from lithium-ion battery cathode materials by heating to ~ 500 °C atmosphere [374]. Together, these experimental data provide strong evidence that LMO surface carbonate is removed by the inert bakeout of LMO at >500 °C. The loss of carbonate at higher temperatures is consistent with the weak binding of CO_2 we calculated in Figure 7.3a-c. For example, the free energy of CO_2 adsorption is -0.1 eV on the LMO(001) surface at room temperature. Additionally, adsorption entropy [377] drives the release of CO_2 from all three model surfaces of LMO at 400 °C in Figure 7.3d. In the experimental system here, the carbonate must decompose before CO_2 is released, which presumably has a higher barrier than simple CO_2 desorption. The surface carbonates we observe are expected to form due to exposure to CO_2 , and the extent of carbonate formation is likely dependent on the storage conditions and age of an LMO supply used in the laboratory. Heat treatment of LMO at >500 °C in argon atmosphere provides a convenient method of removing surface carbonate and could be used immediately to build on prior studies of LMO for more consistent LMO composition. Further studies outside the scope of this work are needed to explore the impact of Ar preanneal temperature and time on carbonate removal and ultimately battery performance.



Figure 7.4.: XPS spectra for the (a) Li 1s, (b) Mn 2p, (c) Al 2p, and (d) O 1s regions for LMO collected following inert transfer after 500°C pre-anneal in argon with TMA and H₂O exposures. The inset in (a) depicts the proposed mechanism for the Li breathing we observe.

In the following, we study the evolution of the LMO surface during TMA/H2O exposures on LMO, which was preannealed in Ar at 500 °C. These studies are under the same conditions and consistent with our prior work where we study the acid-base chemistry of TMA exposure to LMO [261]. Figure 7.4 presents the XPS traces for each constituent element (except carbon) present at the Al_2O_3/LMO surface for bare LMO, LMO after TMA exposure, and LMO after TMA/H₂O exposure. The
corresponding XPS trace of carbon is presented in Figure 7.2b. The data presented in Figure 7.4 correspond to the conditions in the bottom of Table 7.1. Concomitant with the removal of the C 1s carbonate feature at ~288 eV upon TMA exposure, we observe a decrease in the surface lithium concentration for LMO preannealed at both 266 and 500 °C, as delineated in Table 7.1. The observed decrease in surface lithium upon TMA exposure could be partially attributed to the removal of lithium carbonate as outlined above. However, interestingly, the Li 1s XPS peak intensity returns upon H₂O exposure as depicted within Figure 7.4a. Surprisingly, the percentage of Li following TMA/H₂O exposure is higher than the percentage of Li in the bare LMO sample. This result suggests that surface lithium does not leave altogether but is pushed into the subsurface upon TMA exposure and then returns to the surface upon H₂O exposure. The overall surface composition of the Al₂O₃/LMO surface following TMA and H₂O exposures is presented in Table 7.2. These LMO samples were all preannealed under Ar at 500 °C to remove surface carbonates.

Table 7.2.: XPS Surface Stoichiometry of Al_2O_3/LMO Interface of LMO with 500 °C Preanneal in Ar, Including Bare LMO, LMO with TMA Exposure, and LMO with TMA/H₂O Exposure.

$Al_x Li_y Mn_z O_4$	Al_x	Li_y	Mn_z
ideal spinel LMO	0	1	2
bare LMO (500 $^{\circ}$ C)	0.05	0.93	2.76
LMO with 15 s TMA	0.35	0.11	2.06
LMO with TMA/H_2O	0.33	1.10	1.46

The apparent breathing (i.e. reversible spatial redistribution) of lithium to and from the external LMO surface reflected in these data does not seem to be related to the carbonate etching described above, and the XPS traces of other elements are consistent with ideal Al_2O_3 growth on the LMO surface. We observe a monotonic decrease in the Mn 2p counts in Figure 7.4b following both TMA and H₂O exposures, which we attribute to the attenuation of Mn 2p signal by the ALD coating. We observe an increase in the Al 2p intensity upon TMA exposure in Figure 7.4c, which remains relatively constant after H₂O exposure and indicates the reaction of TMA at the surface. We also observe a qualitative change in the O 1s XPS features in Figure 7.4d, which suggests the growth of ALD Al₂O₃ on LMO. We observe an increase in O 1s intensity at a binding energy between 531 and 534 eV, which corresponds to the formation of Al₂O₃ [378], and a decrease in O 1s intensity at a binding energy of 530 eV, which corresponds to an attenuation of the oxygen signal coming from the underlying LMO.



Figure 7.5.: Impact of surface termination on stability of lithium in the LMO(111) surface layer including (a) lithium vacancy formation energy versus depth from the LMO surface for LMO with varying surface terminations expected over the course of TMA/H₂O precursor exposures (b) relaxed surface structure of $-Al(OH)_2$ terminated LMO indicating that Li is drawn into the aluminum oxide surface layer. The values in parentheses of (a) correspond to the number of electrons transferred to LMO in the presence of each charged surface adsorbate.

We suggest that the breathing of Li arises from electrostatic forces at the LMO surface. We propose that Li is pushed away from the external LMO surface upon TMA exposure due to electrostatic repulsion from Al^{3+} incorporated into the surface of the LMO, as well as positively charged -CH₃ groups bound to surface O [261]. This

is analogous to the observation of positively charged Au coatings leading to lithium depletion at the LMO surface [213]. Figure 7.5a presents DFT + U-calculated Li vacancy formation energy vs. depth into the LMO(111) surface. The Li vacancy formation energy in pristine LMO (black data series in Figure 7.5a) is predicted to be ~ 3.9 eV in the bulk and 4.4 eV at the LMO surface (depth of 0 Å in Figure 7.5a). Under the conditions where both Al and $-CH_3$ are present on the surface (orange data series in Figure 7.5a) as expected after a TMA exposure (with the transfer of 4 e^{-1} to LMO to preserve charge neutrality) [225], the Li vacancy formation energy at the LMO surface is significantly reduced to 3.38 eV, which is 0.5 eV more favorable than vacancy formation in the bulk. We therefore expect that upon TMA exposure, Li vacancies will cluster at the LMO surface and Li will be driven into the LMO bulk, as observed experimentally in Figure 7.4a. The exothermicity of the TMA reaction on the LMO surface may help provide thermal energy to overcome kinetic barriers to lithium transport into and out of the subsurface |332|. Upon H₂O exposure, surface CH_3 ligands are expected to leave as CH_4 , while Al and Li are expected to be drawn from the subsurface to form a $\text{Li}_x \text{Al}_{2x/3} \text{O}_3$ surface layer. The increase in surface Li concentration observed by XPS upon TMA/H_2O exposure in Figure 7.4a above the amount observed on bare LMO suggests that this surface layer has a significant amount of Li. If no Li is incorporated into the surface layer, we would expect to see an attenuation of the Li signal consistent with the attenuation of the Mn 2p signal we observe. Instead, we observe an increase in the surface Li concentration from 11% in the bare LMO to 14% after one TMA/H₂O exposure. Assuming that all of the lithium measured by XPS is in the surface layer, the stoichiometry would be $Li_{0.33}Al_{1.89}O_3$. Our DFT + U calculations support these observations. For a model $Al(OH)_2$ -terminated LMO surface (blue data series in Figure 7.5a), designed to represent LMO after TMA/H₂O exposures, Li vacancy formation energy at the surface is predicted to be 4.43 eV, which is 0.5 eV less favorable than in the bulk. We therefore expect that after TMA and H_2O exposures, Li will be drawn from the subsurface and cluster in the aluminum oxide layer. As depicted in Figure 7.5b, the affinity of the surface Al_2O_3 layer for Li is so strong that it causes Li⁺ to relax at a position translated 1.14 Å in the direction of the surface normal. The formation of a lithiumrich aluminum oxide is consistent with prior observations of ALD growth of lithium aluminum oxide, which suggest the favorable incorporation of Li into aluminum oxide layers up to a 1:1 Li/Al ratio [379].

The formation of this Li-rich surface layer upon TMA/H_2O exposure to LMO may help explain the high rate capability observed in Figure 7.1b. The high lithium content is expected to introduce lithium transport pathways and facilitate lithium diffusion between the LMO and electrolyte. Furthermore, the reaction of TMA with LMO to form a Li-rich Li-Al-Mn oxide surface layer is expected to reduce the realizable capacity of the LMO. In Figure 7.1a, we observe a 5 mAh/g decrease in capacity at a 0.1C charge rate from 130 to 125 mAh/g upon TMA/H₂O exposure. Assuming a monodispersed distribution of 0.15 μ m spherical LMO particles based on a BET surface area of $\sim 10 \text{ m}^2/\text{g}$ [225] and an LMO density of $\sim 4 \text{ g/cm}^3$ based on the International Crystal Structure Database structure of LiMn₂O₄ [380], this drop in capacity corresponds to the inactivation of a shell of LMO with a 16 nm thickness. While the high atomic fraction of Al observed after one TMA exposure suggests that Al may occupy interstitial sites near the surface of LMO, leading to some deactivation of the LMO, the expected sub-nanometer coating is not consistent with the deactivation of a 16 nm shell of LMO. Therefore, we suspect that the majority of the additional capacity observed for the uncoated LMO at 0.1C in Figure 7.1a arises from the electrochemical oxidation of surface carbonates and/or SEI formation, which are both mitigated by TMA/H_2O exposure.

7.3 Conclusions

In summary, we identify two substrate effects during the deposition of TMA/H_2O on LMO arising from (1) the reaction of TMA to etch carbonates from the LMO surface and (2) the collective motion, or breathing of Li away from the LMO surface upon TMA exposure, with a return of Li to the surface of LMO upon H₂O exposure. Our study highlights the importance of nonideal/substrate effects in the use of ALD films for battery applications. Batteries require highly reduced (anode) and highly oxidized (cathode) materials, increasing the substrate reactivity with ALD precursors. In a broader scope, this study ties into an increasing number of reports within the ALD community, which have identified nonideal effects that break the mold of conventional ALD and provide new avenues of discovery. A prime example is the recent development of atomic layer etching [381]. Other examples include multilayer deposition of metastable films [382], cation exchange during metal sulfide ALD [383], and sequential infiltration synthesis [384]. Likewise, the importance of substrate reactivity in understanding the nucleation and growth of ALD films we highlight here is increasingly recognized. For example, manganese oxide ALD on soda lime glass was found to leach sodium from the soda lime glass [385], TMA/H₂O on rutheniuminduced redox of the underlying substrate [386], and Al₂O₃ [362, 387].

Within the battery community, the results of this study tie into two emerging themes: (1) the importance of surface carbonates in the electrochemical performance of battery materials and (2) the use of ALD in stabilizing interfaces. This study provides compelling evidence of a surface carbonate present on the surface of LMO, which impacts the first-cycle charging characteristics and rate capability of LMO. This complements other reports identifying the detrimental effect of surface carbonates in Ni-rich cathode materials for lithium-ion batteries [365, 366, 367, 368, 369] and may indicate a broader issue of surface carbonates across cathode materials in general. The routine removal of surface carbonates in battery material studies may be prudent to ensure consistent results. Furthermore, we identify here that either TMA exposure or heat treatment above 400 °C in an inert atmosphere can be used to remove this carbonate layer from LMO. To our knowledge, this is the first report of the use of TMA exposure to remove surface carbonates from lithium-ion battery electrode materials. The removal of surface carbonates may prove to be important for understanding the performance of various cathode materials treated with ALD chemistries [388]. Further

work is required to understand the underlying mechanism and to determine whether the process we observe for LMO is common to other cathode materials.

7.4 Methods

7.4.1 Coin Cell Cycling

For the coil cell cycle rate study, we employed composite cathodes comprised of 84% spinel lithium manganese oxide (LMO, NEI), 8% polyvinylidene fluoride binder (PVDF, Solvay), and 8% conductive carbon (Super P, Timcal). This slurry was applied to an aluminum foil current collector (20 μ thickness) with an 8 MIL doctor blade, and dried overnight under vacuum at 70°C. The mass loading was approximately 5 mg/cm^2 overall and was measured gravimetrically for each of the samples studied in this work to determine the currents for specific cycle rates. For ALD treatment, composite cathodes were loaded into a custom ALD reactor at 200°C [389]. Prior to precursor exposures, the reactor temperature was allowed to stabilize for >15 minutes. The Al_2O_3 ALD cycles consisted of 120 seconds of TMA exposure at a partial pressure of ~ 2 Torr, 60 seconds of N₂ purge, 60 seconds of H₂O exposure at a partial pressure of ~ 3 Torr, and 60 seconds of N₂ purge. The long exposure times for TMA and H_2O were used to allow sufficient time for the TMA to penetrate into the porous network of the composite electrode. Following ALD treatment, the composite electrodes were removed from the reactor, purged in a vacuum oven overnight, then transferred into an argon-filled glovebox for cell assembly. CR2032 coin cells were constructed using 14 mm diameter punches of the LMO composite cathode, 19 mm Celgard separator, 15.9 mm diameter lithium chips (MTI), and $> 50 \ \mu L$ Gen II lithium ion battery electrolyte (ethylene carbonate (EC) and ethyl methyl carbonate (EMC) in a 3:7 ratio by weight, with 1.2 M lithium hexaftuorophosphate $(LiPF_6)$).

7.4.2 X-ray Photoelectron Spectroscopy (XPS) Characterization

We performed XPS measurements using a Thermo Fischer Scientific k-Alpha+ with 1486.6 eV monochromatic Al K α X-rays. We employed an electron beam neutralizer at 0.2V and 130 μ A. Data was obtained and analyzed using Thermo Fischer Scientific Avantage software. All spectra were referenced to the C 1s peak (284.8 eV) and a 30% mixed Gaussian-Lorentzian peak shape was used for both 1s and 2p peaks. Moreover, 2p peaks were constrained according to the spin-orbit split doublet peak areas and full width at half-maximum (fwhm).

XPS was used to examine the surface composition of LMO before and after ALD precursor exposures. We employed stainless steel meshes (Fotofab Inc), each loaded with 100 mg of LMO powder (MTI, ≤ 25 ppb metal impurity), which were pressed under 30 tons of force to yield LMO pellets embedded into mechanically stable supports for handling. These LMO pellets were heated overnight in a vacuum oven at 50°C, then transferred into an argon-filled glovebox (~0.2 ppm O_2 , < 0.5 ppm H_2O). From this point on, LMO samples remained in inert atmosphere during heattreatment, ALD growth, and XPS characterization. For inert transfer into the XPS, LMO samples were loaded into a vacuum-transfer module (Thermo Fisher Scientific). ALD onto these samples was performed using a custom reactor directly connected to the argon-filled glovebox at 266°C [389]. Prior to precursor exposures, the reactor temperature was allowed to stabilize for > 15 minutes. LMO pellets were treated with only TMA exposures, or TMA and H_2O exposures, as noted. A typical timing sequence for TMA and H₂O exposures was comprised of 30 seconds of TMA exposure at a partial pressure of ~ 1 Torr, 120 seconds of Ar purge, 10 seconds of H₂O exposure at a partial pressure of ~ 1 Torr, and 120 seconds of Ar purge. Varying TMA dose times and omission of the H_2O dose were performed in accordance with descriptions in the text, figure captions, and figure labeling. Shorter precursor exposure times were used for LMO pellets versus the composite cathode ALD treatments because the surface sensitivity of XPS does not require coating into the bulk LMO pellet to be coated. Longer Ar purge times were used to ensure excess TMA and reaction byproducts had sufficient time to diffuse out of the LMO pellets before the next precursor exposure.

7.4.3 Density Functional Theory Calculations

We performed spin polarized density functional theory calculations using the Vienna Ab initio Simulation Package (VASP) [160, 168, 161]. The effective cores are treated using the projector augmented wave method [201, 162] and the valence states are expanded in a plane wave basis set to a kinetic energy cutoff of 520 eV. The Li 1s and Mn 3p electronic states are explicitly treated as valence electrons in all calculations. We used the generalized gradient approximation of Perdew, Burke, and Ernzerhof [163] as the exchange-correlation functional with a Hubbard U (PBE+U) correction of 3.5 eV to Mn 3d electronic states. The (001) Mn/O, (111) Li/O, and (511) Li/Mn/O surfaces are used for adsorption and delithiation calculations, where the notation for these terminations corresponds to that which is used in prior work [200]. We applied Gaussian smearing with Fermi temperatures of 0.05 and 0.01 eV for condensed- and gas-phase species, respectively. For CO₂ adsorption/desorption free energy calculations, we applied the Campbell-Sellers model [377] for entropy of adsorption, which empirically relates gas-phase and adsorbate entropies.

M.J.Y., S.L., W.M.D., C.J., and J.W.E. performed the experimental studies in this work and wrote the associated sections of the text. R.E.W. and J.G. performed the *ab initio* calculations and wrote the associated sections of the text.

8. *OPERANDO* OBSERVATIONS AND FIRST-PRINCIPLES CALCULATIONS OF REDUCED LITHIUM INSERTION IN AU-COATED LIMN₂O₄

This chapter is reproduced with the permission of Wiley-VCH Verlag GmbH & Co. KGaA from: Kimberly L. Bassett[‡], Robert E. Warburton[‡], Siddharth Deshpande, Timothy T. Fister, Kim Ta, Jennifer L. Esbenshade, Alper Kinaci, Maria K. Y. Chan, Kamila M. Wiaderek, Karena W. Chapman, Jeffrey P. Greeley, and Andrew A. Gewirth; Operando Observations and First-Principles Calculations of Reduced Lithium Insertion in Au-Coated LiMn₂O₄. Advanced Materials Interfaces **2019**, 6(4), 1801923. ([‡]These authors contributed equally to this work)

The deposition of protective coatings on the spinel $LiMn_2O_4$ (LMO) lithium- ion battery cathode is effective in reducing Mn dissolution from the electrode surface. Although protective coatings positively affect LMO cycle life, much remains to be understood regarding the interface formed between these coatings and LMO. Using *operando* powder X-ray diffraction with Rietveld refinement, it is shown that, in comparison to bare LMO, the lattice parameter of a model Au-coated LMO cathode is significantly reduced upon relithiation. Less charge passes through Au-coated LMO in comparison to bare LMO, suggesting that the reduced lattice parameter is associated with decreased Li⁺ solubility in the Au-coated LMO. Density functional theory calculations show that a more Li⁺-deficient near-surface is thermodynamically favorable in the presence of the Au coating, which may further stabilize these cathodes through suppressing formation of the Jahn-Teller distorted Li₂Mn₂O₄ phase at the surface. Electronic structure and chemical bonding analyses show enhanced hybridization between Au and LMO for delithiated surfaces leading to partial oxidation of Au upon delithiation. This study suggests that, in addition to transition metal dissolution from electrode surfaces, protective coating design must also balance potential energy effects induced by charge transfer at the electrode-coating interface.

8.1 Introduction

Lithium-ion batteries drive the portable electronics industry and appear increasingly in electric and hybrid vehicles. However, Li-ion cathodes remain a stumbling block toward longer-lasting devices and longer-range vehicles due to long term capacity fade [17, 390]. LiMn₂O₄ (LMO) is a common cathode material with low toxicity, high thermal stability, and a high voltage (~4.1 V vs Li/Li⁺). However, LMO exhibits capacity fade upon extended cycling, which is primarily attributed to 1) the formation of a Jahn-Teller distorted Li₂Mn₂O₄ tetragonal phase at low voltages, 2) electrolyte oxidation at high voltages, and 3) Mn ion dissolution from the electrode surface [211, 209, 220]. While formation of tetragonal Li₂Mn₂O₄ and electrolyte oxidation can be mitigated by cycling in a restricted voltage window, other innovative solutions are needed to address Mn dissolution from the LMO surface.

Many approaches have been developed to protect LMO from these mechanisms, such as bulk or surface doping [391, 140, 392] and deposition of protective coatings on the electrode surface [393, 179, 394, 329, 395, 396, 227, 397]. Oxides [393, 329, 395], fluorides [396], graphene [179], and metals [394, 227] have previously been employed as LMO coatings. These coatings sustain capacity upon cycling by mitigating Mn dissolution and decreasing electrolyte decomposition. Although semiconductor coatings, including oxides and fluorides, are predicted to have high electrochemical stability, hydrofluoric acid scavenging characteristics, and have been shown to effectively suppress Mn dissolution, their Li⁺ and electrical conductivity is often poor, which can lead to resistance in the battery [327, 328]. Metal coatings are good candidates to improve electrical conductivity, although many metals will oxidize well below 4.5 V versus Li/Li⁺. Au coatings, however, remain oxidatively stable under these conditions [227, 398] and therefore function as a promising model system to study the influence of a metallic protective coating on LMO. While Au coatings are unlikely to

be economically viable for a commercial battery system, these coatings do provide an interesting model system with which to study the effect of conductive coatings more generally.

One possible effect attendant deposition of a conductive surface coating is changes in the intercalation chemistry of the bulk material. Therefore, examining LMO with a bulk measurement, such as powder X-ray diffraction (XRD), could provide valuable insight into the interactions between an electrode and its coating. Previously, ex situ and in situ XRD studies comparing coated and uncoated LMO observed increased peak broadening, formation of defect phases after extended cycling, and irreversible changes to the lattice parameter for the coated materials [399, 400, 401, 402, 403, 404, 405, 406, 356, 407, 408, 409, 410, 411, 412]. This prior work, however, left unclear how conductive coatings influence LMO intercalation chemistry, which is directly related to the lattice parameter during charge and discharge. It is also unclear how those lattice parameter changes correlate with electrochemical performance. Moreover, very few studies have used theoretical calculations, such as density functional theory (DFT), to directly evaluate physical properties of the interface formed between an electrode and protective coatings [413, 251, 225]. Information regarding the chemical nature of the electrode-coating interface may be able to provide specific insights into experimentally measurable properties, such as the lattice parameter changes and overall electrochemical cycling performance. For instance, one might anticipate contact between a semiconducting cathode and a reducing metal, such as Au, may lead to interfacial charge transfer, which could in turn influence the intercalation chemistry. Such effects can be probed using a combination of operando characterization and theoretical chemistry calculations.

The intent of this work is to develop an understanding of the interactions between the LMO surface and a model conductive Au coating using *operando* XRD followed by Rietveld analysis and DFT calculations. These techniques help elucidate properties of an electrode-coating interface, and how these interfacial effects may influence bulk intercalation chemistry in coated Li-ion cathodes. A more comprehensive description of the electronic and geometric features of electrode-coating interfaces can aid in the design of future functional coatings and other solidsolid interfaces in Li-ion batteries.

8.2 Results

Figure 8.1 shows the cyclic voltammetry (CV) of the bare and Au-coated LMO obtained at a scan rate of 50 V s⁻¹. The two sets of reversible peaks shown are indicative of phase transfor- mations from fully lithiated LiMn₂O₄ (cubic I) to Li_{0.5}Mn₂O₄ (cubic II) to λ -MnO₂ (cubic III) during the anodic sweep and vice versa during the cathodic sweep [204]. Additional capacity in the first cycle (dotted line) at 4.0 V is likely due to irreversible Mn loss from the cathode and solid electrolyte interphase (SEI) formation [414, 415, 416, 417]. During cycling, the charge associated with both the Au-coated and bare LMO decreases, which may be due to various capacity fade mechanisms previously documented in the literature, *e.g.*, Mn loss, SEI formation, oxygen loss, and decoupling of the active material from the conductive support [414, 415, 416, 417]. By the end of six cycles, the charge capacity of the bare LMO (defined as the integrated charge in the CV from 3.5 to 4.4 V) has decreased by an additional 9% from the second charging cycle. The observed capacity fade in our half cells is consistent with our previous work on Au-coated LMO full cells, which also shows a consistent drop in capacity through the first ~75 cycles [227].

The similar peak oxidation/reduction potentials and peak splittings for the coated and bare samples suggest that the Au coatings do not greatly influence kinetics, which agrees with previous results [227]. Figure E.2 in Appendix E shows that the DFT-calculated Li⁺ diffusion barriers in bulk Au are very low, confirming minimal kinetic resistance due to the presence of the coating. The Li⁺ diffusion kinetics are expected to be further enhanced for grain boundary diffusion compared to the bulk DFT predictions [418]. The bare LMO current peak broadening at ~ 3.8 V during the cathodic cubic II to I transition, however, suggests kinetic limitations upon lithiation of the cubic I phase. This hypothesis is supported by the absence of a similar feature during CV at a slower scan rate of 25 μ V s⁻¹ (Figure E.3, Appendix E).



Figure 8.1.: Operando CV of Au-coated (orange) and bare (teal) LMO at 50 V s⁻¹. Current is normalized by the mass of LMO in the electrode pellet. The dotted line shows the first cycle, while the arrow show the direction of capacity and voltage evolution during cycling.

Figure 8.2 shows the *in situ* XRD of the bare (Figure 8.2a) and Au-coated LMO (Figure 8.2b) at open circuit potential (OCP) in fully assembled cells before cycling. The background (yellow line in Figure 8.2) was collected separately and includes diffraction through a cell constructed with a Li anode, separator, and electrolyte. Due to changes in incident flux throughout the experiment, the background was scaled to fit the data.

Figure 8.2 shows that the LMO diffraction peaks are unchanged between the bare and Au-coated samples, where the only new reflections in the Au-coated sample are associated with Au. Rietveld refinement of the LMO-associated peaks gave a lattice parameter of 8.241 (1) Å, consistent with the LMO cubic I phase (8.238-8.248 Å) [132, 419, 420]. These data show that the Au coating does not change the initial LMO structure.

Figure 8.3 shows the potential-dependent XRD obtained at a scan rate of 50 μ V s⁻¹ from both bare (Figure 8.3b) and Au-coated (Figure 8.3c) LMO along with the potential utilized during data collection (Figure 8.3a). For clarity, the spectra



Figure 8.2.: Powder diffraction patterns with Rietveld refinements for a) bare LMO and b) Au-coated LMO in the AMPIX cell at OCP before cycling at 50 μ V s⁻¹. The differences calculated are the Rietveld fits subtracted from the collected data. Visible LMO peaks are indexed.

in the heat maps are normalized by the integration of the entire spectra and then background subtracted. Figure 8.3 shows there are no changes in both the bare and Au-coated LMO diffraction patterns for the first 5.14 h corresponding to a potential sweep between 3 and 3.9 V. After 3.9 V, the cubic I phase begins to delithiate to the cubic II phase.



Figure 8.3.: Operando XRD performed on bare and Au-coated LMO during CV at 50 μ V s⁻¹. a) Potential, b) bare LMO 2 (in degrees), and c) Au-coated LMO 2 θ changes with time and cycle number. A 2 θ range of 8° - 23° is chosen to highlight higher intensity reflections. Diffraction peak intensities at time of 0 h correspond to those at OCP shown in Figure 8.2.

During the first cycle delithiation (starting at 5.3 h and ending at 7.1 h, corresponding to potentials between 3.95 and 4.28 V) for both the bare and Au-coated LMO, the 2θ values of the LMO-related peaks ((111), (311), (222), (400), and (331) at 8.76°, 16.84°, 17.59°, 20.34°, and 22.22°, respectively) begin to increase as the fully lithiated cubic I phase begins to delithiate and moves through the cubic II to cubic III phase. During delithiation, the Rietveld refinements give a lattice parameter change from 8.241(1) to 8.042(1) Å for both the bare and Au-coated LMO. Upon the cathodic sweep (from 8.3 to 13.0 h corresponding to a voltage sweep from 4.5 to 3.5 V), the cubic III \rightarrow II \rightarrow I transitions occur and the peaks shift back to lower 2 θ values. The behavior during delithiation and lithiation seen for the bare LMO is consistent with previous reports [204, 421]. Other persistent peaks include a polytetrafluoroethylene (PTFE) peak at 8.49°, conductive carbon (graphite) peak at 12.38°, and the strong cubic Au peak at 17.78° [365]. Based on XRD, graphite and Au do not undergo any significant changes during cycling, as is expected at these positive potentials. The Au diffraction peaks originate from larger islands (~ 20 nm diameter) and not the ~ 3.5 nm film that coats the majority of the LMO particle surface. Additionally, DFT calculations show that Li-Au alloy coatings are unstable at these potentials (Figure E.5, Appendix E). This is in agreement with previous work from our groups indicating that Li-Au intermetallic surface alloy formation occurs at potentials less than 2.0 V versus Li/Li^+ [422].

During the first delithiation, several new peaks grow in above and below the (111) peak at 8.72° , and 9.27° , above the (311) peak at 17.50° , and below the (440) peak at 20.43°. The peaks at 8.72° , and 9.27° , also change in 2θ during cycling and are most likely defect spinel phases or Li₂MnO₃, as reported previously [399, 423, 356, 407, 408, 409, 424]. Those at 17.5° , and 20.43° are most likely due to compounds within the SEI, such as LiF [423]. Strain, metastable structure, potential texturing, and even degree of crystallinity could contribute to difficulties in indexing these phases [425, 426].

After the first delithiation and lithiation cycle, individual Gaussian fits show the peak areas in the XRD patterns decrease while the peak widths grow wider (Figure E.6, Appendix E), consistent with previous reports [421]. This change is likely caused by the formation of the electrochemically active defect phases seen near the LMO(111) peak or increased strain [425]. After the first CV cycle, the full width at half-maximum (FWHM) of the (111) peak has increased by $\sim 2.4x$ relative to that found at OCP for the bare LMO; the corresponding change is 2x for the Au-coated LMO. The area of the same peak has decreased by $\sim 2.4x$ and 2.6x for the bare and Au-coated LMO, respectively. Likewise, the Rietveld scale factor decreased by an average of $\sim 2.7x$ and 2.2x for the bare and Au-coated LMO, respectively, when comparing the uncycled (at OCP) and cycled (cycles 1-6) lithiated LMO.

Figure 8.4 shows the change in lattice parameter of the lithiated and delithiated Au-coated and bare LMO during cycling at 50 μ V s¹. The lattice parameter was calculated at OCP, just prior to the first delithiation at 3.6 V (at t = 8.2 h), and at 4.5 and 3.5 V versus Li/Li⁺ during the CV. Rietveld refinements produced the lattice parameters and error bars (uncorrected estimated standard deviations produced by those refinements). Figure 8.4a shows that at OCP and before the first delithiation at 3.6 V, both samples exhibited a lattice parameter of 8.241(1) Å, which then decreased to 8.040(1) Å after the first delithiation. Upon the first *operando* lithiation (Figure 8.4a, cycle 1, t = 13.8 h), the lattice parameters of the two samples diverge, with the bare LMO lattice parameter increasing more than that of the Au-coated LMO. During the rest of cycling, the bare LMO exhibits both larger lattice parameters upon lithiation and smaller lattice parameters upon delithiation. Table E.2 in Appendix E provides the lattice parameters for each cycle.

Figure 8.4b shows the relative lattice parameter and relative charge on each cycle compared to the initial bare LMO values after a full lithiation sweep for bare and Aucoated LMO. For lattice parameters, the percentage is calculated relative to the lattice parameters of 8.241 Å at OCP and 8.040 Å following the first delithiation (Figure 8.4a, cycle 1) of bare LMO. Figure 8.4b shows that the relative lattice parameter tracks



Figure 8.4.: Lattice parameter and charge changes during cycling. a) Lattice parameters from Rietveld refinements of selected XRD patterns of the lithiated and delithiated LMO phase at OCP, just prior to the first delithiation at 3.6 V (at t = 8.2 h), at 3.5 V at the end of a lithiation CV half cycle, and at 4.5 V after a delithiation half cycle. b) The relative lattice parameter and relative charge of each cycle compared to the initial bare LMO values after a full lithiation sweep for bare and Au-coated LMO. Charge was calculated without subtracting a capacitive background. Original charge values are plotted in Figure E.4 in Appendix E.

with the relative charge closely for both the bare and Au-coated LMO samples. This shows that changes in lattice parameter reflect changes in the degree of lithiation each sample experiences. Based on the lower lithiated lattice constant and decreased charge, we conclude that Au-coated is less likely to be relithiated to the same extent as bare LMO due to the modified properties of the interface between LMO and the Au coating. To exclude the possibility of kinetic effects driving the observed charge difference between bare and Au-coated LMO at 50 μ V s⁻¹ (~C/5.5), we applied the same approach to data collected at a slower scan rate of 25 μ V s⁻¹ (~C/11) and found the difference negligible. However, we note that while the *operando* half-cell measurements suggest a decrease in capacity for Au-coated LMO that the coating is still effective in reducing Mn dissolution and enhances capacity retention in full cells, as shown when cycled against graphite anodes in our previous work [227]. Additionally, the selected diffraction patterns in Figure E.7 in Appendix E show a tail on the LMO(111) peak during the first lithiation. The tail indicates phase heterogeneity due to slower lithiation in the Au-coated LMO [365]. Figure E.8 in Appendix E shows that the integrated area of the LMO(111) peak decreases with a trend similar to the charge during lithiation as well. We note, however, that this correlation is not maintained for delithiation of LMO (Figure E.9, Appendix E); we suggest that during delithiation other processes are active, including SEI formation and Mn dissolution.

DFT calculations are performed to further understand the nature of the LMO/Au interface at different lithium contents. To address this, we consider the delithiation of LMO(001) surfaces, with and without the Au coating, as discussed in Section 8.4. Here, we apply a periodic model of the Au coating with two atomic layers in order to make the coated electrode computationally tractable to enable insights regarding the interface formed between LMO and the Au coating. We expect that a periodic model should sufficiently capture the effects of the Au coating, which deposits primarily as a film of ~3 nm in thickness with additional islands between 5 and 20 nm wide, sufficiently large in order to screen finite size effects in metal particles [227, 427, 428, 429]. Starting with a Li-terminated [200] LMO(001) surface, Li⁺ are systematically removed from the near-surface region. Figure 8.5a,b shows the most thermodynamically stable configurations at different Li⁺ concentrations for bare and Au-coated LMO, respectively. The main difference between the Li⁺ configurations of the bare and Au-coated LMO is that the Au coating appears to favor delithiation closer to the LMO/Au interface, whereas Li⁺ removal from deeper into the subsurface



Figure 8.5.: Delithiation reactions for DFT-calculated thermodynamics for near surface lithiation and delithiation of bare and Au-coated LMO(001). Low-energy structures at different lithium contents for a) bare and b) Au-coated LMO(001) surfaces. The bottom of the slab is fixed, and a,b) shows only atoms that are relaxed within the permitted lithium removal region. The stoichiometries presented correspond only to the near-surface region in which delithiation is allowed to occur in the calculations, such that the x-values correspond to fractional lithium content with respect to LiMn_2O_4 stoichiometry. A legend of the different atoms types is presented to the right of (a) and (b). Relative energies of bare (teal) and Au-coated (orange) LMO at c) 3.0 V and d) 3.5 V versus Li/Li⁺. The filled in shapes represent the most thermodynamically stable configuration for a given stoichiometry, whose structures are represented in (a) and (b) and are connected by solid lines, whereas metastable lithium configurations are represented by unfilled shapes.

is thermodynamically favored for bare LMO. Figure 8.5c,d at 3.0 and 3.5 V, respectively, show the potential- dependent delithiation thermodynamics for both the bare and Au-coated LMO(001) surfaces, with voltage corrections applied by the formalism in equation 8.1 (see the Section 8.4). The formation energies are reported with respect to the fully lithiated x = 1 phase, and are normalized by the fraction of Li⁺ present per Mn_2O_4 formula unit in the near-surface region in which we allow our delithiation calculations to proceed. There are variations in the most thermodynamically favorable Li⁺ configurations (filled symbols in Figure 8.5c,d) due to the effect of Au. Figure 8.5c,d shows that the Au coating stabilizes more Li⁺-deficient surfaces, with respect to the fully lithiated (x = 1 in the Li_xMn₂O₄ delithiation region of the slab model as shown in Figure E.1, Appendix E) phase. Notably, we observe that there is a thermodynamic energy barrier against full relitiation of LMO back to x= 1 even at U_{Li/Li^+} = 3 V (Figure 8.5c). Moreover, the enhanced thermodynamic stability of Li⁺-deficient surfaces in the presence of the coating may suggest suppressed formation of the near surface $Li_2Mn_2O_4$ static Jahn-Teller tetragonal phase or other defect phases [430]. These trends are consistent with the decreased charge and Li^+ content for the Au-coated LMO (Figure 8.4b), although we note that these calculated near-surface effects cannot fully account for the extent of charge and Li⁺ deficiency observed in experiment. These calculations do suggest, however, a general thermodynamic driving force for decreased Li⁺ concentration in Au-coated LMO in comparison to bare LMO, an effect which is evident from the significant decrease in lattice constant for the lithiated LMO phase seen in Figure 8.4a. Analogous plots for lithiation/delithiation thermodynamics at higher potentials can be found in Figure E.10 in Appendix E. We also obtain similar thermodynamic results using three- and four-layer Au films, the results of which can be found in Figure E.11 (Appendix E).

Figure 8.6 shows the projected density of states (PDOS) and projected crystal orbital Hamilton populations (pCOHP) of near-surface electronic states for the bare (Figure 8.6a,b) and Au- coated (Figure 8.6c,d) LMO(001) surfaces. In each of these plots, the Fermi energy (E_f) is set to the valence band maximum (VBM). In Figure



Figure 8.6.: Atom projected density of states (PDOS) and projected crystal orbital Hamilton population (pCOHP) analysis of surface Mn-O and Au-O bonds for bare $\text{Li}_x \text{Mn}_2 \text{O}_4$ at a) x = 1 and b) x = 0.75, as well as Au-coated LMO at c) x =1 and d) x = 0.75. The Fermi level (E_f) is denoted by the dashed black line in each plot. In the PDOS plots, positive PDOS values (solid lines) correspond to the majority spin channel, whereas negative PDOS values (dashed lines) correspond to the minority spin channel. In pCOHP plots, positive values along the pCOHP axis correspond to bonding states, as shown by the horizontal arrows on the plots, whereas negative values correspond to states that are associated with either anti- or nonbonding orbitals.

8.6, the density of states (DOS) projections are on a surface Mn ion (other topmost layer Mn ions are related by symmetry), the five O ions to which it is coordinated, and the Au atoms in the film. pCOHP pairs are considered to analyze crystal orbital hybridization of MnO and AuO states. Figure 8.6a,b shows the PDOS and pCOHP of bare LMO upon delithiation from x = 1 (Figure 8.6a) to x = 0.75 (Figure 8.6b). Upon Li⁺ removal, electron depletion causes the E_f to move lower into Mn states, which become oxidized. Figure 8.6b illustrates the shift of some Mn states of the x= 0.75 phase above the E_f (marked by *), in comparison to the PDOS of the x = 1phase in Figure 8.6a. In this case, the hole is partially shared between two surface Mn ions, perhaps due to strain imposed by the fixed lattice constant. The states which shift above the Fermi level upon Li⁺ removal are associated with MnO anti- or non-bonding states according to the pCOHP calculations (Figure 8.6b marked by *). The pCOHP calculations for bare LMO are in good agreement with previous work, showing the antibonding MnO nature of valence states directly below E_f , whereas MnO bonding states occur at lower energies [431].

Figure 8.6c,d shows the PDOS and pCOHP analysis for the Au-coated LMO(001) surface. Contrary to trends observed for bare LMO in Figure 8.6a,b, Li⁺ removal from x = 1 (Figure 8.6c) to x = 0.75 (Figure 8.6d) shifts neither the MnO antibonding states above the Fermi level, based on Mn PDOS, nor the cor- responding MnO pCOHP between the two states of charge. These observations suggest a lack of charge neutrality between the electronic states of Li, Mn, and O alone. Instead, the pCOHP analysis in Figure 8.6d shows Au-O antibonding states around the Fermi level. This suggests that Li⁺ removal is associated with partial oxidation of Au, rather than isolated oxidation at the Mn centers as seen in the bare LMO. Moreover, the Au-O pCOHP is comparatively flat at x = 1 (Figure 8.6c), indicating minimal hybridization between Au and O orbitals. However, upon delithiation to x = 0.75 the pCOHP analysis (Figure 8.6d) describes Au-O bonding states at low energies (centered ~-5 eV below E_f and marked by **) as well as antibonding hybridization character directly below E_f . The low energy of the Au-O bonding states with respect

to the Fermi level suggests strong binding between Au and LMO upon Li^+ removal, stabilizing a Li^+ -deficient region near the LMO/Au interface. This observation is consistent with the relevant thermodynamic stability of these configurations shown in Figure 8.5c,d, where we can further attribute the thermodynamic driving forces for decreased Li^+ content in lithiated LMO to the partial oxidation of the Au coating as it interacts with Li^+ -deficient LMO surfaces.

To further investigate the surface redox process upon Li⁺ removal from Au-coated LMO, we perform a charge density difference analysis to determine the nature of charge transfer between the LMO surface and the Au coating. Figure 8.7a shows the planar-averaged charge transfer between the composite LMO/Au interfacial system with respect to its isolated components, determined using the DFT-calculated charge densities (ρ)

$$charge transfer = \rho_{Au/LMO} - (\rho_{LMO} + \rho_{Au}) \tag{8.1}$$

In equation 8.1 and Figure 8.7a, a positive value of the charge transfer corresponds to an increase in electron density, or rather, a buildup of negative charge. Figure 8.7a shows a planar-averaged cross-section of this data for the Au-coated x = 0.75 phase to demonstrate charge transfer normal to the LMO/Au interface. Figure 8.7b shows the integrated charge density difference to illustrate the magnitude of negative and positive charge buildup on LMO and the Au film, respectively. The integrated charge density in Figure 8.7b is determined from integration of the charge transfer (equation 8.1) from the fixed end of the LMO slab to the vacuum region. The formation of the interface with Au leads to an increase in electron density in the LMO nearsurface region, suggesting that the Au film must be partially oxidized to satisfy charge neutrality. We also observe a deviation in the average Mn magnetic moment of the system between bare and Au-coated LMO (Figure E.12, Appendix E). More specifically, the average Mn magnetic moment is consistently higher in the Au-coated LMO surface than that of bare LMO, suggesting a lower average oxidation state for Au-coated LMO since lower-valence Mn ions have more unpaired 3d electrons. These



Figure 8.7.: Charge transfer and work function shifts from LMO/Au interface formation. Charge transfer between Au and LMO(001) surface with x = 0.75 lithium content, including a) planar-averaged charge density difference between Au-coated and bare LMO and b) integrated charge transfer between LMO and Au, starting from the fixed end of the LMO slab up to the vacuum. Positive charge transfer in (a) and (b) refers to an increase in electron density, or, negative charge accumulation. Further details regarding these calculations are provided in the main text. c) Work functions of the most thermodynamically stable x = 1, x = 0.75, and x = 0 surfaces for the bare (teal) and Au-coated (orange) LMO(001) surfaces. The colored arrows in (c) represent the average electron transfer direction when LMO is brought into contact with the Au film. For example, when the Au-coated LMO work function is lower than bare LMO, as it is for stable surfaces ($x \leq 0.75$), the Fermi level is higher in energy, which suggests an electron accumulation in the LMO near-surface and electron depletion in Au is needed to satisfy charge neutrality. This is consistent with the charge density calculations in (a) and (b).

interpretations are consistent with the PDOS and pCOHP analyses of Au-coated LMO in Figure 8.6c,d. These findings further suggest a potential energy driving force for LMO conduction states to become populated upon contact with the Au coating, which would seemingly be in competition upon lithiation with incoming $(Li^+ + e^-)$ pairs which require empty conduction states for intercalation to occur.

Although the thermodynamics (Figure 8.5), chemical bonding analysis (Figure 8.6), and electrode-coating charge transfer (Figure 8.7a,b) calculations all provide an explanation for a Li⁺-deficient near-surface, they do not fully explain how this could lead to a measurable change in the bulk Li⁺ content and lattice parameter as determined from the XRD lattice parameter refinement (Figure 8.4). Thus, we address these interfacial electronic structure effects and consider how they may influence the bulk properties of Au-coated LMO. While the individual Fermi levels of isolated LMO and Au are different, the composite system E_f is pinned when they are brought into contact. This will force the valence and conduction bands of LMO to bend to adjust to the E_f of the composite system. The direction and extent to which the band bending occurs will be driven by the relative work function between bare LMO and the Au coating to determine driving forces for electron transfer, which may protrude further into the bulk of the LMO electrode.

Figure 8.7c shows how the work function (ϕ) of the LMO surface varies between the bare and Au-coated LMO surfaces. Full electrostatic potentials, as well as the electrostatic potential differences between bare and Au-coated LMO, are included in Figure E.13 in Appendix E. The bare and Au-coated LMO ϕ values are estimated at different states of charge (refer to Figure 8.5c,d for relevant potential ranges for each surface) by the potential energy difference between the vacuum level and E_f . As in the PDOS/pCOHP analysis in Figure 8.6, the E_f is set to the VBM in this analysis. While the exact position of E_f between the VBM and the conduction band minimum (CBM) cannot be directly identified for a surface model without rigorous quantification of bulk intrinsic defect levels, we expect that Li⁺ vacancies are the dominant defect that determines E_f during delithiation, justifying its positioning at the VBM. Moreover, we further emphasize that this approach should sufficiently enable trend-based analyses of charge transfer processes at the LMO/Au interface. Compared to the bare LMO, the Au-coated LMO has a lower overall ϕ at both the x = 0.75 and x = 0 states of charge. While the x = 1 phase shows the opposite trend, we note that this state of charge is unlikely to exist in the presence of the Au coating based on our thermodynamic calculations shown in Figure 8.5c,d. This trend is consistent with the formation of a metal-semiconductor junction, wherein $\phi_{Au} < \phi_{LMO}$, and electrons are transferred from Au to LMO due to Fermi level pinning between LMO and Au. The downward band-bending of LMO conduction states in a near-interface electron accumulation region could, in principle, propagate below the surface on the scale of nanometers [432]. As the delithiation calculations (Figure 8.5c,d) suggest, the electronic population of LMO conduction states may make lithiation less favorable for the Au-coated surfaces since these electrochemical reactions require a (Li⁺ + e⁻) pair for insertion.

8.3 Conclusions

Figure 8.8 demonstrates the proposed effect of the Au coating, where the Li⁺deficient near-surface region leads to an overall decrease in bulk Li⁺ concentration as suggested by a decrease in the observed lattice parameter and overall charge transferred to Au-coated LMO. The Li⁺-deficient region near the LMO/Au interface - stabilized by a strong interaction and hybridization between Au and O orbitals - likely leads to an electron accumulation region hindering full lithiation upon discharge.

The region of electron accumulation from the downward bending of LMO conduction states near the metal-semiconductor junction may only protrude into the bulk at the nanometer scale, which would not directly account for the experimentally observed changes in lattice parameter. This interfacial effect, however, could present a kinetic challenge to Li⁺ proceeding into the LMO bulk due to a lower Li⁺ concentration boundary condition at the surface [68]. Li⁺ transport upon lithiation is governed by Fickian diffusion, wherein the driving forces are primarily the surface-to-bulk con-



Figure 8.8.: Influence of Au coating on LMO electrochemistry. The difference in work function between LMO and Au in Au-coated LMO leads to the near-surface accumulation of electrons. This effect also results in partial oxidation of the Au coating near the interface and inhibited reaction of $(\text{Li}^+ + \text{e}^-)$ pairs, leading to an overall reduction in Li⁺ concentration in Au-coated LMO as compared to bare LMO. This change in the near-surface solubility limit may reduce the bulk Li⁺ concentration due to reduced concentration gradients in LMO particles.

centration gradients, in the absence of a significant intraparticle potential gradient: $J_{Li} = -D\nabla c_{Li}$. This effect, depicted in Figure 8.8, inhibits bulk lithiation up to the concentration of stoichiometric LiMn₂O₄, leading to the reduction in electrode lattice parameter and capacity (Figure 8.5).

The findings in this work on a model Au-coated LMO system suggest that, while protective coatings may be effective in suppressing transition metal dissolution from Li-ion battery cathodes [227], interfacial potential energy effects may limit the Li⁺ solubility in the near-surface. Future coatings, conductive or not, will need to balance these potential energy effects with other well-established coating design parameters, such as ionic/electrical conductivity and chemical reactivity with compounds in the organic electrolyte. Additionally, our findings suggest that extensive experimental and theoretical investigations of solid-solid interfaces in Li-ion batteries are necessary in order to tune the performance of the interfaces between electrodes and protective coatings, as well as those between electrodes and solid electrolytes.

8.4 Experimental Section

8.4.1 Electrochemistry and Operando Diffraction

All chemicals were used as received without further purification. Electroless deposition of a continuous Au shell on LMO was performed as previously described [227]. In summary, $LiMn_2O_4$ (LMO) (electrochemical grade, Sigma-Aldrich), $AuCl_3 \cdot 3 H_2O$ (99.9+% metals basis, Sigma-Aldrich), and ethanol (200 proof, Decon Laboratories Inc.) were heated to 60 °C with stirring. A solution of hydroquinone (0.4 g, Sigma-Aldrich) in ethanol (5 mL) was added drop-wise. The mixture was allowed to stir for 10-15 min then removed from heat. The resulting solid was isolated, washed three times with ethanol, and dried at 90 °C under vacuum overnight. As-received (bare) LMO was used to compare with the Au-coated material. Previous reports contain further characterization of Au-coated LMO, and scanning electron micrographs show continuous Au films that are ~3.5 nm thick with a few additional islands between 5 and 20 nm in diameter on the LMO surface [227].

Electrodes for *operando* studies were constructed by mixing carbon black (Vulcan XC-72, Cabot Corporation), graphite (300 mesh, 99%, Alfa Aesar), PTFE binder (Sigma-Aldrich), and as-received or Au-coated LMO in a mass ratio of 1:1:2:6 in a mortar and pestle. ~ 0.024 -0.028 g of slurry was pressed into a 10 mm diameter die at 18-28 thousand PSI for 2 s. The cells were reweighed before cycling, and all cyclic voltammograms are reported with respect to the active material mass in each electrode.

Operando XRD patterns were collected during CV. CVs commenced at open circuit potential and were cycled between 3.5 and 4.5 V versus Li/Li⁺ at 25 or 50 V s⁻¹ in 1 m LiPF₆ (98%, Sigma-Aldrich) in 1:1 (v/v) ethylene carbonate (anhydrous, 99%, Sigma-Aldrich)/ dimethyl carbonate (anhydrous, 99%, Sigma-Aldrich) against a Li counter/reference electrode (99.9%, Alfa Aesar) with a glass fiber separator with CH Instruments potentiostats (models 760D, 660E, 60002E, 610E, and 760E). Potentials are reported with respect to Li/Li⁺. The battery stack was constructed inside a custom AMPIX cell [433]. The AMPIX cell models a coin cell electrode configuration and is equipped with X-ray transmissive windows for *in situ* and *operando* studies. Kapton tape protected the glassy carbon window from Li exposure. Graphite and window peaks seen in the XRD were identical with those reported previously [433].

Operando XRD was performed in transmission mode at beamline 17 BM at the Advanced Photon Source (APS) with a wavelength of 0.72768 Å. Multiple samples were analyzed in parallel using the AMPIX multicell holder. A diffraction pattern was collected for each sample every 10 min with a collection time of 10 s using a Perkin Elmer a-Si Flat Panel PE1621 detector. The beam size was 0.3 x 0.3 mm.

Datasets were analyzed with GSAS II, an open source crystallography package [434]. 2D images were masked and integrated using LaB₆ for calibration. The background scans were performed on cells with the anode, electrolyte, and separator but without a cathode. Rietveld refinements were performed on select 1D diffraction data to evaluate the lattice parameters based on structural models from the Inorganic Crystal Structure Database. Differences between calculated and observed peak heights are large due to masking the original 2D detector image to remove single crystal reflections from the Li counter electrode which overlapped multiple LMO reflections. Therefore, Rietveld structural parameters pertaining to peak height are not reported or analyzed. Rietveld refinements were carried to a weighted profile R-factor (R_{wp}) value of no greater than 6.30. The R_{wp} is the minimized sum of squared differences between the model and data that has been scaled by the weighted intensities [435]. R-factors for all Rietveld refinements performed are reported in Table F.1 in Appendix E.

8.4.2 Density Functional Theory Calculations

Periodic, spin-polarized, and DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) [160, 161, 168]. The electronic cores are treated using the projector augmented wave (PAW) method [201, 162], with [He] and [Ne] $3s^2$ effective core potentials for oxygen and manganese, respectively. All lithium electrons are treated explicitly using the small-core pseudopotential. The generalized gradient approximation of PerdewBurkeErnzerhof (PBE) is used as the exchange and correlation functional [163], with a Hubbard U [102, 103, 104] correction of 3.5 eV applied to the Mn 3d states. A plane wave kinetic energy cutoff of 520 eV was used in all calculations. Total energies were converged to 0.10 meV per unit cell, with a force criterion of 20 meV Å⁻¹ imposed for geometry relaxations.

Delithiation calculations were performed starting from the Li-terminated LMO (001) surface described in the previous work [200]. To reduce spurious supercell interactions, oxygen atoms at the bottom of the slab were passivated with hydrogens, which are initially subject to full ionic relaxation. As in previous work [205, 206, 65], part of the slab was fixed to represent the LMO bulk (see Figure E.1, Appendix E). The delithiation sampling is therefore limited to the range of atoms that are subject to ionic relaxation. Delithiation free energies ($\Delta G_{Li_xMO \to Li_yMO}$) between LMO slabs of two different lithium contents (Li_xMO and Li_yMO) were calculated as a function of cell voltage with respect to the Li/Li⁺ reference electrode (U_{Li/Li^+}) using the electrochemical potential ($g_{Li} - eU_{Li/Li^+}$), where g_{Li}^{bulk} is the intensive bulk Li free energy and e is the charge of an electron of the lithium-ions removed from LMO.

$$\Delta G_{Li_x MO \to Li_y MO} = [G_{Li_y MO} + (y - x)(g_{Li}^{bulk} - eU_{Li/Li^+})] - G_{Li_x MO}$$
(8.2)

Au-coated electrodes were modeled by introducing a two-layer, $2\sqrt{2} \ge 2\sqrt{2}$ Au(001) slab, which has a strain of less than 1% compared to the LMO(001) surface. A 20 Å vacuum layer for slab calculations was introduced, with dipole corrections added to the total energy. Chemical bonding analysis was performed using the crystal orbital Hamilton population (COHP) method within the LOBSTER code [436, 437, 438, 439, 440]. Atom PDOS calculations were performed by projecting wave function character onto the crystal orbitals determined from chemical bonding analysis. A Γ -centered 2 $\ge 2 \ge 1 k$ -point sampling for geometry relaxations was employed, with a denser 4 $\ge 4 \le 1$ grid applied for DOS, work function, and COHP calculations.

Supporting Information for this chapter is included in Appendix E.

R.E.W., S.D., A.K., M.K.Y.C., and J.P.G. performed the first principles calculations. K.L.B., T.T.F., and K.T. performed X-ray and electrochemical data acquisition. K.L.B., J.L.E., K.M.W., and K.W.C. performed sample preparation. K.M.W. and K.W.C. fabricated the operando cell apparatus. K.L.B. performed X-ray and electrochemistry analysis. K.L.B., R.E.W., S.D., J.P.G., and A.A.G. wrote the associated manuscript including the contributions of all authors.

9. THERMODYNAMIC FRAMEWORK FOR EVALUATING SOLUBILITY AND SURFACE SEGREGATION TENDENCIES OF CATIONIC DOPANTS AT LIMN₂O₄ SURFACES

9.1 Introduction

Mn dissolution from the surface of spinel LiMn₂O₄ (LMO) cathodes is one of the main contributors to capacity fade in LMO-based lithium ion battery cells [132, 220, 133, 221, 222]. Transition metal dissolution is also a widespread phenomena, occurring broadly across many different lithium ion battery chemistries beyond LMO [441, 313, 442, 366, 443]. For LMO, Mn disproportionation [228], Mn³⁺ \rightarrow Mn⁴⁺ + Mn²⁺, is proposed to be associated with Mn dissolution wherein the low valent Mn²⁺ ions are soluble in the electrolyte and deposit on the counterelectrode [139]. In order to suppress Mn dissolution from LMO, the problem of electrode/electrolyte interfacial reactivity is often addressed through either interfacial modification strategies such as protective coatings and cationic doping [133, 221].

Protective coatings have been shown to enhance capacity retention and/or rate capability by providing a chemical buffer between LMO and the electrolyte [142, 154, 324, 325, 179, 226, 326, 225] and through chemical removal of surface contaminants by coating precursors [444], although their performance is a strong function of the coating thickness [154, 324, 225], which can increase charge transfer resistance and reduce Li⁺ diffusivity across the electrode/electrolyte interface [325, 225, 213, 445]. Cationic dopants, however, stabilize the metal-oxygen bonds at the LMO surface while minimizing the impedance issues incurred from the deposition of (often electronically insulating) coatings [140]. LMO doped with monovalent [209, 314], divalent [315], and trivalent [316] cations increases the overall $Mn^{4+}:Mn^{3+}$ ratio in the cathode, presumably decreasing the concentration of Mn ions that can undergo the Mn

disproportionation and dissolution reactions. However, selective surface doping with Ti^{4+} cations has also been shown to improve the capacity retention of LMO cathodes [140].

Previous computational studies have been used to examine the influence of dopants in the bulk and at the surface of LMO on the electronic structure of neighboring cations [446, 447, 431, 190]. Additional computational work on layered Li₂MO₃-type (M = Mn, Co, Ni) cathodes has demonstrated that cationic dopants can modulate stability against oxygen loss [448, 449]. Oxygen loss, accompanied by oxygen vacancies on the surface of the cathode, are also compensated by excess charge which will localize on near-surface Mn ions in the case of LMO [200], further decreasing their oxidation state and presumably making them more susceptible to dissolution. Still, there remains a knowledge gap regarding the synthetic control that some dopant chemistries may afford when introduced into the LMO system. For instance, doping may not be selective to the LMO surface, where dopants that have a thermodynamic preference for the bulk and will have minimal utility toward mitigating interfacial reactivity. This paradigm therefore necessitates a theoretical and computational framework to evaluate the thermodynamic driving forces for both dopant insertion into the cathode lattice, rather than toward the formation of a secondary defect phase, as well as the preference for substitution into the near-surface rather than into the bulk.

In this work, we present a framework to isolate design criteria for promising cationic dopants in LMO based on these thermodynamic quantities. The thermodynamic analysis will aid in directing potential synthetic strategies to synthesize functionalized LMO cathodes with the dopants concentrated near the surface in order to mitigate reactivity. We will also use these thermodynamic insights to describe the hypothesized role of dopants inserted into different substitution sites in the context on existing hypotheses related to near-surface oxidation states of Mn ions as well as descriptors related to chemical stability against oxygen and manganese loss.

9.2 Scope and Limitations of the Doping Analysis

We begin by first addressing some potential limitations of the approach within this scope of bulk dopant stability analysis. Only dopant (D) species that are effectively non-reducible are considered, i.e. D reduction and/or oxidation reactions will not be competitive with the Mn^{3+}/Mn^{4+} redox couple. We limit our search in this manner to consider D elements that are inert towards redox chemistry in response to both lithium ion insertion and removal, as well as chemical interactions with the electrolyte. Instead, promising dopants are meant to stabilize the LMO lattice against degradation and Mn dissolution through both chemical stability and by favorably influencing the distributions of ionic and charged defects to mitigate interactions with the electrolyte. On this note, we also do not explicitly include charged and ionic defects (polarons and vacancies/interstitials/anti-sites, respectively) in addition to the aforementioned D substitution or insertion reactions. Such defect levels have recently been evaluated using first principles calculations for LMO [72] and we anticipate that with cationic dopants in dilute concentrations there will be minimal influence on the charge-neutral Fermi level of the system and the corresponding levels of different bulk point defects.

Previous work has shown that the high degree of Mn^{3+}/Mn^{4+} disorder in LMO contributes is representative of the low formation energies for hole and electron polaron defects [72]. As such, we consider each doping reaction to be charge neutral where charge excess or depletion (based on the oxidation state of D) is absorbed as a charge-compensating polaronic defect on Mn centers. It is, in principle, quite feasible to evaluate doping reactions with different charge states in the bulk, as has been done recently for layered LiMO₂ cathode materials [450]. However, we note that the most stable charge states of cationic dopants near the charge-neutral Fermi level were largely consistent the approximations applied in this work. Moreover, such an approach enables consideration of analogous cationic defects at LMO surfaces (to be discussed at greater length later on in this Chapter) in order to determine segregation thermodynamics of dopants from the LMO bulk to surfaces and interfaces. Moreover, we do not explicitly include charge compensating defects where D is accompanied by vacancies (Schottky pairs) or interstitials (Frenkel pairs). Although these are not considered here or in previous work on doped Li-ion cathodes [451, 450], we will comment on how the driving forces for such defects at surfaces may be influenced and their hypothesized role toward Mn dissolution reactions.

9.3 Discussion



Figure 9.1.: Possible dopant (D) siting in bulk LiMn_2O_4 , including substitution for Mn ions (D_{Mn}, octahedral sites) or Li ions (D_{Li}, tetrahedral sites), as well as 16c interstitial sites (D_{interstitial}).

To illustrate the theoretical framework to understand the thermodynamic stability of different compositions of doped LMO cathodes, we first introduce these formalisms for different possible modes of bulk doping mechanisms. In particular, we focus on the dopant (D) inserting in three possible reaction modes: (1) D substitutes for Mn ions in 16d octahedral sites, (2) D substitutes for Li ions in 8a tetrahedral sites, (3) D occupies the 16c interstitial octahedral sites. These different doping patterns are illustrated in Figure 9.1. As mentioned above, we consider the dilute insertion of dopants into LMO. As such, a single D cation insertion into N formula units of
$$N \operatorname{LiMn_2O_4} + \mathrm{D} \to N \operatorname{LiMn_{\frac{2N-1}{N}}D_{\frac{1}{N}}O_4} + \operatorname{Mn}$$
(9.1)

$$N \operatorname{LiMn}_{2}O_{4} + D \to N \operatorname{Li}_{\frac{N-1}{N}}\operatorname{Mn}_{2}D_{\frac{1}{N}}O_{4} + \operatorname{Mn}$$

$$(9.2)$$

$$N \operatorname{LiMn_2O_4} + \mathrm{D} \to N \operatorname{LiMn_2D_{\frac{1}{N}}O_4}$$
(9.3)

The free energy of doping $(\Delta G_{D_i}^{bulk})$ for all possible modes of dilute doping into bulk LMO (the limit as $N \to \infty$) can be expressed in general by

$$\Delta G_{D_i}^{bulk} = G_{D_i} - N g_{LMO} - \sum_i \Delta n_i \mu_i \tag{9.4}$$

where G_{D_i} is the free energy of bulk LMO doped at the *i* site, g_{LMO} is the per forumula unit bulk free energy of defect-free LMO, and Δn_i is the change in the number of atoms of type *i* between the undoped and doped bulk LMO models.

$$\Delta n_i = n_i^{doped} - n_i^{undoped} \tag{9.5}$$

While the free energy of doping expression in equation 9.4 provides a framework for describing the reaction thermochemistry, there remains some ambiguity with respect to the proper reference states for the different μ_i terms (including μ_{Li} , μ_{Mn} , μ_O , and μ_D) in the expression. We have previously addressed similar complexities for the thermodynamic stability analysis of off-stoichiometric LMO surface terminations [200], which require self-consistent definitions of the μ_i reference states. In this previous work, we analyzed surface energy trends within a range of chemical potentials where bulk LMO is defined to be stable, thereby imposing physically meaningful boundary conditions to the surface thermodynamics analysis. For the dopant chemical potential, μ_D , in the case of doped LMO we consider the thermochemistry of D to be inserted into the LMO lattice with respect to a reference state for the most thermodynamically competitive defect phase. For example, this competitive phase for the μ_D reference state may correspond either to an oxide phase (e.g. DO₂ under oxidizing conditions, more positive μ_O values) or metallic D (under more reducing conditions, more negative μ_O values). For a given D- and O-containing phase phase, μ_D and μ_O are constrained by the free energy of the corresponding phase.

$$g_{D_x O_y}^{bulk} = n_D \mu_D + n_O \mu_O \tag{9.6}$$

where g_{bulk} is the bulk free energy per atom and n_i are the number of atoms of type i in the corresponding bulk phase per formula unit.

The phase stability of different D-O compounds can be determined through construction of the convex hull, where the energy relative to the D-O end members, or standard free energy of formation per atom $(\Delta g_f^{D_x O_y})$ is plotted against composition.

$$\Delta g_f^{D_x O_y} = \frac{g_{D_x O_y}^{bulk} - (n_D \mu_D^0 + n_O \mu_O^0)}{n_D + n_O} \tag{9.7}$$

In equation 9.7 the μ_i represent the standard chemical potential at atmospheric pressure and 0 K (i.e. the gas-phase O₂ chemical potential for μ_O^0 at 0 K and the metallic D chemical potential for μ_D^0). Given these definitions, equation 9.7 may alternatively be expressed by the following:

$$\Delta g_f^{D_x O_y} = \frac{n_D}{n_D + n_O} \Delta \mu_D + \frac{n_O}{n_D + n_O} \Delta \mu_O \tag{9.8}$$

where the $\Delta \mu_i$ are the deviations of μ_i in the compound $D_x O_y$ from μ_i^0 and $\frac{n_i}{n_D + n_O}$ is the mole fraction of *i* in $D_x O_y$.

$$\Delta \mu_i = \mu_i - \mu_i^0 \tag{9.9}$$



Figure 9.2.: Dopant (D) reference state determination within the grand canonical ensemble by combining D-O and Li-Mn-O phases diagrams. (a) D-O convex hull accounting for the relative energy of each D- and O-containing phase in composition space. (b) D-O phase diagram in μ_O phase space, derived from the convex hull and phase equilibrium criteria as discussed in the text, equations 9.6-9.11. (c) LiMn₂O₄ chemical potential diagram, adapted from reference [200] with permission from the American Chemical Society. The black polygon outlines the phase stability of LiMn₂O₄ bound by thermodynamic driving forces for the precipitation of competing Li-Mn-O-containing phases, which are labeled on the plot. Based on the chemical environment, denoted by the chemical potentials, the D chemical potential shifts according to the reference phase. The red and blue points on (c) correspond to two sets of conditions, that when referenced to analogous conditions in (b) suggest two different thermodynamically stable reference states. This is meant to serve as a guideline for the competition for the doping into the LMO bulk or surface host, against precipitation into a competing bulk phase.

Stable phases are those which satisfy fundamental thermodynamic stability criteria, where the second derivative of energy relative to the D and O end members with respect to composition must be positive, i.e. a convex energy surface.

$$\left(\frac{\partial^2 g_f^{D_x O_y}}{\partial (\frac{n_i}{n_D + n_O})^2}\right) > 0 \tag{9.10}$$

Figure 9.2a shows an example D-O convex hull, including O₂ and metallic D as the end members, along with different D_xO_y oxide phases containing D⁺, D²⁺, and D³⁺ cations (in the D₂O, DO, and D₂O₃ oxide phases, respectively). In this example, all five of these phases are on the convex hull (second derivatives of standard formation free energies are positive) and represent the low-energy polymorphs for the specified stoichiometries. We further demonstrate how the convex hull may be used to interpret D-O phase stability, where equilibrium conditions between two neighboring phases (α and β) satisfy the criteria of equivalent component chemical potentials.

$$\mu_i^{\alpha} = \mu_i^{\beta} \tag{9.11}$$

Given these equilibrium constraints, the μ_O and μ_D at equilibrium are determined through self-consistent evaluation of equation 9.8 for both the α and β phases subject to the constraints in equation 9.11. Doing so determines the phase stability of the compound in D-O phase phase as a function of component chemical potentials, as shown in Figure 9.2b. This becomes relevant as we apply a similar computational framework, described in further detail in Ref. [200] to evaluate the phase stability of LMO in Li-Mn-O phase space. Figure 9.2c shows the chemical potential diagram for LMO, where the black polygon outlines the phase stability defined by chemical equilibrium with the Li-Mn-O-containing phases on the diagram. Since LMO is a ternary compound, the μ_i equilibrium relationships are a function rather than a single value, where these functions are bound by the intersection of the equilibrium μ_i relationships between LMO and other phases (i.e. the vertices on the polygon in Figure 9.2c).

The stability conditions for both LMO and different dopant-containing phases allows for self-consistent definition of chemical potential reference states in order to evaluate the thermodynamic driving forces for doping reactions according to equation 9.4. Moreover, cross-reference of the chemical potential stability windows for both D- and O-containing phases (Figure 9.2b) with that of LMO (Figure 9.2c) can describe changes in doping reaction thermochemistry as a function of the chemical environment. For instance, under conditions around room temperature (corresponding to a $\Delta\mu_O \sim -0.3$ eV, red lines in Figures 9.2b,c) the DO phase gives the proper reference state for μ_D , whereas at higher temperatures (more reducing conditions; e.g. $\mu_O \sim -1.0$ eV, blue lines in Figures 9.2b,c), $\mu_D = \mu_D^0$ since metallic D is the thermodynamically stable D- and O-containing phase according the the D-O bulk phase diagram.



Figure 9.3.: Surface models and dopant substitution sites. (a) Mn/O-terminated LMO(001), (b) Li/O-terminated LMO(111), and (c) Li/Mn/O-terminated LMO(511) surface models. Surface termination notation is analogous to that which is used in reference [200]. Model dopant locations are labeled according to the legend, and are analogous to those in Figure 9.1.

Since dopants are primarily used to mitigate Mn dissolution from LMO through reduced reactivity with the electrolyte it is desirable for dopants to preferentially insert near the surface, rather than in the bulk. It therefore becomes practical to consider also the segregation energies to identify their preference for surface doping. We consider the three aforementioned doping reaction modes at the low-index (001), (111), and (511) surface models (shown in Figure 9.3). Similar to the bulk doping formation energies, the free energy of surface doping at surface $(\Delta G_{D_i}^j)$ can be expressed by

$$\Delta G_{D_i}^j = G_{D_i}^j - G_{undoped}^j - \sum_i \Delta n_i \mu_i \tag{9.12}$$

where j is the particular LMO surface being considered. The surface segregation energy (ΔG_{seg}^{j}) for a given dopant on surface j in the dilute limit is therefore determined by the following expression.

$$\Delta G_{seq}^j = \Delta G_{D_i}^j - \Delta G_{D_i}^{bulk} \tag{9.13}$$



Figure 9.4.: Thermodynamic criteria for selective doping of different LMO surfaces based on segregation and formation energies.

Through this framework, we propose several combinations of $\Delta G_{D_i}^j$ and $\Delta G_{seg,D_i}^j$ to be applied as thermodynamic criteria to screen for promising dopants, which are demonstrated by the plot in Figure 9.4. The primary aim of this analysis is to identify promising LMO dopant chemistries that will preferentially dope the surface over the bulk, i.e. those in regions (B), (C), and (E) in Figure 9.4 where $\Delta G_{seg}^{j} < 0$. Given the definition of ΔG_{seg}^{j} in equation 9.13, the parity line between ΔG_{seg}^{j} and $\Delta G_{D_{i}}^{j}$ dividing regions (B) and (C) represents the boundary between exothermic and endothermic doping in bulk LMO. As such, we expect that dopants whose surface doping thermodynamics lie in region (C) are likely to be most promising since surface doping is thermodynamically favorable and bulk doping is not. In contrast, region (B) predicts less thermodynamic control over surface vs. bulk doping despite negative segregation energies, since both reactions are exothermic. Despite endothermic surface doping in region (E), where $\Delta G_{D_{i}}^{j} > 0$, dopants that lie within this space may also be promising if the equilibrium constant ($K = exp[-\frac{\Delta G_{D_{i}}^{j}}{k_{B}T}]$) suggests a reasonable concentration of dopant ions near the LMO surface. In (A) and (D) dopant segregation to the LMO surface is not thermodynamically favorable and such dopants are therefore unlikely to be promising in LMO.

While this thermodynamic analysis framework provides certain insights regarding the stability of dopants in the lattice and their propensity to segregate to surfaces, further interpretations are needed to infer potential mechanisms by which they may aid in mitigating interfacial reactivity between the LMO cathode and the electrolyte. As such, there are several scenarios to be considered, which can be evaluated in concert with experimental studies to deduce the role of dopants towards enhanced electrochemical cycling of LMO.

Much of the discussion [221] surrounding Mn dissolution is often related to Mn^{3+} disproportionation into Mn^{2+} and Mn^{4+} , where Mn^{2+} ions are largely considered to be the dissolving Mn species [139, 232, 231], although this remains a subject of debate [229, 230]. Still, the role of surface dopants in LMO is largely hypothesized to influence charge distribution and the electronic structure of surface Mn ions [452]. The presence of the dopant modifies the distribution of Mn^{3+} and Mn^{4+} ions at the surface, the latter of which are hypothesized to be inert to the disproportionation

and dissolution reactions. Given these considerations, we will briefly discuss these potential consequences for the distribution of different Mn ion oxidation states for the D_{Mn} , D_{Li} , and $D_{interstitial}$ dopant modes discussed in the present work. In cases of substitution for surface Mn ions (D_{Mn}) , dopants with a valence $\leq 3+$ will increase the concentration of Mn⁴⁺ ions, presumably making the interface more resilient to dissolution. For Li substitution (D_{Li}) , however, the concentration of low-valent Mn³⁺ ions will increase for dopants with oxidation states $\geq 2+$. Similarly, cationic dopants at interstitial sites $(D_{interstitial})$ will also increase the number of low-valent Mn³⁺, or even Mn²⁺ surface ions.

However, these prescriptions largely rely on the aforementioned arguments related primarily to the electronic structure and distribution of Mn ionic states at the LMO surface. In practice, the mechanisms involved in Mn dissolution may be more complicated, involving chemical reactivity between LMO and the electrolyte. Some degradation mechanisms may also be related to chemical descriptors, such as the formation of oxygen vacancies, which we have recently shown to be directly related to the structure-sensitive atomic layer deposition redox chemistry on LMO surfaces [200]. Oxygen vacancy formation has also recently been evaluated in the context of computational studies of dopants in layered Li_2MO_3 cathodes where it aids in describing the degradation and capacity fade of these cathode materials due to surface oxygen evolution mechanisms [448, 449]. Recent studies of LMO have used morphological [143] and atomic layer deposition of surface coatings [225, 200] that suggest stepped sites such as LMO(511) are more susceptible to dissolution, and we have shown that oxygen vacancy formation is facile on such stepped/defect sites. While some dopant reactions may increase the surface concentration of Mn^{3+} , e.g. D_{Li} and $D_{interstitial}$, they alternatively may suppress vacancy and defect formation since the dopants are in general much less reducible than surface Mn^{4+} . Given these considerations, we propose that the most effective dopants would be those that selectively dope to defect sites, such at the (511) and other stepped/defect surface sites, in order to stabilize these interfacial structures against oxygen and manganese loss. Moreover, low-index terraced surfaces are likely to be more stable against the electrolyte with respect to Mn loss, especially the (111) facet, where Mn ions are in the subsurface and oxygen vacancy formation energies are high [200]. Despite the stability of LMO(001) and (111), however, the presence of dopants near the surface of these low-index planes may further enhance their resiliency against defect formation.

9.4 Conclusions

This chapter has outlined the thermodynamic considerations for cationic surface doping of LMO battery cathodes. A framework to evaluate doping reaction energies was presented, which accounts for dopant insertion at different sites in the bulk LMO lattice with respect to the stability of the dopant in a thermodynamically stable native oxide or metallic phase. This approach was extended to evaluate dopant segregation to low- and high-index LMO surface models. Using the free energy of surface doping and segregation energies we have illustrated several criteria to determine whether a particular dopant is more stable near the surface and can aid in stabilizing the electrode interface against the electrolyte, or if the dopant is more stable in the bulk and will not directly influence interfacial reactivity. We propose that the thermodynamic approach described in this work may be applied to guide feasible synthesis routes for other dilutely-doped oxide systems beyond energy storage, such as promoter atoms embedded in oxide supports for catalytic applications. Following the description of the thermodynamic framework, we have addressed additional criteria to be considered in evaluating the efficacy of a proposed dopant in LMO. In addition to the distribution of Mn ion oxidation states near the LMO surface, we describe the role that dopants may play in modifying chemical descriptors related to oxygen and manganese loss that could influence the driving forces for Mn dissolution in LMO cathodes. The insights gained from these studies may guide the design of doped battery cathodes that can enhance cycle stability and mitigate other problems associated with electrode degradation.

10. CHARGE TRANSFER AND REDOX CHEMISTRY AT THE INTERFACE BETWEEN LITHIUM METAL AND LITHIUM LANTHANUM TITANATE SOLID ELECTROLYTES

This chapter is an excerpt from a manuscript that is being prepared for publication: Robert E. Warburton, Jae Jin Kim, Shane Patel, Jason Howard, Larry A. Curtiss, Chris Wolverton, Paul Fenter, Timothy T. Fister, Jeffrey Greeley; Charge Transfer and Redox Chemistry at the Interface between Lithium Metal and Lithium Lanthanum Titanate Solid Electrolytes. *In Preparation*

10.1 Introduction

Solid-state lithium ion batteries using ceramic superionic conductors as electrolytes are of great interest due to their safety advantages over organic electrolytes, given their decreased flammability and the potential for enhanced electrochemical voltage windows. Solid electrolytes also afford the potential for increased energy densities through enabling the use of Li metal anodes through more controlled nucleation mechanisms at the solid/solid interface between Li and the electrolyte [26, 43, 453]. Moreover, the Li⁺ ionic conductivities of state-of-the-art solid electrolyte materials are approaching those of liquid electrolytes with lithium salts [43]. Enhanced ionic conductivities have achieved through doping [454], and computational studies [455] have further aided in the design of promising superionic conductors using descriptors related to the crystal structure [456] and lattice dynamics described by the phonon density of states [457, 458].

Despite many developments in the materials design space of solid electrolytes there still exists many barriers to practical implementation, many of which can be related to resistivity of the solid/solid interfaces in an all solid-state lithium ion cell. These issues may arise, for instance, from dendrite growth at the Li/electrolyte interface [459] or from poor interfacial wettability between the electrode and the electrolyte [460, 461, 462, 463]. Many of these issues can be understood based on trends in the electrochemical stability windows, which are generally quite wide for oxide solid electrolyte materials, although their respective oxidation and/or reduction potentials often limit their thermodynamic stabilities against either the cathode or anode, respectively [464, 465, 466]. The reactivity of Li/electrolyte interfaces in solid-state batteries can be modified through doping [467, 468] or through deposition of interlayer coatings [464, 469, 470, 471, 472]. However, many solid electrolyte materials are also comprised of many different elemental components, the specific reactivities of which may be exploited to tune reactivity using compatible materials that may be less reactive at the interface with the electrode. A greater understanding the reactivity of different surface terminations of the solid electrolyte 463, for example, may be used to tailor the stability of the Li/electrolyte interfaces in solid-state batteries. Previous computational studies have analyzed the stability of solid electrolyte surface phases [473, 474, 475] and the construction of solid-solid interfacial models have been applied in previous studies of various energy storage systems [467, 469, 476, 477, 478, 213, 479]. Such computational analyses, in concert with experimental characterization, can be used to form a more comprehensive understanding of interfacial reactivity in solidstate batteries.

As an example, the instability of the perovskite lithium lanthanum oxide (LLTO; $Li_{3x}La_{0.67-x}TiO_3$) against the Li metal anode is well-documented in previous reports. X-ray photoelectron spectroscopy (XPS) experiments have shown that LLTO is unstable against Li metal [480] and that reduction occurs around 1.5-1.7 V vs. Li/Li⁺ based on cyclic voltammetry experiments [481, 482, 483]. These material instabilities at low voltages make the Li/LLTO interface a compelling model system to understand and control aspects of solid/solid interfacial reactivity at the atomic scale. In addition to the bulk thermochemistry of the LLTO system, we also aim to introduce surface

and interfacial analyses to form a more comprehensive understanding of interfacial decomposition mechanisms. In some cases, the interface may correspond to a modified equilibrium state that kinetically traps the metastable LLTO phase at low voltages, requiring an overpotential for the decomposition reactions to proceed. Beyond thermodynamics, we also consider trends in band alignment at the metal-semiconductor interface [463, 478, 213] and how the electronic levels of LLTO influence interfacial reactivity with respect to trends in charge transfer across solid/solid interfaces.

In this work, we apply *ab initio* modeling studies to document the interfacial reactivity of the LLTO solid electrolyte and the interface with a Li metal anode. Using first principles density functional theory (DFT) calculations, we describe the driving forces for voltage-dependent LLTO bulk decomposition chemistry. We extend these computational analyses to describe equilibrium surface structures to rationally inform the construction of explicit solid/solid interfacial models between Li and LLTO. These models are used as inputs to *ab initio* molecular dynamics (AIMD) simulations to evaluate the structural evolution and redox chemistry of the Li/LLTO interfaces over short time scales. Lastly, we use insights from bulk thermochemistry and interfacial structure sensitivity, in addition to trends in interfacial band alignment, to propose an interlayer coating to prevent the undesired LLTO interfacial decomposition reactions. These computational simulations and predictions are used to establish the role of the interlayer in mitigating charge transfer and decomposition redox chemistry at the electrode/electrolyte interface.

10.2 Results

10.2.1 Lithium Lanthanum Titanate Bulk and Free Surface Thermodynamics

LLTO perovskites have been synthesized with a range of compositions, with the general chemical formula of $\text{Li}_{3x}\text{La}_{0.67-x}\text{TiO}_3$ representing different Li:La ratios at A-sites, corresponding to different bulk crystallographic properties [482]. The relative Li:La ratio is compensated by A-site vacancies to locally preserve charge neutrality, influencing Li⁺ diffusion where optimal conductivity occurs for $x\sim0.1$ in Li_{3x}La_{0.67-x}TiO₃, which can be further enhanced through substitutional doping [454, 482, 484]. Given the potential structural complexities of LLTO materials, we consider a simplified theoretical model with equivalent Li:La A-site ratios to give a bulk stoichiometry of Li_{0.5}La_{0.5}TiO₃ ($x\sim0.17$ in Li_{3x}La_{0.67-x}TiO₃) with alternating Li and La A-site occupation along the [001] axis. We expect that such a model may describe different modes of LLTO interfacial reactivity, where conclusions may be transferable to a wider stoichiometric design space.



Figure 10.1.: (a) Bulk LLTO crystal structure with Li⁺ distortion in perovskite Asites. (b) Bulk decomposition energies of LLTO at different voltages in a Li-ion cell. The decomposition reactions are listed to the right according to the shaded regions ①-⑨ in the plot. The solid black line is the convex hull of the grand potential phase diagram relative to the LLTO reference (dashed black line).

Figure 10.1a shows the bulk crystal structure of the $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ (LLTO) perovskite, with Ti⁴⁺ions occupying the B-sites in octahedral coordination to O²⁻ anions and ordered mixed A-sites with Li⁺ and La³⁺ ions 12-coordinate to O²⁻ anions. While La³⁺ ions easily coordinate themselves with 12 lattice O²⁻, Li⁺ ions are unstable at the crystallographic center of the A-site cage due to Li-O interatomic distances of ca. 2.86 Å (compared to Li-O bond distances of ca. 1.9 Å) in addition to over-coordination to 12 O²⁻ anions (Li⁺ ions prefer coordination numbers of 4 or 6 according to ref. [485]). Previous computational studies of LLTO have shown a relatively flat potential energy surface, with negative (imaginary) phonon modes associated with both free translation of Li⁺ ions in the A-site cage as well as TiO₆ octahedral tilting [486]. Figure 10.1b shows the bulk LLTO structure with a distortion of the Li⁺ ions to coordinate with O^{2-} ions near the intersection of adjacent A-site cages. This distorted geometry is lower in energy by 0.27 eV per Li_{0.5}La_{0.5}TiO₃ formula unit compared with the undistorted A-site geometry. A similar distortion of the Li⁺ positions in the LLTO A-sites was observed in a previous computational study of various LLTO stoichiometries [487], including the structure in the present work.

Previous work has demonstrated that while LLTO is stable at high voltage against cathodes, it begins to decompose at ca. 1.5 V vs. Li/Li⁺ making it unstable against Li metal anodes [481]. Here, we assess the LLTO thermochemistry, using the energetics of the distorted Li⁺ A-site geometry (Figure 10.1b) as the bulk reference state. Moreover, such distortions will occur due to broken symmetry in subsequent surface and interfacial thermodynamic analysis that could lead to unphysically low (or even negative) surface energies when using the undistorted A-site reference state. To evaluate the bulk thermodynamic stability of LLTO, we apply a Li grand potential analysis [59] to consider potential-dependent decomposition reactions in response to Li-rich (low voltage) or Li-deficient (high voltage) conditions [464, 465, 466, 471, 475, 488].

Figure 10.1c shows the calculated Li grand potential decomposition diagram for LLTO, and the corresponding decomposition products for each range of voltages, indicated by different colored shading and labeling from $(D-\mathcal{G})$ on the plot. The solid black line represents the convex hull, or the combination of bulk compounds in Li-La-Ti-O phase space that minimize the free energy for a given voltage. The data suggests that LLTO is metastable since the convex hull free energy is negative for all potentials between 0 and 5 V vs. Li/Li⁺. Region (\overline{O}) represents stoichiometric decomposition of LLTO into Li₇Ti₁₁O₂₄, La₂Ti₂O₇, and Li₄Ti₅O₁₂. This region, bound by the reduction potential at 1.73 V vs. Li/Li⁺ and the oxidation potential at 3.58 V vs. Li/Li⁺, also indicates the range of voltages for which LLTO is minimally metastable with a decomposition energy of -0.04 eV/atom. We note in particular that the La₂Ti₂O₇ synthesized LLTO [489, 490]. The prediction of reduced Ti phases at voltages below the reduction potential is also consistent with X-ray photoelectron spectroscopy measurements at the Li/LLTO interface [480]. The calculated decomposition products and stability window of the LLTO electrolyte are also relatively consistent with previous DFT calculations using the $Li_{0.33}La_{0.56}TiO_3$ stoichiometry [464].

In addition to identifying the bulk driving forces for the LLTO solid electrolyte decomposition across a solid-state Li-ion cell, it furthermore provides a basis for computational model development of surfaces and interfaces in a solid-state battery system. Specifically, the stable phases across the Li grand potential convex hull elucidates proper thermodynamic reference states for each component in Li-La-Ti-O phase space. For each corresponding set of decomposition products (1)-(9) in Figure 10.1c, the appropriate excess component chemical potential reference states (μ_{Li} , μ_{La} , μ_{Ti} , μ_O) are defined by the stable phases comprising the Li grand potential convex hull. In consideration of the conditions for which LLTO is minimally metastable (region (7)), for example, the μ_i are determined by:

$$\begin{bmatrix} g_{Li_2TiO_3} \\ g_{La_2Ti_2O_7} \\ g_{Li_4Ti_5O_{12}} \\ Voltage \end{bmatrix} = \begin{bmatrix} 2 & 0 & 1 & 3 \\ 0 & 2 & 2 & 7 \\ 4 & 0 & 5 & 12 \\ -1 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \mu_{Li} \\ \mu_{La} \\ \mu_{Ti} \\ \mu_O \end{bmatrix}$$
(10.1)

This enables calculation of LLTO surface energies to determine inherently stable surface terminations of the solid electrolyte which may be present either at grain boundaries in the electrolyte layer or at the interface formed with the electrodes.

Figure 10.2a shows a set of LLTO(010) surface terminations and the stoichiometries of the surface slab models used for the DFT calculations. Here, we consider the (010) surface since this gives mixed Li/La A-site layers in the direction of the surface normal. AO or BO₂ surfaces are commonly employed as models for natural terminations of $\langle 100 \rangle$ -like perovskite surfaces. These AO and BO₂ terminations typically have competitive surface energies, although different chemical environments can favor



Figure 10.2.: LLTO(010) surface thermodynamics. (a) LLTO surface terminations and (b) surface phase diagram in the region of minimal LLTO metastability (region \bigcirc in Figure 10.1) between the calculated reduction and oxidation potentials of 1.73 and 3.58 V vs. Li/Li⁺, respectively.

different terminations (e.g. OER electrocatalysis conditions tend to favor BO₂ surface terminations) [491, 492, 493, 494, 495]. In the case of LLTO, Ti is the only B-site cation so we hereafter employ TiO₂ as the notation for the BO₂-terminated surfaces for this system. In a Li-ion cell with a wide range of very reducing (anode, low voltage) to very oxidizing (cathode, high voltage) operating conditions, the driving forces for different surface terminations or for different types of defects/reconstructions may be favored at the interfaces between the anode and the cathode. Some of these are represented by the structures in Figure 10.2a, primarily concerning oxygen-rich surfaces or AO/TiO_2 terminations containing different concentrations of oxygen vacancies (V_{O}^{-}) .

The surface energy is calculated using the DFT energy of the slab (E_{slab}) along with the component chemical potentials determined from equation 10.1 as the reference states the amount of excess of a given component (Γ_i) with respect to its concentration in the bulk stoichiometry of Li_{0.5}Li_{0.5}TiO₃ $(N_i^{bulkLLTO})$:

$$\gamma = \frac{1}{2A} \left[E_{slab} - N_{fu}^{LLTO} (g_{bulk}^{LLTO} + \sum_{i} \Gamma_{i} \mu_{i}) \right]$$
(10.2)

where the number of LLTO formula units (N_{fu}^{LLTO}) is defined by the stoichiometrically limiting component.

$$N_{fu}^{LLTO} = min(\frac{N_i^{slab}}{N_i^{bulkLLTO}})$$
(10.3)

The excess of the other components in the slab (Γ_i) is therefore calculated by

$$\Gamma_i = \left(\frac{N_i^{slab}}{N_{fu}^{LLTO}} - N_i^{bulkLLTO}\right) \tag{10.4}$$

such that if i is the stoichiometrically limiting component in the slab, $\Gamma_i=0$.

Figure 10.2b shows the surface energies for different LLTO(010) chemical terminations between the reduction and oxidation potentials, where bulk LLTO is minimally metastable. As with previous computational studies of perovskite surfaces, the AO and TiO₂ surface terminations have comparable surface energies for this range of chemical environments. In general, oxygen-rich AO₂ and TiO₃ terminations are highly unstable relative to AO and TiO₂ terminations, although the trends show that oxygen-rich stoichiometries become more favorable at higher voltages. More reduced surfaces formed through oxygen vacancies (TiO₂+ V_{O}), however, become only weakly metastable under reducing conditions near the LLTO reduction potential of 1.73 V. Overall, the insights gained from the surface phase diagrams in Figure 10.2b provide a basis for studying explicit interfacial models between LLTO and a Li anode based on the stable LLTO surfaces and trends in defect formation energies, specifically V_{O}^{-} -type defects.

10.2.2 Interface Between Lithium Metal Anode and Lithium Lanthanum Titanate Electrolyte

Next, we expand upon the computational insights determined from thermodynamic analyses of LLTO bulk and surfaces to directly consider the interface between LLTO and a Li metal anode. To develop explicit Li/LLTO interfacial models, we construct solid/solid interfaces using a lattice matching algorithm to minimize strain between the lattice constants of the Li and LLTO phases [213, 496, 113]. The initial geometries involve straining LLTO(010) by 5.65% and 1.38% in the [001] and [100] directions, respectively, to register to the Li(010) substrate. We assume that strain contributions to interfacial energies will be minimal compared to chemical contributions and that errors will be comparable for similar thicknesses of LLTO layers. As such, interfacial energies are calculated using the same expression used for surface energy calculations (equations 10.2-10.4), where Li is in excess due to the presence of the model Li anode and thus cannot be the stoichiometrically limiting component (due to the presence of a model Li anode). $\mu_{Li} = \mu_{Li}^{bulk}$, and $\mu_{i \neq Li}$ are determined from the three-phase equilibrium between the stable Ti₃O, La₂O₃, and Li₄TiO₄ decomposition products (from region (1) in Figure 10.1c) similar to the example in equation 10.1.



Figure 10.3.: Interfacial structures and energies for (a) AO-terminated, (b) TiO₂-terminated, and (c) TiO₂+ V_O° -terminated LLTO(010) interfaced with Li(100).

Figure 10.3 shows different Li/LLTO interfacial models for both the AO and TiO_2 -terminated LLTO surfaces (Figures 10.3a and 10.3b, respectively) and their interfacial energies calculated from 0 K density functional ionic relaxation. Similar to the thermodynamics of the free surface terminations of LLTO, the interfacial energies of models consisting of both AO and TiO_2 -terminated surface are similar in magnitude. Given the modest oxygen vacancy formation on LLTO surfaces near the LLTO bulk reduction potential (Figure 10.2), similar vacancy formation mechanisms are considered at the interface with Li metal. Figure 10.3c shows that V_O° can form readily at the TiO₂-terminated Li/LLTO interface, where the interfacial energy of the $\text{Li}(100)/\text{LLTO}(010)\text{TiO}_2 + V_O^{\circ}$ is modestly lower than that of $Li(100)/LLTO(010)TiO_2$. We performed a similar analysis for vacancy formation on the Li(100)/LLTO(010)AO model, but found instead that $V_O^{...}$ formation is more favorable in the near-interfacial TiO_2 layer, rather than in the AO layer at the interface. These results are generally consistent with the bulk thermodynamic analysis presented in Figure 10.1c where at the Li anode (0 V vs. Li/Li^+) the stable decomposition products consist of a reduced Ti₃O phase, whereas La³⁺-containing phases (e.g. the native oxide La_2O_3) are more reductively stable under these conditions.

The DFT-relaxed structural models in Figure 10.3 show that due to the oxophilicity and low bulk modulus of Li, there is significant reconstruction at the interface. Given these considerations, along with the relatively flat potential energy surface of LLTO due to Li⁺ dynamics and TiO₆ octahedral tilting, we explicitly consider interfacial dynamics through NVT *ab initio* molecular dynamics (AIMD) simulations. While it may be possible to accelerate the search of conformational space running higher temperature AIMD, the low melting point of Li metal limits these simulations to using a Nosé-Hoover thermostat [169, 497] temperature of 300 K. In particular, we aim to use AIMD simulations of these explicit interfacial models to understand atomic potential atomic scale mechanisms for the onset of decomposition chemistry and the role of the interface in selectively controlling the instability of LLTO as a solid electrolyte against a Li anode. Figure 10.4 shows results from a 40 ps AIMD simulation of the Li(100)/LLTO(010)-AO interfacial model. Figure 10.4a shows the starting ionic positions (left) and the ionic positions after 40 ps of dynamics (right). The different AO layers are labeled (1)-(3), where layer (1) consists of Li, La, and O ions nearest to the interface with Li metal and (3) is the AO layer nearest the middle of the LLTO slab, meant to resemble the bulk of the solid electrolyte. The snapshot after 40 ps illustrates the facile motion of Li⁺ ions in the A-site cages as well as tilting of the TiO₆ octahedra, consistent with the imaginary phonon modes and inherent material instability calculated in previous work [486]. This also shows that Li metal tends to increase its coordination with O in the LLTO near the interface.



10.4.:Figure 300 Κ ab*initio* molecular dynamics simulations of the Li(100)/LLTO(010)-AO interfacial model. (a) Interfacial model at (left) 0 ps and (right) after 40 ps. (b) Projected density of states (pDOS) for Li, La, Ti, and O ions in bulk LLTO. (c-e) pDOS of the explicit interfacial model for (c) Li anode, and the (d) La ions and (e) O ions in LLTO. The color shades correspond to the AO layers as labeled in (a) and (b). The light and dark shades of green in (c) correspond to the Li atoms in the layers closest to the interface (interfacial Li^{0}) and those in the subsurface (bulk Li⁰), respectively. (f) Bader charges of La ions in the explicit interfacial models (data points in blue), calibrated to oxidation states based on linear regression of calculated Bader charges for bulk La_2O_3 and La metal.

Figure 10.4c shows the local projected density of states (pDOS) for the Li anode and Figures 10.4d-e show the La, and O atoms in LLTO in the interfacial model, with the pDOS for each of these species in the LLTO bulk shown in Figure 10.4b for reference. While the Fermi energy (E_f) is a function of the charged defect levels in bulk LLTO within the calculated 2.22 eV band gap, the explicit Li/LLTO interfacial models are metallic and can give trend-based insights regarding charge transfer to/from the Li metal anode to the conduction/valence electronic states of LLTO. Upon interfacial contact between Li and LLTO the conduction states in LLTO (positive $E - E_f$ values in Figure 10.4b) are pinned to the Fermi level of Li metal suggest a driving force for charge transfer from Li into LLTO. The La pDOS (Figure 10.4d) seems to suggest that in the interfacial AO-layers (labeled ① in light purple) there is modest charge transfer due to population of La electronic states are broadened about E_f , suggesting partial occupancy. The O pDOS at the interface (light red data series in Figure 10.4e) shows several gap states, wherein the peaks in the electronic DOS line up with peaks in the interfacial Li⁰ pDOS of the model anode (light green data series in Figure 10.4c) indicating Li-O orbital hybridization, consistent with interfacial reconstruction between the Li anode and the O²⁻ anions in AO layer ① to increase coordination with the oxophilic Li atoms.

To further evaluate the extent of La redox suggesting by the charge transfer observed in the interfacial La pDOS (light purple data series in Figure 10.4d), Bader charge analysis [498, 177, 176, 178] is performed on La ions in the LLTO model and is calibrated to the Bader charges calculated for La₂O₃ (La³⁺ reference) and La metal (La⁰ reference). The calibrated Bader charges in Figure 10.4f show that most La ions are approximately in the 3+ oxidation state (>2.7+), where only one La ion at the interface has a slightly reduced Bader-calibrated oxidation state of ca. 2.4+. Overall, the average calibrated oxidation states of La ions in the Li(100)/LLTO(010)AO model is ca. 2.94+, suggesting minimal redox chemistry between the Li metal anode and La³⁺ ions in LLTO. This finding from explicit interfacial modeling is in agreement as well with the prediction of La₂O₃ bulk stability shown in Figure 10.1b. The results suggest furthermore that the charge transfer between Li and LLTO is primarily associated with bond formation and hybridization between the Li metal anode and O²⁻ ions at the interface.

Given the minimal reactivity of the AO-terminated LLTO with Li over AIMD timescales, we next consider the dynamics of the TiO_2 -terminated LLTO with the



10.5.:ab initio molecular dynamics simulations of the Figure 300 Κ Li(100)/LLTO(010)-TiO₂ interfacial model. (a) Interfacial model at (left) 0 ps and (right) after 40 ps. (b) Partial Ti-O radial distribution function, $g_{Ti-O}(\mathbf{r})$, evolution over the duration of the AIMD run. The white circle corresponds to V_O° formation and O^{2-} anion disproportionation from TiO_5 to TiO_6 and TiO_4 polyhedra at the interface, as marked in the right panel of (a). (c) pDOS for Li, La, Ti, and O ions in bulk LLTO. (d-f) pDOS of the explicit interfacial model for (d) Li anode, and the (e) Ti ions and (f) O ions in LLTO. The color shades in (e) and (f) correspond to the TiO_2 layers as labeled in (a). The light and dark shades of green in (d) correspond to the Li atoms in the layers closest to the interface (interfacial Li⁰) and those in the subsurface (bulk Li⁰), respectively. (g) Bader charges of Ti ions in the explicit interfacial models (data points in blue), calibrated to oxidation states based on linear regressions of calculated Bader charges for bulk TiO₂, Ti₂O, and Ti metal.

Li anode, which the bulk analysis (Figure 10.1) suggests may be more susceptible to redox chemistry at 0 V vs. Li/Li⁺. Figure 10.5 shows results from a 40 ps AIMD simulation of the Li(100)/LLTO(010)-TiO₂ interfacial model. Figure 10.5a shows the starting ionic positions (left) and the ionic positions after 40 ps of dynamics (right). Similar to Figure 10.4a, different TiO₂ layers are labeled 1-3 where layer 1 is nearest to the interface with Li metal and 3 is the TiO₂ layer nearest the middle of the LLTO slab, meant to resemble the bulk of the solid electrolyte. The snapshot after 40 ps illustrates several distinct interfacial reconstructions for the TiO₂-terminated LLTO in comparison to the AO-terminated LLTO interface with Li metal. Specifically, the coordination environments of Ti ions is modified from the initial to final structure. As the initial structure shows (as well as the free TiO₂-terminated LLTO(010) surface in Figure 10.2a, the interfacial TiO₂ layer consists of entirely TiO₅ without the introduction of any point defects, i.e. oxygen vacancies. However, as the system evolves structurally over the course of the AIMD simulation, disproportionation of O^{2-} anions at the interface leads to conversions to TiO₄ and TiO₆ polyhedra (labeled in the right structural model in Figure 10.5a) from the pristine TiO₅ polyhedra-terminated interface.

Similar to the AO-terminated interface (see Figure 10.4a), O^{2-} anions in the interfacial layer distort to increase interactions with the Li anode. This is further facilitated at the TiO₂-terminated interface given the flat potential energy surface of TiO_x polyhedra, where imaginary phonon modes [486] are associated with facile octahedral tilting. This feature is represented in Figure 10.5b by the partial Ti-O radial distribution function (RDF), g_{Ti-O} , which shows a wide range of Ti-O bond lengths between ca. 1.8-2.2 Å that are continuously accessed over the AIMD run. The coordination of O²⁻ anions toward Li metal creates pseudo-vacancy sites in the TiO_x polyhedra, enabling O²⁻ anion disproportionation via vacancy sites to modify the crystal field of TiO₅ at the interface into octahedral and tetrahedral Ti ions (TiO₆ and TiO₄ respectively).

Figure 10.5d shows the local pDOS for the Li anode and Figures 10.5e and 10.5f show the local pDOS for Ti and O ions in LLTO within the explicit interfacial model. The pDOS for each ion in bulk LLTO is shown for reference in Figure 10.5c. Similar to the AO-terminated interface, the conduction states in LLTO are also pinned to the Fermi level of the Li metal suggesting a similar electronic structure-based driving force for charge transfer into LLTO. Comparison between the interfacial Li⁰ (light green data series in Figure 10.5d) and O pDOS (light red data series labeled (1) in Figure

10.5) indicates overlap between the gap states introduced for the O pDOS at the interface and peaks associated with the valence states of interfacial Li⁰, concomitant with the observed reconstruction of TiO_x groups via polyhedral tilting at the interface with Li. Figure 10.5e shows that in comparison to the reference of Ti⁴⁺ ions in bulk LLTO (Figure 10.5c), there is charge transfer to Ti given the broadening of Ti 3d states about E_f . Furthermore, the Bader analysis of Ti atoms in Figure 10.5g, which is calibrated against bulk TiO₂ (anatase and rutile, Ti⁴⁺ reference), Ti₂O (Ti⁺ reference) and Ti metal (Ti⁰ reference), shows that there is significant reduction of Ti ions to the 3+, 2+, 1+, and 0 (metallic) oxidation states. The data suggests that, in contrast to the AO-terminated interface, that titanium oxide-like motifs at the interface between the LLTO electrolyte and a Li metal anode are much more susceptible to redox chemistry. This result, which is specific to the reactivity of TiO_x species with Li metal, is consistent with the theoretical prediction of reduced Ti₃O-like phase (average oxidation state of Ti^{0.67+}) at 0 V vs. Li/Li⁺, as shown in Figure 10.1c.

Given the mobility of the O^{2^-} anions at the TiO₂-termianted interface (Figures 10.5a,b) as well as the comparatively low interfacial energy with the introduction of oxygen vacancies (Figure 10.3), we also perform similar AIMD simulations on the $\text{Li}(100)/\text{LLTO}(010)\text{TiO}_2+V_O^{\circ}$ interfacial model (Figure 10.6). Figure 10.6a shows the starting ionic positions (left) and the ionic positions after 40 ps of AIMD (right), with the TiO₂ layers labeled \oplus - \oplus . The AIMD snapshot after 40 ps shows evidence for the onset of decomposition reactions with the distortion of TiO_x polyhedra at the interface with Li metal. These interfacial reconstructions appear to be facilitated by the introduction of the V_O° point defect. In particular, the coordination of interfacial O^{2^-} anions with the Li metal anode leads to shortened Ti-Ti distances. Figure 10.6b shows the partial Ti-Ti RDF, $g_{Ti-Ti}(r)$, where Ti-Ti interatomic distances of ca. 2.7 Å are present after 5 ps of AIMD, corresponding well to Ti-Ti bond distances in Ti metal.



Figure 10.6.: 300 K *ab initio* molecular dynamics (AIMD) simulations of the Li(100)/LLTO(010)- $\text{TiO}_2+V_{O}^{-}$ interfacial model. (a) Interfacial model at (left) 0 ps and (right) after 40 ps. (b) Partial Ti-Ti radial distribution function, $g_{Ti-Ti}(r)$, evolution over the duration of the AIMD run. (c) pDOS for Li, La, Ti, and O ions in bulk LLTO. The white circle corresponds to the formation of Ti-Ti interatomic distances concomitant with the bulk Ti metal lattice constant of ca. 2.7 Å. (d-f) pDOS of the explicit interfacial model for (d) Li anode, and the (e) Ti ions and (f) O ions in LLTO. The color shades correspond to the TiO₂ layers as labeled in (a) and (b). The light and dark shades of green in (c) correspond to the Li atoms in the layers closest to the interface (interfacial Li⁰) and those in the subsurface (bulk Li⁰), respectively. (f) Bader charges of Ti ions in the explicit interfacial models (data points in blue), calibrated to oxidation states based on linear regressions of calculated Bader charges for bulk TiO₂, Ti₂O, and Ti metal.

Figure 10.6d shows the local pDOS of the Li anode and Figures 10.6e and 10.6f show the pDOS for Ti and O ions in LLTO. While similar overlap is observed between interfacial O (series ① in Figure 10.6f) and interfacial Li⁰ (light green series in Figure 10.6d) to the AO- and TiO₂-terminated interfaces (Figures 10.4 and 10.5, respectively), the data additionally shows an increase in interfacial Ti DOS broadening about the Fermi level, extending to ca. 2 eV below E_f (data series ① in Figure 10.6e). This suggests additional reduction of Ti ions at the interface, which is further supported by Bader analysis (Figure 10.6f) showing several Ti atoms in the explicit interfacial models with reduction to the 3+, 2+, and 0 (metallic) oxidation states.

Overall, these explicit interfacial modeling studies support and augment the insights provided from the bulk LLTO stability analysis at low voltages. The results from these simulations show that LLTO is susceptible to decomposition at the interface with a Li metal anode, but that this is primarily driven by the reactivity of Ti^{4+} ions and the strong thermodynamic driving forces for them to be reduced to lower oxidation states. We observe through AIMD simulations potential atomistic mechanisms for the onset of LLTO decomposition chemistry through interfacial band alignment, as well as $V_O^{::}$ formation and O^{2-} anion transfer between TiO_x polyhedra at the interface.

10.2.3 Vacuum Alignment of Electronic Band Levels at the Li/Electrolyte Interface

Building off of the results from explicit interfacial modeling between LLTO and the Li metal anode, the electrostatic driving forces for charge transfer and redox chemistry between the two materials are analyzed. This analysis is meant to augment the insights afforded from the bulk and interfacial analyses to better understand, and to potentially control, the interfacial reactivity of the LLTO solid electrolyte at the anode. In this section, the electronic band levels are calculated by referencing the free surface ionization potentials to the vacuum electrostatic potential [499]. Similar analyses have been used recently to describe driving forces for charge transfer [463, 213] and for the prediction of space charge layer formation [500] at solid-solid interfaces. For metallic phases, i.e. the Li anode, the ionization potential is simply the difference between the vacuum and Fermi energies, $IP = E_{vac} - E_f$. For semiconductors, this quantity instead refers to the top of the valence band (E_{VBM}) for a given surface, $IP = E_{vac} - E_{VBM}$, and the position of the conduction band minimum can therefore be determined by adding the calculated value of the Kohn-Sham gap of the bulk to the valence band maximum. As a reference, Figure 10.7 shows the electronic band levels for Li metal and the TiO₂- and AO-terminated surfaces of LLTO. Similar to previous DFT analyses of perovskite surfaces [501], there is a significantly large 1.84 eV difference in the ionization potentials of the TiO₂- and AO-terminated LLTO(010) surfaces, suggesting a much larger driving force present for the TiO₂-terminated LLTO(010) surface to be an electron acceptor. In fact, LLTO(010)TiO₂ conduction band (-3.45 eV vs. vacuum) is lower in energy that the Li Fermi level (-3.14 eV vs. vacuum), indicating favorable charge transfer from Li metal to TiO₂-terminated surfaces of LLTO, consistent with the bulk and interfacial analyses discussed previously. In contrast, the AO-terminated LLTO(010) conduction band is 1.53 eV higher in energy than Li, indicating that the native driving forces for charge transfer between these two interfaces is considerably less likely.

These insights from the Li and LLTO band alignment analysis, combined with bulk and explicit interfacial modeling studies, lend further support toward the hypothesis that the instability of Ti^{4+} ions from the thermodynamic and charge transfer driving forces is likely to initiate interfacial decomposition chemistry. Given these insights, however, there is likely to be little synthetic control over the chemical termination of LLTO near the interface with Li, due to both the degeneracy of AO- and TiO_{2^-} terminated surfaces as well as the highly disordered nature of the material. Instead, an interlayer coating can be proposed that applies knowledge gained from the relative stability of AO-terminated LLTO surfaces in addition to the stable bulk decomposition products at 0 V vs. Li/Li⁺. Since La³⁺-containing species, are reductively stable compared to Ti^{4+} at 0 V vs. Li/Li⁺ (Figure 10.1b), this suggests that a La³⁺-rich interface may enable enhanced anodic stability of LLTO solid electrolytes. In particular, the native La₂O₃ oxide phase is calculated to be stable at 0 V vs. Li/Li⁺ and may therefore represent a good proxy for a controlled AO surface termination.

Figure 10.7 incorporates the electronic band levels of La_2O_3 using the low-energy stoichiometric $La_2O_3(001)$ surface. We find that, while the ionization potential of $La_2O_3(001)$ is relatively high (similar to the TiO₂-terminated LLTO slab), the wide



Figure 10.7.: Electronic energy levels for Li anode, TiO_{2} - and AO-terminated LLTO(010) surfaces, and $La_2O_3(001)$. The black dashed horizontal line is the vacuum level, which all other levels are referred to. The horizontal black line for Li is the Fermi level relative to the vacuum. For the semiconductors, horizontal blue lines represent the valence band and horizontal orange lines are the conduction band, determined from the calculated band gap of the semiconducting LLTO and La_2O_3 materials (marked with double-sided red arrows and text). The black arrows and corresponding black text extending from the vacuum level to the valence band or Fermi level indicate the ionization potential.

band gap positions the conduction band minimum to a similar position to that of the AO-terminated LLTO(010) surface. This analysis suggests a minimal driving force for charge transfer from Li to La₂O₃, which may be able to buffer the band alignment between Li metal and the TiO_x-like motifs in LLTO. Additionally, La₂O₃ is a high- κ material [502] that may enable a potential drop across the interlayer. In order to further probe these effects, we next want to consider explicitly the role of La₂O₃ on the band structure and alignment at the Li/LLTO interface in the presence of this interlayer coating.

10.2.4 Controlling Interfacial Reactivity with La₂O₃ Interlayer Coating

We construct a periodic interfacial model that comprises all three components, wherein two La₂O₃(001) bilayer films passivate each TiO₂-terminated LLTO(010) surface as an explicit buffer layer between it and Li(100). Figure 10.8a shows the relaxed structural model wherein the Li(100)/LLTO(010)TiO₂ interface is buffered by a two-monolayer La₂O₃ interlayer coating. The O-La layers in La₂O₃ and the TiO₂ layers in LLTO are labeled (①-⑤ and ⑥-⑦, respectively) for reference to the layer pDOS analysis.

Figure 10.8b shows the pDOS for the Li anode and Figures 10.8c and 10.8d show the O and La pDOS in the La_2O_3 interlayer coating. Upon relaxation the interfacial Li atoms (light green data series in Figure 10.8b) hybridize with O states in La_2O_3 interfacial layer (data series(I) in Figure 10.8c). The La pDOS (Figure 810.8) shows some evidence of modest redox at the Li/La_2O_3 interface (data series (2)), although the character of the La states near and above E_f is largely unchanged between the Li/La_2O_3 and $La_2O_3/LLTO$ interfaces, suggesting that the La_2O_3 bilayer is relatively unreactive with the exception of O^{2-} ion covalency with Li and LLTO. Moreover, the Ti pDOS in LLTO (Figure 10.8e) is effectively indistinguishable between the layers closest to the La_2O_3 -coated Li anode (layer (6)) and those in the center of the slab resembling bulk LLTO (layer (7)). There is minimal broadening of Ti 3d states about E_f suggesting that nearly all Ti ions remain in the 4+ oxidation states. To expand upon the observations from the pDOS analysis, calibrated Bader charge calculations are used to estimate oxidation states of La ions in La_2O_3 and LLTO (Figure 10.8f, dark and light purple data series, respectively) and Ti ions in LLTO (Figure 10.8g). The data supports the aforementioned conclusions from pDOS analysis where La ions in both La_2O_3 and LLTO remain in the 3+ oxidation states, and that all Ti ions in LLTO are in the 4+ oxidation state.

These results indicate that the La_2O_3 interlayer coating may stabilize the LLTO solid electrolyte against anodic decomposition reactions, although such thermody-



Figure 10.8.: Role of La_2O_3 interlayer coating a on band align-(a)ment at the anode/electrolyte interface. DFT-relaxed for structure $Li(100)/La_2O_3(001)/LLTO(010)$ interfacial models. (b-e) pDOS in the $Li/La_2O_3/LLTO$ model for (b) Li anode, (c) La and (d) O ions in La_2O_3 , and the (e) Ti ions in LLTO. The light and dark shades of green in (b) correspond to the Li atoms in the layers closest to the interface with La_2O_3 (interfacial Li⁰) and those in the subsurface (bulk Li^0), respectively. The numbered labels \bigcirc - \bigcirc in each local pDOS plot correspond to the layers marked in the explicit interfacial model shown in (a). Layers (1)-(5) in (c,d) correspond to the O-La-O-La-O stacking of the two-monolayer $La_2O_3(001)$ slab and the layers (6) and (7) correspond to the TiO_2 layers in LLTO at and away from the interface with La₂O₃, respectively. (f,g) Bader charges of (f) La ions and (g) Ti ions in the explicit interfacial models. (f) Bader charges of La ions in La_2O_3 and LLTO are marked in dark and light purple, respectively. The Bader charges are calibrated to bulk La_2O_3 and La metal. (g) Bader charges of Ti ions in LLTO, calibrated to bulk TiO₂, Ti₂O, and Ti metal.

namic driving forces in principle still exist. These insights come from both an understanding of the relative thermodynamic stability of La_2O_3 against Li metal at 0 V vs. Li/Li⁺ but also with respect to the formation of an additional metal-semiconductor junction wherein a potential drop within the interlayer suppresses downward bending of the LLTO conduction band, suppressing charge transfer from Li to the solid electrolyte.

10.3 Conclusions

In this work, we have demonstrated computational strategies to understand and control interfacial reactivity in solid-state batteries. Applying the interface between Li metal and the LLTO solid electrolyte as a model system, we used a Li grand potential thermodynamic analysis to understand the driving forces for LLTO decomposition reactions, providing a baseline for surface and interfacial computational studies. Starting from stable equilibrium LLTO surfaces, we constructed explicit Li/LLTO interfacial models as inputs for AIMD simulations that describe potential atomistic mechanisms for decomposition chemistry at the solid-solid interface. Specifically, these studies demonstrate the reactivity of Ti⁴⁺ ions against Li metal, complementing conclusions from bulk thermodynamics. In contrast, AO-terminated LLTO surfaces (comprised of Li, La, and O) are relatively inert to redox chemistry with Li metal.

We further explore the driving forces for these interfacial reactions through the electronic band levels of different LLTO surface terminations with respect to Li, which directly elucidate an electrostatic driving force for charge transfer from the Li metal anode to the conduction band of TiO₂-terminated LLTO surfaces. Exploiting the structural stability of La³⁺ ions against Li, we demonstrate favorable positions of the La₂O₃(001) valence and conduction bands, which suggest mitigated redox chemistry between Li and LLTO. We further address these predictions through an explicit model of the Li/La₂O₃/LLTO interface, which shows negligible charge transfer between the compounds with only two monolayers of the La₂O₃ interlayer suggesting a high degree of interfacial stability.

In addition to thermodynamic criteria that have been used for the design of coatings [327, 328] and interlayers [464, 470, 471, 503], we suggest that the electronic band level alignment and driving forces for charge transfer must also be considered for stable interlayer coatings in solid-state batteries. Moreover, the substrate for interlayer growth (electrode or electrolyte) is not necessarily inert [504] and near-surface electronic structure and band alignment has been shown to influence the growth of protective oxide coatings [225, 261]. Similar to protective coatings deposited on Liion electrodes in liquid organic electrolytes there is likely to be a significant trade-off between rate capability and interfacial stability as the thickness of the interlayer increases, particularly for high- κ materials such as La₂O₃ that may incur a significant potential drop, even at the nanoscale.

10.4 Methods

10.4.1 Density Functional Theory Calculations

Spin polarized DFT calculations were performed using the generalized gradient approximation of Perdew, Burke, and Ernzerhof [163] in the VASP [160, 168, 161] electronic structure code. The core states were treated using the projector augmented wave method [201, 162], with small core pseudopotentials incorporating the Li 1s and Ti 2p electronic states explicitly modeled as valence states. The valence states are modeled using a plane wave basis set with a kinetic energy cutoff of 520 eV and Gaussian smearing widths of 0.05 eV are applied.

10.4.2 Ab initio Molecular Dynamics Simulations

AIMD simulations of the explicit Li/LLTO interfacial models are performed in the canonical ensemble (NVT) at a Nosé-Hoover [169, 497] thermostat temperature of 300 K in the VASP [160, 168, 161] code. A time step of 2 fs is used in all cases. To reduce computational expense, these calculations are performed non-spin polarized, with Li 1s and Ti 2p states in the core of the pseudopotentials, and at a kinetic energy cutoff of 400 eV. Electronic structure analyses of AIMD snapshots are performed using the more stringent calculation parameters outlined in Section 10.4.1.

R.E.W. performed the DFT and AIMD studies for the bulk, surface, and interfacial calculations. S.P. performed the surface slab vacuum alignment calculations.

11. UNDERSTANDING THE ROLE OF OVERPOTENTIALS IN LITHIUM ION CONVERSION REACTIONS: VISUALIZING THE INTERFACE

This chapter is reproduced with the permission of the American Chemical Society from: Guennadi Evmenenko, Robert E. Warburton, Handan Yildirim, Jeffrey P. Greeley, Maria K. Y. Chan, D. Bruce Buchholz, Paul Fenter, Michael J. Bedzyk, and Timothy T. Fister; Understanding the Role of Overpotentials in Lithium Ion Conversion Reactions: Visualizing the Interface. *ACS Nano* **2019** *13*(7), 7825-7832.

Oxide conversion reactions are known to have substantially higher specific capacities than intercalation materials used in Li-ion batteries, but universally suffer from large overpotentials associated with the formation of interfaces between the resulting nanoscale metal and Li₂O products. Here we use the interfacial sensitivity of *operando* X-ray reflectivity to visualize the structural evolution of ultrathin NiO electrodes and their interfaces during conversion. We observe two additional reactions prior to the well-known bulk, three-dimensional conversion occurring at 0.6 V: an accumulation of lithium at the buried metal/oxide interface (at 2.2 V) followed by interfacial lithiation of the buried NiO/Ni interface at the theoretical potential for conversion (at 1.9 V). To understand the mechanisms for bulk and interfacial lithiation, we calculated interfacial energies using density functional theory to build a potential-dependent nucleation model for conversion. These calculations show that the additional space charge layer of lithium is a crucial component for reducing energy barriers for conversion in NiO.

11.1 Introduction

Lithium ion batteries are a key component of many modern technologies but are still predicated on materials capable of intercalating lithium [505, 390]. While these materials provide improved reversibility and higher voltages than other energy storage technologies, they are intrinsically limited in specific capacity by lithium site density in their crystal structures. Reaching higher lithium content requires a shift from classic insertion materials to the broader class of conversion chemistries where lithium reacts directly with the host material. By removing the crystallographic constraint required for intercalation, conversion reactions, such as those found in a lithium sulfur battery [506] or displacement reactions in binary metal oxides [53] and fluorides [507], can achieve specific capacities many times higher than materials currently used in lithium ion batteries [54]. However, these chemistries universally suffer from poor reversibility, both in their poor Coulombic efficiency and significant overpotentials ($\eta = E_{eq} - E_{exp}$), which have slowed their commercialization.

While irreversible capacity is a known byproduct of the large volume change associated with conversion and can be mitigated by nanoengineering or conductive additives, overpotentials are intrinsic and less understood [52]. In this study, we determine the origins of this overpotential of the well-known displacement reaction of a metal oxide into nanoscale metal and lithium species. The energy density of these materials, given by the product of their reaction voltage and specific capacity, is shown in Figure 11.1 in comparison to standard cathode materials (LCO = $LiCoO_2$, LMNO = $LiMn_{1.5}Ni_{0.5}O_2$, LFP = $LiFePO_4$). Despite their lower intrinsic voltages, the theoretical energy density of conversion reactions is often higher than intercalation materials. The significant overpotentials for oxide conversion severely reduce their energy density, as illustrated in Figure 11.1 [181, 508]. As a result, oxide conversion materials are largely considered to be anodes with limited practical viability.



Figure 11.1.: Comparison of the energy density of intercalation and metal oxide conversion materials. Note that the energy loss in conversion (denoted by arrows) is largely due to the large overpotentials during lithiation, as highlighted for NiO, the subject of this study. Equilibrium ($\eta = 0$) potentials are calculated using bulk, experimental enthalpies; experimental capacities and observed lithiation potentials are taken from reference [52].

The overpotential, which is especially pronounced during the first discharge, has been attributed to the formation of interfaces between the metal and Li_2O products [52]. This energy barrier can involve components related to strain imposed by significant volume change upon conversion, transport of electrons and Li ions through the complex network of nanoparticles formed during lithiation, and the intrinsic nucleation barrier required for phase separation. Many groups have improved the overall reversibility and kinetics of conversion by nanoengineering [509, 510, 511] or with conductive additives [512, 513], but - with a few exceptions [514] - the overpotential appears to be intrinsic. In order to understand the origin of the overpotentials and possible contributions from interfaces, nanoscale *operando* characterization techniques are sorely needed. The spatial resolution of transmission electron microscopy (TEM) has been used to visualize the nucleation and evolution of a conversion reaction [507, 515, 516]. However, the electrochemical conditions of *in situ* TEM are
often ill-defined and the complex, three-dimensional nature of conversion can obscure the atomic scale properties of the interface.

Here we take an alternative route by studying the lithiation of ultrathin (<2 nm thick) films of NiO at well-defined potentials using X-ray reflectivity (XR). X-ray and neutron reflectivity has previously been used to study interfacial reactions in a variety of battery materials, including cathode and solid electrolyte thin films [517, 518, 519, 520, 521, 522, 523, 524], alloying reactions in silicon and silicide composites [525, 526, 527, 528, 529, 530, 531, 532], and reactions associated with lithium plating and solid electrolyte interphase compounds [533, 534, 535, 536, 537, 538, 539]. Here, we reduce the electrode thickness to the typical size of a conversion product. This eliminates much of the 3D complexity of the reaction and can accentuate the subnanometer depth resolution of XR. Such model electrodes largely minimize the contributions of strain and transport to the overpotential and so provide direct insights into the intrinsic barriers for lithiation.

NiO was chosen as a model system due to the simplicity of the reaction, NiO $+ 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Ni} + \text{Li}_2\text{O}$, which does not form any intermediates. In spite of this chemical simplicity, the voltammetry and XR data both reveal two distinct reactions: one near the theoretical potential for lithiation (1.9 V), *i.e.*, with little or no overpotential, and one at the typically observed discharge plateau for the reaction at 0.6 V. The higher potential reaction is initiated at the buried Ni/NiO interface and is preceded by significant accumulation of Li⁺ at this interface. This accumulation is a direct measurement of capacitive lithium storage, which was previously speculated to be a space charge layer giving rise to additional capacity during the first discharge that is ubiquitous for oxide conversion reactions [540, 541]. Using density functional theory (DFT) calculations, we correlate these effects to the dramatically reduced interfacial energy of Li₂O/Ni in the presence of excess lithium at the interface. Similar findings were found for a Ni/NiO/Ni trilayer with improved reversibility. These results help to clarify the fundamental origin of overpotentials in metal oxide

conversion reactions and demonstrate that, at least in principle, conversion can occur at the theoretical limit.

11.2 Results and Discussion

Amorphous Ni and NiO films were grown on annealed R-plane sapphire substrates by pulsed laser deposition (PLD) and measured in a fully immersed, three-electrode cell (Figure F.1) at the Advanced Photon Source, sector 12ID-D. The NiO layer was masked on the sides to enable electrical contact to the bottom Ni current collector. Specular X-ray scattering measurements were performed in the Fresnel regime up to a momentum transfer (q) of 1.2 Å⁻¹, providing a vertical spatial resolution of 2.7 Å. Rocking curves measured between each scan (every 0.1 V) showed no change in width ($\Delta \theta = 0.04^{\circ}$), suggesting that the lateral structure over the 1 x 3 mm² footprint of the beam remained homogeneous throughout the reaction. Similarly prepared NiO/Ni interfaces have been shown by TEM to have nearly ideal and uniform interfaces, consistent with the results of the XR analysis of the as-deposited samples [479]. Samples were lithiated and delithiated by cyclic voltammetry between 3 and 0.3 V vs Li/Li^+ at 0.2 mV/s in 1.0 M LiPF_6 in 1:1 ethylene carbonate (EC)/dimethyl carbonate (DMC). Given the extremely small amount of NiO present (0.28 μ g), we carefully shielded the working electrode connections to minimize the amount of side reactions with the electrolyte.

Fresnel-normalized reflectivity data taken during the lithiation of a 17 Å thick NiO film grown on a 25 Å Ni current collector are shown in Figure 11.2a. The logarithmic intensity of the XR is denoted by color to highlight structural changes during voltammetry, with data and fits overlaying the plot at select potentials. Data were collected continuously during voltammetry so that each XR scan actually takes place over a 0.09 V range. Fits were performed at potentials where the reflectivity was changing slowly. Changes in the XR data correlate well with the current response of the simultaneously measured cyclic voltammetry, shown in Figure 11.2b, with structural changes correlating to the two well-defined reduction events centered at 1.7 and



Figure 11.2.: (a) Fresnel normalized reflectivity (R/R_F) is shown during the first lithiation sweep. The XR intensity is denoted by color so that potential-dependent changes can be compared with the CV in (b). Data were measured continuously during voltammetry with each XR measurement occurring over 0.09 V. Select curves from the fitting overlay the XR map. (c) Electron density profiles and their propagated error bars extracted from fits to the XR data (visible for the 0.3 V data) are shown for select potentials. Reference densities for NiO, Ni, and Li₂O and the average density of the conversion products (Ni + Li₂O) are provided for reference. The area under the open circuit density profile (3.1 V) is colored to emphasize the initial Ni, NiO, and electrolyte layers. Note the strong changes at the Ni/NiO interface near $E_{eq} = 1.9$ V, followed by overall expansion, roughening, and density reduction in the remaining NiO layer approaching $E_{bulk} = 0.6$ V.

0.6 V. The cyclic voltammograms (CVs) appear to have some capacitive response as well and are shifted to negative currents due to side-reactions related to solid electrolyte interface processes or electrolyte decomposition on the exposed current collector. From the raw data alone, the initiation of the lithation reaction at 1.9 V is observed both with a shift of Kiessig fringes in the XR data to lower q, reflecting the overall vertical expansion of the heterostructure, and with an abrupt increase in scattering power due to heightened interfacial contrast. To quantify these structural changes, we show selected fits to the XR data in Figure 11.2c. The extracted electron density profiles show that the higher potential phase change is most pronounced at the buried Ni/NiO interface, followed by expansion and lithiation of the remaining NiO at lower potentials. Even at potentials exceeding E_{eq} , we find a small reduction in electron density at the Ni/NiO interface, consistent with the accumulation of Li⁺ at this buried interface. This capacitive effect reflects the double-layer current measured between 1.9 and 2.5 V and subtle changes in the XR that are most pronounced at high q. The accumulation of Li^+ at this interface, rather than at the surface, suggests that Li⁺ conductivity through the nanocrystalline NiO film is faster than electron transport (consistent with nickel oxides large bandgap of 4.3 eV). Below 1.9 V, this interlayer density drops quickly to the combined density of the conversion products, indicating an interfacial conversion reaction. As the rest of the NiO film lithiates at lower potentials, this interfacial layer eventually reaches the density of pure Li_2O .

During delithiation, the NiO surface continued to roughen, complicating fitting of the bilayer. The first cycle reversibility of both reactions can be seen in the oxidative sweep in Figure 11.2b, but the overall current is noticeably reduced on the second cycle. This latter effect could be tied to partial delamination of improved reversibility, both in the delithiation reaction and in the second lithiation cycle. The density profiles shown in Figure 11.3c also show the presence of a capacitive Li⁺ double layer at both Ni/NiO interfaces at elevated potentials (2.2 V). This is clearly seen in the raw data (Figure 11.3a), which show an abrupt increase in thickness and scattering power at 1.9 V. As with the simpler bilayer, the interfacial component of the reaction continues until ~1.5 V. The derived density profiles (Figure 11.3b) reveal that the bottom interface develops the space charge layer first and begins to undergo conversion at 1.9 V. Both buried interfaces react fully, eventually approaching the density of pure



Figure 11.3.: (a) Normalized reflectivity during lithiation (top) and delithiation (bottom). As in Figure 11.2, select curves overlay the data. CVs taken during the first cycles are shown on the same potential scale as the XR lithiation data for comparison. (b) Electron density profiles from fits to XR data at select potentials show a decrease in density at the interfaces consistent with Li accumulation, followed by lithiation of the NiO interlayer. Minor changes also occur at the surface of the top nickel layer due to its native oxide. Like Figure 11.2, the area under the open circuit density profile (3.1 V) is colored to highlight the initial trilayer structure.

 Li_2O (0.57 e⁻/Å³) with a more Ni-rich (but reacted) interlayer in between. Unlike the first sample, the surface of the exposed Ni overlayer also undergoes a separate conversion reaction with its native oxide. Much like the underlying NiO layer, this native oxide develops a slight dip in electron density consistent with a lithium-rich region that eventually approaches the density of pure Li_2O near 0.6 V.

Similar measurements on a Ni/NiO/Ni trilayer (14 Å thick NiO) were performed to better resolve changes in the NiO film and to improve the structural reversibility of the planar electrodes. Such layered heterostructures help confine the reaction products and provide a stronger interfacial contrast for the overall thickness of the heterostructure [479, 542, 543]. Previous work in multilayer electrodes suggested that Li⁺ transport is possible through sufficiently thin metal interlayers [544]. With the added Ni overlayer, the two-step lithiation is even more apparent in both the XR data and the CV (as seen in Figure 11.3). The CV shows improved reversibility, both in the delithiation reaction and in the second lithiation cycle. The density profiles shown in Figure 3c also show the presence of a capacitive Li⁺ double layer at both Ni/NiO interfaces at elevated potentials (2.2 V). This is clearly seen in the raw data (Figure 11.3a), which show an abrupt increase in thickness and scattering power at 1.9 V. As with the simpler bilayer, the interfacial component of the reaction continues until ~ 1.5 V. The derived density profiles (Figure 11.3b) reveal that the bottom interface develops the space charge layer first and begins to undergo conversion at 1.9 V. Both buried interfaces react fully, eventually approaching the density of pure Li_2O (0.57) $e^{-}/Å^{3}$) with a more Ni-rich (but reacted) interlayer in between. Unlike the first sample, the surface of the exposed Ni overlayer also undergoes a separate conversion reaction with its native oxide. Much like the underlying NiO layer, this native oxide develops a slight dip in electron density consistent with a lithium-rich region that eventually approaches the density of pure Li_2O near 0.6 V.

The present results from both the bilayer and trilayer present a consistent picture for the reaction pathway for the NiO conversion reaction (illustrated schematically in Figure 11.4). The first step involves Li^+ diffusion through the matching the Ni + Li_2O conversion products. Here, the density of the interfacial layer decreases even further, consistent with a pure Li_2O layer at the interface, suggesting that the isolated Ni products from the first reaction aggregate into the Ni electrode.



Figure 11.4.: Schematic of the interfacial and bulk conversion processes during the first lithiation including (a) lithium accumulation, (b) nucleation of conversion products at the buried Ni/NiO interface, (c) formation of Ni and Li₂O layers at the buried interface, and (d) bulk three-dimensional conversion. For reference, an electron density profile (similar to those measured in Figure 11.2) is shown with each picture. In each density profile, the original film is denoted by the black dashed line, and changes in the density profile at each step are highlighted by the representative color of the reacting species.

Given the limited thickness of the interfacial region, our results suggest that the associated lithiation reactions are a relatively small component of the discharge in bulk conversion electrodes, which could be inferred from previous studies of NiO [545]. However, it is striking that in such nanoscale electrodes there is still a strong separation between bulk and interfacial reactions given the nanoscale dimensions of the film. To better understand the origins of this interfacial reaction, we used DFT to calculate interfacial energies (γ) associated with the NiO, Ni, and Li₂O species involved in the reaction. Coupled with the bulk free energy of reaction (ΔG_{bulk}) for NiO conversion, we calculate the intrinsic nucleation barriers and the size of the nucleation products for conversion. This model incorporates geometric considerations from the formation/destruction of different solidsolid interfaces as a result of nucleation at the Ni/NiO interface (ΔA_i). Additionally, the model is potential-dependent due to the presence of a (Li⁺ + e⁻) pair in reactants of the bulk reaction stoichiometry:

$$\Delta G(E,n) = n[\Delta G_{bulk}(E=0\,V) - 2eE] + \sum_{i}^{interfaces} \gamma_i \Delta A_i \tag{11.1}$$

Note that the first term (bulk thermodynamics, which scales with the number of NiO sites, n) becomes negative when E is less than the equilibrium potential (E_{eq}) , and the second term accounts for all new interfaces (with area ΔA) formed upon conversion. While this is a simplification of conversion in a macroscopic electrode, these intrinsic quantities are intended to resemble the simplified geometry of these ultrathin electrodes, where energy barriers due to strain and mass transport are largely minimized.

DFT calculations were performed for all binary permutations of solidsolid interface formation between Ni(111), NiO(100), and amorphous Li₂O. The resulting interfacial energies were incorporated into the nucleation model in equation 11.1 (further details are provided in Appendix F). Based on the XR data, we incorporated a Li₂O layer around an assumed Ni nucleus forming at the Ni/NiO interface into our theoretical model, as illustrated in Figure 11.5a. Using equation 11.1, we calculated a nucleation barrier of 7.32 eV at 1.4 V, while this barrier is gradually reduced to 0.52 eV near the observed bulk potential of 0.6 V. Clearly, the barrier associated with this model is unrealistically large at 1.4 V, whereas the significantly reduced 0.52 eV barrier at 0.6 V suggests only a modest barrier to formation of the discharge product at these potentials.

Although the nucleation model suggests possible mecha- nisms for conversion and growth at 0.6 V, wherein much of the current density from conversion is observed (reference CVs in Figures 11.2b and 11.3a), it does not address the observed interfa-



Figure 11.5.: (a, b) Illustrations of the models used to calculate the total energy required to undergo conversion. (c, d) Solid lines: ΔG (per NiO site), including bulk, interfacial, and total contributions, calculated using $\gamma_{Ni/NiO} = 1.44 \text{ J/m}^2$, $\gamma_{NiO/Li_2O} = 0.35 \text{ J/m}^2$, and $\gamma_{Li_2O/Ni} = 1.86 \text{ J/m}^2$ at 1.4 and 0.6 V, respectively. The dashed lines represent the same model with excess lithium incorporated at the Ni/Li₂O interface, which reduces $\gamma_{Li_2O/Li/Ni}$ to 0.41 J/m². In each case, the presence of excess interfacial lithium leads to a negative interfacial contribution to the free energy change (second term of the energy expression in equation 11.1) due to the destruction of the higher energy Ni/NiO interface and formation of the lower energy NiO/Li₂O and Li₂O/Li/Ni interface, the conversion reaction occurring directly at the buried Ni/NiO interface would be expected to be facile upon introduction of an electrochemical bias.

cial reactions that occur near E_{eq} . To more comprehensively interpret the XR results in this region, we additionally modeled the presence of excess interfacial lithium (shown by the illustration in Figure 11.5b), as observed through XR at $E > E_{eq}$ (see Figures 11.2c and 11.3b). Incorporation of a single lithium monolayer between the Ni(111) substrate and the amorphous Li₂O reduces the calculated interfacial energy to approximately 0.41 J/m². We note that the exact coverage of excess lithium is not known, and the value of one monolayer assumed in the calculations represents a likely upper bound to this quantity, implying that the magnitude of the calculated change in interfacial energy is also an upper bound. Applying the lower Li₂O/Li/Ni interfacial energy to the free energy expression in equation 11.1 leads to a net interfacial contribution to the total ΔG that is negative, since the higher energy Ni/NiO interface is partially destroyed ($\gamma_{Ni/NiO} = 1.44 \text{ J/m}^2$, $\Delta A < 0$), while lower energy $\text{Li}_2\text{O}/\text{Li}/\text{Ni}$ ($\gamma_{Li_2O/Li/Ni} = 0.41 \text{ J/m}^2$) and $\text{NiO}/\text{Li}_2\text{O}$ ($\gamma_{NiO/Li_2O} = 0.35 \text{ J/m}^2$) interfaces are formed ($\Delta A > 0$). The negative interfacial component of ΔG leads to prediction of a barrierless nucleation reaction, as shown in Figure 2.5c,d. This result implies that the formation of the $Li_2O/Li/Ni$ interface is likely to be facile upon introduction of an electrochemical bias, as is also suggested by the interfacial conversion observed by XR at high potentials. We note that the presence of excess lithium appears to be consistent with the formation of a space charge layer that catalyzes the initial conversion reaction at the buried Ni/NiO interface. In addition, we expect that conversion at interfacial defects (e.g., steps, kinks) on the nickel surface is likely to reduce nucleation barriers and overpotentials even further, as previously suggested [476]. These barriers are consistent with the observed conversion processes in the region E > 0.6 V and underline the importance of excess lithium in reducing interfacial energies between Ni- and Li₂O- rich regions of the conversion product. Furthermore, the consumption of the Li^+ to form Li_2O in this region is likely why this phenomenon is self-limiting until bulk conversion is observed near 0.6 V.

11.3 Conclusions

This study enhances the understanding and visualization of the nanoscale interfacial reactions in lithium ion conversion reactions through the use of model NiO thin-film electrodes. We identified an interfacially controlled reaction step in the conversion mechanism, in addition to the known bulk conversion processes. We developed a simple model to understand how the interplay between capacitive and Faradaic processes can lead to an interfacial conversion reaction near the theoretically predicted potentials, revealing that the observed behavior is controlled by the presence of an excess of lithium at the buried Ni/NiO interface. These results suggest that a viable route toward reducing overpotentials in oxide conversion reactions can be achieved by engineering metal/oxide interfaces as a solid-state pseudocapacitor [546]. These principles could be extended to the study and optimization of other conversion battery materials such as fluorides [507, 547], which have higher theoretical equilibrium potentials than oxides in general, but still experience significant overpotentials and voltage hysteresis. While the inherent formation of interfaces remains a fundamental obstacle for oxide conversion reactions, the use of tailored, pre-existing interfaces that can systematically deliver Li to the reaction site could, ironically, be the solution.

11.4 Methods and Experimental

11.4.1 Film Growth

Nickel/nickel oxide bilayer and trilayer thin films were grown by PLD on the 10 3 mm² R-face surfaces of 1 mm thick sapphire α -Al₂O₃ (102) substrates (CrysTec GmbH, Germany) using a PLD/MBE 2300 (PLD Products) system in the Northwestern University Pulsed Laser Deposition Facility. The system employed a 248 nm KrF excimer laser with a 25 ns pulse operating at 5 Hz. The laser was focused to a 1.5 3.5 mm^2 spot size on the targets, which were rotated at 5 rpm to prevent localized heating. The target substrate separation was fixed at 6 cm. Nickel was deposited from a metallic nickel target at a laser energy of 300 mJ per pulse at the chamber base pressure of $\sim 5 \ge 10^{-7}$ Torr. There was a 30% energy loss along the optical train to yield an energy density at the target of 4 J/(pulse $x \text{ cm}^2$). Nickel oxide was deposited from a dense hot-pressed nickel oxide target at an energy of 200 mJ per pulse in a deposition ambient of 5 x 10^{-4} Torr ultra-high-purity (99.994%) oxygen. There was a 30% energy loss along the optical train to yield an energy density at the target of 2.7 J/(pulse x cm^2). The thickness of each deposited layer was controlled by adjusting the number of laser pulses: nickel deposited at 0.01 Å/pulse; NiO deposited at 0.1 Å/pulse. The bottom nickel layer of each heterostructure was masked prior to deposition of subsequent layers to form a $3 \ge 3 \mod^2$ electrical contact with the spring-loaded electrode of the electrochemical cell [530].

11.4.2 X-ray Reflectivity

The operando X-ray reflectivity experiments were performed with an X-ray energy of 20.00 keV at the 12ID-D Advanced Photon Source station at Argonne National Laboratory. The X-ray beam was defocused and collimated to 1.0 x 0.18 mm², and the scattered X-ray pattern was acquired with a Pilatus 100k detector. Full reflectivity data scans were measured in 15 min (every 0.09 V) and were collected repeatedly during electrochemical cycling. Data were analyzed by subtracting the background (linear fit in the sample- ξ direction) in each Pilatus image. Reflectivity was normalized by the incident intensity and beam spill-off, which was proportional to q. The electrochemical cell [530] had separate lithium metal counter and reference electrodes, and the samples were fully immersed in a 1 M solution of LiClO₄ in a 1:1 ratio by volume of EC and DMC. A CHI760E electrochemical workstation was used for electrochemical control of lithiation. *Ex situ* XR studies of test samples were carried out at a Rigaku ATXG diffractometer (NU X-ray Diffraction Facility) E = 8.04 keV (λ = 1.54 Å) X-rays collimated to a 0.1 x 2.0 mm² spot. All XR measurements were performed at ambient laboratory temperature, which ranged between 20 and 25 °C.

XR analysis used Motofit [548] with a multiple-slab model that included a sapphire substrate, Ni and NiO layers, and an electrolyte (*operando*) or air (*ex situ* experiments). Structural parameters for sapphire and the electrolyte were fixed, whereas the parameters for the buffer and active layers (electron density, interface roughness, and layer thickness) were allowed to vary. The electron densities were initially estimated based on the chemical composition of the multilayer electrode components. As discussed in Appendix F, the errors in the structural parameters and their covariances were used to calculate the uncertainty for the overall density profile (*i.e.*, as a function of height). In most cases, the errors in derived electron density are actually smaller than the line-width used in the plots. Individual layer parameters and their errors are reported in Appendix F.

11.4.3 First-Principles Calculations

Spin-polarized DFT calculations were performed using the Vienna *ab Initio* Software Package (VASP) [160, 161, 168]. The generalized gradient approximation (GGA) of PerdewBurkeErnzerhof (PBE) was used as the exchange-correlation functional [163]. Γ -centered k-point grids were used for Brillouin zone sampling, where the product of the number of k-points and the corresponding lattice vector was ~ 30 Å. The projector-augmented wave method [201, 162] was used to treat the effective core potentials, with Li 1s electrons treated explicitly as valence in all calculations. For interfacial models between Ni and amorphous lithium $(a-Li_2O)$, the Kohn-Sham wave functions were expanded in a plane-wave basis set up to kinetic energy of 400 eV. All models containing NiO (interfacial models between NiO/a-Li₂O and Ni/NiO) used a kinetic energy cutoff of 520 eV. Calculations containing NiO used the DFT+Umethod [103, 102, 104, 106] with an effective U value of 6.2 eV applied to the Ni 3delectrons [73]. A U value of 4.0 eV was applied to the 3d states of metallic Ni for Ni/NiO interfacial models to accurately reproduce experimental formation enthalpies for NiO and $LiNiO_2$ as in previous work [549, 203]. Further details are provided in Appendix F.

Interfacial energies were calculated for interfaces between Ni/a-Li₂O, NiO/a-Li₂O, and Ni/NiO. For models containing amorphous lithium, an ensemble of structures is constructed through sampling a bulk supercell of a-Li₂O. The a-Li₂O supercell was generated from a melt and quench approach within classical molecular dynamics simulations performed using the DL_POLY code [550] (see Appendix F for further details). Crystalline Ni/NiO interfaces were made using an in-house lattice matching algorithm to minimize strain between Ni(111) and NiO(100). We sampled several lattice matching ratios about the minimum strain model output from the algorithm to ensure the interfacial energy is well optimized. Interfacial energies, γ , between two compounds, α and β , were evaluated using the general formula

$$\gamma = \frac{1}{2A} \left[E_{total}^{DFT} - \left(n_{\alpha} g_{\alpha}^{bulk} + n_{\beta} g_{\beta}^{bulk} \right) \right]$$
(11.2)

where E_{total}^{DFT} , n_i , and g_i^{bulk} are the total DFT energy of an interfacial model, the number of formula units of compound *i*, and the per formula unit bulk free energy of compound *i*, respectively, for an interface with interfacial area *A*. Structures that included an extra layer of lithium were treated using bulk metallic lithium as reference, since analysis of interfacial electron density suggested a metallic nature for nearly all of the excess lithium in this layer. We used an amorphous Li₂O reference state, as described further in Appendix F.

Supporting Information for this chapter is included in Appendix F.

G.E., T.T.F., M.J.B., and P.F. performed the XR measurements and analyzed the data. D.B.B grew the thin films. R.E.W., H.Y., M.K.Y.C., and J.P.G. performed the DFT and MD calculations. All authors were involved in the writing of the manuscript associated with this chapter.

12. ATOMISTIC STUDIES OF NUCLEATION AND GROWTH IN MULTILAYER ELECTRODES FOR THE NICKEL OXIDE CONVERSION REACTION

This chapter is excerpted from a manuscript being prepared for publication: Robert E. Warburton, Handan Yildirim, Maria K.Y. Chan, Jeffrey Greeley; Atomistic Studies of Nucleation and Growth in Multilayer Electrodes for the Nickel Oxide Conversion Reaction. *In Preparation*

12.1 Introduction

Lithium ion batteries (LIBs) are ubiquitous in consumer electronics and are an increasingly attractive technology for electric vehicles and large-scale grid energy storage [26, 17]. The most prevalent electrode materials in LIBs are currently based on intercalation reactions, wherein Li⁺ ions are reversibly inserted into, and removed from, the interstitial sites of a semiconductor host [21, 22]. Despite the marked success of many electrode chemistries so far, intercalation-based materials exhibit fundamental limits to their energy storage capacity due to the nature of these insertion reactions [551]. Conversion reactions, where metal oxides undergo direct electrochemical reaction with (Li⁺ + e⁻) pairs to form reduced metal nanoparticles within a lithia (Li₂O) matrix, can theoretically extend energy storage capacities well beyond that of traditional intercalation reactions [30, 52]. In practice, there exist several challenges that limit the development of such materials as practical battery electrodes. For instance, conversion reaction electrodes undergo severe volume expansion as a result of the solid-state reaction. Conversion reactions can also proceed through intercalation reactions and/or the formation of metastable intermediate phases [552, 553, 514, 554, 555, 556, 515, 557, 558] prior to full conversion to the final metal and Li₂O discharge product. This class of reactions also exhibits severe overpotentials between charge and discharge, which is related to heterogeneous interface formation upon delithiation. In particular, the problem of excessive overpotentials in these materials is of principal concern, where these inefficiencies may be attributed to the interfacial thermodynamics of the segregated discharge product phases. Nanoscale engineering of electrodes has demonstrated effectiveness toward improved reversibility of these reactions by alleviating the magnitude of some of these interfacial energy penalties [53, 543, 479, 544, 559].

In this work, we aim to describe, at the atomic scale, interfacial thermodynamics as well as their role in the experimentally observed overpotentials during discharge in lithium ion conversion reactions. In particular, we consider the electrochemical conversion of nickel oxide (NiO) to metallic nickel (Ni) and Li_2O as a model Liion conversion reaction. While this reaction has a theoretical equilibrium potential of about 1.86 V vs. Li/Li⁺ [52], However, numerous experimental studies reported significant overpotentials, with lithiation occurring closer to 0.6 V vs. Li/Li⁺ [53, 560, 561, 562, 563, 564, 565, 566, 567]. Such a significant overpotential observed for NiO makes this an interesting case study to probe the role of interfacial reactions on the thermodynamics of conversion reactions. As it is known, intermetallic alloys between Ni and Li are unstable [568, 569, 73] and Ni has even been applied as an inert matrix to control lithiation in the Li-Sn alloying reaction [570]. Conversion of bulk NiO is also not preceded by intercalation [571] or the formation of metastable bulk phases [558] in contrast to other conversion materials such as Co_3O_4 [515] and RuO_2 [554]. To address the role of nanostructured electrodes in catalyzing interface-driven phase transformations, we specifically focus on the Ni/NiO multi-layer electrode architectures described in recent studies by Fister et al. [479, 544, 496] In this particular electrode geometry, the presence of metallic Ni between layers of the NiO electrode seed growth of the Ni/Li₂O discharge product with improved reversibility.

Previous computational studies have considered solid-solid interfaces in LIBs including protective coatings [413, 251, 225, 213] and solid electrolytes [462, 478, 467] at electrode surfaces, in addition to interfaces formed during conversion reactions such as RuO_2 [476], CoO [477], and Cu₂O [572]. Recent studies by Ceder and co-workers have incorporated surface energetics into classical nucleation theory models to understand the interfacial barriers for thermodynamic stability predictions [573, 574, 575]. Similar approaches may be used to apply first principles calculations of solid-solid interfacial to understand the nucleation barriers to conversion reactions beyond those that are predicted by thermodynamic phase equilibrium.

In this study, we integrate first principles density functional theory (DFT) calculations of interfacial thermodynamics with a classical nucleation theory model to explore the interfacial components of the overpotential for NiO conversion reactions. We perform total energy calculations of the binary interfaces formed between Ni/NiO, Ni/Li₂O, and NiO/Li₂O to evaluate the interfacial thermodynamics. We also consider the thermodynamic influence of interfacial lithium at the Ni/Li₂O phase boundary, with a mechanistic explanation for interfacial charge storage beyond bulk stoichiometric limits. We modified the classical nucleation theory approach to account for all the interfaces studied, incorporating the geometry of the Ni/NiO multilayer electrode. Furthermore, we investigate the mechanisms of elementary conversion reaction events, wherein Li⁺ ions react at the Ni/NiO interface to initiate the formation of the Ni + Li₂O discharge product. The nucleation theory-derived overpotentials, and the elementary pre-nucleation reaction events provide further insights into the mechanisms of conversion reactions in nanoscale electrodes, as well as strategies for reducing the voltage hysteresis between the charge and discharge reactions.

12.2 Methods

12.2.1 Construction of Interfacial Models

First principles calculations are performed to evaluate interfacial energies of the solid-solid interfaces between crystalline Ni and amorphous Li_2O (Ni/a-Li₂O), crystalline NiO, and amorphous Li_2O (NiO/a- Li_2O), as well as crystalline Ni and NiO (Ni/NiO). Atomistic interfacial models are constructed using first principles DFT calculations, in addition to classical and *ab initio* molecular dynamics (MD) simulations (further details in Section 12.2.2). Construction of the $Ni/a-Li_2O$ and $NiO/a-Li_2O$ interfacial models involves sampling a large number of small a-Li₂O structural models from the large a-Li₂O structure obtained using classical MD simulations. This sampling was intended to address various terminations for $a-\text{Li}_2O$ at the solid-solid interface as well as to provide richness in the distribution of atoms within the a-Li₂O to provide sufficient statistics. We use a $4x4 \operatorname{Ni}(111)$ and $2x2 \operatorname{NiO}(100)$ unit cells with stoichiometric a-Li₂O unit cells (with 36 to 72 atoms), which are cut from the large a-Li₂O structure obtained using MD simulations by keeping the corresponding lattice to match that of the substrate. For the crystalline Ni/NiO interfaces, an in-house lattice matching algorithm is used in order to minimize the strain between Ni(111)and NiO(100). As is shown in the Section 12.3.1 (Figure 12.4), we sampled several lattice matching ratios from the algorithm to ensure the interfacial energy is well minimized.

12.2.2 Classical Molecular Dynamics Simulations

Classical MD simulations are performed using the DLPOLY code [550] with a core-shell potential whose parameters fit to Hartree-Fock (HF) calculations of bulk Li_2O . These calculations are performed on a cubic Li_2O ($Fd\bar{3}m$) bulk supercell containing 1500 atoms (500 Li₂O formula units). We then proceed through a melt and quench procedure to generate the *a*-Li₂O structure starting from the bulk crystalline phase. We confirmed a melt of Li₂O at 2500 K using the radial distribution function

(RDF), as shown in Figure F.2 in Appendix F. Starting from this melt structure, we gradually reduce the temperature down to 300 K, whereupon the resulting structure is further equilibrated at 300 K for another 300 ps. The resulting RDF and the corresponding structural model (Appendix F, Figure F.2) demonstrate the formation of an amorphous phase with a density of 1.99 g cm⁻³.

12.2.3 Density Functional Theory Calculations

Spin-polarized DFT calculations are performed using the Vienna Ab initio Software Package (VASP) [160, 168, 161]. The effective core potentials are treated using the projector augmented wave (PAW) method [201, 162]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) is used as the exchangecorrelation functional [163]. For interfacial models between Ni and a-Li₂O, the Kohn-Sham valence states are expanded in a plane-wave basis set up to 400 eV. Li PAW potentials include the 1s electrons as valence and all models containing NiO include the 3p states as valence in the PAW potential for Ni with a kinetic energy cutoff of 520 eV. Γ -centered k-point grids are applied for Brillouin zone sampling, with a consistent sampling density chosen such that the number of k-points multiplied into the corresponding real space lattice vector (~ 30 Å). Total energy calculations employ smearing using the tetrahedron method with Blöchl corrections. All atoms are subject to full ionic relaxation, and are converged to energy tolerance of 1 meV/cell and a force criterion of 15 meV Å⁻¹. Calculations involving NiO are performed using the Hubbard-type on-site Coulomb correction (DFT+U) [103, 102, 104] with a U value of 6.2 eV applied to Ni 3d states [73]. For calculations involving the interface between Ni and NiO, the U correction must also be applied to metallic Ni atoms in order to accurately reproduce the bulk NiO thermochemistry as has been detailed in previous work [549, 203]. Using the O_2 correction of -1.27 eV calculated previously [200] in good agreement with the method of Wang et al. [110], we find that a U-value of 4.0 eV on the metallic Ni reference state accurately reproduces standard bulk formation enthalpies between both NiO and LiNiO₂.

12.2.4 Classical Nucleation Theory Model

The results from the first principles calculations are further integrated into a classical nucleation theory (CNT) model. Analogous to previous studies [573, 574, 576], this is exercised to provide insights into the interfacial barriers that may be present under the conditions where the bulk phase transformations are otherwise thermodynamically favorable. In addition to the size of the nucleus (radius, r) we also consider the potential (U) dependence of the total system free energy, which is comprised of both the bulk and interfacial contributions.

$$\Delta G_{total}(U, r) = \Delta G_{bulk} + \Delta G_{interfacial} \tag{12.1}$$

In this expression, ΔG_{bulk} is the free energy of reaction for the overall conversion reaction shown

$$NiO + 2(Li^+ + e^-) \rightarrow Ni + Li_2O \tag{12.2}$$

where the free energy of the (Li⁺ + e⁻) is treated using an analogous computational hydrogen electrode [11, 65] approach. The potential-dependent bulk free energy (per NiO formula unit, Δg_{bulk} of the NiO conversion reaction is therefore

$$\Delta g_{bulk}(U) = (g_{Ni}^{bulk} + g_{Li_2O}^{bulk}) - [g_{NiO}^{bulk} + 2(g_{Li}^{bulk} - eU)]$$
(12.3)

where the free energies, g_i^{bulk} , are assumed to be approximately equal to the DFT calculated total energies - differential entropy contributions are assumed to be small in comparison. Li₂O is treated as amorphous in the bulk reference state, which we have calculated to have an amorphization energy of 0.44 eV per formula unit Li₂O. The equilibrium potential, U_{eq} , is that which makes Δg_{bulk} equal to zero, and is calculated using the electronic structure methods in this work to be 1.90 V and 1.69 V applying the crystalline and amorphous Li₂O reference states, respectively. The interfacial contributions to $\Delta G_{total}(U)$ are determined from the interfacial energies, γ , of the aforementioned solid-solid interface calculated for an interface between compounds α and β by

$$\gamma = \frac{1}{2A} \left[E_{total}^{\alpha/\beta} - \left(n_{\alpha} g_{\alpha}^{bulk} + n_{\beta} g_{\beta}^{bulk} \right) \right]$$
(12.4)

where n_i indicates the number of formula units of each compound in the interfacial model. The calculated γ values are incorporated into the extensive $\Delta G_{interfacial}$ term in equation 12.1 by considering the relative change in the interfacial area for each of the solid-solid interfaces, ΔA_i .

$$\Delta G_{interfacial} = \sum_{i}^{interfaces} \gamma_i \Delta A_i \tag{12.5}$$

Corresponding ΔG_{total} values can be calculated on a per formula unit basis through incorporation of bulk molar densities into the formulation. The value for which ΔG_{total} reaches a maximum at a given U is referred to as the nucleation barrier ΔG_{total} , which is traversed beyond the critical radius of nucleation (r_c) shown below.

$$\Delta G_c = max[\Delta G_{total}(r)] = \Delta G_c(r_c) \tag{12.6}$$

12.3 Results

12.3.1 Heterogeneous Nucleation and Interfacial Thermodynamics

In our previous work [496], operando X-ray reflectivity was used to observe nucleation and growth of the NiO conversion discharge products directly as a function of applied voltage. In the Ni/NiO multilayer electrode geometry we found that the initial lithiation occurs near the equilibrium potential (~1.9 V) at the Ni/NiO interface of the multilayer electrode that is a significantly lower overpotential than is typically observed. Subsequently, growth of the Ni+Li₂O discharge product proceeds outward from the interface as the potential is reduced to ~ 0.6 V. Based on these observations, the reaction is initiated at the Ni/NiO interface with the reaction front moving toward



Figure 12.1.: Heterogeneous nucleation at the interface between nickel and nickel oxide. Schematic of conversion reaction proceeding in the Ni/NiO multilayer electrode, with Li⁺ ions diffusing through nickel oxide and electrons from the current collector through metallic nickel. This model suggests partial destruction of the Ni/NiO interface, accompanied with formation of new interfaces between Ni/Li₂O and NiO/Li₂O.

the electrolyte as the conversion proceeds. Therefore, when a potential bias is introduced, Li⁺ ions are able to effectively diffuse through the NiO layer to the interface with Ni, which is a source of electrons. In addition to the experimental observations of reaction onset at the interface, we expect Li⁺ diffusion through the NiO layer to be more facile than charge transfer through NiO due to its wide band gap (4.3 eV) [577]. At the interface, Li^+ can react with O^{2-} anions in NiO to form Li_2O , with the electrons populating the Ni 3d states and reducing Ni²⁺ cations to metallic Ni⁰. At the onset of nucleation, Ni seeds may form at the Ni/NiO interface, encapsulated by the concurrently formed Li₂O phase. Based on the proposed process for heterogeneous nucleation, as depicted in Figure 12.1b, we consider the interfacial contributions to the conversion discharge product free energy as a means to understand experimentally observed overpotentials. When the conversion is initiated, the formation of the Li_2O -encapsulated Ni seed requires partial destruction of the Ni/NiO interface. In addition to the interface between Li₂O and Ni, Li₂O also forms an interfacial contact with the unreacted NiO. Therefore, the overall picture of heterogeneous nucleation in multilayer electrode morphologies involves all permutations of the binary solid-solid interfaces between Ni, NiO, and Li₂O.



Figure 12.2.: Interfacial models for nickel and nickel oxide with amorphous lithia. a) Bulk supercell of a-Li₂O from classical molecular dynamics simulations and some of the sampled structures for interfacial models between Ni and NiO. b) Examples of converged interfacial models between Ni(111) and a-Li₂O, which have a minimum interfacial energy of approximately 2.51 J m⁻² based on the structures sampled. c) Examples of interfacial models between NiO(100) and a-Li₂O, which have a minimum interfacial energy of approximately 1.18 J m⁻². In a-c, nickel, lithium, and oxygen are grey, green, and red, respectively.

For the remaining of this section, we will describe construction of atomistic models for Ni/Li₂O, Ni/NiO, and NiO/Li₂O interfaces, as well as the associated DFTdetermined interfacial thermodynamics used to describe nucleation and growth mechanisms in these nanostructured electrodes. In order to construct interfacial models involving *a*-Li₂O matrix, we have sampled several configurations from a 500 formula unit supercell generated from a classical MD melt-and-quench procedure (see Section 12.2.2). As shown in Figure 12.2a, we select stoichiometric *a*-Li₂O cells from the bulk supercell (ranging between 36 and 72 atoms). For this sampling procedure, the size of the surface plane is determined by the dimensions of the substrate, either Ni(111) or NiO(100). To reduce the forces in the construction of the heterostructure, the third dimension of the *a*-Li₂O cell is adjusted according to pre-relaxation with 0 K DFT slab calculations before inserting between the periodic images of the substrate. From this approach, we calculate the interfacial energies for the Ni(111)/*a*-Li₂O and NiO(100)/*a*-Li₂O interfaces to be 1.86 J m⁻² and 0.35 J m⁻² respectively. It is likely that the more favorable thermodynamics for the NiO(100)/*a*-Li₂O interface, in comparison to Ni(111)/*a*-Li₂O, is due to favorable interactions between cationic Li⁺ in the *a*-Li₂O region and the O²⁻ anions on the NiO(100) surface. Some representative structures of the Ni(111)/*a*-Li₂O and NiO(100)/*a*-Li₂O interfaces studied are included in Figure 12.2b-c.

Given the relatively high interfacial energy for the Ni(111)/a-Li₂O interface discussed above, we also consider the presence of a Li space-charge layer between metallic Ni⁰ and the ionic a-Li₂O region of the interface. These models are constructed analogously to those of the stoichiometric Ni(111)/a-Li₂O interfaces, with the addition of lithium monolayers inserted between Ni and a-Li₂O (shown in Figure 12.3a). The introduction of off-stoichiometry in this model complicates the thermodynamic analysis, however, as the chemical potential reference state for the excess lithium may depend on its charge state. We suggest that this could be treated within the limits of fully metallic (Li bcc metal reference state) and fully ionic (computational hydrogen/lithium electrode approach [11] for voltage dependence) lithium at the interface. As an estimate, the extent to which lithium is discharged (x denotes fraction of discharge) can be introduced, such that an increase in Li⁺ ions in the excess lithium layer will introduce voltage dependence on calculated interfacial energies.

$$\gamma_{Ni/Li/Li_2O} = \frac{1}{2A} \left[E_{total}^{Ni/Li/Li_2O\,interface} - (n_{Ni}g_{Ni}^{bulk} + (n_{Li}^{Li_2O} + n_O^{Li_2O})g_{Li_2O}^{bulk} + n_{Li}^{excess}(g_{Li}^{bulk} - xeU)) \right]$$
(12.7)

Based on the charge transfer to Ni determined from charge density difference analyses, approximately 13% of the excess Li is ionic, corresponding to an x-value of 0.13



Figure 12.3.: Influence of extra lithium on interfacial energies between nickel and amorphous lithia. a) Representative structural models for Ni(111)/*a*-Li₂O interfacial models with excess Li. Nickel, lithium, and oxygen are shown in grey, green, and red, respectively. b) Interfacial energies for excess Li models in comparison to the stoichiometric Li₂O models, using different thermodynamic treatments (see text for further discussion). The x = 0.13 series (mostly metallic Li) is associated with DFT-calculated charge density difference analysis.

in equation 12.7. From the Li-excess Ni(111)/a-Li₂O models sampled, we estimate an interfacial energy of 0.41 J m⁻² at U = 0 V vs. Li/Li⁺, a significant reduction in comparison to the stoichiometric Ni(111)/a-Li₂O interface. As equation 12.7 indicates for x > 0, however, the interfacial energy increases for positive potentials. Figure 12.3b demonstrates this potential dependence, where the x = 1 case (fully ionic Li⁺) has a higher interfacial energy than the stoichiometric case for U > 0.65V vs. Li/Li⁺, whereas the x = 0.13 and x = 0 cases (charge density analysis and fully metallic Li⁰ case, respectively) each suggest a decreased interfacial energy with respect to the stoichiometric case for voltages well above the bulk conversion reaction equilibrium potential (calculated at 1.89 V vs. Li/Li⁺). Considering the low level of discharge determined from the DFT charge transfer analysis, we suggest that the x= 0 or x = 0.13 cases are most likely to represent the potential-dependent interfacial thermodynamics of the analogous experimental system. Because of the reduction in the Ni/a-Li₂O interfacial energy due to the presence of excess Li, this represents a unique example of interfacial charge storage beyond the theoretical limits governed by the stoichiometry of the bulk conversion reaction [553, 556, 496, 476].



Figure 12.4.: Interfacial energies of crystalline interfaces between nickel and nickel oxide. a-b) Unit cells for (a) Ni(111) and (b) NiO(100) used in lattice matching Moir pattern algorithm. c) Low energy structure for Ni(111)/Ni(100) interface, with an interfacial energy of 1.44 J m⁻² at a ratio of 3:10 NiO:Ni unit cells at the interface. d) Minimum interfacial energy calculated at each Ni:NiO interfacial ratio.

The final interfacial model we studied was the Ni(111)/NiO(100) interface, which is generated upon synthesis of the electrode, prior to introduction of electrochemical bias. As the schematic in Figure 12.1b suggests, the Ni(111)/NiO(100) interface undergoes partial destruction as heterogeneous nucleation proceeds, with the Ni²⁺ ions at the interface being reduced through the acceptance of electrons near the Fermi level from metallic Ni^0 accompanied by O^{2-} anions reacting with incoming Li^+ ions to form Li_2O . We consider a crystalline-crystalline interface between Ni(111) and Ni(100), identifying suitable models from a lattice matching algorithm applied in previous work [113, 112]. Starting from the unit cells for Ni(111) and Ni(100) surfaces, as shown in Figures 12.4a-b, we consider different levels of strain between the two materials to minimize the free energy of the interface. From this analysis, we identify low-energy structure depicted in Figure 12.4c, only requiring expansion by 2.23% and compression by 1.59% of the NiO *a* and *b* lattice vectors. This crystalline interfacial structure results in a modest interfacial energy of 1.44 Jm^{-2} , representing a minimum with respect to different NiO(100)/Ni(111) unit cell ratios as seen in Figure 12.4d.

To summarize, we have described the DFT-calculated interfacial thermodynamics for binary solid-solid interfaces that may be generated and destroyed through heterogeneous nucleation of Ni/NiO multilayer thin film electrodes. In the following section, we integrate these calculated interfacial energies into heterogeneous nucleation models for NiO conversion reaction in these electrodes.

12.3.2 Heterogeneous Nucleation Models for NiO Conversion

Using the DFT-calculated interfacial energies described in the previous section, we incorporate these values into a heterogenous nucleation model. As discussed in Section 12.2, the interfacial component to the total free energy ($\Delta G_{interfacial}$) is dependent upon the change in area for each of the aforementioned interfaces upon conversion. Regarding geometric considerations for heterogenous nucleation at the Ni/NiO interface, we assume a hemispherical Ni seed encapsulated by *a*-Li₂O as the interfacial discharge produce, as depicted in Figure 12.5a. Bulk, interfacial, and total free energies are presented directly as a function of the nucleating Ni seed radius (r), with the outer radius (r_{out}) of the *a*-Li₂O shell (see Figure 12.5a) also determined from r and the density of bulk Li₂O.



Figure 12.5.: Classical nucleation theory analysis of heterogeneous nucleation at the nickel-nickel oxide interface. a) Geometric considerations for classical nucleation model, where interfacial free energy results from changing surface areas of each interface. b-c) Nucleation curves demonstrating bulk and interfacial contributions to total free energy at b) 1.0 V vs. Li/Li⁺ and c) 0.6 V vs. Li/Li⁺. Solid, dashed, dot-dashed, and dotted lines correspond to the stoichiometric Li₂O and excess Li (with x = 1, 0.13, and 0 reference treatments) at the Ni/Li₂O interface, respectively.

Figures 12.5b and 12.5c show the resulting nucleation curves at U = 1.0 V and U = 0.6 V vs. Li/Li⁺, respectively, within different approximations used for the Ni/Li₂O

interfacial energy detailed in the previous section. Using the interfacial energy for the stoichiometric Ni/Li₂O interface ($\gamma_{Ni/Li_2O} = 1.86 \text{ Jm}^{-2}$), we calculate a large nucleation barrier (ΔG_c of 1.30 eV at 1.0 V (solid lines in Figure 12.5b). The ΔG_c is reduced to 0.52 eV at 0.6 V (solid line in Figure 12.5c) as the bulk reaction thermodynamics become more favorable, suggesting only a modest barrier to conversion that is likely to be overcome at room temperature. While this model may suggest nucleation and growth mechanisms that could occur at lower voltages (higher overpotentials), they fail to explain directly the high-voltage conversion reaction mechanisms that appear to be catalyzed by the buried Ni/NiO interface.

As shown in Figure 12.3, the presence of excess lithium layer at the Ni/Li_2O interface can significantly influence the Ni/Li₂O interfacial energies that are input to the classical nucleation theory model. As such, we consider the nucleation and growth scenario depicted in Figure 12.5a incorporating a monolayer of Li at the Ni/Li_2O using the various thermodynamic treatments presented in Figure 12.3. While the fully ionic thermodynamic treatment of the extra Li atoms (x = 1), increases ΔG_c from 1.30 to 5.15 eV at 1.0 V (dashed lines in Figure 12.5b), ΔG_c is slightly decreased from 0.52 to 0.41 eV at 0.6 V (dashed lines in Figure 12.5c). However, most of the Li at the interface is metallic, with minimal charge transfer to the metallic nickel phase. Using both the fraction of ionic Li from the charge density analysis (x =(0.13) and the fully metallic (x = 0) thermodynamic treatments of the extra Li atoms, we predict negligibly small nucleation barriers at both 1.0 V and 0.6 V vs. Li/Li^+ . Moreover, the fully metallic treatment yields a $\Delta G_{interfacial}$ that is negative due to partial destruction of the higher energy Ni/NiO interface ($\gamma_{Ni/NiO} = 1.44 \text{ Jm}^{-2}$) and formation of lower energy NiO/Li₂O ($\gamma_{NiO/Li_2O} = 1.44 \text{ J m}^{-2}$) and Ni/Li₂O $(\gamma_{Ni/Li/Li_2O} = 0.41 \text{ J m}^{-2})$ interfaces. While this is not the case for the charge density analysis treatment of interfacial energies (since $\gamma_{Ni/Li/Li_2O}$ is potential-dependent and increases with increasing voltage), we still predict for each of these models that the negligible barrier to nucleation would suggest a driving force for nearly spontaneous conversion through heterogeneous nucleation at the buried Ni/NiO interface with the discharge product Ni and Li_2O phases separated by a space charge layer of Li that lowers the corresponding interfacial energy.

In summary, we suggest that the x = 1 and x = 0 cases represent upper and lower bounds, respectively, on the predicted nucleation barriers. Given that the DFT charge density analysis suggests that most of the excess Li atoms in the model are metallic, however, the x = 0.13 and x = 0 thermodynamic reference states would appear to be most representative of the Ni/Li₂O interfacial thermodynamics. Given these considerations, the predicted enhancement of heterogeneous nucleation at Li-excess interfaces is qualitatively consistent with XR data revealing electron densities corresponding to an interfacial Li-containing phase data at high potentials preceding bulk conversion (Figure 12.1a). While we find that interfacial Li catalyzes heterogenous nucleation, the XR cannot specifically reveal the stoichiometry of these interfacial regions, which could represent further complexities to the true nature of the conversion reaction and heterogeneous nucleation at the buried Ni/NiO interface in multilayer electrodes.

Building on the nucleation models at the Ni/NiO interface, we extend the analysis to later stages of conversion where the reaction front moves through the the NiO layer and toward the electrolyte. Here, we evaluate the case where the initial reaction at the buried Ni/NiO interface (summarized by the schematic in Figure 12.5a) has taken place and there are now small metallic Ni particles incorporated within a matrix of a-Li₂O (shown on the left side of Figure 12.6a). Embedded Ni particles will enhance the electrical conductivity of the a-Li₂O, enhancing electron transfer to the NiO/a-Li₂O interface where combination with Li⁺ ions can lead to electrochemical conversion. As shown in Figure 12.6a, conversion at the NiO/Li₂O interface likely occurs through reduction of Ni²⁺ cations as Li⁺ ions react with interfacial oxygen atoms.

We apply similar geometric considerations to integrate conversion at the NiO/a-Li₂O interface into our nucleation model, where the identities of the binary interfaces formed and destroyed are modified according to the schematic in Figure 12.6a. Figures 12.6b and 12.6c show the nucleation curves for heterogeneous nucleation at the NiO/Li₂O interface calculated at 1.0 V vs. Li/Li⁺ and 0.6 V vs. Li/Li⁺, respectively.



Figure 12.6.: Classical nucleation theory analysis of heterogeneous nucleation interface between amorphous lithia and nickel oxide. a) Schematic for the conversion reaction at a NiO/Li₂O interface following initial discharge product formation. b-c) Nucleation curves showing the bulk and interfacial contributions to the total free energy at b) 1.0 V vs. Li/Li⁺ and c) 0.6 V vs. Li/Li⁺. Solid, dashed, dot-dashed, and dotted lines correspond to the stoichiometric Li₂O and excess Li (with x = 1, 0.13, and 0 reference treatments) at the Ni/Li₂O interface, respectively.

In comparison to heterogeneous nucleation at the Ni/NiO interface (Figure 12.5b-c), we find that nucleation barriers are, in general, higher for conversion reactions at the NiO/Li₂O interface. This is in large part due to the heterogeneous nucleation occurring at, and therefore leading to the destruction of, a lower energy interface (NiO/Li_2O) which increases $\Delta G_{interfacial}$ in the total free energy expression. What this suggests is that these conversion reactions, given their larger interfacial energy barriers, will proceed at lower voltages (higher overpotentials) than the high-voltage reactions occurring at the buried Ni/NiO interface. Similar to the analysis in Figure 12.5, we find that the reduction in γ_{Ni/Li_2O} with excess Li atoms reduces barriers to nucleation in comparison with the stoichiometric interface, suggesting that conversion could be further catalyzed by interfacial Li even at later stages of the conversion reaction. As shown from experimental STEM images of NiO lithiation [559], as well as recent computational work [558], accumulation of Li⁺ ions at NiO interstitial sites may facilitate the formation of finger-like modes of Ni/Li₂O growth within the NiO bulk. In either case, initial conversion at the Ni/NiO interface to form conductive a-Li₂O with embedded Ni particles enables the reaction of $(Li^+ + e^-)$ pairs to react with NiO to form the Ni + Li_2O discharge product.

12.3.3 Isolated Nucleation Events and Underpotential Conversion Product Formation

Although the heterogeneous nucleation models provide certain insights toward mechanisms for reduced overpotential (η) conversion reactions at a metal-oxide interface, the classical nature of these theories inherently neglect the elementary chemical events that may initiate the nucleation process. In this section, we will evaluate select scenarios in which nucleation events may occur at the engineered Ni/NiO interface, with a particular focus on high-voltages reactions that may lead to lower η , or even underpotentials (higher than the equilibrium potential) that cannot be explicitly captured within a classical nucleation theory formalism.



Figure 12.7.: Lithium substitution at the Ni/NiO interface. Structural models with a top-view of the Ni(111)/NiO(100) interface with Li⁺ substitution for a) 0%, b) 8.3%, c) 16.7%, d) 33.3%, and e) 100% of the Ni²⁺ ions at the interface. f) Thermodynamic formation energies, per atom, per unit area, at the calculated equilibrium potential of 1.89 V. Formation energies are calculated at the equilibrium potential since the stoichiometry is changing and at these conditions, the chemical potentials of Ni atoms in NiO and metallic Ni are equivalent through thermodynamic equilibrium criteria. Further details regarding this formalism may be found in the main text.

First, we consider a hypothetical process wherein Li^+ may accumulate at the interface. Figures 12.7a-e show a series of DFT structural models where a Ni²⁺ in NiO is replaced with Li⁺. For *n* substitutions of this type, the overall reaction within NiO is

$$Ni_x O_x + n(Li^+ + e^-) \rightarrow Ni_{x-n} Li_n O_x + nNi$$
(12.8)

These differential formation energies depend on voltage, due to the transferred $(Li^+ + e^-)$ pair shown in equation 12.8, although the reference state treatment for the removed Ni atoms remains somewhat ambiguous. Thus, we have considered these energies at the bulk equilibrium potential (1.90 V vs. Li/Li⁺) since at bulk equilibrium

rium conditions the chemical potential of Ni atoms in metallic Ni and NiO are by definition equivalent. Figure 12.7f shows the formation energies for this process at different levels of Ni²⁺ replacement with Li⁺, and we observe that each of the substitutions are exothermic. The most stable defect is calculated at 16.7% substitution of the interfacial Ni²⁺ for Li⁺, in a configuration where an O^{2-} anion is shared between two Li⁺ ions (Figure 12.7c). Further substitution to 33.3% (Figure 12.7d) and 100% (Figure 12.7e) is slightly less favorable, likely due to the instability of Li⁺ ions in a bulk rock salt structure that leads to interfacial reconstruction of the lattice. However, these calculations suggest that Li⁺ substitutional incorporation at the Ni/NiO interface is stable in dilute concentrations.

Next, we consider the incorporation of Li⁺ ions into interstitial sites near the Ni/NiO interface and whether such defects could lead to elementary conversion reaction events. Starting with the pristine Ni(111)/Ni(100) interface (first shown in Figure 12.4c), we insert a Li⁺ ion at tetrahedral sites near the Ni/NiO interface. Figure 12.8a demonstrates that the subsequent geometry relaxation proceeds with the Li⁺ occupying the host Ni²⁺ site at the interface, evocative of the substitutional structures presented in Figure 12.7a-e. Further, the displaced Ni²⁺ ion is deposited onto the Ni(111) substrate, and is reduced to Ni⁰. We determined that this process has an equilibrium potential of 1.22 V vs. Li/Li⁺ (η of 0.67 V).

Given that elementary conversion reaction events at the Ni/NiO interface proceed with a relatively low overpotential, it is reasonable to suspect that these overpotentials may be lowered even further for reactions at defect sites. Figure 12.8b shows an example of one such defect, where a kinked step is introduced at the interface. Li⁺ substitution at NiO tetrahedral sites near the Ni/NiO interface leads to Li⁺ occupation of the Ni²⁺ sites and the deposition of a reduced Ni⁰ atom to the edge of the defected Ni step. This reaction is indeed calculated to proceed at a higher potential of 2.04 V vs. Li/Li⁺, corresponding to an underpotential of 0.15 V. Next, we perform calculations on isolated metallic Ni cluster defects at the interface. Figure 12.8c shows a metallic Ni₃ cluster deposited on Ni, where two NiO formula units are removed to



Figure 12.8.: Elementary nucleation events at the Ni/NiO interface. Conversion reaction initiated through insertion of a $(Li^+ + e^-)$ pair interstitial in nickel oxide at a a) clean Ni(111)/NiO(100) interface, b) stepped Ni(111)/NiO(100) interface, and c) a Ni₃ metallic cluster at the Ni(111)/NiO(100) interface (top view). As in Figures 12.2-12.4, Ni, Li, and O atoms are represented by grey, green, and red, respectively. Additionally, the Ni₃ cluster in c), as well as the Ni atoms that become reduced to metallic after lithiation, are represented in blue.

accompany the cluster. Upon Li⁺ insertion, a metallic Ni₄ cluster is generated with an equilibrium potential of 2.29 V vs. Li/Li⁺, an underpotential of 0.38 V. Overall, we conclude that nucleation at such defect sites is likely to occur at higher potentials than either bulk or heterogeneous nucleation. However, we might not expect to observe large-scale bulk nucleation and growth as a result of the initial conversion at such defect sites, since conversion at these healed defects may instead be better represented by the heterogeneous nucleation at more pristine interfaces. Moreover, it may be the case in many such systems that such defects may serve as sites to initiate heterogeneous and bulk nucleation.

12.4 Conclusions

We have performed classical MD simulations and first principles DFT calculations to study relevant solid-solid interfacial models for NiO conversion reaction. These atomistic studies have been coupled with a heterogeneous nucleation theory model to capture the role of interfacial thermodynamics on experimentally observed overpotentials and voltage hysteresis in lithium ion conversion reactions. We have carried out extensive interfacial energy calculations for binary solid-solid interfaces, determining interfacial energies of 1.86 Jm^{-2} , 0.35 m^{-2} , and 1.44 Jm^{-2} for Ni(111)/*a*-Li₂O, NiO(100)/*a*-Li₂O, and Ni(111)/NiO(100) interfaces, respectively. Moreover, we find that excess interfacial lithium may significantly reduce the Ni(111)/*a*-Li₂O interfacial energy, suggesting a thermodynamic driving force for interfacial lithium storage beyond bulk stoichiometric limits. Our heterogeneous nucleation models predict reduced overpotentials with respect to the bulk NiO lithiation at 0.6 V for a Ni/NiO multilayer electrode. The partial destruction of the Ni/NiO interface and the presence of the excess lithium at the interface of the Ni/*a*-Li₂O discharge product contribute to the lower overpotential for heterogenous nucleation.

We also performed a series of calculations for isolated nucleation reaction events at a pristine Ni(111)/NiO(100) interface, as well as in the presence of metallic Ni stepped and clustered defects. Such reaction mechanisms are calculated to be quite favorable
with respect to the predictions from the heterogeneous nucleation model, with the reactions in some cases having almost no overpotential with respect to the bulk reaction thermochemistry. Overall, we proposed that such isolated reaction events, in particular at defect sites, may proceed close to the equilibrium potential as observed in the cyclic voltammograms from our recent work [496]. We anticipate that this result should be generally applicable to other conversion reaction chemistries. Future design of conversion reaction electrode materials with complex morphologies exposing greater concentrations of interfaces and defects may seed greater discharge product formation rates close to the bulk equilibrium potential, enhancing first cycle discharge efficiencies. The reversible maintenance of such morphologies upon extended charge-discharge cycles, however, is likely to remain a challenge to the practical use of such electrodes. We further suggest that the overall conversion reaction processes in this class of materials are likely to be initiated by elementary reaction events, which likely propagate defects that can serve as active sites for seeding bulk nucleation.

13. NEW CLASS OF ELECTROCATALYSTS BASED ON 2-D TRANSITION METAL DICHALCOGENIDES IN IONIC LIQUID

This chapter is reproduced with the permission of Wiley-VCH Verlag GmbH & Co. KGaA from: Leily Majidi, Poya Yasaei, Robert E. Warburton, Shadi Fuladi, John Cavin, Xuan Hu, Zahra Hemmat, Sung Beom Cho, Pedram Abbasi, Márton Vörös, Lei Cheng, Baharak Sayahpour, Igor L. Bolotin, Peter Zapol, Jeffrey Greeley, Robert F. Klie, Rohan Mishra, Fatemeh Khalili-Araghi, Larry A. Curtiss, and Amin Salehi-Khojin; New Class of Electrocatalysts Based on 2D Transition Metal Dichalcogenides in Ionic Liquid. *Advanced Materials* **2019**, *31*(4), 1804453.

The optimization of traditional electrocatalysts has reached a point where progress is impeded by fundamental physical factors including inherent scaling relations among thermokinetic characteristics of different elementary reaction steps, non-Nernstian behavior, and electronic structure of the catalyst. This indicates that the currently utilized classes of electrocatalysts may not be adequate for future needs. This study reports on synthesis and characterization of a new class of materials based on 2D transition metal dichalcogenides including sulfides, selenides, and tellurides of group V and VI transition metals that exhibit excellent catalytic performance for both oxygen reduction and evolution reactions in an aprotic medium with Li salts. The reaction rates are much higher for these materials than previously reported catalysts for these reactions. The reasons for the high activity are found to be the metal edges with adiabatic electron transfer capability and a cocatalyst effect involving an ionicliquid electrolyte. These new materials are expected to have high activity for other core electrocatalytic reactions and open the way for advances in energy storage and catalysis.

13.1 Introduction

Within a broad space of materials that have been explored for electrocatalytic applications, several 2D and quasi-2D structures have recently been reported to exhibit superior properties for the hydrogen evolution reaction and other core electrochemical reactions [578, 579, 580, 581, 582, 583, 584, 585, 586, 587, 588]. In particular, molybdenum disulfide (MoS_2) and a few members of transition metal dichalcogenides (TMDCs) in contact with ionic-liquid (IL) electrolyte have recently shown a great promise to overcome fundamental electronic and thermokinetic limitations for CO_2 reduction reaction, as well as the oxygen reduction and evolution reactions (ORR/OER) [584, 585, 586, 587]. These studies have been conducted on a limited number of TMDCs, and the majority of other TMDCs with a wide range of electronic and potentially catalytic properties have not been investigated. In this study, we report synthesis and characterization of a wide range of TMDCs including sulfides, selenides, and tellurides of group V and VI transition metals and study their electrochemical performance in aprotic medium with Li salts. We employ a wide suite of characterization techniques, such as scanning transmission electron microscopy (STEM), energy dispersive spectroscopy (EDS), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), dynamic light scattering (DLS), and atomic force microscopy (AFM), as well as computational simulations, to elucidate structural, atomic, and electronic characteristics of the synthesized materials.

13.2 Results and Discussion

Bulk TMDCs were synthesized through a direct reaction of pure elements followed by a chemical vapor transport (CVT) process in an evacuated quartz ampule at high temperatures. The powders of the transition metals and chalcogens were mixed in desired stoichiometric ratios and loaded in quartz ampules. The ampules were then evacuated, sealed, and placed in a two-zone furnace for the crystal growth process.



Figure 13.1.: Summary of crystal synthesis and structural characterizations. a) Schematic of the crystal synthesis method including a tube furnace with hot and and cold temperature zones (T_H and T_C). b) Optical microscopy image of the powder crystals formed at the hot zone. Scale bar is 25 m. c) Optical microcopy image of the larger crystals formed at the cold zone through direct transport of the precursor vapors. Scale bar is 25 μ m. d) Photograph of the synthesized solutions of MoS₂, MoSe₂, and MoTe₂ through liquid-phase exfoliation in IPA followed by centrifugation and super- natant collection. e) Raman spectra of all the group V and VI TMDC crystals studied in this report. f) Atomic-resolution TEM images of the transition metal tellurides with different crystalline faces. Insets show the FFT patterns. Scale bar is 1 nm.

Details of the material synthesis are provided in Section 13.4 and Section G.1 of Appendix G. Figure 13.1a shows the schematic of the crystal growth process. After the synthesis process, a powder of TMDC single-crystalline flakes is usually obtained (Figure 13.1b) in the hot zone of the ampule. In the cold zone, single-crystalline chunks of the TMDC are formed through a direct transport of vaporized precursors (Figure 13.1c). Optical images of the synthesized materials in both zones show sharp geometrical features, implying that the reaction products are highly crystalline.

To prepare TMDC nanoflakes suitable for electrochemical experiments, a liquidphase exfoliation technique was used (see Section 13.4), which results in uniform dispersions of atomically thin nanoflakes in the solvent. For ease of exfoliation, we used the powders obtained in the hot-zone of the growth ampule. The material obtained in the cold zone usually requires further processing, *i.e.*, grinding, to facilitate the liquid exfoliation. Figure 13.1d shows a photograph of sample dispersions of MoS_2 , $MoSe_2$, and $MoTe_2$ in isopropyl alcohol (IPA) after sonication, centrifugation, and supernatant collection. In all the samples, the color of the dispersion is primarily determined by the chalcogen type with minor variations due to different transition metals.

Raman spectroscopy was used to verify the successful synthesis of TMDCs. Figure 13.1e shows the sample Raman spectra of all 15 synthesized TMDCs studied in this report, indicating distinct peaks associated with different vibrational modes of the TMDC crystals. For instance, the major representative Raman peaks of WS₂ are observed at 296.6, 350.5, 355.6, and 420.2 cm⁻¹ where the first two peaks match $2LA(M)-2E_{2g}^2(M)$ and 2LA(M), respectively, and the third and fourth peaks represent E_{2g}^1 and A_{1g} [589]. Raman spectrum of TaSe₂ indicates the main peaks at 137.6, 207.3, and 234.5 cm⁻¹ which correspond to E_{1g} , E_{2g}^1 , and A_{1g} , respectively [590]. WTe₂ Raman peaks are also shown at 79.6(A₁), 88.3(A₂), 111.5(A₂), 115.9(A₂), 131.2(A₁), 138.9(A₁), 162.59(A₁), and 209.7(A₁) cm⁻¹ [591, 592, 593].

Figure 13.1f shows atomic-resolution high angle annular dark field (HAADF) images of selected five materials with simulated crystal structures (inserted). We find NbTe₂, TaTe₂, VTe₂ samples are in their 1T' phase (C2/m, monoclinic) from side and top views, while MoTe₂ is in its 1T' phase (P21/m, monoclinic), and WTe₂ is in its Td phase (Pmn21, orthogonal) from side views. X-ray EDS was carried out to probe the chemical composition of the nanoflakes and to determine the presence of impurities (Figure G.1, Appendix G). XPS was also utilized to evaluate the chemical states of synthesized TMDCs. Section G.3 in Appendix G presents the corresponding XPS spectra for all of the synthesized TMDCs.

The liquid exfoliated dispersions were characterized by DLS and AFM to determine the lateral size and thickness distributions of the exfoliated materials (as a representative, see Figures G.6 and G.7 in Appendix 13.4). DLS results indicate an average size of 140-240 nm for all the TMDCs dispersions. AFM height measurements obtained from 30-40 randomly selected exfoliated flakes show the thickness ranging from 2 to 44 nm with an average of about 15-24 nm.



Figure 13.2.: Experimental and theoretical work function and electronic structure of bulk MX₂. a) The experimental and calculated work function of the 15 MX₂ TMDCs. The calculated work function of semiconducting materials is shown as a range representing a tunable region bounded by the valence band maximum and the conduction band minimum measured from the vacuum level. b) Comparison of atomprojected densities of states (DOS) for the transition metal and chalcogen atoms in MoS_2 , $MoSe_2$, and $MoTe_2$. Energies are relative to the vacuum level. On moving from S to Se to Te, both the semi-core states of the chalcogens (shaded) and the Fermi level shift to higher energies. This corresponds to a decrease in work function with increasing chalcogen mass. c) The atom-projected DOS for MoS_2 , WS_2 , VS_2 , NbS_2 , and TaS_2 . The sulfur semi-core states and the work function show little variation other than from one transition metal group to another.

UPS was used to measure work functions of the synthesized TMDCs. The work function has been shown previously to be a good descriptor for catalytic activity in metal catalysts [594]. Moreover, it was shown that for MoS₂, MoSe₂, WS₂, and

 WSe_2 nanoflakes, the catalytic activity for CO_2 reduction increases with decreasing work function [587]. Figure 13.2a shows the comparison among the obtained work functions of the synthesized TMDCs through UPS experiments and their theoretical values calculated using density-functional theory (DFT) within the generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE) [163]. As shown in Figure 13.2a, the UPS-measured work function values for these materials range from 2.95 to 5.14 eV. The lowest measured work function values were recorded for WTe_2 (2.95 eV) and TaTe₂ (3.11 eV). Figure 13.2a also shows the DFT-calculated work functions of the TMDCs. The color gradient bars in Figure 13.2a highlight semiconducting materials and their predicted range of possible work functions. These ranges correspond to the energies between the valence band maximum (VBM) and conduction band minimum (CBM). While the PBE exchange-correlation functional satisfactorily calculates the energy levels of the occupied states including the VBM, it underestimates the energy of the empty states, such as the CBM [595]. Hence, it leads to bandgaps in semiconductors that are smaller than the experimental value [596, 597, 598]. To avoid this issue for the four semiconducting TMDCs (MoS₂, MoSe₂, WS₂, and WSe₂), we have used the experimental value of the bandgap to determine the position of the CBM [599] from the calculated VBM. In general, we find that for each family of TMDCs corresponding to a particular transition metal, the work function decreases from ~ 6 to 4.5 eV as the mass of the chalcogen atom increases. For a given chalcogen atom though, we find a less dramatic change in the work function on varying the transition metal atom. However, we find a discrepancy between the experimental and theoretical values for MoTe₂, WTe₂, and the TaX₂ compounds. Discrepancies in work functions can possibly be attributed to a small oxidation of the surface that was observed in STEM EDS experiments. Formation of a very thin oxide layer, for instance on tantalum, has been shown to reduce its work function [600]. Nevertheless, the calculated trends for all the compounds are in excellent agreement with the experiments.

To understand how the composition of a TMDC affects its work function and if there is any correlation with catalytic activity, we have calculated the electronic structure of the TMDCs with selective variation of either the chalcogen or the transition metal. Figure 13.2b shows the atom-projected density of states (DOS) for MoS_2 , $MoSe_2$, and $MoTe_2$, where the energy is normalized with respect to the vacuum level. We observe that the semi-core *s*-states of the chalcogen atoms, indicated by the shaded region, shift to higher energies for heavier chalcogens. This trend is similar to the reduction in the work function for heavier chalcogens. Figure 13.2c, on the other hand, shows the atom-projected DOS of MoS_2 , VS_2 , NbS_2 , WS_2 , and TaS_2 . The semi-core *s*-states of the sulfur atoms do not show any appreciable variation. Likewise, we found that the work functions of the five compounds do not indicate much variation either, except when there is a transition from metal (Group V cation) to semiconductor (Group VI cation). We conclude that the work function reduction found in TMDCs with heavier chalcogens is directly correlated to the shift in the chalcogen semi-core states to higher energies.

After thorough characterization of the synthesized TMDCs, we examined their catalytic performances by carrying out electrochemical cyclic voltammetry (CV) experiments during ORR and OER. The dispersed TMDCs in IPA were used to prepare the cathodes through layer by layer coating on gas diffusion layer (GDL) substrates. The CV experiments were performed in a three electrode cell within a nonaqueous oxygen saturated electrolyte, containing 0.1 M lithium bis(trifluoromethanesulfonyl)imide salt and a hybrid electrolyte of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄) ionic liquid and dimethyl sulfoxide (DMSO) with a volumetric ratio of 1 to 3, respectively, which produces the maximum ORR and OER among other compositions [584]. In our three-electrode cell experiments, the synthesized TMDC catalysts on GDL were used as the working electrode and lithium chips (99.9%) as the auxiliary and reference electrodes. The CV experiments were performed in the potential range 2.0-4.2 V versus Li/Li⁺ with a scan rate of 20 mV s⁻¹.



Figure 13.3.: a,b) Performance comparison of synthesized TMDC catalysts in IL/DMSO mixture electrolyte for the oxygen reduction reaction (ORR) (a), and oxygen evolution reaction (b). c,d) ORR and OER of NbS₂, MoS₂, VS₂, VSe₂ and other reported catalysts in aprotic media with Li salt [601, 602, 603, 604, 605, 606, 607, 608]. The Y axis labels in (c) and (d) are the same as in (a) and (b). e,f) TOF of NbS₂, MoS₂, VS₂, VSe₂ at different applied overpotentials during ORR and OER, respectively.

Figure 13.3a, b demonstrates the obtained current density results for all the synthesized TMDC catalysts for ORR and OER at potentials of 2.0 and 4.2 V versus Li/Li⁺, respectively. This set of results depicts the catalytic activity of various TMDC chemistries toward ORR and OER, which had not been considered previously. There are four catalysts among the synthesized TMDCs which show remarkably high activity in both ORR and OER: MoS₂, NbS₂, VS₂, and VSe₂. Figure 13.3c,d compares the electrochemical performance for these bifunctional catalysts with the state of the art catalysts in aprotic media such as noble metals (*i.e.*, Pt) [602, 601, 603, 609], metal oxides $(i.e., Mn_3O_4)$ [604, 605], perovskite $(i.e., La_{0.5}Sc_{0.5}CoO_{2.91})$ [606], and doped carbon nanomaterials (*i.e.*, N-doped graphene) [607]. The data were extracted from various references and the current density values were normalized based on the geometrical surface area of the cathode [601, 604, 605, 606, 607]. At a potential of 2.0 V, NbS₂ presents the best ORR performance with a high current density of 47.39 mA cm^{-2} , which is ~15 times higher than that of Au, Pt, or commonly used oxides (*i.e.*, Mn_3O_4 [604] at the same potential. NbS₂ also shows a current density of 5.22 mA cm^{-2} at a potential of 4.2 V during OER, which is higher than the best reported catalyst (mesoporous $La_{0.5}Sc_{0.5}CoO_{2.91}$) [606] in aprotic media for OER (current density of 4.5 mA cm⁻², Figure 13.3d) obtained through rotating-disk electrode measurement in 1 m solution of LiPF_6 in ethylene carbonate/dimethyl carbonate electrolyte. It is worth mentioning that the mesoporous $La_{0.5}Sc_{0.5}CoO_{2.91}$ catalyst shows an onset potential of ~ 4.0 V during OER, which is much higher than the TMDC materials reported in this work. This would increase the energy efficiency in TMDC compared to $La_{0.5}Sc_{0.5}CoO_{2.91}$ catalyst. VS₂ exhibits a current density of 39.72 and 7.17 mA $\rm cm^{-2},$ respectively, for the ORR and OER. $\rm VSe_2$ and $\rm MoS_2$ also have high current densities for both ORR and OER indicating a bifunctional behavior with remarkable performance for both ORR and OER in aprotic media. However, comparing Figure 13.2a with Figure 13.3a,b, we clearly see that lower work functions do not correlate with higher ORR/OER activity, as was seen for CO_2 electroreduction [587]. Furthermore, in order to explore the intrinsic activity of our catalysts, a roughness factor technique [585, 586, 587, 610, 611] was used to measure the number of active sites and turn over frequency (TOF) values for MoS_2 , NbS_2 , VS_2 , and VSe_2 . TOF of these catalysts were calculated based on the current densities recorded at different overpotentials during ORR and OER. As depicted in Figure 13.3e, all of the four catalysts show similar TOF values during ORR where VSe_2 reaches the highest TOF of 3.28 s⁻¹ at the overpotential of 950 mV. Figure 13.3f shows the TOF values of these four catalysts during OER. At the overpotential of 800 mV, VSe_2 shows the highest TOF number of 0.7 s⁻¹. (see Section G.8 of Appendix G).

To better understand the mechanisms of ORR and OER on TMDC nanoflakes, we carried out more detailed computations using DFT and classical molecular dynamics (MD) simulations. In particular, MD simulations were used to determine distribution of electrolyte at the MoS_2 -solution interface. Figure 13.4a shows the density profile of EMIM⁺, BF_4^- , and DMSO molecules across the simulation box normal to the MoS_2 surface. Under equilibrium conditions, mostly DMSO and BF_4^- molecules are interacting with the MoS_2 surface, due to the positive charge density of the surface, while EMIM⁺ cations are forming the dense wall a bit further away from the surface (inset of Figure 13.4a). Application of an electric field normal to the MoS_2 surface (as described in Section G.9 of Appendix G) forces BF_4^- anions away from the surface and makes it accessible to EMIM⁺ molecules (Figure 13.4a,b). Figure 13.4c,d shows the orientation of $EMIM^+$ cations near the Mo terminated MoS_2 sheets. As shown in Figure 13.4c,d, the majority of EMIM⁺ molecules lie parallel to the interface, align with MoS_2 sheets, and lie between two adjacent sheets. A fraction of $EMIM^+$ cations are positioned at a $\sim 50^{\circ}$ -60° angle with respect to the surface, with the ring closer to the surface and the carbon tail further away and making a $\sim 30^{\circ}-40^{\circ}$ angle with each MoS_2 sheet.

Constrained density functional theory (CDFT) calculations were then carried out on MoS_2 and WS_2 to investigate the nature of the electron transfer in the ORR and OER mechanisms to obtain insight into the high electrocatalytic activity of these materials. The presence of diabatic electron transfer during ORR or OER would involve



Figure 13.4.: Molecular dynamics simulation results. a) Density profile of the $\rm EMIM^+/BF_4^-/DMSO$ mixture at its interface with metal-terminated sheets under an applied voltage bias obtained from molecular dynamics simulations. Inset represents the density profiles under equilibrium condition. The blue curve represents the density profile of sulfur atom of DMSO molecule, the green curve represents the density profile of boron atom of BF4⁻, and the orange curve represents the density profile of the carbon atom of EMIM⁺, which is shown in (b). b) Snapshot of the simulation system showing 60 Å of the mixture near the metal-terminated surface, and molecular structure of the simulated ionic liquids and DMSO. c) The angle distribution of EMIM⁺ cations with respect to the MoS₂ sheets obtained from molecular dynamics trajectories. Inset shows the defined vector along the length of EMIM⁺ cations. d) Snapshots of the metalmixture interface from different viewpoints showing the orientation of interacting molecules.

direct electron hopping, as opposed to electron transfer upon adsorption/desorption, between the catalyst and O_2 or Li_2O_2 , *i.e.*, adiabatic electron transfer. CDFT is used here because it allows for proper charge localization between groups of atoms corresponding to the donor (\mathcal{D}) and acceptor (\mathcal{A}) states during charge transfer. Fur-



Figure 13.5.: Molecular cluster models used for constrained density functional theory (CDFT) calculations. a) $M_{15}X_{29}$ cluster with two (EMIM⁺ + e⁻) pairs adsorbed on the metal-terminated edge, where M represents the metal cations and X represents the chalcogen anions. The isolated metal site between the EMIM⁺ molecules represents the active site for electron transfer during oxygen reduction and evolution. b) Charge hopping from [$M_{15}X_{29}$] to convert O₂ to O₂⁻ (superoxide ion) during ORR. c) Charge hopping from Li₂O₂ monomer to [$M_{15}X_{29}$] with a hole localized on the activate site, converting the Li₂O₂ (peroxide anion) to Li₂O₂⁻ (superoxide anion).

ther, this enables calculation of electronic couplings (H_{ab}) between initial and final electronic states, in order to gain insights into the kinetics of electron transfer, *i.e.*, through Marcus theory for diabatic charge transfer [118].

The catalytically active sites of MoS_2 and WS_2 are typically at the edges [612], which STEM experiments have determined to be metal-terminated for this particular synthesis process [587]. We applied a cluster model with periodic boundary conditions (shown in Figure 13.5a), modified from the one used previously by Huang et al. [613] to expose a metal-terminated edge with adsorbed (EMIM⁺ + e⁻) pairs, which bind strongly to the cathode [585]. The edges are passivated with 0.5 ML of the chalcogen ion (sulfur in this case), with an additional sulfur ion positioned at the free corner (opposite side of cluster from adsorbed EMIM⁺ ions and active metal site, Figure 13.5a). This ensures that unpaired electrons on the isolated metal site of the flake edge represent the highest occupied molecular orbital (HOMO) of the system. For ORR, we consider charge hopping from the flake to an O₂ molecule, leading to superoxide ion (O_2^-) formation (Figure 13.5b). The subsequent reaction with Li⁺ ions to form the Li₂O₂ in the EMIM⁺/BF₄⁻ solvent is facile, as shown previously [585]. OER, however, involves the oxidation of the O₂²⁻ anions in Li₂O₂. As a model for the onset of OER, we introduce a hole onto the catalyst, corresponding to electron removal from the flake HOMO, which is calculated to be thermodynamically favorable under OER conditions (Figure G.7, Appendix G). We then consider the transfer of an electron from a neutral Li₂O₂ monomer to fill the induced hole on the flake, such that the O₂ anion in Li₂O₂ is oxidized from O₂²⁻ (peroxide) to O₂⁻ (superoxide), as shown in Figure 13.5c.

A summary of the Marcus rate parameters for ORR and OER is included in Table 13.1. The electronic couplings are exponential in distance between the donor and acceptor (r_{D-A}) due to the exponential decay of wave functions as a function of separation. A regression of the CDFT-calculated couplings is used to fit H_{ab} to the form: $H_{ab} = A \exp(-\frac{\alpha}{2}r_{D-A})$ where A is a pre-exponential factor and α is the decay rate. In general, we found that the H_{ab} decays more slowly for ORR, in comparison to OER, by approximately a factor of two. The reorganization energies (λ) for OER, largely due to relaxation of the O₂⁻ anion in Li₂O₂, are considerably larger than for ORR. The consequence is that the lower λ for ORR, in combination with a more unfavorable driving force (ΔG) for charge transfer, makes the activation energy (E_{act}) for this proposed diabatic charge hopping process prohibitively high. The O_2 binds to TMDC nanoflake edges very strongly [585], however, whereupon it is likely to be reduced adiabatically due to the large ground state charge transfer associated with binding to the nanoflake edge. With a higher λ for OER, the E_{act} for diabatic charge transfer is reduced. Moreover, it is unlikely that O_2 anions bound to Li^+ ions will be stable at the catalyst edge, based on calculated binding energies and reduction potentials (see discussion in Section G.11 of Appendix G). It is therefore reasonable that the OER may proceed via diabatic charge transfer from the Li_2O_2 charge product, which may also help explain why OER rates are considerably lower

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Reaction	Transition	$\Delta G \ [eV]$	$\lambda [eV]$	E_{act} [eV]	A [eV]	$\alpha [{ m \AA}^{-1}]$
ORR	$[Mo_{15}S_{32}]^0[O_2]^0 \rightarrow [Mo_{15}S_{32}]^+[O_2]^-$	2.94	0.39	7.14	325	1.61
ORR	$[W_{15}S_{32}]^0[O_2]^0 \rightarrow [W_{15}S_{32}]^+[O_2]^-$	2.85	0.44	6.14	92	1.35
OER	$[Mo_{15}S_{32}]^{+}[Li_{2}O_{2}]^{0} \rightarrow [Mo_{15}S_{32}]^{0}[Li_{2}O_{2}]^{+}$	0.87	1.01	0.87	20541	2.49
OER	$[W_{15}S_{32}]^+[Li_2O_2]^0 \rightarrow [W_{15}S_{32}]^0[Li_2O_2]^+$	0.96	0.98	0.96	50681	2.58

than ORR rates for these materials. The adiabatic nature of the ORR can explain the high electrocatalytic activity for ORR.

13.3 Conclusions

In summary, we synthesized 15 members of TMDC family through CVT method and explored their potential for electrocatalysis applications such as ORR and OER. Various characterization techniques were employed to understand the electronic and structural properties of these materials. It was shown that most of the tested catalysts exhibit bifunctionality for ORR and OER, four members including NbS₂, MoS₂, VS₂, and VSe₂ depicted excellent performances, exceeding those of the well-known catalysts in aprotic media for both of these reactions. These results show a great potential to seek highly efficient bifunctional catalysts among TMDCs which have been rarely studied for electrochemical reactions beyond hydrogen evolution.

13.4 Experimental Section

13.4.1 Crystal Growth

A total of 1 g of precurser powders of transition metal and chalcogen with a 1:2 stochiometric ratio were loaded in an evacuated and sealed quartz ampule. The ampule was then placed in a two-zone furnace and the temperature of the both zones was raised to 1080 °C in one day. The temperature of the empty part of the ampule (cold zone) was then gradually cooled down to 950 °C in four days, while the other end was maintained at 1080 °C. The system was then slowly cooled down to room temperature in one day.

13.4.2 Synthesis of TMDC Nanoflakes

TMDC nanoflakes were synthesized using a liquid exfoliation method by sonicating a solution containing a mixture of 300 mg of the TMDC powder dispersed in 60 mL IPA. The sonication was carried out for 30 h using a probe sonicator (Vibra Cell Sonics 130 W). The resultant dispersions were centrifuged for 60 min at 2000 rpm, and the supernatant was collected.

13.4.3 Raman Spectroscopy

The Raman spectra were obtained using a Horiba LabRAM HR Evolution confocal Raman microscope using a 532 nm laser wavelength and 50x objective with Horiba Andor detector.

13.4.4 XPS

A Thermo Scientific ESCALAB 250Xi instrument was used to obtain XPS results. All spectra were calibrated based on the C-C bond binding energy at 284.8 eV. Thermo Avantage software was used to analyze and process each elements data.

13.4.5 AFM

A Bruker ICON Dimension was used to obtain the topography maps of drop-cast flakes which are analyzed to get the statistical flake thickness distributions. Exfoliated TMDC dispersions in IPA were drop-cast on silicon substrates. The substrates were carefully washed by acetone, IPA, and deionized water before experiment to remove the solvent residues.

13.4.6 DLS Measurement

Flake size measurements were carried out using the Malvern Zetasizer Nano ZSP system at 25 °C. The instrument includes a 10 mW semiconductor laser with 633 nm emissions. TMDC NFs dispersed in IPA were used for the measurements.

13.4.7 Transmission Electron Microscopy (TEM)

Aberration corrected JEOL ARM200CF (S) TEM microscope, equipped with a cold field emission gun allowing for 0.8Å spatial resolution and an Oxford X-max 100TLE windowless X-ray detector, was utilized for atomic resolution imaging and EDS. HAADF detector with 90 mrad inner-detector angle and 22 mrad probe convergence angle was utilized to obtain Z contrast images.

13.4.8 UPS

The UPS experiment was performed with He I UV source and in ultrahigh vacuum with the pressure of 8.0 10^{-10} mbar. A silver metal was used to first calibrate the analyzer based on the metal Fermi edge, and a bias of -10 V was applied in all cases to distinguish the sample energy cut-off from the cut-off of the spectrometer. Thermo Avantage software was used to analyze and process each synthesized materials data.

13.4.9 Electrochemical Experiments

The catalytic activity of the synthesized TMDCs nanoflakes for ORR and OER were studied by electrochemical experiments in a standard three-electrode cell (Section G.8 of Appendix G). To prepare the cathode electrode, 100 mg of catalyst was coated onto a 1 cm² carbon paper (TGP-H-030, purchased from FuelCellsEtc) as a gas diffusion layer and dried overnight in an argon filled glove box.

13.4.10 Constrained DFT Calculations

To assess charge hopping rates (k_{CT}) between nanoflakes and reaction intermediates, CDFT calculations were performed [123, 122], as implemented [126, 127] in the QUANTUM-ESPRESSO code [614]. The generalized gradient approximation of PBE as the exchange-correlation functional was used [163]. The core states were treated using the optimized norm-conserving Vanderbilt pseudopotentials with a wave function kinetic energy cutoff of 80 Ry (1088 eV) [615, 616]. Supporting Information for this chapter is included in Appendix G.

L.M. synthesized the TMDCs and their nanoflakes, and carried out the electrochemical experiments. L.M. and Z.H. performed UPS. I.L.B. supervised UPS analyses. Z.H. and B.S. performed Raman experiments. P.A., Z.H., P.Y., and L.M. carried out XPS and obtained AFM and DLS results. A.S.-K. supervised the electrochemical and characterization experiments. S.F. and F.K.-A. performed classical molecular dynamics simulations. J.C., S.B.C., and R.M. carried out computational work function measurements. R.E.W., L.C., P.Z., M.V., J.G., and L.A.C. carried out the computational studies (CDFT) of TMDC/IL systems. X.H. and R.F.K. performed STEM and EELS experiments. All of the authors contributed to the associated manuscript.

14. A LONG-CYCLE-LIFE LITHIUM-CO₂ BATTERY WITH CARBON NEUTRALITY

This chapter is reproduced with the permission of Wiley-VCH Verlag GmbH & Co. KGaA from: Alireza Ahmadiparidari[†], Robert E. Warburton[†], Leily Majidi[†], Mohammad Asadi[†], Amir Chamaani, Jacob R. Jokisaari, Sina Rastegar, Zahra Hemmat, Baharak Sayahpour, Rajeev S. Assary, Badri Narayanan, Pedram Abbasi, Paul C. Redfern, Ahn Ngo, Márton Vörös, Jeffrey Greeley, Robert Klie, Larry A. Curtiss, Amin Salehi-Khojin; Long-Cycle-Life Lithium-CO₂ Battery with Carbon Neutrality. *Advanced Materials* **2019** *31*, 1902518. ([†]These authors contributed equally to this work)

Lithium-CO₂ batteries are attractive energy-storage systems for fulfilling the demand of future large-scale applications such as electric vehicles due to their high specific energy density. However, a major challenge with Li-CO2 batteries is to attain reversible formation and decomposition of the Li₂CO₃ and carbon discharge products. A fully reversible LiCO₂ battery is developed with overall carbon neutrality using MoS₂ nanoflakes as a cathode catalyst combined with an ionic liquid/dimethyl sulfoxide electrolyte. This combination of materials produces a multicomponent composite (Li₂CO₃/C) product. The battery shows a superior long cycle life of 500 for a fixed 500 mAh g⁻¹ capacity per cycle, far exceeding the best cycling stability reported in Li-CO₂ batteries. The long cycle life demonstrates that chemical transformations, making and breaking covalent C-O bonds can be used in energy-storage systems. Theoretical calculations are used to deduce a mechanism for the reversible discharge/charge processes and explain how the carbon interface with Li₂CO₃ provides the electronic conduction needed for the oxidation of Li₂CO₃ and carbon to generate the CO_2 on charge. This achievement paves the way for the use of CO_2 in advanced energy-storage systems.

14.1 Introduction

Lithium-ion batteries are widely used as electrochemical energy storage systems for consumer electronics [30]; however, technologies with higher specific energy are needed for electrified transportation applications [617]. Therefore, beyond Li-ion battery chemistries such as rechargeable Li-O₂ batteries have recently garnered much attention due to their higher theoretical energy density [506, 618]. Li-O₂ batteries generally have limited cyclability, though several studies have reported new concepts that have achieved long cycle life [584, 619]. Although far less studied, the Li-CO₂ battery is another beyond Li-ion technology with a theoretical energy density of 1876 Wh kg⁻¹ [620, 621], far exceeding that of Li-ion batteries (~265 Wh kg⁻¹). This type of battery involves CO₂ reduction and evolution reactions during discharge and charge, respectively, on the surface of a porous cathode with an electrolyte based on lithium salts.

Despite the potentially high-energy density of $LiCO_2$ batteries, the electrochemical reactions remain poorly understood. Generally, it is believed that the discharge products in a Li-CO₂ battery should involve formation of Li_2CO_3 and carbon to balance the reaction stoichiometry, while charge results in regeneration of CO₂, although other possible products, such as O₂, have been observed. Previous Li-CO₂ battery studies have shown evidence for Li_2CO_3 upon discharge and for its disappearance upon charge with cycle life generally less than 100 cycles [622, 623, 624, 625, 626, 627, 628, 629, 630, 631]. However, none of these studies have achieved full reversility during cycling where carbon can react with Li_2CO_3 to regenerate CO₂ in the charging process. Recently, two studies have provided evidence for carbon reversibility in a Li-CO₂ battery using Raman spectroscopy [632, 82], but not for more than one cycle. This is important since during the discharge process, other side reactions can occur that can degrade the electrolyte. Moreover, accumulation of carbon and other side products on the catalyst surface can lead to clogging of active sites, which results in the battery failure. Thus, it is crucial to operate Li-CO_2 batteries under a carbon neutral condition in order to reversibly balance the electrochemical reactions during discharge and charge processes.

Our recent findings on the superior electrocatalytic activity of nanostructured transition metal dichalcogenides for CO_2 reduction [633, 587, 634, 586] and O_2 reduction in a Li- O_2 battery [584, 242, 585], have led us to investigate whether this type of catalyst would enable carbon and Li₂CO₃ reversibility in a Li- CO_2 battery. Using a MoS₂ electrocatalyst with an ionic liquid/dimethyl sulfoxide (DMSO) electrolyte, we have been able to achieve a long-cycle-life Li- CO_2 battery with evidence from various *in situ* and *ex situ* techniques for reversibility with carbon neutrality.

14.2 Results and Discussion

We assembled a custom-made Swagelok type Li-CO₂ cell using lithium as the anode and MoS₂ nanoflakes (NFs) coated on a gas diffusion layer as the cathode with the electrolyte composed of an 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄)/DMSO (25%/75%) solvent with 0.1 M LiTFSI as a lithium salt. The MoS₂ NFs synthesis and characterization were performed and confirmed based on our previously established methods [634, 242, 585]. The assembled cell was first purged with pure CO₂ and then connected to a battery analyzer for cycling experiments. This Li-CO₂ battery was found to cycle up to 500 consecutive discharge and charge cycles with a capacity of 500 mAh g⁻¹ per cycle at a current density of 500 mA g⁻¹ as shown in Figure 14.1a. Comparing the discharge voltage of the first (2.92 V) and 500th (2.75 V) cycles at the capacity of 500 mAh g⁻¹ indicates only a 5% decrease in the discharge potential. The charge potential also shows about a 12% increase during 500 cycles. These results confirm the stable and sustainable performance of the cell during 500 continuous cycles.

We also tested the rate capability of the Li-CO₂ battery at different current densities of 100, 500, and 1000 mA g⁻¹. Figure 14.1b-d illustrates the polarization gap



Figure 14.1.: The electrochemical performance of Li-CO₂ battery using MoS₂ NFs as cathode materials and a hybrid electrolyte (IL/DMSO) with 0.1 M LiTFSI. a) Discharge and charge voltages profile up to 500 cycles with the capacity of 500 mAh g^{-1} per cycle. b-d) Polarization gap (V) for 500 mAh g^{-1} capacity as a function of number of cycles at different current densities.

of the cell as a function of the number of cycles up to 200 cycles. The results indicate that at the current density of 100 mA g⁻¹, the battery shows the lowest polarization gap (0.7 V) at the first cycle and then this potential gap increases to ~1.45 V after 200 cycles (Figure 14.1b). Polarization gaps of 1.7 and 2.45 V were also obtained for higher current densities of 500 and 1000 mA g⁻¹ after 200 cycles, respectively (Figure 14.1c,d). These are 0.25 and 1 V larger than the polarization gap obtained at the current density of 100 mA g⁻¹.

To identify the composition of discharge/charge products during cycling especially the fate of carbon that should be formed during discharge, we used X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The XPS was performed on the surface of cycled cathodes of MoS_2 NFs coated on Al mesh. Figure 14.2a,b depicts the XPS spectra of the cathode at the first discharge and charge cycles. All spectra were calibrated based on C-C bonding energy at 284.8 eV. The O-C-O and C-C peaks in the XPS spectra are representatives of the so called adventitious carbon contamination which has been discussed in the literature extensively [635, 636, 637]. The C 1s and Li 1s spectra of the product show peaks at 289.5 and 55.2 eV, respectively, corresponding to formation of Li_2CO_3 [584, 629, 632]. This is consistent with our X-ray diffraction pattern (XRD) results (Section H.4, Appendix H).



Figure 14.2.: Spectroscopic investigation of MoS₂ NFs cathode coated on Al mesh. a,b) The XPS spectra of C 1s and Li 1s after the first discharge, and c,d) after the first charge cycle. e) Raman spectra showing the reversible formation/decomposition of Li₂CO₃ and carbon during the first cycle (D and G stand for the disordered and graphitic peaks of carbon, respectively). f) CO₂ moles during the first discharging process after the cell was discharged up to 1600 mAh g⁻¹. g) CO₂ moles detected before and after the charge process in first cycle.

Comparing the XPS spectra of C 1s and Li 1s for the discharge and charge cycles indicates that Li₂CO₃ is completely decomposed in the charge process, confirming the reversible formation and decomposition of Li₂CO₃. The XPS results also did not show any evidence of other products such as Li₂O, Li₂O₂, or LiOH. *Ex situ* Raman spectroscopy was also performed on the cathodes at the first charge and discharge cycles and results are shown in Figure 14.2e. The Raman spectra in discharge consist of three distinct Raman peaks at around 1580 and 1350 cm⁻¹ corresponding to carbon and 1088 cm⁻¹ corresponding to Li₂CO₃. Both the carbon and Li₂CO₃ Raman peaks completely disappeared on the charge, providing further evidence for the reversibility of the Li-CO₂ cell, i.e., Li₂CO₃ and carbon formation and decomposition during cycling.

In situ differential electrochemical mass spectroscopy (DEMS) was carried out to determine the gases produced during first charge and discharge cycles in the Li- CO_2 cell. Figure 14.2f shows DEMS profile to measure the e^{-}/CO_2 ratio during first cycle of the discharge process. The experiments were performed by discharging the battery up to 1600 mAh g^{-1} capacity and comparing the moles of CO₂ in the headspace of the cell before and after first cycle of the discharge process. It was observed that moles of CO_2 noticeably decreased compared to that of the cell before the discharge process, suggesting the consumption of the CO_2 during this process. The measurements indicate an e^{-}/CO_2 ratio of 4.05 for the discharge process. Figure 14.2g presents the DEMS results during the first charge cycle, which was pre-discharged up to 2000 mAh g⁻¹. The results indicate an immediate rise only in the CO_2 partial pressure confirming that CO_2 is the only gas evolved during the charge process. The e^{-}/CO_{2} ratio of 4.07 during the first cycle of the charge process was obtained by comparing the evolved moles of CO_2 with calibration data (Figure H.3, Appendix H). This indicates a four-electron transfer process during the evolution of CO_2 gas. No evidence of other evolved gases (e.g., O_2 , CO, and H_2) was observed during the charge process (Figure H.6, Appendix H). The DEMS results for the charge and discharge processes indicate that they both involve a four-electron reaction confirming the full

reversibility of the battery at the first cycle. In order to quantify the discharge product, we used the Coulometry approach (equation 14.1) that was previously used by McCloskey et al. [638] to determine the cathode weight gain;

$$\frac{3.6}{Fb}M_i = \Delta w_i [\text{mg mAh}^{-1}]$$
(14.1)

where Δw_i is the cathode weight increase by formation of *i* species, *F* is the Faraday constant, *b* is the number of transferred electrons, and M_i is the molecular weight of *i* species. Considering $b = 4.05 \text{ e}^{-}/\text{CO}_2$ obtained from DEMS and molecular weight of 78.89 for Li₂CO₃, we obtained $\Delta w_i = 0.726 \text{ mg mAh}^{-1}$, which is 98.8% of the theoretical value of 0.735 mg mAh⁻¹ for a four-electron transfer process. Knowing the current of 500 mA over 1 h time period in our system, the amount of Li_2CO_3 was found to be 0.03 μ g during the discharge process.



Figure 14.3.: SEM and TEM images of cathode sample after 25 cycles working in the $LiCO_2$ battery. a,b) SEM image of cathode surface after discharge (a) and charge (b) processes. c) TEM image showing the three components present in the sample: crystalline Li_2CO_3 , amorphous carbon and MoS_2 catalyst. d) Li_2CO_3 crystals oriented toward [103] zone axis. e) Experimental diffraction pattern. f) HRTEM image of an MoS_2 NFs. g) The intensity across the blue line. The spacing is consistent with MoS_2 interlayer spacing. h) Raman spectra showing the reversible formation/decomposition of Li_2CO_3 and carbon up to 100 cycles.

We also performed additional characterizations at higher cycles to examine the reversibility of product formation and decomposition. Figure 14.3a,b shows scanning electron microscopy (SEM) images of the cathode after 25 cycles of discharge and charge processes. The SEM images confirmed the presence of discharge products in the form of nanoparticles with an average size of 100-200 nm. The deposited nanoparticles on the surface of cathode completely disappeared after the charge experiment (Figure 3b) verifying the XPS and Raman data. A typical cathode area after 25 discharge cycles is depicted in the transmission electron microscopy (TEM) image shown in Figure 14.3c. Our electron energy-loss spectroscopy (EELS) and TEM results show the presence of four major components: i) crystalline Li₂CO₃, ii) amorphous carbon, iii) crystalline carbon, and iv) the MoS₂ NF catalyst. The elemental assignments shown in Figure 14.3c) for the MoS₂ catalyst, the Li₂CO₃ and amorphous carbon,

is based on EELS, high-resolution imaging, and electron diffraction pattern analysis, similar to the previously reported results by Asadi et al. [584]

For example, crystalline Li_2CO_3 is found using high-resolution phase contrast (HRTEM) imaging and electron diffraction (Figure 14.3d-f), while HRTEM images of the surface of the cathode after 25 discharge cycles is used to identify crystalline MoS₂ NFs (Figure 14.3f). This was further confirmed by measuring the intensity spacing across the blue line (6.2 nm), which is consistent with MoS₂ interlayer spacing (Figure 14.3g). We also performed EELS of the C-K edge to distinguish between crystalline and amorphous forms of carbon (Section H.5, Appendix H).

Raman spectroscopy was also performed on the cycled cathodes up to 100 charge / discharge cycles and results further confirm the reversibility at higher cycles (Figure 14.3h). Electrochemical impedance spectroscopy (Section H.6, Appendix H) and XPS results (Figure H.1, Appendix H) carried out at 10th cycle of charge and discharge also provide a strong evidence for the reversible formation and decomposition of products.

To examine the stability of the electrolyte, we performed ¹H NMR and ¹³C NMR experiments on the fresh and used electrolyte (after 100 discharge/charge cycles). Results shown in Figure H.10 in Appendix H indicate that there is no evidence of electrolyte degradation for the used electrolyte.

Moreover, we studied the deep discharge of this system for possible application in primary batteries where no reversibility is needed. The experiments were performed at the same current densities used for the cycling experiments (Section H.8, Appendix H). Results shown in Figure H.11 in Appendix H illustrate a discharge/charge capacity of about 60 000 mAh g⁻¹ (600 h charge and discharge) at a current density of 100 mA g⁻¹. Capacities of 35 000 mAh g⁻¹ (70 h) and 30 000 mAh g⁻¹ (30 h) were also obtained at current densities of 500 and 1000 mA g⁻¹, respectively.

The experimental investigations have provided evidence for carbon neutrality during long-term cycling of this Li-CO₂ battery, i.e., both the presence of carbon in the discharge product and its reincorporation into CO_2 gas with Li₂CO₃ decomposition. Despite these observations, many of the relevant mechanistic details of these reactions still remain unclear. In turn we carried out computational studies to provide further insight into the charge and discharge mechanisms during cycling experiments at a capacity of 500 mAh g⁻¹. This involved initially determining energies for some possible reactions using highly accurate quantum chemical wave-function-based calculations, followed by more detailed density functional theory (DFT) studies of possible reaction steps. The mechanisms are likely to be very complex since the discharge products are a mixture of crystalline Li_2CO_3 and amorphous carbon based on the TEM studies (Figure 14.3c) and our studies are meant to provide insight into feasible mechanisms.

Energies for four possible discharge reactions have been determined with the very accurate G4MP2 method [639] with the following assumptions: i) the effects of solvation have been added to gas phase G4MP2 energies in our calculations using a continuum model (SMD [640]), assuming DMSO as the solvent, although these effects on the reaction energies do not change any conclusions (see Table H.3, Appendix H), ii) in the discharge reactions, the carbon and lithium are assumed to be in atomic form and the rest of the species CO, CO₂, Li₂CO₃, and Li₂O, are in their molecular forms. The results of these energies, when combined with experimental results, provide evidence for the overall reaction on discharge.

The first reaction examined was a two-electron reduction with CO gas being one of the products along with Li_2CO_3 :

$$2\text{Li} + 2\text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{CO} \quad \Delta G = -3.82 \text{ eV}$$
 (14.2)

This two-electron reduction reaction is very thermodynamically favorable, but since no CO is observed during discharge this is not the likely reaction mechanism for formation of Li_2CO_3 . This reaction may be unfavorable due to kinetic factors (energy barriers) for the reaction mechanism or because other reactions involving solid-state products are more favorable. The second reaction examined involves formation of Li_2O and CO:

$$2\text{Li} + \text{CO}_2 \rightarrow \text{Li}_2\text{O} + \text{CO} \quad \Delta G = -2.22 \text{ eV}$$
 (14.3)

This reaction is also exothermic according to the calculations. However, Li_2O , as well as CO, are not observed experimentally, so this can also be ruled out as a discharge reaction. The third reaction is similar to reaction 14.3 but involves carbon formation:

$$4\text{Li} + \text{CO}_2 \rightarrow 2\text{Li}_2\text{O} + \text{C} \quad \Delta G = 1.91 \text{ eV}$$
(14.4)

Since reaction 14.4 is endothermic, it is not likely, and also Li_2O is not observed. The fourth reaction we examined involves the formation of carbon and Li_2CO_3 :

$$2\text{Li} + \frac{3}{2}\text{CO}_2 \to \text{Li}_2\text{CO}_3 + \frac{1}{2}\text{C} \quad \Delta G = -1.33 \text{ eV}$$
 (14.5)

Reaction 14.5 is thermodynamically favorable and is the most likely reaction based on the lack of experimental evidence for reactions 14.2-14.4. The TEM and Raman studies also show the presence of carbon and DEMS shows a four-electron reduction, which are consistent with reaction 14.5.

In addition to above results, the observed discharge potential of ~2.9 V is consistent with the calculated thermodynamic potential for reaction 14.5 of ~2.90 V versus Li/Li^+ [641]. The calculated thermodynamic potential for reaction 14.4, which involves formation of Li₂O is 1.89 V, much lower than observed in Figure 14.1, further confirming that this reaction is unlikely to occur. Thus, we conclude that the discharge process involves reduction of CO₂ followed by reaction with (Li⁺ + e⁻) pairs to form a mixture of discharge products including crystalline Li₂CO₃ and some form of carbon.

The schematic in Figure 14.4a illustrates the formation of the discharge product where reduction of CO_2 is considered the first step in the eventual formation of Li_2CO_3 and C. However, based on DFT calculations the reduction of CO_2 ($CO_2 + e^- \rightarrow CO_2^-$) in solution occurs at ~0.6 V versus Li/Li⁺, much lower than the discharge potential. This would indicate that the MoS₂ interface with adsorbed CO₂ greatly affects the electron transfer. To investigate the electron transfer mechanism, con-



Figure 14.4.: Theoretical calculations of Li-CO₂ battery charge and discharge mechanisms. a) Schematic showing discharge and charge processes of a model for an Li₂CO₃/C composite on an MoS₂ cathode. b) Mo₁₅S₂₁ cluster model used for CDFT calculations of diabatic charge hopping from MoS₂ NF to CO₂. c) CDFT calculations of electronic couplings between $[Mo_{15}S_{21}]^0[CO_2]^0$ and $[Mo_{15}S_{21}]^+[CO_2]^-$ as a function of separation between the active site and CO₂. The fit gives $H_{ab} = 2712e^{-0.85r_{Mo}-CO_2}$. d) Potential-dependent mechanistic analysis of CO₃²⁻ ion formation on MoS₂/IL cocatalyst that can lead to Li₂CO₃/C discharge product growth. Potential dependence is calculated through a computational hydrogen electrode approach and all voltages are with reference to the Li⁺/Li electrode. e) Cluster model C₅₅H₁₈/(Li₂CO₃)₂ used as model of amorphous carbon and lithium carbonate to calculate the charge potential for decomposition of Li₂CO₃/C. f) A reaction sequence that was investigated for oxidation, Li⁺ elimination and CO₂ elimination from cluster in (e) of an Li₂CO₃ dimer bonded to cluster (hydrogens are not shown in the diagram).

strained DFT (CDFT) calculations [122, 126, 127] were used to investigate the role of the MoS_2/IL co-catalyst system for CO_2 reduction. Using an $Mo_{15}S_{21}$ cluster model with adsorbed (EMIM⁺ + e⁻) pairs to expose an isolated Mo atom on the catalyst edge, we consider the process of non-adiabatic electron hopping from the catalyst to a CO₂ molecule as shown in Figure 14.4b. Figure 14.4c shows the electronic couplings (H_{ab}) between the $[Mo_{15}S_{21}]^0[CO_2]^0$ and $[Mo_{15}S_{21}]^+[CO_2]^-$ charge states calculated as a function of distance between the active site and CO₂. The CDFT-calculated H_{ab} values decrease exponentially as expected, due to exponential decay of the diabatic wave function overlap as a function of donoracceptor separation. However, we found that the coupling between the two diabats is strong even at large separation, suggesting that charge transfer is most likely adiabatic (i.e., CO₂ is spontaneously reduced due to the strong binding to the edge of the flake). Thus, this suggests that the discharge potential will correspond to the thermodynamic potential of the reaction, i.e., ~2.9 V.

To further investigate the mechanism of the Li_2CO_3/C discharge product formation, a mechanistic study was performed on a periodic MoS2 nanoribbon with the presence of EMIM cations, shown in Figure 14.4b. Potential dependence is calculated through a computational hydrogen electrode approach and all voltages are referenced to the Li/Li^+ electrode [11] and is shown in Figure 14.4d. Following the initial adsorption of CO_2 (downhill by 1.58 eV), we found that dissociative adsorption of a second CO_2 molecule is also favorable (by 0.60 eV), which leads to the formation of a co-adsorbed carbonate (CO_3^*) and carbon monoxide (CO^*) . The CO* desorption is unfavorable by 2.23 eV, consistent with the experimental result wherein CO is not detected as a gaseous byproduct. Adsorbed CO_3^* is assumed to react with Li⁺ ions in solution to form Li_2CO_3 , where this electrochemical step is favorable below 2.31 V versus Li/Li⁺, which is approximately consistent with the experimental discharge potential. What remains unclear, however, is the process by which the amorphous carbon forms to satisfy the bulk reaction stoichiometry. Our DFT calculations suggest that a third CO_2 could, in principle, react with the edge containing adsorbed CO^* to form a second CO_3^* and a single carbon atom (C^{*}), although we found that the thermodynamics for such a process are uphill by 0.94 eV. We speculate that this CO^* conversion into CO_3^* and C^* will be favorable in the presence of defect sites on the catalyst or carbon product leading to amorphous carbon growth.

Based on the DEMS and Raman data, the charge process involves decomposition of crystalline Li_2CO_3 and amorphous carbon. The decomposition of Li_2CO_3 and carbon:

$$2\text{Li}_2\text{CO}_3 + \text{C} \rightarrow 3\text{CO}_2 + 4\text{Li}^+ + 4\text{e}^-$$
 (14.6)

will occur at 2.9 V based on thermodynamics [641, 642]. However, the observed charge potential always occurs much higher around 3.8-4.5 V in our work and other experimental studies [632, 82]. The reason is probably because of an overpotential due to the oxidation potential of Li_2CO_3 required for the electrochemical reaction. From B3LYP density functional calculations, the oxidation potentials of Li_2CO_3 monomer and dimer are 4.2 and 4.4 V versus Li/Li⁺, respectively. The lower charge potential in Figure 14.1 of ~ 4 V for the earlier cycles may be due to the mechanism by which decomposition occurs. The amorphous carbon may provide an electrically conducting network to enable the charge process that has to start with oxidation of the discharge product since Li_2CO_3 is not electronically conductive [643]. From B3LYP density functional calculations, the oxidation potential of molecular Li_2CO_3 is lowered if it is bound to a carbon defect site in a model for amorphous carbon. Thus, the decomposition may occur at the interface between carbon and Li_2CO_3 . This would require maintenance of an interface between Li₂CO₃ and carbon throughout decomposition to CO_2 and C. Our DFT calculations on a model system show that maintenance of such an interface is possible with loss of CO_2 and C (see Figure H.12, Appendix H).

We have also investigated the energy for reaction 14.6 by investigating in detail various reaction pathways for sequential oxidation and decomposition of a cluster model of $\text{Li}_2\text{CO}_3/\text{C}$ (see Section H.11, Appendix H for details). We used a C_{54} cluster model for amorphous carbon (with 18 hydrogens on the edges) and a single carbon adatom (representing a defect site) as shown in Figure 14.4. Sequential reactions involving oxidation, loss of Li⁺, and CO₂ elimination were found with an upper charge potential of ~4 V, consistent with experiment, with the highest energy step involving oxidation of the cluster. One of these reaction cycles is shown in Figure 14.4f. The exact role of the MoS_2 catalyst during charge other than providing a conductive network with the amorphous carbon is unclear based on this mechanism.

14.3 Conclusions

In summary, we developed a rechargeable Li-CO₂ battery based on MoS₂ NFs that shows reversible cycling at 500 mAh g⁻¹ for 500 cycles, as well as a very high charge/discharge capacity of 60 000 mAh g⁻¹ for one cycle. Our experimental investigation confirmed the presence of crystalline Li₂CO₃ and amorphous C as the main discharge products, with evidence that they are reversibly decomposed in the subsequent charge cycle, i.e., it maintains carbon neutrality. Computational studies have provided new insight into feasible discharge and charge mechanisms involving formation and decomposition of the Li₂CO₃/C composite. The long cycle life demonstrates that complex C-O bond making and breaking chemical transformations can be used in energy storage systems, in addition to the widely studied alkali metal (Li, Na, K)-oxygen bond making and breaking transformations.

Supporting Information for this chapter is included in Appendix H.

A.S.K. and L.A.C. conceived the idea. A.A., M.A., L.M., B.S., and A.C. performed/analyzed/verified all electrochemical experiments. A. A., M.A., P.A. performed the DEMS and verified the data analysis. P.A., L.M. performed XPS and verified the data analysis. Z. H. and S. R. carried out Raman experiments. S.R. performed NMR experiments. R.E.W., R.S.A., B.N., P.C.R., A.N., M.V., J.G. and L.A.C. performed the computational studies of the MoS₂/IL and reaction mechanisms during charge/discharge cycling. J.J. and R.K. performed the TEM and HRTEM experiments. A.S.K., L.A.C., A.C., M.A., R.E.W., R. K. wrote the manuscript of the associated publication. All of the authors discussed the results and reviewed the manuscript.

15. LITHIUM-COUPLED ELECTRON TRANSFER KINETICS IN LICOO₂ FROM NON-ADIABATIC RATE THEORIES

15.1 Introduction

Extended charge and discharge cycling of lithium ion (Li-ion) batteries depends on the reversibility of bulk Li-coupled electron reactions in the anode and cathode [26, 17]. The capacity of the typical intercalation-based Li metal oxide cathode material is related to the number of interstitial sites available to Li⁺ ions, along with the associated electronic energy levels of transition metal redox couples within a suitable voltage range for operation of the cell. In addition to the capacity and voltage limits set by Li-coupled electron transfer reactions, the mobility of Li⁺ ions and electrons (or holes) in the bulk or at the surface of an electrode represent a theoretical limit to the kinetics of such reactions. Notably, computational work has shown that ion diffusion in semiconductor oxides can be highly dependent on the oxidation states of transition metal ions along the ion diffusion coordinate [644]. Similar effects have been observed for Li-ion battery materials, where local environments can determine diffusion barriers for Li⁺ ion bulk mobility [57]. Such effects are likely to be especially pronounced under conditions for extreme fast charging where Li⁺ ion and electron/hole mobility are on different time-scales.

Electronic conductivity mechanisms have been proposed extensively in the literature for energy storage materials. Band conduction mechanisms are expected in materials with a continuous distribution of electronic states at the Fermi level or where charge spontaneously delocalizes, *i.e.* metallic systems, or at the surface of topological insulators such as Li_2O_2 [63]. For the aforementioned systems, electronic conductivity can be evaluated from the material bandstructure and charge carrier effective masses using models such as the Boltzmann transport equation [645]. Most Li-ion battery electrodes, however, have more localized electronic structure such that charge carrier conduction occurs via charged defects called polarons sites accompanied by local lattice distortions. Electron and hole polaron hopping mechanisms have been studied using density functional theory (DFT) calculations for various energy storage materials including spinel LiMn₂O₄ [72] and olivine LiMPO₄ (M=Fe,Mn) [70] Li-ion cathodes, as well as solid compounds associated with beyond Li-ion systems such as Li₂CO₃ [643], Li₂O₂ [643, 50, 71, 646], and Li₂S [647]. In each of these previous examples, these polaron hopping mechanisms were assumed to be adiabatic, which implicitly assumes a strong electronic coupling between initial and final charge states and a Born Oppenheimer potential energy surface for charge transfer. Recent work has shown, however, that non-adiabatic effects are sometimes necessary for accurate treatment of charge transfer rates between charged defects in solids [648, 649, 240, 239]. In particular, very recent work by Siegel and co-workers has demonstrated the importance of non-adiabaticity in polaron transport in α -sulfur and Li₂S for lithium-sulfur batteries [241].

Despite these recent efforts to include non-adiabatic effects into first principles solid-state conductivity studies, such work has yet to be extended to the intercalationchemistry based Li metal oxide materials that are ubiquitous as the cathodes in Liion batteries. Here, we describe a general framework that can be used to describe relative conductivities of electron and hole polaron hopping events in energy storage materials in the adiabatic and non-adiabatic limits. To demonstrate this concept, we focus on describing charge transfer within the prototypical layered LiCoO₂ Li-ion cathode [22] material in the low- and high-voltage limits. We use constrained density functional theory calculations (CDFT) [122, 123] to evaluate electronic couplings for two-state configuration interactions to determine charge transmission probabilities and reorganization energies in the limit of non-adiabatic charge transfer.

15.2 Methods

Spin polarized, plane-wave, density functional theory (DFT) calculations were performed using the Quantum Espresso [614] code. The van der Waals-inclusive opt-B88 [650, 651, 652, 653] exchange and correlation functional was used to provide accurate treatment of interlayer CoO₂ binding energies as described by Aykol and co-workers [654]. A Hubbard U correction [102, 103, 104, 106] of 3.3 eV [110] is applied to correct for over delocalization of the highly correlated Co 3d states in Li_xCoO₂. The core states are treated using the optimized norm-conserving Vanderbilt pseudopotentials [615, 616] and valence states are expanded in a plane wave basis set with a kinetic energy cutoff of 80 Ry (1088 eV). Bound polaron defects are introduced into 75 formula unit (5 x 5 x 3) Li₇₅Co₇₅O₁₅₀ and Co₇₅O₁₅₀ supercells to minimize Coulombic interactions across periodic boundary conditions. Given the size of the supercells, all calculations were performed at the Γ -point. Total energies are converged to 1 x 10⁻⁶ Ry (1.36 x 10⁻⁵ eV) per unit cell and ionic relaxations are subject to a force criterion of 1 x 10⁻³ Ry/Bohr (2.57 x 10⁻² eV/Å).

In the adiabatic limit (strong electronic coupling), transition state theory is valid to treat charge transfer rates (k_{CT}^{TST}) , where the activation energy (E_{act}) can determined using the nudged elastic band method [170, 341].

$$k_{CT}^{TST} = \frac{k_B T}{h} exp(-\frac{E_{act}}{k_B T})$$
(15.1)

In equation 15.1, k_B is the Boltzmann constant, T is the temperature (300 K in this work), and h is the Planck constant.

In the limit of non-adiabatic charge (very weak electronic coupling), charge transfer rates follow a Marcus [118] rate theory treatment:

$$k_{CT}^{Marcus} = |H_{ab}|^2 \sqrt{\frac{\pi}{\hbar^2 k_B T \lambda}} exp(-\frac{E_{act}}{k_B T})$$
(15.2)
where E_{act} in this case is evaluated from the determined from the intersections of diabatic potential energy surfaces within a Marcus parabolic construction depending on the reaction driving forces (ΔG) and reorganization energies (λ) defined by:

$$E_{act} = \frac{(\Delta G + \lambda)^2}{4\lambda} \tag{15.3}$$

$$\Delta G = (\mathcal{D}_f^f + \mathcal{A}_f^f) - (\mathcal{D}_i^i + \mathcal{A}_i^i)$$
(15.4)

$$\lambda = (\mathcal{D}_i^f + \mathcal{A}_i^f) - (\mathcal{D}_f^f + \mathcal{A}_f^f)$$
(15.5)

where $\mathcal{D}_x^y \mathcal{A}_x^y$ are the donor and acceptor sites for charge transfer, respectively, in the *x* electronic state and *y* atomic configuration. The electronic coupling (H_{ab}) between the two diabatic states (a and b) is by definition:

$$H_{ab}[\rho_a, \rho_b] = \langle \psi(\rho_b) | H | \psi(\rho_a) \rangle \tag{15.6}$$

and represents the two-state configuration interaction between the a and b electronic states as off-diagonal solutions to the Schrödinger eigenvalue problem.

To account for the transition between the adiabatic and non-adiabatic limits, the Landau-Zener rate expression is used:

$$k_{CT}^{LZ} = \left(\frac{P_{LZ}}{1 + P_{LZ}}\right)\nu \exp\left[-\frac{1}{k_B T}\left(E_{act} - |H_{ab}| - \frac{\lambda}{2}\right) + \sqrt{\frac{\lambda^2}{4} + |H_{ab}|}\right]$$
(15.7)

which includes the adiabaticity correction (Δ) [649] added to the exponential:

$$\Delta = |H_{ab}| + \frac{\lambda}{2} - \sqrt{\frac{\lambda^2}{4} + |H_{ab}|} \tag{15.8}$$

and accounts for the probability of a charge transmission event occurring based on the magnitudes of H_{ab} and λ :

$$P_{LZ} = 1 - exp\left[-\frac{|H_{ab}|^2}{\hbar\nu}\sqrt{\frac{\pi}{k_B T \lambda}}\right]$$
(15.9)

Since H_{ab} and λ depend explicitly on the charge density and total energies of an excited electronic state, respectively, these parameters are not directly accessible through ground state DFT calculations. As such, constrained DFT (cDFT) [122, 123] calculations, as implemented into the Quantum Espresso code by Galli and co-workers [126, 127], are used to determine these parameters in the non-adiabatic rate expressions of equation 15.2 and 15.7. In cDFT, a constraining potential (V_i) is applied as a Lagrange multiplier to enforce charge separation (N_0) between donor (\mathcal{D}) and acceptor (\mathcal{A}) atomic groups. The cDFT free energy ($F^{cDFT}[\rho(\mathbf{r})]$) incorporates this term is added as a Lagrange multiplier to the DFT total energy ($E^{DFT}[\rho(\mathbf{r})]$):

$$F^{cDFT}[\rho(\mathbf{r})] = E^{DFT}[\rho(\mathbf{r})] - V_i(\int_{\Omega} w(\mathbf{r}\rho(\mathbf{r})d^3r - N_0)$$
(15.10)

where $w(\mathbf{r})$ is a weight function based on real-space Hirshfeld charge partitioning [128] between \mathcal{D} and \mathcal{A} .

$$w_i(\mathbf{r}) = \frac{\sum_i^{\mathcal{D}} \rho_i(\mathbf{r}) - \sum_i^{\mathcal{A}} \rho_i(\mathbf{r})}{\rho(\mathbf{r})}$$
(15.11)

A charge separation convergence criterion of 1 x 10^{-5} e⁻ is enforced for all cDFT calculations in this work.

15.3 Results

Fully lithiated LiCoO₂ is a hexagonal $R\bar{3}m$ crystal structure with O3 stacking of the CoO₂ layers and Li⁺ ion occupation of interstitial octahedral sites [22]. Following a series of delithiated phase transitions with increasing voltage [655, 56], the CoO₂ layers eventually adopt an O1 stacking sequence in the fully delithiated CoO₂ phase [182]. Figure 15.1 shows the defect-free bulk structures for the low-voltage LiCoO₂ (Figure 15.1a) and high-voltage CoO₂ (Figure 15.1b) phases, representing the fully



Figure 15.1.: Defect-free bulk unit cells of (a) fully-lithiated (low voltage phase) O3-LiCoO₂ and (b) delithiated (high voltage phase) O1-CoO₂. Side (left) and top (right) views are presented to show the O3 and O1 stacking of Co ions within the CoO₂ layers of LiCoO₂ and CoO₂, respectively, as well as the octahedral positions of Li⁺ ions between CoO₂ layers. Lithium, cobalt, and oxygen ions are depicted in green, blue, and red, respectively. The black outline represents the unit cell, which has been repeated in the [100] and [010] directions.

lithiated and delithiated limits of the Li_xCoO_2 phase diagram. In order to study electron and hole transport in the Li_xCoO_2 cathode system we introduce bound polarons into the two bulk phases in Figure 15.1 with dilute modification of the Li^+ ion content. For example, introducing a single Li^+ vacancy (V'_{Li}) into a LiCoO_2 supercell introduces a hole polaron (or a single oxidized Co^{4+} ion) in the lattice to preserve overall charge neutrality. Similarly, introduction of a Li^+ interstitial (Li_i) in CoO_2 introduces an electron polaron (or a single reduced Co^{3+} ion). Using a modified version of the approach described by Deskins and Dupuis [244, 246, 245], we locally relax hole and electron polarons at different positions in the lattice relative to either their associated charge-compensating defect $(V'_{Li} \text{ and } Li_i)$ for LiCoO₂ and CoO₂, respectively). Further, to minimize interactions within the periodic boundary conditions, these calculations are performed within the 75 formula unit supercells as described in Section 15.2.



Figure 15.2.: Configurations of lithium ion vacancies (V'_{Li}) and bound hole polarons (Co^{4+}) in $\mathrm{Li}_{74}\mathrm{Co}_{75}\mathrm{O}_{150}$ supercell calculations. In each top panel (top view) of (a-h) the * indicates the position of V'_{Li} whereas the arrows in the bottom panels (side view) point to the layer where V'_{Li} is located. The Co^{4+} hole polaron positions are labeled by the cyan polyhedra in (a-h) and the atomic color scheme for the rest of the defect-free lattice is consistent with that of Figure 15.1. (i) The relative energies of each hole polaron as labeled in (a-h) plotted as a function of the charge compensating V'_{Li} -Co⁴⁺ defect separation distance.

Figure 15.2a-h shows the different positions of hole polarons (Co⁴⁺ shown by cyan polyhedra) relative to the positions of V'_{Li} (marked by * and arrows in top and bottom panels, respectively) in LiCoO₂. Figure 15.2i shows the relative energies of each of the Co⁴⁺ hole polarons relative to the location of V'_{Li} . Several equivalent positions (**a**, **b**, **c**) are relaxed to account for hole transport between structurally identical sites in the lattice within the same CoO₂ layer (between **a** and **b**) and for tunneling between CoO₂ layers (between **a**/**b** to **c**). As might be expected [656], there exists a general trend favoring close proximity the of V'_{Li} and Co⁴⁺ to maximize local charge neutrality, with the relative energies of these defect pairs increasing with increased separation. Eventually, the trend plateaus (see positions **g** and **h** in Figure 15.2i) approaching the limit of infinitely separated charged defects.



Figure 15.3.: Configurations of lithium interstitials (Li_i) and bound electron polarons (Co^{3+}) in LiCo₇₅O₁₅₀ supercell calculations. In each top panel (top view) of (a-h) the * indicates the position of Li_i . The Co³⁺ electron polaron positions are labeled by the gold polyhedra in (a-h) and the atomic color scheme for the rest of the defect-free lattice is consistent with that of Figure 15.1. (i) The relative energies of each electron polaron as labeled in (a-h) plotted as a function of the charge compensating Li_i -Co³⁺ defect separation distance.

Figure 15.3a-h shows the locations of Co^{3+} electron polarons (marked by gold polyhedra) relative to Li_i (marked by * in the top panels) in the 75 forumla unit CoO_2 supercell. Figure 15.3i shows the relative energies for the defect pairs, with the same general trends observed for hole polaron localization in LiCoO_2 (Figure 15.2i). The exception to this general thermodynamic trend with defect pair separation is position **b**, which appears to be less thermodynamically favorable than its Li_i -Co³⁺ separation might suggest. We note that the key structural difference for position **b** is that the

 Co^{4+} site is localized in a CoO_2 layer where only one O^{2-} anion is coordinated to the interstitial Li⁺ ion, whereas the layer above has three O^{2-} coordinated to Li⁺, since the O1-stacking of CoO_2 leads to tetrahedral interstitial sites. This suggests that prior to charge compensation with a Co^{3+} polaron, introduction of Li⁺ at tetrahedral sites breaks degeneracy of Co^{4+} conduction states to which the electron will be promoted from the resulting asymmetry of the local crystal field.

Following localization of hole and electron polarons at different positions within the supercell lattice, driving forces (ΔG) for charge transfer can be determined. In order to account directly for non-adiabatic effects on charge transfer rates, however, the electronic coupling between two polaronic charge states (H_{ab}) and the reorganization energies (λ) must be calculated. These parameters in the Marcus (equation 15.2) and Landau-Zener (15.6) rate expressions are inaccessible based on results of the ground state DFT calculations in Figure 15.2-15.3 and depend directly on the metastable state charge density as shown in equations 15.5 and 15.6. The H_{ab} corresponds to is the two-state configuration interaction between the ground and selected metastable charge state (equation 15.6), which can be determined through effective \mathcal{D} and \mathcal{A} charge partitioning in cDFT calculations. The ($\mathcal{D}_i^f + \mathcal{A}_i^f$) term in the reorganization energy λ expression (equation 15.5) can be approximated by the cDFT free energy (equation 15.10) for the metastable charge state diabat, since the Lagrange multiplier term associated with the cDFT constraining potential becomes vanishingly small as the charge separation convergence criterion is satisfied.

Using the ground state polaron structures in Figures 15.2 and 15.3, cDFT calculations are used to evaluate the H_{ab} and the reorganization energies λ relevant to non-adiabatic charge transfer. In contrast to our previous work, where the cumulative \mathcal{D} and \mathcal{A} atom groups were always spatially separated during charge partitioning [242, 243] (see weight function, $w(\mathbf{r})$, formulation in equation 15.11), charge transport in LiCoO₂ involves covalent bonding between \mathcal{D} and \mathcal{A} atomic groups in the case of nearest-neighbor charge transport (as in top panel of Figure 15.4a) or other atoms in the lattice. These considerations of covalency make a consistent charge partitioning



Figure 15.4.: Charge partitioning within constrained density functional theory (cDFT) calculations for bound hole transport in LiCoO₂ between (a) neighboring CoO₆ octahedra that share two O²⁻ anions and (b) spatially separated CoO₆ octahedra. The top panel images in (a) and (b) show the donor and acceptor (\mathcal{D} - \mathcal{A}) as defined by the cDFT calculation input. The bottom panel shows the isosurfaces for the lowest single particle molecular orbital (LUMO), or conduction band minimum, for the Γ -point calculation performed within cDFT for each diabatic electronic state. For hole transport (and electron transport in the case of O1-CoO₂) between both neighboring and spatially separated CoO₆, the LUMO isosurfaces and site-projected magnetic moments correspond to polaron localization at a single Co ion site in the bulk lattice.

scheme within cDFT non trivial. We also consider charge transport between nextnearest neighbors or between CoO_2 layers (as shown in top panel of Figure 15.4b) through the van der Waals gap. Within cDFT, the charge scheme must treat each of these situations consistently, where constrained charged defects are consistent with the electronic structure of either Co^{4+} (for hole polarons in $LiCoO_2$) or Co^{3+} (for electron polarons in CoO_2).

The top panels in Figures 15.4a and 15.4b show an example of the charge partitioning scheme for polaron localization between neighboring and spatially separated CoO_6 octahedra. In each case, the \mathcal{D} and \mathcal{A} atom groups are always defined by the Co ion where the polaron is transferred to or from, in addition to the six O^{2-} anions to which it forms covalent bonds. The full CoO_6 octahedra are therefore defined as the \mathcal{D} and \mathcal{A} between which charge partitioning (as defined in equation 15.11) is enforced by cDFT, even when the \mathcal{D} and \mathcal{A} atomic groups overlap (see top panel of Figure 15.4a). The bottom portion of Figures 15.4a and 15.4b demonstrate the localization of ground and excited state hole polarons in LiCoO₂ within cDFT, where we plot the differential isosurfaces for the band decomposed energy densities of the conduction band minimum (CBM), *i.e.* lowest single particle molecular (LUMO), at the Γ point for each diabat for the corresponding charge transfer event. These results show that the cDFT charge partitioning approach consistently localizes holes onto the desired Co ions with the LUMO isosurface adopting the shape of a non-bonding type 3datomic orbital. We also use this charge partitioning approach within cDFT to properly localize the ground and excited states for bound electron polarons in CoO_2 to enable calculation of H_{ab} and λ . For each cDFT calculation, the site projected magnetic moments are consistent with proper polaron localization observed in the ground state DFT calculations performed in Figures 15.2 and 15.3 (magnetic moments of 0 μ_B and 1 μ_B for Co³⁺ and Co⁴⁺, respectively), providing further corroboration to the band decomposed charge density analysis of electron and hole polarons in $Li_{x}CoO_{2}$.

Table 15.1 shows the parameters associated with the rate expressions for polaron transport relative to the charge-compensating Li⁺ defect between the positions as labeled in Figures 15.2 and 15.3 for LiCoO₂ and CoO₂, respectively. As mentioned above, driving forces (ΔG) are determined from ground-state thermodynamics of the different polaron positions as determined from the data in Figures 15.2i and 15.3i, whereas H_{ab} and λ are determined using the ground and excited state wave functions determined from cDFT calculations. To reduce computational expense, we perform cDFT calculations only for a polaron transport reaction in one forward direction. The

Table 15.1.: Kinetic parameters for non-adiabatic charge transfer of bound electron polarons in CoO_2 and bound hole polarons in $LiCoO_2$. The notation in the "transition" column refers to the polaron positions as labeled in Figure 15.2 for $\rm LiCoO_2$ and Figure 15.3 for CoO_2.

transition	$\Delta G [eV]$	$\lambda [eV]$	E_{act} [eV]	H_{ab} [eV]	P_{LZ}	k_{Marcus} [s ⁻¹]	$k_{LZ} [\mathrm{s}^{-1}]$
				C_0O_2			
$a \rightarrow b$	0.11	0.20	0.12	$1.33 \mathrm{x} 10^{-2}$	0.28	$5.97 \mathrm{x} 10^{10}$	$6.39 \mathrm{x} 10^{10}$
$a \rightarrow c$	0.00	0.05	0.01	2.93	1.00	$4.28 \mathrm{x} 10^{17}$	$1.54 \mathrm{x} 10^{13}$
$\mathbf{a} \to \mathbf{d}$	0.05	0.29	0.10	3.35	Ц	$7.33 \mathrm{x} 10^{15}$	$5.33 \mathrm{x} 10^{13}$
$a \rightarrow e$	0.13	0.37	0.17	0.58	Ч	$1.35 \mathrm{x} 10^{13}$	$6.38 \mathrm{x} 10^{12}$
$\mathbf{a} \to \mathbf{f}$	0.27	0.32	0.27	$5.84 \mathrm{x} 10^{-4}$	$5.08 \mathrm{x} 10^{04}$	$2.93\mathrm{x}10^{5}$	$2.99\mathrm{x}10^5$
$a \rightarrow g$	0.28	0.49	0.30	$3.91 \mathrm{x} 10^{-4}$	$1.83 \mathrm{x} 10^{-4}$	$2.80\mathrm{x}10^4$	$2.85\mathrm{x}10^4$
$\mathbf{a} \to \mathbf{h}$	0.29	0.50	0.31	$1.93 \mathrm{x} 10^{-3}$	$4.40 \mathrm{x} 10^{-3}$	$4.98 \mathrm{x} 10^5$	$5.32\mathrm{x}10^{5}$
$\mathbf{d} \to \mathbf{e}$	0.08	0.20	0.10	2.75	1.00	$6.22 \mathrm{x} 10^{15}$	$1.06 \mathrm{x} 10^{13}$
$\mathrm{d} \to \mathrm{g}$	0.23	0.26	0.23	0.02	0.44	$1.39\mathrm{x}10^9$	$1.43 \mathrm{x} 10^9$
$\mathbf{d} \to \mathbf{h}$	0.24	0.28	0.24	$4.71 \mathrm{x} 10^{-4}$	$3.54 \mathrm{x} 10^{-4}$	$6.17\mathrm{x}10^{5}$	$6.28\mathrm{x}10^{5}$
$\mathbf{g} \to \mathbf{h}$	0.01	0.01	0.01	3.01	1.00	$9.90 \mathrm{x} 10^{17}$	$9.45 \mathrm{x} 10^{12}$
				$LiCoO_2$			
$a \rightarrow c$	0.00	0.21	0.05	4.76	1.00	$1.03 \mathrm{x} 10^{17}$	$7.45 \mathrm{x10^{13}}$
$\mathbf{a} \to \mathbf{b}$	0.00	0.58	0.15	$6.20 \mathrm{x} 10^{-3}$	$4.16 \mathrm{x} 10^{-2}$	$2.95\mathrm{x}10^9$	$3.52\mathrm{x}10^9$
$\mathbf{a} \to \mathbf{d}$	0.01	0.29	0.08	4.02	1.00	$2.47 \mathrm{x} 10^{16}$	$1.13 \mathrm{x} 10^{14}$
$a \rightarrow e$	0.10	0.49	0.18	$4.79 \mathrm{x} 10^{-2}$	0.94	$5.29 \mathrm{x} 10^{10}$	$4.95 \mathrm{x} 10^{10}$
$\mathbf{a} \to \mathbf{f}$	0.10	0.39	0.15	3.90	1.00	$1.10 \mathrm{x} 10^{15}$	$4.23 \mathrm{x} 10^{13}$
$a \rightarrow g$	0.17	0.70	0.27	$8.90 \mathrm{x} 10^{-4}$	$7.90 \mathrm{x} 10^{-2}$	$4.68\mathrm{x}10^{5}$	$4.83 \mathrm{x} 10^{5}$
$\mathrm{a} \rightarrow \mathrm{h}$	0.17	0.64	0.26	$1.64 \mathrm{x} 10^{-2}$	0.24	$2.71\mathrm{x}10^{8}$	$3.53 \mathrm{x} 10^8$
$\mathbf{d} \to \mathbf{e}$	0.09	0.28	0.12	3.47	1.00	$3.13 \mathrm{x} 10^{15}$	$1.75 \mathrm{x} 10^{13}$
$\mathbf{d} \to \mathbf{f}$	0.09	0.28	0.12	4.28	1.00	$5.45 \mathrm{x} 10^{15}$	$2.12 \mathrm{x} 10^{13}$
$\mathbf{e} \to \mathbf{f}$	-0.01	0.22	0.05	4.02	1.00	$7.90 \mathrm{x} 10^{16}$	$8.71 \mathrm{x} 10^{13}$
$\mathbf{g} \to \mathbf{h}$	0.00	0.22	0.05	3.89	1.00	$6.58 \mathrm{x} 10^{16}$	$7.30 \mathrm{x} 10^{13}$

rates in the backward direction can be calculated using the relationship between the two λ within the Marcus diabatic parabola construction, along with the assumption that H_{ab} and H_{ba} are approximately equal. Diabatic activation energies (E_{act}) are determined from ΔG and λ as shown in equation 15.4.

In consideration of polaron transport between nearest neighbor Co ion sites (hop distance of ca. 2.8 Å) H_{ab} is in general quite large (between 2.75 and 4.76 eV) with Landau-Zener charge transmission probabilities (P_{LZ}) near unity. This finding suggests adiabatic nearest neighbor electron and hole transport in $\text{Li}_x \text{CoO}_2$, with rates that can be well-modeled by transition state theory and barriers from nudged elastic band calculations. These adiabatic charge transfer rates are comparably high but not necessarily reversible, since significantly large driving forces can lead to several orders of magnitude difference in between a forward and reverse charge transfer rate, *e.g.* two orders of magnitude difference in rates between the a \rightarrow e and e \rightarrow a transitions in LiCoO₂.

 H_{ab} between next-nearest neighbors and more spatially separated defects such as interlayer charge transfer, however, becomes vanishingly small, sharply decreasing P_{LZ} and approaching the non-adiabatic (Marcus theory) charge transfer limit. Accordingly, charge transfer rates are also much lower in comparison to nearest neighbor electron and hole transport. We note, however, that such a conclusion would not be reached from a comparison of E_{act} for different charge transfer events and that direct consideration of non-adiabaticity involving calculation of H_{ab} and providing an estimate of P_{LZ} is necessary to understand the true contributions of these charge transfer modes to the overall material electronic conductivity. These results suggest that, due to the layered structure of $Li_x CoO_2$, lower charge transfer rates associated with interlayer tunneling lead to significant anisotropy in electronic conductivity driven primarily by non-adiabaticity. This has shown by various experimental orientation-dependent resistivity and conductivity measurements showing several orders of magnitude difference between in-layer and inter-layer charge transfer rates [657, 658].

15.4 Conclusions

This work describes a general approach and methodology to calculate the dependence of charge transfer rates on proximity to charge compensating Li⁺ ion vacancy or interstitial defects. Li⁺ ion defect concentrations are likely to determine the Fermi level position as the dominant defect in intercalation-based Li-ion battery cathodes under electrochemical potential bias, underpinning the driving forces for bulk Li⁺coupled electron transfer reactions. We have shown through consideration of bound electron and hole polaron defects in $Li_x CoO_2$ that nearest neighbor charge transport is adiabatic due to strong electronic coupling between the two polaronic charge states. However, next-nearest neighbor and more spatially separated Co-ion redox centers have much weaker electronic couplings and charge transmission probabilities from Landau-Zener theory, suggesting non-adiabatic charge transfer kinetics that cannot be captured using transition state rate theories. In the case of layered Li_xCoO_2 , there is also low probability of interlayer tunneling suggesting highly anisotropic electronic conductivities in agreement with previous experimental measurements. Moreover, we note that activation energies for polaron transport are not representative of relative charge transfer rates in the non-adiabatic limit. The results in this work suggest that non-adiabatic contributions to charge transfer may be highly relevant in bulk materials with more spatially separated redox centers for polaron hopping (as shown recently for $BiVO_4$ [240, 239]) or less covalency between transition metal d and oxygen 2p states. Similar systematic approaches to evaluate dependence of concerted and decoupled charge and ion transport may be applied to parameterized multiscale models parameterized using *ab initio* calculations to further understand rate capabilities of ordered and disorder battery electrodes, especially at the accelerated charge/discharge rates necessary for fast charging applications.

16. SUMMARY AND PERSPECTIVE

This dissertation describes the computational analysis of several different model reactions in rechargeable battery systems. These *ab initio* modeling studies, in concert with experimental characterization efforts, are able to provide a greater understanding of interfacial reactions relevant to battery chemistry, and provide insight into new physics that can further aid in the rational design of functionalized battery materials.

Jean-Marie Tarascon and Michel Armand wrote in their 2001 review that "tackling interfacial issues is both tedious and complex" [659] - a statement which, in my opinion, is further borne out by the work that has been described here. Even in the case of the long hypothesized Mn³⁺ disproportionation reactions on LMO to form soluble Mn²⁺ ions, the search for feasible reaction pathways (Chapter 4) is not trivial and likely involves explicit electrolyte oxidation and acid dissociation mechanisms at stepped and defected surfaces. Through the development of a suite of LMO surface models (Chapter 2), computational studies of the ALD growth mechanisms of coatings (Chapters 5-7) show significant heterogeneity in their reactivity towards coating precursors. Previously, battery electrodes as substrates for ALD have implicitly been considered inert, whereas this work sheds important light on the rich inorganic acidbase chemistry between the reactants and the substrate that can be further optimized to tailor morphology and growth chemistry of functionalized electrode materials.

Through examination of different solid-solid interfacial models, this work has additionally presented several key insights. Analysis of the role of nanostructure in the NiO conversion reaction (Chapters 11 and 12) have used nucleation theory to illustrate how an engineered interface can be used to overcome voltage hysteresis in LIB conversions reactions. The analysis of solid-state battery systems (Chapter 10) again illustrates the importance of surfaces and interfaces to compliment understanding of bulk thermodynamics, wherein the specific reactivity of the LLTO electrolyte with the Li metal anode is due to unstable Ti⁴⁺ cations catalyzing the onset of decomposition chemistry. These specific interfacial insights are used to point to metal-semiconductor band alignment (also shown in Chapter 8 to influence the lithiation reactions of Aucoated LMO) as a potential strategy for the development of descriptors that can be applied in the computational screening of new interlayer coating materials for solid-state batteries.

In addition to theoretical predictions and trend-based analyses of surface science and interfacial chemistry, these studies also highlight the importance of combining computational and experimental techniques in order to gain a more holistic understanding of complex interfacial systems. While it is certainly important to apply computational methods to gain an understanding of experimental results (and vice versa), I am of the opinion that these studies also highlight strategies in which the theory can help guide the experiments based on a deeper understanding of the physical characteristics that underpin experimentally observable properties.

This thesis has also demonstrated several examples of charge transfer as they relate to interfacial redox mechanisms (Chapters 13 and 14) and has outlined a framework to understand ion-coupled electronic conductivities of energy storage materials (Chapter 15). In the latter analysis of the LCO cathode material, in particular, these studies demonstrate that non-adiabatic effects may be necessary in some cases to accurately describe charge transfer in intercalaction-based battery electrodes. It is reasonable to suspect that for systems where conductivity issues are more pronounced that a Marcus rate theory treatment may be even more critical to an understanding and control of charge transfer mechanisms.

Many of the approaches and insights described within this thesis will play a role in the design of promising materials for electrochemistry applications. When it comes to computational modeling of solids, especially multicomponent materials, and understanding of the thermodynamics will always be paramount to developing realistic models that can suitably represent experimental systems. While computational electrochemical analyses should begin by an overall understanding of bulk driving forces prior to developing complex models of surfaces and interfaces, these analyses may not always be sufficient to understand the performance of a material, especially with respect to side reactions and modes of degradation. On a related note, is also important to realize that the properties of surfaces can vary widely from the bulk properties, and key properties such as ionization potentials and vacancy formation thermodynamics are highly sensitive to the particular surface facet and chemical termination. In the near future, studies of charge transfer will need to be further applied to understand ion-coupled electron transfer mechanisms in materials for electrochemistry. Within the space of batteries, I belive that Marcus rate theory analyses could play an important role in the design of materials for fast-charging applications where thermodynamics are non-equilibrated and Butler-Volmer kinetics are not valid. These types of investigations may be coupled with concerted and sequential ion diffusion in alloyed intercalation electrodes (such as NCA and NMC cathodes), as well as multivalent electrodes where ion diffusion may be coupled to multiple charge transfer steps. Beyond batteries, these charge transfer studies may also be applied toward electrocatalytic and photoelectrocatalytic reactions where concerted proton coupled electron transfer mechanisms comprise the elementary steps that determine reactivity and selectivity of a given material toward catalysis.

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A. SUPPLEMENTARY INFORMATION FOR "THERMODYNAMIC STABILITY OF LOW- AND HIGH-INDEX SPINEL LIMN₂O₄ SURFACE TERMINATIONS"

A.1 Calculation Details

The PBE+U calculations for key low energy surface structures have been benchmarked using the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional [94] in VASP [160, 161]. Here, we find that the PBE+U calculations give excellent agreement for the net slab magnetism (Table A.2). Additionally, the atomic Bader charges are analyzed using the Bader Charge Analysis program from the Henkelman group [176, 177, 178]. Figure A.1 demonstrates that the Bader charges scale linearly for each system analyzed using hybrid functionals.

Alternate antiferromagnetic (AFM) orderings have been considered for the (111) Li/O surface, which has been determined to be stable from the analysis of ferromagnetic (FM) slabs in the main text (see Figure 2.5). Although the bulk analysis has suggested that the FM and AFM orderings are nearly degenerate, we consider the possibility that alternate magnetic orderings at the surface could affect the thermodynamics of the LMO interface. The results from the analysis are included in Table A.3, where the surface energies are reported with respect to the FM (111) Li/O slab ($\Delta\gamma$ in the table represents the difference between the AFM and FM surface energies).

A.2 Relationship Between Li Chemical Potential and Half Cell Voltage

As defined previously, $\Delta \mu_{Li}$ is defined as the difference between the chemical potential of Li in the LMO slab, μ_{Li}^{LMO} , and the chemical potential of bulk Li, μ_{Li}° .

$$\Delta \mu_{Li}^{LMO} = \mu_{Li}^{LMO} - \mu_{Li}^{\circ} \tag{A.1}$$

Table A.1.: k-point densities used for slab calculations. Included are the magnitudes of calculation cell lattice parameters (||x|| and ||y||) in the directions where the system is periodic. These correspond to the lattice vectors orthogonal to the specified Miller direction (surface normal). The k-points used are specified, as well as the k-point density in each periodic direction. Here, N represents the number of k-points used in each direction.

surface	x [Å]	y [Å]	k-points	$\frac{N x }{2\pi}$	$\frac{N y }{2\pi}$
(001)	8.21	8.21	2x2x1	2.6	2.6
(010)	8.79	8.21	2x2x1	2.8	2.6
(100)	8.21	8.79	2x2x1	2.6	2.8
(011)	8.21	12.03	2x2x1	2.6	3.8
(101)	12.03	8.21	2x2x1	3.8	2.6
(110)	11.58	8.79	2x2x1	3.7	2.8
(111)	11.58	12.03	2x2x1	3.7	3.8
(113)	5.79	13.08	4x2x1	3.7	4.2
(131)	6.01	13.81	4x2x1	3.8	4.4
(311)	12.96	6.01	2x4x1	4.1	3.8
(133)	13.08	6.01	2x4x1	4.2	3.8
(313)	12.96	13.08	2x2x1	4.1	4.2
(331)	13.81	13.81	2x2x1	4.4	4.4
(115)	5.79	20.99	4x1x1	3.7	3.3
(151)	6.01	22.35	4x1x1	3.8	3.6
(511)	20.91	6.01	1x4x1	3.3	3.8
(135)	10.16	24.39	2x1x1	3.2	3.9
(153)	10.54	25.19	2x1x1	3.4	4
(315)	12.96	20.99	2x1x1	4.1	3.3
(351)	13.81	22.35	2x1x1	4.4	3.6
(513)	20.91	13.08	1x2x1	3.3	4.2
(531)	22.35	13.81	1x2x1	3.6	4.4

	Total magn	etic moment $[\mu_B]$	Average ma	agnetic moment $[\mu_B]$
	PBE+U	HSE06	PBE+U	HSE06
(001) Li	152.0	152.0	3.45	3.45
(001) Mn/O	156.0	156.0	3.55	3.55
(111) Li/O	140.0	140.0	3.18	3.18

Table A.2.: Slab magnetic moments

If Li in the LMO slab is in equilibrium with the Li⁺ and e⁻ pairs, their respective chemical potentials must be equivalent.

$$\mu_{Li}^{LMO} = \mu_{Li^+} + \mu_{e^-} \tag{A.2}$$

As has been discussed previously [11], the chemical potential of the Li⁺ and e⁻ pair may be corrected for voltage, U, with respect to standard conditions by the general relationship in equation A.3.

$$\mu_{Li^+}(U_{Li/Li^+}) + \mu_{e^-}(U_{Li/Li^+}) = (\mu_{Li^+}^{\circ} + \mu_{e^-}^{\circ}) - eU_{Li/Li^+}$$
(A.3)

In equation A.3, this U value corresponds to the Li foil electrode. Moreover, the chemical potential of the Li⁺ and e⁻ pair at standard conditions can be assumed to be approximately equal to the chemical potential of the bulk Li metal as determined through DFT calculations. Thus, the $\Delta \mu_{Li}$ value may be directly related to a voltage by the following relationship.

$$\mu_{Li}^{LMO} = \mu_{Li}^{\circ} - eU_{Li/Li^+} \tag{A.4}$$

$$\Delta \mu_{Li} = -eU_{Li/Li^+} \tag{A.5}$$

Table A.3.: Surface energies and magnetic orderings for the (111) Li/O surface. Surface energies are recalculated for the (111) Li/O termination using a different AFM ordering at the surface. For the AFM structures, the bulk magnetic ordering is $\uparrow\uparrow\downarrow\downarrow\downarrow$ along the [110] direction. The Mn atoms shown in each of the structural models are arranged by either the bulk magnetic ordering, or such that Mn with the same spin will cluster into islands or arrange in linear ribbons at the surface. The Mn atoms in subsurface layers are not modified further from the bulk AFM ordering. Each of these calculated surface energies are taken as a deviation, $\Delta\gamma$, from the surface energy for FM ordering of the slab. In each of the structures below, purple atoms represent Mn atoms that are spin- up, whereas the gold atoms represent Mn atoms that are spin-down.





Figure A.1.: Bader charges with PBE+U and HSE06 functionals. Bader charges are calculated for the (001) Li, (001) Mn/O and (111) Li/O surface terminations (left to right). The figures indicate that Bader charges scale linearly with one another in all cases.

A.3 Additional Atomic Structures and Surface Phase Diagrams

Table A.4.: LMO (001) oxygen vacancy formation energies. Vacancy formation energies are calculated for the two distinct oxygens at the surface of the Li and Mn/O terminations of LMO (001). The O1-type vacancy is an oxygen atom that is bound to both Mn atoms in the surface and subsurface layers. The O2-type vacancy is the oxygen that is only bound to surface Mn atoms.

	$\Delta E_{vac}^{O1} \ [eV \ atom^{-1}]$	$\Delta E_{vac}^{O2} \; [eV \; atom^{-1}]$
(001) Mn/O	1.96	2.21
(001) Li	3.64	3.07



Figure A.2.: (001) surface terminations. Included are the surface terminations considered for the LMO (001) surface. As mentioned in the main text, the Li and Mn/O terminations represent the two planes that make up the stoichiometric repeat units of LMO along the (001) Miller direction. Additional oxygen atoms are added to the surface Mn for the Li and Mn/O surface terminations to generate the Li/O and O-rich terminations, respectively. The Li/O and O-rich structures represent surface Mn that are fully coordinated, with respect to bulk MnO₆ polyhedra.



Figure A.3.: (010) surface phase diagram



Figure A.4.: (100) surface phase diagram



Figure A.5.: (110) surface terminations. Included are the surface terminations considered for the LMO (110) surface. Defects may be introduced to the terminations associated with the distinct (110) layering structure, Li/Mn/O and Mn/O, to generate their respective stoichiometric terminations. Furthermore, the Li/Mn/O and Mn/O terminations may be further passivated with oxygen to fully coordinate MnO₆ polyhedra, as in the Li/O and O-rich surface structures.



Figure A.6.: (011) surface phase diagram



Figure A.7.: (101) surface phase diagram



Figure A.8.: Reduction of (110) Li/O surface through oxygen vacancies. Predicted Mn oxidation states on (a) clean LMO (110) Li/O surface without oxygen vacancies, (b) LMO (110) Li/O-1Ovac surface termination (Li/O termination with one oxygen vacancy present), (c) LMO (110) Li/O-2Ovac surface termination (Li/O termination with two oxygen vacancic present). For further details, Figure 2.3 may be referenced.

unreconstructed	reconstructed	$\Delta E_{rec} \; [\text{eV atom}^{-1}]$	reconstruction type
Mn/O Li ₂₄ Mn ₆₀ O ₁₂₈	Mn/O-rec Li ₂₄ Mn ₆₀ O ₁₂₈	-0.39	Li diffusion
Li/Mn/O Li ₂₄ Mn ₅₂ O ₉₆	Li/Mn/O-rec Li ₂₄ Mn ₅₂ O ₉₆	-1.31	inverse spinel surface
Mn/O-stoich Li ₂₄ Mn ₄₈ O ₉₆	Li-stoich Li ₂₄ Mn ₄₈ O ₉₆	-1.39	inverse spinel surface
Li Li ₃₂ Mn ₅₂ O ₉₆	Li-rec Li ₃₂ Mn ₅₂ O ₉₆	-1.26	inverse spinel surface

Table A.5. (111) surface reconstructions





Figure A.9.: (111) surface terminations



Figure A.10.: (111) phase diagram for Li defect formation on Li/O-terminated surface. Phase diagram is determined at a constant $\Delta \mu_O$ value corresponding to atmospheric conditions ($p_{O_2} = 0.21$ atm, T = 298 K). Under these conditions and in a Li-deficient environment, the formation of defects on the Li/O-terminated surface is calculated to be thermodynamically favorable. The excess Li with respect to the bulk LMO stoichiometry (ξ_{Li}) is analogous to the notation applied in the main text. These defect sites represent a local surface structure identical to the Mn/O termination, which may undergo facile reconstruction via Li diffusion to the Mn/O- rec termination. The Li/O-defect termination therefore represents an intermediate stoichiometry between that of the Li/O and Mn/O-rec terminations to demonstrate that such features may be present on LMO(111) terraces.



Figure A.11.: Reduction of (111) Li/O surface through oxygen vacancies. Predicted Mn oxidation states on (a) clean LMO (111) Li/O surface without oxygen vacancies and (b) LMO (111) Li/O-10vac surface termination (Li/O termination with one oxygen vacancy present).



Figure A.12.: Reduction of (111) Li-rich surface through oxygen vacancies. Predicted Mn oxidation states on (a) clean LMO (111) Li-rich surface without oxygen vacancies and (b) LMO (111) Li-rich-10vac surface termination (Li/-rich termination with one oxygen vacancy present). While the defect-free Li/O termination has surface Mn with approximately equivalent oxidation states, we note that the defect-free Li-rich surface contains one reduced Mn as a result of the extra Li at the surface (calibrated Bader charge of +2.91). Neighboring Mn atoms also become reduced upon introduction of the low energy oxygen vacancy in the Li-rich-10vac termination.



Figure A.13.: (311) surface terminations



Figure A.14.: (113) surface phase diagram



Figure A.15.: (131) surface phase diagram



Figure A.16.: Reduction of (311) Li/Mn/O surface through oxygen vacancies. Predicted Mn oxidation states on (a) clean LMO (311) Li/Mn/O surface without oxygen vacancies, (b) LMO (311) Li/Mn/O-1Ovac surface termination (Li/Mn/O termination with one oxygen vacancy present). We note that the multiple vacancies appearing in (b) are due to inclusion of multiple periodic images of the supercell.



Figure A.17.: (331) surface terminations



Figure A.18.: (133) surface phase diagram



Figure A.19.: (313) surface phase diagram



Figure A.20.: Reduction of (331) Li/O surface through oxygen vacancies. Predicted Mn oxidation states on (a) clean LMO (331) Li/O surface without oxygen vacancies, (b) LMO (311) Li/ O-10vac surface termination (Li/ O termination with one oxygen vacancy present), (c) LMO (331) Li/O-20vac surface termination (Li/O termination with two oxygen vacancies).



Figure A.21.: (511) surface terminations



Figure A.22.: (115) surface phase diagram



Figure A.23.: (151) surface phase diagram



Figure A.24.: Reduction of (511) Li/Mn/O surface through oxygen vacancies. Predicted Mn oxidation states on (a) clean LMO (511) Li/Mn/O surface without oxygen vacancies, (b) LMO (511) Li/Mn/O-1Ovac surface termination (Li/Mn/O termination with one oxygen vacancy present). We note that the multiple vacancies appearing in (b) are due to multiple periodic images of the supercell.



Figure A.25.: Reduction of (511) Li surface through oxygen vacancies. Predicted Mn oxidation states on (a) clean LMO (511) Li surface without oxygen vacancies, (b) LMO (511) Li-10vac surface termination (Li termination with one oxygen vacancy present). We note that the multiple vacancies appearing in (b) are due to multiple periodic images of the supercell.



Figure A.26.: (531) surface terminations



Figure A.27.: (135) surface phase diagram



Figure A.28.: (153) surface phase diagram



Figure A.29.: (315) surface phase diagram



Figure A.30.: (351) surface phase diagram



Figure A.31.: (513) surface phase diagram

	resp	ond t	o the v	ertice	s of the six-	sided polygo	on in Figure				
	2.11	0									
					${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${ m LiMn_2O_4}$	
surface termination	E_{slab}	\mathbf{N}_{Li}	\mathbf{N}_{Mn}	N_O	MnO_2	MnO_2	${\rm Mn_2O_3}$	$\rm LiMnO_2$	$\rm Li_2 MnO_3$	$\rm LiMnO_2$	
					0	${\rm Mn_2O_3}$	$\mathrm{Mn}_3\mathrm{O}_4$	$\rm Li_2 MnO_3$	0	${\rm Mn}_3{\rm O}_4$	
(001) Li	-1077.18	24	44	88	0.88	0.88	0.67	0.60	0.81	0.60	
(001) Li/O	-916.79	20	36	80	1.32	1.68	2.32	2.30	1.25	2.45	
(001) Mn	-933.80	20	44	72	6.04	5.34	3.85	3.82	6.11	3.51	
(001) Mn/O	-1056.44	20	44	88	0.62	0.62	0.83	06.0	0.69	0.90	
(001) Mn/O-rec	-1053.35	20	44	88	0.98	0.98	1.20	1.26	1.06	1.26	
(001) Li-stoich	-1067.25	22	44	88	0.70	0.70	0.70	0.70	0.70	0.70	
(001) Mn/O-stoich	-964.90	20	40	80	1.27	1.27	1.27	1.27	1.27	1.27	
(001) O-rich	-890.98	16	36	80	1.66	2.01	3.08	3.19	1.73	3.35	
(100) Li	-1076.42	24	44	88	0.91	0.91	0.71	0.65	0.84	0.65	
$(100) { m Mn}$	-933.27	20	44	72	5.71	5.05	3.65	3.63	5.77	3.34	
$(100) \mathrm{Mn/O}$	-1056.19	20	44	88	0.60	0.60	0.80	0.87	0.67	0.87	

Table A.6. Surface energies, in J m⁻², calculated for all surface terminations considered in this work. Values are calculated at three-phase equilibrium points, which correspond to the vertices of the six-sided polygon in Figure

continued on next page

					$\rm LiMn_2O_4$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	$\rm LiMn_2O_4$
surface termination	\mathbb{E}_{slab}	N_{Li}	N_{Mn}	N_O	MnO_2	MnO_2	${\rm Mn_2O_3}$	$\rm LiMnO_2$	$\rm Li_2 MnO_3$	$LiMnO_2$
					0	${\rm Mn_2O_3}$	$\mathrm{Mn}_3\mathrm{O}_4$	${\rm Li}_2{\rm MnO}_3$	0	$\mathrm{Mn}_3\mathrm{O}_4$
(100) Li-stoich	-1066.86	22	44	88	0.69	0.69	0.69	0.69	0.69	0.69
(100) Mn/O-stoich	-964.04	20	40	80	1.28	1.28	1.28	1.28	1.28	1.28
(010) Li	-1076.42	24	44	88	0.91	0.91	0.71	0.65	0.84	0.65
(010) Mn	-937.69	20	44	72	5.21	4.56	3.16	3.14	5.28	2.85
$(010) { m Mn/O}$	-1055.99	20	44	88	0.63	0.63	0.83	0.89	0.69	0.89
(010) Li-stoich	-1066.85	22	44	88	0.70	0.70	0.70	0.70	0.70	0.70
(010) Mn/O-stoich	-966.09	20	40	80	1.05	1.05	1.05	1.05	1.05	1.05
(110) Li/Mn/O	-1067.61	24	44	88	1.34	1.34	1.20	1.15	1.29	1.15
(110) Li/Mn/O-stoich	-959.03	20	40	80	1.30	1.30	1.30	1.30	1.30	1.30
$(110) { m Mn/O}$	-1044.22	20	44	88	1.37	1.37	1.51	1.56	1.42	1.56
(110) Mn/O-stoich	-959.89	20	40	80	1.23	1.23	1.23	1.23	1.23	1.23
(110) Li/O	-1115.75	24	44	96	0.58	0.81	1.23	1.22	0.53	1.32
(110) Li/O-1Ovac	-1104.75	24	44	94	0.68	0.86	1.14	1.12	0.64	1.20
(110) Li/O-2Ovac	-1093.05	24	44	92	0.85	0.96	1.11	1.08	0.80	1.13
(110) O-rich	-1118.41	20	44	104	1.58	2.05	3.32	3.43	1.63	3.63

Table A.6. continued

continued on next page

										1
				$\rm LiMn_2O_4$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	$\rm LiMn_2O_4$	
\mathbf{E}_{slab}	N_{Li}	\mathbf{N}_{Mn}	N_O	MnO_2	MnO_2	$\mathrm{Mn_2O_3}$	$\rm LiMnO_2$	$\rm Li_2 MnO_3$	$\rm LiMnO_2$	
				0	${\rm Mn_2O_3}$	$\mathrm{Mn}_3\mathrm{O}_4$	${\rm Li}_2{\rm MnO}_3$	0	${\rm Mn}_3{\rm O}_4$	
-968.87	24	36	88	1.61	2.08	2.79	2.72	1.47	2.92	
-1068.72	24	44	88	1.29	1.29	1.14	1.10	1.24	1.10	
-957.53	20	40	80	1.46	1.46	1.46	1.46	1.46	1.46	
-1045.08	20	44	88	1.34	1.34	1.49	1.53	1.39	1.53	
-960.64	20	40	80	1.21	1.21	1.21	1.21	1.21	1.21	
-1116.51	24	44	96	0.53	0.77	1.21	1.20	0.48	1.30	
-1105.50	24	44	94	0.64	0.82	1.12	1.09	0.60	1.17	
-1094.09	24	44	92	0.79	0.91	1.06	1.03	0.74	1.08	
-1068.71	24	44	88	1.29	1.29	1.14	1.10	1.24	1.10	
-957.38	20	40	80	1.47	1.47	1.47	1.47	1.47	1.47	
-1044.99	20	44	80	1.35	1.35	1.49	1.54	1.40	1.54	
-960.66	20	40	80	1.21	1.21	1.21	1.21	1.21	1.21	
-1116.52	24	44	96	0.53	0.77	1.21	1.19	0.48	1.30	
-1105.47	24	44	94	0.65	0.83	1.12	1.10	0.60	1.18	
-1094.16	24	44	92	0.78	0.90	1.05	1.02	0.74	1.07	
	E_{stab} -968.87 -968.87 -1068.72 -957.53 -1045.08 -1045.08 -1116.51 -1116.51 -1105.50 -1094.09 -1068.71 -1068.71 -957.38 -1044.99 -960.66 -1116.52 -1116.52 -1116.52 -1105.47	E_{stab} N_{Li} -968.87-968.87-968.8724-1068.7224-957.5320-1045.0820-1116.5124-1105.5024-1105.5024-1094.0924-1068.7124-1068.7124-1068.7124-1068.7124-1068.7124-1068.7124-1068.7124-1068.7124-1068.7124-1068.7124-1069.6620-1116.5224-1105.4724-1105.4724-1105.4724-1004.1624	E_{stab} N_{Li} N_{Mn} -968.872436-1068.722444-957.532040-1045.082040-1045.082040-1045.082040-1045.082040-1045.082040-1045.082444-1055.502444-1105.502444-1094.092444-1068.712444-1068.712444-1068.712444-1068.712444-1074.992040-1116.522444-1105.472444-1105.472444-1094.162444	E_{stab} N_{Li} N_{Mn} N_O -968.87243688-1068.72244488-957.53204080-1045.08204080-1045.08204488-1045.08204486-1116.51244496-1116.51244496-1105.50244496-1105.50244496-1094.09244496-1044.99204080-1068.71244496-1068.71244496-1068.71244496-1068.71244496-1068.71244496-1068.71244496-1068.71244496-1068.71244496-1068.71244496-1068.72244496-1105.47244496-1105.47244492-1094.16244492-1094.16244492	E_{stab} N_{Li} N_{Mn} N_O MnO_2 -968.872436881.61-1068.722444881.61-968.872444881.61-1068.722444881.29-957.532040801.46-1045.082044881.29-1045.082044881.29-1045.082044881.24-1045.082444960.53-1105.502444960.79-1094.092444881.29-1068.712444881.29-1068.712444881.35-1068.712444960.53-1068.712444960.53-1068.712444960.53-1068.712444960.53-1068.712444960.53-1068.712444960.53-1068.712444960.53-1105.472444920.53-1105.472444920.53-1105.472444920.53-1105.472444920.53-1094.162444920.78-1094.162444920.78-1094.162444920.78	E_{siab} N_{Li} N_{Mi} N_O MiO_2 MiO_2 -968.87 24 36 88 1.61 2.08 -968.87 24 44 88 1.61 2.08 -968.87 24 44 88 1.29 1.29 -968.87 24 44 88 1.29 1.29 -968.87 24 44 88 1.29 1.29 -967.53 20 40 80 1.46 1.29 -960.64 20 44 88 1.24 1.24 -1116.51 24 44 96 0.53 0.77 -1105.50 24 44 92 0.79 0.91 -1004.09 24 44 92 0.79 0.91 -1004.09 24 44 88 1.29 1.29 -1004.09 24 44 88 1.29 0.77 -1004.09 20 40 80 1.47 1.47 -1004.09 20 44 88 1.29 0.91 -1004.09 20 44 88 1.29 0.77 -1004.09 20 44 88 1.29 0.71 -1004.09 20 44 88 1.29 0.71 -1004.09 20 44 88 1.29 0.71 -1004.09 20 44 88 1.24 0.65 -1004.09 24 44 96 0.53 0.77 <	E_{stab} N_{Li} N_{Mi} N_O MinO2Min2O3Min2O3 -968.87 24 36 88 1.61 2.08 2.79 -968.87 24 36 88 1.61 2.08 2.79 -968.87 24 44 88 1.61 2.08 2.79 -968.87 24 44 88 1.29 1.29 1.14 -957.53 20 40 80 1.46 1.46 1.46 -1045.08 20 44 88 1.29 1.21 1.21 -1045.08 20 44 88 1.21 1.21 1.21 -1045.08 20 44 80 1.21 1.21 1.21 -1105.50 24 44 92 0.53 0.77 1.21 -1105.50 24 44 92 0.79 1.21 1.21 -1004.09 20 40 80 1.21 1.21 1.21 -1044.99 20 40 80 1.21 1.21 1.21 -1044.99 20 40 80 1.22 1.47 1.47 -1044.99 20 40 80 1.22 1.42 -1044.99 20 40 80 1.21 1.21 -1044.99 20 40 80 1.22 1.47 -1044.99 20 40 80 1.21 1.21 -1044.99 20 40 80 1.21 <	E_{sids} N_{Li} N_{Mn} N_O MnO_2 Mn_2O_3 Mn_3O_4 $LiMnO_2$ -968.872436881.612.082.792.72-1068.722444881.612.082.792.72-957.532040801.461.461.461.46-1045.082040801.211.211.21-1068.722444960.530.771.211.21-1045.082040801.241.491.491.46-1045.082040801.211.211.21-1045.082040801.211.211.21-1116.512444940.640.821.141.10-1105.502444930.771.211.201.20-1068.712444920.790.911.061.03-1068.712444981.291.291.141.10-1068.712444981.291.291.1471.21-1064.092040801.211.211.201.20-1064.092040801.291.291.1471.47-1044.992040801.211.211.211.21-1044.992040801.291.291.291.24-1064.652444	E_{slab} N_{L_1} N_{M_1} N_0 MnO_2 $LiMnO_2$ Li_2MnO_3 Li_2MnO_3 Li_2MnO_3 O -968.87 24 36 88 1.61 2.08 2.72 1.47 -968.87 24 44 88 1.29 1.29 1.146 1.46 1.24 -957.53 20 40 80 1.29 1.29 1.146 1.24 1.24 -1068.72 24 44 88 1.29 1.29 1.29 1.24 -1045.08 20 44 88 1.21 1.21 1.21 1.29 1.24 -1045.08 20 44 96 0.53 0.77 1.21 1.29 1.24 -1116.51 24 44 96 0.53 0.77 1.21 1.24 1.24 -1116.51 24 44 96 0.53 0.77 1.21 1.24 1.24 -1116.51 24 24 <	E_{alab} N_{Li} N_{Mi} N_0 MmO_2 MmO_2 Li_2MmO_2 Li_2MmO_2 Li_2MmO_2 Lim_0O_2

Table A.6. continued

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					$\rm LiMn_2O_4$	${\rm LiMn_2O_4}$	$\rm LiMn_2O_4$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${ m LiMn_2O_4}$
surface termination	E_{slab}	\mathbf{N}_{Li}	\mathbf{N}_{Mn}	N_O	MnO_2	MnO_2	${\rm Mn_2O_3}$	$\rm LiMnO_2$	$\rm Li_2 MnO_3$	$\rm LiMnO_2$
					0	${\rm Mn_2O_3}$	$\mathrm{Mn}_3\mathrm{O}_4$	${\rm Li}_2{\rm MnO}_3$	0	$\mathrm{Mn}_3\mathrm{O}_4$
(111) Li	-1219.06	32	52	96	2.96	2.77	1.94	1.81	2.84	1.72
(111) Li/Mn/O	-1189.23	24	52	96	1.91	1.71	1.36	1.37	1.94	1.28
(111) Li/Mn/O-rec-4	-1200.32	24	52	96	1.18	0.98	0.63	0.64	1.22	0.56
(111) Li/Mn/O-rec-5	-1589.92	32	68	128	1.22	1.03	0.67	0.68	1.26	0.60
(111) Mn	-1260.37	24	00	96	3.48	2.90	1.84	1.87	3.60	1.62
(111) Mn/O	-1459.95	24	00	128	0.48	0.68	1.50	1.64	0.60	1.72
(111) Mn/O-rec2-4	-1463.08	24	09	128	0.28	0.47	1.30	1.44	0.40	1.52
$(111) \operatorname{Mn/O-rec2-5}$	-1853.24	32	76	160	0.28	0.48	1.30	1.44	0.40	1.52
$(111) \operatorname{Mn/O-stoich}$	-1155.20	24	48	96	1.01	1.01	1.01	1.01	1.01	1.01
(111) Li-stoich	-1160.77	24	48	96	0.65	0.65	0.65	0.65	0.65	0.65
(111) Li/O	-1119.63	24	44	96	0.23	0.42	0.77	0.76	0.19	0.85
(111) Li/O AFM bulk	-1119.33	24	44	96	0.24	0.44	0.79	0.78	0.21	0.87
(111) Li/O AFM islands1	-1119.38	24	44	96	0.24	0.44	0.79	0.78	0.20	0.86
(111) Li/O AFM islands ²	-1119.45	24	44	96	0.24	0.43	0.79	0.77	0.20	0.86
(111) Li/O AFM ribbons1	-1118.60	24	44	96	0.29	0.49	0.84	0.83	0.25	0.91
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Table A.6. continued
					${\rm LiMn_2O_4}$	$\rm LiMn_2O_4$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${ m LiMn_2O_4}$
surface termination	E_{slab}	\mathbf{N}_{Li}	\mathbf{N}_{Mn}	N_O	MnO_2	${\rm MnO}_2$	${\rm Mn_2O_3}$	$\rm LiMnO_2$	$\rm Li_2 MnO_3$	$\rm LiMnO_2$
					0	${\rm Mn_2O_3}$	$\mathrm{Mn}_3\mathrm{O}_4$	$\rm Li_2 MnO_3$	0	${\rm Mn}_3{\rm O}_4$
(111) Li/O AFM ribbons2	-1118.42	24	44	96	0.30	0.50	0.85	0.84	0.27	0.93
(111) Li/O-10vac	-1107.04	24	44	94	0.42	0.57	0.80	0.79	0.38	0.85
(111) Li/O-def	-1097.13	20	44	96	0.19	0.39	0.98	1.04	0.23	1.12
(111) $2x-inv Li/Mn/O-rec$	-2366.90	48	100	192	1.45	1.25	0.90	0.91	1.49	0.83
(111) 2x-inv Li-stoich	-2321.63	48	$\overline{00}$	192	1.29	1.29	1.29	1.29	1.29	1.29
(111) Li/O-invSpin-bulk1	-1880.18	40	26	160	1.53	1.72	2.08	2.07	1.49	2.15
(111) Li/O-invSpin-bulk2	-1892.48	40	92	160	0.72	0.92	1.27	1.26	0.68	1.35
(111) Li-rich	-1159.56	32	44	96	0.62	0.81	0.70	0.54	0.42	0.62
(111) Li-rec	-1229.60	32	52	96	2.27	2.08	1.25	1.12	2.15	1.03
(111) Li/Mn/O-2	-1319.56	32	52	112	1.42	1.61	1.73	1.64	1.30	1.73
(113) Li/Mn	-516.58	12	23	40	2.60	2.29	1.46	1.40	2.58	1.26
(113) $\rm Li/Mn/O$	-567.03	12	23	48	0.91	1.01	1.20	1.20	0.88	1.24
(113) Li/Mn/O-10vac	-556.26	12	23	46	1.07	1.07	1.01	0.99	1.05	0.99
(113) Li/Mn/O-20vac	-543.03	12	23	44	1.58	1.48	1.16	1.12	1.56	1.08
(113) Mn	-505.05	10	23	40	2.61	2.29	1.72	1.74	2.67	1.60

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					${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$
surface termination	E_{slab}	\mathbf{N}_{Li}	N_{Mn}	N_{O}	MnO_2	MnO_2	$\mathrm{Mn}_2\mathrm{O}_3$	$\rm LiMnO_2$	$\rm Li_2 MnO_3$	$\rm LiMnO_2$
					0	${\rm Mn_2O_3}$	$\mathrm{Mn}_3\mathrm{O}_4$	$\rm Li_2 MnO_3$	0	$\mathrm{Mn}_3\mathrm{O}_4$
(113) Mn/O	-553.79	10	23	48	1.15	1.26	1.70	1.78	1.22	1.82
(113) Stoich	-1057.98	22	44	88	1.07	1.07	1.07	1.07	1.07	1.07
(131) Li/Mn	-514.77	12	23	40	2.72	2.42	1.64	1.58	2.70	1.45
(131) Li/Mn/O	-566.07	12	23	48	0.99	1.09	1.27	1.27	0.97	1.31
(131) Li/Mn/O-1Ovac	-555.80	12	23	46	1.08	1.08	1.02	1.00	1.06	1.00
(131) Li/Mn/O-2Ovac	-543.39	12	23	44	1.46	1.36	1.06	1.02	1.44	0.98
(131) Mn	-505.66	10	23	40	2.40	2.10	1.56	1.57	2.46	1.44
$(131) { m Mn/O}$	-553.09	10	23	48	1.19	1.29	1.72	1.79	1.25	1.83
(131) Stoich	-1056.66	22	44	88	1.11	1.11	1.11	1.11	1.11	1.11
(311) Li/Mn	-514.77	12	23	40	2.72	2.42	1.64	1.58	2.70	1.45
(311) Li/Mn rec	-517.90	12	23	40	2.30	2.00	1.21	1.15	2.28	1.03
(311) Li/Mn rec2	-515.34	12	23	40	2.65	2.35	1.56	1.50	2.63	1.37
(311) Li/Mn/O	-566.24	12	23	48	0.97	1.07	1.25	1.25	0.95	1.29
(311) Li/Mn/O-1Ovac	-555.99	12	23	46	1.06	1.06	1.00	0.98	1.04	0.98
(311) Li/Mn/O-2Ovac	-543.43	12	23	44	1.45	1.35	1.05	1.02	1.43	0.97
continued on next page										

					${\rm LiMn_2O_4}$	$\rm LiMn_2O_4$	${\rm LiMn_2O_4}$	$\rm LiMn_2O_4$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$
surface termination	E_{slab}	N_{Li}	\mathbf{N}_{Mn}	N_O	MnO_2	MnO_2	${\rm Mn_2O_3}$	$\rm LiMnO_2$	$\rm Li_2 MnO_3$	$\rm LiMnO_2$
					0	${\rm Mn_2O_3}$	$\mathrm{Mn}_3\mathrm{O}_4$	${\rm Li}_2{\rm MnO}_3$	0	$\mathrm{Mn}_3\mathrm{O}_4$
(311) Li/Mn/O rec	-566.31	12	23	48	0.96	1.06	1.24	1.24	0.94	1.28
(311) Mn	-505.67	10	23	40	2.40	2.10	1.56	1.57	2.46	1.44
(311) Mn rec	-505.65	10	23	40	2.40	2.10	1.56	1.58	2.46	1.45
(311) Mn rec2	-505.65	10	23	40	2.40	2.10	1.56	1.58	2.46	1.45
(311) Mn/O	-554.24	10	23	48	1.04	1.14	1.56	1.63	1.10	1.68
(311) O-rich	-578.16	10	23	54	1.70	2.10	3.25	3.36	1.76	3.53
(311) Li/O	-591.98	12	23	54	1.39	1.79	2.70	2.73	1.37	2.90
(311) Stoich	-1057.50	22	44	88	1.05	1.05	1.05	1.05	1.05	1.05
(133) Li	-786.24	18	33	64	1.85	1.77	1.44	1.39	1.80	1.35
(133) Li/O	-832.31	18	33	72	1.05	1.28	1.71	1.70	1.00	1.80
(133) Li/O-1Ovac	-823.33	18	33	20	0.98	1.14	1.37	1.35	0.94	1.42
(133) Li/O-2Ovac	-812.33	18	33	68	1.13	1.21	1.25	1.22	1.08	1.25
(133) Li/Mn-1	-894.51	18	39	72	2.02	1.79	1.36	1.37	2.07	1.27
(133) Li/Mn-2	-776.93	16	33	64	1.62	1.54	1.40	1.41	1.64	1.37
(133) Li/Mn/O-1	-916.21	18	39	76	1.76	1.68	1.63	1.67	1.81	1.63

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					${\rm LiMn_2O_4}$	$\rm LiMn_2O_4$	$\rm LiMn_2O_4$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$
surface termination	\mathbf{E}_{slab}	N_{Li}	N_{Mn}	N_O	MnO_2	MnO_2	${\rm Mn_2O_3}$	$\rm LiMnO_2$	$\rm Li_2 MnO_3$	$\rm LiMnO_2$
					0	${\rm Mn_2O_3}$	$\mathrm{Mn}_3\mathrm{O}_4$	${\rm Li}_2{\rm MnO}_3$	0	$\mathrm{Mn}_3\mathrm{O}_4$
(133) Li/Mn/O-2	-905.62	16	39	76	1.66	1.59	1.73	1.82	1.77	1.79
(133) Mn/O	-939.41	18	39	80	1.34	1.42	1.75	1.80	1.39	1.84
(133) O-rich	-973.15	18	39	88	1.84	2.22	3.31	3.41	1.88	3.58
(133) Stoich	-1730.66	36	72	144	1.33	1.33	1.33	1.33	1.33	1.33
(313) Li	-785.63	18	33	64	1.91	1.84	1.51	1.45	1.87	1.42
(313) Li/O	-831.96	18	33	72	1.09	1.32	1.75	1.73	1.04	1.83
(313) Li/O-1Ovac	-822.67	18	33	70	1.05	1.21	1.44	1.42	1.01	1.49
(313) Li/O-2Ovac	-811.82	18	33	68	1.18	1.26	1.31	1.27	1.14	1.31
(313) Li/Mn-1	-893.86	18	39	72	2.09	1.85	1.43	1.44	2.13	1.34
(313) Li/Mn-2	-776.92	16	33	64	1.62	1.54	1.40	1.41	1.64	1.37
(313) Li/Mn/O-1	-916.21	18	39	76	1.76	1.68	1.63	1.67	1.81	1.63
(313) Li/Mn/O-2	-905.64	16	39	76	1.66	1.58	1.73	1.82	1.77	1.78
(313) Mn/O	-939.42	18	39	80	1.34	1.42	1.75	1.80	1.39	1.84
(313) O-rich	-973.45	18	39	88	1.80	2.19	3.28	3.38	1.85	3.55
(313) Stoich	-1730.75	36	72	144	1.33	1.33	1.33	1.33	1.33	1.33

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					${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	$\rm LiMn_2O_4$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$
surface termination	E_{slab}	N_{Li}	\mathbb{N}_{Mn}	N_O	MnO_2	MnO_2	${\rm Mn_2O_3}$	$\rm LiMnO_2$	$\rm Li_2 MnO_3$	$\rm LiMnO_2$
					0	${\rm Mn_2O_3}$	$\mathrm{Mn}_3\mathrm{O}_4$	${ m Li}_2{ m MnO}_3$	0	$\mathrm{Mn}_3\mathrm{O}_4$
(331) Li	-786.39	18	33	64	1.79	1.71	1.39	1.34	1.74	1.30
(331) Li/O	-832.15	18	33	72	1.04	1.27	1.68	1.67	0.99	1.77
(331) Li/O-1Ovac	-822.74	18	33	70	1.02	1.17	1.40	1.38	0.97	1.44
(331) Li/O-2Ovac	-811.69	18	33	68	1.17	1.24	1.29	1.25	1.12	1.29
(331) Li/Mn-1	-892.93	18	39	72	2.13	1.90	1.49	1.50	2.18	1.40
(331) Li/Mn-2	-777.13	16	33	64	1.56	1.48	1.35	1.35	1.57	1.32
(331) Li/Mn/O-1	-917.09	18	39	76	1.62	1.55	1.50	1.54	1.67	1.50
(331) Li/Mn/O-2	-906.08	16	39	76	1.57	1.50	1.64	1.73	1.68	1.69
(331) Mn/O	-939.97	18	39	80	1.25	1.33	1.65	1.70	1.30	1.73
(331) O-rich	-973.56	18	39	88	1.75	2.13	3.19	3.28	1.79	3.44
(331) Stoich	-1728.75	36	72	144	1.40	1.40	1.40	1.40	1.40	1.40
(115) Li	-760.43	16	31	64	0.83	0.91	1.05	1.04	0.82	1.07
(115) Li-10vac	-750.10	16	31	62	0.91	0.91	0.86	0.84	0.89	0.84
(115) Li-20vac	-736.45	16	31	00	1.32	1.24	1.01	0.99	1.30	0.95
(115) $Li/Mn/O$	-750.40	14	31	64	0.68	0.76	1.08	1.13	0.73	1.17

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					${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$
surface termination	E_{slab}	N_{Li}	N_{Mn}	N_O	MnO_2	MnO_2	$\mathrm{Mn}_2\mathrm{O}_3$	$\rm LiMnO_2$	$\rm Li_2 MnO_3$	$\rm LiMnO_2$
					0	${\rm Mn_2O_3}$	$\mathrm{Mn}_3\mathrm{O}_4$	${ m Li}_2{ m MnO}_3$	0	$\mathrm{Mn}_3\mathrm{O}_4$
(115) Li/Mn/O-1Ovac	-740.29	14	31	62	0.73	0.73	0.87	0.91	0.78	0.91
(115) $\rm Li/Mn/O-2Ovac$	-727.05	14	31	60	1.10	1.03	0.98	1.02	1.15	0.98
(115) Mn	-690.15	12	31	56	1.74	1.51	1.28	1.35	1.84	1.25
(115) Mn/O	-737.74	12	31	64	0.80	0.88	1.38	1.49	0.91	1.53
(151) Li	-759.57	16	31	64	0.77	0.83	0.95	0.94	0.76	0.97
(151) Li-10vac	-748.97	16	31	62	0.85	0.85	0.81	0.80	0.84	0.80
(151) Li-20vac	-736.60	16	31	60	1.09	1.03	0.83	0.81	1.08	0.79
(151) Li/Mn/O	-749.58	14	31	64	0.64	0.70	0.97	1.02	0.68	1.05
(151) $\rm Li/Mn/O-1Ovac$	-738.83	14	31	62	0.74	0.74	0.85	0.89	0.78	0.89
(151) $\rm Li/Mn/O-2Ovac$	-725.64	14	31	60	1.04	0.98	0.94	0.97	1.08	0.94
(151) Mn	-689.74	12	31	56	1.49	1.30	1.11	1.16	1.58	1.08
(151) Mn/O	-737.28	12	31	64	0.71	0.77	1.20	1.29	0.80	1.32
(511) Li	-759.76	16	31	64	0.75	0.82	0.93	0.93	0.74	0.96
(511) Li-10vac	-749.06	16	31	62	0.85	0.85	0.81	0.80	0.83	0.80
(511) Li-20vac	-736.63	16	31	60	1.09	1.02	0.83	0.81	1.07	0.78

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					${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	$\rm LiMn_2O_4$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$
surface termination	\mathbf{E}_{slab}	N_{Li}	N_{Mn}	N_O	MnO_2	MnO_2	$\mathrm{Mn}_2\mathrm{O}_3$	$\rm LiMnO_2$	$\rm Li_2 MnO_3$	$\rm LiMnO_2$
					0	${\rm Mn_2O_3}$	$\mathrm{Mn}_3\mathrm{O}_4$	${\rm Li}_2{\rm MnO}_3$	0	${\rm Mn}_3{\rm O}_4$
(511) Li/Mn/O	-749.59	14	31	64	0.64	0.70	0.97	1.02	0.68	1.05
(511) Li/Mn/O-10vac	-738.84	14	31	62	0.74	0.74	0.85	0.89	0.78	0.89
(511) Li/Mn/O-20vac	-725.70	14	31	00	1.04	0.98	0.94	0.96	1.08	0.94
(511) Mn	-689.06	12	31	56	1.55	1.36	1.16	1.22	1.64	1.14
(511) Mn/O	-737.72	12	31	64	0.67	0.74	1.16	1.25	0.76	1.28
(511) Stoich	-1335.62	28	56	112	1.29	1.29	1.29	1.29	1.29	1.29
(531) Li	-809.44	18	33	68	1.03	1.08	1.12	1.09	0.99	1.12
(531) Li-10vac	-797.88	18	33	66	1.17	1.17	1.07	1.04	1.14	1.04
(531) Li-20vac	-785.31	18	33	64	1.40	1.34	1.10	1.06	1.36	1.04
(531) Li/Mn	-773.96	16	33	64	1.39	1.33	1.23	1.23	1.40	1.21
(531) Li/Mn/O	-798.04	16	33	68	1.02	1.08	1.24	1.26	1.03	1.29
(531) Mn	-764.28	14	33	64	1.25	1.19	1.23	1.27	1.31	1.25
$(531) \mathrm{Mn/O}$	-788.05	14	33	68	0.91	0.96	1.27	1.33	0.96	1.35
(531) Mn/O-1Ovac	-777.08	14	33	66	1.01	1.01	1.18	1.23	1.07	1.23
(531) Mn/O-2Ovac	-766.05	14	33	64	1.12	1.06	1.09	1.14	1.17	1.12

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					${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$
surface termination	E_{slab}	N_{Li}	\mathbf{N}_{Mn}	N_{O}	MnO_2	MnO_2	$\mathrm{Mn}_2\mathrm{O}_3$	$\rm LiMnO_2$	$\rm Li_2 MnO_3$	$\rm LiMnO_2$
					0	${\rm Mn_2O_3}$	$\mathrm{Mn}_3\mathrm{O}_4$	${\rm Li}_2{\rm MnO}_3$	0	${\rm Mn}_3{\rm O}_4$
(531) Mn/O-3Ovac	-753.02	14	33	62	1.37	1.26	1.16	1.20	1.43	1.15
(531) Stoich	-1525.05	32	64	128	1.35	1.35	1.35	1.35	1.35	1.35
(153) Li	-810.58	18	33	68	0.95	1.01	1.04	1.02	0.92	1.04
(153) Li-10vac	-799.18	18	33	99	1.09	1.09	0.99	0.95	1.05	0.95
(153) Li/Mn	-774.18	16	33	64	1.39	1.33	1.23	1.23	1.40	1.21
(153) $\rm Li/Mn/O$	-798.71	16	33	68	0.98	1.04	1.21	1.23	0.99	1.25
$(153) { m Mn}$	-763.84	14	33	64	1.30	1.24	1.28	1.32	1.36	1.30
(153) Mn/O	-788.19	14	33	68	0.91	0.96	1.27	1.33	0.96	1.36
(153) Mn/O-1Ovac	-777.30	14	33	66	1.01	1.01	1.18	1.23	1.06	1.23
(153) Mn/O-2Ovac	-765.84	14	33	64	1.15	1.09	1.12	1.17	1.20	1.15
(315) Li	-810.56	18	33	68	0.98	1.04	1.08	1.05	0.95	1.08
(315) Li-10vac	-799.05	18	33	66	1.13	1.13	1.03	0.99	1.10	0.99
(315) Li/Mn	-773.86	16	33	64	1.46	1.40	1.29	1.29	1.47	1.27
(315) Li/Mn/O	-798.89	16	33	68	1.00	1.06	1.23	1.25	1.01	1.28
(315) Mn	-764.35	14	33	64	1.30	1.24	1.28	1.32	1.36	1.30

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					${\rm LiMn_2O_4}$	$\rm LiMn_2O_4$	${\rm LiMn_2O_4}$	$\rm LiMn_2O_4$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$
surface termination	\mathbf{E}_{slab}	N_{Li}	N_{Mn}	N_O	MnO_2	MnO_2	$\mathrm{Mn}_{2}\mathrm{O}_{3}$	$\rm LiMnO_2$	$\rm Li_2 MnO_3$	$\rm LiMnO_2$
					0	$\mathrm{Mn}_2\mathrm{O}_3$	$\mathrm{Mn}_3\mathrm{O}_4$	${\rm Li}_2{\rm MnO}_3$	0	${\rm Mn}_3{\rm O}_4$
(315) Mn/O	-789.07	14	33	68	0.87	0.93	1.24	1.31	0.93	1.33
(315) Mn/O-1Ovac	-777-	14	33	66	0.99	0.99	1.17	1.22	1.05	1.22
(315) Mn/O-2Ovac	-766.42	14	33	64	1.14	1.08	1.11	1.16	1.20	1.14
(351) Li	-809.15	18	33	68	1.05	1.10	1.14	1.11	1.01	1.14
(351) Li-10vac	-797.58	18	33	66	1.20	1.20	1.09	1.06	1.16	1.06
(351) Li/Mn	-773.77	16	33	64	1.40	1.34	1.24	1.24	1.41	1.22
(351) Li/Mn/O	-798.04	16	33	68	1.02	1.08	1.24	1.26	1.03	1.29
(351) Mn	-764.06	14	33	64	1.27	1.21	1.24	1.29	1.32	1.26
$(351) \mathrm{Mn/O}$	-788.05	14	33	68	0.91	0.96	1.27	1.33	0.96	1.35
(351) Mn/O-10vac	-777.09	14	33	66	1.01	1.01	1.18	1.23	1.07	1.23
(351) Mn/O-2Ovac	-766.05	14	33	64	1.12	1.06	1.09	1.14	1.17	1.11
(513) Li	-810.57	18	33	68	0.95	1.01	1.04	1.02	0.92	1.04
(513) Li-10vac	-799.19	18	33	66	1.09	1.09	0.99	0.95	1.05	0.95
(513) Li/Mn	-774.22	16	33	64	1.38	1.33	1.22	1.23	1.40	1.20
(513) Li/Mn/O	-798.86	16	33	68	0.97	1.03	1.20	1.22	0.98	1.24

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continued on next page

					${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$	${\rm LiMn_2O_4}$
surface termination	\mathbf{E}_{slab}	N_{Li}	N_{Mn}	N_O	MnO_2	MnO_2	$\mathrm{Mn}_{2}\mathrm{O}_{3}$	$\rm LiMnO_2$	$\rm Li_2 MnO_3$	$\rm LiMnO_2$
					0	$\mathrm{Mn_2O_3}$	$\mathrm{Mn}_3\mathrm{O}_4$	${\rm Li}_2{\rm MnO}_3$	0	${\rm Mn}_3{\rm O}_4$
(513) Mn	-763.84	14	33	64	1.30	1.24	1.28	1.32	1.36	1.30
$(513) \mathrm{Mn/O}$	-788.53	14	33	68	0.88	0.94	1.25	1.31	0.94	1.33
$(513) \mathrm{Mn/O-10vac}$	-777.41	14	33	66	1.00	1.00	1.17	1.22	1.05	1.22
$(513) \mathrm{Mn/O-2Ovac}$	-765.92	14	33	64	1.14	1.08	1.12	1.16	1.20	1.14
(135) Li	-810.54	18	33	68	0.99	1.04	1.08	1.05	0.95	1.08
(135) Li-10vac	-799.12	18	33	66	1.13	1.13	1.02	0.99	1.09	0.99
(135) Li/Mn	-773.82	16	33	64	1.46	1.40	1.29	1.30	1.47	1.27
(135) Li/Mn/O	-798.87	16	33	68	1.00	1.06	1.24	1.25	1.01	1.28
$(135) { m Mn}$	-764.32	14	33	64	1.30	1.24	1.28	1.33	1.36	1.30
$(135) \mathrm{Mn/O}$	-789.10	14	33	68	0.87	0.92	1.24	1.30	0.92	1.33
$(135) \mathrm{Mn/O-10vac}$	-777.91	14	33	66	0.99	0.99	1.17	1.22	1.05	1.22
$(135) \mathrm{Mn/O-2Ovac}$	-766.45	14	33	64	1.13	1.08	1.11	1.16	1.19	1.13

B. SUPPLEMENTARY INFORMATION FOR "ORIENTED LIMN $_2O_4$ PARTICLE FRACTURE FROM DELITHIATION DRIVEN SURFACE STRESS"

For the lithiation of $L_{0.5}$ MO surfaces, we first screen over all possible intercalant sites within the lithiation region with low accuracy settings (plane wave energy cutoffs of 400 eV). This is done to speed up calculations to identify and eliminate structures that are relatively unstable. We then choose structures within 0.3 eV of the most stable structure and optimize them the standard, higher accuracy calculation settings which have been outlined in Section 3.2.4 of the main text. We then proceed, using most stable structure(s) and repeat this procedure to calculate further lithiated states.



Figure B.1.: SEM of LMO particle fracture. SEM micrographs of the LMO composite cathode (a) before and (b,c) after electrochemical cycling. The yellow arrows in (c) indicate the cracked regions in multiple LMO particles.



Figure B.2.: LMO(111) delithiation thermodynamics. (a) Low-energy structures of the LMO(111) surface at different lithium contents. (b-d) Relative energies of delithiated LMO at (b) 3.0 V, (c) 3.5 V, (d) 4.0 V, and (e) 4.5 V vs. Li/Li⁺. The filled circles in (b-e) represent the most stable structures for a given stoichiometry, as shown in (a). The unfilled circles in (b-e) denote metastable lithium configurations.



Figure B.3.: LMO(001) delithiation thermodynamics. (a) Low-energy structures of the LMO(001) surface at different lithium contents. (b-d) Relative energies of delithiated LMO at (b) 3.0 V, (c) 3.5 V, (d) 4.0 V, and (e) 4.5 V vs. Li/Li⁺. The filled circles in (b-e) represent the most stable structures for a given stoichiometry, as shown in (a). The unfilled circles in (b-e) denote metastable lithium configurations.

Figure B.4 shows the lithiation of the partially lithiated $L_{0.5}$ MO phase at the (001) near-surface, with the most stable structures calculated at each Li⁺ concentration shown in Figure B.4a. Figure B.4b shows the calculated thermodynamics for these phases, suggesting that the x = 0.5 is the most stable near-surface phase leading up to the α -peak ($L_{0.5}$ MO/LMO bulk equilibrium) upon lithiation (discharge). While more Li-rich near surface phases (x = 0.625, 0.75) are more stable for lower potentials (Fig. B.4d), a full phase transition from $L_{0.5}$ MO to LMO would be expected under these conditions. Due to the limited range of near-surface Li⁺ concentrations, mechanical properties associated with lithiation of the $L_{0.5}$ MO phase are likely driven by the bulk phase transitions. This finding, in contrast with the increased surface tensile stress observed upon delithiation (Fig. 3.3e-f) is in agreement with the chemo-mechanical measurements of an ansynchronous stress-strain relationship between delithiation and lithiation by Çapraz et al. [192]



Figure B.4.: Lithiation thermodynamics of $L_{0.5}MO(001)$



Figure B.5.: TKD Phase Map of $LiMn_2O_4$. Regions of the mapped area from Figure 3.5 that were indexed to $LiMn_2O_4$ are colored red, corresponding to the entire region in which crystallographic analysis is performed. White regions indicate where there was no successful indexing to any phase due to sample quality.



Figure B.6.: Additional TEM and Diffraction Analysis of Cracked Region. (a) Medium magnification image of the cracked region highlighted in Figure 6. White arrows mark the same stacking faults seen in Figure 3.6c. The faceted crack can be seen parallel to both the (1-11) and (-111) planes. (b) Selected area electron diffraction of the cracked region from (a).



Figure B.7.: TKD analysis of cracking in additional LMO particle after extended cycling. (a) SEM image of additional cross section sample. The white boxed area indicates the mapping region. The sample orientation axes are also shown. (b) Inverse Pole Figures for the entire mapping region in the x, y, and z sample directions.



Figure B.8.: LMO(111) and LMO(001) delithiation sites. Starting lithiated structures for (a) LMO(111) and (b) LMO(001) for computational delithiation studies. The region of the slab highlighted in gray indicates the portion where ions are not permitted to relax upon delithation and from which delithiation is not permitted to occur. Structures are instead sampled from the Li⁺ ions nearest to the surface (above the region of the slab shaded in gray).

C. SUPPLEMENTARY INFORMATION FOR "MECHANISM FOR AL_2O_3 ATOMIC LAYER DEPOSITION ON LIMN₂O₄ FROM *IN SITU* MEASUREMENTS AND *AB INITIO* CALCULATIONS"

C.1 Supplemental Experimental Data



Figure C.1.: (a) An expanded view of reaction products generated during the 3 ALD cycles. (b) QMS intensity background for CH_4 during TMA and H_2O pulses in an empty reactor. Time sequence is $[10x(0.3-5.0)TMA, 10x(0.3-5.0)H_2O]$. (c) Surface area of uncoated LMO and ball-milled LMO.



Figure C.2.: In-situ FTIR. (a) Difference spectra in low frequency for the first TMA pulse onto LMO at 150 °C after annealing at 200 °C. (b) Difference spectra in high frequency for the first TMA pulse onto LMO at 150 °C after annealing at 200 °C.



Figure C.3.: In situ FTIR measurements of Al_2O_3 ALD on LMO following 400 °C anneal. (a)-(f) Difference spectra following TMA (red) and H_2O (blue) exposures for ALD cycles 1-6, respectively. (g) Absolute spectra referenced to the bare LMO recorded after ALD cycles 1-6.





Figure C.4.: In situ FTIR measurements of Al_2O_3 ALD on LMO following 200 °C anneal. (a)-(f) Difference spectra following TMA (red) and H_2O (blue) exposures for ALD cycles 1-6, respectively. (g) Absolute spectra referenced to the bare LMO recorded after ALD cycles 1-6.



Figure C.5.: *Ex-situ* XPS of coated LMO samples in a second spot. (a) $1xAl_2O_3$ LMO on AAO substrate. (b) $3xAl_2O_3$ LMO on AAO substrate.



Figure C.6.: *Ex-situ* SEM and AFM images of sputtered LMO on silicon substrates at room temperature. (a) SEM of LMO film without post-annealing, (b) AFM image of LMO film without post-annealing. (c) SEM of LMO film with post-annealing at 500 °C. (d) AFM image of LMO film with post-annealing at 500 °C.



Figure C.7.: QCM Growth per cycle of ALD Al_2O_3 on an LMO film for duplicate measurement of in-situ QCM.



Figure C.8.: SEM images of LMO powders. (a) SEM of uncoated LMO. (b) SEM of 1 cycle ALD Al₂O₃ coated LMO (designated as $1xAl_2O_3$ LMO thereafter). (c) $2xAl_2O_3$ LMO. (d) $4xAl_2O_3$ LMO. (e) $6xAl_2O_3$ LMO. (f) $10xAl_2O_3$ LMO. Scale bars are 1 μ m.



Figure C.9.: (a-b) TEM image of $10xAl_2O_3$ on LMO. (c) HRTEM image of LMO indicating the 0.48 nm interplanar *d*-spacing along the [111] direction



Figure C.10.: Charge-discharge measurements for uncoated and coated LMO at 0.5 C at room temperature. (a) Cycling results. (b) Capacity retention upon the 100^{th} cycle tested at 0.5 C at RT. (c) Charge-discharge measurements and (d) capacity retention upon the 100^{th} cycle for uncoated and coated LMO at 0.5 C at room temperature vs. graphite in full cells. (e) Charge-discharge measurements for uncoated and coated LMO at 0.5 C at 55 °C. (f) EIS of half-cells before cycling with the equivalent circuit shown in the inset. R_e , R_{ct} , C_d , and Z_w in the equivalent circuit correspond to the electrolyte and SEI resistance, electrode/electrolyte interfacial charge resistance, double layer capacitance, and Warburg impedance, respectively.

Sample	$R_e (\Omega)$	$R_{ct} (\Omega)$
Uncoated LMO	10.17	66.06
$1 \ge Al_2O_3 \ge O_3$	10.79	92.85
$2 \ge Al_2O_3 \ge C_3$	10.63	104.85
$4 \ge Al_2O_3 \ge C_3$	10.14	108.72
$6 \ge Al_2O_3 \ge O_3$	12.40	110.66
$10 \ge Al_2O_3 \ge C_3$	11.58	144.81

Table C.1.: Fitting parameters for EIS data in Figure C.10e



Figure C.11.: Electrochemical measurements cycled at 0.5 C for stoichiometric LMO (Carus) at room temperature. (a) Cycling results. (b) Voltage vs. capacity profile for the 1th cycle. (c) Voltage vs. capacity profile for the 100^{th} cycle. (d) Coulombic efficiency during cycling beginning from the first cycle. (e) Coulombic efficiency during cycling beginning from the second cycle.





Figure C.12.: Charge-discharge measurements for stoichiometric LMO (Carus) cycled at (a) 1 C at room temperature, (b) at 0.5 C at 55 °C.

C.2 Hydroxyl Formation on LMO

We consider the formation of hydroxyls on the Li/O-terminated LMO(111) surface. On LMO(111), the nearest-surface Mn ions are octahedrally coordinated and are thus unlikely to form further bonds to O₂ from atmospheric H₂O. Thus, the overall reaction (equation C.3) for hydroxyls, H^{*}, on the surface may be decomposed into two steps corresponding to a two-part mechanism involving oxygen vacancy (V_O°) formation (equation C.1) and dissociative adsorption of H₂O (equation C.2).

$$2* \to 2V_O^{\circ} + O_2(g) \tag{C.1}$$

$$V_O^{\cdot \cdot} + * + H_2 O(g) \to 2H* \tag{C.2}$$

$$Overall: * + \frac{1}{2}H_2O \to H * + \frac{1}{4}O_2(g)$$
 (C.3)

The free energy of formation for n hydroxyls on the surface, $\Delta G_{f,nH*}$, may therefore be expressed in the form

$$\Delta G_{f,nH*}(T, P_{H_2O}) = [G_{nH*} + \frac{n}{4}\mu_{O_2}(T, P_{O_2})] - [E_* + \frac{n}{2}\mu_{H_2O}(T, P_{H_2O})]$$
(C.4)

Here, we use the DFT-calculated vibrational frequencies of adsorbed hydroxyls for zero-point and vibrational entropy corrections within the harmonic approximation. Since experiments have been performed in ultrahigh vacuum, we also assume an ideal gas harmonic partition function to determine gas phase entropy corrections for a given set of temperatures and pressures [660]. The lowest hydroxyl bending frequency is calculated to be a reasonably high 600 cm⁻¹, suggesting that a harmonic entropy treatment is a reasonable approximation even at moderately high temperatures. For the oxygen partial pressure, we assume the chemical potential reference is fixed via a partial pressure of 0.21 atm.

 H_2O adsorption may also occur at surface Li atoms. In these cases, adsorption energies are calculated by the following expression.

$$\Delta G_{ads,H_2O} = G_{H_2O} - [E_* + \mu_{H_2O}(T, P_{H_2O})] \tag{C.5}$$

For the close shell H₂O adsorbate, we treat the entropy using the method of Campbell and Sellers [377], which has demonstrated validity for the entropy of adsorbed species for entropies up to $\sim 50R$. The resulting phase diagram for hydroxyls and water on LMO(111) Li/O (Figure C.13) suggests light water coverage may be present under low temperatures and moderate H₂O partial pressures. Given the pretreatment N₂ purge at 400 °C, however, the *ab initio* predictions would suggest that overall hydroxyl coverage is likely to be low, consistent with depressed CH₄ signal in QMS measurements during the first ALD pulse. We note that hydroxyls may form during the TMA pulse, however, through a relatively facile dehydrogenation of adsorbed CH₃* fragments (Figure C.14).



Figure C.13.: *Ab initio* phase diagram for hydroxyl formation on Li-O terminated LMO (111) surface.



Figure C.14.: Dissociation of adsorbed CH_3^* to form surface hydroxyls. CH_3^* may undergo further decomposition to $CH_2^* + H^*$ once adsorbed to surface oxygen atoms. (a) Dehydrogenation of CH_3^* leading to an intermediate state forming an Li-O-CH₃ complex. This involves oxygen breaking bonds with Mn and forming a bond with Li at the surface. (b) Further relaxation of the intermediate state to adsorbed CH_2^* bridging two surface oxygen atoms.

C.3 TMA Decomposition Thermodynamics

Since each ALD half-reaction is self-terminating, multiple exothermic reaction coordinates may be exploited as the TMA precursor decomposes to the surface, effectively blocking stable sites towards further decomposition. These alternate pathways may proceed during initial, as well as intermediate ALD cycles, to complete the full monolayer film observed after ~10 cycles of TMA/H₂O pulses. For each step along the reaction coordinate, the energy relative to the clean surface and gas-phase TMA for a particular adsorbate ($G_{rel.ads}$)

$$G_{rel,ads*} = G_{ads*} - [G_* + G_{TMA}(g)] \tag{C.6}$$

where $G_{rel,ads}$ refers to the DFT-calculated energy of a particular adsorbate species, including adsorbed CH₃^{*} groups at infinite separation (separate calculations) to balance the chemical equation with the TMAgas-phase reference. The decomposition energy (ΔG_{decomp}), and the intrinsic transition state energy ($E_{TS,intrinsic}$) are reported for each pathway presented.

$$\Delta G_{decomp} = G_{Al(CH_3)_{x-1}+CH_3*} - G_{Al(CH_3)_{x*}} \tag{C.7}$$

$$E_{TS,intrinsic} = G_{TS} - G_{Al(CH_3)_{x^*}} \tag{C.8}$$

As an estimate for the feasibility a kinetic process occurring for a given intrinsic barrier, a simplified transition state theory approximation for a rate expression of the form

$$r \sim \frac{k_B T}{h} e^{-\frac{E_{TS,intrinsic}}{k_B T}} \tag{C.9}$$

where k_B and h represent the Boltzmann and Planck constants, respectively. Given the approximation in equation C.9, demethylation processes with E_{TS} , intrinsic of 1.22 eV and 1.39 eV would be likely to occur on the time scale of seconds and minutes, respectively, at 200 °C. As such, barriers less than these are assumed to be accessible at reaction conditions under the time scale of the TMA and H₂O pulses. Demethylation, involving a net change in total spin, requires estimation of the kinetic barrier through analysis of a spin-orbit-coupled diabatic minimum energy path [343, 342]. The procedure outlined in Ref. [307] is followed accordingly, using the Landau-Zener equation [120] and the spin-orbit coupling energy, taken from the literature [344], to provide reasonable estimates. In each case, the Landau-Zener calculated spin-crossing probability is close to unity.

For decomposed surface intermediates, the relative thermodynamics between a given structure corresponding structure and the most stable configuration of the previous step in the reaction coordinate $(G_{Al(CH_3)_x * \to Al(CH_3)_{x-1}*})$ is shown:

$$G_{Al(CH_3)_{x^*}} \to Al_{(CH_3)_{x-1^*}} \tag{C.10}$$

where, again, the energies of the adsorbed methyl groups in equation C.10 are taken at infinite separation. Adsorption sites are referred to according to the notation outlined in Figure 5.5c.

Figure C.15 illustrates two example reactions, which may occur at the LMO surface, for TMA* decomposition to DMA* with the decomposed CH_3^* fragment coadsorbed to the surface. Figure C.15a demonstrates such a process for decomposition from the low-energy O_b adsorption site. If such sites may be locally blocked by CH_3^* or other adsorbates, however, the process outlined in Figure C.15b may occur, wherein TMA adsorbs through O_a and decomposed to the DMA* and CH_3^* molecular fragments accordingly.

Decomposition from DMA^{*} to MA^{*} with coadsorbed CH₃^{*} is shown in Figure C.16. In this case, two adsorption configurations are presented for DMA^{*}, including the low-energy configuration in Figure C.16a (3f-d site) and an alternate configuration (2f-b) in Figure C.16b. As indicated by the corresponding relative thermodynamics to TMA^{*}, $\Delta G_{TMA \rightarrow DMA^*}$, each configuration is considerably exothermic with respect to the low-energy adsorption configuration for TMA^{*}. As mentioned in the main text, this decomposition process leads to a net reduction of two Mn cations through the promotion of two electrons to the Mn 3d states, typically involving reduction of near-surface Mn, which directly participate in bonding to adsorbates, elongating or



Figure C.15.: TMA^{*} \rightarrow DMA^{*} + CH₃^{*}. (a) TMA^{*} adsorbed at O_b site, with decomposed DMA^{*} to a 2f-a site. (b) Further relaxation of DMA^{*} + CH₃^{*} from 2f-a site in (a) to a 2f-b site. (c) TMA^{*} adsorbed at O_a site, with decomposed DMA^{*} to a 2f-a site. (d) TMA^{*} adsorbed at O_a site, with decomposed DMA^{*} to a 2f-a site, with CH₃^{*} group at O_a on other side of 16c site.

breaking Mn-O bonds. In some cases, sub-surface charge redistribution may occur to compensate for the electronic structure changes of near surface Mn cations and the total electron count in the oxide. Moreover, Figure C.16c depicts a facile diffusion process for MA^{*} diffusion away from the coadsorbate to an alternate three-fold site.

Two processes for the final decomposition step, MA^{*} demethylation to Al^{*} and coadsorbed CH_3^* , are presented in Figure C.17. As Figure C.17a indicates, decomposition from the low-energy configuration of MA^{*} at the 3f-d site is unlikely to proceed due to endothermic thermodynamics and a prohibitively high kinetic barrier. However, as these sites become saturated and effectively blocked, decomposition to MA^{*} may occur at alternate three-fold sites, with the next most stable being the 3f-c site depicted in Figure C.17b. From here, as mentioned in Chapter 5 the thermodynamics



Figure C.16.: DMA^{*} \rightarrow MA^{*} + CH₃^{*}. (a) DMA^{*} adsorbed at 3f-d site, with decomposed MA^{*} to the same 3f-d site. (b) DMA^{*} adsorbed at 2f-b site, with decomposed MA^{*} to 3f-a site. (c). Diffusion of MA^{*} from 3f-a site to 3f-b site due to effect of coadsorbed CH₃^{*}. Further diffusion to 3f-a, 3f-c and 3f-d sites at infinite separation are exothermic by 0.44 eV, 0.46 eV, and 1.61 eV, respectively.

are highly favorable due to octahedral coordination of Al^{*} at the interstitial 16c site in the final state, accompanied by a modest kinetic overbarrier, predicted to be accessible under ALD conditions. Thermodynamic and structural information regarding the isolated Al^{*} adsorbates (no CH3^{*} present in calculation cell) are included in the subsequent Figure C.18.

C.4 Intermediates in the Oxidation Half-Cycle

Oxidation of Al-containing adsorbates are considered from MA^{*} on the reaction coordinate from the two sites discussed in Figures C.17a and C.17b. These sites are labeled 3f-c and 3f-d in Figure 5.5c of Chapter 5, referring to the positions of the analogous bulk crystallographic 16c and 16d sites, respectively [132]. The thermo-

(a)



Figure C.17.: $MA^* \rightarrow Al^* + CH_3^*$. (a) MA^* adsorbed at 3f-16d site, with decomposed Al* to the same 3f-16 site (b) MA* adsorbed at 3f-16c site, with decomposed Al* forcing Li cations further into subsurface, and adopting octahedral coordination to lattice oxygens as previously depicted in Chapter 5.



Figure C.18.: Al^{*} adsorption sites. (a) Al^{*} adsorbed at interstitial 16c site with octahedral coordination to lattice oxygen atoms. (b) Al^{*} adsorbed at three-fold coordinated 16d position.

dynamics of these steps are included in Figure C.19. For each H_2O molecule that reacts, we assumed that protons are either transferred to surface oxygen atoms to form hydroxyl groups, or rather, react with CH_3^* coadsorbates to form CH_4 and remove carbon-containing compound from the surface, as the experimental portion of this study may suggest.

From the 3f-c (or, 16c sites), the DFT calculations suggest that hydroxyl formation on Al is thermodynamically unfavorable, represented by the uphill nature of its reaction coordinate from full decomposition to Al* in the first half cycle. Hydroxylation is likely unfavorable in this case due to a significant energetic penalty to disrupt the highly stable octahedral coordination of Al^{*} at the interstitial site. At the 3fd site (16d), however, initial hydroxyl formation to AlOH^{*} with byproduct CH₄ is exothermic. Subsequent hydroxylation to Al(OH)₂^{*}, or O-H dissociation to AlO^{*} + H^{*}, is not calculated to be stable as shown in Figure C.19. As demonstrated in Table C.2, based on reaction thermochemistry in the H₂O half-reaction, there is likely to be a net increase in the Mn³⁺:Mn⁴⁺ ratio, based on stable surface compounds on LMO(111). This finding is also consistent with *ex-situ* XPS measurements as presented in Chapter 5. More oxidized compounds may be present on surface facets with undercoordinated Mn, leading to moderate oxidation of surface or near-surface Mn, as has been demonstrated recently through DFT calculations on LMO(001) [142]. However, the (111) surface is likely to comprise the majority of LMO particle surface area, based on both theoretical calculations [64, 200] and experimental observations [145].


Figure C.19.: Thermodynamics of $Al(O_xH_y)$ species possible during water halfreaction on LMO(111) Li/O surface. Red and blue series on the free energy diagram correspond to Al-containing species oxidation proceeding from the 3f-c (16c) and 3f-d (16d) sites, respectively (notation refers to that used in Figure 5.5c). Energies are taken with respect to the pristine (111) slab and gas-phase TMA, in addition the corresponding gas-phase references for each step along the reaction coordinate (number of CH₄, H₂O molecules).

Surface	Number of Mn	Number of Mn
compound	reduced	oxidized
Al*	3	0
AlOH*	2	0
$Al(OH)_2^*$	1	0
$Al(OH)_3^*$	0	0
AlO*	1	0
AlO_2^*	0	1
AlO_3^*	0	3

Table C.2.: Oxidized Al species during water half cycle and implications for Mn redox

D. SUPPLEMENTARY INFORMATION FOR "DESCRIPTOR-BASED ANALYSIS OF ATOMIC LAYER DEPOSITION ON SPINEL LIMN $_2O_4$ LITHIUM ION BATTERY CATHODES"



Figure D.1.: Surface slab models used in this work. The notation for each of the terminations corresponds to that established in Ref. [200], and the region shaded grey corresponds to atoms which are fixed during adsorption calculations.



Figure D.2.: TMA decomposition reactions on the Li/O-terminated LMO(111) surface. (a-d) TMA* \rightarrow DMA* + CH₃*, (e-g) DMA* \rightarrow MA* + CH₃*, and (h,i) MA* \rightarrow Al* + CH₃* reaction pathways, as well as (j,k) isolated Al* ions adsorbed on the surface. In each image, G_{rel} is the free energy relative to the clean LMO(111) Li/O slab and gas phase TMA, ΔG_{decomp} is the energy for a given decomposition step, E_A , intrinsic is the barrier as determined from nudged elastic band calculations as outlined in Section 6.2.1 in Chapter 6, and $\Delta G_{Al(CH_3)_x \rightarrow Al(CH_3)_{x-1}*}$ corresponds to the free energy difference between Al(CH₃)_x* and Al(CH₃)_{x-1}* adsorbates, with the corresponding CH₃* groups also adsorbed on the surface at infinite separation.



Figure D.3.: TMA decomposition reactions on the Li-rich-terminated LMO(111) surface. (a) TMA^{*} \rightarrow DMA^{*} + CH₃^{*}, (b-d) DMA^{*} \rightarrow MA^{*} + CH₃^{*}, and (e) MA^{*} \rightarrow Al^{*} + CH₃^{*} reaction pathways, as well as (f,g) isolated Al^{*} ions adsorbed on the surface. The notation for different thermodynamic and kinetic parameters is described in the caption of Figure D.2.



Figure D.4.: TMA decomposition reactions on the Mn/O-rich-terminated LMO(001) surface. (a-c) TMA^{*} \rightarrow DMA^{*} + CH₃^{*}, (d,e) DMA^{*} \rightarrow MA^{*} + CH₃^{*}, and (f-h) MA^{*} \rightarrow Al^{*} + CH₃^{*} reaction pathways, as well as (i) isolated Al^{*} ions adsorbed on the surface. The notation for different thermodynamic and kinetic parameters is described in the caption of Figure D.2.



Figure D.5.: TMA decomposition reactions on the Li-terminated LMO(001) surface. (a-c) TMA* \rightarrow DMA* + CH₃*, (d-f) DMA* \rightarrow MA* + CH₃*, and (g,h) MA* \rightarrow Al* + CH₃* reaction pathways, as well as (i) isolated Al* ions adsorbed on the surface. The notation for different thermodynamic and kinetic parameters is described in the caption of Figure D.2.



Figure D.6.: TMA decomposition reactions on the Li/Mn/O-terminated LMO(511) surface. (a,b) LMO(511) step model from (a) side and (b) top views. The blue and orange arrows are used to mark the step edge and point along the (001) and (111) planes, respectively. (c,d) TMA^{*} \rightarrow DMA^{*} + CH₃^{*}, (e,f) DMA^{*} \rightarrow MA^{*} + CH₃^{*}, and (g,h) MA^{*} \rightarrow Al^{*} + CH₃^{*} reaction pathways, as well as (i,j) isolated Al^{*} ions adsorbed on the surface. The notation for different thermodynamic and kinetic parameters is described in the caption of Figure D.2.



Figure D.7.: TMA decomposition reactions on the Li/Mn/O-10vac -terminated LMO(511) surface. (a,b) TMA^{*} \rightarrow DMA^{*} + CH₃^{*}, (c-f) DMA^{*} \rightarrow MA^{*} + CH₃^{*}, and (g,h) MA^{*} \rightarrow Al^{*} + CH₃^{*} reaction pathways, as well as (i,j) isolated Al^{*} ions adsorbed on the surface. The notation for different thermodynamic and kinetic parameters is described in the caption of Figure D.2. The blue and orange arrows are used to mark the step edge and point along the (001) and (111) planes, respectively. Reference Figures D.6a,b for the relation between the top and side views of the step.



Figure D.8.: CH_3^* diffusion from Mn to O adsorption sites on the Mn/O-terminated LMO(001) surface. Although some decompositions to Mn sites proceed with very low barriers (Figure D.4c, Figure D.5c), diffusion to O sites is more thermodynamically favorable (main text, Figure 6.3) and proceeds with accessible barriers at 200°C.

E. SUPPLEMENTARY INFORMATION FOR "*OPERANDO* OBSERVATIONS AND FIRST-PRINCIPLES CALCULATIONS OF REDUCED LITHIUM INSERTION IN AU-COATED LIMN₂O₄"



Figure E.1.: Starting lithiated structures for the (a) bare and (b) Au-coated LMO(001) surfaces. Delithiation calculations are limited to the region wherein atoms are allowed to relax. The stoichiometry of the delithiation region (as described in Section 8.4 of Chapter 8) in the fully lithiated state is $\text{Li}_8\text{Mn}_{16}\text{O}_{32}$, which is reduced to $\text{Li}\text{Mn}_2\text{O}_4$ in order to report formation energies with respect to the number of Mn_2O_4 formula units.

Sample	Cycle number	\mathbf{R}_p	\mathbf{R}_{wp}	\mathbf{R}_{exp}	(Reduced χ^2) ^{1/2}
	OCP	3.27	4.82	0.95	5.11
	0	2.95	4.67	0.94	5.02
	1	2.12	3.55	1.10	3.24
Lithiated	2	2.54	4.19	0.99	4.26
Bare LMO	3	2.54	4.35	1.12	3.93
	4	2.94	5.31	1.15	4.64
	5	2.82	4.45	1.07	4.20
	6	2.50	4.24	0.95	4.51
	OCP	2.65	4.36	1.02	4.30
	0	3.12	4.66	1.00	4.67
	1	2.69	4.35	1.25	3.66
Lithiated	2	3.23	5.70	1.02	5.62
Au-coated	3	3.17	4.94	1.14	4.36
LMO	4	2.98	5.07	1.17	4.38
	5	3.17	5.09	1.10	4.65
	6	4.07	6.30	1.01	4.97
	1	3.49	4.59	1.00	4.62
	2	2.47	3.99	1.35	2.97
Delithiated	3	2.25	3.57	0.97	3.70
Bare LMO	4	2.33	3.67	1.15	3.23
	5	2.42	4.01	1.13	3.57
	6	2.93	4.31	1.03	4.21
	1	2.62	3.62	1.08	3.37
Delithiated	2	3.36	4.60	1.54	3.01
Au-coated	3	3.46	4.82	1.04	4.67
LMO	4	2.74	4.13	1.16	3.58
	5	3.10	4.51	1.15	3.96
	6	2.40	3.79	1.07	3.57

Table E.1.: Goodness of fit indicators for all Rietveld refinements performed

Sample	Cycle number	Time [hr]	Potential [V vs. Li/Li^+]	a [Å]
	OCP	0.6722	3.120	8.241(1)
	0	3.3389	3.600	8.242(1)
	1	13.8389	3.510	8.215(1)
Lithiated	2	24.9539	3.509	8.217(1)
Bare LMO	3	36.1111	3.501	8.209(1)
	4	47.2944	3.511	8.215(1)
	5	58.2611	3.509	8.206(1)
	6	69.4611	3.501	8.198(1)
	OCP	0.6389	3.114	8.240(1)
	0	3.3056	3.594	8.239(1)
	1	13.9700	3.514	8.199(1)
Lithiated	2	24.9150	3.516	8.183(1)
Au-coated	3	36.0833	3.506	8.182(1)
LMO	4	47.2555	3.504	8.190(1)
	5	58.4222	3.514	8.183(1)
	6	69.4222	3.506	8.184(1)
	1	8.3389	4.500	8.041(1)
	2	19.5056	4.490	8.044(1)
Deithiated	3	30.6222	4.489	8.044(1)
Bare LMO	4	41.6111	4.491	8.047(1)
	5	52.7611	4.499	8.046(1)
	6	63.9611	4.489	8.046(1)
	1	8.3056	4.494	8.041(1)
Deithiated	2	19.4722	4.496	8.055(1)
Au-coated	3	30.4167	4.474	8.048(1)
LMO	4	41.7555	4.486	8.050(1)
	5	52.7555	4.494	8.049(1)
	6	63.9222	4.496	8.051(1)

Table E.2.: Lattice parameters (a) of Au-coated and bare LMO as shown in Figure 8.4a and 8.4b.



Figure E.2.: Vacancy-mediated diffusion of Au and Li⁺ in bulk Au. The low diffusion barrier of 0.28 eV for Li⁺ in Au suggests that the Au coating is not limiting in terms of Li⁺ ion conductivity of Au-coated LMO.



Figure E.3.: Operando CV of Au-coated (orange) and bare (teal) LMO at 25 μ V/s. Current is normalized by the mass of LMO in the electrode pellet.



Figure E.4.: Charge calculated for each sweep in the CV for both (a) lithiation and (b) delithiation. The charge was calculated without subtracting a capacitive background and by integrating between 3.5 to 4.4 V vs Li/Li⁺.



Figure E.5.: Equilibrium potentials for Li substitution within a 4 layer Au film on $\text{Li}_{0.75}\text{Mn}_2\text{O}_4$, calculated for when the ΔG in equation 8.1 is equal to zero. As the Li substitution position moves from the Au surface (far left) to the LMO/Au interface (far right), the substitution becomes more favorable. However, even the highest substitution equilibrium potential ($U_{eq} = 2.36 \text{ V} \text{ vs. Li/Li}^+$ at the LMO/Au interface) is well outside the normal operation of LMO as a cathode and would instead be closer to anodic potentials.



Figure E.6.: Gaussian fits of background subtracted diffraction of (a) bare LMO at OCP, (b) lithiated bare LMO after the first CV cycle, (c) Au-coated LMO at OCP, and (d) Au-coated LMO after the first CV cycle. After the 1^{st} CV cycle, the FWHM of the (111) peak has increased by 2.4x and 2x for the bare and Au-coated LMO, respectively. The area has decreased by 2.4x and 2.6x for the bare and Au-coated LMO, respectively. Although the Rietveld refinement parameters pertaining to height are not examined because of masking the original area detector image, the same mask was used for every diffraction pattern for a given sample. Therefore, its valid to examine peak height changes over time for a particular peak of a sample.



Figure E.7.: Selected diffraction patterns of bare and Au-coated LMO during the first lithiation at 50 μ V/s. The arrows draw attention to a tail on the LMO(111) peak.



Figure E.8.: Gaussian fits of background subtracted (111) LMO peak of bare and Au-coated LMO after (a) lithiation and (b) delithiation.



Figure E.9.: The relative lattice parameter and relative charge of each cycle compared to the initial bare LMO values after a full delithiation sweep for bare and Au-coated LMO. For this figure 100% of the lattice parameter is approximately 8.040(1) Å and any larger number is considered a decrease in percentage because the LMO material isnt fully delithiating and utilizing all available capacity.



Figure E.10.: Relative energies of bare (teal) and Au-coated (orange) LMO at (a) 3.0 V, (b) 3.5 V, (c) 4.0 V, and (d), 4.5 V vs. Li/Li⁺. The filled in shapes represent the most thermodynamically stable configuration for a given stoichiometry, whose structures are represented in Figures 8.5a and 8.5b of Chapter 8, and are connected by solid lines, whereas metastable lithium configurations are represented by unfilled shapes.



Figure E.11.: Relative energies of bare (teal) and Au-coated (orange) LMO with different Au layer thicknesses (different shades of orange, as labeled in (a)) at (a) 3.0 V, (b) 3.5 V, (c) 4.0 V, and (d) 4.5 V vs. Li/Li⁺. The data points represent the most thermodynamically stable configuration for a given stoichiometry.



Figure E.12.: Average Mn oxidation states for bare (teal) and Au-coated (orange) LMO as a function of Li⁺ content. The dashed lines correspond to the magnetic moment reference for Mn^{3+} (which has four unpaired 3*d* electrons) and Mn^{4+} (which has three unpaired electrons).



Figure E.13.: Electrostatic potentials for (a) bare and (b) Au-coated LMO for x = 0, 0.75, and 1 in $\text{Li}_x \text{Mn}_2 \text{O}_4$. The vacuum level is used to determine work functions plotted in Figure 8.8 of Chapter 8. (c) Difference in the electrostatic potential between Au-coated and bare LMO, each normalized to the vacuum level, which is equivalent in all six systems by definition. The negative end of the plot is cut off to focus on the electrostatic potential differences between the Mn-O layers of the bare and Au-coated LMO, as labeled in (a) and (b). We note that oscillations in the difference function may also be partially due to slight geometric differences in the relaxed bare and Au-coated structures for a given Li⁺ content.

F. SUPPLEMENTARY INFORMATION FOR "UNDERSTANDING THE ROLE OF OVERPOTENTIALS IN LITHIUM ION CONVERSION REACTIONS: VISUALIZING THE INTERFACE"

F.1 Electrochemical Cell



Figure F.1.: Electrochemical X-ray Cell. (a) Fully assembled cell and (b) exploded view of cell with each part label A-M. This cell is referred to as a transmissiongeometry cell because the X-rays pass through the circular opening in the cell. The sample is fully immersed in the1:1 EC/DMC + 1 M LiClO₄ electrolyte, in analogy with a traditional beaker electrochemical cell. The individual labeled parts are: (A) Kel-f cell body; (B) Al goniometer adaptor; (C) Kel-f working electrode clamp; (D) stainless steel working electrode plungers; (E) Kel-f plunger shells; (F) 20-30 kfm O-ring (PSI); (G) 0.024 in. OD stainless steel compression spring (Lee, CIM010ZA); (H) 10x3x1 mm3 sample; (I) Kel-f sample holder; (J) 2-56 stainless steel set screw for sample height adjustment; (K) doubled 75 m Kapton windows; (L) Teflon flange; (M) Kel-f window clamp.

The electrolyte inlet and outlet (syringe + stopcock + Teflon tubing, not shown) are attached via PVDF compression fittings on the cell bodys NPT fittings. The counter/reference electrode is a piece of lithium foil crimped to a copper wire and laid above the sample in the cell. The copper wire is epoxied to glass tubing (to seal

from outside air) and attached using a compression fitting. The other NPT fittings are capped, but could be used for additional electrodes or a bubbler.

The working electrode has a primary O-ring seal at the sample using a custom miniature O-ring and secondary O-ring seals at the working clamp. The cell is mostly assembled outside of the glovebox; the lithium metal, windows, and electrolyte are attached inside an Ar-filled glovebox ($O_2 < 1$ ppm).

Analog voltages corresponding to the potential and current from the CHI potentiostat were saved in the SPEC file used to record the XR data.

F.2 Reflectivity Fits

Table F.1.: Mass densities (ρ) and calculated electron densities (ρ_e) of components of the Ni/NiO multilayer electrode.

	Density	X-ray scattering	Effective electron
Compound	ρ	length density	density (20 keV)
	(g/cm^3)	$(20 \text{ keV}, \text{x}10^{-5} \text{ e}^{-}\text{Å}^{-2})$	$\rho_e \; (\mathrm{e}^- \mathrm{\AA}^{-3})$
1 M LiPF_6			
EC/DMC	1.2	1.07	0.38
(1:1 v/v)			
NiO	6.67	5.51	1.95
Ni	8.90	7.30	2.59
Li_2O	2.01	1.60	0.57
sapphire	3.97	3.31	1.17

The scattering length density of each layer at 20 keV was calculated using Motofit. In the forward scattering limit, the electron density can be calculated by dividing the SLD by the classical electron radius (2.82 x 10^{-5} Å).

F.3 Bilayer Reflectivity Fits

Fits were performed using genetic model followed by Levenberg-Marquadt optimization of ξ^2 in Motofit [548]. Statistical errorbars were found to undervalue the overall accuracy of the measurement. Based on observed variance in the XR at high q, we adopted a minimum error bar of 5% for the entire measurement. Each interface in the electron density prole is calculated using an error function, *e.g.*

$$\rho_{tot}(z) = \rho_0 + \sum_{i=1}^{N} (\rho_i - \rho_{i-1}) [1 + erf(\frac{z - z_i}{\sqrt{2\sigma_{i,i-1}}})]$$
(F.1)

for an N-layer system with top density ρ_0 (the electrolyte) and substrate density ρ_N and interfacial roughness $\sigma_{i,i-1}$. An example of how multiple layers form an overall density profile is given in fits below. The parameters used in the each fit are shown in the accompanying tables.

As discussed by Nelson [548], the reflectivity, R, is calculated from these parameters using a matrix approach functionally equivalent to Parrat's recursive method for a stratified thin film.

$$R = \left|\frac{M_{11}}{M_{21}}\right|, \text{ where } M = \prod_{i=0}^{N} c_{i,i+1}$$
 (F.2)

where $r_{i,i+1} = \frac{k_i - k_{i+1}}{k_i + k_{i+1}}$ and $k_i = \sqrt{4\pi^2 - 4\pi(\rho_i - \rho_0)}$.

Fits were evaluated by find a minimum reduced ξ^2 for a minimally covarying $\rho(z)$. Error bars of $\rho(z)$ were calculated using the covariance matrix $V_{i,j}$ and standard deviations, σ_i , for each parameter, x_i :

$$\sigma_{\rho}(z) = \left[\sum_{i,j} V_{i,j} \sigma_i \sigma_j \frac{\partial \rho}{\partial x_j} \frac{\partial \rho}{\partial x_j}\right]^{1/2}$$
(F.3)

F.4 Classical Molecular Dynamics Simulations

Classical molecular dynamics simulations are performed using the DLPOLY code [550]. A core-shell potential is fit using parameters from Hartree-Fock calculations. The MD simulations are performed on a supercell containing 500 Li₂O formula units (1500 total atoms) and we confirm a melt of Li₂O to an amorphous phase by the radial distribution functions (RDF) in Figure F.2a. The RDF, along with the structural

model (Figure S3b) demonstrate the formation of an amorphous phase with a density of 1.99 g cm⁻³. Density functional geometry relaxations of 72 and 144 atom models cut from the amorphous cell suggest an average Li₂O amorphization energy of 0.44 eV per Li₂O formula unit. This amorphous reference state is applied for the bulk Li₂O thermodynamics as described in the main text for calculation of interfacial energies and the potential-dependent bulk reaction thermodynamics.



Figure F.2.: a) Radial distribution functions for (top to bottom) Li-Li, Li-O, and O-O ion pairs for the a-Li₂O at 300 K (purple) and those corresponding to the melt (shown by black, blue, and red lines). b) Snapshot of a-Li₂O structure obtained at 300 K.

F.5 Interfacial Structures

Interfacial models for Ni(111)/a-Li₂O, NiO(100)/a-Li₂O, and Ni(111)/NiO(100) are constructed using the approach outlined in the Methods section of Chapter 11. Representative models of the structures sampled to estimate their respective interfacial energies are shown in Figure F.3. Further description of these interfaces and the nucleation model are highlighted in Chapter 12.



Figure F.3.: Interfacial models for (a) Ni/*a*-Li₂O with an interfacial energy of 1.86 J m⁻², (b) Ni/Li/*a*-Li₂O with an interfacial energy of 0.41 J m⁻², (c) Ni/NiO with an interfacial energy of 1.44 J m⁻², and (d) NiO/*a*-Li₂O with an interfacial energy of 0.35 J m⁻². In (a)-(d), Ni, Li, and O atoms are depicted in silver, green, and red, respectively.

G. SUPPLEMENTARY INFORMATION FOR "NEW CLASS OF ELECTROCATALYSTS BASED ON 2-D TRANSITION METAL DICHALCOGENIDES IN IONIC LIQUID"

G.1 Synthesis of TMDCs through CVT

A total of one gram of precurser powders of transition metal and chalcogen (>99.99% trace metal basis purity) with a 1:2 stochiometric ratio were loaded in a quartz ampule with 1 cm internal diameter and 20 cm length. A $\sim 3\%$ additional chalcogen was also loaded to serve as the transport agent and to ensure the structure would not be chachogen-defficient. The ampule was then evacuated with a turbo molecular pump ($<10^{-6}$ mbar) and sealed with a hydrogen torch. The ampule was then placed in a two-zone CVD furnace and the temperature of the both zones was raised to 1080 °C in one day. The temperature of the empty part of the ampule (cold zone) was then gradually cooled down to 950 °C in four days, while the other end was maintained at 1080 °C, in order to form single crystalline grains with pristine structure via direct vapor transport. The system was then slowly cooled down to room temperature in one day and the material was taken out for tests and characterizations. It is worth noting that the excess of chalcogens would condense at the end of the cooling cycle (due to a lower evaporation temperature compared to the crystal growth temperature) and does not affect the crystalline structure of the TMDCs. It can also be easily removed through annelaing in vacuum.

G.2 Electron diffraction X-ray Spectroscopy (EDX) Results

EDX is performed to obtain the elemental composition of the synthesized TMDCs and identify presence of impurities in the synthesized crystals. The EDX spectra obtained from the tellurides are shown in Figure G.1. Except copper signal that originates from the TEM grid, and minor hydrocarbons observed in the 0-1 KeV range (i.e., 0.277 eV for C, 0.525 eV for O), no other impurities were detected.



Figure G.1.: Electron diffraction X-ray Spectroscopy (EDX) results for telluride based TMDCs. (a-e) EDS spectra of MTe_2 nanoflakes (M = V, Nb, Ta, Mo, W). All the peaks are labeled, except the peaks in the 0-1 KeV range which originate from C and O in the hydrocarbon contaminants and solvent residues.

G.3 X-ray Photoelectron Spectroscopy (XPS) Results

XPS experiments were performed on all the synthesized materials, and the complete results for all the 15 compounds are presented in Figures G.2-G.4 (for sulfides, selenides, and tellurides, respectively). All the spectra were calibrated based on the C-C bond binding energy at 284.8 eV.

For all the figures, the transition metal spectra are shown on top, and the chalcogen spectra are shown at the bottom row. In all cases the spectra are analyzed, and the corresponding peaks are identified. For instance, in the case of VTe₂, the corresponding V 2p spectrum possesses four main peaks located at ~514.6 eV and ~517.2 eV for V 2p_{3/2} and ~522.2 and ~525.0 eV for V 2p_{1/2}. These peaks represent vanadium in different oxidation states of 4 and 5 (Figure G.4a). Figure G.4b indicates the Nb core levels of NbTe₂ at ~207.2 and ~210.0 eV, corresponding to Nb $3d_{5/2}$ and Nb $3d_{3/2}$, respectively. The observed Ta 4f spectrum in Figure G.4c shows two peaks at ~26.6 and ~28.6 eV, referring to Ta $4f_{7/2}$ and Ta $4f_{5/2}$. For a representative chalcogen, e.g., telluride, the Te 3d region obtained from VTe₂ sample is shown in Figure G.4f, exhibiting two main peaks of Te $3d_{5/2}$ and Te $3d_{3/2}$ located at 571.4 and



581.9 eV. Two smaller fitted peaks are spotted at 572.9 and 583.6 eV which originate from the Te-O bonding.

Figure G.2.: XPS spectra of the synthesized MS_2 nanoflakes (M = V, Nb, Ta, Mo, W).



Figure G.3.: XPS spectra of the synthesized MSe_2 nanoflakes (M = V, Nb, Ta, Mo, W).

G.4 Lateral and Thickness Distribution of the Nanoflakes (DLS and AFM)

Dynamic light scattering spectroscopy (DLS) and atomic force microscopy (AFM) techniques are employed to determine the lateral size and thickness distributions of



Figure G.4.: XPS spectra of the synthesized MTe_2 nanoflakes (M = V, Nb, Ta, Mo, W).

the exfoliated materials. The results for telluride based TMDCs and the selected four catalysts (MoS_2 , NbS_2 , VS_2 , and VSe_2) are shown in Figure G.6 and G.7, respectively.



Figure G.5.: Dispersions of exfoliated TMDC nanoflakes in IPA.



Figure G.6.: (a-e) Size distribution and (f-j) flake thickness of different transition metal tellurides obtained from DLS and AFM topography maps, respectively.



Figure G.7.: (a-d) Size distribution from DLS measurements and (e-h) statistical flake thickness distribution by AFM on 40 flakes for each of selected catalysts. (i-l) Typical AFM images of exfoliated nanoflakes. (Scale bar in each image is 200 nm)

G.5 Work Function Measurements through UPS

To perform UPS, a bias of -10 V was applied in all cases to distinguish the sample energy cut-off from the cut-off of spectrometer. To measure the work function, a metal such as silver was used to first calibrate the analyzer based on the metal Fermi edge. The calibration was performed in a way that Fermi edge of silver was located at 0 eV binding energy, therefore, the whole spectrum was shifted by a specific number. In the next step, UPS measurements were performed for all of the TMDCs samples and the corresponding spectra were shifted according to the amount of shift in silvers spectrum. Finally, the work function numbers were calculated through the equation $\phi_{TMDC} = h\nu - E_c$. $h\nu$ is the exciting photon energy of the ionization source (He I) which is 21.2 eV. E_c refers to binding energy of secondary edge cut-off corresponding to lower kinetic energy [661]. The obtained work function measurement results for the synthesized TMDCs are shown in Figure G.8. Experiments were performed for three points on each sample and errors bigger than 0.1 eV are shown with error bars.



Figure G.8.: Ultraviolet Photoelectron Spectroscopy (UPS) results for the synthesized TMDCs

G.6 Work Function Calculations

The work function of a material is a property determined by the difference between the electronic Fermi level and the vacuum energy outside a specific surface. In our calculations, the surface is defined as the TMDC basal planes. In semiconductors, the Fermi level lies in the band gap, between the conduction band minimum (CBM) and the valence band maximum (VBM), where the position of the Fermi level depends on various factors, e.g. dopant levels, point defects, voltage. Work function calculations were performed with VASP. Geometric optimization of the observed bulk phases of each of the TMDCs was performed using Grimmes zero damping van der Waals correction [662] applied to Perdew-Burke-Ernzerhof exchange-correlation functional [163]. Layered structures of each slab were created from the optimized bulk structures. The slabs consisted of seven layers of TMDC with at least 15 Å of vacuum to minimize image interactions. The slabs were optimized with in-plane lattice vectors fixed to the bulk values, and the ions of the central layer fixed to best mimic the surface of a bulk material. A single-step static calculation was performed, and the work function was determined by the difference of the resulting vacuum energy and the Fermi level. All calculations were performed with a kinetic energy cutoff of 450 eV. All k-points meshes were Γ -centered. The number of k-points, N_i , used along direction b_i related to direct lattice vector a_i such that is equal to ~25 Å for relaxations and ~75 Å for for static calculations. Since spin-orbit coupling (SOC) effects are stronger in materials with heavier atoms, we repeated calculations on TMDCs with tungsten or tellurium accounting for SOC. While adding spin-orbit coupling significantly effects calculated band gaps, we found that it changes the work functions by at most 1.6% in WTe₂ and by less in lighter TMDCs. Predicted work functions presented in Figure 13.2a are from calculations with SOC for the seven aforementioned TMDCs (WS₂, WSe₂, WTe₂, MoTe₂, NbTe₂, VTe₂ and TaTe₂). All DOS plots in Figure 13.2b and 13.2c are from calculations without SOC.

G.7 Three-Electrode Electrochemical Cell for ORR and OER

The cyclic voltammetry (CV) experiments for both ORR and OER were performed inside the three-electrode electrochemical cell. The cell was composed of one working electrode (WE) which each time included one of the 15 synthesized TMDCs, one counter electrode (CE) and one reference electrode (RE) which included lithium chips (Purity of 99.99% purchased from Sigma Aldrich). The electrolyte consisted of EMIM-BF4 ionic liquid and dimethyl sulfoxide (DMSO) with the volumetric ratio of 1 to 3 respectively containing 0.1 M of Lithium Bis(Trifluoromethanesulfonyl)Imide (LiTFSI) as salt. The three-electrode cell was sealed properly. The O_2 gas was bubbled into the solution along with stirring to minimize the mass transfer effect and complete saturation. The bubbling was continued for approximately 20 minutes before running the CV experiment. The applied voltage was swept between 2 and 4.2 V vs. Li/Li⁺ with 20 mV/s scan rate. CV curves were recorded using a Voltalab PGZ100 potentiostat (purchased via Radiometer Analytical SAS) calibrated with a RCB200 resistor capacitor box. The potentiostat was connected to a PC using Volta Master (version 4) software.

G.8 Turn Over Frequency (TOF) Measurements

To calculate TOF values for MoS₂, NbS₂, VS₂ and VSe₂ catalysts, a roughness factor (RF) method [610, 611, 587, 586] was used to measure the number of active sites in MoS₂, NbS₂, VS₂ and VSe₂ catalysts that have shown the best performance for both ORR and OER. CV experiments were performed in 0.5M H₂SO₄ electrolyte with different scan rates ranging from 20 to 300 mV s⁻¹ and in a low overpotential and non-Faradaic region [610, 663, 585]. Double layer capacitance (C_{dl}) of each catalyst was calculated based on the slope of current densities recorded at a certain potential in different scan rates [610, 585]. Figure G.9 shows a typical CV experiment and C_{dl} calculated for MoS₂ catalyst in this study.


Figure G.9.: (a) Cyclic voltammetry (CV) curves at different scan rates recorded for MoS_2 nanoflakes. (b) Current densities versus scan rate recorded from CV experiments at potential 0.2V vs RHE. Double layer capacitance of MoS_2 is represented by the slope of the line.

RF values for MoS_2 and three other catalysts were calculated based on the MoS_2 flat standard capacitance as their physical properties are similar. Details are provided in Refs [587, 586]. The number of active sites for the catalysts were also obtained through equation G.1 [610, 587, 586, 585].

density of active sites (sites
$$cm^{-2}$$
) = density of standard (sites cm^{-2}) x RF (G.1)

Table G.1 summarizes the values for C_{dl} , RF and number of active sites for MoS₂, NbS₂, VS₂ and VSe₂.

Catalyst	$C_{dl} \ (\mathrm{mF} \ \mathrm{cm}^{-2})$	Roughness factor	Number of active sites
MoS_2	2.10	35	$4.07 \mathrm{x} 10^{16}$
NbS_2	2.50	41.6	$4.84 \mathrm{x} 10^{16}$
VS_2	1.90	31.6	$3.68 \mathrm{x} 10^{16}$
VSe_2	1.48	24.66	$2.86 \mathrm{x} 10^{16}$

Table G.1.: Number of active sites for the selected catalysts.

The number of TOF for each catalyst during ORR and OER is measured based on equation G.2 using the current densities at different overpotentials [585].

$$TOF = \frac{i_0}{\text{density of active sites}} \ge 1.602 \ge 10^{-19} \ge [2e^-/O_2]$$
(G.2)

G.9 Classical Molecular Dynamic Simulations

Classical Molecular Dynamics (MD) simulations were carried out using the software package GROMACS 5 [664, 665] with the OPLS-All atom force field [666] for DMSO molecules and ionic liquids, and the MoS_2 [667]. All simulations were carried out using isotropic constant pressure control using the Berendsen Barostat [668], with a coupling constant of 1.0 ps and a compressibility of 2.755×10^{-5} bar⁻¹. Temperature was kept at 300 K using the Velocity Rescaling Thermostat [669] with a coupling constant of 0.1 ps. A time step of 2 fs was used. The Verlet cut-off scheme was used. Coulomb interactions were calculated using the PME method [670] with the Coulomb radius set to 1.4 nm. Van der Waals forces were evaluated using a switching function from 0.8 to 1.4 nm. The bond lengths were restrained using the LINCS algorithm [671]. The simulation box contains an MoS_2 slab and the electrolyte has a cross section of 100 100 Å x 100 Å and is 145 Å. long. The 15 Å-thick MoS_2 slab is made up of 16 metal (Mo) terminated sheets and includes 5120 Mo atoms and 9728 S atoms. The electrolyte is prepared using an $[EMIM]^+[BF_4]^-$: DMSO ratio of 1:3 (volume fractions of 25% IL) and 0.1M $[Li]^+[BF_4]^-$ and includes 6358 DMSO molecules, 984 $\rm [EMIM]^+[BF_4]^-$ pairs , 60 Li^+ ion and 188 additional $\rm BF_4^-$ to neutralize the total charge of the simulation box. The system was equilibrated using the following steps: first the $[\text{EMIM}]^+[\text{BF}_4]^-$ was equilibrated for 30 ns at constant pressure and temperature (NPT ensemble) to reach a stable volume; next Li^+ ions and additional $BF_4^$ were randomly inserted in the mixture and was equilibrated in the presence of the MoS_2 stack for 480 ns at NPT ensemble. Following the equilibration simulations, an electric field of 4.5 V/nm (63 V) is applied perpendicular to the MoS_2 slab. The resulted potential drop calculated, considering the reaction field of the mixture was 60 V across the MoS₂ Slab. This potential drop was calculated using VMD PMEpot plugin [672]. This setup is simulated for 560 ns and the last 280 ns is used for analysis.

To quantify the orientation of EMIM⁺ cations, a vector along the cation is defined as shown in Figure 13.4c. The angle between this vector and each Cartesian axis is measured for the EMIM⁺ cations within 8 of the MoS_2 surface (those in the first pick near the surface and forming an interaction with Mo atoms) for every 10 frame of the trajectory and averaged over last 280 ns.

G.10 Scanning Transmission Electron Microscopy (STEM) image of MoS₂

Scanning Transmission Electron Microscopy (STEM) was used to investigate the atomic structure of MoS_2 nanoflakes. From the low magnification LAADF image in Figure G.10, we found that the edges of the MoS_2 nanoflake are along the [100] or [010] direction as shown by the contour of the edges. The angle formed between two dashed red lines is 121 degrees, which is close to a perfect angle between these two symmetric directions, 120 degrees. In Figure G.10, the high magnification image presents the distinctive atomic configuration of MoS_2 with a sharp contrast between Mo (bright) and S (dark) atoms. The overall uniformity and completeness of the structures show that there is no clear defect in the few-layer MoS_2 .



Figure G.10.: The LAADF image of the MoS_2 nanoflake with a high magnification LAADF image zoomed in the blue square area. The red lines present the contour of the edge.

G.11 DFT Calculations

Charge hopping rates are determined using a Marcus theory [118] formalism, with the appropriate parameters evaluated using procedures outlined previously in the literature and briefly discussed below. The nanoflake models are modified from the cluster model of Huang et al. [613] The resulting triangular model that we used for the charge transfer calculations (shown in Figure 13.5a of Chapter 13) gives O_2 adsorption energies that are consistent (within 0.1 eV) with both periodic models (discussed below) and a more symmetric hexagonal cluster (similar to 2-D Wulff constructions presented elsewhere [673]), both of which contain analogous coverage of (EMIM⁺ + e⁻) on the metallic edges to produce isolated metal sites. As discussed in the main text, the triangular flake is used to constrain charge transfer between O_2/Li_2O_2 and the metallic edge of the flake, ensuring that there is no degeneracy in states at the HOMO/LUMO during ORR/OER corresponding to sites on the basal planes of the cluster that are not physically relevant for the catalysis. Calculations are performed using a cubic box with a length of 32 Å with donor and acceptor states separated at various distances to evaluate the distance-dependence of electronic coupling (H_{ab}) between two diabatic states. These are then used to calculate rates using the Marcus rate expression,

$$k_{CT} = |H_{ab}|^2 \sqrt{\frac{\pi\beta}{\hbar^2 \lambda}} exp(-\beta E_{act}) \tag{G.3}$$

where β is $\frac{1}{k_BT}$, H_{ab} is the electronic coupling, ΔG is the driving force, λ is the reorganization energy, and E_{act} is the activation energy. E_{act} is determined from ΔG and λ through the Marcus parabola construction:

$$E_{act} = \frac{(\Delta G + \lambda)^2}{4\lambda} \tag{G.4}$$

where ΔG and λ are defined by the following expressions.

$$\Delta G = (\mathcal{D}_f^f + \mathcal{A}_f^f) - (\mathcal{D}_i^i + \mathcal{A}_i^i) \tag{G.5}$$

$$\lambda = (\mathcal{D}_i^f + \mathcal{A}_i^f) - (\mathcal{D}_f^f + \mathcal{A}_f^f)$$
 (G.6)

In the expressions above, \mathcal{D}_x^y and \mathcal{A}_x^y are the total energies of the donor and acceptor, respectively, in the x atomic configuration and y electronic state. Each of the \mathcal{D}_x^y and \mathcal{A}_x^y quantities are estimated with the single-point and relaxed geometries considered in isolation within the calculation cell, with a jellium background charge [674] introduced to charged systems with total energies determined using the Makov-Payne correction [675]. To determine formation energies of holes on the active site (most relevant at high potentials), we modify the well-established reduction potential (E_{red}) formalism through adjustment of the electron free energy reference to the proton solvation energy and the reversible hydrogen electrode [676, 677, 678]. The resulting phase diagram in Figure G.11 is used to rationalize the charge state of the nanocluster models used for CDFT calculations of ORR and OER charge transfer.

Some adsorption energy calculations were performed using periodic DFT within the Vienna Ab initio Software Package (VASP) [168, 160, 161], with the projector augmented wave method used to treat the effective core potentials [201, 162]. The nanoflake supercell was constructed using optimized lattice constants for MoS₂ and WS₂ with 6 metal atoms terminating the flake edge. Two (EMIM⁺ + e⁻) pairs are included per unit cell, separated by an isolated metal atom (catalytic site), as in previous work [585]. VASP calculations are subject to full ionic relaxation, and utilize a kinetic energy cutoff of 400 eV with a Γ -centered 2x1x1 k-point grid. Using the computational hydrogen electrode approach [11], we calculate that (Li⁺ + e⁻) pairs bind to adsorbed O₂ ions on MoS₂ only for potentials lower than 1.19 V vs. Li/Li⁺. Such a mechanism would suggest higher discharge overpotentials than are experimentally observed, and is thus consistent with the solution-phase discharge product formation described in our previous work [585].



Figure G.11.: Potential-dependent charge state of the nanoflake cluster models. DFT calculations suggest that hole formation becomes favorable under OER potentials, consistent with the charge state used for the diabatic charge transfer mechanism for OER described in Chapter 13.

H. SUPPLEMENTARY INFORMATION FOR "A LONG-CYCLE-LIFE LITHIUM-CO₂ BATTERY WITH CARBON NEUTRALITY"

H.1 Materials Preparation

 MoS_2 nanoflakes (NFs) were used as the active cathode materials in the Li-CO₂ cells. MoS_2 NFs were synthesized following a modified liquid exfoliation method [585, 242, 584]. Briefly, 300 mg of MoS_2 powder (Sigma Aldrich) was first dispersed in a 60 mL of 2-propanol (IPA) solvent and sonicated for 20 h using a sonication probe (Vibra Cell Sonics 130W).

H.2 Cell Assembly

Cathodes were prepared using MoS₂ NFs solution in IPA on the Toray carbon paper gas diffusion layer (GDL) followed by drying process at 80°C under vacuum for 24 hours. The loading of MoS₂ NFs was 0.1 ± 0.002 mg/cm². The liquid electrolyte was also prepared by dissolving 0.1 M lithium bis(trifluoromethane) sulfonamide (LiTFSI) in 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM BF₄)/dimethyl sulfoxide (DMSO) solution (vol: 25/75). For a cell assembly, presoaked glass microfiber filter separator (Whatman GF/D) with 35 μ L electrolyte was placed between the lithium chip (99.9%) as an anode and as-prepared MoS₂ NFs cathode on GDL in a Swagelok cell. All electrolyte preparations and cell assemblies were performed in an Ar-filled glovebox.

H.3 Characterization and Measurement

Galvanostatic charge/discharge tests were performed using MTI battery analyzer at various current densities in the range of 100, 500 and 1000 mA/g at room temperature. After cycling, the MoS₂ cathodes were recovered from the cells under Ar and were further characterized using X-ray Photoelectron Spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi), Raman spectroscopy (Renishaw inVia Reflex Raman microscope with a 532 nm laser and a 50x objective lens), Scanning Electron Microscopy (SEM, Raith e-LiNE electron beam lithography systems) and Transmission Electron Microscopy (TEM, aberration corrected JEOL ARM200CF equipped with a cold field emission gun and 1.2 Å spatial resolution). For XPS and Raman analysis, the Li-CO₂ cells were assembled using carbon-free MoS₂ NFs coated on the Al mesh to avoid possible interference of the carbon peak of our Toray carbon GDL in the analysis. Results for the XPS at 10^{th} charge and discharge cycles of the cathode are shown in Figure H.1.



Figure H.1.: The C 1s and Li 1s spectra show the X-ray Photoelectron Spectroscopy (XPS) results from the cathode surface including MoS_2 NFs coated on Al mesh after (a-b) the 10^{th} discharge, and (c-d) the 10^{th} charge cycle.

The DEMS experiment was performed in a custom-made Swagelok cell design. Details are provided below.

Figure H.2 shows the schematic of the cell integrated with DEMS through a transfer line with a 500 μ L standard volume loop. The cell is composed of a 0.5 mm stainless steel spacer, 0.25 mm thick Lithium chip, a 0.26 mm thick glassy fiber separator, a 150 μ m catalyst coated gas-diffusion layer and 55 μ m Aluminum Mesh Foil as a current collector. The cell configuration creates a 1 mm thick head space resulting in ~115 μ L head space. This results in a total volume of ~615 μ L (cell and transfer line) connected to the Kf-25 vacuum flange. A pressure gague was also directly mounted at the inlet of the cell to monitor cell and transfer line pressure.



Figure H.2.: A schematic of the Swagelok DEMS cell and its process flow diagram.

The cell head space volume was calibrated using the volume exchange technique. In this method, the assembled cell volume without electrolyte was calibrated by comparing the partial pressure variation with five different standard volume loops i.e., 50, 100, 250, 500 and 1000 μ L (purchased from Valco instrument) filled with ultra-high purity (UHP)Argon (99.99%) at known pressure [638].

The DEMS apparatus was also calibrated to determine CO_2 partial pressure using various vol% of CO_2 mixed in UHP Argon e.g., 3, 6, and 10 vol%. In brief, the cell was assembled inside the Ar-filled glove-box and directly connected to DEMS. Prior connecting to the DEMS, the cell and transfer line were flushed with Ar to remove all possible impurities. Then, the cell was filled with the known vol% of CO_2 at 1.5 bar e.g., 3, 6, and 10 vol%. Next, the DEMS valve was opened to inject the existing gas in the transfer line into the DEMS, the cell outlet valve was closed at this stage. The partial pressure of CO_2 was monitored at this stage until reaching to its initial baseline. Then, the outlet value of the cell was opened to expand the CO_2 to the transfer line and directly injected to the DEMS. Figure H.3 shows the calibration curve of CO_2 and the fitted line with respect to number of the moles of the CO_2 considering zero mole of CO_2 at the reference line. The calibration has been made by comparing the partial pressure variation of CO_2 with respect to the reference baseline. This is linearly proportional to the number of moles of CO_2 using ideal gas law.

Table H.1.: Mole quantities of CO₂ before and after charge experiment.

Mole of CO_2 before	Mole of CO_2 after	Consumed moles	e^{-}/CO_{2}
discharge	discharge	of CO_2	ratio
$3.12 \mathrm{x} 10^{-6}$	$1.465 \mathrm{x} 10^{-6}$	$1.655 \mathrm{x} 10^{-6}$	4.05



Figure H.3.: DEMS calibration points and corresponding fitted line based on different CO₂ concentrations.

For discharge reaction, the cell and DEMS capillary were first purged with argon to remove any impurities. The cell was then purged with pure CO_2 (99.99%, research grade, Praxair) for 15 minutes to saturate the electrolyte with CO_2 . The head space of the cell was then filled with 1.5 bar pure CO_2 (99.99% research grade, Praxair) and directly injected to the DEMS. The same experiment was performed after an hour discharge process (Figure H.4). The calibration curve was then used to calculate the number of CO_2 molecules based on the variation of CO_2 partial pressure before and after the discharge process.



Figure H.4.: Differential Electrochemical Mass Spectrometry (DEMS) profile of the cell during the 1^{st} discharging process.

The charge reaction was also studied by in-situ monitoring of evolved gasses during the first cycle using DEMS (Figure H.5). The experiment was performed at the current density of ~150 mA/g. In-situ measurements of O₂, CO₂, and H₂O signals were performed by Secondary Electron Multiplier (SEM) mode during the term of charging reaction. Our results indicate an average CO₂ evolution rate of 4.14×10^{-12} moles/s, which results in $4.07 \text{ e}^{-}/\text{CO}_{2}$ ratio during charging reaction [679, 680].

In order to investigate the possibility of oxygen evolution, the partial pressure of oxygen was also monitored during the first charge process. As shown in Figure H.6, there is no change in partial pressure of oxygen throughout the charging process which is an indication of no evolved gas other than CO_2 .



Figure H.5.: Differential Electrochemical Mass Spectrometry (DEMS) profile of the cell during the 1^{st} charging process.

Table H.2.: Mole quantities of CO₂ before and after charge experiment.

Mole of CO ₂ before	Mole of CO_2 after	Evolved CO_2	e^{-}/CO_{2}
charge	charge	moles	ratio
$34.68 \text{x} 10^{-8}$	$6.375 \mathrm{x} 10^{-7}$	$2.9 \mathrm{x} 10^{-8}$	4.07



Figure H.6.: Differential Electrochemical Mass Spectrometry (DEMS) profile of the cell during the 1^{st} charging process.

H.4 X-ray Diffraction

X-ray diffraction experiment was performed using Rigaku Smartlab instrument. In order to perform X-ray diffraction, the battery was ran for 10 consecutive cycles and stopped at the end of discharge process. Then, cathode material was taken out from cell and was firstly washed with dimethyl carbonate and sequentially dried and stored in an Argon glove box for 24 hours prior to testing. Diffraction pattern was obtained at 40 KV and 160 mA with 0.03 step and 5 deg/min between 10° to 60° 2 Θ range (Figure H.7). The peaks located at 26° and 54° refer to substrate [681, 682].



Figure H.7.: XRD pattern of discharged cathode after 10 cycles.

H.5 Electron Energy Loss Spectroscopy of the Cathode

We performed electron energy loss spectroscopy (EELS) of the C K-edge which can discriminate between crystalline and amorphous forms of carbon. We note that direct imaging of carbon is difficult due to beam sensitivity and the similarity in contrast between the lithium carbonate and carbon fractions. EELS maps were taken from many different areas of the specimen. Maps were used to minimize damage, and the extracted spectra were averaged to improve the signal to noise ratio. EELS revealed the presence of both amorphous and crystalline forms of carbon in the sample. EELS spectra taken from two different regions are shown in Figure H.8. The upper panel corresponds to amorphous carbon, as can be seen in the References [679, 680] and from the EELS atlas data (Gatan, Inc.). The lower panel, taken from the region outlined in the inset, shows additional features associated with more crystalline carbon, highlighted by the arrows, which appear due to electronic transitions associated with covalent bonding [679, 680].

While some variation between the presence of amorphous and crystalline carbon was observed, it is difficult to correlate this with a particular feature of the sample. We note that in sample preparation, the sonication step effectively pulverizes the specimen, meaning that components are redistributed somewhat and phases that may have been adjacent to each other prior to processing will likely be separated. In order to ensure all components could be detected, relatively large areas were examined in the spectra. This also allows the dose and dose rate to be limited to limit electron beam damage, which must be considered for these specimens as they are susceptible to damage.



Figure H.8.: Averaged, normalized EELS spectra of the carbon K edge extracted from EELS maps of the marked areas in the insets. The scale bar is 200 nm. A) shows an EELS spectrum from a portion of the sample showing amorphous carbon. B) EELS from a portion of the spectrum showing a mixture of crystalline and amorphous character.

H.6 Electrochemical Impedance Spectroscopy

EIS was done using a Voltalab PGZ100 Potentiostat. The amplitude of Signal was kept at 10mV and the frequency range was set 10KHz to 100MHz. Figure H.9 shows the resistance of cathode material for Pristine, 10^{th} charge and discharge cycle. As can be seen, the cell, in charged state, shows the same behavior to pristine condition after 10 consecutive cycles. These results are consistent with other characterizations confirming the reversibility of products formation and decomposition.



Figure H.9.: Averaged, normalized EELS spectra of the carbon K edge extracted from EELS maps of the marked areas in the insets. The scale bar is 200 nm. A) shows an EELS spectrum from a portion of the sample showing amorphous carbon. B) EELS from a portion of the spectrum showing a mixture of crystalline and amorphous character.

H.7 Nuclear Magnetic Resonance Experiments

To examine the stability of electrolyte, we performed ¹H NMR and ¹³C NMR experiments on the fresh and used electrolyte (after 100 discharge/charge cycles) by using a 500 MHz Agilent system. All the samples were prepared in the glove box with less than 1 ppm of oxygen. In order to deuterate the electrolyte, tetrahydrofuran (THF-d8) was used. The electrolyte consists of EMIM-BF₄ and DMSO with the ratio of 1 to 3 and 0.1 M LiTFSI salt. The used electrolyte was extracted from the cathode and separator after running the cell for 100 cycles. The spectra for ¹H NMR and ¹³C NMR was obtained after 256 scans from 0-14 ppm and 0-250 ppm respectively. Results shown in Figure H.9 indicate that there is no evidence of electrolyte degradation for the used electrolyte.



Figure H.10.: Nuclear Magnetic Resonance (NMR) results of fresh and used electrolytes at (a)¹H NMR and (b)¹³C NMR in THF-d8

H.8 Deep Discharge Behavior



Figure H.11.: Deep discharge profiles under different applied current densities of (a)100 mA/g, (b) 500 mA/g, and (c) 1000 mA/g.

H.9 Periodic Density Functional Theory Calculations

Periodic, plane-wave density functional theory calculations are performed using the VASP code [160, 161, 168] to investigate CO₂ reduction mechanisms on the edge of the MoS₂ catalyst. We use a nanoribbon model with a thickness of 4 layers with 6 Mo atoms on the Mo edge and 12 S atoms on the S edge. We explicitly include two (EMIM⁺ + e⁻) pairs adsorbed on the Mo edge, as in our previous work [585], exposing isolated Mo atoms as the catalytically active site. We use the generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE) as the exchange and correlation functional [163], and the valence states are expanded in a plane-wave basis set up to 400 eV. Electronic energies are converged to 10^{-4} eV and the cell is subject to full ionic relaxation (at a fixed cell volume) with a force criterion of 20 meV Å⁻¹.

H.10 Constrained Density Functional Theory Calculations

Constrained density functional theory (CDFT) calculations [122, 123] are performed to assess the adiabaticity of charge transfer during CO₂ reduction. We use the CDFT version recently implemented [127, 126] in the QUANTUM-ESPRESSO code [614] to calculate electronic coupling between the initial and final diabatic electronic states of a spatially separated MoS₂ nanoflake (NF) cluster model and CO₂ molecule. PBE is used as the exchange and correlation functional [163]. The core states are modelled with the optimized norm-conserving Vanderbilt (ONCV) pseudopotentials and the valence states are expanded in a plane-wave basis set with an energy cutoff of 80 Ry (1088 eV) [615, 616]. The charge separation between donor and acceptor states is converged to a tolerance of 10^{-5} electrons.

The NF cluster models are modified from that used by Huang et al. [613] in order to accompany the adsorbed (EMIM⁺ + e⁻) pairs on the Mo-terminated edge as in the periodic model used in this and previous work [585]. The dichalcogenide portion of the cluster model has stoichiometry Mo₁₅S₂₁ and the calculations are performed in a cubic box with dimensions of 32 Å. The Brillouin zone is sampled using a single k-point (Γ). We also use these models to estimate reduction potentials of adsorbed CO₂ using standard DFT, in which case we apply a jellium background charge [674] to compensate charged systems, and total energies are determined using the Makov-Payne correction [675]. The reduction potential is computed as

$$E_{red} = -\frac{\Delta G_{red}}{F} - 1.24V \tag{H.1}$$

where ΔG_{red} is the free energy of reaction for the addition of an electron to the system, F is the Faraday constant, and the correction by -1.24 V converts to the reduction potential to the scale of the Li/Li⁺ reference electrode, through adjustment of the electron free energy reference to the proton solvation and the reversible hydrogen electrode [676, 677, 678].

H.11 DFT Calculations on a Model System for a Li₂CO₃/C Interface

To investigate the interaction of amorphous carbon with Li_2CO_3 , *ab-initio* molecular dynamics (AIMD) simulations were performed using the VASP code [160, 161]. The exchange-correlation functional was treated within the generalized gradient approximation (GGA) of Perdew-Burke- Ernzerhof (PBE) [163] with Γ -point Brillouin zone sampling and a 600 eV plane-wave energy cutoff. A time step of 1 fs was used for the integration of the equations of motion and a 10^6 eV energy convergence criterion. An NVT-ensemble simulation at the temperature T=1000 K was employed. For the initial amorphous carbon structure, we employed the melt-quench method using the AIREBO potential to generate atomic configurations of diamond-like carbon (DLC) with high sp^3 bond fraction (85%) similar to that found in previous experiments [683]. A computational supercell with dimensions 3.6 nm x 3.6 nm x 3.6 nm (8000 C atoms) is used in which the positions of the carbon atoms correspond to a perfect diamond lattice. Periodic boundary conditions are employed along all directions. All the classical molecular dynamics simulations are performed using LAMMPS [684]. The system is first equilibrated at 9000 K (beyond the melting point of diamond) within a canonical ensemble for 1 ns. The molten system is then quenched to 300 K over a period of 100 ps; thereafter the system is equilibrated at 300 K for 1 ns under constant pressure conditions to obtain DLC. Finally, we cut a spherical cluster of ~ 1.4 nm diameter (152 atoms) from the prepared DLC block and deposited it on the Li₂CO₃ surface to perform AIMD simulations.

H.12 Investigation of Reaction Pathways for Sequential Oxidation and Decomposition of a Cluster Model of Li₂CO₃/C for the Reaction $2Li_2CO_3 + C \rightarrow 3CO_2 + 4Li^+ + 4e^-$

DFT calculations have been carried out to investigate various reaction pathways for sequential oxidation and decomposition of a cluster model of $\text{Li}_2\text{CO}_3/\text{C}$ (2Li₂CO₃+ $\text{C} \rightarrow 3\text{CO}_2 + 4\text{Li}^+ + 4\text{e}^-$). We used a C₅₄ cluster model for amorphous carbon (with 18 hydrogens on the edges) and a single carbon adatom (representing a defect site)



Figure H.12.: Model showing possible restructuring of amorphous carbon Li_2CO_3 interface that occur during charge: a, Initial structure of amorphous carbon cluster and a Li_2CO_3 surface, b, AIMD results showing formation of interface of carbon cluster with Li_2CO_3 , c, Structure with removal of $2Li_2CO_3$ and C from (b); d, AIMD results showing restructuring of the amorphous carbon Li_2CO_3 interface after removal of two Li_2CO_3 molecules.

as shown in Fig. 14.4e in the Chapter 14. The calculations were carried out at the B3LYP/6-31+G(2df,p) level of theory with the SMD solvation model. The energies are relative to Li/Li^+ . Sequential reactions involving oxidation, loss of Li^+ and CO_2 elimination were investigated in different orders. One of these reaction cycles with favorable energetics is shown in Figure H.4g.

Table H.3.: Possible reaction free energy in different solvents. ^{*a*} denotes a neutral doublet and ^{*b*} represents a neutral triplet. Gas phase calculations are performed at G4MP2 level of theory. Solvation energy calculations are performed at B3LYP/6-31G(2df,p) level of theory using SMD solvation model.

		$\Delta G(eV)$				
Entry	Reaction	Gas phase	Diethyl ether	Acetone	DMSO	Water
1	$2\mathrm{Li}^a + 2\mathrm{CO}_2 \rightarrow$	-4.22	-4.61	-4.81	-4.82	-5.25
	$Li_2CO_3 + CO$					
2	$2\mathrm{Li}^a + \mathrm{CO}_2 \rightarrow$	-1.55	-2.00	-2.25	-2.22	-2.91
	$Li_2O + CO$					
3	$4\mathrm{Li}^a + \mathrm{CO}_2 \rightarrow$	+2.75	+1.82	+1.31	+1.36	-0.07
	$2\mathrm{Li}_{2}\mathrm{O} + \mathrm{C}^{b}$					
4	$2\mathrm{Li}^a + \frac{3}{2}\mathrm{CO}_2 \rightarrow$	-1.30	-1.70	-1.91	-1.91	-2.37
	$Li_2CO_3 + C^b$					

VITA

Robert Warburton was born on April 13th, 1990 in Canton, Ohio to Scott and Lori Warburton, and has four younger siblings, Jillian, Abigail, Matthew, and Isabelle. He married Michelle Warburton (Rasicci) on August 1st, 2015 in North Canton, Ohio. He has a dog named Louie and his favorite baseball player in Jim Thome.

He earned a Bachelor of Science degree with Honors Research Distinction in Chemical Engineering from The Ohio State University in 2014. While at Ohio State, he began his research career working with Prof. Aravind Asthagiri using DFT simulations to understand the role of solvation on oxygen reduction reaction intermediates on nitrogen-doped graphene electrocatalysts. He began his graduate studies in the Davidson School of Chemical Engineering at Purdue University in August 2014. Under his advisor, Prof. Jeffrey Greeley, his graduate research involved the application of DFT-based computational methods toward applications in surface and interfacial science in energy storage materials within the Center for Electrochemical Energy Science. Through a Department of Energy Office of Science Graduate Student Research Fellowship, he also spent eight months working in the Materials Science Division at Argonne National Laboratory under the guidance of Dr. Larry Curtiss, where his fellowship research focused on modeling charge transfer kinetics in energy storage materials. He will receive his Ph.D. in Chemical Engineering in December 2019 and afterward will begin a research position as a postdoctoral associate under the supervision Prof. Sharon Hammes-Schiffer in the Department of Chemistry at Yale University where he will study proton-coupled electron transfer chemistry at electrochemical interfaces. He plans to pursue a career in academia, applying computational techniques combined with electronic structure, thermodynamic, and kinetic rate theories to the study of energy storage and conversion materials.

PUBLICATIONS

Notes: ‡ = equal contribution; * = corresponding author(s)

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