

ABSTRACT

Title of Dissertation: COMPUTATIONAL STUDY OF SOLID-CATHODE INTERFACES AND COATINGS FOR LITHIUM-ION BATTERIES

Adelaide M. Nolan
Doctor of Philosophy, 2021

Dissertation Directed by: Professor Yifei Mo
Dept. of Materials Science and Engineering

All-solid-state batteries, which use a solid electrolyte, are a promising technology for improving the safety of currently commercialized batteries based on liquid electrolytes. However, to enable all-solid-state batteries with high energy densities, we need to integrate solid electrolytes with high-voltage and high-capacity cathodes. The interface between solid electrolytes and high-energy cathodes is often thermodynamically unstable, which can lead to reactions and the formation of decomposition products which cause high interfacial resistance. One solution to improve resistance and poor contact at the interface is the application of a coating layer, which can act as a physical barrier between the solid electrolyte and the cathode and prevent decomposition.

I performed first-principles computation and thermodynamic analyses to study the thermodynamic stability and Li-ion transport in coating layers for solid-solid interfaces. I used a high-throughput systematic analysis of phase diagrams based on a materials database to study the decomposition energy and products of reactions

between coating layer chemistries and layered and high-voltage cathodes. My thermodynamic stability analysis revealed that the strong reactivity of lithiated and delithiated cathodes greatly limits the possible choice of materials that are stable with the cathode under high-voltage cycling. The computation results reaffirmed previously demonstrated coating chemistries and identified several new chemistries for high energy cathodes. In particular, I found that lithium quaternary phosphates and lithium ternary fluorides were two promising materials classes, with good stability with high-voltage cathodes and sufficient lithium content to enable Li-ion transport.

I next studied the interface stability between solid electrolytes and common cathodes. The lithium garnet solid electrolytes are promising among known solid electrolytes because of their high temperature stability, good stability in air and moisture, and wide electrochemical window, but have limited stability against a variety of cathodes. To guide the development of coating layers for the garnet-cathode interface, I analyzed the stability of garnet with families of lithium ternary oxide (Li-M-O) coating chemistries and revealed factors governing the stability of materials with LLZO garnet and high-energy NMC cathodes. In addition to classifying known coating layers, I provide detailed guiding tables for coating layer selection and identify and discuss several new promising coating layer materials for stabilizing the interface between garnet and high-capacity cathodes.

The crystal structure of a coating material plays a major role in transport properties such as Li-ion diffusivity and conductivity, which are required in the coating layer to achieve low interfacial resistance and good battery performance.

Alumina is widely used as a coating layer in batteries and other applications, and has decent stability against a wide range of solid electrolytes and cathodes. I used first-principles molecular dynamics simulations and nudged-elastic band calculations to study Li-ion transport and migration barriers in several crystalline polymorphs and amorphous alumina. I found structural features in the Al framework, specifically the Li-Al distance variation, determined migration barriers in both crystalline and amorphous structures. Based on this structure-property relationship, I investigated how Li content, defects and off-stoichiometry changed the Li-ion transport within selected polymorphs, and suggest lowering the Al-ion content as a strategy to achieve stable and Li-diffusive alumina coatings.

With this work, I provide an understanding of trends in stability between coating layers, cathodes, and the garnet solid electrolyte, new promising coating layer materials and families, and rational guidance for coating layer design and interfacial engineering for energy dense all-solid-state batteries. My thesis provides guiding principles for selecting materials with long-term cycling stability and good Li diffusivity as coatings for energy dense Li-ion batteries.

Computational Study of Solid-Cathode Interfaces
and Coatings for Lithium-Ion Batteries

by

Adelaide M. Nolan

Dissertation submitted to the Faculty of the Graduate School of the
University of Maryland, College Park in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
2021

Thesis Committee:

Professor Yifei Mo, Chair/Advisor

Professor Eric Wachsman

Professor Liangbing Hu

Dr. Michelle Johannes, Naval Research Laboratory

Professor Chunsheng Wang, Dean's Representative

© Copyright by
Adelaide Mei-Chun Nolan
2021

Acknowledgments

My advisor, Dr. Yifei Mo, deserves a lot of credit for taking me on as a student given my background (or lack thereof). I came to my group not knowing anything about lithium-ion batteries or solid electrolytes, or having done any research projects. Now, almost at the end of my PhD, I appreciate how little I knew then, and paradoxically, I can appreciate how little I know now. I've gotten far enough up the mountain that I can see how much we have yet to discover. I am really grateful to everyone who broke trail before me, taught me to find my own way, and helped me to climb and hike through difficult parts.

One of those trailblazers is Dr. Yizhou Zhu, who took me on as a mentee when she was a senior graduate student in the group. She sat with me and patiently explained basic concepts—chemical potential, how we calculate phase diagrams, how to navigate the Materials Project—probably many times over. She was incredibly helpful as a teacher and a friend, and I'm really glad she was there to teach me when I first started. Thank you, Yizhou.

I also want to thank Dr. Michelle Johannes, who directed my most recent project on Li^+ transport in Al_2O_3 . She's owed many kudos for taking on a remote summer intern during a global pandemic (and navigating extensions into a fall, then winter, then spring intern), for fielding my many questions and providing insights,

and for shielding me from bureaucracy. Michelle, thanks for all your help, for sharing the alumina project and coaching me through various errors in VASP, for your sense of humor, and for your friendship. It's been wonderful to work with you this past year.

As I've mentioned, I'm so glad my advisor, Professor Mo, was willing to take me on as a student. He's patiently coached me through my beginnings as a graduate student, waded through my inept early drafts, and taught me to question, take initiative, and be a researcher in my own right. He's also been the source of many incredible opportunities I've had throughout my PhD. He's not only encouraged me to apply to fellowships and present at conferences, but he's also given feedback and worked with me on every application and presentation. I've been the beneficiary of his strong network in the battery community as well—his connections have opened doors to collaborations with other experimental groups and provided the opportunity for me to intern at NRL. Professor Mo, you have my deep gratitude for all the countless hours you've invested in me and my growth.

I've made many other friends at UMD that have helped me throughout my PhD, and I'm grateful to them all. Thanks also to everyone in Professor Mo's group, past and present, including Dr. Xingfeng He, Dr. Qiang Bai, Alex Epstein, Pei-yin Lee, Luo Zhe, Shafiqul Islam, Dr. Shuo Wang, Dr. Menghao Yang, and Alex Hall, for your discussions, help, and friendship. Special thanks to my classmate and office mate Yunsheng Liu, who started the same time as me. Thanks for always answering my questions about methodology, how to interpret strange data, and offering ideas on research direction and philosophy alike.

Thanks to Glenn, my partner and dearest friend, for your experimental perspective on various questions I've had throughout my PhD, and for your love and respect. Thanks for your willingness (or for dragging me out) to run, play games, orienteer, disc golf, and for your companionship.

To my family—my grandparents, aunts, uncles, and cousins—thank you for your support. Thanks to Mei-An especially for talking, listening, and for the laughs.

Finally, thank you to my parents for their love and support, for housing me, feeding me, telling me that quitting in the first month of my PhD would be ridiculous, and helping me to succeed all those years before that. You're the best.

Table of Contents

Acknowledgements	ii
Table of Contents	v
List of Tables	vii
List of Figures	viii
List of Abbreviations	x
Chapter 1: Introduction	1
1.1 Stability of solid-state chemistries with high-voltage cathodes	3
1.2 Stabilization of the garnet-cathode interface	5
1.3 Li^+ transport in Al_2O_3 coating	6
1.4 Outline of thesis	8
Chapter 2: Computational methods	9
2.1 Thermodynamic analyses: stability of two materials in contact	9
2.2 Density functional theory calculations: Li-ion migration in Al_2O_3	12
2.2.1 Static relaxation parameters	12
2.2.2 Crystalline supercell size and parameters	13
2.2.3 Creation of amorphous Al_2O_3 and comparison to experiment	14
2.2.4 Li^+ site identification	15
2.2.5 NEB parameters	16
2.2.6 AIMD simulations	16
2.2.7 Analysis of site and pathway	18
Chapter 3: Stability at the interface with high-voltage cathodes	20
3.1 Thermodynamic stability of two materials in contact	21
3.2 Stability of lithiated and delithiated LiCoO_2 with lithium ternary oxides	23
3.3 Comparisons between reactivity of LiCoO_2 and of high-voltage cathodes	26
3.4 Influence of Li content of coating chemistry	27
3.5 Comparison of binary oxides, Li polyanion oxides, and Li ternary fluorides	28
3.6 Discussion	30
Chapter 4: Stability at the interface between LLZO and NMC	33

4.1	Garnet-cathode interface stability	36
4.2	Materials stable with garnet and NMC	41
4.3	Stability between LLZO and the Li-M-O composition space	46
4.4	Stability between the cathode and Li-M-O composition space	50
4.5	Discussion	52
Chapter 5: Li transport in Al_2O_3		58
5.1	Li^+ sites and dilute Li^+ migration in α , κ , γ , θ , and amorphous Al_2O_3	61
5.2	Effect of Li^+ concentration in Al_2O_3	70
5.3	Li^+ migration in defected Al_2O_3	76
5.4	Discussion	79
Chapter 6: Conclusions and future work		83
6.1	Conclusions	83
6.2	Future work	85
Chapter 7: Publications and presentations		87
7.1	Publications	87
7.2	Presentations	90
Appendix A: Further analysis on stability of coatings with cathodes		92
Appendix B: Stability of materials with garnet and NMC		96
Appendix C: Li-ion migration in Al_2O_3		104
Bibliography		111

List of Tables

4.1	Decomposition energy and phase equilibria of cathodes with LLZO	39
4.2	Li-M-O materials stable with LLZO and NMC 111	45
B.1	Stability of LLZO–NMC 111 pseudo-binary under changing μ_{Li}	102
B.2	Stability of LLZO–NMC 111 pseudo-binary under changing μ_O	103

List of Figures

1.1	Schematic illustration of solid-state battery	3
2.1	RDFs of am- Al_2O_3	14
2.2	RDFs of Li-O and Li-Al spectra	19
3.1	Thermodynamic stability between two materials	22
3.2	E_d of Li-M-O with lithiated and delithiated cathodes	24
3.3	Schematic of Li source and Li sink	28
3.4	Reactivity of Li ternary fluorides and comparison of coating layer classes	29
4.1	Heatmap of LLZO, NMC, and d-NMC with ternary oxides	42
4.2	Li-Al-O and Li-Nb-O ternary heatmaps	47
4.3	Heatmaps of stability between LLZO and selected Li-M-O	48
4.4	Li-Al-O ternary heatmap with NMC	51
5.1	Li-ion sites in crystalline Al_2O_3	63
5.2	Theta and amorphous Arrhenius relation	65
5.3	Energy barrier in crystalline alumina vs. LDV	67
5.4	Li-ion transport in amorphous alumina	69
5.5	Effect of increasing Li^+ concentration in α , θ , and am- Al_2O_3	71
5.6	Al^{3+} off-stoichiometry and Li^+ migration.	77
A.1	Swarmplot of cathode stability with Li-M-O	92
A.2	Stability of binary oxides with cathodes	93
A.3	Stability of polyanion oxides with cathodes	93
A.4	Boxplot of stability of binary oxides with cathodes	94
A.5	Cathodic and anodic limits of coatings	94
A.6	E_d with LCP vs electrochemical limit for selected oxides	95
B.1	Binary oxides stability with LLZO and NMC	96
B.2	Polyanion oxides stability with LLZO and NMC	97
B.3	Ternary halides stability with LLZO and NMC	98
B.4	Boxplot of garnet stability with materials classes	99
B.5	Garnet and cathode μ_{Li} windows	99
B.6	Stability of Li-Al-O with LNO, LMO, and LCO	100
B.7	Li-Al-O and d-NMC ternary heatmap	100
B.8	Li-Nb-O and LLZO electrochemical stability	101

B.9	Li-Al-O electrochemical stability	101
C.1	Defect calculations for α and θ	104
C.2	Li migration barrier and structure parameters	105
C.3	Concentration dependence in θ -Al ₂ O ₃	105
C.4	NEB for θ surface	106
C.5	MD in θ -Al ₂ O ₃	106
C.6	NEB in amorphous Al ₂ O ₃	107
C.7	Connected migration path in amorphous surface	107
C.8	NEB barrier in amorphous surface	108
C.9	MSD of amorphous surface	108
C.10	Effect of O ₂ deficiency	109
C.11	Barrier for hopping in vacancy cluster in α -Al ₂ O ₃	109
C.12	NEB of amorphous with Al deficiency	110

List of Abbreviations

AIMD or MD	<i>ab-initio</i> molecular dynamics
DFT	Density Functional Theory
E_a	Activation energy, energy of migration barrier
E_d	Energy of decomposition (thermodynamic)
LCO	LiCoO ₂ , lithium cobalt oxide
LCP	LiCoPO ₄ , lithium cobalt phosphate
LDV	Li-Al distance variation
LiB	Lithium-ion battery
LLZO	Li ₇ La ₃ Zr ₂ O ₁₂ , lithium lanthanum zirconium oxide
LMNO	lithium manganese nickel spinel
LNO	LiNiO ₂ , lithium nickel oxide
MSD	Mean squared displacement
NCA	Lithium nickel-cobalt-aluminum oxide
NEB	Nudged elastic band (calculation)
NMC	Lithium nickel-manganese-cobalt oxide
RDF	Radial distribution function
SE	Solid electrolyte

Chapter 1: Introduction

Lithium-ion batteries (LiBs) power the majority of the world’s smartphones, laptops, and electric vehicles. These LiB operate by the intercalation of graphite anodes and layered oxide cathodes [1]. The discovery and conceptualization of this mechanism, fundamental to battery development, was awarded the 2019 Nobel Prize in Chemistry [2]. Over three decades of research, major energy density gains have been achieved through optimization of cathode composition, manufacturing processes, battery management systems, and tuning of salts and solvents in the electrolyte, but modern commercial LiBs are still largely based on similar chemistries using liquid electrolytes and intercalation electrodes [1, 3]. These chemistries often suffer from safety issues, and further potential increases in energy density are limited [4–6]. To surpass the limits of traditional chemistries, one potential direction is to implement energy dense electrodes such as the Li metal anode and high-voltage cathodes using solid electrolytes, which are Li-ion conducting ceramics regarded to have better compatibility with these energy dense electrodes than liquid electrolytes [7].

Although the implementation of high-voltage cathodes will enable more energy dense batteries, most high-voltage cathodes are reactive with the electrolyte, includ-

ing solid electrolytes, and their reaction will cause the formation of decomposition products that can cause capacity fade and performance degradation as the battery cycles [6, 8, 9]. Coating layers, which can be applied to the cathode before battery assembly, have been shown to prevent these decomposition reactions by acting as a physical barrier or chemically stable interlayer between the electrolyte and the electrode [10, 11]. However, coating layer selection often relies on trial-and-error for a given materials system, and there is a lack of how different coating chemistries affect their stability at the interface. To guide coating layer selection for a given chemical system, we need a fundamental understanding of the reactions between the coating layer, the cathode, and the electrolyte, accounting for how changes in chemistry and composition of the coating and cathode will affect their interfacial stability and decomposition products. Further, by understanding the relationships between the coating layer structure and the ionic transport, we can develop rational design strategies to optimize coating layer performance.

Buried solid-solid interfaces are difficult to study and characterize in experiments. In this thesis, I use computational modeling to analyze the thermodynamic stability and decomposition products at the interface between coating layers, cathodes, and solid electrolytes, and the relationship between coating layer structure and ionic transport. I demonstrate how we can apply our understanding to provide guidance for coating layer selection, design, and processing.

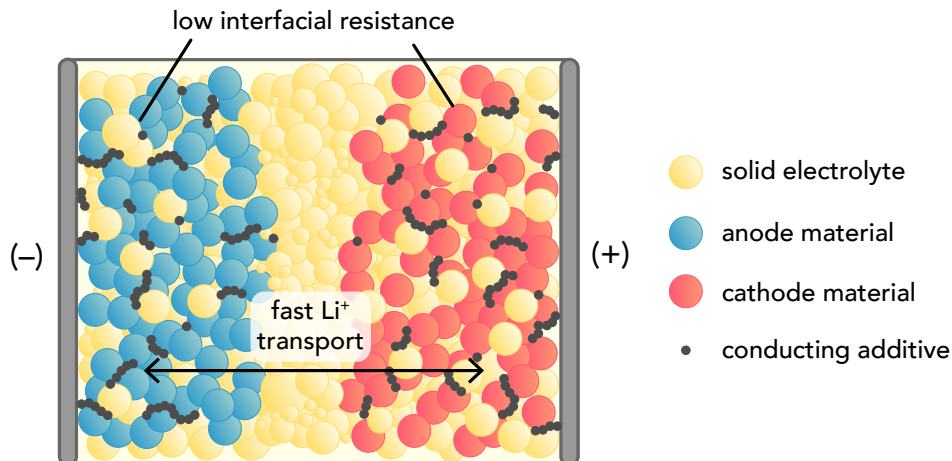


Figure 1.1: Schematic illustration of a solid state battery, depicting two key requirements for good performance: (1) low interfacial resistance between electrolyte and cathode, and (2) good ionic transport across the interface. The properties of applied coating layers are key for successful, long cycling all-solid-state batteries. Reproduced from Ref [12].

1.1 Stability of solid-state chemistries with high-voltage cathodes

Increasing demand for high capacity, long-cycling batteries, such as in electric vehicles or portable electronic devices, requires improvements in the energy density of current LiB systems. One route to improved energy density is to use high voltage or high-energy cathode materials, which widen the operating voltage range or increase the capacity of the battery [13]. Several high-energy cathode materials, such as nickel-rich $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ (NMC) and $\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$ (NCA) have been adopted to increase the energy density and capacity of fuel cells beyond those based on LiCoO_2 (LCO) [14, 15]. High-voltage cathodes such as spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ or olivine LiCoPO_4 , which discharge to a higher voltage than LCO, are also used to increase the energy density of full cells [8, 16].

However, most high-energy cathodes have poor compatibility with other com-

ponents of the cell, reacting at high voltages or delithiated states. High-energy cathodes often have oxidation limits beyond the 2 – 4 V electrochemical window of liquid electrolytes, which means that they tend to react and oxidize the electrolyte as cycling proceeds. These reactions lead to the buildup of decomposition products that can cause capacity fade and eventual failure of the battery [17–19].

Applied coating layers can block direct contact between the cathode and electrolyte and prevent undesirable side reactions or transition metal dissolution of the cathode into the liquid electrolyte. Binary oxide coating layers such as Al_2O_3 , TiO_2 , and SiO_2 have been demonstrated to improve the cycle life, Coulombic efficiency, and cyclability of high-voltage cathodes in full cells [20–22]. Solid electrolyte materials have also been explored as coating layers for high-voltage cathodes, but reactions between the cathode and solid electrolyte have been reported [17, 18, 23, 24]. To design energy dense batteries with long-term stability, systematic understanding and guidance for coating layers that are stable during electrochemical cycling with high-voltage cathode chemistries is still needed.

In Chapter 3, I use thermodynamic analyses to understand what factors affect the stability of materials in contact with the cathode and what types of materials are stable with given cathodes under high-voltage cycling. I investigate the stability of a wide range of materials with high-voltage cathodes and describe the trends in the stability of the lithiated and delithiated cathodes and high-voltage cathodes, and how stability changes across different coating layer materials classes and chemistries. I provide general guidelines for the stability between the coating and the high-voltage cathodes, and highlight particular solid-state chemistries that may be strong

candidates as coating layers.

1.2 Stabilization of the garnet-cathode interface

Currently commercialized LiB are based on liquid electrolytes comprised of a lithium salt and an organic solvent. The organic solvent is flammable and has been deemed responsible for several well-documented thermal runaway events and safety issues of LiB. A class of inorganic ceramic Li-ion conducting materials known as solid electrolytes have garnered attention as a potential replacement for the liquid electrolyte and a route to safer and more energy dense LiB [4,25]. Several categories of solid electrolytes are being explored, including high Li-conductivity sulfides such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) [26], oxides such as $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) [27,28], and most recently halides with wide electrochemical windows such as Li_3YCl_6 and Li_3YBr_6 [29].

In particular, garnet-structured LLZO is one of the most promising known solid electrolytes due to its relative stability in moisture and air compared with sulfides, its high Li conductivity [27,28], and its good compatibility with the Li metal anode [30–34]. However, the integration of LLZO with high-energy cathodes is still a significant challenge for the development of a long-cycling all-solid-state battery. High-temperature sintering, which is commonly required during assembly to provide a good bond between LLZO and the cathode, also results in the formation of secondary phases and decomposition products at the LLZO-cathode interface [35–39]. This reactivity has also been observed in computational studies of the

interface between garnet and cathodes [40, 41].

Again, coating layers offer a solution. A number of coating layer chemistries have been identified to improve cycling life and lower interfacial resistance between LLZO and cathodes such as LLZO or NMC [42–45]. To achieve long-term thermodynamic stability, coating layers applied to the garnet-cathode interface should be stable with Li garnet and the lithiated and delithiated cathode. However, current understanding of the effects of materials chemistry, lithium content, and composition of the coating layer on its stability at the interface is limited. In Chapter 4, I conduct a comprehensive study on the thermodynamic stability between LLZO, NMC, and ternary oxide coating layer chemistries. I focus on the high-energy cathode NMC as the cathode chemistry, which is needed to achieve high energy density in all-solid-state batteries. I use our insights to offer guidance for the selection of coatings and further development of interfacial engineering to enable energy dense all-solid-state batteries.

1.3 Li^+ transport in Al_2O_3 coating

Al_2O_3 is commonly used as a coating layer for battery electrodes due to its chemical and electrochemical stability, its cheap cost, and because it can be easily deposited using available conformal coating techniques, such as chemical vapor deposition (CVD) or atomic layer deposition (ALD). Al_2O_3 coatings have been used to reduce interfacial resistance and improve cycling life of high energy and high capacity cathodes [46–49]. In computational studies, Al_2O_3 coatings have also been predicted

to have good thermodynamic stability with a range of cathode materials [50, 51].

However, in addition to thermodynamic stability, coating layers also must exhibit decent Li diffusivity to enable good rate capability and performance. Al_2O_3 has a band gap higher than the operating voltage of most LiBs and extremely high activation barriers for Li^+ migration in the room-temperature α (corundum) and amorphous phases, making it hard to explain the evidence from cycling data that Li ions are moving through the coating layer. This discrepancy has prompted previous investigations of Li^+ migration in Al_2O_3 [52–55], but these studies have only focused on the room temperature crystalline phase, $\alpha\text{-Al}_2\text{O}_3$, and amorphous Al_2O_3 (am- Al_2O_3). Since some evidence suggests Al_2O_3 may not always be deposited in the amorphous phase, and may form crystalline domains in phases other than $\alpha\text{-Al}_2\text{O}_3$ [56], a study of how structure influences diffusion in Al_2O_3 is relevant to understanding how Li^+ moves through Al_2O_3 coatings, and will enable better understanding of diffusive coatings that can protect the cathode.

Computation can be used to identify and quantify how changes in the crystal structure affect macroscale properties such as Li^+ diffusivity and conductivity. In Chapter 5, I use first-principles computation, including nudged elastic band (NEB) and *ab-initio* molecular dynamics (MD) simulations to study Li^+ diffusion in α , am-, and metastable polymorphs γ , θ , and $\kappa\text{-Al}_2\text{O}_3$ to understand how structural differences affect Li^+ diffusion and to ultimately enable guidance on the development and synthesis of fast-conducting coating layers.

1.4 Outline of thesis

The aim of my thesis is to provide a theoretical understanding of the requirements for stable and high-conductivity coating layers, and thereby guide the discovery of new materials and the experimental development of solid-state batteries with high energy density. Computational modeling has been demonstrated to be a valuable tool for coating layer screening [50, 57], fast conductor materials discovery [58, 59], and prediction of interface stability [24, 51, 60]. I provide an overview of the computation methods used in this thesis in Chapter 2. In the following chapters, I investigate stability between solid-state chemistries and high-energy cathodes (Chapter 3), systematically analyze and identify coatings for the LLZO-NMC interface (Chapter 4), and explore the effects of crystal structure and Li concentration on Li-ion diffusion in Al_2O_3 coating layers (Chapter 5). In Chapter 6, I discuss conclusions and future work.

Chapter 2: Computational methods

In this chapter, I discuss the computational methods used in this thesis. The methods used can be broadly divided into two categories: (1) thermodynamic analyses used to study the thermodynamic stability of materials in contact and under applied voltage, and (2) first-principles density functional theory (DFT) calculations for analyzing kinetic properties such as migration energy and conductivity.

2.1 Thermodynamic analyses: stability of two materials in contact

To evaluate the decomposition energy and phase equilibria between two materials, we constructed compositional phase diagrams, which use computed materials energies from first-principles calculation databases. The database used in the calculations in this thesis is the Materials Project [61], accessed using the *pymatgen* Python package [62]. The version of the Materials Project database used for calculations throughout this thesis is v2020.9.14, and all calculations, including those reproduced from previously published papers, have been updated to be consistent with this version. To obtain the chemical stability between two materials A and B,

we considered a pseudo-binary with the composition

$$C_{pseudo-binary}(C_A, C_B, x) = xC_A + (1 - x)C_B \quad (2.1)$$

where C_A and C_B are the compositions of A and B, normalized to one atom per formula unit, and x is the molar fraction of A. In this study, the pseudo-binary was is a paired combination of material A and material B, where A and B were are a layered oxide cathode, coating layer, or the solid electrolyte LLZO. The energy of the pseudo-binary $E_{pseudo-binary}(A, B, x)$ is given by

$$E_{pseudo-binary}(A, B, x) = xE_A + 1 - xE_B \quad (2.2)$$

where E_A and E_B are the energies of materials A and B, respectively. This phase equilibria of the pseudo-binary is the lowest energy set of stable phases comprising the same composition and is identified in the compositional phase diagram. The decomposition energy is calculated as the energy of the phase equilibria (products), E_{eq} , minus the energy of the pseudo-binary (reactants):

$$\Delta E_D(A, B, x) = E_{eq}(C_{pseudo-binary}(C_A, C_B, x)) - E_{pseudo-binary}(A, B, x) \quad (2.3)$$

Since $\Delta E_D(A, B, x)$ includes the decomposition energy of material A or material B if they are not stable, $\Delta E_{D,mutual}(A, B, x)$ was calculated as

$$\Delta E_{D,mutual}(A, B, x) = \Delta E_D(A, B, x) - x\Delta E_D(A) - (1 - x)\Delta E_D(B) \quad (2.4)$$

where $\Delta E_D(A)$ and $\Delta E_D(B)$ are the energy above the hull of materials A and B, respectively. The minimum of $\Delta E_{D,mutual}(A, B, x)$ over the entire range of x from 0 to 1 was taken as the decomposition energy E_d used throughout this thesis. Heatmaps of the decomposition energy for cathode-coating and LLZO-coating interfaces, including the Gibbs triangle heatmaps, were constructed by finding the value of $\Delta E_{D,mutual}(A, B, x)$ for the cathode/LLZO substrate (A) and coating layer composition (B). All decomposition energies were normalized to per atom of the composition of the pseudo-binary. The software package python-ternary was used to construct visualizations of the Gibbs triangle heatmaps in Chapter 4 [63]. Additional details can be found in previous studies [24, 64].

We used grand potential phase diagrams to evaluate the electrochemical stability of a material mixture in equilibrium with applied potential ϕ [24]. As in previous studies, ϕ was referenced to the chemical potential of Li

$$\mu_{\text{Li}}(\phi) = \mu_{\text{Li}}^0 - e\phi \quad (2.5)$$

where μ_{Li}^0 is the chemical potential of Li metal. Given a phase with composition C, and energy E_C , grand potential phase diagrams provide the energy of the phase equilibria $E(C_{eq}(C, \mu_{\text{Li}}))$ and decomposition energy $E_D^{\text{open}}(C, \phi)$ of the phase in equilibrium with Li at a set chemical potential

$$E_D^{\text{open}}(C, \phi) = E(C_{eq}(C, \mu_{\text{Li}})) - E_C - \Delta n_{\text{Li}} \mu_{\text{Li}}(\phi) \quad (2.6)$$

To evaluate the electrochemical stability of the interface of two materials A and B, similar to the previous section, we defined the mutual reaction of the pseudo-binary of these two materials:

$$\Delta E_{D,mutual}^{open}(A, B, x, \phi) = \Delta E_D^{open}(A, B, x, \phi) - x\Delta E_D^{open}(A, \phi) - (1 - x)\Delta E_D^{open}(B, \phi) \quad (2.7)$$

the decomposition energies of the individual phases A and B, $\Delta E_D^{open}(A, \phi)$ and $\Delta E_D^{open}(B, \phi)$, were excluded. The minimum of the mutual reaction energy under applied voltage $\min(\Delta E_{D,mutual}^{open}(A, B, x, \phi))$ over the entire range of x from 0 to 1 was taken as the decomposition energy ΔE_d^{open} used throughout this thesis. Additional details can be found in previous studies [24].

2.2 Density functional theory calculations: Li-ion migration in Al_2O_3

In this section, I provide the methods and calculation parameters used to perform density functional theory (DFT) calculations and analyses for studying Li-ion migration in Al_2O_3 , the work discussed in Chapter 5.

2.2.1 Static relaxation parameters

All DFT calculations were performed using the Perdew-Burke-Ernzerhof (PBE) [65] generalized gradient approximation in the Vienna Ab initio Simulation Package (VASP) [66]. Static relaxations of structures were performed using a plane-wave cutoff of 520 eV and a Γ -centered 1 x 1 x 1 k-point mesh consistent with parameters

used by the Materials Project [61]. Structures were relaxed with an energy cutoff of 1×10^{-7} eV/atom and until residual forces were less than 0.01 eV/Å.

2.2.2 Crystalline supercell size and parameters

Initial crystalline supercells of 160 atoms (64 Al atoms and 96 O atoms) for the α and θ structures and 120 atoms (48 Al atoms and 72 O atoms) for the κ structure were generated using *pymatgen* and statically relaxed. For the γ structure, a supercell with 106 atoms (42 Al atoms and 64 O atoms) was generated by creating Al^{3+} vacancies in the parent spinel Al_3O_4 structure, following the method established in our previous work [67]. All subsequent nudged elastic band and molecular dynamics calculations were conducted using these supercells. To study the effect of Li^+ concentration, as compared to Li^0 , on diffusion in the θ and amorphous structures, Li^+ ions were added to the supercells. We used both a $\text{V}_{\text{Al}}^{3+}\text{-3Li}^+$ defect complex method as well as the “jellium” method (reducing the overall number of electrons and compensating by a uniform charge background) to model the Li^+ ions. For bulk systems, we found a significant difference between the jellium method and the defect complex method, in general finding in MD simulations that Li^+ diffusion was facilitated in structures with Al^{3+} vacancies. For the surface cells, to prevent collapse of the vacuum layer and to prohibit the charged vacuum environment from pulling Li^+ out of the structure, we used the defect complex method. We used surface slabs with a thickness of at least 10 Å, with a symmetric vacuum layer approximately 14 Å thick.

2.2.3 Creation of amorphous Al_2O_3 and comparison to experiment

We created amorphous samples using ab-initio molecular dynamics (AIMD) with the same potentials and cutoffs used in other parts of this project. Three different $\gamma\text{-Al}_2\text{O}_3$ structures were used as starting points, since this crystal structure is already intrinsically disordered, being a defected Al_3O_4 spinel. We chose Al vacancies in the parent structure at octahedral sites, tetrahedral sites and a combination of octahedral and tetrahedral sites. We melted the system at 2700 K with variable cell shape and size until the system was visibly liquid, and then continued at this temperature for 20 ps, cooled from 2700 K to 1700 K at a slow rate of 0.5 K/fs, and then more quickly from 1700 K to 100 K at 1 K/fs. After the melt-quench sequence, all amorphous structures produced extremely similar radial distribution functions (RDFs) that match well with experiment [68] and with previous simulations (Figure 2.1) [69].

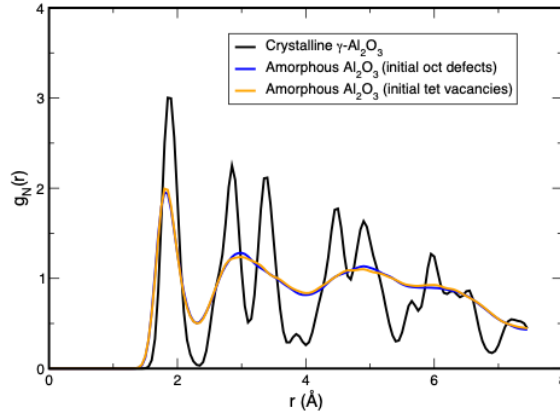


Figure 2.1: Radial distribution functions (RDFs) of am- Al_2O_3 as produced from liquid quenching of defected $\gamma\text{-Al}_2\text{O}_3$ structures.

2.2.4 Li^+ site identification

Li^+ sites in amorphous Al_2O_3 were identified using a combination of topological Voronoi analysis of the space in the structure and bond valence considerations to identify sites with reasonable spatial and chemical characteristics for Li^+ occupation. For the Voronoi analysis, the space between Al framework atoms was partitioned using the Voronoi-Dirichlet algorithm as implemented in Zeo++ [70], and candidate Li sites were further down-selected by bond valence. Partitioned volumes in the structure were selected as candidate sites if Li could be placed in the volume at least 1.8 Å away from any adjacent Al cations. Candidate sites were merged to an average of the original positions if multiple sites were closer than 1.6 Å. The bond valence of the Li atoms was set to between 0.4 and 1.2, which are the bounds for Li-containing oxides. The software used to identify sites is documented as part of the open-source package Topological_Analysis at https://github.com/mogroupumd/Topological_Analysis. More details are in previous studies [58]. The identified sites were statically relaxed using DFT until the Li ion moved in to a position of local equilibrium. Li^+ sites in crystalline α , κ , γ , and θ structures were selected by a combination of the same Voronoi analysis used for the amorphous structure and hand-selection of candidate sites with octahedral or tetrahedral coordination. The identified sites were then statically relaxed to obtain a structure with an Li interstitial at local equilibrium.

2.2.5 NEB parameters

Nudged elastic band (NEB) calculations were performed to determine the migration path and energy barrier for Li hopping between neighboring sites in Al_2O_3 structures. Initial and final states for the migration were statically relaxed, then starting guesses for the migration pathway were constructed by linear interpolation of images between the two states. All calculations were conducted using a Γ -centered $1 \times 1 \times 1$ k-point Brillouin-zone sampling. NEB paths were relaxed until the change in the forces was less than 1×10^{-4} eV/Å. The barrier for Li migration, or activation energy E_a was calculated as the difference between the highest and lowest energies from the converged NEB path.

2.2.6 AIMD simulations

Ab-initio molecular dynamics (AIMD) simulations were performed using non-spin polarized DFT calculations with a Γ -centered $1 \times 1 \times 1$ k-point grid. After relaxation, the temperature of the cells was set to 100 K. Structures were heated to the final temperatures at a constant rate by velocity scaling during a period of 2 ps. The timestep during heating was set to 2 fs. All simulations adopted the NVT ensemble with the Nosé-Hoover thermostat and a Nosé mass corresponding to a period of 40 time steps was chosen (SMASS = 0). The NVT ensemble was adopted in order for diffusivity data to be comparable to AIMD performed for other Li-conducting materials in previous studies [71, 72]. For the amorphous structure, 5 cells with increasing Li concentrations were initialized with random Li positions

among the available sites, relaxed, and then AIMD simulations were conducted at temperatures of 1900 K to compare the effect of Li^+ concentration on diffusivity. For the cell with a concentration of $\text{Li}_{0.19}\text{Al}_2\text{O}_3$, corresponding to 6 Li ions in our 160 atom supercell, additional simulations were conducted at temperatures of 1200, 1400, 1300, 1500, 1700, 1800, and 2000 K to obtain an Arrhenius relationship. The timestep was set to 1 fs. For the θ structure, supercells with 1, 2, 3, or 4 Li ions were randomly initialized and relaxed. AIMD simulations were performed at 1300 K for cells with 1, 2, 3, or 4 Li-ions, and additionally at 1500, 1600, 1700, and 1800 K for the cell with 1 Li ion. The timestep was set to 2 fs. The trajectories of Li^+ were recorded during the simulations and their mean squared displacement (MSD) was calculated as the average of the squared displacement of N ions at each timestep:

$$MSD(t) = \frac{1}{N} \sum_{i=0}^N (r_i(t) - r_i(t_0))^2 \quad (2.8)$$

For a cell with a single ion, the mean squared displacement as defined in this thesis would be equivalent to the squared displacement, because the squared displacement would be averaged over one. All plots of the MSD in this thesis were generated using the above method.

In calculating the diffusivity, the total mean squared displacement (TMSD) of Li ions was used, which is evaluated as

$$TMSD(\Delta t) = \sum_{i=1}^N \frac{1}{N_{\Delta t}} \sum_{t=0}^{t_{tot}-\Delta t} |r_i(t + \Delta t) - r_i(t)|^2 \quad (2.9)$$

where r_i is the trajectory of lithium ion i and $N_{\Delta t}$ is the total number of time intervals Δt during the duration t_{tot} of the MD simulation. Because TMSD is an averaged value, in simulations with multiple ions, TMSD represents the total diffusion of all lithium ions over the simulation time. The diffusivity D of Li^+ in the structure was then calculated according to the Einstein relation as

$$D = \frac{1}{N} \frac{TMSD(\Delta t)}{2d\Delta t} \quad (2.10)$$

Where N is the number of mobile carriers (Li-ions) and d is the dimension, 3. To ensure a statistically significant number of effective hopping events were captured, MD simulations for am- and θ - Al_2O_3 used for the Arrhenius relationship were run until the standard deviation of the diffusivity was approximately 20-30% of the diffusivity or less, as recommended in previous studies [71].

2.2.7 Analysis of site and pathway

We conducted analyses of the structure and geometry of Li sites in crystalline and amorphous Al_2O_3 to determine relationships between the migration barrier and the local structural configurations. For each image in the nudged elastic band calculation, corresponding to a point along the Li migration pathway, we collected Li-O distances within a cutoff of 2.8 Å, Li-Al distances within a cutoff of 3 Å, DFT energies, coordination number, number of nearest neighbors, locations of 1st and 2nd peaks for the RDF for Li-Al and Li-O distributions, and site volumes as quantified by Voronoi node analysis, for the moving Li ion. The distances used for

the Li-Al and Li-O cutoffs were determined by the average of the minimum between the 1st and 2nd RDF peaks for Li-O and Li-Al in crystalline and amorphous Al_2O_3 (Figure 2.2). The average Li-Al distance for each image in the migration path was calculated by averaging the distances of the neighboring Al to the Li. The Li-Al distance variation (LDV) for each migration path was calculated by taking the range of the average Li-Al distances, or maximum average Li-Al distance – minimum average Li-Al distance.

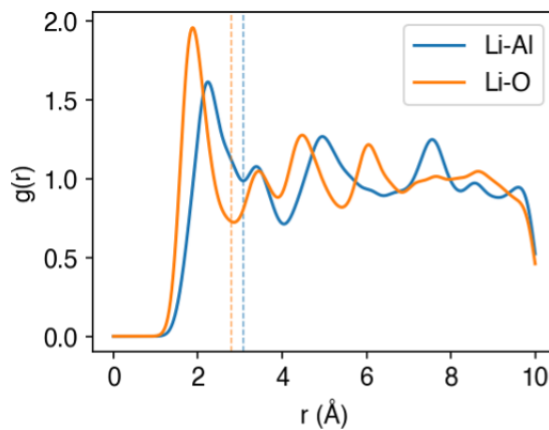


Figure 2.2: Averaged Li-Al (blue) and Li-O (orange) RDF spectra for all crystalline polymorphs, with dotted lines indicating first minima at 3 Å and 2.8 Å, respectively.

Chapter 3: Stability at the interface with high-voltage cathodes¹

By enabling high-voltage cathodes, we can significantly improve the energy density of current lithium-ion batteries. An outstanding challenge for high-voltage cathodes is that they are not stable throughout their operating voltages and tend to decompose or undergo phase transformations when in the discharged state, resulting in short battery lifetimes and poor performance [73, 74]. Coating layers have been used to enhance stability of the high-voltage cathode while cycling, acting as a physical barrier to prevent chemical reaction, a “bridge” to match the Li chemical potential of the electrolyte and the cathode, a scavenger of corrosive species such as hydrogen fluoride, or serving several of these functions at once [24, 50, 57].

Previous computation approaches using materials databases have been successful in developing screening schemes for finding coating layer materials for particular applications. However, there still exists a gap in the knowledge of materials chemistries that are stable with high-voltage cathodes. In this chapter, I performed comprehensive analysis of the stability of various materials chemistries with lithiated and delithiated cathode materials. I focused on the cathodes LCO, LiNiO₂ (LNO), high-voltage spinel LiNi_{0.5}Mn_{1.5}O₄ (LMNO), and high-voltage olivine-structured

¹Parts of this chapter have been published in or paraphrased from **A.M. Nolan**, Y. Liu, Y. Mo, Solid-State Chemistries Stable with High-Energy Cathodes for Lithium-Ion Batteries. *ACS Energy Letters*, 4 (10), 2444-2451 (2019).

LiCoPO₄ (LCP). I chose to investigate LiNiO₂ because it is a material representative of the family of high-capacity Ni-rich cathodes NCA and NMC. The goal of this analysis is to provide thermodynamic principles to guide future development of materials stable with high-voltage cathodes under cycling.

3.1 Thermodynamic stability of two materials in contact

To assess the potential use of a particular material as a coating layer, the thermodynamic stability of the material with the cathodes at charged and discharged (lithiated and delithiated) states was evaluated. This evaluation condition was chosen because prospective coating layer materials should be stable with both the lithiated and delithiated states of the cathode to prevent side reactions and cathode deterioration throughout the cycling voltage range of the battery. The interface stability was evaluated between common cathodes and a wide range of contacting materials, including lithium ternary oxides, binary oxides, lithium polyanion oxides, and lithium ternary fluorides. The cathode and coating material were considered as a pseudobinary mixture of the two materials, as established in previous studies by Zhu et al., and the reactions of the cathode and contacting material to form more stable phase equilibria were identified (Fig. 3.1) [24]. See additional details on computational methods in Chapter 2.

The decomposition energy, E_d , was defined as the minimum of the mutual decomposition energy between two phases, and was evaluated using density functional theory (DFT) energies from the Materials Project database [61]. Using this

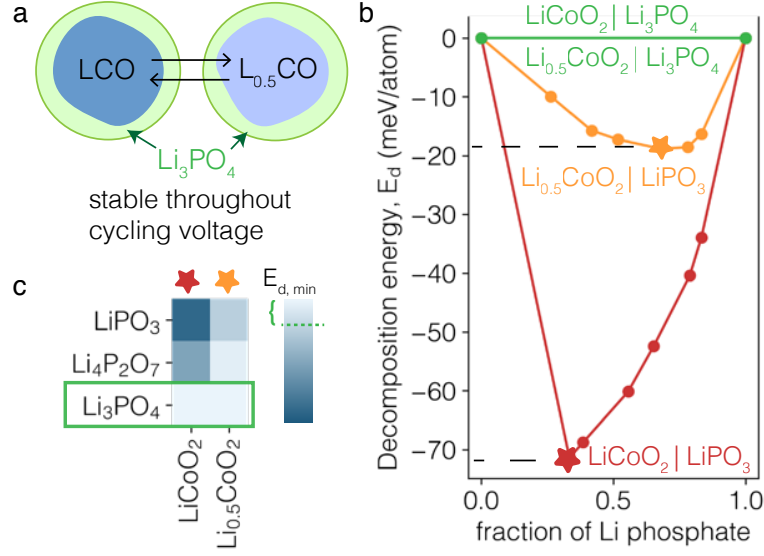


Figure 3.1: Thermodynamic analysis of the stability between cathode and contacting materials. (a) Illustration showing the stable interface between lithiated and delithiated LCO cathode particles coated with Li_3PO_4 . (b) Mutual reaction energy of LiPO_3 – LiCoO_2 (red), LiPO_3 – $\text{Li}_{0.5}\text{CoO}_2$ (orange), Li_3PO_4 – LiCoO_2 (green), and Li_3PO_4 – $\text{Li}_{0.5}\text{CoO}_2$ (green) as a function of the mixing fraction in the pseudobinary. The minimum mutual reaction energy for each pair of materials (marked by a star) corresponds to the possible reaction with the lowest energy. (c) Heatmap of the minimum mutual reaction energies of different compositions of lithium phosphates with lithiated and delithiated LCO.

methodology, chemistries thermodynamically stable with cathodes at both lithiated and delithiated states could be identified. The values of the decomposition energies of each material with the lithiated and delithiated cathodes were then encoded into a heatmap (Fig. 1c), allowing for easy visual identification of materials that are stable. The more favorable (more negative) the decomposition energy between two materials, the darker the corresponding shade on the heatmap. The stable combinations are indicated in the lightest shade.

Finally, in this study, several limits were imposed on the materials studied. To exclude coating layer materials that were potentially redox-active, only materi-

als where cations are at their highest common oxidation state were included. All metastable and unstable materials ($E_{hull} > 0$) were excluded from examination, and all materials containing elements with atomic numbers greater than 84 ($Z > 84$) or radioactive elements were excluded.

3.2 Stability of lithiated and delithiated LiCoO_2 with lithium ternary oxides

We began by systematically investigating lithium ternary oxides for their stability with cathodes (Fig. 3.2). Lithium ternary oxides have been identified as promising coating layers for high-voltage cathodes and as solid electrolyte materials. We found that different lithium ternary oxides exhibit different stabilities with the cathode. For example, among the three lithium phosphates, Li_3PO_4 is stable with both lithiated LCO and delithiated $\text{L}_{0.5}\text{CO}$, but by contrast, LiPO_3 exhibits a favorable reaction of -71 meV/atom with LCO and -19 meV/atom with $\text{L}_{0.5}\text{CO}$.

In general, $\text{L}_{0.5}\text{CO}$ tends to react with the compositions with highest lithium content, drawing Li out from the coating layer into the delithiated cathode. This can be readily understood by examining the phase equilibria of individual reactions. For example, $\text{L}_{0.5}\text{CO}$ reacts with Li_5TaO_5 , a highly lithiated Li-Ta-O compound, with a favorable decomposition energy of $E_d = -38$ meV/atom to form the phase equilibria Li_3TaO_4 , Li_2CoO_3 , and $\text{Li}_9\text{Co}_7\text{O}_{16}$. The phases formed are a less lithiated Li-Ta-O compound, Li_3TaO_4 , and more lithiated forms of LCO, Li_2CoO_3 , and $\text{Li}_9\text{Co}_7\text{O}_{16}$, which indicate that Li was drawn from Li_5TaO_5 and into $\text{L}_{0.5}\text{CO}$.

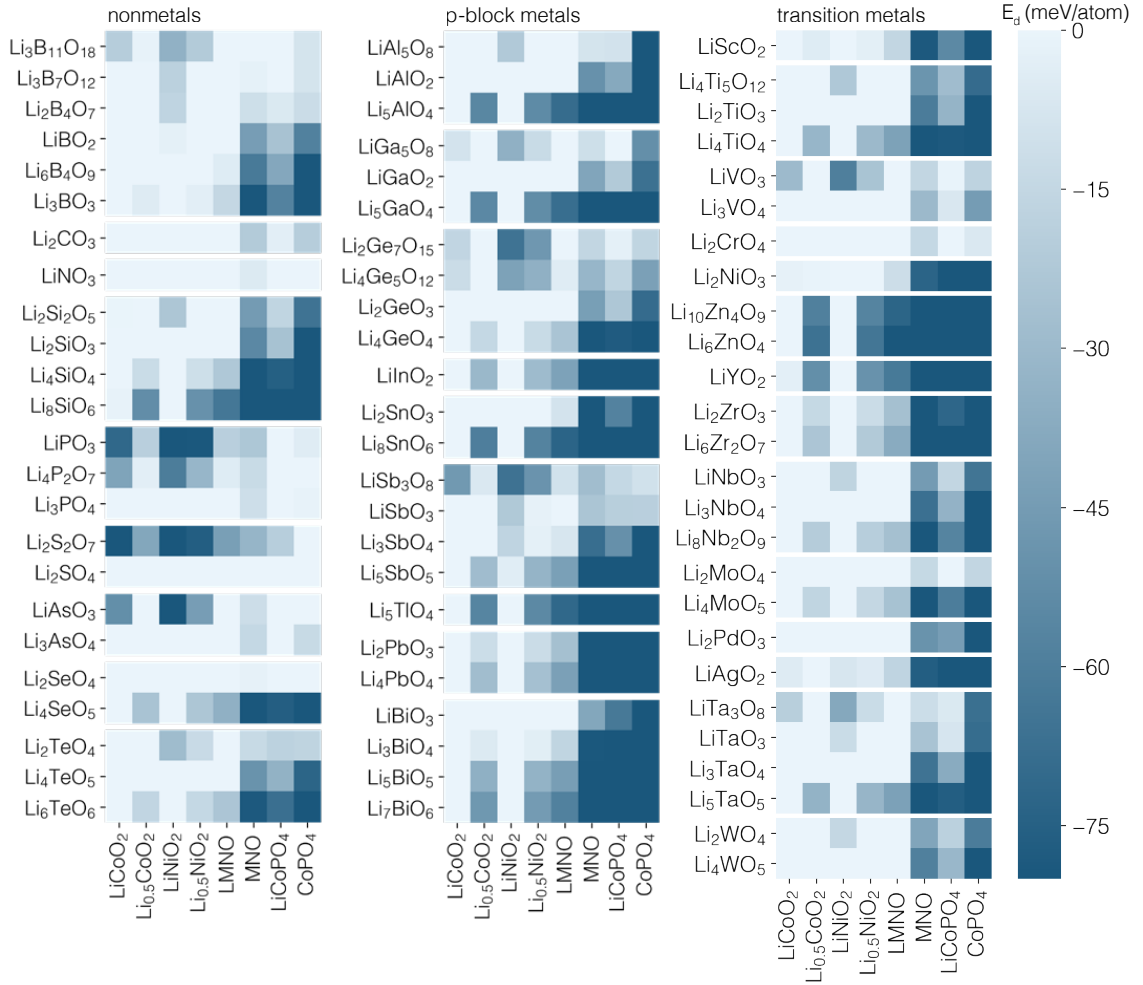


Figure 3.2: Decomposition energies of lithium ternary oxides with cathodes at lithiated and delithiated states. The color of each square in the heatmap corresponds to the minimum decomposition energy (E_d) of the cathode and contacting material. Groups of materials with the same elemental composition are ordered by increasing lithium content down the column.

By contrast, LCO tends to react with compositions with lower lithium content, although it is much less reactive than $\text{L}_{0.5}\text{CO}$ overall (see Figure A.1). LiCoO_2 reacts with LiTa_3O_8 , a less lithiated phase, with a reaction energy of $E_d = -18$ meV/atom, to form Co_3O_4 , $\text{Li}_{0.5}\text{CoO}_2$, and LiTaO_3 . LiTaO_3 is a more lithiated form of LiTa_3O_8 , while spinel Co_3O_4 and $\text{Li}_{0.5}\text{CoO}_2$ are both delithiated forms of LCO, indicating that the Li has been drawn out of the LCO and into the coating layer to form LiTaO_3 . The formation of spinel Co_3O_4 has been observed at the surface of LCO particles after cycling or at high voltages, and is generally indicative of cathode degradation [75, 76]. Coating materials that degrade the cathode should be avoided.

Overall, delithiated $\text{L}_{0.5}\text{CO}$ is stable with fewer lithium ternary oxides than lithiated LCO and generally reacts with a more negative (more favorable) energy of decomposition than LCO for a given lithium ternary oxide composition. This trend suggests that the delithiated cathode is less stable and there is greater difficulty in finding materials chemistries stable with highly charged cathodes. Further, this trend in the instability of delithiated cathodes agrees with other computational calculations [77] and experimental thermal stability analysis [78]. The opposite reactions of LCO and $\text{L}_{0.5}\text{CO}$ with the same material compositions underscore the importance of finding suitable coating layers to protect the cathode and achieve stability over long-term cycling.

3.3 Comparisons between reactivity of LiCoO_2 and of high-voltage cathodes

LNO, a nickel-rich analogue to LCO, was studied because it is expected to behave similarly to high-energy cathodes NMC and NCA, and exhibit similar reactivity to ternary compositions. We found that Ni-rich layered cathodes are more reactive than Co-based cathodes, reacting with more materials and reacting with a more negative (more favorable) energy of decomposition. For LNO, the delithiated $\text{L}_{0.5}\text{NO}$ is slightly more reactive than the lithiated LNO, similar to the difference between the stability of delithiated and lithiated LCO. In addition, like $\text{L}_{0.5}\text{CO}$, delithiated $\text{L}_{0.5}\text{NO}$ tends to react with the more lithiated coating compositions, resulting in delithiated coatings and lithiated LNO phases. For example, using the Li-Ta-O family of compositions again, $\text{L}_{0.5}\text{NO}$ reacts with Li_5TaO_5 to form Li_2NiO_3 , Li_3TaO_4 , and NiO , with a decomposition energy $E_d = -32$ meV/atom. The phase equilibria in reactions with delithiated $\text{L}_{0.5}\text{NO}$ are distinct from that of Co-based cathodes, and tend to contain rocksalt NiO or layered LiNiO_2 and Li_2NiO_3 rather than spinel Ni_3O_4 . The preferred formation of layered Li-Ni-O phases over spinel is confirmed by experimental findings [79].

The high-voltage cathodes LMNO and LCP are even more reactive with the lithium ternary oxides than LCO and LNO cathodes. Similar to the layered LNO and LCO cathodes, their delithiated states, $\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (MNO) and CoPO_4 (CP), are more reactive with materials as their lithium content of the oxide increases. This

is evidenced by the increasing decomposition energy for MNO and CP while moving down a group of materials with the same elemental composition in the heatmap (Fig. 3.2). This larger decomposition energy can be attributed to the greater reactivity of high-voltage cathodes and their stronger tendency to attract Li, especially at delithiated states.

3.4 Influence of Li content of coating chemistry

The groups of materials in the heatmap (Fig. 3.2) are organized by Li content, such that the Li content of the compositions increases down a group. Because of this organization, it is straightforward to visualize the effect of Li content on the various cathodes studied. Among all cathodes, the reaction energy of delithiated cathodes decreases (becomes more favorable) as the Li content of the coating layer increases. In general, this is because the delithiated cathode materials act as a Li sink, drawing Li out of the coating material, and the higher the Li content of the coating material, the more favorable the reaction, or exchange of Li species (Fig. 3.3). By the same token, lithiated cathodes tend to be more stable with materials with high Li content. These conflicting requirements for stability illustrate the challenge of finding materials stable with both the lithiated and delithiated cathodes. Overall, for lithium ternary oxides, the delithiated cathode is more reactive and reacts with a more favorable decomposition energy, so should be considered a priority.

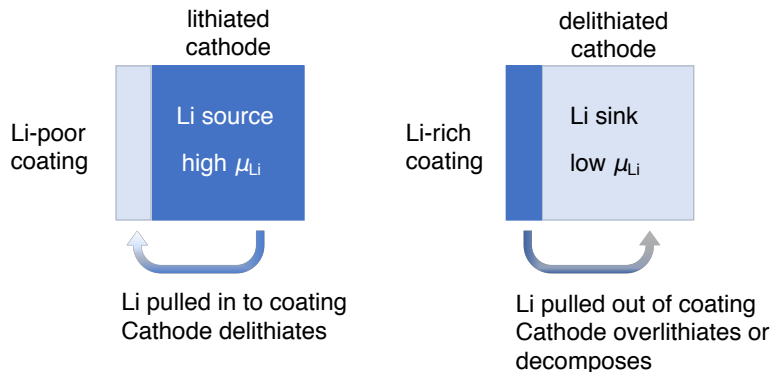


Figure 3.3: Schematic illustration of chemical reactivity of lithiated and delithiated cathodes with Li-poor and Li-rich coating layers, and general trend of species in phase equilibria.

3.5 Comparison of binary oxides, Li polyanion oxides, and Li ternary fluorides

In addition to lithium ternary oxides, we also investigated binary oxides (Fig. A.2), lithium polyanion oxides (Fig. A.3), and lithium fluorides (Fig. 3.4a) for their stability with the cathode materials. According to the trend found previously with the lithium ternary oxide compounds, because binary oxides contain no Li, they may be more stable with the delithiated cathodes. In general, this was found to be the case: binary compounds tend to be slightly more stable with the delithiated and high voltage cathodes than the lithiated cathodes (Fig. 3.4b). In general, binary oxides that contained alkali metals, alkaline earth metals, and nonmetals (except BeO, MgO, and SiO₂) tended to be much less stable with the cathodes. By contrast, binary transition metal oxides and p-block oxides showed good stability with high voltage cathodes LMNO and LCP (Fig. A.4). Consistent with this computational

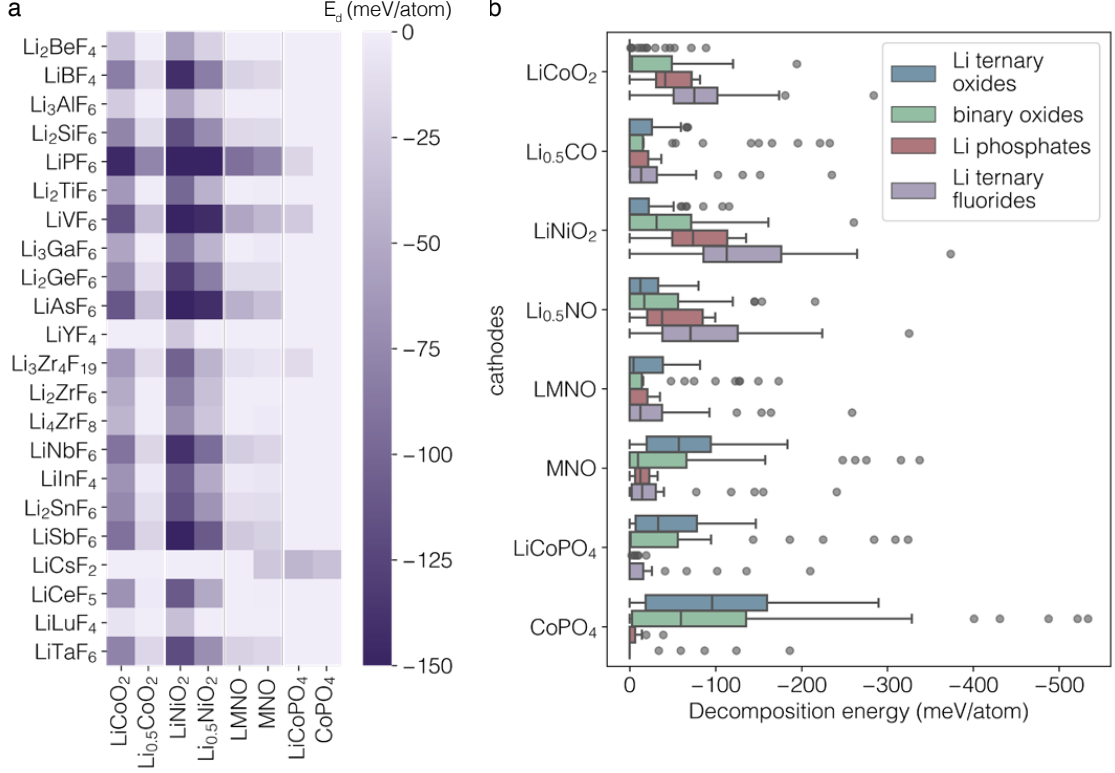


Figure 3.4: (a) Heatmap of decomposition energies E_d , of lithium ternary fluorides with cathodes, similar to Figure 2. (b) Grouped boxplot of decomposition energies of all cathodes with lithium ternary oxides, binary oxides, lithium polyanion phosphates, and lithium ternary fluorides. The center line of each box indicates the median of the data set, the outer edges represent the first and third quartiles, and the end points are marked by either the most extreme value on either end or 1.5 times the interquartile range, whichever is smaller. Data outside of the end points are marked individually as gray circles.

result, many of these materials, such as Al_2O_3 , SiO_2 , and Ta_2O_5 , were experimentally implemented as coating layers for LMNO [48, 80–82] and LCP [83]. However, binary oxides may be less suitable as coatings because they do not contain Li (rendering them unable to conduct Li-ions).

Lithium polyanion compounds were investigated because they have shown recent success as coating layers and solid electrolyte chemistries [84]. Delithiated $\text{L}_{0.5}\text{CO}$ and $\text{L}_{0.5}\text{NO}$ exhibited better stability with all the lithium polyanion

chemistries than compared to the lithium ternary oxides. Many of the lithium borates and lithium silicates had good stability with these layered cathodes. Surprisingly, the lithium polyanion phosphates had better stability overall with the lithiated and delithiated high-voltage cathodes compared to the layered oxides. The stability of the phosphates may be attributed to their high oxidation limits, which match the high oxidation limits of delithiated high-voltage cathodes.

Similar to the lithium phosphates, the lithium ternary fluorides, which have extremely high oxidation limits, tend to be highly reactive with lithiated cathodes but less reactive with high-voltage cathodes and delithiated cathodes (Fig. 3.4a). A number of fluorides such as CeF_3 and AlF_3 have been reported as cathode coating layers [85,86]. Other lithium ternary halides such as the chloride Li_3YCl_6 have been reported as good candidate solid electrolytes with high Li^+ conductivity and good stability with LCO cathodes [29,87].

3.6 Discussion

Our thermodynamic analyses illustrate that the stability of the cathode and a given material varies with the Li content, cation, and anion chemistries of both the cathode and the coating layer. Thus, the interface stability or compatibilities should be individually evaluated for each pair of cathode and coating compositions. For example, lithium phosphates are more stable with high voltage cathodes (LMNO and LCP) and less stable with layered oxide cathodes (LCO and LNO), while lithium borates and silicates are more stable with the layered oxide cathodes. While the

type of metal cation in the cathodes and coatings greatly affects their stability, poor stability between a coating layer and cathode can in general be attributed to the high oxidation potential of delithiated cathodes (4.5 V or greater), often beyond the oxidation limit (3.5—4V) of most oxides (Figs. A.5 and A.6). Thus, many reported binary oxide coatings have low or no Li content and correspondingly high oxidation limits. Because Li content is desired for Li-ion transport, in order to simultaneously achieve good ionic conductivity and high-voltage stability, lithium polyanion phosphates, which have naturally high oxidation limits, are a promising chemistry for coatings or solid electrolytes. One proof-of-concept is in phosphate solid electrolytes such as $\text{Li}_{1.4}\text{Al}_{0.6}\text{Ti}_{1.6}(\text{PO}_4)_3$, which has been reported with excellent oxidation stability and good cycling stability with oxide cathodes [84, 88, 89]. In addition, the lithium ternary fluorides we investigated have naturally high oxidation limits and are promising candidates to serve as coating layers for stability with delithiated cathodes at high voltage. Therefore, we suggest lithium polyanion phosphates and lithium fluorides as strong potential candidates for coating layers to stabilize high voltage cathodes while still containing sufficient Li to maintain good Li conductivity through the coating layer.

In summary, we investigated the thermodynamic stability between a broad range of solid-state chemistries and current cathode materials in Li-ion batteries. Our thermodynamic analyses of high-energy and high-voltage cathodes emphasized their strong reactivity, in particular, at delithiated or charged states, which causes undesirable side reactions and deterioration in battery performance. Our results suggest that the thermodynamic stabilities of the lithiated and delithiated cathode

with the contacting material are effective criteria for identifying promising coatings or solid electrolytes that can exhibit long-term stability with the cathode. Indeed, many experimentally demonstrated coating materials for oxide cathodes such as ZrO_2 [46,76], Al_2O_3 [47], and SiO_2 [10] on layered cathodes and Li_3PO_4 , LiNbO_3 , and LiTaO_3 in all-solid-state batteries [11] were confirmed by our thermodynamic criteria for their good stability with the cathode at all states of charge. For the binary oxides, minor reactions, such as between Al_2O_3 and lithiated LCO, may provide enhanced interfacial binding between the coating and LCO and introduce lithium into the coating to provide Li^+ transport [54]. The good agreement between experimental work and computation results suggests that the new chemistries identified in this chapter can guide future development of coatings or solid electrolytes stable with high-voltage cathodes.

Chapter 4: Stability at the interface between LLZO and NMC¹

All-solid-state batteries (ASBs), which use a ceramic solid electrolyte (SE), have the potential to improve upon the safety and energy density of current commercial Li-ion batteries with liquid electrolytes [90, 91]. A number of solid electrolyte materials with different chemistries have been developed. Currently, sulfide solid electrolytes have high lithium-ion conductivity, but suffer poor stabilities, including limited electrochemical windows, poor interface compatibility with anodes and cathodes, and poor air and moisture stability [92, 93]. Compared to sulfides, oxide solid electrolytes in general exhibit significantly better stabilities. In particular, Li garnets such as $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) have both high ionic conductivity and good electrochemical stability, and are regarded as promising solid electrolytes to enable high-energy density all-solid-state lithium batteries [27, 28].

While all-solid-state lithium metal cells using LLZO electrolytes have been demonstrated with good cycling performance [30–32, 34, 94], the integration of high-energy cathodes with stable, low resistance interfaces with garnet remains a significant challenge for the development of ASBs. High-temperature sintering between

¹This chapter has been published in or paraphrased from **A.M. Nolan**, E.D. Wachsman, Y. Mo, Computation-Guided Discovery of Coating Materials to Stabilize the Interface Between Lithium Garnet Solid Electrolyte and High-Energy Cathodes. *Energy Storage Materials*, (2021), *Under revision*.

the SE and the cathode to is often required in manufacturing to produce good physical contact, but this sintering also leads to side reactions at the interface. Several studies have examined the thermal stability of LLZO with LCO cathode, and have observed the formation of secondary phases including LaCoO_3 and $\text{La}_2\text{Zr}_2\text{O}_7$ at sintering temperatures of 600 °C and higher [35–39]. Miara et al. reported the formation of lithiated secondary phases during sintering of LLZO with high-energy spinel cathodes [40]. Energetically favorable reactions between LLZO and cathodes were also reported in computational studies on their thermodynamic stability [19, 41]. The limited stability between Li-garnet SEs and high-energy cathodes is a major impediment to the development and manufacturing of garnet-based all-solid-state batteries.

The application of coating layers between the SE and cathode is an effective strategy to impede the undesired side-reactions during sintering. For example, Li_3BO_3 has been demonstrated in several studies as a coating for LLZO and LCO ASBs [38, 95–97], and improves the interfacial stability by suppressing the decomposition that occurred during sintering without the coating [38]. In addition, coating layers between garnet and the cathode are also needed for achieving low interfacial resistance and stable electrochemical cycling performance of ASBs. Both experiments and computational studies indicate that cathodes such as LCO and high-voltage $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ are oxidized with LLZO after cycling, leading to materials degradation, increased interfacial resistance, and poor cell cycling performance [19, 24, 38, 98]. A similar issue has been observed for high-capacity $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ (NMC), which has poorer sintering stability and higher inter-

facial resistance with LLZO than LCO [35,36,39,99]. A number of coating materials, including LiNbO_3 , Li_2SiO_3 , and polymeric coatings, have been demonstrated to improve cycling stability of the LLZO-NMC interface [42–45].

So far, the development of coating materials for SEs and cathodes has largely relied on trial-and-error. The coating layer should be stable with Li garnet and also with the cathode, but understanding of the underlying thermodynamic mechanisms that govern the stability between garnet-coating and garnet-NMC is very limited. Thermodynamic analyses based on first-principles computation databases have been employed to study the chemical and electrochemical reactions between SEs and cathodes and predict materials that are stable with SE or cathode at the interface [12,64,100,101]. Using this approach, high-throughput computational studies have been performed to screen coating materials for sulfide SEs and cathode interface [57], Li metal anode [60], high-voltage cathodes [51], and coating layers to scavenge the reactive hydrogen fluoride [50]. Computational thermodynamic analyses can offer fundamental understanding about the interface stability of garnet SE with cathodes, and rationally guide the identification of promising coating materials for LLZO-cathode interfaces to enable garnet-based ASBs.

In this chapter, I systematically analyze the thermodynamic stability of LLZO garnet and high-energy cathodes including NMC with a wide range of materials chemistries with different cations, compositions, and lithium content, and identify the promising materials that can stabilize the LLZO-cathode interface, in order to guide the further development of the LLZO-cathode interface for stable sintering and cycling. I focused on high-energy cathodes such as NMC, which is needed

to achieve high energy density of these ASBs. A systematic study of the thermodynamic stability of materials with LLZO and NMC has not yet been performed. Here, I use thermodynamic analyses based on first-principles computation data to analyze the stability between LLZO garnet and a wide range of commonly used high-energy cathodes. I perform a high-throughput study to identify materials systems that have good stability with LLZO and NMC chemically or electrochemically at applied voltage. For the most promising Li ternary oxide Li-M-O systems, I systematically analyze and identify the composition ranges that can stabilize the LLZO-NMC interface. I provide fundamental mechanistic understanding of the thermodynamic stability of materials with LLZO and cathodes, and rational guidance for further development of coating and interface engineering to enable high energy density garnet-based ASBs.

4.1 Garnet-cathode interface stability

I evaluated the thermodynamic stability of the interface between LLZO and several cathodes, including the NMC cathodes $\text{LiNi}_{0.3}\text{Mn}_{0.3}\text{Co}_{0.3}\text{O}_2$ (NMC 111), $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC 622), and $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC 811), and cathodes with a single transition metal cation such as LCO, LiNiO_2 (LNO), LiMnO_2 , and LiMn_2O_4 (LMO). To evaluate the stability between two materials, we consider their pseudo-binary mixture and identify the mixture of compositions that give the lowest energy (i.e. phase equilibria) and corresponding decomposition energy, using the energies from the Materials Project database and the same scheme established in

previous studies [24, 51]. In all calculations, I used materials that had an existing identification number in the International Crystal Structure Database (ICSD), to ensure all phases used in the calculations have been experimentally synthesized or characterized. Further details on the calculation parameters are in Chapter 2.

LLZO reacts with a negative (exothermic) energy of decomposition (E_d) with most oxide cathodes (Table 4.1). In general, when LLZO reacts with a cathode, the phase equilibria is comprised of lithiated TM oxides, such as Li_2NiO_3 and Li_2MnO_3 , and delithiated LLZO products, such as La_2O_3 and $\text{La}_2\text{Zr}_2\text{O}_7$. The decomposition product $\text{La}_2\text{Zr}_2\text{O}_7$ suggests a tendency for LLZO to lose Li in reaction with the cathode, and that this Li loss is the dominant mechanism for the interface instability between LLZO and the cathode. The formation of $\text{La}_2\text{Zr}_2\text{O}_7$ is also observed in experimental studies of high-temperature sintering of LLZO and oxide cathodes [39, 40]. In our computation we see the formation of $\text{La}_2\text{Zr}_2\text{O}_7$ in reactions with LLZO and delithiated cathodes. A possible explanation may be the simplification in our computation that all lithium remains in the composite mixture, such that Li loss from the sample during high-temperature sintering is not considered. Kim et al. [99] attributes the discrepancy in computational and experimental findings to the presence of CO_2 in the sintering environment (air) which reacts to form Li_2CO_3 , drawing Li from LLZO and NMC and preventing the formation of Li-rich TM oxides predicted theoretically. To test this, we added CO_2 to the mixture of LLZO and cathodes and found that the addition of even a small amount of CO_2 (0.0004 CO_2 per atom of LLZO) causes partial decomposition of LLZO into Li_2CO_3 , $\text{La}_2\text{Zr}_2\text{O}_7$, and La_2O_3 , which are in agreement with phases observed in experiments.

This formation of Li_2CO_3 or other interphase layers may passivate the interface between LLZO and cathode, and kinetically inhibit further degradation reactions to form other lithiated oxides as suggested by thermodynamics. Nevertheless, both our computation and previous experiments confirm that Li loss from LLZO is the major factor causing the decomposition at the LLZO-cathode interface and during sintering.

$C_{cathode}$	x_{LLZO}	E_d with LLZO (meV/atom)	Phase equilibria at x_{LLZO}
LiCoO ₂	—	0	—
Li _{0.5} CoO ₂	0.33	-21	O ₂ , La ₂ O ₃ , LiCoO ₂ , La ₂ Zr ₂ O ₇
LiNiO ₂	—	0	—
Li _{0.5} NiO ₂	0.46	-35	Li ₂ NiO ₃ , NiO, La ₂ Zr ₂ O ₇ , LaNiO ₃
LiMnO ₂	—	0	—
LiMn ₂ O ₄	0.46	-60	Li ₂ MnO ₃ , LiMnO ₂ , La ₂ Zr ₂ O ₇ , LaMnO ₃
MnO ₂	0.70	-123	La ₂ O ₃ , Li ₂ MnO ₃ , La ₂ Zr ₂ O ₇
NMC 111	0.57	-87	Li ₂ O, LiCoO ₂ , Li ₆ Zr ₂ O ₇ , Li ₂ NiO ₃ , NiO, La ₂ MnCoO ₆
d-NMC 111	0.60	-132	LiCoO ₂ , Li ₆ Zr ₂ O ₇ , Li ₂ NiO ₃ , Li ₂ ZrO ₃ , Li ₂ O ₂ , La ₂ MnCoO ₆
NMC 622	0.44	-63	Li ₂ O, Li ₆ Zr ₂ O ₇ , Li ₂ NiO ₃ , NiO, La ₂ MnCoO ₆
d-NMC 622	0.48	-117	Li ₂ NiO ₃ , Li ₂ ZrO ₃ , ZrO ₂ , NiO, La ₂ MnCoO ₆
NMC 811	0.29	-38	Li ₂ O, Li ₆ Zr ₂ O ₇ , Li ₂ NiO ₃ , NiO, La ₂ MnCoO ₆
d-NMC 811	0.44	-80	Li ₂ NiO ₃ , ZrO ₂ , NiO, La ₂ MnCoO ₆ , La ₂ Zr ₂ O ₇

Table 4.1: The minimum mutual decomposition energy and phase equilibria of lithiated and delithiated LiCoO₂, LiNiO₂, LiMnO₂, LiMn₂O₄, and NMC cathodes with LLZO. Delithiated NMC cathodes (Li_{0.5}Ni_xMn_yCo_{1-x-y}O₂) are denoted with the prefix “d-”.

To understand the effect of different TM cations on the garnet-cathode interface stability, we compared the stability of garnet LLZO with lithiated and delithiated cathodes NMC 111, NMC 622, and NMC 811, and their endpoint compositions, such as LCO, LMO, and LNO. The LLZO-cathode mixture has a high propensity for reaction with all compositions of NMC, and less so for LCO. In co-sintering experiments, the LLZO-NMC 111 mixture was found to have poorer stability and a

larger amount of decomposition products or impurity phases than the LLZO-LCO mixture [35, 36], which agrees with our result that the LLZO-NMC mixture has a more thermodynamically favorable, exothermic reaction energy. Comparing LCO, LNO, and LMO, we found LCO is the most stable with LLZO, and LMO is the least stable (Table 4.1). Similarly, in different compositions of NMC, higher Mn content leads to poorer stability with garnet (Table 4.1). In agreement with our computation, the co-sintering experiments by Ren et al. [35] found that LMO had poorer stability with LLZO than LCO and that the LMO-LLZO interface decomposed starting at 400 °C to form lithiated Mn oxides such as Li_2MnO_3 , and formed $\text{La}_2\text{Zr}_2\text{O}_7$ and $\text{La}_{1-x}\text{MnO}_{3+\delta}$ at 600 – 800 °C. These experimentally detected phases agree well with our predicted decomposition products of Li_2MnO_3 , $\text{La}_2\text{Zr}_2\text{O}_7$, and LaMnO_3 . For sintered LLZO-NMC 111, Ren et al. [35] found evidence of a mixed composition of LaMnO_3 , LaCoO_3 , and LiNiO_3 , which is consistent with the formation of LaCoMnO_3 predicted by our computation. Slightly different decomposition products, such as LaNiO_3 [36] and $\text{LaNi}_{0.5}\text{Co}_{0.5}\text{O}_3$ [99] were reported in other sintering studies of the LLZO-cathode mixture. We also find the formation of LaNiO_3 in the reaction of delithiated LNO with LLZO, which may be similar to the products formed from Li loss during sintering experiments for high-Ni cathodes. While it has not yet been established what causes the differences in experiments, all studies reported the formation of LaMO_3 perovskite ($\text{M} = \text{Ni}, \text{Mn}, \text{Co}$, or a combination), in agreement with our computational prediction [35, 36, 99].

4.2 Materials stable with garnet and NMC

A coating layer can serve as a physical barrier to impede the side reaction between SE and cathode during sintering or electrochemical cycling. A good coating material should be chemically and electrochemically stable with both cathode and electrolyte to avoid detrimental reactions which may cause high interface resistance and poor electrochemical performance. To determine the appropriate coating materials, we evaluated a wide range of materials chemistries, including binary oxides, lithium ternary oxides, quaternary lithium phosphates, borates, and silicates, and ternary lithium halides, for their stabilities with lithiated and delithiated NMC cathode and LLZO SE (Figures B.1, B.2, and B.3). Among these chemistries examined, the lithium ternary oxides in general have better stability with LLZO (Figure B.4) than other chemistries, and so are the focus of this chapter.

As identified by our computation, a small number of lithium ternary oxide compositions are chemically stable (near zero decomposition energy $|E_d|$) with both LLZO and lithiated and delithiated NMC (Fig. 4.1). Similar to our previous study, [51] we found the lithium content of the compound is a major factor affecting its stability with the LLZO or NMC. In general, the materials with higher Li content tend to be more stable with LLZO, while the materials with lower Li content tend to be less stable with LLZO. By contrast, an opposite trend is observed for NMC, in that the materials with lower Li content tend to be more stable with NMC, in particular with delithiated NMC or at high voltages (e.g. 5 V). These opposite trends in the stabilities of materials with LLZO and NMC may be explained by the

different equilibrium Li chemical potential (μ_{Li}) in LLZO and NMC. LLZO has a high Li content and a high μ_{Li} , and can achieve equilibrium with materials with a similar level of high μ_{Li} , such as lithium metal and compounds with high Li content (Fig. 3.1). If the materials in contact cannot achieve this equilibrium of Li chemical potential μ_{Li} , LLZO has the tendency to lithiate materials in contact and to lose lithium as a result. The high-energy cathode materials, such as NMC, have lower μ_{Li} , and tend to absorb lithium from lithium-rich sources. The chemical potential windows of LLZO and delithiated cathodes have little to no overlap for range of chemical potentials where both materials are in equilibrium (Figure B.5). Therefore, these differences in the Li chemical potentials in LLZO and cathode are the origin of their poor interfacial stability [24, 38, 41]. The resulting conflicting requirements for Li content give rise to challenges in identifying appropriate coating materials that are stable with both LLZO and NMC. As shown in our analyses (Fig. 3.1), only a small number of materials among all lithium ternary oxide compounds are stable with both materials. Our heatmap (Fig. 3.1) provides guidance for selecting those compounds that can be stable with both LLZO and NMC as potential coating layers.

We also evaluated the electrochemical stability of coating-LLZO and coating-NMC pseudo-binary mixtures under the voltage of 3 – 5 V, using the same scheme as in previous studies [24] (see Chapter 2 for further details). As would be expected because a high voltage is equivalent to a low Li chemical potential, the LLZO-coating interface tends to be less stable at higher voltage, whereas the NMC-coating interface tends to be more stable at higher voltage. The phase equilibria of the

interfacial reactions at the interface under applied voltage are dominated by the delithiation of LLZO or NMC. In agreement with the aforementioned results, the tendency of Li loss from LLZO is also a key factor driving the interface instability during electrochemical cycling.

We identified the compositions with little or no chemical reactions (with a small magnitude of $|E_d| < 0.05$ eV/atom) with LLZO and NMC (Table 2). For most Li ternary oxide families, there is at least one composition that is stable or has minor reactions with both LLZO and NMC. For example, Li_3BO_3 , the Li-Si-O compounds (Li_2SiO_3), and Li-Nb-O compounds ($\text{Li}_8\text{Nb}_2\text{O}_9$) have a small magnitude of $|E_d| < 0.05$ eV/atom or less with LLZO and NMC. These compositions were reported in experimental studies as coating layers to stabilize the LLZO-NMC or LLZO-LCO interface by blocking side reactions between LLZO and the cathode [42, 44, 102–104]. This good agreement with experiments confirms our analyses can identify and predict stable coatings for the LLZO-NMC interface. Our heatmap (Fig. 4.1) also identifies a number of other lithium ternary oxides as promising coating layers to stabilize the LLZO-NMC interface.

M in Li-M-O	M stable with LLZO?	Compositions stable with LLZO, NMC111 and d-NMC
B		Li ₃ BO ₃ , LiBO ₂ , Li ₆ B ₄ O ₉
C	Stable	Li ₂ CO ₃
N	Stable	LiNO ₃
Mg	$ E_d < 0.003$ eV/atom	MgO
Al		LiAlO ₂ , Li ₅ AlO ₄
Si		Li ₂ SiO ₃
P		Li ₃ PO ₄
Sc		Sc ₂ O ₃ , LiScO ₂
Ti	$ E_d < 0.03$ eV/atom	Li ₂ TiO ₃ , Li ₄ TiO ₄
V	Stable	Li ₃ VO ₄
Cr	Stable	LiCrO ₂ , Li ₂ CrO ₄
Zn	Stable	ZnO
Ga	Stable	Li ₅ GaO ₄ , LiGaO ₂
Ge	Stable	Li ₄ GeO ₄ , Li ₂ GeO ₃ , Li ₈ GeO ₆
Zr	$ E_d < 0.005$ eV/atom	ZrO ₂ , Li ₆ Zr ₂ O ₇ , Li ₂ Zr ₂ O ₃
Y		Y ₂ O ₃ , LiYO ₂
Nb	Stable	Li ₈ Nb ₂ O ₉ , Li ₃ NbO ₄
Mo	Stable	Li ₂ MoO ₄ , Li ₄ MoO ₅
Sn	Stable	Li ₂ SnO ₃
Sb	Stable	Li ₅ SbO ₅ , Li ₃ SbO ₄
Ta	Stable	Li ₃ TaO ₄
W	Stable	Li ₄ WO ₅

Table 4.2: Materials stable with LLZO and NMC 111 (in the decomposition reactions of the pseudo-binary mixture, $|E_d| < 0.05$ eV/atom). Li₂O and Li₂O₂ are stable with both LLZO and NMC and are not explicitly listed in the table. Complete decomposition energies and phase equilibria of all the thermodynamically stable compositions in these systems and all other Li-M-O systems studied can be found in the SI.

4.3 Stability between LLZO and the Li-M-O composition space

The thin-layer coating at the SE-cathode interfaces may not be the exact stoichiometric compounds as coated, and may change as a result of interdiffusion, sintering, or electrochemical cycling to become amorphous, off-stoichiometric, or mixed compositions (such as LiBO-LiCO) [105]. Here, we study the trends in stability with LLZO throughout the ternary Li-M-O space, in order to identify all compositions that are stable with LLZO. The decomposition energy E_d of each composition with LLZO is illustrated by a heatmap of Li-M-O Gibbs ternary diagram (Fig. 4.2). For example, in the Li-Al-O system (Fig. 4.2a), LLZO is stable with Li_2O , Li_2O_2 , LiAlO_2 and Li_5AlO_4 , and with all mixed compositions of these compounds in their enclosed region (yellow region outlined by green dashed lines in Fig. 4.2a). Al-rich compositions near the Al corner show poor stability with LLZO, as the Al-LLZO pseudo-binary has a decomposition energy $E_d = -181$ meV/atom. These decompositions with a large magnitude of reaction energy tend to form products such as $\text{La}_2\text{Zr}_2\text{O}_7$, due to the tendency of LLZO to lose Li and the corresponding lithiation of the transition metal oxides.

Li-M-O systems with different cations M exhibit significantly different stability with LLZO. For the Li-Nb-O system (Fig. 4.2b), LLZO is stable with Nb, LiNbO_2 , $\text{Li}_8\text{Nb}_2\text{O}_9$, Li_2O , and Li_2O_2 , and any mixed compositions within this space are also stable with LLZO. Compared to the Li-Al-O system, a significantly wider range of Li-Nb-O compositions are stable with garnet LLZO. Multiple experimental studies reported that Li-Nb-O coatings with a range of compositions can stabilize garnet-

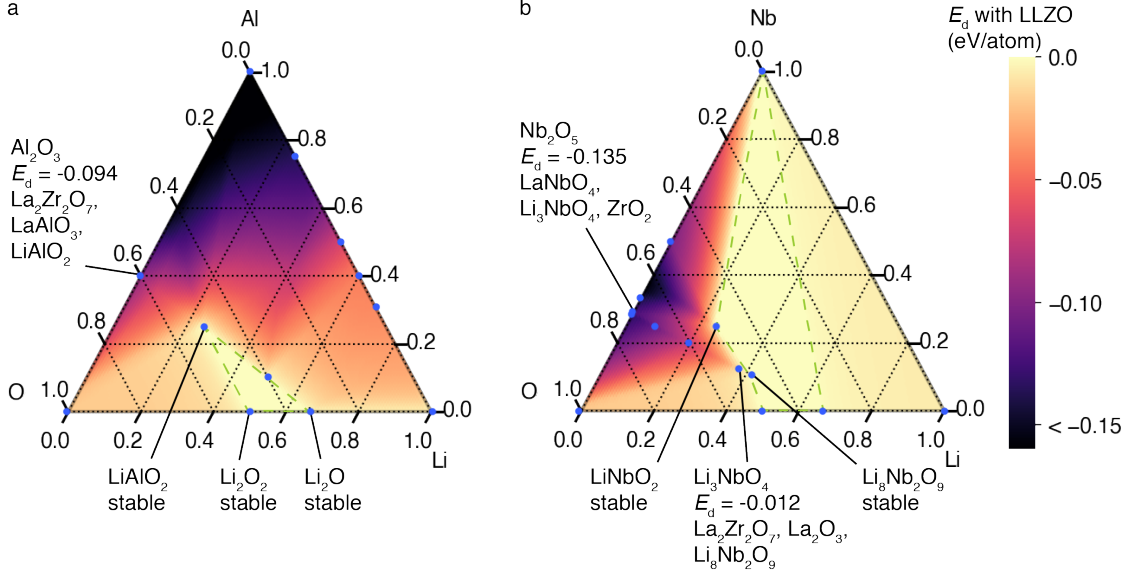


Figure 4.2: Heatmaps of the decomposition energy of a) Li-Al-O and b) Li-Nb-O compositions with LLZO. Regions of complete stability between the Li-M-O composition and LLZO are outlined by the dashed green line. Known stable compounds in the ternary phase space are marked by blue points. Decomposition products of the reaction with LLZO are provided for selected known stable compositions.

cathode interfaces to achieve low interfacial resistance. For example, Kato et al. reported that an interlayer of Nb metal at the LLZO-LCO interface was lithiated to form an amorphous LiNbO_3 and LiNb_3O_8 layer and suppressed interface side reactions for prolonged cycling life [44]. Sastre et al. reported that amorphous Li-Nb-O coatings speculated as Li_3NbO_4 , LiNbO_3 , LiNb_3O_8 or their mixtures significantly reduced the LLZO-LCO interfacial resistance [106]. In agreement with these experimental studies, these Li-Nb-O compositions are shown to have good stability with LLZO in our analysis. The wide range of Li-Nb-O compositions stable with garnet may explain the success of these Li-Nb-O coatings in experiments, because the varied compositions of coatings would remain stable at the interface during sintering or voltage cycling.

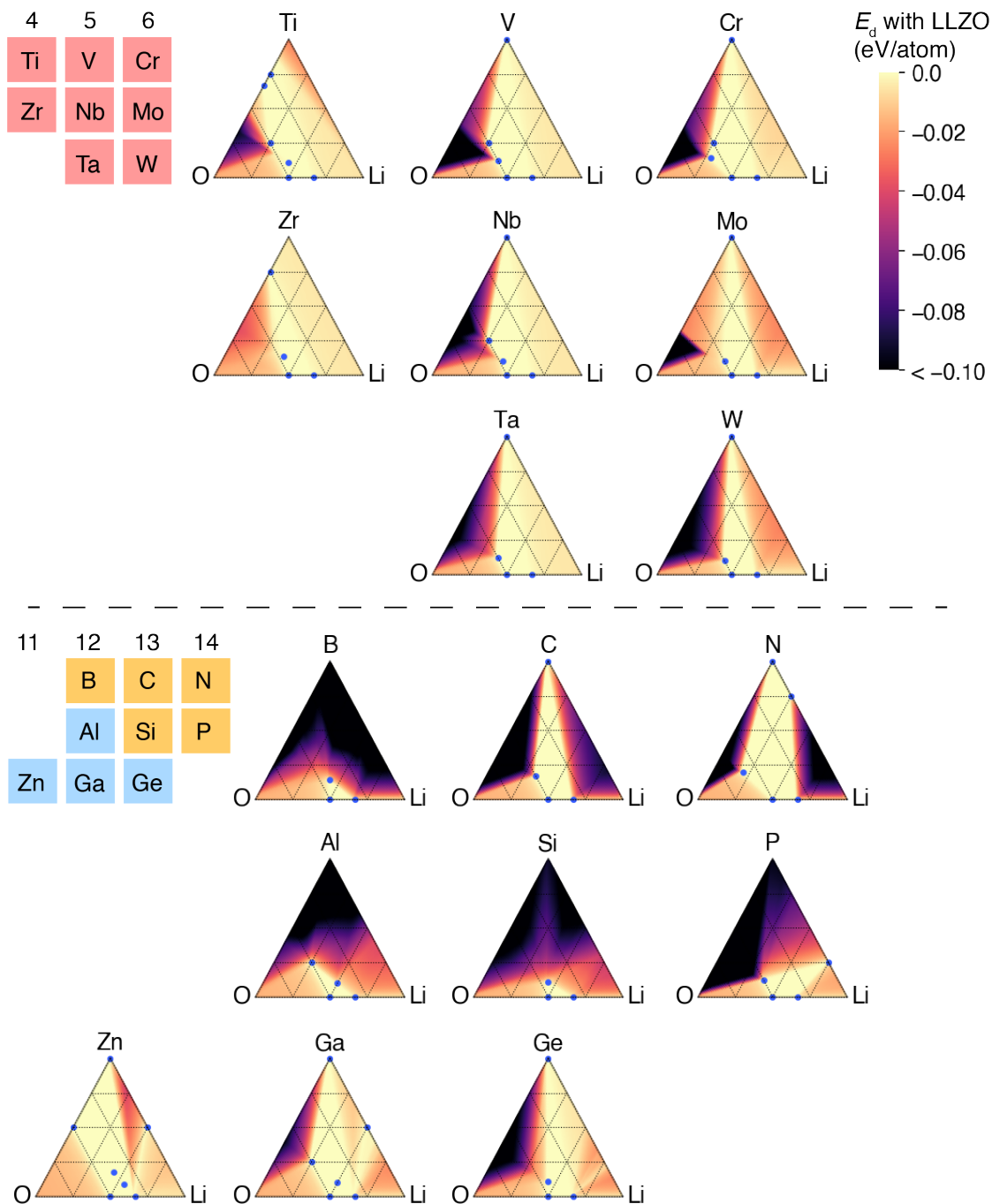


Figure 4.3: Heatmaps of chemical stability (E_d) of Li-M-O (M = B, C, N, Al, Si, P, Ti, V, Cr, Zr, Nb, Mo, Zn, Ga, Ge, Ta, or W) with LLZO. Known compounds that are stable with LLZO are marked with blue points.

We extended our analysis to other Li-M-O systems for cations $M = \text{B, C, N, Al, Si, P, Ti, V, Cr, Zr, Nb, Mo, Zn, Ga, Ge, Ta, or W}$, which are commonly considered and used for coatings (Fig. 4.3). Similar to the Li-Al-O system, many systems with nonmetal M such as Li-B-O, Li-Si-O, and Li-P-O only have one or two ternary Li-M-O compositions (along with Li_2O and Li_2O_2) stable with LLZO, leading to a narrow compositional space with LLZO stability. Compositions of coatings for garnet from these Li-M-O systems should be selected within the stable compositional space, as the compositions outside this space react exothermically with LLZO and may cause side reactions and interfacial degradation.

Similar to Nb, the transition metal elements V, Cr, Ta, Zn, Ga, Ge and non-metals C and N are stable with garnet, and a wider Li-M-O compositional space of ternary Li-M-O oxides have good stability with LLZO. For cations $M = \text{Ti and Zr}$, the M metal exhibits minor reactions with LLZO, but the binary oxides M-O are stable with LLZO, leading to a wide compositional space stable with LLZO. Notably, for the Li-Zn-O system, Zn metal, ZnO oxide, and LiZn alloy are stable with LLZO. Thus, this system has the widest composition space stable with LLZO, and so should be a promising system for garnet coatings as has been demonstrated in experiments [107–109]. In general, our heatmaps of the stability between LLZO and Li-M-O provide a guiding map for selecting compositions for garnet coating layers.

4.4 Stability between the cathode and Li-M-O composition space

Here, we analyze the stability of the entire Li-M-O composition space with NMC and other cathodes, since the coating layer should be stable with the cathode in addition to the LLZO solid electrolyte. Our analyses found that the stability trends are similar for all layered oxide cathodes, such as LCO, LNO, LMO, and NMC cathodes investigated (Figure B.6), so only the results for NMC 111 are shown. As shown in the heatmap of Li-Al-O with NMC 111 (Fig. 4.4), the NMC cathode is stable with Li_2O and LiAlO_2 , and all compositions along the tie-line including Li_5AlO_4 , which can be stable coating layer choices for cathodes. Al_2O_3 has good stability with NMC 111, with E_d of -0.015 eV/atom, and is stable with LCO, and thus the compositions along the Li_2O - Al_2O_3 tie-line have decent cathode stability. The compositions towards the Li/Al-rich and O-poor side of the Li_2O - Al_2O_3 tie-line show poor stability with cathode, and may be unsuitable as coating layers. By contrast, the compositions towards the Li-poor and O-rich side of the Li_2O - Al_2O_3 tie-line, i.e., the compositional space enclosed by Al_2O_3 , O_2 , and Li_2O , which may correspond to oxygen-rich mixed or off-stoichiometric compositions, still show decent stability with NMC ($|E_d| < 0.03$ eV/atom). This trend indicates that the cathode stability of the coating would not be significantly affected by the potential delithiation of the coating layer or oxygen enrichment of the composition at the coating layer surface, which may happen at high voltage or in the discharged state of the cathode.

We perform the same analyses on a number of other Li-M-O systems. Similar

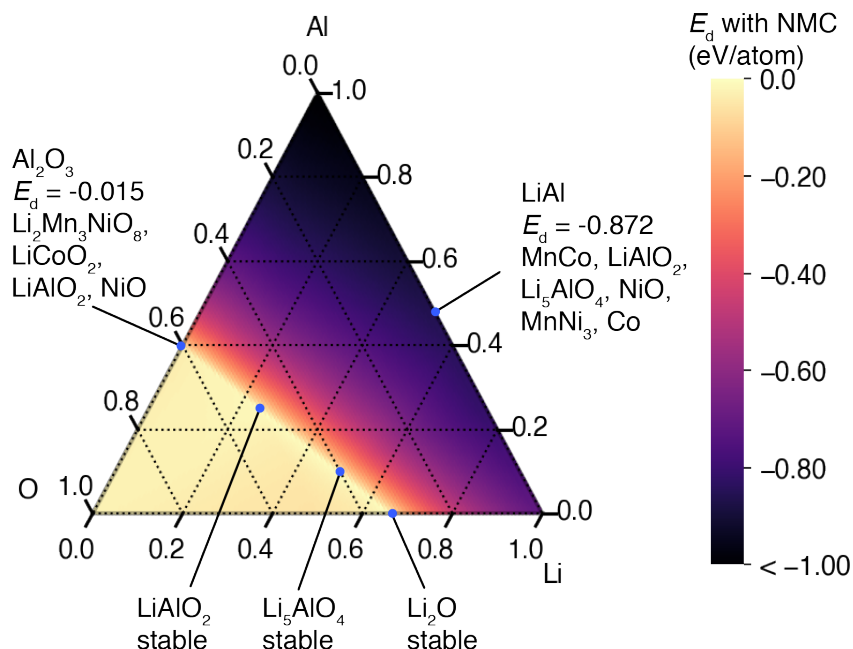


Figure 4.4: Heatmap of the decomposition energy and phase equilibria of selected representative Li-Al-O compositions with NMC 111. The composition space enclosed by Al_2O_3 , O_2 , and Li_2O has good stability with the NMC cathode.

to Li-Al-O, the only Li-M-O compositions stable with the cathode are along the tie-line of Li_2O and M-O metal oxides, and the cathode stability is generally good for O-rich compositions. The same analyses performed for delithiated NMC show similar conclusions for stable compositions as lithiated NMC and the other cathodes (Figure B.7). Analyses performed to examine the electrochemical stability of the Li-M-O systems with the cathode under applied voltage (Figures B.8 and B.9) also found a similar stability trend. Therefore, the best choices of cathode coating compositions are along the tie-line of Li_2O and M-O metal oxide, including Li-M-O ternary compositions and their mixtures, as these coating interfaces would remain stable at the delithiated state of the cathode and under applied voltage during battery cycling.

Since the coating layer between the SE and the cathode should be stable with both SE and cathode, we compare the heatmaps and stable regions of Li-M-O with LLZO (Figs. 4.2 and 4.3) and those with NMC (Fig. 4.4). The stability regions of Li-M-O with LLZO and with NMC have little overlap. This is consistent with our former analyses (2.2) showing the conflicting stability trends of LLZO and cathode caused by the discrepancy in their equilibrium lithium chemical potential. Fortunately, the materials compositions along the tie-line of Li_2O to M-O oxides, including multiple ternary oxides, show decent stability with both LLZO and NMC with a small magnitude of decomposition energy E_d . Therefore, these Li-M-O compositions are identified as potential coating layer materials (Table 4.2) for $M = \text{B, C, N, Na, Mg, Al, Si, P, Sc, Ti, V, Cr, Zn, Ga, Ge, Y, Nb, Mo, Ta, Sn, Sb, and W}$. These listed coating materials would meet the conflicting stability requirements with both LLZO and the NMC cathode to provide good interface stability during sintering and battery cycling.

4.5 Discussion

Using thermodynamic analyses based on first principles computation data, we systematically examined the stability between LLZO garnet with commonly used cathodes including LCO, NMC, LMO, and LNO. Our analyses found that the poor stability between LLZO garnet and cathodes is thermodynamically intrinsic, and is caused by the imbalance of the lithium chemical potentials between these two materials. Specifically, LLZO, a Li-rich material with high Li chemical potential,

has a strong tendency to lose lithium, leading to degradation reactions with the cathode and CO_2 during sintering as observed in experiments [35, 36, 38, 39, 99]. The thermodynamic intrinsic instability between LLZO and cathodes also causes interfacial degradation during electrochemical cycling especially at high voltages, leading to high interfacial resistance and poor electrochemical cycling stability, as reported in experiments [37, 40, 98]. The results of the LLZO-cathode instability and the formation of decomposition products such as $\text{La}_2\text{Zr}_2\text{O}_7$ and LaMO_3 ($\text{M} = \text{Ni}, \text{Co}, \text{Mn}$) agree with multiple experimental studies, which confirm the validity of our thermodynamic analyses. Given that the stability between garnet and cathodes are thermodynamically intrinsic and the decomposition products have poor Li-ion conduction, a buffer coating layer is critical to stabilize and protect the LLZO-cathode interfaces during sintering and electrochemical cycling.

We further performed systematic analysis of the thermodynamic stabilities of a wide range of the Li-M-O compositions with LLZO and NMC cathode, providing guidance for the selection of coating layers for garnet SE, NMC cathode, or to stabilize LLZO-NMC interfaces (Table 4.2). A coating layer on the garnet SE may protect it from forming surface contamination layers, such as Li_2CO_3 or LiOH , which need to be removed before battery assembly to achieve low interfacial resistance [30]. Our study finds that the stability between LLZO and Li-M-O materials is highly dependent on Li content and M cation choices. While for any cation M, one Li-M-O ternary composition may be stable with LLZO, certain Li-M-O systems such as $\text{M} = \text{C}, \text{N}, \text{Mg}, \text{V}, \text{Cr}, \text{Zn}, \text{Ga}, \text{Ge}, \text{Nb}, \text{Mo}, \text{Sn}, \text{Sb}, \text{Ta}, \text{and W}$ have a wide composition range that is stable with garnet LLZO (Fig. 4.2 and Table 4.2). Such materials

systems are promising coatings for protecting garnet LLZO, because these coatings would remain stable with LLZO even with composition changes during sintering, electrochemical cycling, or side reactions. A noteworthy example is the Li-Nb-O system, where Nb metal and a wide range of Li-Nb-O compositions are stable with LLZO, which are demonstrated in multiple experimental studies [43, 44, 106]. For a similar reason, Ge [94], Sn [110], Li-Mg alloys [111, 112], and ZnO [107–109] have also been reported as good coatings for LLZO in solid-state batteries. We predict several promising coatings that have not yet been tried experimentally. Guidance for selecting coatings for LLZO is summarized in Figures 4.1–4.3 and Table 4.2.

For oxide cathodes such as NMC, the stable coating materials are the compositions along the tie-line of Li_2O and M-O oxides, with usually one ternary composition that is stable with NMC. For cathode coatings, good stability is generally retained for variations of the coating layer composition with increased oxygen content or Li loss. Our computation analyses found several coatings also reported in experiments to improve the performance of NMC or other high-voltage cathodes, such as LiAlO_2 and Al_2O_3 [14, 49], Li_3PO_4 [113], Li_2SiO_3 [42, 114], TiO_2 and Li_2TiO_3 [80, 115], and Li_3VO_4 [116], which confirm the validity of our computation. We identify many other predicted coatings for guiding engineering of the cathode surface, as summarized in Fig. 4.1 and Table 4.2.

We identify materials that are stable with both LLZO and NMC as coating layers to stabilize the LLZO-NMC interface. As revealed by our thermodynamic analyses, the disparity of lithium chemical potentials in garnet SE and cathodes give rise to conflicting requirements for the coatings that can be stable with both materi-

als. Fortunately, for most materials systems, at least one Li-M-O ternary oxide and mixed compositions along their tie-line with Li_2O are stable with both LLZO and cathodes. The stable coating with LLZO-NMC interfaces should be limited to this narrow composition range, as summarized in Table 4.2. Well-demonstrated LLZO-cathode coatings, such as Li_3BO_3 [38, 95–97], Li_xNbO_y [44, 106], and Li_2SiO_3 [42], are confirmed in our computation analyses. The mixed composition of these predicted stable coating materials are also promising coating layers. For example, the mixed Li_3BO_3 - Li_2CO_3 coating has been demonstrated for LLZO-cathode interlayer with good stability and improved conductivity [105]. To name a few, new candidate coatings such as Li_2ZrO_3 , Li_2TiO_3 , LiGaO_2 , Li_2GeO_3 , Li_2SnO_3 , LiScO_2 , LiYO_2 , and Li_4WO_5 have good chemical and electrochemical stability with LLZO, NMC, and d-NMC, and have not yet been experimentally studied. We offer the full list of all possible materials for readers to choose based on their own interfacial processing approach.

Our approach identified the materials that have thermodynamic stability with LLZO and cathodes, which is a key criterion for stabilizing the interface. While the thermodynamic stability determines the ultimate stability between materials, a limited amount of minor reaction may be beneficial to form a good coverage of coating layer with strong chemical bonding. For example, Yoon et al. [117] applied Co_xB metallic coatings that reacted favorably with the NMC 811 cathode and infiltrated within the grain boundaries, forming strong bonds with the cathode surface, which greatly reduced intragranular cracking and side reactions with the electrolyte and enabled excellent cycling stability. We list materials with a minor

reaction energy ($|E_d| < 0.05$ eV/atom) in Table 4.2 and plot all heatmaps with reaction energies, which guide the selection of coatings if a certain level of reaction is desired. After a minor reaction, the final formed interphase layers would be within the identified thermodynamically stable composition spaces.

Our computation scheme only considers thermodynamics using first-principles computation data, and we have not considered the effects of temperature, time duration, environment, and reaction kinetics during sintering. Although only the DFT energies at 0 K were used, the thermodynamic analyses are adequate to capture the major trends in the reaction and stability, as our results are in agreement with previous experimental studies. To consider the high-temperature effect during sintering, one may perform a grand potential phase diagram approach by setting the chemical potential of oxygen, lithium, or CO₂ as a function of temperature, which has been demonstrated for modeling the thermal runaway of the Li metal anode with solid electrolytes at elevated temperatures [118]. In our analyses of the effect of altering the Li/O chemical potential (Table B.1 and B.2), we observe similar stability trends and reactions as in our original calculations (Table 4.1). In addition to the effects of temperature, models including the effects of time duration, environments, and reaction kinetics during sintering may be a future research direction to guide the sintering experiments. Nonetheless, our results capture the major trends in interface stability, which is the key criteria for identifying good interface coatings.

In addition, we note that chemical and electrochemical stability is one requirement of interfacial coating layers. As we previously described, the adhesion between coating and SE/cathode is desired to promote strong bonding and improve

physical contact, and this criteria can be evaluated using minor reaction energies from our analyses. Other properties, such as ionic transport, electronic conductivity, and mechanical properties are also critically important for the coating layer to achieve low interfacial resistance and to maintain robust interfacial coverage during electrochemical cycling [119,120]. Future studies to assess other required properties of the coating layer are needed to further optimize and design coating layers for all-solid-state batteries.

In conclusion, we conducted a systematic thermodynamic analysis of the chemical and electrochemical stability of Li-M-O chemistries with garnet LLZO and NMC. We revealed the thermodynamic mechanisms and factors governing the stabilities of materials with different cations, Li content, and compositions. Our results provide new materials candidates and guiding principles to identify promising coatings for garnet-based SE, high-energy cathodes, and for stabilizing the SE-cathode interfaces, which are critically needed to enable all-solid-batteries with high-energy cathodes. Our computation approach can be further applied to investigate and screen interphase or coating materials for stabilizing interfaces in other applications.

Chapter 5: Li transport in Al_2O_3 ¹

Improvements in Li-ion battery (LIB) safety and energy density require stabilization of electrode surfaces in the electrochemical environment, which in turn depend on advances in coating layer technology [8, 10]. Oxide coatings can suppress transition metal dissolution, scavenge corrosive species in the electrolyte, improve cyclability, and prevent chemical, structural, or electrochemical reaction of high energy electrodes during cycling [46, 50, 121–123]. Al_2O_3 is commonly used as a coating in many applications, including for battery electrodes, due to its high stability in a wide range of voltages, its relatively low cost and the availability of conformal coating techniques, such as atomic layer deposition (ALD), to accommodate virtually any electrode geometry. Thin coatings of Al_2O_3 have enabled better cyclability and stability in high-voltage spinel cathodes and high capacity layered cathodes [48, 124], and ALD-grown Al_2O_3 coatings have been used to improve cycle life and mitigate the effects of high volume expansion in anodes such as Si and MoO_3 by providing surface protection against electrolyte infiltration [125, 126].

Computation has indicated that Al_2O_3 has relatively good thermodynamic stability with a range of cathode materials [51], in good agreement with decades

¹This chapter has been published in or paraphrased from **A.M. Nolan**, D. Wickramaratne, N. Bernstein, Y. Mo, and M.D. Johannes, Li^+ diffusion in amorphous and crystalline Al_2O_3 for battery electrode coatings. *In preparation*, 2021.

of experimental findings that have shown that Al_2O_3 remains intact during cycling when coated on electrodes in lithium ion batteries with both liquid and solid electrolytes [31, 80, 127]. However, Al_2O_3 has been measured and calculated to have a band gap higher than operating voltage of LIBs in all crystalline and amorphous phases [128], and a Li^+ hopping barrier of greater than 1.5 eV in the most common crystalline α (corundum) phase [52, 129] and 0.5 – 1.5 eV in the amorphous phase [53, 55], making it hard to explain the strong evidence from cycling data that both Li ions and electrons are successfully passing through the material.

Several other groups have recognized and sought to understand this discrepancy. Authors of previous studies have proposed concentration-dependent diffusivity [54, 55], electron tunneling [130], or structural reconstruction due to heavy electron doping [54] as possible necessary conditions for Al_2O_3 cyclability. These studies have focused only on the room-temperature crystalline phase, corundum-structured alpha (α) Al_2O_3 , and amorphous Al_2O_3 (which we abbreviate as am- Al_2O_3 to avoid confusion with the α phase) [52–55]. Furthermore, no conclusive atomistic mechanism has been established to explain how conductivity is activated in an otherwise “dead” material. Since some evidence suggests that Al_2O_3 coatings may be not always be deposited in the amorphous phase, but might instead form crystalline domains other than α - Al_2O_3 [56], a detailed and systematic atomistic analysis of Li^+ migration in other phases of Al_2O_3 is relevant to understanding the mechanism by which Li moves through nanoscale Al_2O_3 coatings. In this chapter, we provide such an analysis, connecting global and local structural properties to Li^+ hopping barriers using nudged elastic band (NEB) calculations, and further

investigate the connection between Li^+ concentration to diffusivity with *ab initio* molecular dynamics (MD) in the context of our findings regarding the importance of local structure.

Beyond the thermodynamically stable $\alpha\text{-Al}_2\text{O}_3$, Al_2O_3 crystallizes into several other metastable polymorphs including the gamma (γ), theta (θ), kappa (κ), chi (χ), eta (η), and delta (δ) phases. The synthesis and characterization of these phases is the subject of several other works and reviews [131–133]. Among these phases, only the structures of κ and θ have been experimentally resolved, although there is general agreement that γ is a disordered cubic spinel [131, 134, 135]. The γ phase is the polymorph most commonly found in commercial applications such as catalysis or coatings [134, 136]. ALD-grown Al_2O_3 has been demonstrated to favorably form in the γ , α , or amorphous phase depending on conditions of strain energy, surface energy, and lattice mismatch of the substrate [137]. Further, the γ , θ , and κ phases of Al_2O_3 can reliably be formed with various deposition temperatures and substrates using chemical vapor deposition (CVD) [138–140]. In this work, we focus on the stable α phase and the metastable γ , θ , and κ polymorphs because of their structural confirmation in experiments and their accessibility via common processing routes. These metastable polymorphs have not yet been studied for Li-ion diffusion. An understanding and comparison of the mechanisms by which Li^+ diffuses through these different crystalline and amorphous structures can enable progress toward the development of reproducible, conductive coatings that protect electrode surfaces.

With first-principles computation, we can directly investigate the effect of atomic level differences in crystal structure on macroscale properties such as Li^+

diffusivity and conductivity. A fundamental understanding of Li diffusion within different phases of Al_2O_3 will guide experimental synthesis and fabrication of Al_2O_3 coatings for optimal battery coating layer performance. Here, we examine Li-ion diffusivity in Al_2O_3 as a function of structure and Li^+ concentration. We use first-principles nudged elastic band calculations and ab initio molecular dynamics simulations to observe Li^+ diffusion in the different structures of α , κ , γ , θ , and amorphous Al_2O_3 . We find that simple geometric properties such as the Li-Al distance correlate with the Li^+ migration barrier in both crystalline and amorphous Al_2O_3 , and use this to demonstrate how the migration barrier can be lowered by inducing of Al^{3+} deficiencies.

5.1 Li^+ sites and dilute Li^+ migration in α , κ , γ , θ , and amorphous Al_2O_3

We first demonstrate that lithium is incorporated in Al_2O_3 as lithium ions, Li^+ , rather than as metallic Li, Li^0 . This is the most common assumption based on the availability of Li ions in the electrolyte during cycling and is also relevant to the question of how concentration may affect Li^+ conductivity. The findings of Jung et al. [54] suggest that it is actually Li^0 that is added to Al_2O_3 and subsequently ionized, dumping charge into the Al-O bonds, weakening the overall structure, and creating more diffusive pathways. This would also heavily n-dope the material, rendering it metallic, which is in contradiction to in-situ cycling data [125]. Our defect energy calculations for Li^0 and Li^+ conclusively show that the formation

energy for Li^0 is prohibitively high for all chemical potentials and Fermi energies and thus, only Li^+ should be considered as feasible for incorporation in the matrix (Figure C.1). We continue from here under this assumption, as have most other previous computational investigations [55, 141].

An overview of the crystalline structures α , κ , γ , and θ - Al_2O_3 and the potential sites for Li^+ sites in these phases are shown in Figure 5.1. We identified candidate Li^+ sites in α , κ , γ , θ , and amorphous Al_2O_3 by using a combination of Voronoi analysis to find appropriately-sized volumes for Li^+ occupation, and bond valence analysis to identify sites with proper chemical environments for the Li^+ ion. We performed a static relaxation to converge the lattice parameters and atomic positions to their lowest energy configurations at each candidate Li^+ site. Parameters, cutoffs, and detailed methodology for all calculations can be found in Chapter 2.

For our initial calculations, all structures maintain perfect stoichiometry so that the only relevant differences between crystalline lattices are in the organization of the oxygen anion sublattice and the ratio of tetrahedral to octahedral Al^{3+} cations. The α phase, which has a corundum structure (space group $\text{R}\bar{3}\text{c}$), is the room temperature phase of Al_2O_3 , while orthorhombic κ (space group $\text{Pna}2_1$), cubic spinel γ (space group $\text{Fd}\bar{3}\text{m}$), and monoclinic θ (space group $\text{C}2/\text{m}$) are all metastable high-temperature phases. In α and κ , the oxygen anions are ordered in hexagonal lattice planes, with oxygen planes in α organized as ABAB packing, and in κ organized as ABAC packing. In α , two-thirds of the octahedral interstitials are occupied by Al^{3+} atoms in an ordered array. All Al^{3+} cations are octahedrally coordinated in α , while in κ , 25% of Al^{3+} cations are tetrahedrally coordinated and the other 75%

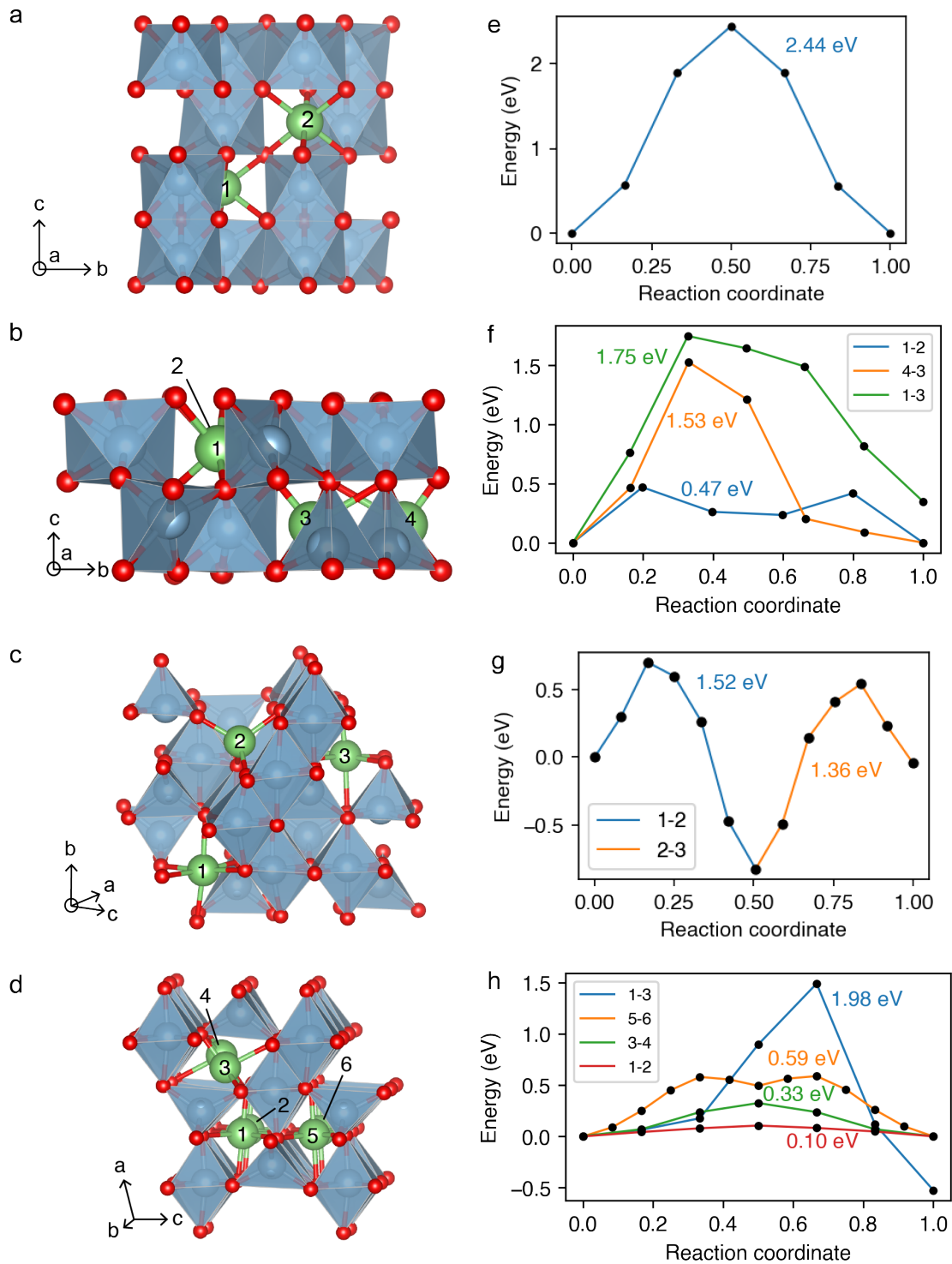


Figure 5.1: Structures and Li⁺ sites of crystalline a) α , b) κ , c) γ , and d) θ -Al₂O₃, where open channels in the b-direction can be seen. Aluminum, oxygen, and lithium atoms are represented by gray spheres in polyhedra, red spheres, and green spheres, respectively. NEB paths with normalized reaction coordinates for Li site hops in the e) α , f) κ , g) γ , and h) θ structures.

occupy octahedral interstitials.

In γ and θ - Al_2O_3 , the oxygen anion sublattice is arranged in a fcc structure, and Al^{3+} ions occupy either tetrahedral or octahedral interstitial sites. The γ structure is best understood as a defected cubic spinel, and has a disordered structure with lattice parameters and atomic positions that have yet to be fully experimentally resolved [134, 135]. In γ - Al_2O_3 , some of the octahedral and tetrahedral sites are occupied by Al^{3+} in a disordered array. Previous computational studies suggest 25–37.5% of Al^{3+} in γ may occupy tetrahedrally coordinated sites, while the other Al^{3+} cations occupy octahedrally coordinated sites [141]. In θ - Al_2O_3 , 50% of the Al^{3+} ions are tetrahedrally coordinated and 50% of the Al^{3+} ions are octahedrally coordinated. As observed by Wolverton and Hass, the increasing percentage of tetrahedrally coordinated Al^{3+} ions from γ to θ also matches the order in which they form from dehydration of a boehmite precursor [141].

Within each structure, Li^+ sites are coordinated by four (tetrahedral), five (pentahedral), or six (octahedral) oxygen anions. Li^+ migration occurs between neighboring octahedral sites in α , octahedral-tetrahedral sites in γ , and as octahedral-octahedral, octahedral-pentahedral, or pentahedral-pentahedral site hops in κ . We used nudged elastic band (NEB) calculations to calculate the energy of the migration barrier (E_a) and transition state energy for Li^+ hops between adjacent sites in each material. To calculate E_a , we took the energy difference of the highest and lowest energy images in the converged NEB path. In all crystalline and amorphous structures, we first examined migration barriers in the dilute case, corresponding to a Li concentration of approximately $x = 0.03$ in $\text{Li}_x\text{Al}_2\text{O}_3$ (one Li^+ per supercell),

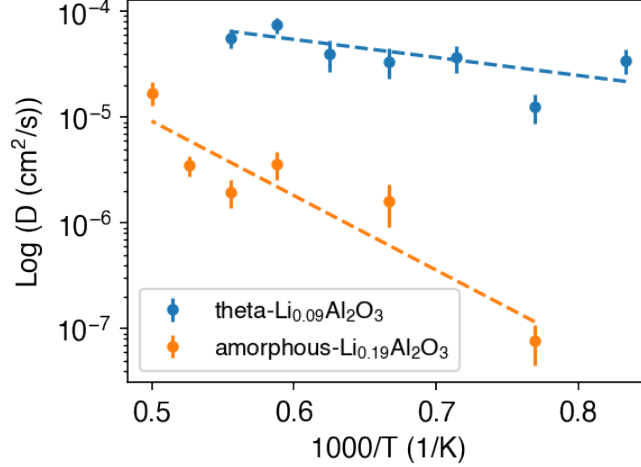


Figure 5.2: Arrhenius relationship for θ and amorphous Al_2O_3 with dilute Li concentrations.

with charge neutrality enforced by adding in a uniform positive background charge (or “jellium”, see Chapter 2 for further details). We later explored higher concentrations of Li in selected structures, as previous studies have suggested a dependence of diffusivity on Li concentration in amorphous Al_2O_3 [54, 55].

In the α , κ , and γ structures, the Li^+ migration barrier is high, above 1.5 eV for most paths. Li^+ has the largest migration energy barrier in α - Al_2O_3 , with $E_a = 2.44$ eV, in good agreement with previous studies. This barrier is prohibitively high for rapid migration through the coating layer, even for coatings as thin as 1 nm [52]. As further confirmation of this result, we found no Li^+ migration in ab-initio molecular dynamics (MD) simulations of Li^+ in α - Al_2O_3 at temperatures within 100 K of the melting point. In κ - Al_2O_3 , the energy barrier for migration between octahedral sites (sites 1 and 2 in Fig. 5.1b) is relatively low at $E_a = 0.47$ eV, but migration between pentahedral sites (sites 3 and 4 in Fig. 5.1b) requires a large activation energy of $E_a = 1.53$ eV. Migration between adjacent pentahedral

and octahedral sites in κ also has a large activation energy of $E_a = 1.75$ eV. Finally, in γ - Al_2O_3 , hopping occurs between octahedral and tetrahedral sites. The energy barriers found for different octahedral-tetrahedral hops were between 1.3 and 1.5 eV (Figure 5.1g). Overall, the high energy barrier for Li^+ migration indicate that fast (or even moderate) room temperature Li^+ conduction is unlikely to occur in α - Al_2O_3 , κ - Al_2O_3 , or γ - Al_2O_3 .

Compared to these structures, the barrier for Li^+ migration in the θ structure is very low. In θ - Al_2O_3 , Li^+ occupies sites in wide, open channels between oxygen planes, which run in the b-direction (Fig. 5.1d). The Li^+ sites in the channels are either tetrahedral or octahedral, with DFT energies slightly lower for the tetrahedral Li^+ than the octahedral Li^+ . Channels with tetrahedral sites are asymmetric in the a-c plane, with elongation along the c-axis (sites 3 and 4 in Fig. 5.1d), or elongation along the a-axis (sites 5 and 6), while channels with octahedral sites are more symmetric in the a-c plane. Tetrahedral-tetrahedral Li^+ migration has an energy barrier of $E_a = 0.3$ eV (hopping from site 3 to 4) or 0.6 eV (sites 5 and 6) and octahedral-octahedral migration in these channels has a barrier of $E_a = 0.1$ eV (sites 1 and 2 in Fig. 5.1d), the lowest Li^+ migration barrier for all crystalline materials studied. Hops between channels from octahedral to tetrahedral sites have high barriers of about $E_a = 1.5$ eV. The low barriers for Li^+ migration indicate that θ - Al_2O_3 is likely to exhibit fast Li^+ conduction, but that it would likely be confined to 1-D conduction along the b-axis channel. MD simulation results indicate θ - Al_2O_3 has an extrapolated room-temperature Li^+ conductivity of 0.004 mS cm^{-1} (lower bound $1.74 \times 10^{-4} \text{ mS cm}^{-1}$), upper bound 0.134 mS cm^{-1}) in the b-direction

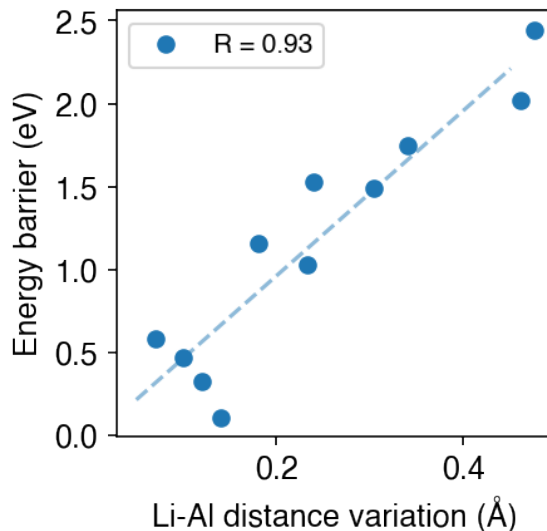


Figure 5.3: Energy barrier vs. Li-Al distance variation (LDV, see Chapter 2) for crystalline structures. Each point represents a migration path in a crystalline structure. The dotted line is a linear regression for the points, with Pearson’s correlation coefficient $R = 0.93$.

(Figure 5.2).

The wide variation in the energy of Li^+ migration barriers can only be attributed to differing structural parameters of the crystalline polymorphs. To understand how these parameters are related to the migration barriers, we plotted relationships between the migration barrier and the Li-Al distance, average Li-O bond length, Li site volume, migration path length, Li coordination number, and number of nearest Al neighbors (Chapter 2) for migrating Li in each image of the migration paths in the various crystalline structures. We found that the range of the average Li-Al distance for each path, referred to here as the Li-Al distance variation (LDV) (Chapter 2), has by far the strongest correlation with the migration barrier in the crystalline polymorphs, with a correlation coefficient $R = 0.93$ (Figure 5.3). The LDV measures the change in the average Al neighbor distance as the

Li^+ migrates along a given path. Our work shows that as this variation increases, so does the activation barrier. Other variables we examined, including the Li site volume, average Li-O distances, average Li-Al distances, and coordination number did not significantly correlate with the migration barrier (Figure C.2). Therefore, Li^+ migration is facilitated when the Al-neighbor environment remains constant throughout the migration channels. Further, this suggests that in crystalline structures, a lower barrier is more favorable for structures where Li^+ sites are large and far from neighboring Al^{3+} cations. The Coulomb repulsion between the high positive charge of Al^{3+} and Li^+ , badly screened by the dielectric environment, is the most likely underlying factor determining this relationship.

In sharp contrast to the crystalline polymorphs, where sites are mainly tetrahedrally or octahedrally coordinated and are symmetric within each structure, Li^+ sites in amorphous Al_2O_3 , as found through Voronoi analysis, have a range of O coordination numbers and local environments, resulting in varying Li^+ energies and barriers for migration (Figure 5.4a and b). Low barriers certainly exist throughout the amorphous structure, but any path allowing Li^+ to move a reasonable distance is likely to also contain some sites with very low energies relative to neighboring spots. These low-energy sites can act as trapping sites for Li^+ , resulting in lower diffusivity.

In our study of 135 sites in the 160-atom amorphous supercell, Li-ions tended to predominantly occupy 3-, 4-, 5-coordinated sites in am- Al_2O_3 , and rarely 6-coordinated sites. The median site energy increased with coordination number, where 3-coordinated sites had the lowest median energy and 6-coordinated sites had

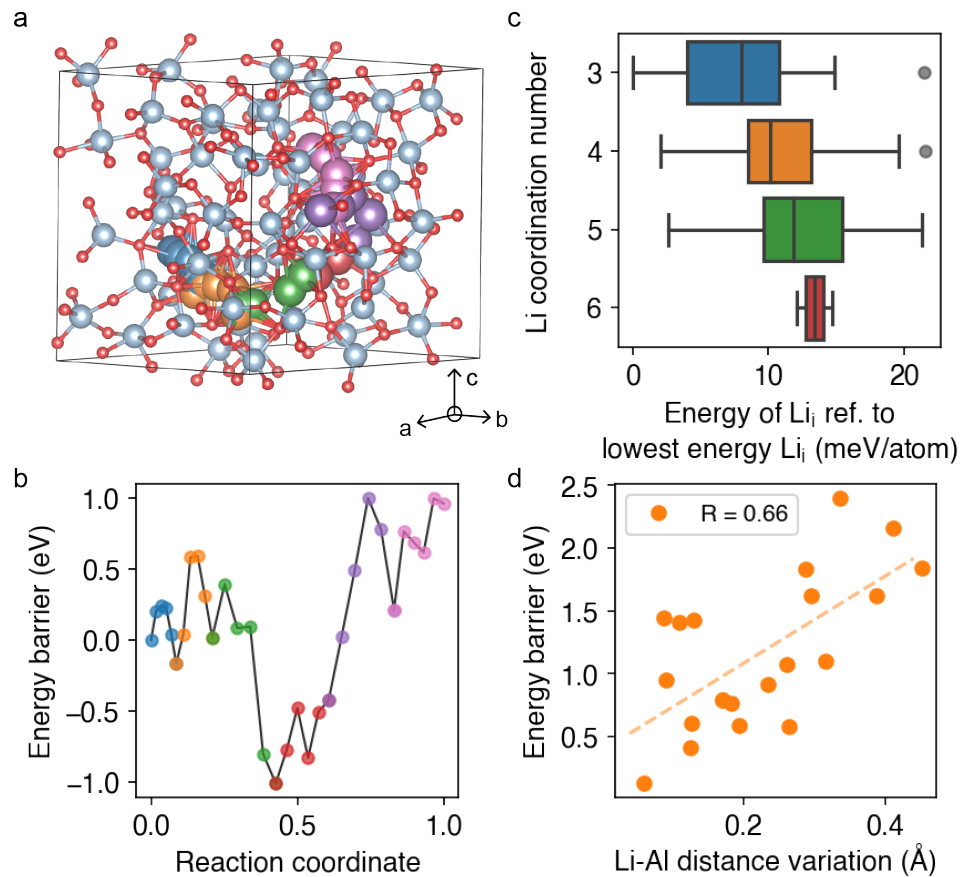


Figure 5.4: Li⁺ transport in am-Al₂O₃. a) Amorphous structure with Al (light blue), O (light red), and Li sites (large spheres, multiple colors) from NEB calculations and b) corresponding connected NEB path. Colors of Li in structure correspond to points plotted in path. c) Boxplots of distribution of the energy of Li⁺ interstitials in am-Al₂O₃, Li_i, referenced to the lowest energy Li_i found for the structure, grouped by coordination number. All Li sites and NEB images were used. The center line in each box indicates the median of the data, the edges of the box indicate the first and third quartiles, and the whiskers indicate the range of the data or 1.5 times the interquartile range, whichever is smaller. Points outside the whiskers (outliers) are marked with gray circles. d) Energy barrier vs Li-Al distance variation for all studied migration paths in amorphous Al₂O₃. The dotted line is a linear regression of the points with correlation coefficient $R = 0.66$.

the highest (Figure 5.4c). However, the energy difference between sites with different O coordination numbers was small and the range in energies overlapped for all coordination numbers, which provides an explanation for why we did not find a trend between energy barrier and Li-O coordination number or Li-O distance. Among the migration paths we studied ($N = 21$), some could be connected together across the cell, and these connected paths had overall migration barriers of approximately 2 eV (Figure 5.4b). However, these connected paths may not be representative of the average migration barrier for Li^+ in amorphous. From our MD simulations, Li^+ migration in am- $\text{Li}_{0.2}\text{Al}_2\text{O}_3$ had an $E_a = 1.39 \pm 0.137$ eV (Figure 5.2), which agrees well with the activation energy for dilute Li^+ concentrations in amorphous Al_2O_3 from previous computational studies [55]. We found a positive correlation between migration barrier and LDV similar to that in the crystalline materials (Figure 5.4d), indicating that the strong dependence of Li^+ migration on the repulsion from nearby Al^{3+} holds in the amorphous system.

5.2 Effect of Li^+ concentration in Al_2O_3

Previous studies have shown Li^+ diffusivity increases slightly with concentrations higher than $x = 0.3$ in amorphous $\text{Li}_x\text{Al}_2\text{O}_3$ [55]. In our MD simulations of $\alpha\text{-Al}_2\text{O}_3$, we observed only two Li^+ hopping events in $\alpha\text{-Li}_{0.56}\text{Al}_2\text{O}_3$, but none for those with lower Li concentrations. For amorphous- $\text{Li}_x\text{Al}_2\text{O}_3$, our MD simulations of Li concentrations from $x = 0.09$ to 0.25 show small shifts in diffusivity with concentration, but little trend (Figure 5.5a). By contrast, in MD simulations of $\theta\text{-Al}_2\text{O}_3$, we

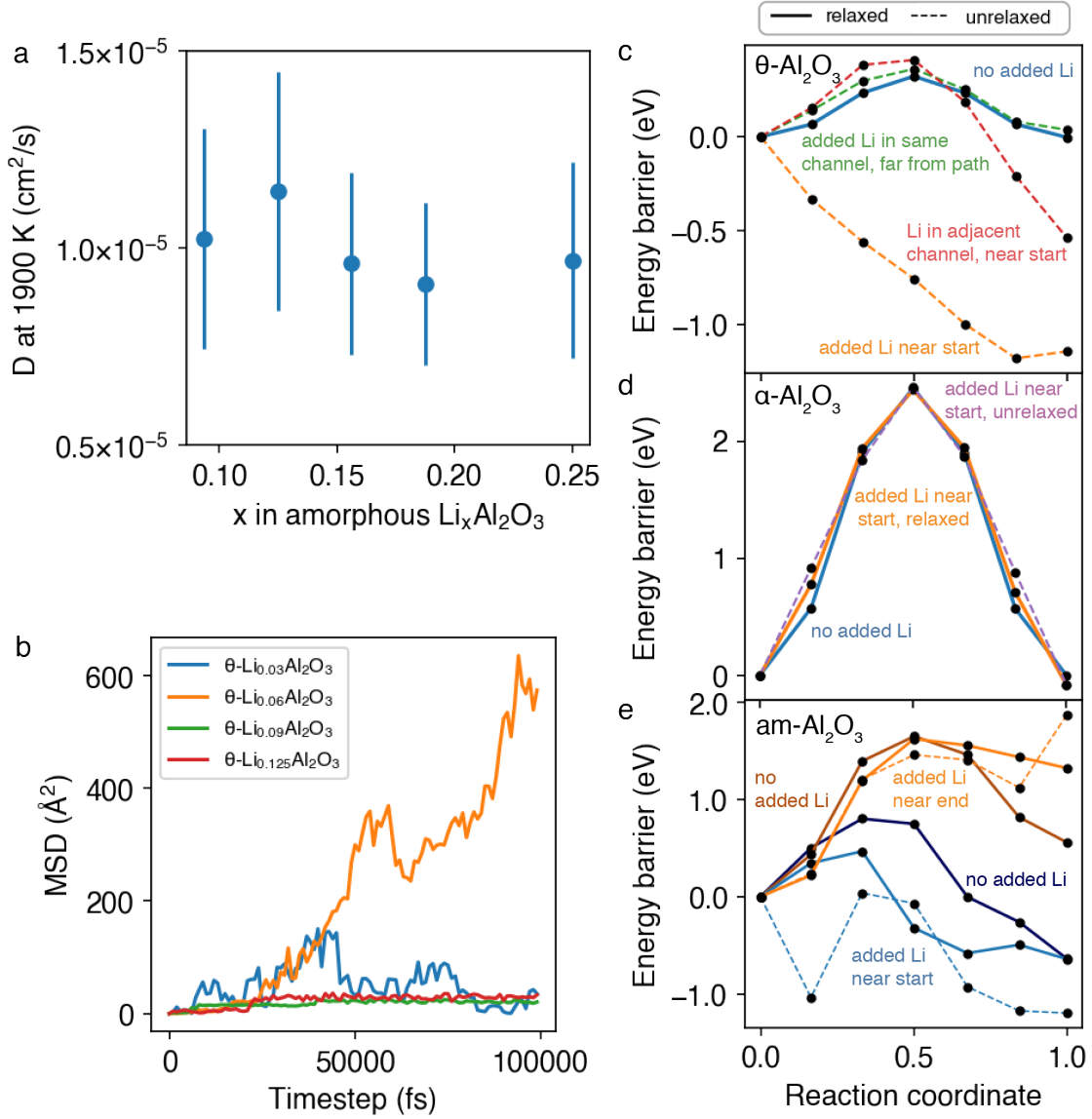


Figure 5.5: Effect of increasing Li^+ in α , θ , and am- Al_2O_3 . a) Li diffusivity in am- Al_2O_3 from MD simulations at 1900 K as function of Li^+ concentration. b) Mean squared displacement (MSD) of Li^+ ions in $\theta\text{-Al}_2\text{O}_3$ with increasing Li concentration at 1300 K. Migration energy barriers for selected paths in c) θ , d) α , and e) amorphous Al_2O_3 , comparing relaxed paths (solid lines) with unrelaxed paths with an added Li^+ near the start or end of the path (dashed lines). In (c), the relaxed path (solid blue line) is the 3-4 path as shown in Fig. 5.1d, corresponding to a tet-tet hop.

found that the number of Li hops of Li^+ decreased as Li^+ concentrations increased (Figure 4b), implying that the cells with higher concentrations ($x > 0.06$) do not show fast diffusion. The mechanism driving these shifts in diffusivity as a function of Li concentration could involve direct Li^+ - Li^+ repulsion in the relatively unscreened environment of the Al_2O_3 matrix, gradual filling of the lowest energy (trap) sites such that at higher concentrations Li^+ can easily hop between the remaining high energy sites left available [142], local or global structural distortions that affect the favorability of available pathways, or competition or cooperation between any of these factors. To distinguish between these possibilities and uncover the origin of the different behaviors in different structures, we examined the atomistic effect of Li^+ concentration in am- Al_2O_3 , θ - Al_2O_3 (the most intrinsically conductive crystal), and α - Al_2O_3 (the least intrinsically conductive crystal) by adding an extra Li^+ near to endpoints of the hopping paths previously calculated for Li ions in the pristine Al_2O_3 matrix.

To isolate the effect of Li^+ - Li^+ Coulombic interactions, we placed an extra Li^+ near the endpoints of the migration path and recalculated the energies along the path, first without any structural relaxation and subsequently re-relaxing the entire NEB path. In some cases we found that the added Li^+ so strongly repelled the existing Li^+ that the path itself was altered, eliminating the option of a direct comparison between relaxed migration paths with and without added Li^+ . Ions placed in positions near (1.5 Å) the start or end points of the migrating ion dramatically changed the path energies due to direct Li^+ - Li^+ repulsion (evaluated without relaxation), and in many cases also had additional strong effects through lattice

relaxation.

For θ -Al₂O₃, both intra- and cross-channel Li⁺-Li⁺ interactions appear to be relatively unscreened, as migrating Li were strongly “pushed” away from added ions (Fig. 5.5c), especially within the channel. The range of Li⁺-Li⁺ interactions is fairly localized; ions added 3 Å or more away did not change the migration barrier. After relaxation of extra Li⁺ at nearby sites (< 2 Å apart), the added Li-ions did not stay at their initial proximity and instead moved further apart due to electrostatic repulsion (and low intrinsic migration barrier). Therefore, we could not directly compare relaxed paths without and with an additional Li⁺ in close proximity, but we can gauge the overall effect of relaxation through calculations of the migration path with added Li⁺ at greater distances. We performed these for a variety of Li⁺ concentrations. Li⁺ concentration-induced relaxation raises the barrier in θ -Al₂O₃ (Figure C.3). For all concentrations $x > 0.03$ (one Li⁺ per supercell) in θ -Li_xAl₂O₃, Li⁺ migration barriers increased. This can be traced to shrinkage or collapse of the channels in response to added Li⁺ that makes the pathway less favorable for migration. We also studied the θ surface and found extremely distorted channels near the vacuum layer (Figure C.4), resulting in an increased migration barrier. This highlights the fact that the integrity of the 1D channels in θ is critical to fast diffusion within the structure, and that this integrity is compromised by structural relaxation in response to increasing Li⁺ concentration. Our MD simulations showed that at concentrations of Li⁺ where $x > 0.06$, in addition to constriction of the channels, framework Al³⁺ occasionally swapped positions with Li⁺, blocking the fast-conducting channels, and causing overall structural changes reminiscent of a

phase transition (Figure C.5). Thus, we conclude that in the case of θ -Al₂O₃, it is structural effects, specifically choking of the 1D channels, that are the dominant effect of increasing Li⁺ content and that these are detrimental to ionic conductivity.

In α -Al₂O₃, we found that the addition of a Li⁺ had virtually no effect on the migration barrier or the symmetry of the energy barrier for hopping between the two identical sites (Fig. 5.5d), indicating that the migrating Li⁺ is not “pushed” as it was in θ -Al₂O₃. Li⁺ sites in the α structure are spaced widely at approximately 3.3 Å apart, and we have already established that almost no direct Coulombic repulsion is operative at this distance. Additionally, the surrounding Al³⁺ framework atoms are closer to the migrating Li⁺ than they are in the θ structure (between 2.0 and 2.8 Å), which may result in increased screening of direct Li⁺-Li⁺ interaction. A relaxation of the NEB path with the extra Li⁺ recovers almost exactly the original path energies and barrier, demonstrating that the added Li⁺ does not change or distort the Al³⁺ framework, but also does not enhance migration. These findings are in alignment with our MD simulations that show increasing Li⁺ concentration in α appeared to have little effect on the number of observed hopping events. From this result, we conclude that increasing Li⁺ concentration in α is not likely to increase the conductivity, as no strong Li⁺-Li⁺ interactions exist at relevant site distances in this structure.

In amorphous Al₂O₃, Li⁺-Li⁺ interactions were readily observed for Li⁺ close to one another (approximately 1.5–2.0 Å apart) (Fig. 5.5e). We found Li⁺-Li⁺ repulsion affected path energies in both high and low barrier paths, and at a variety of sites with different energies and Al³⁺ environments. Since hops in am-Al₂O₃

occur between sites of different energies, the migration paths are intrinsically non-symmetric. As before, we place an extra Li^+ near to the endpoints of the migration path and recalculate path energies without relaxation. For am- Al_2O_3 , the energies of the initial and final sites differ, resulting in more calculations. For both endpoints, and for both the high and low energy barrier paths we chose, the Li^+ is “pushed” away from the extra Li^+ by Coulomb repulsion. Very large shifts in energy were seen for nearby site energies and the overall barrier for the higher energy hop was lowered by approximately 1 eV. We also found that when a nearby low energy site is occupied, the energy barrier for migration in the vicinity of the site is lowered (Figure C.6). These results suggest that the atomistic mechanism for the dependence of diffusivity on concentration found in previous studies [55] is the occupation of very low energy sites, which not only eliminates trapping sites, but also lowers the migration barrier for nearby migrating ions. Previous studies also suggested an increased concentration of Li^+ up to a formula of $\text{Li}_{3.5}\text{Al}_2\text{O}_3$ is energetically favorable over the dilute case [54], suggesting that lithiation of the amorphous coating is a viable method to improve Li^+ diffusivity in the material. Our investigation of a surface model of amorphous Al_2O_3 indicates that the amorphous surface is likely to behave similarly to the bulk, with a similar average migration barrier and concentration dependence, regardless of structural distortions of the surface (Figure C.7-C.9). Therefore, we suggest that in coatings of amorphous Al_2O_3 , the weak dependence of diffusivity on increasing Li^+ concentration originates from gradual filling of the lowest energy sites.

To summarize our findings, we suggest that increased Li concentration im-

proves diffusivity in structures with “hilly” energy landscapes, i.e. a mixture of low energy trapping sites and high energy sites, such as am- Al_2O_3 . Added Li^+ occupy and thereby eliminate the low energy trapping sites, which also facilitates Li^+ migration in adjacent sites. Li^+ - Li^+ interactions are poorly screened in the dielectric environment of Al_2O_3 , which may drive Li^+ through the lattice during charge and discharge as a concentration gradient is imposed. There are also structural changes precipitated by Li^+ concentration. For the case of the intrinsically diffusive 1D channels in θ - Al_2O_3 , Li^+ -driven perturbation of the structure impedes Li^+ transport. The high intrinsic migration barrier of α - Al_2O_3 is relatively insensitive to Li^+ incorporation except at very high Li^+ concentrations sufficient to alter the structural framework.

5.3 Li^+ migration in defected Al_2O_3

Because defect energies for Al^{3+} and O^{2-} vacancies are calculated to be low in Al_2O_3 according to our work and that of others [143], and because of the strong relationship we found between LDV and Li^+ migration barrier in crystalline and amorphous Al_2O_3 , we next studied how native defects affect Li^+ migration. We removed O^{2-} and Al^{3+} at varying concentrations, compensated with jellium or added Li^+ , respectively, relaxed the structures to allow for accommodation of the removed/added atoms, and performed MD simulations and NEB calculations. We did not find any marked effect of O^{2-} off-stoichiometry on Li^+ hopping (Figure C.10), which is consistent with the lack of dependence of the Li^+ migration barrier on the Li-O distance

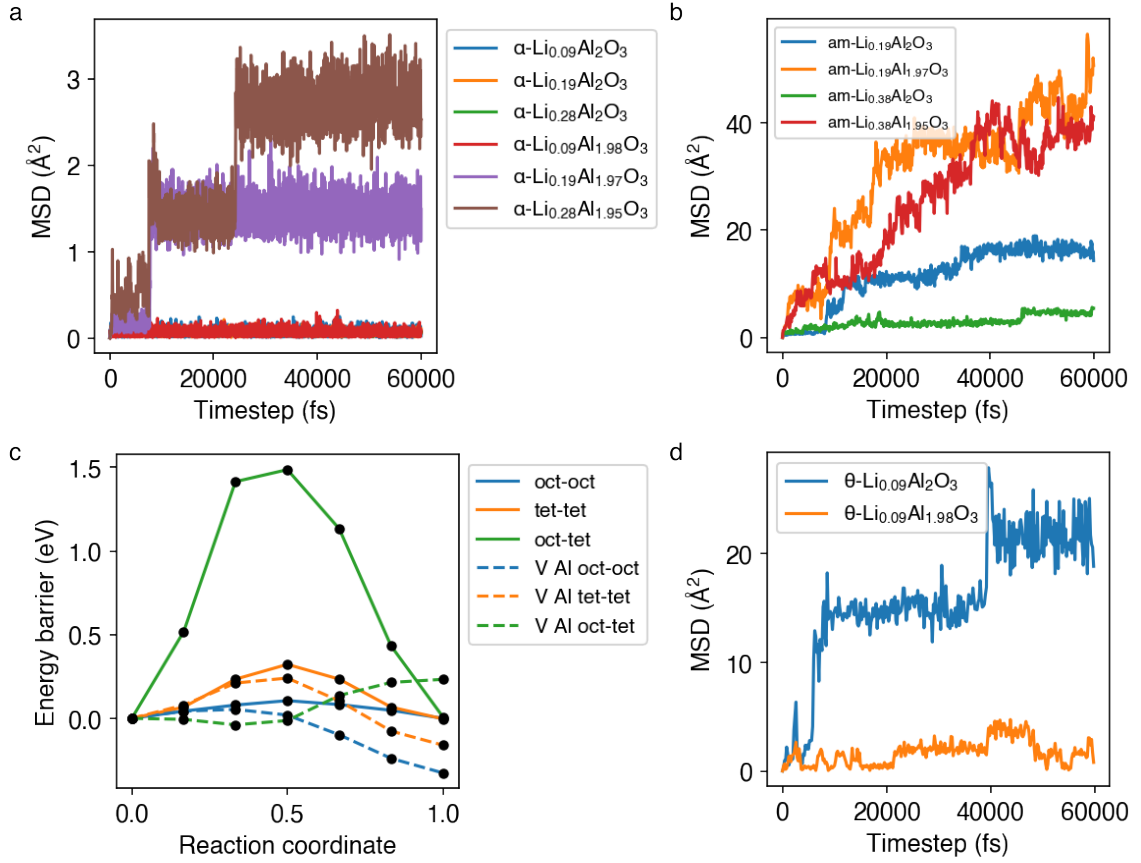


Figure 5.6: Al^{3+} off-stoichiometry and Li^+ migration. MSD of Li^+ for several Li^+ concentrations in pristine and off-stoichiometric a) α and b) amorphous Al_2O_3 , both at 1300 K. c) Energy barriers for paths in pristine (solid line) $\theta\text{-Li}_{0.09}\text{Al}_2\text{O}_3$ and Al^{3+} vacancy defected (dotted line) $\theta\text{-Li}_{0.09}\text{Al}_{1.94}\text{O}_3$. d) MSD of Li^+ in $\theta\text{-Li}_{0.09}\text{Al}_2\text{O}_3$ and Al^{3+} vacancy defected $\theta\text{-Li}_{0.09}\text{Al}_{1.94}\text{O}_3$ at 1300 K.

in amorphous or crystalline Al_2O_3 polymorphs. We therefore focused on the effect of Al^{3+} off-stoichiometry on the migration energy barrier. We studied Li^+ migration in α , θ , and am- Al_2O_3 with various levels of Al^{3+} deficiency, compensating for the charge difference by adding 3 Li^+ for each Al^{3+} removed (see further details in Chapter 2). Overall, the number of Li^+ hopping events increased in Al^{3+} -deficient crystalline α (Figure 5.6a) and amorphous Al_2O_3 (Figure 5.6b) compared to stoichiometric structures with the same Li^+ concentration (but charge compensated by a uniform positive background). Our MD simulations of Al^{3+} vacancy-defected α structures showed several hopping events in α , whereas the same duration of MD of the pristine lattice with the same Li concentration showed no movement of Li interstitials. Visual inspection of our MD simulations revealed that Li hopping in α occurred within enlarged Li^+ sites formed by Al^{3+} vacancies in the lattice (Figure C.11). The calculated migration barrier for the Li^+ hops mediated by Al^{3+} vacancies was also drastically lower than the barrier for Li migration in pristine α . In amorphous Al_2O_3 , we fully relaxed structures with Al^{3+} removed and compensating Li^+ added, resulting in a bond network that rearranged to accommodate the missing Al. The migration barriers in these structures with Al^{3+} off-stoichiometry were also lowered compared to the non-defected case (Figure C.12), though to a lesser extent than in the crystalline α structure. In the Al^{3+} off-stoichiometric structures, Li^+ occupied the vacant Al^{3+} sites after relaxation, which indicates that the improved Li^+ transport was not specifically vacancy-driven, i.e., Li^+ did not travel via a string of vacancies connected through the structure. Rather, increased movement was a result of the changed Li-Al environment and lowered Coulombic repulsion. Overall,

our findings suggest that an increase in Al^{3+} sub-stoichiometry may facilitate Li^+ migration in both α and amorphous Al_2O_3 . This finding squares with our previous result that a smaller LDV lowers the Li^+ migration barrier, and identifies $\text{Li}^+ - \text{Al}^{3+}$ as the dominant charge interaction in this material.

By contrast, in $\theta\text{-Al}_2\text{O}_3$, in which Li diffusion is fastest in the non-defected structure, almost all of the energy barriers were similar or slightly higher in defected structures. The exception was for the high barrier cross-channel hops near the Al^{3+} vacancy, which were instead lowered (Figure 5.6c). This can again be explained by structural distortions that drive local constriction along the high mobility 1D channels. The Al^{3+} vacancies in the θ framework were occupied by a Li^+ substituent, which caused asymmetry in the LDV and Li site volume for paths in the channel, increasing the migration barrier. This is consistent with our studies of the migration energy landscape in θ which indicate that even minor structural distortion raises migration barriers (Figure C.4). However, we found the opposite effect for hopping across channels, where reduction of LDV was not offset by channel constriction. These microscopic observations are supported by MD simulations in which Li^+ migration was more sluggish in the Al-defected structure than in the pristine one (Figure 5.6d).

5.4 Discussion

In this study, we systematically analyzed the effects of crystal structure and ionic concentration on Li^+ diffusion in Al_2O_3 . We observed that the varied Li^+

migration barriers in the α , κ , γ , and θ crystalline Al_2O_3 polymorphs and amorphous Al_2O_3 were strongly correlated with Li-Al distance variation (LDV, see Chapter 2), which is a measure of the variation of the distance between Li and neighboring Al along the migration path. This correlation suggests that Al_2O_3 crystal structures with minimal fluctuation in the size of the Al framework channels connecting Li sites will most readily conduct Li ions. This is consistent with the very low barrier for Li migration in the θ structure, as θ - Al_2O_3 has characteristic wide channels and large Li sites far from adjacent Al^{3+} . In other structures, such as α - and κ - Al_2O_3 , the dense packing of Al^{3+} ions and constriction of the site, with closer neighboring Al atoms at the transition point, raise the barrier energy and cause sluggish Li^+ migration.

The concentration of Li^+ in the structures is relevant for Li^+ diffusion in all structures studied, but in varying ways. In amorphous Al_2O_3 , we found that because of the strong Li^+ - Li^+ interactions, the addition of a Li-ion near the start of a migration path would lower the migration barrier through Coulomb repulsion. These interactions, along with a gradual filling of the lowest energy trap sites, comprise the mechanism for increased diffusivity. In a battery charge/discharge process, there is a natural directional gradient to Li^+ density that could serve to drive movement through the coating. This implies that pre-lithiation of the amorphous coating may be a viable option to increase conductivity, both by pre-filling trap sites and by increasing repulsion. In α - Al_2O_3 , where the Li^+ migration barrier in the dilute case is so high as to effectively block Li^+ transport, the number of hopping events in MD simulations increased only in extremely lithiated structures, but remained essen-

tially zero at small concentrations. The number of hopping events did not increase with increasing Li^+ concentration in $\theta\text{-Al}_2\text{O}_3$, where increasing Li^+ concentration disrupted the migration channels in the structure, especially in high-temperature MD simulations where it appeared to precipitate a phase transition, causing slower diffusion than in the dilute case. Our work suggests that amorphous Al_2O_3 provides the best optimization between favorable repulsion and unfavorable distortion and that efforts to synthesize highly conductive $\theta\text{-Al}_2\text{O}_3$ for anode/cathode coating materials would be fruitful only at the very beginning of the charge/discharge where Li^+ density is low enough that the structure is preserved, and disadvantageous deeper in the cycle.

For off-stoichiometric α , θ , and amorphous Al_2O_3 , we found that while O^{2-} and Al^{3+} defects would affect diffusivity, Al^{3+} off-stoichiometry in α and amorphous materials could effectively lower the migration barrier and increase the number of hopping events compared to the non-defected lattices. In defected $\alpha\text{-Al}_2\text{O}_3$, Al^{3+} vacancy clusters drastically lowered the barrier for migration. MD simulations also suggested that Al^{3+} off-stoichiometry resulted in a greater number of hopping events in α and amorphous Al_2O_3 . As with Li^+ concentration, the Al^{3+} off-stoichiometry advantage in θ was offset by structural distortion and incipient phase transition that choked off the conductive channels.

Overall, our key findings are that stable, fast Li^+ diffusivity in Al_2O_3 may be achieved via a combination of high Li^+ concentration and lower concentration of Al^{3+} (off-stoichiometry) in amorphous materials. Since typical Al_2O_3 synthesis and coating methods do not involve Li, one route to conductive coatings would be

to manipulate the Al^{3+} vacancy concentration of deposited coatings, perhaps by synthesis in an O-rich environment, and increase the Li^+ concentration in-operando during cycling. In this case, lithiation would require a depletion of the Li capacity in the electrode during the first cycle, suggesting that coating a Li-rich anode (such as Li metal) against dendrite formation may be a more fruitful path towards improved battery performance than protectively coating the relatively Li-poorer cathode. However, since Li^+ and $\text{V}_{\text{Al}}^{3+}$ are compensating defects that form a neutral $\text{V}_{\text{Al}}^{3+}\text{-3Li}^+$ defect complex, it may be possible to achieve an optimal material at the synthesis level. Our work suggests that a Li-enriched, Al-deficient am- Al_2O_3 coating would be highly conductive and suitable for both anode and cathode protection.

Chapter 6: Conclusions and future work

6.1 Conclusions

I used thermodynamic analyses based on first-principles computation data to systematically examine the stability between high-voltage cathodes and solid-state chemistries. I found that the thermodynamic stability of coating layers with high voltage cathodes is highly influenced by the Li content (atomic Li fraction) of the coating. A match or overlap between the Li chemical potential (μ_{Li}) of coating and cathode is important for stability. Coatings with a higher Li content will tend to be stable with layered cathodes, while coatings with a lower Li content will tend to be stable with delithiated or high-voltage cathodes. Because the stability varies with the Li content and cation chemistries, the interface stability or compatibilities should be individually evaluated for each pair of cathode, coating, and solid electrolyte compositions. Among the classes of materials that I studied, I found that lithium quaternary phosphates and lithium ternary fluorides both had good stability with high-voltage cathodes and sufficient Li content for Li transport, and may be useful to investigate as coating materials.

I further evaluated the stability between different cathodes and a specific solid electrolyte, garnet-structured LLZO, which is promising because of its high Li-ion

conductivity and wide electrochemical stability window. I found that LLZO and most oxide cathodes are intrinsically thermodynamically unstable, and, similarly to the high-voltage cathode and coating layers, this instability is caused by a mismatch of the μ_{Li} between the two materials. The intrinsic instability causes interfacial degradation during cycling, especially at high voltages, leading to high interfacial resistance and poor stability, which has also been reported in experiments. Given this instability, a coating will be critical to stabilize and protect LLZO-cathode interfaces. Through systematic analysis with lithium ternary oxide coating layer chemistries, I found the stability of LLZO with a Li-M-O coating is highly dependent on the identity of the element M. For elements M that are stable with garnet, Li-M-O coatings will have a wide composition range that is stable with garnet. These types of materials are promising coatings for protecting garnet, since they would remain stable with LLZO throughout compositional fluctuations due to sintering, electrochemical cycling, or side reactions. The overlap of Li-M-O compositions stable with LLZO and NMC occurs for O-rich and Li-rich compositions generally along the tie-line between Li_2O and M-O oxides. Based on these trends, I identified a number of promising new coating layers and provide guiding tables and figures for experimental coating layer selection (see Chapter 4).

Finally, I used first-principles computation to analyze the effects of crystal structure and composition on Li^+ migration in Al_2O_3 , a common coating layer. I observed that the migration barriers in the α , κ , γ , and θ crystalline phases and amorphous Al_2O_3 was strongly correlated with Li-Al distance variation, such that larger distances between Li^+ and neighboring Al^{3+} in the structure are a good proxy for

low Li⁺ migration barriers in both crystalline and amorphous polymorphs. Among the polymorphs I studied, I found θ -Al₂O₃ has the lowest migration barrier and the fastest Li⁺ diffusion, but its 1D diffusion channels are delicate and susceptible to distortion, which disrupts easy migration. The incorporation of higher concentrations of Li⁺ increased the number of observed hopping events in amorphous and α -Al₂O₃, but caused distortion and a phase transition in θ -Al₂O₃, preventing fast diffusion. Although O²⁻ vacancies were largely inert, I found that Al³⁺ vacancies and off-stoichiometry could lower the migration barrier and increase the number of hopping events in α and amorphous Al₂O₃. Therefore, lowering the Al³⁺ content, perhaps through introduction of vacancy defects or synthesis in an O-rich environment, could be a viable method to achieve stable and Li-diffusive Al₂O₃ coatings.

6.2 Future work

Although this thesis work has provided understanding of the interface, thermodynamic stability of coating layers, and Li-ion transport in Al₂O₃, additional studies are needed to guide the development of the solid electrolyte-cathode interface. For example, we have yet to understand the effects of experimental conditions such as high-temperature sintering or varied processing conditions, and how these environmental changes affect the stability of components at the interface, the ionic conductivity of the coating, and other properties of interest such as mechanical strength or stiffness. These remaining knowledge gaps articulate key future directions for this work.

The thermodynamic analyses performed in this thesis rely on DFT energies calculated for materials at 0 K. One of the core questions for this type of analysis is how it can translate to reactions at room temperature or higher temperatures, since processing of the electrolyte-cathode interface generally occurs at higher temperatures. A valuable future research effort would be to conduct thermodynamic analyses to model the high temperature reactions between solid electrolyte, cathode, and coating layer. Kinetics and surface structure or morphology will also play a role at high temperatures, and these variables may be taken into consideration with large-scale molecular dynamics simulations separate from the thermodynamic analyses used here.

The ionic conductivity of the coating layer is also a major factor in its success in lowering interfacial resistance and improving battery performance. As can be seen from my work on Li^+ transport in Al_2O_3 , Li-ion conductivity within the coating layer is highly individualized depending on the chemistry, and chemistries with multiple polymorphs can have a wide range of Li^+ migration energies and diffusivities. Further work on successful chemistries within a particular system would be useful to improve our understanding of how to synthesize and process coating layers. For example, the amorphous Li-Nb-O system is successful as a coating layer with LLZO garnet and layered oxide cathodes, but there is little understanding of how the Li content and overall stoichiometry affect Li^+ conduction. An in-depth study of the Li^+ migration in additional experimentally demonstrated coatings for a particular system (e.g. LLZO-NMC) would allow us to fine-tune the chemistry for best Li^+ diffusivity and thermodynamic stability.

Chapter 7: Publications and presentations

7.1 Publications

1. **Adelaide M. Nolan**, Yunsheng Liu, and Yifei Mo. Solid-State Chemistries Stable with High-Energy Cathodes for Lithium-Ion Batteries. *ACS Energy Letters*, 4(10):2444–2451, 2019.
2. **Adelaide M. Nolan**, Eric D. Wachsman, and Yifei Mo. Computation-Guided Discovery of Coating Materials to Stabilize the Interface Between Lithium Garnet Solid Electrolyte and High-Energy Cathodes. *Under revision*, 2021.
3. **Adelaide M. Nolan**, Darshana Wickramaratne Noam Bernstein, Yifei Mo, and M.D. Johannes. Li^+ diffusion in amorphous and crystalline Al_2O_3 for battery electrode coatings. *In preparation*, 2021.
4. **Adelaide M. Nolan**, Yizhou Zhu, Xingfeng He, Qiang Bai, and Yifei Mo. Computation-Accelerated Design of Materials and Interfaces for All-Solid-State Lithium-Ion Batteries. *Joule*, 2(10):2016–2046, 2018.
5. **Adelaide M. Nolan** and Yifei Mo. A Solid with Liquid-like Diffusion: A

- Unique Superionic Conductor. *Chem*, 5(9):2289–2290, 2019.
6. Yirong Gao[§], **Adelaide M. Nolan**[§], Peng Du[§], Yifan Wu, Chao Yang, Qianli Chen, Yifei Mo, and Shou-Hang Bo. Classical and emerging characterization techniques for investigation of ion transport mechanisms in crystalline fast ionic conductors. *Chemical reviews*, 120(13):5954–6008, 2020. [§]co-first authors
 7. Xuetian Ma, **Adelaide M. Nolan**, Shuo Zhang, Jianming Bai, Wenqian Xu, Lijun Wu, Yifei Mo, and Hailong Chen. Guiding synthesis of polymorphs of materials using nanometric phase diagrams. *Journal of the American Chemical Society*, 140(49):17290–17296, 2018.
 8. Rusong Chen, **Adelaide M. Nolan**, Jiaze Lu, Junyang Wang, Xiqian Yu, Yifei Mo, Liquan Chen, Xuejie Huang, and Hong Li. The thermal stability of lithium solid electrolytes with metallic lithium. *Joule*, 4(4):812–821, 2020.
 9. Md Shafiqul Islam, **Adelaide M. Nolan**, Shuo Wang, Qiang Bai, and Yifei Mo. A Computational Study of Fast Proton Diffusion in Brownmillerite $Sr_2Co_2O_5$. *Chemistry of Materials*, 32(12):5028–5035, 2020.
 10. Jian Duan, Wangyan Wu, **Adelaide M. Nolan**, Tengrui Wang, Jiayun Wen, Chenchen Hu, Yifei Mo, Wei Luo, and Yunhui Huang. Lithium–Graphite Paste: An Interface Compatible Anode for Solid-State Batteries. *Advanced Materials*, 31(10):1807243, 2019.
 11. Yao Liu, Qiang Bai, **Adelaide M. Nolan**, Yongning Zhou, Yonggang Wang,

- Yifei Mo, and Yongyao Xia. Lithium ion storage in lithium titanium germanate. *Nano Energy*, 66:104094, 2019.
12. Daxian Cao, Yubin Zhang, **Adelaide M. Nolan**, Xiao Sun, Chao Liu, Jinzhi Sheng, Yifei Mo, Yan Wang, and Hongli Zhu. Stable thiophosphate-based all-solid-state lithium batteries through conformally interfacial nanocoating. *Nano letters*, 20(3):1483–1490, 2019.
 13. Yunsheng Liu, Shuo Wang, **Adelaide M. Nolan**, Chen Ling, and Yifei Mo. Tailoring the Cation Lattice for Chloride Lithium-Ion Conductors. *Advanced Energy Materials*, 10(40):2002356, 2020.
 14. Menghao Yang, Yunsheng Liu, **Adelaide M. Nolan**, and Yifei Mo. Interfacial Atomistic Mechanisms of Lithium Metal Stripping and Plating in Solid-State Batteries. *Advanced Materials*, 33(11):2008081, 2021.
 15. Xingfeng He, Qiang Bai, Yunsheng Liu, **Adelaide M. Nolan**, Chen Ling, and Yifei Mo. Crystal structural framework of lithium super-ionic conductors. *Advanced Energy Materials*, 9(43):1902078, 2019.
 16. Ying Zhang, Xingfeng He, Zhiqian Chen, Qiang Bai, **Adelaide M. Nolan**, Charles A Roberts, Debasish Banerjee, Tomoya Matsunaga, Yifei Mo, and Chen Ling. Unsupervised discovery of solid-state lithium ion conductors. *Nature communications*, 10(1):1–7, 2019.
 17. Shan Xiong, Xingfeng He, Aijie Han, Zhantao Liu, Zhensong Ren, Brian McElhenny, **Adelaide M. Nolan**, Shuo Chen, Yifei Mo, and Hailong Chen.

Computation-Guided Design of LiTaSiO_5 , a New Lithium Ionic Conductor with Sphene Structure. *Advanced Energy Materials*, 9(22):1803821, 2019.

18. Chengwei Wang, Kun Fu, Sanoop Palakkathodi Kammampata, Dennis W McOwen, Alfred Junio Samson, Lei Zhang, Gregory T Hitz, **Adelaide M. Nolan**, Eric D Wachsman, Yifei Mo, et al. Garnet-type solid-state electrolytes: materials, interfaces, and batteries. *Chemical reviews*, 120(10):4257–4300, 2020.

7.2 Presentations

1. AM Nolan, X Ma, H Chen, Y Mo. Poster. “Nanoscale Phase Tuning: A Computational and Experimental Study of Phase Changes in Metallic Cobalt Nanoparticles.” ResearchFest 2018, College Park, MD. June 29, 2018.
2. AM Nolan, Y Zhu, X He, Y Mo. Presentation. “Computation Accelerated Design of Advanced Materials for Novel Energy Applications.” Clearwater Clean Energy Conference, Clearwater, FL. June 18, 2019. ***Second runner up, Best Student Paper***
3. Adelaide M. Nolan, Yunsheng Liu, Yifei Mo. Presentation. “Solid-State Chemistries Stable with High-Energy Cathodes for Lithium-Ion Batteries.” 2020 MRS Spring/Fall Meeting. Virtual. November 28, 2020. ***Best Student Presenter Award for Symposium***
4. Adelaide M. Nolan, Yifei Mo. Presentation. “Computation-Guided Discovery

of Materials for Stabilizing Interfaces in High-Energy Solid-State Lithium-Ion Batteries.” 2021 MRS Spring Meeting. Virtual. April 21, 2021.

Appendix A: Further analysis on stability of coatings with cathodes

This appendix contains additional information about the stability of oxide cathodes with different solid-state chemistries.

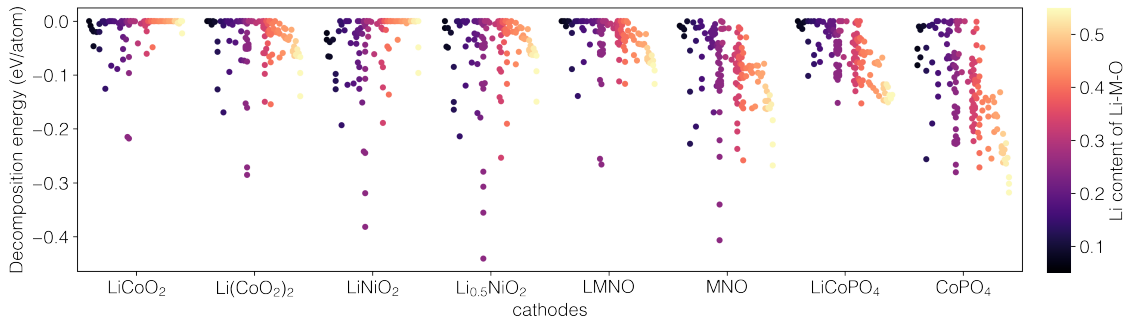


Figure A.1: Swarmplot comparing the minimum mutual decomposition energy E_d of all the lithium ternary oxide (Li-M-O) compounds with each of the cathodes. The pseudo-binary of the Li-M-Os and each cathode is denoted by a cluster of points. Within each cluster, a point represents a single Li-M-O compound. The color of the point indicates the lithium content of the composition. In each cluster, points are grouped by their lithium content. Delithiated cathodes tend to react more vigorously with the most lithiated compounds (Li content 0.45-0.5 or greater) than lithiated cathodes. The decomposition energies of LNO cathodes are more negative than the LCO cathodes, which indicates they tend to have slightly larger decomposition energies.

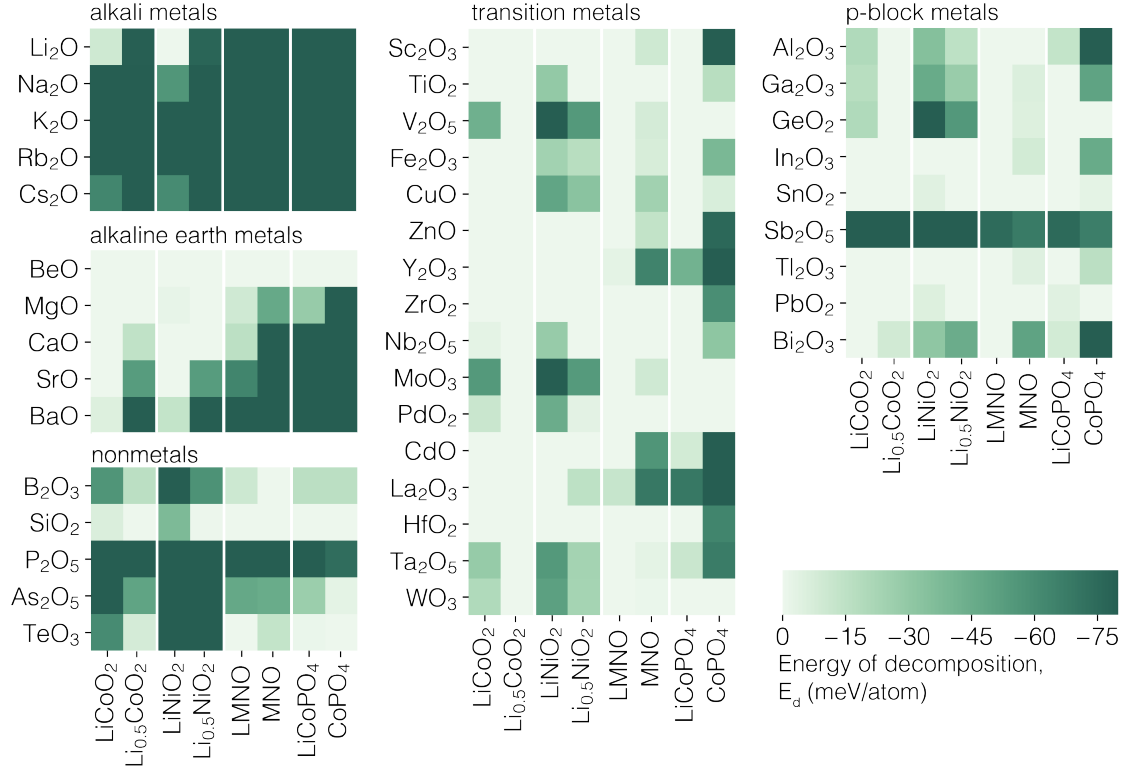


Figure A.2: Heatmap of decomposition energies E_d of binary oxides with cathodes, similar to Fig. 3.2.

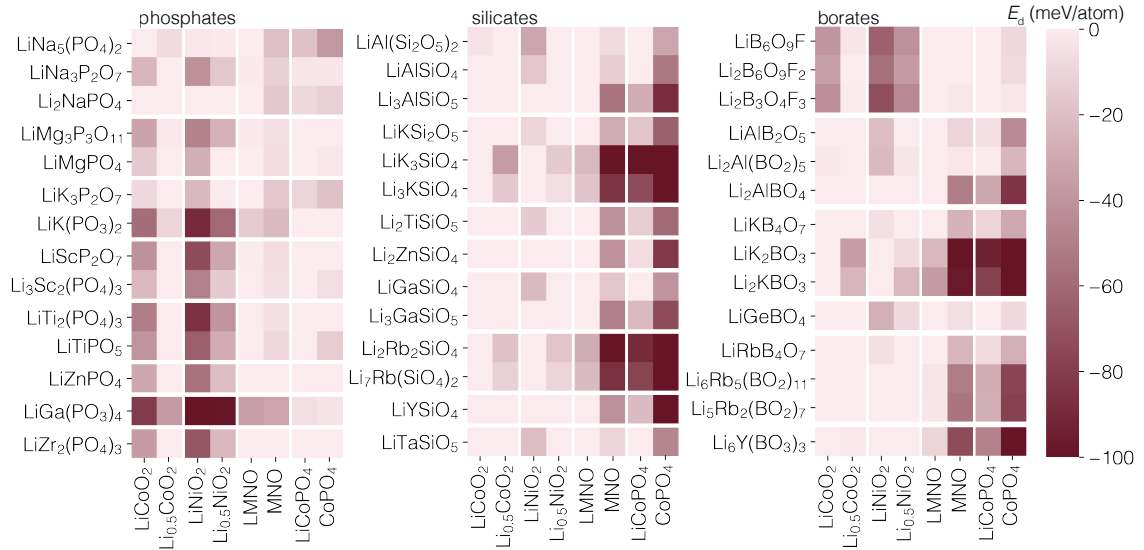


Figure A.3: Heatmap of decomposition energies E_d of selected lithium polyanion compounds (composition Li-M-X-O , where $\text{X} = \text{B, Si, or P}$) with cathodes, similar to Fig. 3.2.

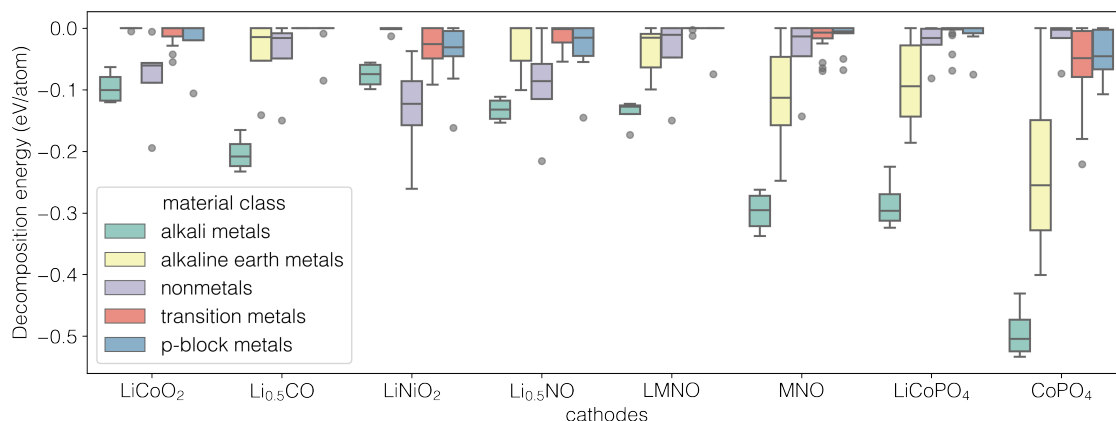


Figure A.4: Boxplot comparing the decomposition energies of each of the groups of binary oxides with all the cathodes. Data outside the whiskers (outliers) are marked individually as gray circles.

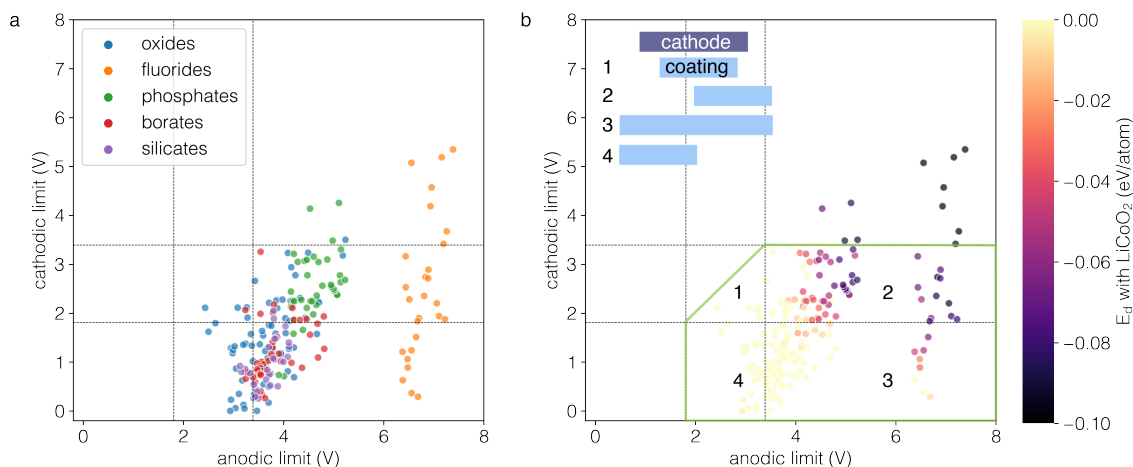


Figure A.5: Cathodic vs anodic limits of all lithium-containing materials studied. (a) Colored by materials classes. (b) Colored by decomposition energy with LiCoO_2 . Outlined green area indicates region where there is overlap between the electrochemical window of the cathode and the coating, with the type of overlap specified by the legend. Overlap of the electrochemical windows of the two materials does not necessarily mean the two materials are stable.

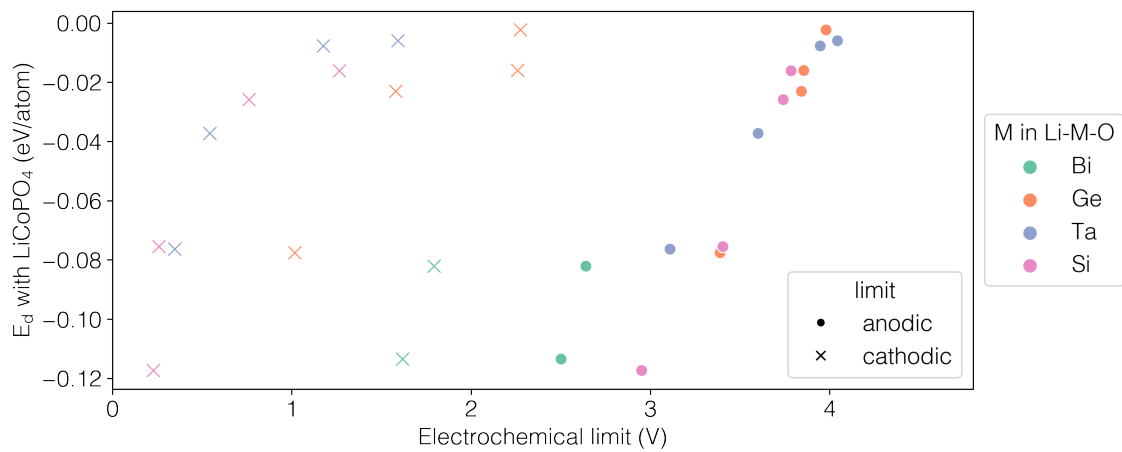


Figure A.6: Decomposition energy of LiCoPO₄ with Li-M-O oxides vs the anodic and cathodic limits of the oxides. The materials with higher anodic limit (oxidation limit) generally exhibit better interface stability.

Appendix B: Stability of materials with garnet and NMC

This appendix contains additional information about the stability of garnet and NMC with various coating layer materials.

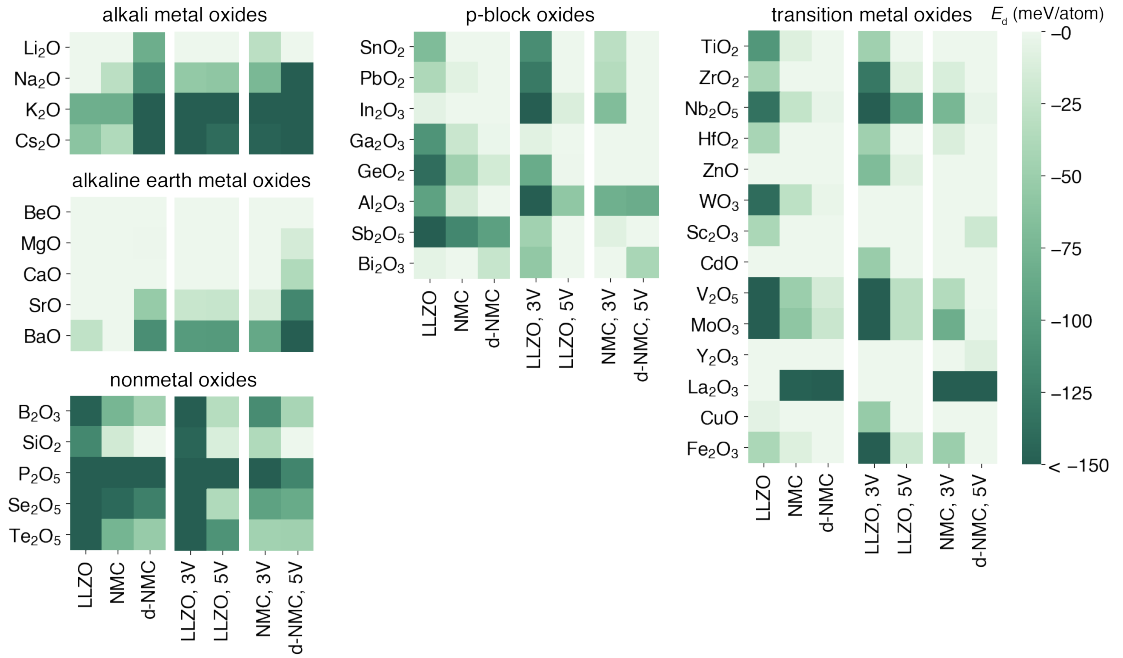


Figure B.1: Heatmaps of the chemical and electrochemical (at 3 and 5 V) decomposition energy of binary oxides with LLZO, LiNi_{0.3}Mn_{0.3}Co_{0.3}O₂ (NMC), and delithiated Li_{0.5}Ni_{0.3}Mn_{0.3}Co_{0.3}O₂ (d-NMC).

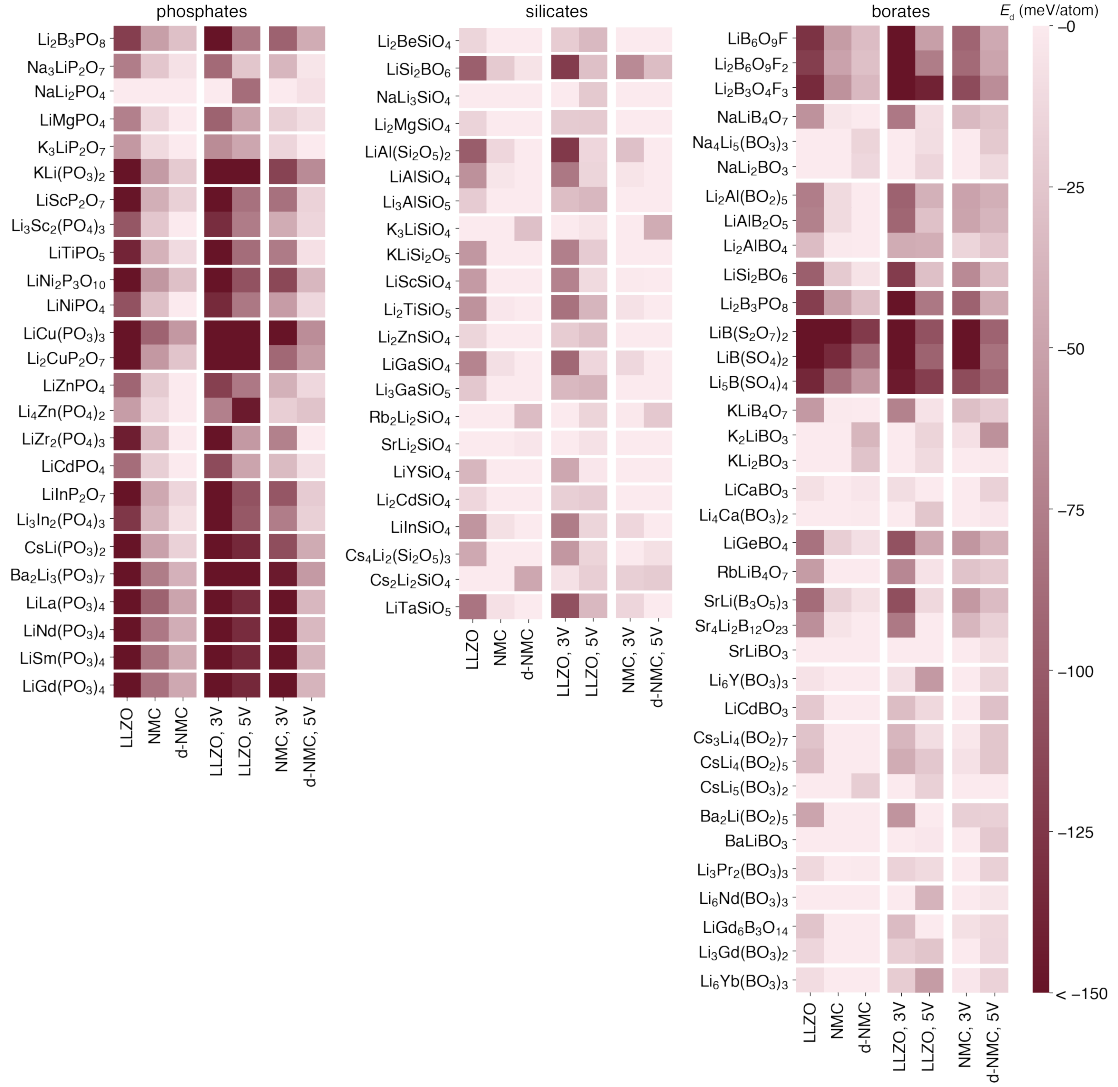


Figure B.2: Heatmaps of the chemical and electrochemical (at 3 and 5 V) decomposition energy of quaternary phosphates, silicates, and borates with LLZO, NMC, and d-NMC.

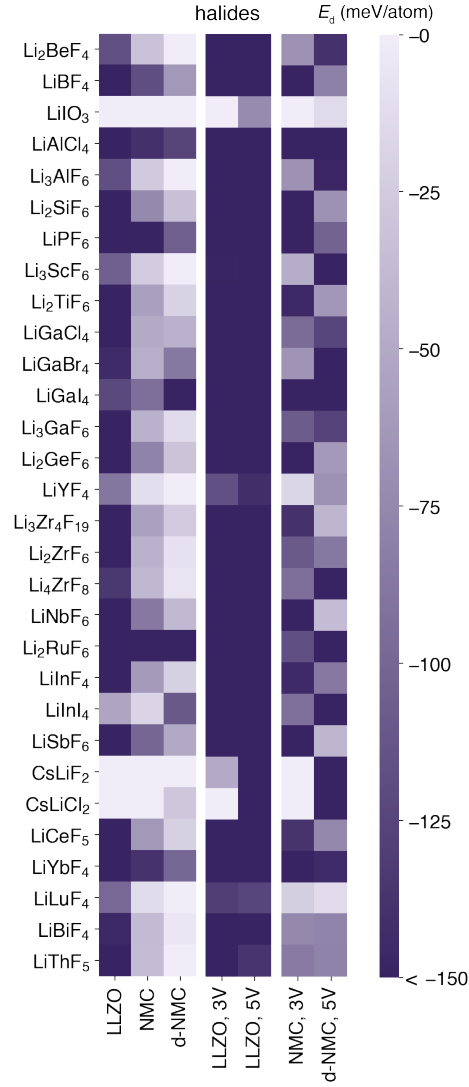


Figure B.3: Heatmap of the chemical and electrochemical (at 3 and 5 V) decomposition energy of ternary halides with LLZO, NMC, and d-NMC.

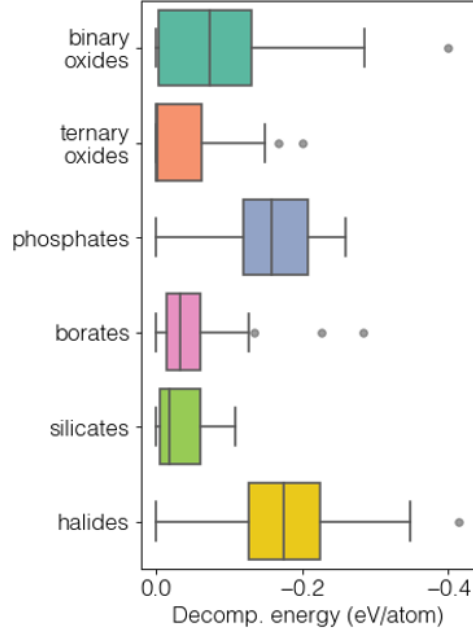


Figure B.4: Boxplot showing distribution of decomposition energies of garnet LLZO with binary oxides and lithium ternary oxides, phosphates, borates, silicates, and halides. Among the materials classes studied, the lithium ternary oxides have the lowest median reaction energy with LLZO, at approximately 0 eV/atom, indicating a large proportion of this material class has good stability with LLZO.

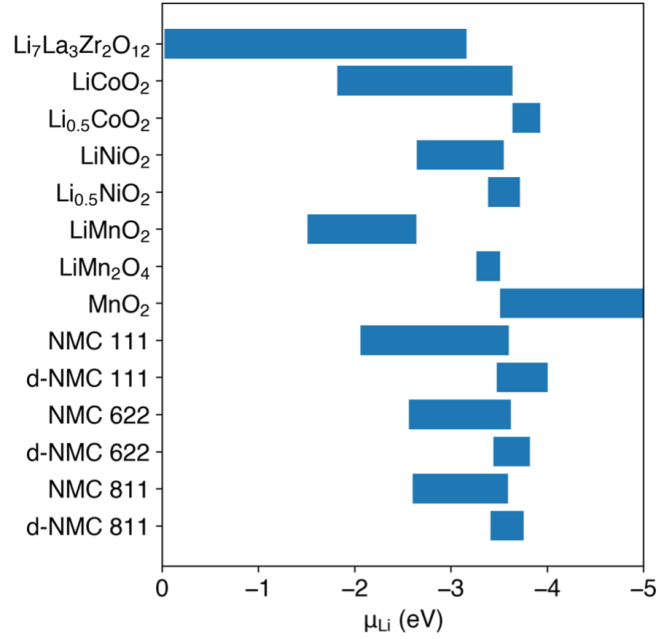


Figure B.5: Li chemical potential (μ_{Li}) windows of LLZO garnet and selected oxide cathodes.

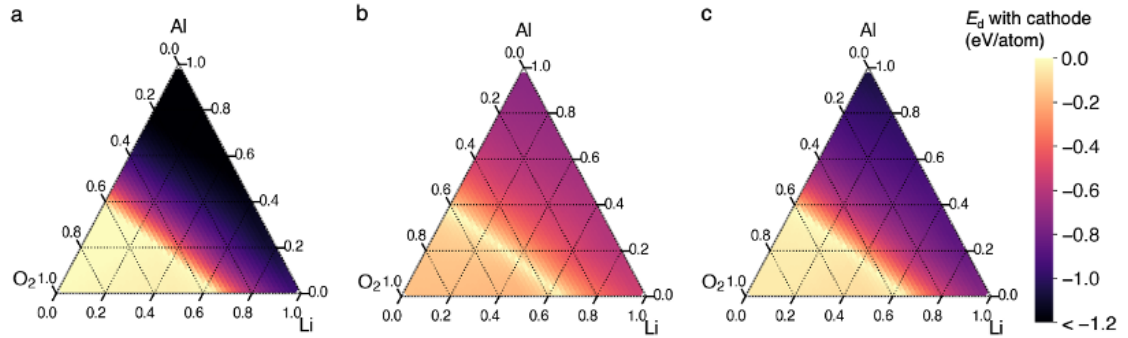


Figure B.6: Heatmaps of the decomposition energies of Li-Al-O compositions with cathodes a) LiNiO_2 , b) LiMnO_2 , and c) LiCoO_2 . All heatmaps are normalized to the same energy.

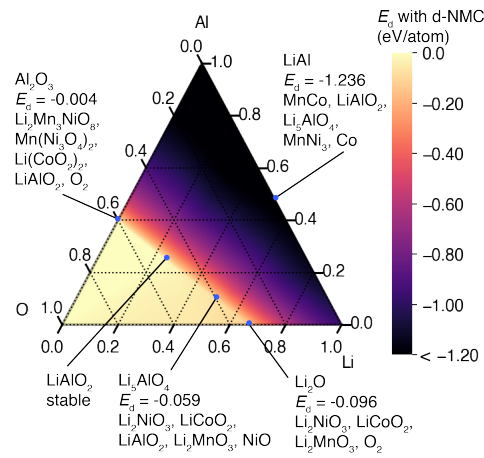


Figure B.7: Heatmap of the decomposition energies of Li-Al-O compositions with delithiated cathode d-NMC.

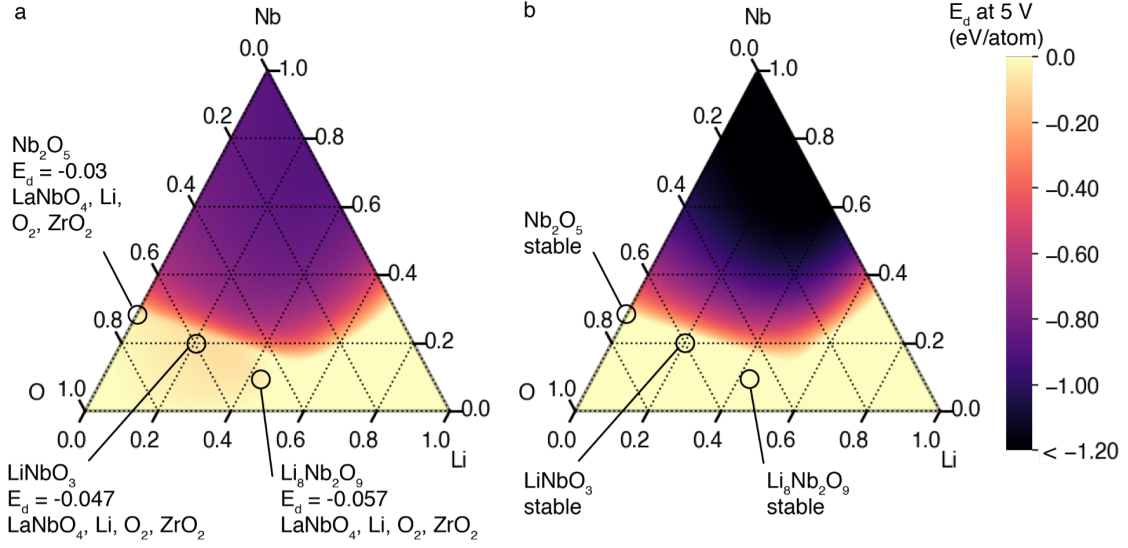


Figure B.8: Electrochemical stability of the (a) LLZO — Li-Nb-O interface and the (b) NMC — Li-Nb-O interface at 5V.

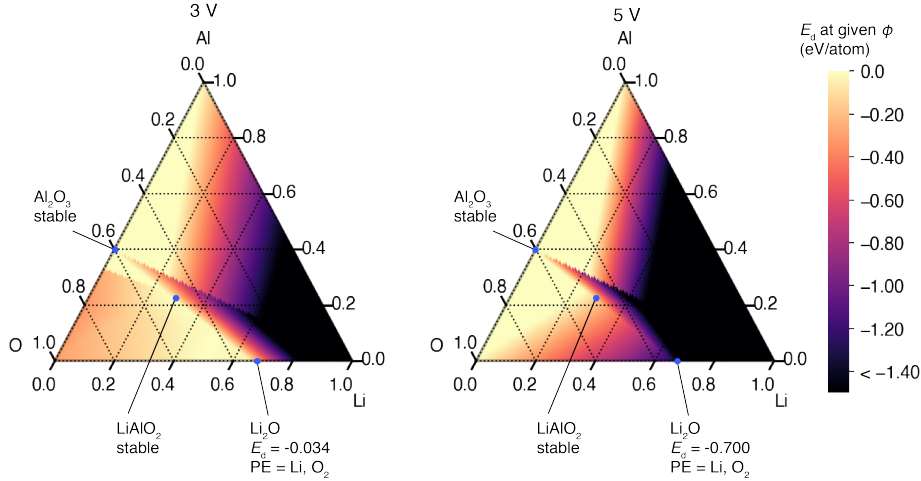


Figure B.9: Decomposition energy and products of Li-Al-O at 3 V and 5 V. Under 5 V, the most stable regions are Al- and O-rich compositions. The O-rich region of the coating layer is stable between 3 – 5 V, the typical cathode cycling voltage. Binary Al_2O_3 is stable throughout the 3 – 5 V range. Highly lithiated compositions, which tend to be less stable as voltage increases, will decompose into Al_2O_3 and O_2 or Al metal.

μ_{Li} (eV)	ratio of NMC 111	ratio of LLZO	Rxn. E. (meV /atom)	Mutual Rxn. E. (meV /atom)	Phase equilibria
0	0.43	0.57	-796	-81	La ₂ O ₃ , Li ₂ O, ZrCo ₂ , ZrMn ₂ , ZrNi ₃
-0.25	0.75	0.25	-1080	-29	La ₂ O ₃ , Li ₂ O, MnCo, Zr ₆ Co ₂₃ , ZrNi ₃
-0.5	1.00	0.00	-1156	0.00	Co, Li ₂ O, MnCo, MnNi ₃
-1	0.53	0.47	-376	-27	Co, La ₂ MnCoO ₆ , Li ₂ O, Li ₆ Zr ₂ O ₇ , MnNi ₃
-1.25	0.43	0.57	-270	-87	Co, La ₂ MnCoO ₆ , Li ₂ O, Li ₆ Zr ₂ O ₇ , Ni
-1.75	0.43	0.57	-194	-155	La ₂ MnCoO ₆ , Li ₂ O, Li ₆ CoO ₄ , Li ₆ Zr ₂ O ₇ , Ni
-2	0.43	0.57	-157	-151	La ₂ MnCoO ₆ , Li ₂ O, Li ₆ Zr ₂ O ₇ , LiCoO ₂ , Ni
-2.25	0.43	0.57	-139	-139	La ₂ MnCoO ₆ , Li ₂ O, Li ₆ Zr ₂ O ₇ , LiCoO ₂ , NiO
-2.75	0.43	0.57	-125	-125	La ₂ MnCoO ₆ , Li, Li ₂ NiO ₃ , Li ₂ O, Li ₆ Zr ₂ O ₇ , LiCoO ₂
-3	0.43	0.57	-138	-138	La ₂ MnCoO ₆ , Li, Li ₂ NiO ₃ , Li ₂ O ₂ , Li ₆ Zr ₂ O ₇ , LiCoO ₂
-3.25	0.43	0.57	-156	-146	La ₂ MnCoO ₆ , Li, Li ₂ NiO ₃ , Li ₂ O ₂ , Li ₂ ZrO ₃ , LiCoO ₂
-3.5	0.43	0.57	-202	-140	La ₂ MnCoO ₆ , Li, Li ₂ NiO ₃ , LiCoO ₂ , O ₂ , ZrO ₂
-3.75	0.43	0.57	-291	-158	La ₂ MnCoO ₆ , Li, Li(CoO ₂) ₂ , NiO, O ₂ , ZrO ₂
-4	0.43	0.57	-385	-168	CoO ₂ , La ₂ MnCoO ₆ , Li, NiO, O ₂ , ZrO ₂

Table B.1: Stability of LLZO–NMC 111 pseudo-binary under μ_{Li} ranging from 0.0 to -6.0 eV.

μ_O (eV)	ratio of NMC 111	ratio of LLZO	Rxn. E. (meV /atom)	Mutual Rxn. E. (meV /atom)	Phase equilibria
0.00	0.43	0.57	-141	-141	La ₂ MnCoO ₆ , Li, Li ₂ NiO ₃ , Li ₂ O ₂ , Li ₆ Zr ₂ O ₇ , LiCoO ₂
-0.25	0.43	0.57	-160	-145	La ₂ MnCoO ₆ , Li, Li ₂ NiO ₃ , Li ₂ O ₂ , Li ₂ ZrO ₃ , LiCoO ₂
-0.50	0.43	0.57	-213	-141	La ₂ MnCoO ₆ , Li, Li ₂ NiO ₃ , LiCoO ₂ , O ₂ , ZrO ₂
-0.75	0.43	0.57	-306	-160	La ₂ MnCoO ₆ , Li, Li(CoO ₂) ₂ , NiO, O ₂ , ZrO ₂
-1.00	0.43	0.57	-400	-168	CoO ₂ , La ₂ MnCoO ₆ , Li, NiO, O ₂ , ZrO ₂

Table B.2: Stability of LLZO–NMC 111 pseudo-binary under μ_O ranging from 0.0 to -1.0 eV.

Appendix C: Li-ion migration in Al_2O_3

This appendix contains additional information on Li-ion migration in Al_2O_3 .

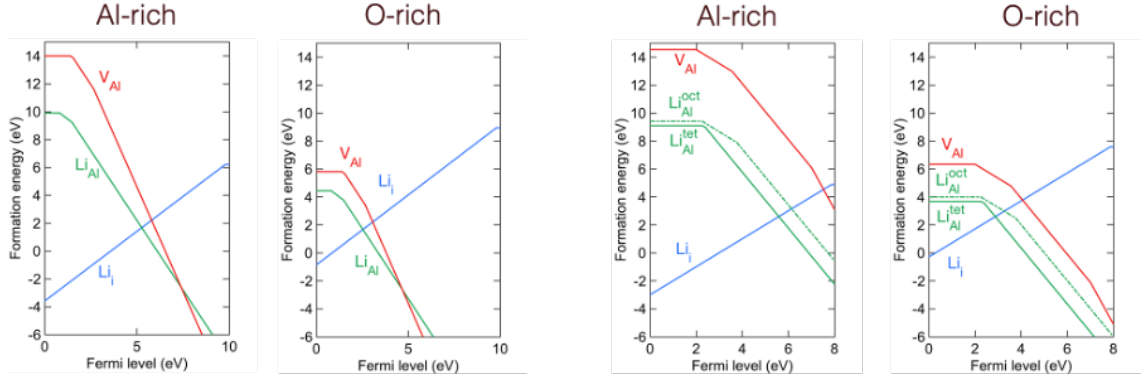


Figure C.1: Defect calculations for α (left) and θ (right) Al_2O_3 . V_{Al} denotes an isolated Al vacancy, Li_{Al} corresponds to lithium substituted on an Al site, and Li_i corresponds to an isolated Li interstitial. The slope of the line denotes the defect's charge state. Li_i is stable in the positive charge state (given by the slope of the line) for all values of the Fermi level within the bandgap of α and θ Al_2O_3 .

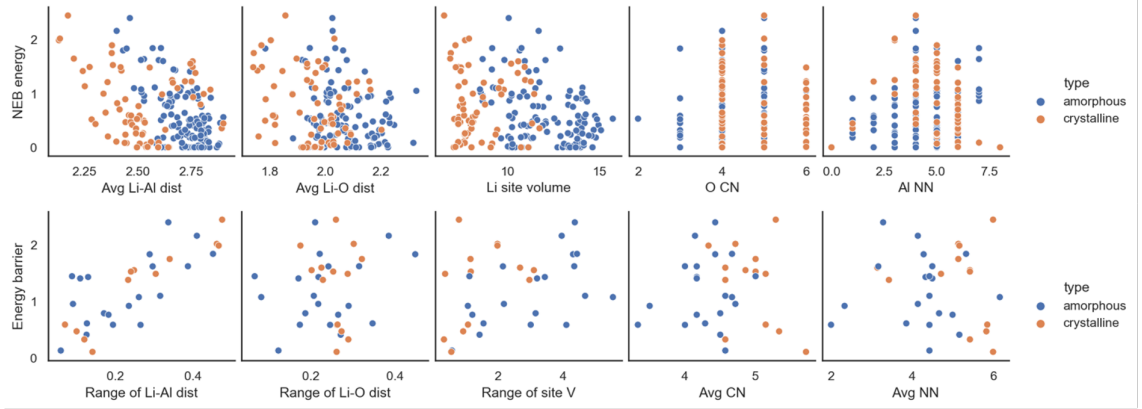


Figure C.2: Example correlations investigated between migration energy barrier and structural parameters of crystalline (orange) and amorphous (blue) Al_2O_3 . Migration energy and energy barrier vs average Li-Al distance at transition state ($\text{\AA}$), average Li-O distance at transition state ($\text{\AA}$), volume of transition state ($\text{\AA}^3$), O coordination number, and number of nearest neighbors at transition state. See Chapter 2 for a description of how each parameter was calculated.

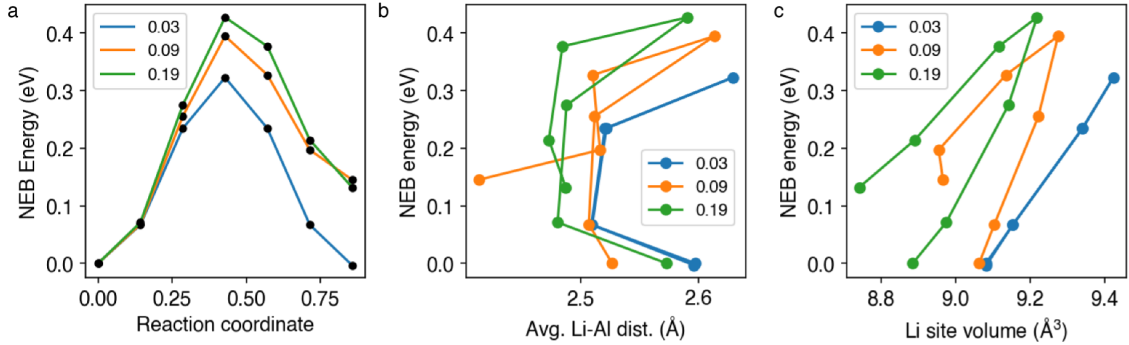


Figure C.3: Concentration dependence in $\theta\text{-Al}_2\text{O}_3$. a) NEB paths for a tet-tet hop in cells with varying Li^+ concentration in a range of $x = 0.03$ to 0.25 for x in $\theta\text{-Li}_x\text{Al}_2\text{O}_3$. NEB energy vs b) average distance to neighboring Al and c) site volume for each Li site in path, for selected concentrations of $x = 0.03, 0.09$, and 0.19 .

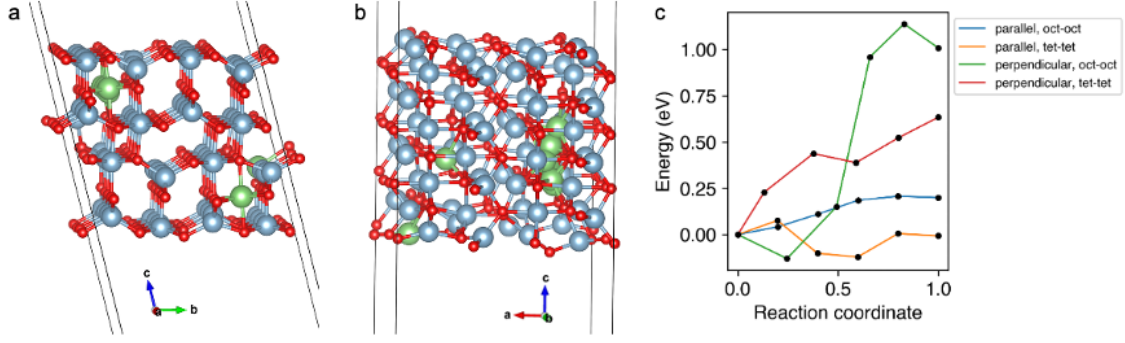


Figure C.4: NEB for θ surface. a) Tet-tet migration path in surface orientation with channels parallel to surface, b) tet-tet migration path in channels perpendicular to surface, c) energy barriers for surface orientations with channels parallel and perpendicular to surface for tet-tet and oct-oct hops. For orientations of the surface parallel to the vacuum layer, the channels did not distort and the migration barrier did not change drastically compared to the bulk. In the perpendicular direction, channels were highly distorted and there was a corresponding increase in the migration barrier.

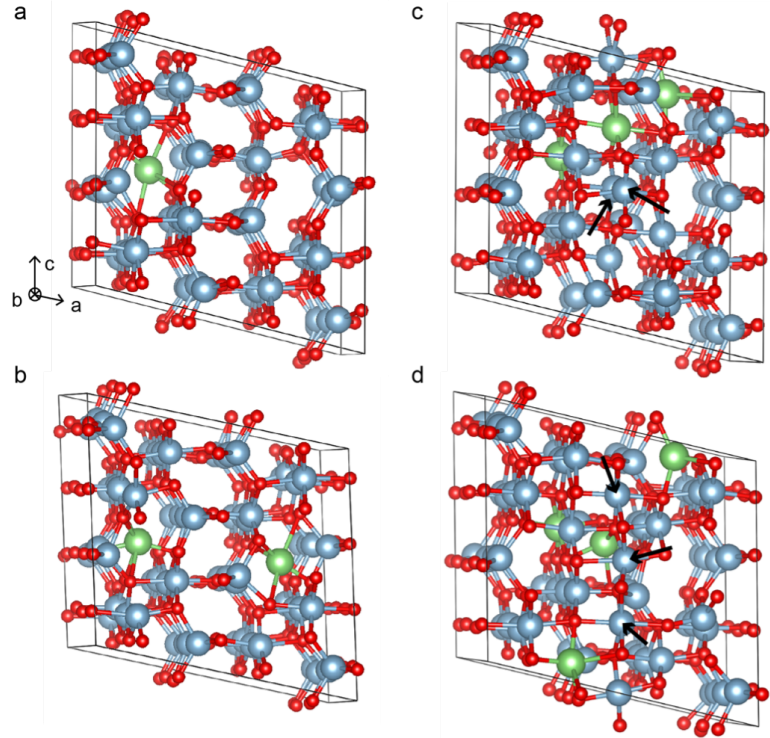


Figure C.5: Snapshots of molecular dynamics simulations at 25 ps of simulation time in $\theta\text{-Li}_x\text{Al}_2\text{O}_3$, with increasing Li concentrations of a) 0.03, b) 0.06, c) 0.08, and d) 0.125. Black arrows indicate Al^{3+} that has swapped with Li^{+} and migrated into the channel, causing potential blockages for Li^{+} migrating in the b-direction.

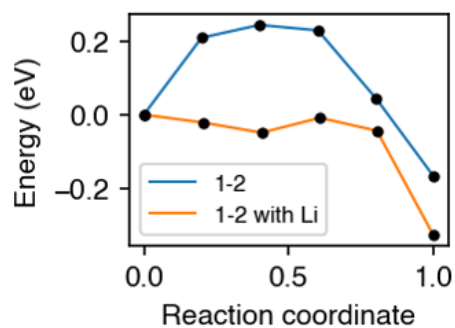


Figure C.6: NEB in amorphous Al_2O_3 , comparing the same path without and with an added Li in a nearby low energy site.

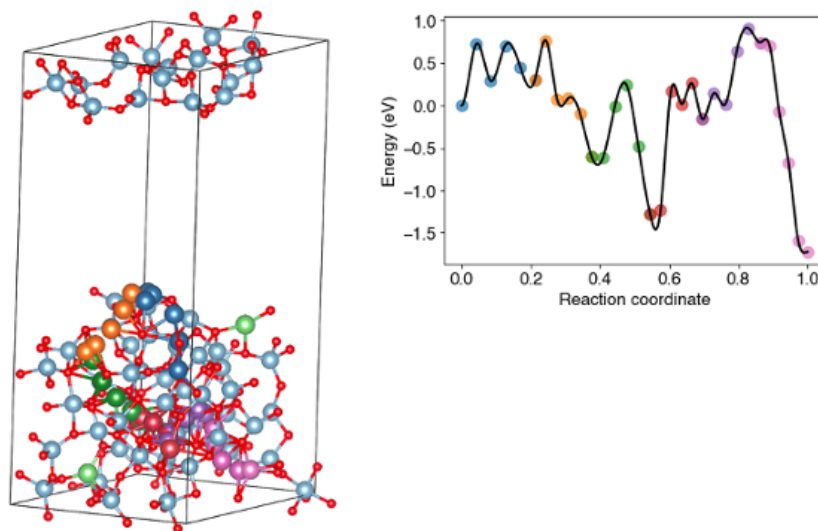


Figure C.7: Connected migration path in amorphous surface. The average migration barrier for Li in the surface model was 1.08 eV ($N = 18$), similar to the average migration barrier in the bulk.

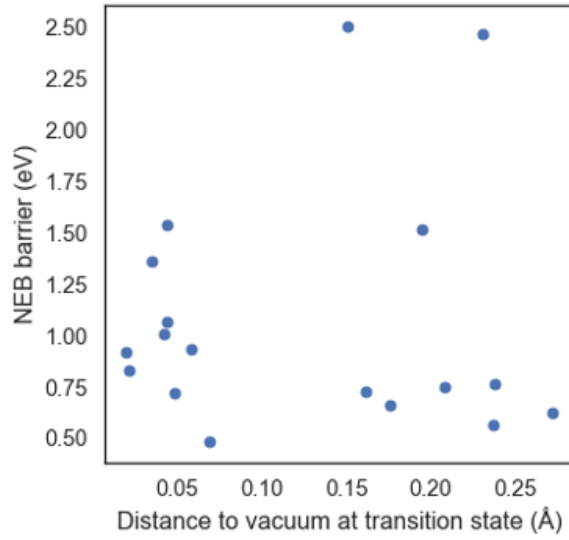


Figure C.8: NEB barrier of amorphous surface vs distance of transition site to vacuum layer. Excluding three outliers (with $E_a > 1.5$ eV), the trend indicates that NEB barriers are higher for transition states closer to the vacuum layer, suggesting that structural distortions caused by the vacuum layer may marginally increase the migration barrier near the interface.

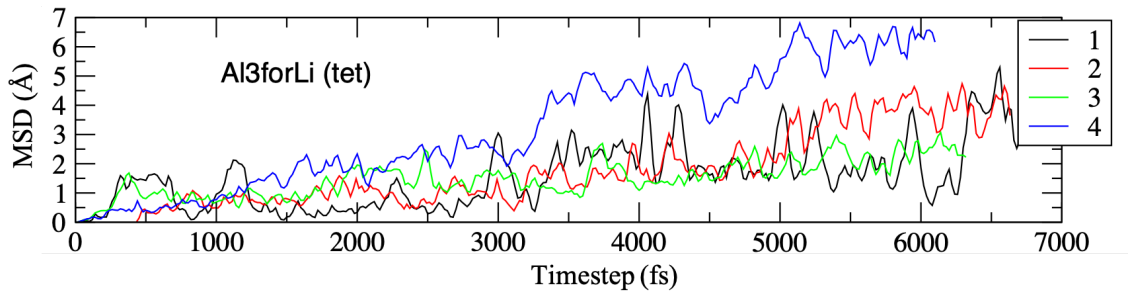


Figure C.9: MSD of Li^+ in amorphous surface for increasing Li concentrations of am- $\text{Li}_{0.09}\text{Al}_{1.98}\text{O}_3$ (1), am- $\text{Li}_{0.19}\text{Al}_{1.97}\text{O}_3$ (2), am- $\text{Li}_{0.28}\text{Al}_{1.95}\text{O}_3$ (3), and am- $\text{Li}_{0.38}\text{Al}_{1.94}\text{O}_3$ (4).

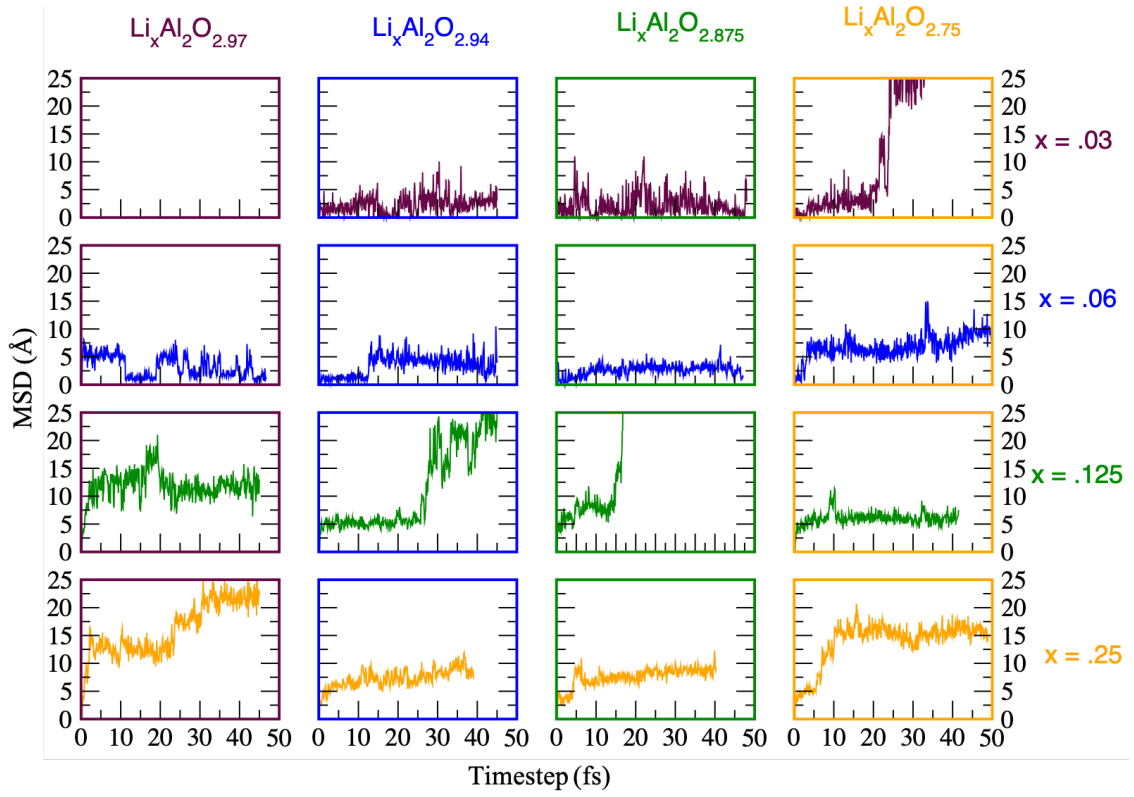


Figure C.10: MSD of Li-ions for γ - Al_2O_3 structures with different Li^+ concentrations and O^{2-} vacancies, demonstrating minimal dependence of hopping events on O^{2-} vacancy concentration.

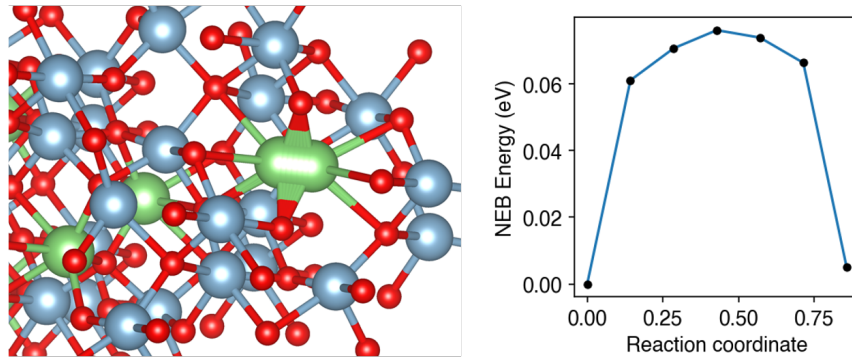


Figure C.11: Visualization and energy of NEB path across vacancy cluster in Al-defected α - $\text{Li}_{0.28}\text{Al}_{1.95}\text{O}_3$. The initial and final sites were obtained by visualizing the hopping event in a MD simulation of the structure.

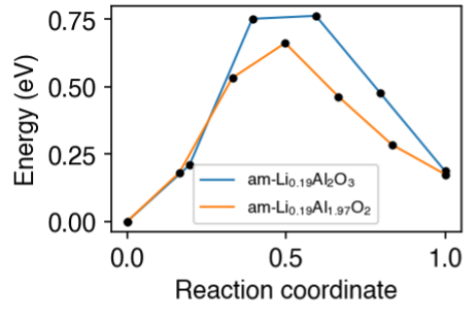


Figure C.12: Migration path in amorphous Al₂O₃ for the same starting and ending hops without (blue) and with added Al³⁺ vacancies (orange). Li concentrations are the same for both paths.

Bibliography

- [1] John B. Goodenough and Kyu Sung Park. The Li-ion rechargeable battery: A perspective. *Journal of the American Chemical Society*, 135(4):1167–1176, Jan 2013.
- [2] Davide Castelpvecchi and Emma Stoye. Chemistry Nobel honours world-changing batteries. *Nature*, 574(7778):308, Oct 2019.
- [3] J. M. Tarascon and M. Armand. Issues and challenges facing rechargeable lithium batteries. *Nature*, 414(6861):359–367, Nov 2001.
- [4] Jürgen Janek and Wolfgang G. Zeier. A solid future for battery development. *Nature Energy*, 1(9):1–4, sep 2016.
- [5] Brent C. Melot and J. M. Tarascon. Design and preparation of materials for advanced electrochemical storage. *Accounts of Chemical Research*, 46(5):1226–1238, 2013.
- [6] John B. Goodenough and Youngsik Kim. Challenges for rechargeable Li batteries. *Chemistry of Materials*, 22(3):587–603, 2010.
- [7] Simon Randau, Dominik A. Weber, Olaf Kötz, Raimund Koerver, Philipp Braun, André Weber, Ellen Ivers-Tiffée, Torben Adermann, Jörn Kulisch, Wolfgang G. Zeier, Felix H. Richter, and Jürgen Janek. Benchmarking the performance of all-solid-state lithium batteries. *Nature Energy*, 5(3):259–270, 2020.
- [8] Wangda Li, Bohang Song, and Arumugam Manthiram. High-voltage positive electrode materials for lithium-ion batteries. *Chemical Society Reviews*, 46(10):3006–3059, 2017.
- [9] Magali Gauthier, Thomas J. Carney, Alexis Grimaud, Livia Giordano, Nir Pour, Hao Hsun Chang, David P. Fenning, Simon F. Lux, Odysseas Paschos,

- Christoph Bauer, Filippo Maglia, Saskia Lupart, Peter Lamp, and Yang Shao-Horn. Electrode-Electrolyte Interface in Li-Ion Batteries: Current Understanding and New Insights. *Journal of Physical Chemistry Letters*, 6(22):4653–4672, Nov 2015.
- [10] Daxian Zuo, Guanglei Tian, Xiang Li, Da Chen, and Kangying Shu. Recent progress in surface coating of cathode materials for lithium ion secondary batteries. *Journal of Alloys and Compounds*, 706:24–40, Jun 2017.
- [11] Sean P. Culver, Raimund Koerver, Wolfgang G. Zeier, and Jürgen Janek. On the Functionality of Coatings for Cathode Active Materials in Thiophosphate-Based All-Solid-State Batteries. *Advanced Energy Materials*, page 1900626, May 2019.
- [12] Adelaide M. Nolan, Yizhou Zhu, Xingfeng He, Qiang Bai, and Yifei Mo. Computation-Accelerated Design of Materials and Interfaces for All-Solid-State Lithium-Ion Batteries. *Joule*, 2(10):2016–2046, Oct 2018.
- [13] Yang Kook Sun, Seung Taek Myung, Byung Chun Park, Jai Prakash, Ilias Belharouak, and Khalil Amine. High-energy cathode material for long-life and safe lithium batteries. *Nature Materials*, 8(4):320–324, 2009.
- [14] Debasish Mohanty, Kevin Dahlberg, David M. King, Lamuel A. David, Athena S. Sefat, David L. Wood, Claus Daniel, Subhash Dhar, Vishal Mahajan, Myongjai Lee, and Fabio Albano. Modification of Ni-Rich FCG NMC and NCA Cathodes by Atomic Layer Deposition: Preventing Surface Phase Transitions for High-Voltage Lithium-Ion Batteries. *Scientific Reports*, 6:1–16, Feb 2016.
- [15] Seung-Taek Myung, Filippo Maglia, Kang-Joon Park, Chong Seung Yoon, Peter Lamp, Sung-Jin Kim, and Yang-Kook Sun. Nickel-Rich Layered Cathode Materials for Automotive Lithium-Ion Batteries: Achievements and Perspectives. *ACS Energy Letters*, 2(1):196–223, Jan 2017.
- [16] Qiming Zhong, Arman Bonakdarpour, Meijie Zhang, Yuan Gao, and J. R. Dahn. Synthesis and electrochemistry of $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$. *Journal of The Electrochemical Society*, 144(1):205–213, 1997.
- [17] Raimund Koerver, Felix Walther, Isabel Aygün, Joachim Sann, Christian Dietrich, Wolfgang G. Zeier, and Jürgen Janek. Redox-active cathode interphases in solid-state batteries. *Journal of Materials Chemistry A*, 5(43):22750–22760, 2017.
- [18] Raimund Koerver, Isabel Aygün, Thomas Leichtweiß, Christian Dietrich, Wenbo Zhang, Jan O. Binder, Pascal Hartmann, Wolfgang G. Zeier, and Jürgen Janek. Capacity Fade in Solid-State Batteries: Interphase Formation and Chemomechanical Processes in Nickel-Rich Layered Oxide Cathodes and Lithium Thiophosphate Solid Electrolytes. *Chemistry of Materials*, 29(13):5574–5582, Jul 2017.

- [19] William D. Richards, Lincoln J. Miara, Yan Wang, Jae Chul Kim, and Gerbrand Ceder. Interface Stability in Solid-State Batteries. *Chemistry of Materials*, 28(1):266–273, 2016.
- [20] Yoongu Kim, Nancy J. Dudney, Miaofang Chi, Surendra K. Martha, Jagjit Nanda, Gabriel M. Veith, and Chengdu Liang. A Perspective on Coatings to Stabilize High-Voltage Cathodes: $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ with Sub-Nanometer Lipon Cycled with LiPF_6 Electrolyte. *Journal of The Electrochemical Society*, 160(5):A3113–A3125, 2013.
- [21] Pinar Karayaylali, Ryoichi Tatara, Yirui Zhang, Kuei-Lin Chan, Yang Yu, Livia Giordano, Filippo Maglia, Roland Jung, Isaac Lund, and Yang Shao-Horn. Editors’ Choice—Coating-Dependent Electrode-Electrolyte Interface for Ni-Rich Positive Electrodes in Li-Ion Batteries. *Journal of The Electrochemical Society*, 166(6):A1022–A1030, 2019.
- [22] Wengao Zhao, Jianming Zheng, Lianfeng Zou, Haiping Jia, Bin Liu, Hui Wang, Mark H. Engelhard, Chongmin Wang, Wu Xu, Yong Yang, and Ji-Guang Zhang. High Voltage Operation of Ni-Rich NMC Cathodes Enabled by Stable Electrode/Electrolyte Interphases. *Advanced Energy Materials*, 8(19):1800297, Jul 2018.
- [23] Atsushi Sakuda, Akitoshi Hayashi, and Masahiro Tatsumisago. Interfacial observation between LiCoO_2 electrode and $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolytes of all-solid-state lithium secondary batteries using transmission electron microscopy. *Chemistry of Materials*, 22(3):949–956, 2010.
- [24] Yizhou Zhu, Xingfeng He, and Yifei Mo. First principles study on electrochemical and chemical stability of solid electrolyte–electrode interfaces in all-solid-state Li-ion batteries. *J. Mater. Chem. A*, 4(9):3253–3266, 2016.
- [25] Yaosen Tian, Guobo Zeng, Ann Rutt, Tan Shi, Haegyeom Kim, Jingyang Wang, Julius Koettgen, Yingzhi Sun, Bin Ouyang, Tina Chen, Zhengyan Lun, Ziqin Rong, Kristin Persson, and Gerbrand Ceder. Promises and challenges of next-generation “beyond Li-ion” batteries for electric vehicles and grid decarbonization, 2021.
- [26] Noriaki Kamaya, Kenji Homma, Yuichiro Yamakawa, Masaaki Hirayama, Ryoji Kanno, Masao Yonemura, Takashi Kamiyama, Yuki Kato, Shigenori Hama, Koji Kawamoto, and Akio Mitsui. A lithium superionic conductor. *Nature Materials*, 10:682, jul 2011.
- [27] Venkataraman Thangadurai, Sumaletha Narayanan, and Dana Pinzar. Garnet-type solid-state fast Li ion conductors for Li batteries: Critical review. *Chemical Society Reviews*, 43(13):4714–4727, Jul 2014.

- [28] Alfred Junio Samson, Kyle Hofstetter, Sourav Bag, and Venkataraman Thangadurai. A bird’s-eye view of Li-stuffed garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ceramic electrolytes for advanced all-solid-state Li batteries. *Energy and Environmental Science*, 12(10):2957–2975, Oct 2019.
- [29] Tetsuya Asano, Akihiro Sakai, Satoru Ouchi, Masashi Sakaida, Akinobu Miyazaki, and Shinya Hasegawa. Solid Halide Electrolytes with High Lithium-Ion Conductivity for Application in 4 V Class Bulk-Type All-Solid-State Batteries. *Advanced Materials*, 30(44):1803075, nov 2018.
- [30] Asma Sharafi, Eric Kazyak, Andrew L Davis, Seungho Yu, Travis Thompson, Donald J Siegel, Neil P Dasgupta, and Jeff Sakamoto. Surface Chemistry Mechanism of Ultra-Low Interfacial Resistance in the Solid-State Electrolyte $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. *Chem. Mater*, 29:7961–7968, 2017.
- [31] Xiaogang Han, Yunhui Gong, Kun Fu, Xingfeng He, Gregory T. Hitz, Jiaqi Dai, Alex Pearce, Boyang Liu, Howard Wang, Gary Rubloff, and et al. Negating interfacial impedance in garnet-based solid-state li metal batteries. *Nature Materials*, 16(5):572–579, 2017.
- [32] Wei Luo, Yunhui Gong, Yizhou Zhu, Kun Kelvin Fu, Jiaqi Dai, Steven D Lacey, Chengwei Wang, Boyang Liu, Xiaogang Han, Yifei Mo, and et al. Transition from superlithiophobicity to superlithiophilicity of garnet solid-state electrolyte. *Journal of the American Chemical Society*, 138(37):12258–12262, Sep 2016.
- [33] Kun Kelvin Fu, Yunhui Gong, Boyang Liu, Yizhou Zhu, Shaomao Xu, Yonggang Yao, Wei Luo, Chengwei Wang, Steven D. Lacey, Jiaqi Dai, and et al. Toward garnet electrolyte-based li metal batteries: An ultrathin, highly effective, artificial solid-state electrolyte/metallic li interface. *Science Advances*, 3(4):1–12, 2017.
- [34] Gregory T. Hitz, Dennis W. McOwen, Lei Zhang, Zhaohui Ma, Zhezhen Fu, Yang Wen, Yunhui Gong, Jiaqi Dai, Tanner R. Hamann, Liangbing Hu, and et al. High-rate lithium cycling in a scalable trilayer li-garnet-electrolyte architecture. *Materials Today*, 22:50–57, Jan 2019.
- [35] Yaoyu Ren, Ting Liu, Yang Shen, Yuanhua Lin, and Ce Wen Nan. Chemical compatibility between garnet-like solid state electrolyte $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ and major commercial lithium battery cathode materials. *Journal of Materiomics*, 2(3):256–264, 2016.
- [36] Nian Zhang, Xinghui Long, Zhi Wang, Pengfei Yu, Fudong Han, Jiamin Fu, Guoxi Ren, Yanru Wu, Shun Zheng, Wencheng Huang, and et al. Mechanism study on the interfacial stability of a lithium garnet-type oxide electrolyte against cathode materials. *ACS Applied Energy Materials*, 1(11):5968–5976, Nov 2018.

- [37] Sven Uhlenbruck, Jürgen Dornseiffer, Sandra Lobe, Christian Dellen, Chih Long Tsai, Benjamin Gotzen, Doris Sebold, Martin Finsterbusch, and Olivier Guillon. Cathode-electrolyte material interactions during manufacturing of inorganic solid-state lithium batteries. *Journal of Electroceramics*, 38(2–4):197–206, 2017.
- [38] Kyusung Park, Byeong Chul Yu, Ji Won Jung, Yutao Li, Weidong Zhou, Hongcai Gao, Samick Son, and John B. Goodenough. Electrochemical Nature of the Cathode Interface for a Solid-State Lithium-Ion Battery: Interface between LiCoO_2 and Garnet- $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. *Chemistry of Materials*, 28(21):8051–8059, 2016.
- [39] Gülin Vardar, William J. Bowman, Qiyang Lu, Jiayue Wang, Richard J. Chater, Ainara Aguadero, Rachel Seibert, Jeff Terry, Adrian Hunt, Iradwikarnari Waluyo, and et al. Structure, Chemistry, and Charge Transfer Resistance of the Interface between $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Electrolyte and LiCoO_2 Cathode. *Chemistry of Materials*, 2018.
- [40] Lincoln Miara, Anna Windmüller, Chih Long Tsai, William D. Richards, Qianli Ma, Sven Uhlenbruck, Olivier Guillon, and Gerbrand Ceder. About the compatibility between high voltage spinel cathode materials and solid oxide electrolytes as a function of temperature. *ACS Applied Materials and Interfaces*, 8(40):26842–26850, 2016.
- [41] Lincoln J. Miara, William Davidson Richards, Yan E. Wang, and Gerbrand Ceder. First-Principles Studies on Cation Dopants and Electrolyte—Cathode Interphases for Lithium Garnets. *Chemistry of Materials*, 27(11):4040–4047, 2015.
- [42] George V. Alexander, Nataly Carolina Rosero-Navarro, Akira Miura, Kiyoharu Tadanaga, and Ramaswamy Murugan. Electrochemical performance of a garnet solid electrolyte based lithium metal battery with interface modification. *Journal of Materials Chemistry A*, 6(42):21018–21028, Oct 2018.
- [43] George V. Alexander, M. S. Indu, Selvajyothi Kamakshy, and Ramaswamy Murugan. Development of stable and conductive interface between garnet structured solid electrolyte and lithium metal anode for high performance solid-state battery. *Electrochimica Acta*, 332:135511, Feb 2020.
- [44] Takehisa Kato, Tadashi Hamanaka, Kazuo Yamamoto, Tsukasa Hirayama, Fumihiro Sagane, Munekazu Motoyama, and Yasutoshi Iriyama. In-situ $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}/\text{LiCoO}_2$ interface modification for advanced all-solid-state battery. *Journal of Power Sources*, 260:292–298, 2014.
- [45] Eongyu Yi, Hao Shen, Stephen Heywood, Judith Alvarado, Dilworth Y. Parkinson, Guoying Chen, Stephen W. Sofie, and Marca M. Doeff. All-solid-state batteries using rationally designed garnet electrolyte frameworks. *ACS Applied Energy Materials*, 3(1):170–175, Jan 2020.

- [46] Yong Jeong Kim, Jaephil Cho, Tae-Joon Kim, and Byungwoo Park. Suppression of Cobalt Dissolution from the LiCoO_2 Cathodes with Various Metal-Oxide Coatings. *Journal of The Electrochemical Society*, 150(12):A1723, 2003.
- [47] J. Cho, Y. J. Kim, and B. Park. Novel LiCoO_2 cathode material with Al_2O_3 coating for a Li ion cell. *Chemistry of Materials*, 12(12):3788–3791, 2000.
- [48] J. Liu and A. Manthiram. Kinetics Study of the 5 V Spinel Cathode $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Before and After Surface Modifications. *Journal of The Electrochemical Society*, 156(11):A833, 2009.
- [49] Wen Liu, Xifei Li, Dongbin Xiong, Youchen Hao, Jianwei Li, Huari Kou, Bo Yan, Dejun Li, Shigang Lu, Alicia Koo, and et al. Significantly improving cycling performance of cathodes in lithium ion batteries: The effect of Al_2O_3 and LiAlO_2 coatings on $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$. *Nano Energy*, 44(November 2017):111–120, Feb 2018.
- [50] Muratahan Aykol, Soo Kim, Vinay I. Hegde, David Snyder, Zhi Lu, Shiqiang Hao, Scott Kirklin, Dane Morgan, and C. Wolverton. High-throughput computational design of cathode coatings for Li-ion batteries. *Nature Communications*, 7(1):13779, Dec 2016.
- [51] Adelaide M. Nolan, Yunsheng Liu, and Yifei Mo. Solid-State Chemistries Stable with High-Energy Cathodes for Lithium-Ion Batteries. *ACS Energy Letters*, 4(10):2444–2451, oct 2019.
- [52] Shenzhen Xu, Ryan M. Jacobs, Ha M. Nguyen, Shiqiang Hao, Mahesh Mahanthappa, Chris Wolverton, and Dane Morgan. Lithium transport through lithium-ion battery cathode coatings. *Journal of Materials Chemistry A*, 3(33):17248–17272, Aug 2015.
- [53] Shiqiang Hao and C. Wolverton. Lithium transport in amorphous Al_2O_3 and AlF_3 for discovery of battery coatings. *Journal of Physical Chemistry C*, 2013.
- [54] Sung Chul Jung and Young-Kyu Han. How Do Li Atoms Pass through the Al_2O_3 Coating Layer during Lithiation in Li-ion Batteries? *The Journal of Physical Chemistry Letters*, 4(16):2681–2685, Aug 2013.
- [55] Jianli Cheng, Eric Sivonxay, and Kristin A. Persson. Evaluation of Amorphous Oxide Coatings for High-Voltage Li-Ion Battery Applications Using a First-Principles Framework. *ACS Applied Materials and Interfaces*, 2020.
- [56] Hyun Soo Kim and Steve W. Martin. Synthesis and electrochemical characteristics of Al_2O_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials for lithium ion batteries. *Electrochimica Acta*, 52(3):1316–1322, Nov 2006.
- [57] Yihan Xiao, Lincoln J. Miara, Yan Wang, and Gerbrand Ceder. Computational Screening of Cathode Coatings for Solid-State Batteries. *Joule*, 2:1–24, 2019.

- [58] Xingfeng He, Qiang Bai, Yunsheng Liu, Adelaide M Nolan, Chen Ling, and Yifei Mo. Crystal Structural Framework of Lithium Super-Ionic Conductors. *Advanced Energy Materials*, 9(43), 2019.
- [59] William D. Richards, Yan Wang, Lincoln J. Miara, Jae Chul Kim, and Gerbrand Ceder. Design of $\text{Li}_{1+2x}\text{Zn}_{1-x}\text{PS}_4$, a new lithium ion conductor. *Energy Environ. Sci.*, 9(10):3272–3278, 2016.
- [60] Yizhou Zhu, Xingfeng He, and Yifei Mo. Strategies Based on Nitride Materials Chemistry to Stabilize Li Metal Anode. *Advanced Science*, 4(8):1–11, 2017.
- [61] Anubhav Jain, Shyue Ping Ong, Geoffroy Hautier, Wei Chen, William Davidson Richards, Stephen Dacek, Shreyas Cholia, Dan Gunter, David Skinner, Gerbrand Ceder, and Kristin A. Persson. Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. *APL Materials*, 1(1):011002, Jul 2013.
- [62] Shyue Ping Ong, William Davidson Richards, Anubhav Jain, Geoffroy Hautier, Michael Kocher, Shreyas Cholia, Dan Gunter, Vincent L. Chevrier, Kristin A. Persson, and Gerbrand Ceder. Python Materials Genomics (pymatgen): A robust, open-source python library for materials analysis. *Computational Materials Science*, 68:314–319, Feb 2013.
- [63] Marc Harper. python-ternary: Ternary plots in python. *Zenodo 10.5281/zenodo.594435*, 2015.
- [64] Yizhou Zhu, Xingfeng He, and Yifei Mo. Origin of Outstanding Stability in the Lithium Solid Electrolyte Materials: Insights from Thermodynamic Analyses Based on First-Principles Calculations. *ACS Applied Materials and Interfaces*, 7(42):23685–23693, 2015.
- [65] John P. Perdew, Matthias Ernzerhof, and Kieron Burke. Rationale for mixing exact exchange with density functional approximations. *Journal of Chemical Physics*, 105(22):9982–9985, Dec 1996.
- [66] G. Kresse and J. Furthmüller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B - Condensed Matter and Materials Physics*, 54(16):11169–11186, Oct 1996.
- [67] R. Goswami, C. S. Pande, N. Bernstein, M. D. Johannes, C. Baker, and G. Villalobos. A high degree of enhancement of strength of sputter deposited Al/ Al_2O_3 multilayers upon post annealing. *Acta Materialia*, 2015.
- [68] P. Lamparter and R. Kniep. Structure of amorphous Al_2O_3 . *Physica B: Condensed Matter*, 234–236:405–406, Jun 1997.
- [69] Gonzalo Gutiérrez and Börje Johansson. Molecular dynamics study of structural properties of amorphous Al_2O_3 . *Physical Review B - Condensed Matter and Materials Physics*, 65(10):1–9, Feb 2002.

- [70] Thomas F. Willems, Chris H. Rycroft, Michael Kazi, Juan C. Meza, and Maciej Haranczyk. Algorithms and tools for high-throughput geometry-based analysis of crystalline porous materials. *Microporous and Mesoporous Materials*, 149(1):134–141, Feb 2012.
- [71] Xingfeng He, Yizhou Zhu, Alexander Epstein, and Yifei Mo. Statistical variances of diffusional properties from ab initio molecular dynamics simulations. *npj Computational Materials*, 4(1), 2018.
- [72] Xingfeng He, Yizhou Zhu, and Yifei Mo. Origin of fast ion diffusion in superionic conductors. *Nature Communications*, 8(May):1–7, 2017.
- [73] Li Yang, Boris Ravdel, and Brett L. Lucht. Electrolyte Reactions with the Surface of High Voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathodes for Lithium-Ion Batteries. *Electrochemical and Solid-State Letters*, 13(8):A95, Aug 2010.
- [74] K. Edström, T. Gustafsson, and J.O. Thomas. The cathode–electrolyte interface in the Li-ion battery. *Electrochimica Acta*, 50(2-3):397–403, Nov 2004.
- [75] Na Liu, Hong Li, Zhaoxiang Wang, Xuejie Huang, and Liquan Chen. Origin of Solid Electrolyte Interphase on Nanosized LiCoO_2 . *Electrochemical and Solid-State Letters*, 9(7):A328, Jul 2006.
- [76] Hajime Miyashiro, Atsushi Yamanaka, Mitsuharu Tabuchi, Shiro Seki, Masanobu Nakayama, Yasutaka Ohno, Yo Kobayashi, Yuichi Mita, Akira Usami, and Masataka Wakihara. Improvement of Degradation at Elevated Temperature and at High State-of-Charge Storage by ZrO_2 Coating on LiCoO_2 . *Journal of The Electrochemical Society*, 153(2):A348, 2006.
- [77] L. Wang, T. Maxisch, and G. Ceder. A first-principles approach to studying the thermal stability of oxide cathode materials. *Chemistry of Materials*, 19(3):543–552, 2007.
- [78] J. R. Dahn, E. W. Fuller, M. Obrovac, and U. von Sacken. Thermal stability of Li_xCoO_2 , Li_xNiO_2 and $\lambda\text{-MnO}_2$ and consequences for the safety of Li-ion cells. *Solid State Ionics*, 69:265–270, 1994.
- [79] Matteo Bianchini, Maria Roca-Ayats, Pascal Hartmann, Torsten Brezesinski, and Jürgen Janek. There and Back Again-The Journey of LiNiO_2 as a Cathode Active Material. *Angewandte Chemie International Edition*, 58(31):10434–10458, 2019.
- [80] Hyung Man Cho, Michael Vincent Chen, Alex C. MacRae, and Ying Shirley Meng. Effect of Surface Modification on Nano-Structured $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Spinel Materials. *ACS Applied Materials and Interfaces*, 7(30):16231–16239, 2015.

- [81] Liubin Ben, Hailong Yu, Yida Wu, Bin Chen, Wenwu Zhao, and Xuejie Huang. Ta₂O₅ Coating as an HF Barrier for Improving the Electrochemical Cycling Performance of High-Voltage Spinel LiNi_{0.5}Mn_{1.5}O₄ at Elevated Temperatures. *ACS Applied Energy Materials*, 1:5589–5598, 2018.
- [82] Wei Kong Pang, Hsiu Fen Lin, Vanessa K. Peterson, Cheng Zhang Lu, Chia Erh Liu, Shih Chieh Liao, and Jin Ming Chen. Enhanced Rate-Capability and Cycling-Stability of 5 v SiO₂- and Polyimide-Coated Cation Ordered LiNi_{0.5}Mn_{1.5}O₄ Lithium-Ion Battery Positive Electrodes. *Journal of Physical Chemistry C*, 121(7):3680–3689, 2017.
- [83] Ali Eftekhari. Surface Modification of Thin-Film Based LiCoPO₄ 5 V Cathode with Metal Oxide. *Journal of The Electrochemical Society*, 151(9):A1456, 2004.
- [84] Jia-Yan Liang, Xian-Xiang Zeng, Xu-Dong Zhang, Peng-Fei Wang, Jing-Yuan Ma, Ya-Xia Yin, Xiong-Wei Wu, Yu-Guo Guo, and Lijun Wan. Mitigating Interfacial Potential Drop of Cathode-Solid Electrolyte via Ionic Conductor Layer to Enhance Interface Dynamics for Solid Batteries. *Journal of the American Chemical Society*, 140(22):6767–6770, May 2018.
- [85] Chao Lu, Hao Wu, Yun Zhang, Heng Liu, Baojun Chen, Naiteng Wu, and Sen Wang. Cerium fluoride coated layered oxide Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O₂ as cathode materials with improved electrochemical performance for lithium ion batteries. *Journal of Power Sources*, 267:682–691, 2014.
- [86] Y. K. Sun, S. W. Cho, S. T. Myung, K. Amine, and Jai Prakash. Effect of AlF₃ coating amount on high voltage cycling performance of LiCoO₂. *Electrochimica Acta*, 53(2):1013–1019, 2007.
- [87] Shuo Wang, Qiang Bai, Adelaide M. Nolan, Yunsheng Liu, Sheng Gong, Qiang Sun, and Yifei Mo. Lithium Chlorides and Bromides as Promising Solid-State Chemistries for Fast Ion Conductors with Good Electrochemical Stability. *Angewandte Chemie International Edition*, 58(24):8039–8043, Jun 2019.
- [88] Xingang Liu, Jiang Tan, Ju Fu, Ruoxin Yuan, Hao Wen, and Chuhong Zhang. Facile Synthesis of Nanosized Lithium-Ion-Conducting Solid Electrolyte Li_{1.4}Al_{0.4}Ti_{1.6}(PO₄)₃ and Its Mechanical Nanocomposites with LiMn₂O₄ for Enhanced Cyclic Performance in Lithium Ion Batteries. *ACS Applied Materials & Interfaces*, 9(13):11696–11703, Apr 2017.
- [89] Hee-Soo Kim, Yoong Oh, Ki Hoon Kang, Ju Hwan Joosun Kim, Ju Hwan Joosun Kim, and Chong Seung Yoon. Characterization of Sputter-Deposited LiCoO₂ Thin Film Grown on NASICON-type Electrolyte for Application in All-Solid-State Rechargeable Lithium Battery. *ACS Applied Materials and Interfaces*, 9(19):16063–16070, May 2017.

- [90] Kian Kerman, Alan Luntz, Venkatasubramanian Viswanathan, Yet-Ming Chiang, and Zhebo Chen. Review—Practical Challenges Hindering the Development of Solid State Li Ion Batteries. *Journal of The Electrochemical Society*, 164(7):A1731–A1744, 2017.
- [91] Lei Fan, Shuya Wei, Siyuan Li, Qi Li, and Yingying Lu. Recent progress of the solid-state electrolytes for high-energy metal-based batteries. *Advanced Energy Materials*, 8(11), Apr 2018.
- [92] Kun Joong Kim, Moran Balaish, Masaki Wadaguchi, Lingping Kong, and Jennifer L. M. Rupp. Solid-State Li–Metal Batteries: Challenges and Horizons of Oxide and Sulfide Solid Electrolytes and Their Interfaces. *Advanced Energy Materials*, 11(1):2002689, Jan 2021.
- [93] Yoon Seok Jung, Dae Yang Oh, Young Jin Nam, and Kern Ho Park. Issues and challenges for bulk-type all-solid-state rechargeable lithium batteries using sulfide solid electrolytes. *Israel Journal of Chemistry*, 55(5):472–485, 2015.
- [94] Wei Luo, Yunhui Gong, Yizhou Zhu, Yiju Li, Yonggang Yao, Ying Zhang, Kun Kelvin Fu, Glenn Pastel, Chuan Fu Lin, Yifei Mo, and et al. Reducing Interfacial Resistance between Garnet-Structured Solid-State Electrolyte and Li-Metal Anode by a Germanium Layer. *Advanced Materials*, 29(22):1–7, 2017.
- [95] Shingo Ohta, Shogo Komagata, Juntaro Seki, Tohru Saeki, Shinya Morishita, and Takahiko Asaoka. Short communication: All-solid-state lithium ion battery using garnet-type oxide and Li_3BO_3 solid electrolytes fabricated by screen-printing. *Journal of Power Sources*, 2013.
- [96] Ting Liu, Yaoyu Ren, Yang Shen, Shi Xi Zhao, Yuanhua Lin, and Ce Wen Nan. Achieving high capacity in bulk-type solid-state lithium ion battery based on $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ electrolyte: Interfacial resistance. *Journal of Power Sources*, 324:349–357, Aug 2016.
- [97] Mao Shoji, Hirokazu Munakata, and Kiyoshi Kanamura. Fabrication of All-Solid-State Lithium-Ion Cells Using Three-Dimensionally Structured Solid Electrolyte $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Pellets. *Frontiers in Energy Research*, 4(AUG):32, Aug 2016.
- [98] Christian Hänsel, Semih Afyon, and Jennifer L.M. Rupp. Investigating the all-solid-state batteries based on lithium garnets and a high potential cathode- $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$. *Nanoscale*, 8(43):18412–18420, Nov 2016.
- [99] Younggyu Kim, Dongha Kim, Roland Bliem, Gülin Vardar, Iradwikanari Waluyo, Adrian Hunt, Joshua T. Wright, John P. Katsoudas, and Bilge Yildiz. Thermally driven interfacial degradation between $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ electrolyte and $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode. *Chemistry of Materials*, 32(22):9531–9541, 2020.

- [100] Alexander Urban, Dong-Hwa Hwa Seo, and Gerbrand Ceder. Computational understanding of Li-ion batteries. *npj Computational Materials*, 2(1):16002, Nov 2016.
- [101] Yihan Xiao, Yan Wang, Shou-Hang Bo, Jae Chul Kim, Lincoln J. Miara, and Gerbrand Ceder. Understanding interface stability in solid-state batteries. *Nature Reviews Materials*, 5(2):105–126, 2020.
- [102] Shingo Ohta, Juntaro Seki, Yusuke Yagi, Yuki Kihira, Takao Tani, and Takahiko Asaoka. Co-sinterable lithium garnet-type oxide electrolyte with cathode for all-solid-state lithium ion battery. *Journal of Power Sources*, 265:40–44, Nov 2014.
- [103] Shingo Ohta, Tetsuro Kobayashi, Juntaro Seki, and Takahiko Asaoka. Electrochemical performance of an all-solid-state lithium ion battery with garnet-type oxide electrolyte. *Journal of Power Sources*, 202:332–335, 2012.
- [104] Fan Deng, Yongmin Wu, Weiping Tang, Shufeng Song, Zhaoyin Wen, Masashi Kotobuki, Li Lu, Jianyao Yao, Ning Hu, and Janina Molenda. Conformal, nanoscale γ -Al₂O₃ coating of garnet conductors for solid-state lithium batteries. *Solid State Ionics*, 342:115063, Dec 2019.
- [105] Fudong Han, Jie Yue, Cheng Chen, Ning Zhao, Xiulin Fan, Zhaohui Ma, Tao Gao, Fei Wang, Xiangxin Guo, and Chunsheng Wang. Interphase engineering enabled all-ceramic lithium battery. *Joule*, 2(3):497–508, 2018.
- [106] Jordi Sastre, Xubin Chen, Abdessalem Aribia, Ayodhya N. Tiwari, and Yaroslav E. Romanyuk. Fast Charge Transfer across the Li₇La₃Zr₂O₁₂ Solid Electrolyte/LiCoO₂ Cathode Interface Enabled by an Interphase-Engineered All-Thin-Film Architecture. *ACS Applied Materials and Interfaces*, 12(32):36196–36207, Aug 2020.
- [107] Yiren Zhong, Yujun Xie, Sooyeon Hwang, Qian Wang, Judy J. Cha, Dong Su, and Hailiang Wang. A highly efficient all-solid-state lithium/electrolyte interface induced by an energetic reaction. *Angewandte Chemie International Edition*, 59(33):14003–14008, Aug 2020.
- [108] Chengwei Wang, Yunhui Gong, Boyang Liu, Kun Fu, Yonggang Yao, Emily Hitz, Yiju Li, Jiaqi Dai, Shaomao Xu, Wei Luo, and et al. Conformal, Nanoscale ZnO Surface Modification of Garnet-Based Solid-State Electrolyte for Lithium Metal Anodes. *Nano Letters*, 17(1):565–571, Jan 2017.
- [109] Chengtian Zhou, Alfred Junio Samson, Kyle Hofstetter, and Venkataraman Thangadurai. A surfactant-assisted strategy to tailor Li-ion charge transfer interfacial resistance for scalable all-solid-state Li batteries. *Sustainable Energy and Fuels*, 2(10):2165–2170, Sep 2018.

- [110] Minghui He, Zhonghui Cui, Cheng Chen, Yiqiu Li, and Xiangxin Guo. Formation of self-limited, stable and conductive interfaces between garnet electrolytes and lithium anodes for reversible lithium cycling in solid-state batteries. *Journal of Materials Chemistry A*, 6(24):11463–11470, Jun 2018.
- [111] Thorben Krauskopf, Boris Mogwitz, Carolin Rosenbach, Wolfgang G. Zeier, and Jürgen Janek. Diffusion Limitation of Lithium Metal and Li–Mg Alloy Anodes on LLZO Type Solid Electrolytes as a Function of Temperature and Pressure. *Advanced Energy Materials*, 9(44):1902568, Nov 2019.
- [112] Chunpeng Yang, Hua Xie, Weiwei Ping, Kun Fu, Boyang Liu, Jiancun Rao, Jiaqi Dai, Chengwei Wang, Glenn Pastel, and Liangbing Hu. An electron/ion dual-conductive alloy framework for high-rate and high-capacity solid-state lithium-metal batteries. *Advanced Materials*, 31(3):1804815, Jan 2019.
- [113] Suk Woo Lee, Myeong Seong Kim, Jun Hui Jeong, Dong Hyun Kim, Kyung Yoon Chung, Kwang Chul Roh, and Kwang Bum Kim. Li_3PO_4 surface coating on Ni-rich $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ by a citric acid assisted sol-gel method: Improved thermal stability and high-voltage performance. *Journal of Power Sources*, 360:206–214, 2017.
- [114] Dandan Wang, Xiaoping Zhang, Ruijuan Xiao, Xia Lu, Yaping Li, Tinghua Xu, Du Pan, Yong-Sheng Hu, and Ying Bai. Electrochemical performance of Li-rich $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.17}\text{Co}_{0.07}]\text{O}_2$ cathode stabilized by metastable Li_2SiO_3 surface modification for advanced Li-ion batteries. *Electrochimica Acta*, 265:244–253, 2018.
- [115] Haifu Deng, Ping Nie, Haifeng Luo, Yi Zhang, Jie Wang, and Xiaogang Zhang. Highly enhanced lithium storage capability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by coating with Li_2TiO_3 for Li-ion batteries. *Journal of Materials Chemistry A*, 2(43):18256–18262, Nov 2014.
- [116] Liubin Song, Fuli Tang, Zhongliang Xiao, Zhong Cao, and Huali Zhu. Energy Storage and Thermostability of Li_3VO_4 -Coated $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ as Cathode Materials for Lithium Ion Batteries. *Frontiers in Chemistry*, 6:546, Nov 2018.
- [117] Moonsu Yoon, Yanhao Dong, Jaeseong Hwang, Jaekyung Sung, Hyungyeon Cha, Kihong Ahn, Yimeng Huang, Seok Ju Kang, Ju Li, and Jaephil Cho. Reactive boride infusion stabilizes ni-rich cathodes for lithium-ion batteries. *Nature Energy*, pages 1–10, Mar 2021.
- [118] Rusong Chen, Adelaide M Nolan, Jiaze Lu, Liquan Chen, Xuejie Huang, Hong Li, Junyang Wang, Xiqian Yu, and Yifei Mo. The Thermal Stability of Lithium Solid Electrolytes with Metallic Lithium. *Joule*, 4:812–821, 2020.
- [119] Abhik Banerjee, Hanmei Tang, Xuefeng Wang, Ju-Hsiang Cheng, Han Nguyen, Minghao Zhang, Darren H. S. Tan, Thomas A. Wynn, Erik A. Wu,

- Jean-Marie Doux, and et al. Revealing nanoscale solid–solid interfacial phenomena for long-life and high-energy all-solid-state batteries. *ACS Applied Materials & Interfaces*, 2019.
- [120] Abhik Banerjee, Xuefeng Wang, Chengcheng Fang, Erik A. Wu, and Ying Shirley Meng. Interfaces and interphases in all-solid-state batteries with inorganic solid electrolytes. *Chemical Reviews*, 120(14):6878–6933, 2020.
 - [121] Xunhui Xiong, Zhixing Wang, Guochun Yan, Huajun Guo, and Xinhai Li. Role of V_2O_5 coating on $LiNiO_2$ -based materials for lithium ion battery. *Journal of Power Sources*, 245:183?193, 2014.
 - [122] Ho-Ming Cheng, Fu-Ming Wang, Jinn P Chu, Raman Santhanam, John Rick, and Shen-Chuan Lo. Enhanced Cycleability in Lithium Ion Batteries: Resulting from Atomic Layer Deposition of Al_2O_3 or TiO_2 on $LiCoO_2$ Electrodes. *J. Phys. Chem. C*, 116:16, 2012.
 - [123] David C. Miller, Ross R. Foster, Yadong Zhang, Shih Hui Jen, Jacob A. Bertrand, Zhixing Lu, Dragos Seghete, Jennifer L. O’Patchen, Ronggui Yang, Yung Cheng Lee, and et al. The mechanical robustness of atomic-layer- and molecular-layer-deposited coatings on polymer substrates. *Journal of Applied Physics*, 105(9):093527, May 2009.
 - [124] Xinran Wang and Gleb Yushin. Chemical vapor deposition and atomic layer deposition for advanced lithium ion batteries and supercapacitors. *Energy and Environmental Science*, 8(7):1889?1904, Jul 2015.
 - [125] Collin R. Becker, S. M. Prokes, and Corey T. Love. Enhanced Lithiation Cycle Stability of ALD-Coated Confined a-Si Microstructures Determined Using in Situ AFM. *ACS Applied Materials and Interfaces*, 8(1):530?537, Jan 2016.
 - [126] Leah A. Riley, Andrew S. Cavanagh, Steven M. George, Yoon Seok Jung, Yanfa Yan, Se Hee Lee, and Anne C. Dillon. Conformal surface coatings to enable high volume expansion Li-Ion anode materials. *ChemPhysChem*, 11(10):2124?2130, Jul 2010.
 - [127] Ke Du, Hongbin Xie, Guorong Hu, Zhongdong Peng, Yanbing Cao, and Fan Yu. Enhancing the Thermal and Upper Voltage Performance of Ni-Rich Cathode Material by a Homogeneous and Facile Coating Method: Spray-Drying Coating with Nano- Al_2O_3 . *ACS Applied Materials & Interfaces*, 8(27):17713?17720, Jul 2016.
 - [128] Elena O. Filatova and Aleksei S. Konashuk. Interpretation of the Changing the Band Gap of Al_2O_3 Depending on Its Crystalline Form: Connection with Different Local Symmetries. *Journal of Physical Chemistry C*, 119(35):20755?20761, Aug 2015.

- [129] J. Pan, J. Öijerholm, A. B. Belonoshko, A. Rosengren, and C. Leygraf. Self-diffusion activation energies in α -Al₂O₃ below 1000°C - Measurements and molecular dynamics calculation. *Philosophical Magazine Letters*, 84(12):781?789, Dec 2004.
- [130] Pengfei Ma, Wenhao Guo, Jiamin Sun, Jiacheng Gao, Guanqun Zhang, Qian Xin, Yuxiang Li, and Aimin Song. Electron transport mechanism through ultrathin Al₂O₃ films grown at low temperatures using atomic-layer deposition. *Semiconductor Science and Technology*, 34(10):105004, Sep 2019.
- [131] Guido Busca. *Structural, Surface, and Catalytic Properties of Aluminas*, volume 57. Elsevier Inc., 1 edition, 2014.
- [132] C. Vinod Chandran, Christine E.A. Kirschhock, Sambhu Radhakrishnan, Francis Taulelle, Johan A. Martens, and Eric Breynaert. Alumina: Discriminative analysis using 3D correlation of solid-state NMR parameters. *Chemical Society Reviews*, 48(1):134?156, Jan 2019.
- [133] Michael F. Peintinger, Michael J. Kratz, and Thomas Bredow. Quantum-chemical study of stable, meta-stable and high-pressure alumina polymorphs and aluminum hydroxides. *Journal of Materials Chemistry A*, 2(32):13143?13158, Aug 2014.
- [134] Igor Levin and David Brandon. Metastable alumina polymorphs: Crystal structures and transition sequences. *Journal of the American Ceramic Society*, 81(8):1995?2012, 1998.
- [135] Henry O. Ayoola, Stephen D. House, Cecile S. Bonifacio, Kim Kisslinger, Wissam A. Saidi, and Judith C. Yang. Evaluating the accuracy of common γ -Al₂O₃ structure models by selected area electron diffraction from high-quality crystalline γ -Al₂O₃. *Acta Materialia*, 182:257?266, Jan 2020.
- [136] Libor Kovarik, Mark Bowden, and János Szanyi. High temperature transition aluminas in δ -Al₂O₃/ θ -Al₂O₃ stability range: Review. *Journal of Catalysis*, 393:357?368, Jan 2021.
- [137] M. B. Katz, M. E. Twigg, and S. M. Prokes. Formation and stability of crystalline and amorphous Al₂O₃ layers deposited on Ga₂O₃ nanowires by atomic layer epitaxy. *Journal of Applied Physics*, 2016.
- [138] S. Rupp and A. Larsson. Chemical vapour deposition of κ -Al₂O₃. *Thin Solid Films*, 388(1?2):50?61, Jun 2001.
- [139] Baban P. Dhonge, Tom Mathews, and A. K. Tyagi. Synthesis of mesocrystalline Al₂O₃ nano-platelet coatings using combustion chemical vapor deposition (C-CVD). *Surface and Coatings Technology*, 254:418?422, Sep 2014.

- [140] Ming Gao, Akihiko Ito, and Takashi Goto. Preparation of γ -Al₂O₃ films by laser chemical vapor deposition. *Applied Surface Science*, 340:160?165, Jun 2015.
- [141] C Wolverton and K C Hass. Phase stability and structure of spinel-based transition aluminas. *Physical Review B - Condensed Matter and Materials Physics*, 63(2), 2001.
- [142] M. Schäfer and K. M. Weitzel. Site energy distribution of ions in the potential energy landscape of amorphous solids. *Materials Today Physics*, 5:12?19, Jun 2018.
- [143] J. R. Weber, A. Janotti, and C. G. Van De Walle. Native defects in Al₂O₃ and their impact on III-V/Al₂O₃ metal-oxide-semiconductor-based devices. *Journal of Applied Physics*, 109(3):033715, Feb 2011.