Operando Visualization of Li Metal Anodes

by

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This dissertation is dedicated to my parents. You both have given me the best life I could ever live and I am truly grateful to be your son.
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Preface

A technique called plan-view *operando* video microscopy is utilized heavily throughout this work. This technique synchronizes optical video microscopy with the electrochemical response of the system and is best viewed in a video format. However, flash player is no longer supported at the time of writing this dissertation, which inhibits video integration. To view these videos, they can be found in their respective publication.
# TABLE OF CONTENTS

Dedication ................................................. ii
Acknowledgements ........................................ iii
Preface ..................................................... iv
List of Figures ............................................ vii
List of Tables ............................................. xi
List of Abbreviations ..................................... xii
Abstract .................................................. xiv

Chapter

1 Introduction ............................................. 1
   1.1 Motivation ........................................ 1
   1.2 Outline .......................................... 3
   1.3 Individual and Group Research Statement ............ 4

2 Background .............................................. 6
   2.1 Battery Basics .................................... 7
      2.1.1 Thermodynamic Potentials .................... 8
      2.1.2 The Thermodynamics of Batteries ............. 9
      2.1.3 Kinetics ................................... 10
      2.1.4 Classical Nucleation Theory ................. 14
   2.2 Lithium Metal Batteries ............................ 16
      2.2.1 Motivation .................................. 16
   2.3 Challenges Facing lithium (Li) Metal Anodes ...... 17
      2.3.1 Solid Electrolyte Interphase Formation ...... 17
      2.3.2 Deposition and Dendrite Formation .......... 19
      2.3.3 Dissolution and Pit Formation ............... 21
      2.3.4 Dead Li Formation .......................... 23
      2.3.5 State-of-The-Art Lithium Metal Anodes ...... 24

3 Plan-View Operando Video Microscopy .................. 26
   3.1 Plan-View Design .................................. 26
# Identifying the Coupled Relationships among Nucleation, Morphology, and Reversibility

4.1 Experimental Methods .................................................. 37  
4.2 Results and Discussion .................................................. 37  
4.3 Conclusions ................................................................. 52  

# Anisotropic Evolution and Faceting of Lithium

5.1 Experimental Methods .................................................. 55  
5.2 Results and Discussion .................................................. 57  
   5.2.1 Focus variation microscopy for 3-D dimensional analysis .... 57  
   5.2.2 Anisotropic in-plane vs. through-plane expansion of individual pits 61  
   5.2.3 Faceting of pits during expansion ............................... 65  
   5.2.4 Influence of electrode microstructure on pit morphology .... 68  
   5.2.5 Implications of anisotropic pit expansion on Li metal anode cycling 72  
   5.2.6 Conclusions ............................................................ 75  

# Conclusions and Future Work

6.1 Conclusions ................................................................. 77  
6.2 Future Work ............................................................... 79  

# Bibliography

Bibliography ................................................................. 83
# LIST OF FIGURES

**FIGURE**

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Estimated U.S. Energy consumption by source and sector for 2020.</td>
<td>2</td>
</tr>
<tr>
<td>2.1</td>
<td>Schematic of Li-ion battery.</td>
<td>8</td>
</tr>
<tr>
<td>2.2</td>
<td>Schematic of the Gibbs free energy for an arbitrary chemical reaction where</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>the reactants rearrange into the products.</td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>A) Diagram of the Gibbs free energy for a single electron transfer reaction</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>at dynamic equilibrium. B) Energy profile for single electron transfer</td>
<td></td>
</tr>
<tr>
<td></td>
<td>reaction when electrode potential is increased from ( E_{eq} ) to ( E ).</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C) Zoom-in of the transition state.</td>
<td></td>
</tr>
<tr>
<td>2.4</td>
<td>A) Schematic of hemispherical cluster of electrodeposited metal on substrate</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>surface and B) Gibbs free energy for a cluster as a function of cluster</td>
<td></td>
</tr>
<tr>
<td></td>
<td>radius.</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>Schematic depicting two models of the SEI structure, a) mosiac-like and b)</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>multi-layered.</td>
<td></td>
</tr>
<tr>
<td>2.6</td>
<td>Schematic of dendrite formation showing A) a pristine anode surface, B)</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>current focusing at local hot spots, C) fracture of the SEI, D) dendrite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>growth. E) optical image of a mossy growth that was deposited on a Li metal</td>
<td></td>
</tr>
<tr>
<td></td>
<td>anode at 3 mA cm(^{-2}) inside of the plan-view cell and detached from</td>
<td></td>
</tr>
<tr>
<td></td>
<td>the electrode surface (the growth is floating in electrolyte). F) SEM of</td>
<td></td>
</tr>
<tr>
<td></td>
<td>different mossy growth on a Li metal anode after 0.1 mA h cm(^{-2}) of</td>
<td></td>
</tr>
<tr>
<td></td>
<td>charge was deposited at 3 mA cm(^{-2}).</td>
<td></td>
</tr>
<tr>
<td>2.7</td>
<td>Schematic of pit formation A) pristine surface, B) preferential stripping</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>that leads to void formation, and C) accumulation of voids into a pit, D)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SEI collapse into the pit. Ex situ SEM image of a pit formed on a Li metal</td>
<td></td>
</tr>
<tr>
<td></td>
<td>anode from the plan-view cell.</td>
<td></td>
</tr>
<tr>
<td>2.8</td>
<td>A) Mossy growth on a Li metal anode, B) preferential stripping at the base</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>of the mossy growth, and C) dead Li formation.</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>COMSOL model of current density distribution in <em>operando</em> visualization</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>cells. A) Current density distribution along the working electrode surface</td>
<td></td>
</tr>
<tr>
<td></td>
<td>for both the optimized and non-optimized cells when 1mA cm(^{-2}) is</td>
<td></td>
</tr>
<tr>
<td></td>
<td>applied. B) A schematic showing the geometry of the plan-view cell.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Isometric views of C) a non-optimized cell and D) the optimized-cell with</td>
<td></td>
</tr>
<tr>
<td></td>
<td>the current density in the cell electrolyte shown in color on a cross section</td>
<td></td>
</tr>
<tr>
<td></td>
<td>plot (current focuses at electrode edges). Current density streamlines are</td>
<td></td>
</tr>
<tr>
<td></td>
<td>also shown.</td>
<td></td>
</tr>
</tbody>
</table>
3.2 Current density distribution in the plan-view cell at different current densities. Current density in the plan-view cell shown on a cross section plot (CE is the counter electrode) when the applied current density is A) 3 mA cm$^{-2}$, C) 5 mA cm$^{-2}$, E) 7 mA cm$^{-2}$. Current density along the working electrode surface when the applied current density is A) 3 mA cm$^{-2}$, C) 5 mA cm$^{-2}$, E) 7 mA cm$^{-2}$.

3.3 Frames from plan-view video microscopy of the working electrode in a Li-Li symmetric cell cycled at 3 mA cm$^{-2}$ and 0.2 mAh cm$^{-2}$. The frames show the electrode morphology and voltage trace at various stages: A) before cycling; B) end of the first plating half-cycle; C) onset of dead Li formation; D) end of first dissolution half-cycle; E) during second deposition half-cycle. F) Zoomed views of D and E showing pit formation and subsequent nucleation of dendrites into existing pits.

3.4 A) PEIS spectra taken during deposition, where each spectrum was taken after 0.01 mAh cm$^{-2}$ of deposition. B) Two electrode measurement of cell polarization of a plan view visualization cell cycling at 3 mA cm$^{-2}$. C) COMSOL model showing a cross-sectional view of the voltage inside the plan-view cell where CE is the counter electrode. D) Three-electrode measurement showing the voltage of the working electrode vs. the reference electrode in a plan-view visualization cell depositing Li at 3 mA cm$^{-2}$.

3.5 Schematic of three-electrode plan-view cell.

4.1 Panels A-C are optical images of the working electrode surface from three different Li-Li symmetric cells after 0.0025 mAh cm$^{-2}$ of Li was deposited at the respective current density; A) 3 mA cm$^{-2}$; B) 5 mA cm$^{-2}$; C) 7 mA cm$^{-2}$. Red circles were added to A-C to improve visibility of dendrite nucleation. D-F are optical images of the working electrode surface from three different Li-symmetric cells after 0.2 mAh cm$^{-2}$ of Li was stripped at the respective current density; D) 3 mA cm$^{-2}$; E) 5 mA cm$^{-2}$; F) 7 mA cm$^{-2}$.

4.2 A) Nucleation density measurements for both dendrites and pits. B) Diagram depicting the heterogenous Li surface with spatially varying Gibbs energy for nucleation ($G_{nuc}$). C) Diagram showing the impact of increasing current density on nucleation density for a heterogenous surface with spatially varying $G_{act}$. 

4.3 A) Optical image of pristine Li surface before deposition with grain boundaries highlighted in red. B) Pristine Li surface before dissolution with grain boundaries highlighted in red. C) Surface shown in A after 0.01 mAh cm$^{-2}$ of Li was deposited. D) Surface shown in C after 0.2 mAh cm$^{-2}$ of Li was stripped.

4.4 Histograms showing the minimum distance between the nuclei and the nearest surface grain boundary for A) dendrites and B) pits.
4.5 A) Li electrode with an SEI before any cycling, (B) Li electrode after a half-cycle of dissolution in Which pits have formed on the surface, (C) Dendrite formation during deposition, where nucleation occurs inside of the pit, (D) Dead Li formation and expansion of initial pits after dissolution, and (E) Dendrite nucleation inside of the expanded pit and upward displacement of Dead Li.

4.6 A) Process of calculating effective dendrite volume through a spherical approximation. B) Tracking of four individual dendrite effective volumes throughout the first cycle in a Li-Li symmetric cell at a current density of 3 mA cm\(^{-2}\).

4.7 Panels A-C show \(V_{\text{max}}\) vs. \(V_{\text{dead}}\) for the first two cycles of three Li-Li symmetric cells cycling at the same current density (3 mA cm\(^{-2}\)) but to different capacities of Li: A) 0.2 mAh cm\(^{-2}\); B) 0.1 mAh cm\(^{-2}\), C) 0.025 mAh cm\(^{-2}\). Panels D-F show the first dissolution half cycle and the second dissolution half cycle to illustrate differences in the second peak position. The second peak is quantified as a percentage of the half cycle to allow for comparisons across all cells.

4.8 A) Voltage traces of three Li-Li symmetric coin cells cycling at 3 mA cm\(^{-2}\). The amount of Li passed in the first cycle varied between the three cell (0.2 mAh cm\(^{-2}\), 0.1 mAh cm\(^{-2}\), and 0.025 mAh cm\(^{-2}\)). The same capacity (0.2 mAh cm\(^{-2}\)) was passed in the second cycle for all cells. Second peak positions when the capacity passed in the first cycle is B) 0.2 mAh cm\(^{-2}\), C) 0.1 mAh cm\(^{-2}\) and D) 0.025 mAh cm\(^{-2}\).

4.9 A), B), and C) optical images of dendrite nucleation at pit edge after 0, 0.16, and 0.33 mAh cm\(^{-2}\) of deposition respectively.

4.10 A) SEM image of pit on Li surface. B) Nucleation of dendrite along the perimeter of a pit. C) Cross-sectional image of pit that has been milled using a focus ion beam (FIB).

5.1 Schematic of MATLAB segmentation code that outlines pit.

5.2 a) Example AFM image with averaging border depicted. b) Example image produced with focus variation microscopy with averaging border depicted. Variables and constraints that define the border dimensions are listed.

5.3 a) Schematic of the plan-view cell used for operando analysis. b) Current density distribution within electrolyte body along a cross-section when charge is stripped from the working electrode at 5 mA cm\(^{-2}\) (area based on working electrode surface area). c) Current density at working electrode and counter electrode surface when charge is stripped from working electrode surface at same rate in c). d) Current density along working electrode surface across the X axis.

5.4 (a) Schematic depiction of focus variation microscopy, where a focal series is captured and saved as a vertical image stack. After postprocessing, (b) the output is a composite optical image of the pit, which enables 3D reconstruction of the pit from (c) an isometric view, and cross sections of the pit along the (d) YZ and (e) XZ-planes.
5.5 Images of three different pits captured through (a–c) ex situ focus variation microscopy and (d–f) ex situ AFM on Li metal electrodes. Li was stripped at a current density of 5 mA cm$^{-2}$ in each coin cell. The depth of discharge was 0.027 mAh cm$^{-2}$ in Pit A (left column), 0.041 mAh cm$^{-2}$ in Pit B (middle column), and 0.055 mAh cm$^{-2}$ in Pit C (right column). (g) The average pit width and (h) maximum pit depth of for each pit were measured by focus variation microscopy and AFM.

5.6 3D reconstructions of a pit from an (a–c) isometric view and (d–f) cross sections of pit along the YZ-plane produced by operando focus variation microscopy. Each column represents a point in time during the half cycle, 240 s (left column), 430 s (middle column), and 730 s (right column).

5.7 Cell polarization (left axis) and the pit aspect ratio (right axis) as a function of time for a single pit.

5.8 a) Optical image of the working electrode from a plan-view cell after 1.1 mAh cm$^{-2}$ of charge was stripped. b-g) Pit aspect ratio as a function of time for the pits labeled in a). Dashed line is an aspect ratio of 2, which is the expected value for isotropic expansion. Values greater than 2 indicate faster in-plane expansion.

5.9 (a–c) Optical images of a pit, (d–f) outlines of pit edge with normal vectors to pit edge, and (g–i) histograms of all normal vector angles with respect to the X-axis at different points in time of the stripping half cycle, 41 s (left column), 204 s (middle column), and 653 s (right column).

5.10 (a–c) Optical images of a pit, (d–f) outlines of pit edge with normal vectors to pit edge, and (g–i) histograms of all normal vector angles with respect to the X-axis at different points in time of the stripping half cycle, 184 s (left column), 286 s (middle column), and 643 s (right column).

5.11 (a–c) Optical images of a pit and (d–f) polar plots showing the radial distance from the pit center to the edge as a function of polar angle $\theta$ at different points in time of the stripping half cycle, 240 s (left column), 430 s (middle column), and 730 s (right column).

5.12 (a–c) Optical images of two pits with (d–f) cartoon depictions at different points in time of the stripping half cycle, 81 s (left column), 163 s (middle column), and 743 s (right column).

5.13 Optical image of electrode surface extracted from a Li-Li symmetric coin cell after 1.1 mAh cm$^{-2}$ of charge was stripped from the surface at 5 mA cm$^{-2}$. Local groupings of similar polygonal shapes were observed. The shape of each grouping varied across the electrode surface.

5.14 Optical images of deposition into faceted pits at a rate of 5 mA cm$^{-2}$ at different points in time (A) 0 s, (B) 143 s, and (C) 183 s. Scale bar in (a) the same for all images.
LIST OF TABLES

TABLE

3.1 COMSOL model variable and constant definitions ........................................ 28
3.2 COMSOL model parameters ............................................................................ 28
LIST OF ABBREVIATIONS

2-D  two-dimensional

3-D  three-dimensional

AFM  atomic force microscopy

BCC  body-centered-cubic

CE   Coulombic efficiency

DFT  density functional theory

DOD  depth-from-defocus

EBSD  electron backscatter diffraction

EIS  electrochemical impedance spectroscopy

EV   electric vehicle

EC   ethylene carbonate

EMC  ethyl methyl carbonate

FIB  focus ion beam

Li   lithium
Mg  Magnesium

PEIS  potentiostatic electrochemical impedance spectroscopy

SEM  scanning electron microscopy

SEI  solid electrolyte interphase

SHE  standard Hydrogen electrode

TEM  transmission electron microscopy

XRD  x-ray diffraction
ABSTRACT

A pressing challenge facing the 21st century world is replacing fossil fuels with a competitive and renewable energy source. However, enabling widespread renewable energy sources requires improvement in the energy density of current battery technology, especially for transportation applications. A promising approach to increase the energy density of current state-of-the-art Li-ion batteries is to replace the graphite anode with pure metallic Li. These anodes offer a specific capacity that is 10x greater than that of graphite and are a critical component of next-generation batteries, such as Li-Air and Li-Sulfur. Incorporating a Li metal anode into a rechargeable battery would be a breakthrough technology that could further aid in the electrification of vehicles. However, the commercialization of metallic Li is limited by poor cycle life and safety concerns, which are impacted by the dynamic morphological evolution of the anode surface during cycling.

The goal of this thesis is to improve our understanding of the morphological evolution of the Li surface and the relationship between surface morphology and performance. A platform for plan-view operando video microscopy is developed, which simultaneously affords optical access to the anode surface and achieves a uniform current distribution across the working electrode surface. Using this platform, various factors that govern the morphological evolution of the Li surface are explored. Nucleation is characterized as a function of current density and electrode microstructure. A positive correlation is observed between nucleation density and current density for both dendrites and pits. However, pit nucleation is found to be more sensitive to current density than dendrite nucleation. Furthermore, surface grain boundaries are observed to be preferential nucleation sites for dendrite and pits.
during initial cycling. However in subsequent cycles, preferential nucleation is found to transition from the surface grain boundaries to the pit edges.

The degree of reversibility during Li plating and stripping is then explored. The size of individual dendrites is tracked throughout cycling by quantifying their volumetric contraction. A clear correlation between dendrite size and reversibility is not observed, however reversibility is found to be sensitive to pitting. Dendrite reversibility is observed to improve when nucleation occurs at a pit edge compared to a pristine surface. Additionally, this reversibility is found to be sensitive to the size of the pits in which nucleation occurred. Overall, dead Li formation is found to be more sensitive to nucleation than growth.

Operando focus variation microscopy is then integrated with the plan-view platform to better understand the mechanisms that link pit formation to dendrite nucleation and reversibility. Using this upgraded capability, the nucleation and growth of individual pits is mapped in three dimensions. Pit expansion is observed to be highly anisotropic, where expansion occurs more rapidly along the anode surface than into the depth of the electrode. Concurrently, facets are observed to form at the pit edges, indicating that the underlying mechanism for anisotropic stripping is determined by the properties of the electrode crystal lattice. Additionally, pit expansion is observed to preferentially occur along surface grain boundaries, highlighting the importance of electrode microstructure on anode morphology.

Overall, this thesis provides mechanistic insight into the morphological evolution and poor reversibility of Li metal anodes through the use of plan-view operando optical analyses. In the future, the understanding developed can inform rational solutions that are aimed at improving the performance of next-generation Li metal batteries.
CHAPTER 1

Introduction

1.1 Motivation

Fossil fuels, such as petroleum, natural gas, coal, and oil have been an enabling technology in the advancement of industrialized civilizations, and they currently serve as the dominant resource for global energy consumption.\(^1\) However, these resources are non-renewable and release greenhouse gases, such as CO\(_2\), that contribute to global warming and climate change.\(^2\) The changes in the global climate threaten natural ecosystems and humans and are occurring at an alarming rate.\(^3,4\) Therefore, there is an immediate need to replace fossil fuels with a competitive energy source that is renewable.

Figure 1.1 shows the energy consumption by source and sector for the United States (U.S.) in the year 2020. The majority of the total energy produced came from the combustion of fossil fuels (79\%), while a significantly smaller portion (12\%) was provided by renewable sources. Approximately 40\% of the total energy produced was utilized to generate electrical energy, which was largely used by the residential and commercial sectors. In contrast, electricity was scarcely used by the industrial and transportation sectors; instead, fossil fuels were the dominant energy source. The transportation sector consumed the most energy, with 95\% of production coming from fossil fuels and only 5\% from renewable sources. The electrification of vehicles would be an effective pathway to reduce greenhouse emissions, since this would alleviate the use of fossil fuels in one of the largest
Vehicle electrification is gaining interest, as the global sales of electric vehicle (EV) has increased from less than 10,000 to millions of vehicles solid within the past two decades. Advancements in Li-ion batteries, including improvements to specific energy and reduced manufacturing costs, have made EV more readily available to consumers. However, widespread vehicle electrification is still limited by battery performance and costs. The U.S. Department of Energy has identified that a step improvement in battery technology is needed for widespread vehicle electrification.

Incorporating metallic Li into rechargeable batteries is a promising pathway to enable a new generation of high-energy-density batteries. Replacing the graphite anode with pure metallic Li can increase the specific capacity of the anode by a factor of 10. However, several challenges restrict the use of metallic Li in a secondary battery, such as poor Coulombic efficiency (CE) and safety concerns. The following chapter will discuss the
current state-of-the-art in Li metal batteries, and the primary bottlenecks preventing their commercialization.

1.2 Outline

The goal of this dissertation is to improve our understanding of the factors that govern the morphological evolution of Li metal anodes, and to identify how these factors impact performance. First, a custom platform for operando video microscopy is presented and validated against previous studies. This tool is then used to characterize nucleation on Li metal and elucidate the impact of the initial surface microstructure on nucleation behavior and performance. Subsequently, the platform is upgraded to perform focus variation microscopy, which is used to study the anisotropic nature of Li metal stripping.

Chapter 2 will describe background concepts from thermodynamics and kinetics that influence battery performance. The current state-of-the-art understanding of the morphological evolution and sources of poor performance of Li metal anodes will also be covered. The background information presented in this chapter will provide a basis for the discussion throughout the remainder of this thesis.

Chapter 3 introduces a custom plan-view optical microscopy platform that enables real-time visualization of Li metal anodes and quantitative analysis of Li nucleation. The design simultaneously enables a plan-view perspective and achieves a uniform current distribution across the working electrode surface. The ability to monitor the morphological evolution of a Li metal anode, and to time-synchronize the electrochemical voltage signatures using the plan-view platform, are demonstrated. The plan-view platform is then validated against previous operando video microscopy studies to demonstrate that the observations from the plan-view cell are consistent with other form factors and are representative of Li metal anodes in batteries.

Chapter 4 identifies the coupled relationships between the nucleation, morphology, and
 reversibility of Li metal anodes through the use of the plan-view platform. The nucleation density of both dendrites and pits are quantified as a function of current density to explore how surface heterogeneity impacts nucleation. Pit nucleation is found to be more sensitive to current density, providing evidence of fundamental differences in the nucleation behavior of dendrites and pits. Surface grain boundaries are found to be “hot” spots for the formation of both dendrites and pits. However, in subsequent cycles, nucleation preferentially occurs along the edges of pits rather than surface grain boundaries. Lastly, dendrite reversibility is studied as a function of dendrite size. A strong correlation between dendrite size and reversibility is not observed. However reversibility is observed to be sensitive to the size of the pits within which nucleation occurred.

Chapter 5 explores the anisotropic morphological evolution of pits during Li metal stripping. The plan-view platform is upgraded to perform focus variation microscopy, which is a technique that captures the areal surface topography of a sample. Using this new capability, the three-dimensional expansion of individual pits is monitored, and pits are observed to expand more rapidly along the surface of the electrode than into the depth. The faceting of pits is also observed, indicating that the electrode crystallographic orientation influences Li metal stripping. The impact of electrode microstructure on stripping is also studied, and surface grain boundaries are found to influence the preferential expansion of pits.

Chapter 6 summarizes the primary contributions of this thesis towards enabling Li metal anodes in the future. Additionally, several opportunities to expand upon this work are presented, which focus on an improved understanding how nucleation and surface morphology impact performance.

1.3 Individual and Group Research Statement

The work presented in this thesis was a collaborative effort with many others from the Dasgupta Research lab at the University of Michigan. A brief summary of the contributions
from all co-workers and co-authors is presented below.

Chapter 3 was adapted from Sanchez, et al. 2020. Adrian J. Sanchez performed the COMSOL simulations, designed and fabricated the final generation of the plan-view platform, and performed visualization experiments. Eric Kazyak assisted in the design of the plan-view platform. Yuxin Chen performed three-electrode measurements. Neil P. Dasgupta supervised the research.

Chapter 4 was adapted from Sanchez, et al. 2020. Adrian J. Sanchez designed and fabricated the plan-view operando video microscopy platform, gathered operando video microscopy data, and wrote the manuscript. Eric Kazyak assisted with manuscript writing and performed scanning electron microscopy (SEM)/focus ion beam (FIB) analysis. Yuxin Chen aided in gathering operando video microscopy data. Kuan-Hung Chen helped analyze data. Ethan Pattison aided in image processing. Neil P. Dasgupta supervised the research, provided guidance and assisted with manuscript writing.

Chapter 5 was adapted from Sanchez, et al. 2021. Adrian J. Sanchez developed focus variation microscopy in the plan-view platform, gathered focus variation microscopy data, and wrote the manuscript. Eric Kazyak assisted with manuscript writing and data analysis, Yuxin Chen aided in the development of the focus variation microscopy technique. Jose Lasso aided in data and image processing. Neil P. Dasgupta supervised the research, provided guidance, and assisted with manuscript writing.
CHAPTER 2

Background

Since the introduction of commercial Li-ion batteries by Sony in 1991, our modern society has been transformed by the accelerated development of portable electronics, such as phones and laptops.\textsuperscript{14} The high energy density offered by Li-ion batteries has made this chemistry the predominant choice for rechargeable batteries.\textsuperscript{15} For the pioneering work on Li-ion batteries, the 2019 Nobel Prize in Chemistry was awarded to John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino.\textsuperscript{16} M. Stanley Whittingham first demonstrated the ability to host Li in a titanium disulfide electrode, but the performance of the rechargeable battery was limited by the Li metal anode. John B. Goodenough built upon this system by developing the Li\textsubscript{x}CoO\textsubscript{2} (LCO) electrode that allowed for further energy storage, but performance was still limited by the Li metal anode. Akira Yoshino developed the graphite anode to replace the metallic Li, which when paired with the LCO electrode, gave rise to the Li-ion battery.

As energy demands continually grow and we approach the theoretical limitations of Li-ion batteries, efforts are underway to develop a “beyond Li-ion” technology. A promising technology is a rechargeable battery that incorporates an anode made of pure metallic Li.\textsuperscript{17} However, many challenges limit the application of a Li metal anode in a rechargeable battery. The focus of this thesis is to understand the poor performance of Li metal anodes during cycling. Before delving into the main body of this thesis, a brief background is provided in this chapter to aid in understanding of the presented work.
2.1 Battery Basics

A battery is an electrochemical device that directly converts chemical energy into electrical energy. The internal structure of a traditional battery consists of a cathode, anode, separator, electrolyte, and current collectors. A simple schematic of a battery (Li-ion depicted) is shown in Figure 2.1. In Li-ion batteries, the anode and cathode are responsible for hosting $\text{Li}^+$, which is responsible for the stored chemical energy. During discharge, $\text{Li}^+$ is liberated at the anode surface and is transferred to the cathode. To facilitate the transport of $\text{Li}^+$, the battery contains a liquid electrolyte that occupies the pores of the electrodes and separator. This electrolyte is capable of conducting ions but is not electronically conductive. The electrons that are liberated during the interfacial charge transfer reactions are transferred from the anode to the cathode through an external circuit. This circuit can be connected to a device to allow for useful electrical work to be performed. Current collectors are mounted to both electrodes to support the conduction of electrons.

When describing electrochemical cells, the anode and cathode are defined as the electrodes that facilitate oxidation and reduction, respectively.\textsuperscript{18} This means that the graphite electrode in a Li-ion battery alternates between serving as the anode and cathode as the battery cycles. While the battery is discharged and charged, the graphite electrode serves as the anode and cathode, respectively. However, the negative electrode (electrode with a lower potential) is commonly referred to as the anode, to avoid switching terms continuously. For example, the graphite electrode is commonly referred to as the anode for Li-ion batteries.

The next chapter provides a background on the fundamental principles that govern the performance of a battery, including thermodynamics and kinetics. This information is then discussed in the context of Li metal batteries.
2.1.1 Thermodynamic Potentials

Gibbs free energy is a thermodynamic potential that is often used in the analysis of electrochemical cells. Below is brief background on Gibbs free energy, which is primarily based on “Equilibrium Thermodynamics” by C.J Adkins et al. and “Fuel Cell Fundamentals” by Ryan O’Hayre et al.\textsuperscript{19,20} For a system with two degrees of freedom, there are four state functions (dependent only on the initial and final state, not the path between) that can be used to describe thermodynamic equilibrium.\textsuperscript{19} One of these functions is Gibbs free energy (equation 2.1).\textsuperscript{19} The definition of this function (considering a system that is subjected to hydrostatic pressure) is provided in equation 2.1 where $S$ is entropy, $T$ is temperature, $V$ is volume, and $p$ is pressure.\textsuperscript{19}

\begin{equation}
G = U - TS + pV
\end{equation}

A factor that makes Gibbs free energy useful for the description of electrochemical cells is that the independent variables are pressure and temperature (these are often known or controlled). The change in Gibbs free energy represents the maximum electrical work that can be performed by an electrochemical process. This is best expressed by the differential form of Gibbs free energy for a closed system subjected to hydrostatic pressure and electrical work ($W_{elec}$) (equation 2.2).
\[ dG = -SdT + Vdp - dW_{\text{elec}} \] (2.2)

When temperature and pressure are held constant \((dT = dp = 0)\), the maximum electrical work that can be performed by the system is the negative change in Gibbs free energy.\(^{20}\) When the change in Gibbs free energy is negative, the electrochemical process is spontaneous and can perform electrical work, while a positive change indicates the process requires input work to proceed.\(^{20}\)

### 2.1.2 The Thermodynamics of Batteries

The voltage between the cathode and anode of a battery \((V_{OC})\) is a measure of the ability to do electrical work.\(^{20}\) The relationship between the open circuit voltage of a battery and Gibbs free energy is shown in equation 2.3, where \(z\) is charge number and \(F\) is Faraday’s constant.\(^{21}\)

\[ \Delta G = -W_{\text{elec}} = -zFV_{OC} \] (2.3)

The difference in the energy levels of the electrons in the cathode and anode produce this voltage.\(^{21}\) There are quantized energy states that an electron can occupy in each electrode, and electrons fill these states starting with the lowest energy level and progressing to higher energy levels.\(^{22}\) The Fermi level \((E_F)\) is defined as the level at which there is a 50% probability of occupation.\(^{22}\) The open circuit voltage of a battery is determined by the difference in the Fermi level between the cathode and anode as shown in equation 2.4, where \(\mu_e^-\) and \(\mu_e^+\) are the chemical potential of the electrons in the anode and cathode respectively.\(^{21}\)

\[ V_{OC} = -\frac{\Delta E_F}{F} = \frac{\mu_e^- - \mu_e^+}{F} \] (2.4)
The chemical potential of species $i$ is the change in Gibbs free energy of a system when an infinitesimal amount of species $i$ is introduced while temperature and pressure are held constant.\textsuperscript{20} The mathematical description is given in equation 2.5

$$
\mu_i = \left( \frac{\delta G}{\delta N_i} \right)_{T,P}
$$

(2.5)

This chemical potential can further be expressed as a function of the chemical potential under standard conditions and the activity of the species ($a_i$) as shown in equation 2.6.\textsuperscript{20}

$$
\mu_i = \mu_{i}^o + RT \ln(a_i)
$$

(2.6)

The Nernst equation can be derived by combining equations 2.7, 2.5, and 2.6, where $a_i^-$ and $a_i^+$ are the activity of species $i$ in the negative and positive electrode respectively. This relationship (equation 2.7) is ubiquitous in electrochemistry and defines the open circuit voltage of an electrochemical cell.\textsuperscript{20}

$$
V_{OC} = \frac{-RT}{z_i F} \ln \frac{a_i^+}{a_i^-}
$$

(2.7)

2.1.3 Kinetics

The Nernst equation detailed in Section 2.1.2 defines the open circuit voltage of a battery when it is at equilibrium (no net current). However, a finite current is produced under normal operating conditions, and the voltage of the battery deviates from the Nernst equation under non-equilibrium conditions. The deviation is due to kinetic and mass transport effects. This section overviews the underlying principles that describe these voltage differences and is primarily based off of “Electrochemical Methods Fundamentals and Applications” by Allen J. Bard et al.\textsuperscript{18}

To describe the reaction that occurs at the electrode surface, the general redox couple $O + ne \rightleftharpoons R$ will be considered, where species $O$ is the oxidizing agent, species $R$ is the
reducing agent, and \( n \) is the number of electrons transferred. Under open circuit conditions, the forward and reverse reaction rates of the given redox couple are equal. Therefore, there is no net current, and the system is in dynamic equilibrium.\(^{18}\) The rate of the forward and backward directions can be expressed as the product of a rate constant and the concentration of the respective species at the electrode surface, raised to a specified power based on the reaction order. Equations 2.8 and 2.9 show the general forms of the reaction rates where \( k_f \) and \( k_b \) are the rate constants of the forward and reverse reaction respectively, \( C_O(0, t) \) and \( C_R(0, t) \) are the concentrations of the oxidizing and reduction agent respectively at the electrode surface, \( R \) is the gas constant, and \( T \) is temperature.\(^{18}\)

\[
\nu_f = k_f C_O(0, t) = \frac{i_c}{nFA} \tag{2.8}
\]

\[
\nu_b = k_b C_R(0, t) = \frac{i_a}{nFA} \tag{2.9}
\]

These expressions were further expanded to show the cathodic \((i_c)\) and anodic \((i_a)\) currents that are associated with each reaction, where \( A \) is area. The rate constants in equations 2.8 and 2.9 can be described with the Arrhenius relationship (equation 2.10), where \( \beta \) is the frequency factor and \( \Delta G_{act} \) is the activation energy.\(^{18}\)

\[
k = \beta \exp \left( \frac{-\Delta G_{act}}{RT} \right) \tag{2.10}
\]

Figure 2.2 depicts the Gibbs free energy profile of an arbitrary chemical reaction to illustrate the concept of the activation energy. In the energy profile, an overall decrease is observed as the reaction moves forward, which indicates that the process is thermodynamically downhill. However, there is a local barrier between the between initial and final states, which represents the activation energy for this reaction. This energetic barrier must be surmounted for the reaction to move forward.\(^{18}\)

The activation energy for the forward and backward reactions listed above is sensitive
to the electrode potential. Figure 2.3A shows the Gibbs free energy profile for the redox couple when the electrode is at equilibrium. The activation barrier for the forward and reverse reactions are labeled as $\Delta G_{act,f}$ and $\Delta G_{act,b}$ respectively. When the voltage of the electrode changes from the equilibrium potential ($E_{eq}$) to potential $E$, the energy of the electrons in the electrode changes by $-F(E - E_{eq})$. The change in voltage alters the energy landscape of the redox as shown in Figure 2.3B. The dashed line represents the energy profile at equilibrium, while the solid line represents the profile at a potential $E (E > E_{eq})$. The activation barriers for the forward and reverse reactions are impacted differently by the change in potential. The forward activation barrier increases to a new value, $\Delta G'_{act,f}$, while the reverse activation barrier decreases to $\Delta G'_{act,b}$. Figure 2.3C shows a zoom-in of the transition point in the energy profile to better display the change in activation barriers. The activation barriers are changed by a fraction of $F(E - E_{eq})$. The forward activation barrier is increased by a factor of $\alpha F(E - E_{eq})$ while the reverse activation barrier is decreased by a factor of $(1-\alpha)F(E - E_{eq})$, where $\alpha$ is the transfer coefficient of the redox couple. The transfer coefficient describes the symmetry of the intersection shape and ranges from 0 to 1. With the activation barriers thus defined as a function of the electrode potential, the forward and reverse rate constants can be expressed as:
Figure 2.3: A) Diagram of the Gibbs free energy for a single electron transfer reaction at dynamic equilibrium. B) Energy profile for single electron transfer reaction when electrode potential is increased from $E_{eq}$ to $E$. C) Zoom-in of the transition state.

\[ k_f = \beta_f \exp \left( -\frac{\Delta G_{act,f}}{RT} \right) \exp \left( -\frac{\alpha F(E - E_{eq})}{RT} \right) \]  

(2.11)

\[ k_b = \beta_b \exp \left( -\frac{\Delta G_{act,b}}{RT} \right) \exp \left( \frac{(1 - \alpha) F(E - E_{eq})}{RT} \right) \]  

(2.12)

The prefactors in equations 2.11 and 2.12 are equivalent to each other and can be represented as a standard rate constant $k^o$ of the reaction. To obtain the relationship between the electrode potential and net current ($i$), the difference in the cathodic ($i_c$) and anodic ($i_a$) current is calculated, which results in the following expression:

\[ j = Fk^o \left[ C_O(0, t) \exp \left( -\frac{\alpha F(\eta)}{RT} \right) - C_R(0, t) \exp \left( \frac{(1 - \alpha) F(\eta)}{RT} \right) \right] \]  

(2.13)

where $\eta$ is defined as the overpotential ($E - E_{eq}$). The overpotential can be viewed as the voltage loss that is needed to drive a current. In electrochemistry, current is typically normalized by area so that direct comparisons can be made between the performance of different cells. Furthermore, the above relationship can be expressed as a function of the exchange current density (Equation 2.14) where $C^*_O$ and $C^*_R$ are the bulk concentrations of...
the oxidizing and reducing agents respectively. Normalizing current by area and incorporating the exchange current density leads to the generalized Butler-Volmer relation. This equation is ubiquitous to electrochemistry and describes the change in voltage required (overpotential) to drive a given current density.

\[ j_o = Fk^\alpha C^{(1-\alpha)}_O C^{\alpha}_R \]  
\[ j = j_o \left[ \frac{C_O(0, t)}{C^*_O} \exp \left( -\frac{\alpha \eta}{RT} \right) - \frac{C_R(0, t)}{C^*_R} \exp \left( \frac{(1 - \alpha) \eta}{RT} \right) \right] \]

Redox couples with a high exchange current density display superior kinetics and do not require relatively large overpotentials to drive large currents. A lower exchange current density indicates poor kinetics, and thus relatively large voltage changes are needed to drive a given current. When there are no mass transport limitations (surface and bulk concentration are equivalent) and the electrode is at equilibrium (net current is 0), the Butler-Volmer equation can be reduced to the Nernst relation.

2.1.4 Classical Nucleation Theory

Nucleation is explored heavily throughout this thesis, therefore a brief overview of classical nucleation theory is presented, which is largely based off of “Electrochemistry for Materials Science” by Waldfried Plieth et al. and “Theory and Practice of Metal Electrodeposition” by Yuliy D. Gamburg et al.. During the electrodeposition of a metal, the metal cations in the electrolyte are reduced at the electrode surface to form adatoms. These adatoms diffuse across the electrode surface and form clusters of atoms that can become unstable and break apart or become stable and grow. The change in Gibbs free energy of the nucleation and growth of these clusters determines whether the cluster is stable. A schematic of
a hemispherical cluster is shown in Figure 2.4A. The Gibbs free energy of the growing cluster \( \Delta G_{\text{cluster}} \) is the summation of the bulk energy \( \Delta G_{\text{bulk}} \) and the surface energy \( \Delta G_{\text{surface}} \) as shown in equation 2.16

\[
\Delta G_{\text{cluster}} = \Delta G_{\text{Bulk}} + \Delta G_{\text{Surface}} = -\frac{2\pi}{3} r^3 \frac{\Delta G_m}{V_m} + 2\pi r^2 \sigma \quad (2.16)
\]

where \( \Delta G_m \) is the change in molar Gibbs free energy, \( r \) is the radius of the nuclei, \( V_m \) is the molar volume of the deposited metal, and \( \sigma \) is the surface free energy. This equation shows two competing terms. The volumetric expansion of the cluster produces a negative change in the Gibbs free energy (thermodynamically favorable) while the newly created surface produces a positive change in Gibbs free energy.\(^{23,24}\) The energy profile as a function of the cluster size is shown with the bulk and surface contributions displayed in Figure 2.4B. Overall, the creation of a new surface forces the total change in Gibbs energy to increase. However, as the cluster expands, the bulk term begins to dominate, creating a local apex in the total free energy followed by a rapid decrease. The apex in the total energy profile represents the transition from unstable to stable growth, and the radius at which this occurs is labeled as \( r_{\text{crit}} \). Clusters with a radius smaller than \( r_{\text{crit}} \) are unstable and break apart, while clusters with a larger radius will undergo stable growth. Calculating the derivative of equation 2.16 and setting it equal to 0 can be used to determine the critical radius (equation 2.17).\(^{23,24}\)

\[
r_{\text{crit}} = \frac{2\sigma}{\Delta G_m} V_m \quad (2.17)
\]
2.2 Lithium Metal Batteries

2.2.1 Motivation

Li-ion batteries have been instrumental in enabling portable electronics, however, as we approach the theoretical limitations of this battery chemistry, a new generation of high-energy density batteries is needed to satisfy future energy demands. The graphite anode in a Li-ion battery is a bottleneck in achieving higher energy densities. The graphite anode displays a scaffolded structure and majority of the mass comes from the host material. The capacity and energy of the cell derive from the Li content in the cell, and therefore additional mass and volume beyond that hinders energy density.

A promising pathway to boost the energy density of state-of-the-art Li-ion batteries is to replace the graphite anode with metallic Li. Li metal anodes offer a specific capacity of 3,860 mAh/g, which is ten times greater than that of graphite (372 mAh/g). Additionally, they offer a highly negative electrochemical potential of -3.04 V vs. the standard Hydrogen electrode (SHE), making them an ideal anode for high energy density batteries. Li metal anodes can enable a new generation of high energy density batteries, such as Li-air and
Research into Li metal batteries has expanded exponentially in the past decade and is viewed as the key to “beyond Li-ion” battery technology.\textsuperscript{26–28}

2.3 Challenges Facing Li Metal Anodes

Metallic Li offers superior theoretical energy storage capabilities when compared to graphite anodes; however, several factors limit the practical use of Li in a rechargeable battery. These include poor CE, electrolyte decomposition, poor cycle life, and safety concerns about thermal runaway. Many of the challenges facing Li metal anodes stem from the electrochemical instability of Li against liquid electrolytes.\textsuperscript{29,30} The following sections detail the interplay between the electrochemical instability and formation of three-dimensional (3-D) structures, and how this negatively impacts performance.

2.3.1 Solid Electrolyte Interphase Formation

Due to low electrochemical potential of Li (-3.04V vs. SHE), the electrolyte can be spontaneously reduced when it comes into contact with a Li metal anode. This produces a layer of decomposition products known as the solid electrolyte interphase (SEI) at the electrode/electrolyte interface.\textsuperscript{31,32} The electrochemical instability demonstrated by Li promotes a poor cycle life for several reasons. First, continuous SEI formation consumes the active Li inventory, even while the cell is at rest. Nearly 2-3\% of the total capacity can be lost to SEI formation when the cell is at rest for 24 hours.\textsuperscript{33} Second, the continuous decomposition of the electrolyte can cause the internal cell resistance to increase, which can result in an early end-of-life.\textsuperscript{34–36} Lastly, the heterogeneous nature of the SEI layer can promote current focusing, exacerbating the formation of 3-D structures during plating and stripping (further discussion in Section 2.3.2).\textsuperscript{29}

Numerous studies have been conducted to understand the physical and chemical structure of the SEI since it was first conceptualized by Peled et al.\textsuperscript{37} Initially, it was proposed...
that the structure of the SEI was mosaic-like, however another model developed by Aurbach et al. suggested that the structure of the SEI is multi-layered. A schematic of the two prominent SEI models is shown in Figure 2.5 where the mosaic-like and multi-layered structure display spatial variations in chemical composition. The chemistry of the SEI is not limited to the compounds listed. These are only intended to illustrate the variations in chemical composition and overall structure.

With the development of cryo-electron microscopy for Li metal battery research, the SEI was observed to concurrently display both a mosaic-like and multi-layered structure. The chemical composition of the SEI can be impacted by many factors including current density, temperature, and external pressure. However, the chemistry of the SEI is predominantly determined by the electrolyte composition. Species such as Li₂O, LiF, Li₂N, Li₂CO₃, ROCO₂Li, and ROLi have been observed across various carbonate and ether-based electrolytes.

Though the structure and chemical composition of the SEI is system dependent, there is a generally accepted description of how SEI formation occurs. First, the electrolyte is reduced spontaneously when it contacts the Li surface, producing a thin layer of soluble multiphase organic species. Once the cell charges/discharges, these species become inor-
ganic compounds and form the inner layer of the multi-layered SEI structure. With further electrolyte reduction, organic species are formed, creating the outer layer.\textsuperscript{56} The initial condition of the SEI plays a critical role on performance where highly porous structures were found to exacerbate electrolyte decomposition, and a compact, conductive layer impedes SEI growth.\textsuperscript{57} Artificial SEI layers have also been developed to tune the mechanical and electrochemical properties of the SEI and support better performance.\textsuperscript{58–60}

### 2.3.2 Deposition and Dendrite Formation

A factor limiting the performance of Li metal anodes is the formation of dendrites during electrodeposition. Figures 2.6A-D show how dendrite growth occurs on a pristine anode surface (Figure 2.6A). Due to surface inhomogeneities such as local variations in surface chemistry, microstructure, and morphology, current focuses at local “hot spots” (Figure 2.6B). The volumetric expansion at these hot spots can fracture the SEI and expose fresh Li (Figure 2.6C). This leads to uncontrolled growth and the formation for dendrites (Figure 2.6D).\textsuperscript{36,61} These highly branched, high-surface-area structures hinder the application of metallic Li in a rechargeable battery for several reasons. First, they exacerbate electrolyte decomposition by continuously exposing fresh Li. Second, there are safety concerns about dendrite formation, since the resulting morphology can promote short-circuiting and cause thermal runaway. Lastly, dendrite formation is largely irreversible and promotes significant capacity losses (further discussion in Section 2.3.4).\textsuperscript{62}

Fundamental studies have explored the origins and the dynamic evolution of dendrite formation. Dendrite nucleation was found to be sensitive to many experimental conditions, including surface chemistry. For example, through time-of-flight secondary ion mass spectroscopy measurements, preferential nucleation has been observed at LiF rich regions when the anode surface was not mechanically treated.\textsuperscript{63} Furthermore, the nucleation density of dendrites was shown to have a positive correlation with current density, which is in good agreement with classical nucleation theory.\textsuperscript{64} However, further studies observed
that nucleation density is also sensitive to diffusion through the SEI.\textsuperscript{65} Many other experimental factors can impact the nucleation of metallic Li. Cryo-transmission electron microscopy (TEM) has recently been used to demonstrate that current density can govern the crystallinity of metallic Li.\textsuperscript{66} Higher current densities promoted crystalline deposition, and the associated nanostructures have been shown to have poor reversibility compared to amorphous deposition.\textsuperscript{66} Furthermore, electrolyte additives can cause facet-dependent kinetics. Recent studies have shown that electrolyte additives or cross-contaminants from the cathode can induce preferential deposition on specific crystallographic planes.\textsuperscript{67}

Dendrite morphologies are system-dependent. In carbonate electrolytes, needle-like morphologies are observed at current densities below 0.5 mA cm\textsuperscript{-2}.\textsuperscript{68} However, at higher current densities (>0.5 mA cm\textsuperscript{-2}), mossy-like growth is observed in carbonate electrolytes.\textsuperscript{61,69,70} A recent study has demonstrated that a fractal-like morphology can develop when the concentration of Li cation species at the electrode-electrolyte interface is depleted (Sand’s time).\textsuperscript{71} The fractal-like morphology has been shown to more easily penetrate the separator of a battery compared to mossy growth.\textsuperscript{71}

The morphology of plated Li is critical to performance and influences the reversibility of Li plating and stripping.\textsuperscript{62} Columnar-like morphologies can help to alleviate capacity loss by minimizing the physical and/or electrical isolation of Li, which is known as “dead Li” (further discussion in Section 2.3.4).\textsuperscript{62} With carbonate electrolytes, the plated morphology is highly porous and significant capacity losses occur through dead Li formation.\textsuperscript{72} Additives and ether-based electrolytes promote denser morphologies that exhibit a nodule-like morphology, which help alleviate capacity loss through dead Li formation.\textsuperscript{73–78} Furthermore, the application of an external stack pressure to the cell can impact the porosity of plated Li and consequently CE.\textsuperscript{79,80}

Figure 2.6 shows mossy dendrites, which are the primary morphology explored throughout this thesis. Figure 2.6E shows an optical image of mossy growth inside of the plan-view cell presented in this thesis (Chapter 3), which has detached from the electrode.
Figure 2.6: Schematic of dendrite formation showing A) a pristine anode surface, B) current focusing at local hot spots, C) fracture of the SEI, D) dendrite growth. E) optical image of a mossy growth that was deposited on a Li metal anode at 3 mA cm\(^{-2}\) inside of the plan-view cell and detached from the electrode surface (the growth is floating in electrolyte). F) SEM of different mossy growth on a Li metal anode after 0.1 mAh cm\(^{-2}\) of charge was deposited at 3 mA cm\(^{-2}\).

Figure 2.6F shows an ex situ SEM image of a different mossy deposit that was deposited on a Li metal anode inside of the plan-view cell. The origins and mechanisms that promote mossy growth are not fully understood.\(^{70}\)

2.3.3 Dissolution and Pit Formation

Current focusing during electrodissolution can promote the formation of 3-D surface structures known as pits. Few studies have explored the origins and evolution of pits, and a comprehensive understanding of how pit formation impacts Li metal anode performance is lacking.\(^{81–84}\) Pit formation is posed to occur in several stages as shown in Figure 2.7. Figure 2.7A shows a pristine Li metal anode. Once electrodissolution occurs, current focuses
at local hot spots, forming voids at the electrode-SEI interface (Figure 2.7B). These voids should diffuse into the bulk electrode; however, they can accumulate when the diffusion rate cannot compete with the rate of void creation. The accumulation of voids underneath the SEI forms a crater-like structure known as a pit (Figure 2.7C). With further electrode-dissolution, the SEI collapses into the pit as shown in Figure 2.7D.\textsuperscript{81} An example of the pit morphology is included in Figure 2.7E. The morphology is drastically different from the dendrites discussed in Section 2.3.2.

Pit formation has been shown to influence the morphological evolution of a Li metal anode. Dendrite nucleation has been observed to occur within pits that form in the previous half-cycle in both carbonate and ether based electrolytes. Recent studies have explored the impact of pitting a Li metal electrode during the initial half-cycle, but there is little known

\textbf{Figure 2.7: Schematic of pit formation} A) pristine surface, B) preferential stripping that leads to void formation, and C) accumulation of voids into a pit, D) SEI collapse into the pit. Ex situ SEM image of a pit formed on a Li metal anode from the plan-view cell.

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\textsuperscript{81} This text seems to reference a specific study or literature, but the number is not standard and might be a typographical error.
about the relationship between pit formation and performance.

### 2.3.4 Dead Li Formation

The physical and/or electrical isolation of metallic Li from the electrode surface is known as dead Li formation. This negatively impacts Li metal anode performance for two primary reasons. One is that significant capacity losses occur through dead Li formation. Second is that the accumulation of dead Li can cause capacity fade in full cells. This occurs because the accumulated dead Li can cause mass transport limitations, which increases the overpotential at the negative electrode and causes the cell to reach cut-off voltage limits early in the cycle. Figure 2.8 shows a schematic of how dead Li formation is thought to occur. First, a mossy deposit forms on the electrode surface during deposition due to current focusing (Figure 2.8A). During electrodissolution, the volume of the mossy growth decreases; however, charge is preferentially removed from the base of the mossy growth (Figure 2.8B). Continued stripping at the base isolates the active Li that is located at the top of the structure (Figure 2.8C). The causes of preferential stripping at various locations along the surface are not fully understood; however, local variations in SEI thickness has been shown to promote current focusing on Li nano-whiskers.\(^\text{70}\)

![Figure 2.8: A) Mossy growth on a Li metal anode, B) preferential stripping at the base of the mossy growth, and C) dead Li formation.](image)
2.3.5 State-of-The-Art Lithium Metal Anodes

Numerous methods have been developed to improve the reversibility of Li plating and stripping. These include variation of the electrolyte composition,\textsuperscript{85,86} mechanical deformation of the anode surface,\textsuperscript{87,88} modification of the electrode/electrolyte interface chemical composition and structure,\textsuperscript{89–91} application of 3-D electrode architectures,\textsuperscript{92–95} and \textit{in situ} electrochemical treatments.\textsuperscript{82,96} These methods have been shown to effectively boost the CE of Li metal, but the CE enabled by recent improvements has plateaued around 99.5%.\textsuperscript{97} This efficiency is inadequate for a rechargeable battery since the remaining percentage has a compounding impact on the battery cycle life.

Fundamental studies have been conducted to identify the factors that contribute to Coulombic inefficiency, such as current density and depth of discharge, low stack pressure, electrolyte composition, and dead Li formation.\textsuperscript{62,98–101} An immense effort has also been placed on understanding the origins and morphological evolution of dendrite formation.\textsuperscript{68,69,102–106} Exploration into dendrite formation has produced a better understanding of the preferential nucleation of dendrites,\textsuperscript{63,107} dendrite growth mechanisms,\textsuperscript{70,71} and how the physical isolation of plated Li occurs.\textsuperscript{62,98–101}

Great progress has been made in understanding dendrite formation. Surface chemistry has been shown to play a critical role in dendrite nucleation.\textsuperscript{63} The morphological evolution of whisker-like growth has been linked to local stress build-up.\textsuperscript{70} Furthermore, recent studies have highlighted that the crystallinity of Li evolves during deposition, and that the crystallographic orientation of plated Li has an important role in performance.\textsuperscript{66,67,101} However, a comprehensive model on the origins and evolution of dendrite formation has not been fully established. Important remaining questions about dendritic growth include: 1) How does the electrode microstructure impact dendrite nucleation? 2) What is the relationship between reversibility and dendrite morphology? and 3) How does a dendrite transition to dead Li?

As mentioned in Section 2.3.3, preferential nucleation of dendrites has been observed
to occur within in pits formed in the previous half-cycle. However, pitting on the electrode surface has not been study extensively. There is a lack of understanding in: 1) the morphological evolution of pits; 2) the influence of pit formation on extended cycling behavior; and 3) the relationship between pit formation and the reversibility of Li plating and stripping. The overall goal of this thesis is to address these knowledge gaps and better understand the dynamic morphological evolution of Li metal and the impact of this dynamic behavior on performance. This information is key for informing new strategies on how to address the poor performance of Li metal anodes.
CHAPTER 3

Plan-View Operando Video Microscopy


A previous study has applied operando video microscopy to elucidate the 'peaking' behavior exhibited in the voltage profile of a Li-Li symmetric cell when under galvanostatic conditions. This platform provided a cross-section perspective of the anode surface that was effective at capturing the growth of individual dendrites. For this thesis, a new cell design was developed that enables imaging from a plan-view perspective of the electrode surface without introducing artifacts that would otherwise arise from a non-uniform current distribution. This plan-view perspective facilitates quantitative measurements of nucleation on Li metal and allows for tracking of individual dendrite morphologies as they evolve in real time. In this chapter, the plan-view design and optimization are detailed.

3.1 Plan-View Design

Owing to the opaque nature of Li metal, a parallel electrode configuration does not allow for plan-view imaging during operation. Thus, to enable operando plan-view imaging, a new cell geometry was developed. During cell design, care was taken to avoid artifacts
that can arise from a non-uniform current distribution along the working electrode. Previous designs have placed the electrodes adjacent to each other (which may be in the same plane or offset vertically), or have alternatively utilized a parallel plate configuration with a small viewing hole in the counter electrode. Herein, we introduce a new design that simultaneously enables a uniform current distribution over a 15mm diameter electrode and affords optical access to the entire surface over a large field of view. This plan-view platform allows for statistical analysis of variables including areal nucleation density of dendrites and pits, the projected size of individual dendrites and pits, and the relative quantity of dead Li present along the entire electrode surface.

To optimize the cell geometry, the spatial distribution of current density within the electrolyte was modeled using finite-element analysis in COMSOL (Figure 3.1). The Tertiary Current module in COMSOL was used to establish the governing Electrochemistry and Physics for a Li-Li symmetric cell. The module uses the Nernst-Planck equation (Eqn. 3.1) to describe mass transport in the electrochemical cell, while enforcing electroneutrality (Eqn. 3.2). The convection term in the Nernst-Planck equation was neglected. The reaction kinetics at the electrode-electrolyte interface were described by Butler-Volmer equation (Eqn. 3.3). The definition of each equation variable and constant is provided in Table 3.1, while the parameters used in the COMSOL model are provided in Table 3.2.

\[
[bt]I = F + \sum_{i=1}^{n} Z_i \left( -D_i \nabla C_i - Z_i \mu_i F C_i \nabla \phi \right)
\]  

(3.1)

\[
[bt] \sum_{i=1}^{n} Z_i C_i = 0
\]  

(3.2)

\[
[bt]I = I_o \left[ \frac{C_{red}}{C_{bulk}} \exp \left( \frac{\alpha F \eta}{RT} \right) - \frac{C_{ox}}{C_{bulk}} \exp \left( -\frac{\alpha F \eta}{RT} \right) \right]
\]  

(3.3)

The optimized design (Figure 3.1D and 3.1F) incorporates a concentric ring geometry where a height offset is present between the working and counter electrodes. A physical
Table 3.1: COMSOL model variable and constant definitions

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_o$</td>
<td>Exchange Current Density</td>
</tr>
<tr>
<td>$Z_i$</td>
<td>Net charge of species i</td>
</tr>
<tr>
<td>$D_i$</td>
<td>Diffusion coefficient of species i</td>
</tr>
<tr>
<td>$C_i$</td>
<td>Concentration of species i</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday’s constant</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Charge transfer coefficient</td>
</tr>
<tr>
<td>$\mu_i$</td>
<td>Mobility of species i</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Electric Potential</td>
</tr>
</tbody>
</table>
| $C_{\text{red}}$ | Concentration of species to be oxidized |}

Table 3.2: COMSOL model parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_o$</td>
<td>2.17 mA cm$^{-2}$</td>
<td>111</td>
</tr>
<tr>
<td>$D_{Li^+}$</td>
<td>$1.6 \times 10^{-6}$ cm$^2$/s</td>
<td>112</td>
</tr>
<tr>
<td>$D_{PF_{6}^+}$</td>
<td>$1.6 \times 10^{-6}$ cm$^2$/s</td>
<td>112</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.5</td>
<td>61</td>
</tr>
<tr>
<td>$T$</td>
<td>298.75 K</td>
<td></td>
</tr>
</tbody>
</table>

barrier is also placed between the direct line-of-sight of the electrodes. The combination of these features results in a uniform current distribution along the working electrode surface (Figure 3.1A), with a spatial variation of less than 1%.

Without these optimizations, current would otherwise heavily focus at the edges of the working electrode as shown in Figure 3.1C and E. To overcome this challenge, in the optimized cell, the gradient in current density between the two electrodes was intentionally offset vertically from working electrode surface (Figure 3.1D). This allows for the current density along the working electrode surface to be uniform (Figure 3.1F). The uniform current distribution predicted by this model is consistent with our experimental observations in this study of a uniform distribution of dendrites and pits along the entire electrode area without edge effects. This current uniformity achieved across current densities from 3 – 7 mA cm$^{-2}$ as shown with the cross-section profiles in Figure 3.2. This range of current
Figure 3.1: COMSOL model of current density distribution in operando visualization cells. A) Current density distribution along the working electrode surface for both the optimized and non-optimized cells when 1mA cm\(^{-2}\) is applied. B) A schematic showing the geometry of the plan-view cell. Isometric views of C) a non-optimized cell and D) the optimized-cell with the current density in the cell electrolyte shown in color on a cross section plot (current focuses at electrode edges). Current density streamlines are also shown.

densities was chosen because it facilitated a statistical analysis of dendrite nucleation and growth. Current densities below 3mA cm\(^{-2}\) produced sparse dendrite nucleation that hindered a statistical analysis. Current densities above 7mA cm\(^{-2}\) led to excessive dendrite agglomeration that inhibited the tracking of individual dendrite size.

Using this optimized platform, optical recordings of the working electrode surface in a Li-Li symmetric cell were collected and synchronized with the corresponding electrochemical response. A 1M LiPF\(_6\) 1:1 v/v ethylene carbonate (EC):ethyl methyl carbonate (EMC) electrolyte was used, in order to produce optically-visible mossy dendrites that
Figure 3.2: Current density distribution in the plan-view cell at different current densities. Current density in the plan-view cell shown on a cross section plot (CE is the counter electrode) when the applied current density is A) 3 mA cm\(^{-2}\), C) 5 mA cm\(^{-2}\), E) 7 mA cm\(^{-2}\). Current density along the working electrode surface when the applied current density is A) 3 mA cm\(^{-2}\), C) 5 mA cm\(^{-2}\), E) 7 mA cm\(^{-2}\) can be individually resolved from a plan-view perspective. Detailed explanations of how the evolution of surface morphology impacts the shape of voltage traces during galvanostatic cycling can be found in our previous work.\(^{61,113}\) This understanding will be briefly described here, to confirm that the plan-view cell provides consistent and comparable results with the cross-sectional visualization cell, and contextualize the remaining discussion throughout the manuscript. Snapshots of the electrode morphology at different stages of cycling is shown in Figure 3.3.

Prior to cycling, the working electrode surface is planar, and the surface microstructure
Figure 3.3: Frames from plan-view video microscopy of the working electrode in a Li-Li symmetric cell cycled at 3 mA cm$^{-2}$ and 0.2 mAh cm$^{-2}$. The frames show the electrode morphology and voltage trace at various stages: A) before cycling; B) end of the first plating half-cycle; C) onset of dead Li formation; D) end of first dissolution half-cycle; E) during second deposition half-cycle. F) Zoomed views of D and E showing pit formation and subsequent nucleation of dendrites into existing pits.

can be clearly observed (Figure 3.3A). Upon Li deposition, large mossy dendrites nucleate and grow (Figure 3.3B). The corresponding decay in cell polarization can be attributed to 1) the increase in electrode surface area; 2) the formation of lower-impedance electrode-electrolyte interfaces along the dendrite surface; and 3) a decreasing distance to counter electrode. When the cell polarity switches (Figure 3.3C) the dendrites on the working electrode shrink until they become electrically and/or physically isolated from the electrode surface, which is referred to as “dead Li” formation. A small peak is observed at the beginning of the second half-cycle, which is due to the nucleation of dendrites on the
counter electrode. This is consistent with previous studies, and further details on the origins of these voltage peaks can be found in our previous work. After the formation of dead Li, subsequent electrodissolution on the anode surface occurs on the bulk electrode, and pits begin to form (Figure 3.3D). This transition in reaction pathways along the electrode surface, from initially stripping from dendrites to subsequently stripping from the bulk electrode, corresponds with a second peak in voltage. As the polarity switches a second time (Figure 3.3E and 3.3F), dendrites are observed to nucleate exclusively inside of pits, which correlates with a decay in cell polarization. These results are fully consistent with operando video microscopy performed from a standard parallel-electrode geometry, which validates the use of this geometry as a representative platform for analysis.

We note that a larger cell polarization is observed in the plan-view cells than previous cross-sectional experiments. This is due to the larger IR drop across the electrolyte, which arises from the plan-view geometry. To deconvolute the contributions to total cell polarization, three-electrode experiments, electrochemical impedance spectroscopy (EIS), and computational modelling were performed. The total cell polarization ($V_{\text{cell}}$) can be described as the sum of the individual electrode overpotentials ($\eta$) and the potential drop due to the cell internal resistance $\Delta V_{IR}$:

$$V_{\text{cell}} = \eta_{\text{working}} + \Delta V_{IR} + \eta_{\text{counter}}$$  (3.4)

It has been previously shown through galvanostatic intermittent titration technique (GITT) measurements that in the initial cycles, contributions to cell polarization from relaxation of concentration gradients are negligible, and therefore are not considered in this analysis. To measure the IR drop across the electrolyte in the plan-view cell, potentiostatic electrochemical impedance spectroscopy (PEIS) measurements were performed. Li was deposited on to the working electrode of a plan-view Li-Li symmetric cell at a current density of 3 mA cm$^{-2}$. PEIS was performed every 0.01 mAh cm$^{-2}$. The frequency range for the measurement was 1 Hz – 500 kHz. The evolution of the PEIS spectrum is shown in
Figure 3.4: A) PEIS spectra taken during deposition, where each spectrum was taken after 0.01 mAh cm\(^{-2}\) of deposition. B) Two electrode measurement of cell polarization of a plan view visualization cell cycling at 3 mA cm\(^{-2}\). C) COMSOL model showing a cross-sectional view of the voltage inside the plan-view cell where CE is the counter electrode. D) Three-electrode measurement showing the voltage of the working electrode vs. the reference electrode in a plan-view visualization cell depositing Li at 3 mA cm\(^{-2}\).

As shown in Figure 3.4A, the high-frequency intercept remains constant during charging, which can be attributed to the IR drop across the cell.\(^{18}\) The value of the cell internal resistance of the plan-view cell was measured as 230 Ω. The IR drop caused by this resistance at a current density of 3 mA cm\(^{-2}\) is 1.21 V. This constitutes a large portion of the total cell polarization in the plan-view cell, as shown in Figure 3.4B, which plots the cell polarization of a plan-view visualization cell cycling at 3 mA cm\(^{-2}\). After subtracting the IR drop from the total cell polarization, the magnitude of the remaining cell polarization ranges from 0.3 V - 0.5 V.

The large internal resistance of the cell is also supported by the COMSOL model de-
tailed above. Figure 3.4C shows a cross section plot of the voltage distribution inside the plan-view cell at a current density of 3 mA cm$^{-2}$. The predicted IR drop is 1 V. The resistance associated with this IR drop was calculated to be 190.5 $\Omega$. This large resistance reasonably agrees with the internal cell resistance experimentally measured in Figure 3.4A. The COMSOL results support that the larger cell polarization is created by an ohmic drop across the electrolyte.

Lastly, a three-electrode cell was fabricated to provide further evidence that the kinetic overpotential on the working electrode ($\eta_{\text{working}}$) is consistent with previous cross-sectional experiments.$^{61}$ The three-electrode cell has a similar geometry to the plan-view cell used in this study but has a reference electrode 1.5 mm away from the working electrode as shown in Figure 3.5. Using this cell, 0.2 mAh cm$^{-2}$ of Li was deposited onto the working electrode at 3 mA cm$^{-2}$. The voltage of the working electrode was measured with respect to the reference electrode and is shown in Figure 3.4D. The voltage peaks at -0.326 V and decays to -0.134 V. This voltage range agrees with the ranges observed in previous cross-sectional experiments.$^{61}$

Despite the larger IR drop, the magnitude of electrode overpotentials in the plan-view cells after IR compensation are in close agreement previous cross-sectional cells. As we
have previously demonstrated, the variations in cell polarization that lead to the “peaking”
behavior in the initial cycles is due to spatial variations in kinetics along the electrode
surface, and not a result of concentration polarization or ohmic drop across the electrolyte.\textsuperscript{61}
Therefore, the results in this thesis regarding nucleation and growth behavior should be
directly comparable to the other cell geometries.
CHAPTER 4

Identifying the Coupled Relationships among Nucleation, Morphology, and Reversibility


To gain a better understanding of the evolving relationships between surface heterogeneity, nucleation, and reversibility, and how they relate to CE, the plan-view platform detailed in Chapter 3 was utilized to record Li metal anodes under operating conditions. Utilizing this platform we demonstrate the following: 1) the differences in nucleation density of both dendrites and pits as a function of current density; 2) the critical role of pits on plated Li morphology and reversibility; 3) the correlation of microstructural features on the electrode surface with the location of “hot spots” for nucleation; and 4) the impact of dendrite volume on reversibility and dead Li formation. The results in this study provide quantitative insight into the coupled relationships between electrochemistry, surface properties, and morphological evolution of Li metal anodes during cycling.
4.1 Experimental Methods

Li foil (750 µm thick) from Alfa Aesar and a LiPF6 1:1 (v/v) EC/EMC electrolyte from Soulbrain were used in all experiments. After each cell assembly, the batch of Li was repackaged with an aluminized nylon and polyethylene film purchased from Gaylord Archival and stored in an argon glovebox with water and oxygen levels of <0.5 ppm. The working and counter electrodes were each cut to an area of 1.76 cm² using a razor blade. The as-received Li was used to form the electrodes without any chemical or other mechanical treatment. A 10 min rest period was maintained between the end of assembly and the beginning of cycling. A Biologic SP-200 potentiostat was used for galvanostatic cycling. All visualization experiments were conducted inside of an argon glovebox where water and oxygen levels were <0.5 ppm. The optical equipment used to record the electrode surfaces was a Nikon Eclipse LV150 microscope paired with a Nikon Lu Plan Flour 5× objective. The camera used was a model UI-3080SE-C-HQ camera from Imaging Development Systems GmbH. A ring light-emitting diode from AmScope was used to illuminate the working electrode surface. All videos were recorded at 1 frame/s with the uEye cockpit software from Imaging Development Systems GmbH and postprocessed with MATLAB and Adobe Premiere Pro. The two-dimensional (2-D) projected areas were manually measured, while all data analysis along with synchronization was done in MATLAB. SEM imaging and the FIB experiments were performed by a Thermo Fischer Helios 650 Nanolab SEM/FIB instrument. FIB was conducted at 21 nA gallium ion beam with a 30 kV accelerating voltage.

4.2 Results and Discussion

To quantitatively evaluate the effect of current density on nucleation using the plan-view platform, Li was plated onto the working electrode of three separate Li-Li symmetric cells at 3, 5, and 7 mA cm⁻². In a different set of samples, Li was stripped from the working electrode under the same current densities. The resulting microscopy analysis of the
Figure 4.1: Panels A-C are optical images of the working electrode surface from three different Li-Li symmetric cells after 0.0025 mAh cm\(^{-2}\) of Li was deposited at the respective current density; A) 3 mA cm\(^{-2}\); B) 5 mA cm\(^{-2}\); C) 7 mA cm\(^{-2}\). Red circles were added to A-C to improve visibility of dendrite nucleation. D-F are optical images of the working electrode surface from three different Li-symmetric cells after 0.2 mAh cm\(^{-2}\) of Li was stripped at the respective current density; D) 3 mA cm\(^{-2}\); E) 5 mA cm\(^{-2}\); F) 7 mA cm\(^{-2}\).

surfaces of the six experiments are shown in Figure 4.1. These images were used to quantify areal nucleation density along the electrode surface, which is shown in Figure 4.2A. A positive correlation between the nucleation density and current density is observed for both dendrites and pits. However, the nucleation density for pits was greater for all current densities.

The positive correlation between current density and areal nucleation density for dendrite nucleation is consistent with previous \textit{ex situ} observations.\textsuperscript{24,63,65} However, pit nucleation density vs. current density has not been previously explored in detail, which represents a knowledge gap in the Li metal anode literature. We note that the exact quantification of nucleation density is system-dependent. Factors such as electrolyte composition, stack pressure, presence of a separator, cell geometry, and electrode surface preparation will influence nucleation on Li metal. However, the trends shown in Figure 4.2 provide insights into the role of surface heterogeneity on nucleation behavior.
Figure 4.2: A) Nucleation density measurements for both dendrites and pits. B) Diagram depicting the heterogeneous Li surface with spatially varying Gibbs energy for nucleation ($G_{\text{nucl}}$). C) Diagram showing the impact of increasing current density on nucleation density for a heterogeneous surface with spatially varying $G_{\text{act}}$.

An increase in heterogeneous nucleation density with increasing current density is expected according to classical nucleation theory. The change in Gibbs free energy during nucleation and growth can be divided into a bulk and surface term (Eqn. 4.1)

$$
\Delta G_{\text{Nucl}} = \Delta G_{\text{Bulk}} + \Delta G_{\text{Surf}} = -\frac{2\pi}{3}r^3 \frac{\Delta G_m}{V_m} + 2\pi r^2 \sigma
$$

where $\Delta G_m$ is the change in molar Gibbs free energy, $r$ is radius, $V_m$ is molar volume, and $\sigma$ is surface free energy. The local activation barrier for nucleation ($\Delta$) will vary spatially across the surface (shown schematically in Figure 4.2B) due to the heterogeneous nature of the surface of a Li metal electrode. The nature of this heterogeneity could be affected by several structural and compositional variables, including surface composition,
microstructure, topographical defects, etc. For example, in previous studies of electrodeposition, features such as dislocations, grain boundaries, and interfaces have been shown to result in spatial variations in the nucleation barrier.\textsuperscript{117-121} This concept is shown schematically in Figure 4.2B., where the yellow regions on the electrode surface have smaller activation barriers for nucleation relative to the red regions. During electrodeposition and dissolution, the driving force to overcome these activation barriers increases as the electrode overpotential increases.\textsuperscript{61}

The overpotential will increase with current density, as described by the Butler-Volmer relationship (Eqn. 4.2)

\[
i = F K^o \left\{ c_{Li} \exp \left[ \frac{(1 - \alpha)F}{RT} \right] - c_{Li^+} \exp \left[ -\frac{\alpha F}{RT} \eta \right] \right\}
\] (4.2)

where \( i \) is current, \( K^o \) is the standard heterogeneous rate constant, \( F \) is Faraday’s constant, \( R \) is the gas constant, \( T \) is temperature, \( \eta \) is overpotential, \( \alpha \) is the charge transfer symmetry coefficient, \( C_{Li} \) is the surface concentration of Li, and \( C_{Li^+} \) is the local electrolyte concentration of Li\(^+\).

While the positive correlation between overpotential and current density will generally lead to higher nucleation density with increasing current density in all electrodeposition processes, this relationship is also directly impacted by the surface heterogeneity. As current density is increased, a larger fraction of the spatially varying activation barriers across the surface can be overcome by the increased overpotential. As shown in Figure 4.2C, the yellow regions are accessed by relatively lower currents. However, as the current density increases, the spatial locations with a higher activation barrier (orange and red regions) start to facilitate nucleation as a result of the larger overpotential.

The results presented in Figure 4.2A suggest that there is a fundamental difference in the nucleation process of pits and dendrites. One potential factor causing this difference is that the heterogenous nature of the starting Li metal electrode surface (grains, grain boundaries, defects, SEI, etc.) may have different impacts on the local activation barrier.
for nucleation of dendrites and pits. To support this hypothesis, direct evidence of the role of surface microstructure on nucleation behavior for both dendrites and pits is provided in the subsequent results and discussion, where we demonstrate that surface grain boundaries serve as preferential nucleation sites for both dendrites and pits, and pits have a higher nucleation density along grain boundaries than dendrites.

In addition to surface heterogeneities arising from microstructure and composition, there may be additional factors that further influence the differences observed between nucleation of dendrites and pits. Examples include differences in transition times between nucleation to growth, critical radius size, and electro-chemo-mechanical phenomena that influence nucleation. Studying these factors is beyond the capabilities of the current optical video microscopy platform, as these dynamic nucleation phenomena occur at length and time scales below the resolution limit.

Overall, these results point to the critical role of surface heterogeneity on nucleation. Further investigation is needed to unveil the exact mechanistic origins of how surface heterogeneity affects the dynamic evolution of nucleation and growth phenomena for both dendrites and pits. Multiple aspects of Li surface heterogeneity, such as surface chemistry, microstructure and morphology will likely influence the way nucleation occurs.

To help facilitate this understanding, the plan-view microscopy platform enables us to directly observe the spatial location of heterogenous features on the Li surface, such as local variations in topography and surface grain boundaries. This enables surface features to be identified before cycling, and to be subsequently correlated with the nucleation location of dendrites and pits.

To study the impact of microstructure on nucleation, two Li-Li symmetric cells were compared. Li was deposited onto the working electrode in the first cell, while Li was stripped from the working electrode in the second cell. The locations of the initial surface grain boundaries on the Li metal surface can then be correlated with location of dendrite and pit nucleation.
Figure 4.3: A) Optical image of pristine Li surface before deposition with grain boundaries highlighted in red. B) Pristine Li surface before dissolution with grain boundaries highlighted in red. C) Surface shown in A after 0.01 mAh cm$^{-2}$ of Li was deposited. D) Surface shown in C after 0.2 mAh cm$^{-2}$ of Li was stripped.

The initial working electrode surfaces of these two cells are shown in Figures 4.3A and 4.3B. The surface grain boundaries are highlighted in red to improve their visibility. Figure 4.3C shows the Li surface after electrodeposition, while Figure 4.3D shows the Li surface after electrodissolution.

The location of initial dendrite nucleation shown in Figure 4.3C correlates with the location of surface grain boundaries. Similarly, pits are observed to form in the vicinity of surface grain boundaries (Figure 4.3D), which is consistent with previous ex situ observations. Figure 4.4 shows the minimum distance between a given nuclei and the nearest surface grain boundary for all dendrites and pits observed in Figure 4.3. The histograms
Figure 4.4: Histograms showing the minimum distance between the nuclei and the nearest surface grain boundary for A) dendrites and B) pits.

display prominent peaks near 0 µm, indicating majority of the nuclei have nucleated on a surface grain boundary. Furthermore, a higher nucleation density along grain boundaries is observed for pits than for dendrites. This is consistent with the trends in overall nucleation density described in Figure 4.2A.

In general, we note that the spatial variation in nucleation along the Li surface may be impacted by variables including surface pre-treatments (e.g. mechanical/chemical polishing), the chemical composition of the surface, electrolyte composition, etc. We note that not all “hot spots” are along grain boundaries, and not all grain boundaries serve as hot spots. However, a statistical preference of nucleation location to surface grain boundaries is clearly evident under these conditions, illustrating the importance of surface microstructure on nucleation.

One possible contributing factor that influences the preferential nucleation of dendrites and pits near surface grain boundaries is the variation in local SEI composition. This hypothesis is consistent with a previous study that identified dendrite “hot spots” as LiF-rich regions that formed near surface topographical features such as ridges and striations. In the future, multi-modal operando studies that enable correlation of structural, chemical, and electrochemical phenomena at a local scale will be critical to gain a comprehensive
mechanistic understanding of the role that surface heterogeneity plays on nucleation.

While the results shown in Figure 4.3 were collected from the initial half-cycle, the impact of surface structure on dendrite nucleation evolves during extended cycling. To probe this evolution, a Li-Li symmetric cell was cycled 20 times. Dendrites were observed to nucleate in the vicinity of surface grain boundaries during the first cycle, and nucleate within existing pits in the second cycle. Interestingly, new pits rarely form after the first cycle. Dendrites continue to nucleate inside of the pits formed in the first cycle for the entire recording. Since the CE is less than 100%, this indicates that the initial pits grow larger at the end of the subsequent dissolution half cycles (Figure 4.5), as the reaction pathway on the electrode surface transitions from stripping from plated dendrites to stripping from pits.

As the pits grow larger, new surface area becomes available for subsequent dendrite nucleation as shown in Figure 4.5. In Figure 4.5A, the initial planar electrode surface is covered by a heterogeneous SEI. When an anodic potential is applied (Figure 4.5B), localized pit formation occurs at “hot spots” on the electrode surface, and the SEI and native surface layers eventually collapse into the pit. During subsequent electrodeposition (Figure 4.5C), dendrites nucleate inside of the pits and grow into large mossy structures. Dissolution (Figure 4.5D) first leads to the formation of dead Li, which subsequently transitions to the expansion of pits. The surface area introduced from the pit expansion facilitates dendrite nucleation in subsequent deposition, which vertically displaces the dead Li away from the electrochemically active metal surface (Figure 4.5E). We have previously shown that this process leads to a compact and tortuous dead-Li interphase, which impacts mass transport through the electrolyte during extended cycling. Overall, these observations demonstrate that the location of pits formed in the initial cycle remain as dendrite “hot spots” during extended cycling.

The evolution in the size of the initial pits, and nucleation of subsequent dendrites in these same pit locations, highlights the impact that the initial surface structure has on subse-
Figure 4.5: A) Li electrode with an SEI before any cycling, (B) Li electrode after a half-cycle of dissolution in which pits have formed on the surface, (C) Dendrite formation during deposition, where nucleation occurs inside of the pit, (D) Dead Li formation and expansion of initial pits after dissolution, and (E) Dendrite nucleation inside of the expanded pit and upward displacement of Dead Li.

quent cycling performance. This further helps to rationalize why initial surface treatments prior to cycling (such as mechanical deformation, chemical modification, etc.) can have a strong impact on extended cycle life and CE. To further demonstrate the impact of surface morphology on cycling performance and dead Li formation, the dynamic evolution of dendrite morphology during cycling is explored below.

To gain quantitative insight into how the dynamic evolution of the Li surface morphology impacts cycling performance, the size of multiple individual dendrites was tracked in parallel. As shown in Figure 4.6A, the 2-D projected areas of individual dendrites were measured periodically throughout the growth and stripping processes. Based on the projected area measurements, the radius of a circle with an equivalent area is calculated. This effective radius is then used to compute the volume of a sphere, which is used as a first-order approximation of the dendrite volume. This calculation assumes both an isotropic growth in three dimensions, and a constant relative density of the individual Li deposits over this range of growth. We note that both of these approximations are imperfect, and are subject to influence from experimental variables, including batch-to-batch variation in the Li source material. However, this analysis allows us to observe quantitative trends within a set of experiments, including a direct comparison of the relative volumetric growth rate of individual dendrites.

Figure 4.6B shows the effective volume of multiple dendrites being tracked during one
Figure 4.6: A) Process of calculating effective dendrite volume through a spherical approximation. B) Tracking of four individual dendrite effective volumes throughout the first cycle in a Li-Li symmetric cell at a current density of 3 mA cm\(^{-2}\).

cycle. The left plot in Figure 4.6B shows the effective volume of the four dendrites as the dendrites grow. Time stamps T1 – T10 represent the points in time when the effective volumes were recorded. The optical images that correlate with these times are labeled with the corresponding time stamp and are shown on the right. The four dendrites measured are labeled with numbers and are color-coded in both the left plot and the optical image T2. Initially, the effective volume of all dendrites increases during the deposition half-cycle. When the polarity switches, the effective volume of all dendrites decreases until dead Li forms simultaneously across the electrode surface. Variations in the growth and contraction rate of individual dendrites are observed, which leads to differences in effective volume among the individual dendrites.

To study the influence of dendrite size on reversibility, the effective volume of individual dendrites were measured in three Li-Li symmetric cells. The current density was held constant at 3 mA cm\(^{-2}\) across all cells, while the total depth of charge per cycle was varied between the different cells. Measurements were only taken in the first two cycles because the presence of dead Li convolutes measurements past the second cycle. Addition-
ally, only isolated dendrites were considered; dendrites that physically contacted others or agglomerated into one were not considered for the analysis.

Figure 4.7A-C shows the results from this analysis. Each plot shows the effective volume of individual dendrites at the end of deposition (maximum effective volume, $V_{\text{max}}$) versus at the end of dissolution (dead Li effective volume, $V_{\text{dead}}$) for a given experiment. An inset plot is provided for each experiment to improve the visibility of measurements taken during the second cycle, since the dendrite volumes were smaller than in the first cycle. A linear regression was performed for each cycle data set, and the fitted line from the regression is shown as solid line in each plot. The y-intercept of all fits were fixed at the origin. Interestingly, $R^2$ (coefficient of determination) values above $> 99\%$ were achieved in all data sets, indicating a strong linear relationship between $V_{\text{max}}$ and $V_{\text{dead}}$ within each cycle, which is independent of the initial dendrite size and location. We define the ratio of $V_{\text{dead}}:V_{\text{max}}$ as $V_c$, which is the inverse of the fitted line slope (Eqn. 4.3).

$$V_c = \frac{V_{\text{dead}}}{V_{\text{max}}} = \frac{1}{\text{slope fit}}$$  (4.3)

$V_c$ is bounded between 1 and 0, where 1 indicates that the dendrite showed poor reversibility with no volumetric contraction, while 0 signifies that the dendrite was fully reversible. We note that capacity loss in Li metal anodes may be attributed to both dead Li and SEI formation. Recently, titration gas chromatography has demonstrated that the dominant contribution to Coulombic inefficiency in carbonate electrolytes is unreacted metallic Li, rather than SEI. This provides further justification for the use of $V_c$ as a meaningful proxy for reversibility.\textsuperscript{62} Additionally, this proxy helps identify reversibility trends in Li-Li symmetric cells where a CE cannot be measured.

The strong linear relationship between $V_{\text{max}}$ and $V_{\text{dead}}$ indicates that the reversibility of plating and stripping does not depend on individual dendrite size within an single cycle. However, the fitted $V_c$ values all decreased between the first and second cycle in each experiment, indicating that improved reversibility occurs in the second cycle across all of
Figure 4.7: Panels A-C show $V_{\text{max}}$ vs. $V_{\text{dead}}$ for the first two cycles of three Li-Li symmetric cells cycling at the same current density (3 mA cm$^{-2}$) but to different capacities of Li: A) 0.2 mAh cm$^{-2}$; B) 0.1 mAh cm$^{-2}$, C) 0.025 mAh cm$^{-2}$. Panels D-F show the first dissolution half cycle and the second dissolution half cycle to illustrate differences in the second peak position. The second peak is quantified as a percentage of the half cycle to allow for comparisons across all cells.

Further evidence of the improved reversibility between the first two cycles is present in the voltage traces of the Li-Li symmetric cells. It has previously been shown that the temporal variation of this second peak during the dissolution half cycle correlates with the CE of the Li metal anode. As shown in Figure 3.3, the second peak in the voltage trace during the dissolution half-cycle corresponds with the onset of dead Li formation. Therefore, if the second peak occurs later in the half-cycle, this is an indication of higher CE. Figures 4.7D-F shows the voltage profile of the dissolution half-cycles from the first and second cycles. To allow comparisons of the second peak position across all data sets, the horizontal axes in Figures 4.7D-F are expressed as the percentage of the half cycle that is completed.

Across all cells, the second voltage peak occurred at a later time in the second cy-
cle, which indicates improved reversibility. Notably, $V_c$ and the second peak position decrease/increase monotonically with the capacity of Li passed in the second cycle. However, these quantities do not correlate with the amount of Li passed in the first cycle.

To confirm that these observations of relative reversibility are not an artifact of the plan-view cell design, coin cells were cycled under similar conditions. $V_c$ values cannot be directly obtained with coin cells because of the lack of optical access. However, the second peak position can still be measured. Each coin cell was cycled at a rate of 3 mA cm$^{-2}$ for two cycles. The capacity passed during the first cycle differed for each cell to establish different pit sizes across the cells (0.025 mAh cm$^{-2}$, 0.1 mAh cm$^{-2}$, and 0.2 mAh cm$^{-2}$). The voltage profiles of each coin cell are shown in Figure 4.8A, where the second cycle initiates at 0s. Figures 4.8B-C show the second peak positions in the dissolution half cycles for each coin cell. The overall trends in second peak position are similar to those observed in the plan-view platform. The second peak position increases between the first and second cycle indicating improved reversibility. Additionally, the second peak position increases monotonically with the amount of Li passed in the second cycle, while a trend is not present in the first cycle.

To rationalize these observations, the optical recordings from all of the plan-view visualization cells tested were used to analyze the evolution of the Li surface morphology during the first and second cycles. For all cells, dendrite nucleation occurs at singular points when current is initially applied in the first cycle. In contrast, the Li surface is not pristine in the second cycle. Instead, the electrode surface is pitted, and these pits facilitate dendrite nucleation.

Interestingly, nucleation inside of a pit does not occur at a singular point. Instead, we observed that nucleation occurs along the perimeter of the pits. A high-magnification view of the plating location inside of several pre-existing pits is provided in Figure 4.9. Plating can be seen to occur along the perimeter of the pits before extending into the center of the pits, indicating preferential nucleation at the pit edges. To further illustrate this effect, _ex
Figure 4.8: A) Voltage traces of three Li-Li symmetric coin cells cycling at 3 mA cm\(^{-2}\). The amount of Li passed in the first cycle varied between the three cell (0.2 mAh cm\(^{-2}\), 0.1 mAh cm\(^{-2}\), and 0.025 mAh cm\(^{-2}\)). The same capacity (0.2 mAh cm\(^{-2}\)) was passed in the second cycle for all cells. Second peak positions when the capacity passed in the first cycle is B) 0.2 mAh cm\(^{-2}\), C) 0.1 mAh cm\(^{-2}\) and D) 0.025 mAh cm\(^{-2}\).

**situ** SEM images were taken of a newly formed pit (Figure 4.10A) and of the initial stages of deposition within a pit (Figure 4.10B and 4.3C). Mossy Li deposition can be observed along the pit edges, indicating plating is occurring along the perimeter of the pits.

Since the prevailing understanding of “dead Li” formation is that electronic isolation occurs at the base of a dendrite,\(^{62,70}\) the local morphology of the dendrite base should impact reversibility. We therefore conclude that the higher nucleation area along the pit edges compared to a singular point contributes to the improved reversibility observed in the second cycle, compared to the first cycle.

Following this logic, the introduction of pits helps to rationalize the observation that both \(V_c\) and the second peak position are sensitive to the amount of charge passed in the second cycle, but not in the first cycle. In the second cycle, the morphology of the dendrite base will be impacted by the amount of Li that was stripped during the previous cycle. As
the depth of discharge increases in a stripping cycle, the pit area and perimeter will also increase, since $V_c$ is always greater than zero. In contrast, the morphology of the dendrite base in the first cycle is not determined by the depth of charge, since nucleation occurs at singular points along the electrode surface, rather than in pre-existing pits.

Overall, the summation of these observations suggest that dead Li formation is influenced more by the nature of dendrite nucleation than the extent of dendrite growth. As a result, the heterogeneity of the nucleation surface likely has a stronger impact on CE than SEI growth along the dendrite surface. This is also consistent with the conclusion that the extent of lithium loss during cycling is impacted more from unreacted (dead) Li than SEI formation.\textsuperscript{62}

Finally, these observations help to explain how initial surface modifications, such as mechanical deformation of the Li surface and thin-film coatings, can improve reversibility and extended cycle life by influencing the heterogeneity of nucleation along the Li metal surface.\textsuperscript{87–89,91} Surface modifications will alter the nature and local morphology of the initial dendrite and pit nucleation, which in turn, results in improved reversibility and reduced dead Li formation during extended cycling. As the research community continues to seek improved methods of achieving high CE Li metal anodes, we hope that these mechanistic insights provided in this study into the importance of nucleation will aid in the rational design of electrode architectures and surfaces.

\textbf{Figure 4.9:} A), B), and C) optical images of dendrite nucleation at pit edge after 0, 0.16, and 0.33 mAh cm$^{-2}$ of deposition respectively.
4.3 Conclusions

In this work, an *operando* optical microscopy cell was developed, which enables a plan-view perspective of the electrode surface and uniform current distribution along the working electrode. Using this cell, the following insights into Li metal nucleation and reversibility were developed:

1. **Nucleation density is higher for pits than dendrites.** Areal nucleation density was observed to increase for both dendrites and pits as a function of current density. However, the nucleation density of pits was greater than that of dendrites. A potential mechanism that contributes to this difference is the different influences of surface...
heterogeneity on the spatially varying nucleation activation barrier for dendrites and pits. The quantitative data provided in this manuscript can be incorporated into future modeling efforts of electrodissolution behavior.

2. **Surface heterogeneity in the Li metal microstructure influences nucleation behavior.** Preferential nucleation of both dendrites and pits along surface grain boundaries was observed in the first half cycle. This serves as an example of the influence surface heterogeneity has on nucleation behavior, and highlights the role of surface microstructure on nucleation. After the first half cycle, the pit edges were observed to be preferential hot spots for dendrite nucleation. This behavior continues throughout subsequent cycling.

3. **Dead Li formation is influenced more by nucleation than growth.** The effective volume of individual dendrites was tracked during cycling to identify trends in reversibility. It was found that the individual dendrite size within a single cycle did not have a consistent impact on reversibility. Instead, the morphology of the dendrite nucleation sites was found to have a much larger influence on reversibility. The results suggest that dead Li formation is impacted more by the nature of dendrite and pit nucleation than growth. These insights help to rationalize why different surface treatments improve performance even after the initial surface treatment has been eroded during cycling, and point to the importance of rational design of electrode surface structure and composition to further improve CE.
CHAPTER 5

Anisotropic Evolution and Faceting of Lithium


The results presented in Chapter 4 demonstrate that pit formation plays a non-negligible role in Li metal anode performance. Using, the plan-view platform, Dendrites were observed to preferentially nucleate along the perimeter of pits formed in the previous half-cycle, and this nucleation within pits leads to improved reversibility when compared to nucleation at singular points along the electrode surface. Furthermore, the reversibility of individual dendrites was observed to be sensitive to the size of the pits within which nucleation occurred. However, the complete mechanisms that link pit formation to dendrite nucleation and reversibility are not fully understood. Therefore, an improved understanding of how pit geometry dynamically evolves, and the influence of electrode surface properties on pit morphology, are critical for optimizing the CE and cycle life of Li-metal batteries.

This chapter explores the dynamic evolution of Li metal surface morphology during stripping. A platform for operando focus variation microscopy is presented and used to reveal strong anisotropy and faceting in surface pits, which correlates with surface microstructure. Specifically, this study: (1) maps the dynamic morphological evolution of individual pits in 3-dimensions; (2) demonstrates anisotropic pit expansion in both in-plane and through-plane directions; (3) correlates anisotropy with surface grain boundaries and
crystallographic texture; and (4) demonstrates faceted edges in pits, which align within individual grain orientations. The results presented provide greater insight into the fundamental nature of Li stripping reactions and raise new questions about the role of microstructure in reversible cycling of Li metal.

5.1 Experimental Methods

The electrolyte used in all experiments was 1M LiPF$_6$ in 1:1 v/v EC/EMC (Soulbrain) and 750 µm thick Li foil (Alfa Aesar) was used as the electrodes. All cells were assembled in an Argon glovebox with oxygen and water levels below 0.5 ppm. Coin cell electrodes were punched to an area of 1.6 cm$^2$, while the plan-view electrodes were cut to size with a razor blade. Atomic force microscopy (AFM) imaging was conducted on a MFP-3D Origin+ (Asylum Research) in tapping mode. A Keyence VHX-7000 digital microscope was used for all optical microscopy analysis. The 5000x objective was used for ex situ measurements while the 400x objective was used for operando measurements. All image analysis was performed in MATLAB®.

3-D renders were produced by a multi-step process. First, the topographical information produced by the Keyence microscope was converted into a point cloud file in MATLAB®, which is a file containing the spatial coordinates of all pixels. Using the “Scanto3D” add-on in DS SOLIDWORKS®, the point cloud was meshed into a surface and saved as an object file. The object file was then imported in the Autodesk 3DS Max®, and the stored surface was rendered.

A segmentation code was developed in MATLAB® to differentiate a pit from the bulk surface. The general workflow of the script is depicted in Figure 5.1. First a threshold to the luminance of the RGB image was applied to convert pixels exceeding the threshold to white and the remaining pixels to black (built-in function ‘im2bw’). Second, to fill missing pockets in the pit, thresholds were applied to spatial information provided by focus
Figure 5.1: Schematic of MATLAB segmentation code that outlines pit.

Variation microscopy. Pixels with a Z-coordinate below the average Z-coordinate of the bulk surface and a 3-D gradient below the gradient measured at the pit edge were filled with black. Furthermore, a subsequent flood-fill operation was applied to further fill any missing pockets (built-in function ‘imfill’). Third, the black regions were segmented into individual shapes, and then filtered based on area (built-in function ‘bwarea’). The region with the largest area was retained, and all others were removed. Lastly, the remaining pit outline was structured with square elements (built-in function ‘strel’) and smoothed with a Savitsky-Golay filter with a moving average of 5 pixels. The resulting binary image highlighted with pit surface with black and the remaining regions with white.

The pit aspect ratio was defined as the difference in Z-coordinate between the average bulk surface and minimum Z-coordinate within the pit. The average Z-coordinate of the bulk surface was calculated over a square border surrounding the pit as shown in Figure 5.2. The dimensions of the square border that were used to compare focus variation microscopy and AFM images in Figure 5.5 are shown in Figure 5.2 A. The width of the pit border (W) was defined as 5% of the AFM image side length (S_{AFM}). Furthermore, the outer side length of the border (S_{out}) was equated to the side length of the AFM image (S_{AFM}). The border dimensions were defined differently for Figure 5.7, where AFM was not used. These dimensions are shown in Figure 5.2 B. First, the averaging border was centered with the initial pit centroid (centroid during nucleation). The inner side length of the border (s_{in}) was defined by enforcing the border to be at least 2 microns away from the pit edge. To do
5.2 Results and Discussion

5.2.1 Focus variation microscopy for 3-D dimensional analysis

The plan-view *operando* video microscopy platform detailed in Chapter 3 was updated to achieve high-magnification imaging, which is shown in Figure 5.3A. The cell design is still based on a concentric ring counter electrode, which is positioned with a vertical offset...
Figure 5.3:  a) Schematic of the plan-view cell used for operando analysis. b) Current density distribution within electrolyte body along a cross-section when charge is stripped from the working electrode at 5 mA cm\(^{-2}\) (area based on working electrode surface area). c) Current density at working electrode and counter electrode surface when charge is stripped from working electrode surface at same rate in c). d) Current density along working electrode surface across the X axis.

from the Li metal working electrode. However, the diameter of the working electrode was reduced to 5 mm and also brought closer to the quartz window to minimize the amount of electrolyte, through which to image.

COMSOL simulations of the current density distribution inside the cell are shown in Figures 5.3B-D. A uniform color is observed at the working electrode surface in Figures 5.3B and C, indicating a uniform current density distribution at the working electrode surface. The magnitude of the current density is larger at the working electrode than the counter electrode because of a smaller surface area (0.1963 cm\(^2\) and 1.0292 cm\(^2\)). The variations in current density along the X-axis of the working electrode surface are shown in Figure 5.3D where \(-X_o\) and \(X_o\) are the edges of the working electrode along the X-axis. The spatial variations in current density are within 2\%.

In addition to the high-magnification upgrade, the plan-view platform was integrated with a Keyence VHX-7000 optical microscope. This digital microscope can perform focus
Figure 5.4: (a) Schematic depiction of focus variation microscopy, where a focal series is captured and saved as a vertical image stack. After postprocessing, (b) the output is a composite optical image of the pit, which enables 3D reconstruction of the pit from (c) an isometric view, and cross sections of the pit along the (d) YZ and (e) XZ-planes.

Figures 5.4 shows the application of this new capability on a stripped Li electrode. First, the motorized objective scans along the out-of-plane-axis and captures images of the Li surface at various focal planes. An encoder integrated into the objective stepper motor records the position of each image along the out-of-plane axis with a spatial resolution of 100 nm. These images are collected into a vertical stack where the objective position is used to determine the depth of each plane. A depth-from-defocus (DOD) algorithm is then applied to identify which plane produces the highest focus quality for a given pixel. Focus quality is quantified by calculating the standard deviation of surrounding pixel grey values, where a higher standard deviation indicates stronger contrast between pixels and better focus quality. Once all pixels have been assigned to corresponding planes, a composite optical image is produced with the entire field-of-view in focus (Figure 5.4B). Furthermore, the depth of each pixel is quantified based on the position of the corresponding plane. This depth information enables 3-D reconstructions of the electrode surface, as shown in Figures 5.4C–E. The 3-D information allows for quantitative analysis of the surface topography. This microscopy technique has been previously used for applications ranging from archaeology to metrology for additive manufacturing.

To validate the applicability of this 3-D imaging capability for Li metal anodes, focus
Figure 5.5: Images of three different pits captured through (a–c) ex situ focus variation microscopy and (d–f) ex situ AFM on Li metal electrodes. Li was stripped at a current density of 5 mA cm\(^2\) in each coin cell. The depth of discharge was 0.027 mAh cm\(^2\) in Pit A (left column), 0.041 mAh cm\(^2\) in Pit B (middle column), and 0.055 mAh cm\(^2\) in Pit C (right column). (g) The average pit width and (h) maximum pit depth of for each pit were measured by focus variation microscopy and AFM.

Variation microscopy and AFM were performed on the same electrodes. Three different samples (labeled Pit A, Pit B, and Pit C in Figure 5.5) were extracted from Li–Li symmetric coin cells, where varying amounts of charge were stripped in each cell at a current density of 5 mA cm\(^2\). Figures 5.5A–C show images of individual pits produced through focus variation microscopy, while Figures 5.5D–F show the corresponding AFM images of the same surface locations. The measurements conducted by the two microscopy techniques were consistent with regards to geometric shape and pit dimensions.

To provide a quantitative comparison, the average width and maximum depth of each
pit were measured. The average pit width was calculated from the mean value of 180 cross-sectional measurements taken through the pit centroid. Furthermore, the maximum pit depth was measured from the difference in depth between the surrounding bulk surface and the lowest point in the pit. To differentiate the bulk electrode surface from the pit, a segmentation algorithm was developed in MATLAB®. The algorithm applies a threshold to the luminance of the optical image in greyscale and to the 3-D gradient of the spatial coordinates. Details of the algorithm are provided in the Experimental Methods (Section 5.1).

Figures 5.5G and H show the measured dimensions of each pit, demonstrating good agreement between the optical microscope and AFM measurements. However, the time needed for data acquisition differs significantly between the two microscopy techniques. The optical microscope performed each scan, spanning multiple pits, in approximately twenty seconds, while the duration of an AFM scan for a single pit was approximately five minutes. This affords the optical microscope superior temporal resolution for operando analysis, while simultaneously providing a larger field of view that spans multiple pits. Therefore, focus variation microscopy is well suited to capture the dynamic morphology of the working electrode surface throughout a dissolution half-cycle. In the following discussion, this capability is used to quantify anisotropic pit expansion and demonstrate the role of crystallographic orientation and surface microstructure during electrodissolution.

5.2.2 Anisotropic in-plane vs. through-plane expansion of individual pits

To study the morphological evolution of individual pits, operando focus variation microscopy was performed on the working electrode of a Li–Li symmetric cell. An areal capacity of 1.1 mA h cm\(^2\) was stripped at 5 mA cm\(^2\) in a 1 M LiPF\(_6\) in 1:1 v/v EC:EMC electrolyte. 3-D reconstructions were generated at different points in the stripping half-cycle, as shown in Figure 5.6. The centroid of the pit was calculated and plotted with a red
sphere to quantitatively track translational motion of the pit.

Figures 5.6A–C present isometric views of the pit expansion where the centroid is observed to monotonically translate in the negative Z-direction. This is expected since the pit expands into the bulk Li. However, there is negligible translation of the centroid in the XY-plane. The centroid remains close to the coordinate origin and translates less than one micron in the lateral directions. The lack of in-plane translation indicates that the expansion of the pit remains centered around the initial nucleation point in the XY-plane.

Strong anisotropy in the pit geometry was observed in the 3-D reconstructions. Figures 5.6D–F show cross-sections of the pit along the YZ-plane. In each frame, the pit width is consistently more than two times larger than the maximum pit depth. Using the previously described segmentation method to define the pit edges, the pit width along the YZ-plane expands from 38.2 µm to 58.3 µm, while the maximum pit depth increases from 4.9 µm to 13.6 µm. The asymmetric profile of the pit cross-section demonstrates that the pit expands more rapidly in the in-plane directions than in the out-of-plane direction.

To further quantify the anisotropy between the in-plane and out-of-plane directions, the aspect ratio of the average pit width to the maximum pit depth was calculated throughout...
the half-cycle as shown in Figure 5.7. If pit expansion occurred in an isotropic manner, an aspect ratio of 2 would be observed. However, the measured values remained greater than 3, indicating that the pit width expanded faster than the pit depth. This trend was consistently observed across all pits along the electrode surface (the aspect ratio as a function of time for multiple pits are provided Figure 5.8).

The observed anisotropic expansion will be influenced by crystallographic texture of the underlying Li electrode. For example, density functional theory (DFT) modeling of Li metal anodes has shown that the thermodynamic overpotential for plating and stripping varies in different crystallographic directions.\textsuperscript{127} The overpotential for stripping was predicted to be higher on the 100 family of planes than on the 110 family, which will influence the relative rates of electrodissolution according to Butler–Volmer kinetics. These variations can drive anisotropic pit expansion similar to the results in Figures 5.6D–F. For the Li foil used in this study, a strong [100] out-of-plane orientation has been measured by pole-figure diffraction analysis, which is a consequence of the rolling process commonly used to manufacture commercial Li foils.\textsuperscript{67,128} Owing to the preferential [100] alignment in the normal direction, a slower rate of electrodissolution will occur normal to the Li surface.
Figure 5.8: a) Optical image of the working electrode from a plan-view cell after 1.1 mAh cm$^{-2}$ of charge was stripped. b-g) Pit aspect ratio as a function of time for the pits labeled in a). Dashed line is an aspect ratio of 2, which is the expected value for isotropic expansion. Values greater than 2 indicate faster in-plane expansion.

because of the higher stripping overpotential relative to kinetically-fast crystallographic directions in the orthogonal in-plane directions.

Since Li is a body-centered-cubic (BCC) system, the 100 family of planes is also present along the in-plane directions. This should cause anisotropic in-plane expansion, with preferential stripping along kinetically-faster crystallographic directions. As a result, facets can form as pits expand laterally, which will be described below. The anisotropic dissolution demonstrated here for Li is analogous to the preferential stripping that occurs on the (0001) basal plane of Magnesium (Mg) in a 1 M ethyl magnesium bromide electrolyte.$^{129}$

Another factor that can contribute to dissolution anisotropy is the growth of surface films, such as the SEI. For example, previous studies have suggested that the dissolution behavior of Mg is dependent on the growth of surface films.$^{129,130}$ In a 0.01 M NaCl solution, the (0001) plane was shown to be the most resistant to dissolution, while in a 0.01
M NaCl/0.00001 M dichromate solution, the (0001) plane was less resistant to dissolution than the prismatic planes. Additionally in pitting corrosion of metals, anisotropic pit expansion has been attributed to the growth of surface films, which is influenced by the crystallographic orientation of the substrate and by the presence of impurities and alloying elements. In Li metal, variations in the SEI growth rate along the electrode surface have been linked with spatially-varying kinetic rate constants along the surface. Thus, the anisotropic evolution of Li pit morphology shown here motivates additional investigations of how SEI growth kinetics depend on surface orientation of Li metal grains, to elucidate the role of surface films on spatially varying kinetics during stripping. We also note that the anisotropic pit expansion has also been observed in less reactive metals where an SEI does not form, such as 316L stainless steel.

In addition to the crystallographic factors described above, a third contributing factor to the observed anisotropy in Li pits is the geometric curvature of the pit edge, which can induce local current focusing. This is consistent with our previous observation that nucleation of Li plating preferentially occurs along the perimeter of pits formed in the previous half-cycle, which has been shown to influence CE.

Overall, the dependence of stripping overpotential on crystallographic direction, SEI formation, presence of impurities, and current focusing can all contribute to the through-plane anisotropy observed in the operando measurements. We hope that the experimental observations in this study will motivate future modeling work to understand the dynamic interplay between thermodynamics, kinetics, and mass transport during anisotropic pit evolution. In the following results and discussion, we further demonstrate the critical roles of crystallographic texture and surface microstructure on pit morphology.

### 5.2.3 Faceting of pits during expansion

In addition to through-plane anisotropy, in-plane anisotropy was also observed. As individual pits grow in size, faceted edges were observed to form along their perimeter. Figures
5.9A–C show the geometric evolution of an individual pit. To quantify this faceting behavior, the perimeter of the pit was discretized into equidistant points, and the normal vectors of the edge were calculated at each point (Figures 5.9D–F). The angle of each normal vector was then measured with respect to the X-axis and binned into histograms as shown Figures 5.9G–I.

In the initial stages of the half cycle, the pit morphology did not demonstrate any clear faceting (Figure 5.9A). The surface normal vectors pointed out radially (Figure 5.9D), and the histogram (Figure 5.9G) shows a relatively uniform distribution. However, as the
Figure 5.10: (a–c) Optical images of a pit, (d–f) outlines of pit edge with normal vectors to pit edge, and (g–i) histograms of all normal vector angles with respect to the X-axis at different points in time of the stripping half cycle, 184 s (left column), 286 s (middle column), and 643 s (right column).

half-cycle progressed, the pit developed four-fold symmetry (Figure 5.9B), as indicated by grouping of the normal vector directions (Figure 5.9E). The groups of angles are centered around 180°, 90°, 0° and 90° (Figure 5.9H). The grouping of normal vector angles indicates that facets developed at the pit edge. The four-fold symmetry and facets observed in the middle column of Figure 5.9 were maintained as stripping proceeded, as shown in right column of Figure 5.9.

The results above provide further evidence that crystallographic texture is a contributing factor in the anisotropic dissolution of Li metal. Analogous faceting behavior has been
observed in pitting corrosion, where BCC metals, such as iron, have been demonstrated
to form polygonal pits.\textsuperscript{138} These facets can develop when the dissolution rate varies with
respect to the crystallographic planes.\textsuperscript{133,139} Moreover, the quadrilateral shape displayed in
Figure 5.9 was not the only polygonal shape observed. Other examples of faceting, such
as hexagons, were also commonly observed. An example of a hexagonal pit is shown in
Figure 5.10. The variations in shapes indicate that other factors, in addition to the crystallo-
graphic texture, contribute to dissolution anisotropy. One important factor is the Li surface
microstructure, which is described below.

5.2.4 Influence of electrode microstructure on pit morphology

To explore the impact of the Li microstructure on dissolution anisotropy, pit expansion was
studied near surface grain boundaries. Figures 5.11A–C show the growth of a pit through-
out the stripping half-cycle. To quantify the influence of the surrounding surface grain
boundaries, the distance between the pit centroid and the edge was measured at varying
polar angles. These measurements are shown in Figures 5.11D–F where the radial distance
from the pit center to the edge is expressed a function of polar angle (\(\theta\)).

Consistent with previous results, the pit shown in Figure 5.11 developed facets dur-
ding the intermediate stages of the stripping half-cycle. However, an additional source of
in-plane anisotropy was observed. Throughout all stages of the stripping half-cycle, pref-
erential pit expansion was observed along a surface grain boundary. The intersection of
the pit with this surface grain boundary is labeled with a dashed circle. A local apex was
observed in Figures 5.11D–F at this intersection, indicating more rapid expansion along
the surface grain boundary.

We note that preferential expansion was not observed along all the surface grain bound-
daries labeled in Figure 5.11A. For example, no apex is present at \(\theta = 30^\circ\) in Figures
5.11D–F. In our previous publication, preferential nucleation of pits was observed along
surface grain boundaries.\textsuperscript{12} However, not all nucleation “hot spots” were along grain bound-
aries, and not all grain boundaries were hot spots. The same trend is exhibited during the expansion of pits shown here. Not all surface grain boundaries cause preferential pit expansion, which may be attributed to variations in local kinetics and/or diffusion along grain boundaries with different angular mismatch between the adjacent grains. For example, recent modelling work has shown that the self-diffusion of Li can play an important role in the morphological evolution of the electrode–electrolyte interface, which will be influenced by surface grain boundary orientation. Overall, the results highlight the importance of the Li microstructure on the morphological evolution of the electrode surface.

To further study the influence of the Li microstructure on dissolution anisotropy, pit morphology was tracked with respect to the surrounding grains. Figures 5.12A–C show optical images of two pits expanding from the experiment described in Figure 5.6. These pits nucleated on the same surface grain boundary and were surrounded by the same grains.
at the top and bottom of the images. The pits and surface grain boundaries are labeled in the corresponding schematics in Figures 5.12D–F.

Initially, the two pits nucleated on the same surface grain boundary and expanded into the same grains at the top and bottom of the images as shown in Figures 5.12A and D. The preferential nucleation of pits along surface grain boundaries is consistent with previous studies. As these pits expanded, they preferentially grew along the surface grain boundary that connects them (Figures 5.12B and E). Evidence for this is shown by the vertices along the pit edges that align with the surface grain boundary. We also note that not all grain boundaries led to preferential pit expansion, as the right (green) pit preferentially expanded along the boundary to the left, but not along the boundary to the right. Before merging, the average width of these pits reaches 32.7 µm (left pit) and 27 µm (right pit), which is smaller than the average surface grain size of the Li foil used in this study (150 µm).

The merging of pits will be impacted by the grain size, since this determines the distance between grain boundaries. At the end of the half cycle (Figure 5.12 right column), the pits formed similar facets and display an octagonal shape with the same orientation.

In summary, multiple factors that lead to anisotropic in-plane expansion were demon-
strated by the two pits shown in Figure 5.12. Preferential expansion was observed along specific surface grain boundaries, and facets developed at intermediate stages of the stripping half cycle. Additionally, the similar geometry (octagons with parallel facets) developed by the two pits suggest that the surrounding grains and grain boundaries impact the morphological evolution of individual pits.

In contrast to its out-of-plane texture, the Li foil used in this study does not display a preferred in-plane crystallographic texture based on pole-figure diffraction analysis. Therefore, the directions of preferential in-plane pit expansion will vary from grain to grain, and consequently the direction of pit facets are expected to also vary among different grains. This helps to explain why different geometric shapes (rectangles, hexagons, etc.) can all be observed in the same electrode. For example, the number of edges and interior angles of each polygon will be influenced by both the underlying crystal structure and the angular misorientation between adjacent grains. However, in the case where multiple pits expand into the same set of grains (as shown in Figure 5.12), the observed consistencies in polygonal shape and facet orientation can be rationalized by the underlying crystal structure. Similar behavior is known to occur in pitting corrosion, where the pit polygonal shape can abruptly change when crossing a grain boundary, which is a direct result of the different orientation of the adjacent crystallite. The parallel faceting among several adjacent pits was also observed in coin cells as shown in Figure 5.13, which confirms that the trends reported throughout this study also occur under cells with applied stack pressure and a polymer separator. Overall, these results demonstrate that Li microstructure, grains and surface grain boundaries, all contribute to the anisotropic expansion of pits on Li metal anodes.
5.2.5 Implications of anisotropic pit expansion on Li metal anode cycling

The results of this study highlight the importance of the electrode crystallographic orientation and microstructure on the morphological evolution of Li metal anodes during stripping (discharge). These properties of the electrode surface directly impact pit morphology, which in turn plays a critical role in Li metal anode performance. For example, the pits that form during stripping in the first cycle have been shown to improve the CE of the subsequent cycle. This improved reversibility is attributed to preferential nucleation of plated
Li within pits, and the extent of this improvement was shown to be sensitive to the size of the pits. Furthermore, the initial pits formed in the first cycle serve as the preferential nucleation sites for subsequent plating throughout the extended cycle life of the electrode. It has also been shown that by controlling the manner in which pits are formed in the first cycle, improved reversibility and cycle life can be achieved.\textsuperscript{82,87}

Together, these observations suggest that by engineering the crystallographic texture and surface microstructure of a Li metal anode, the evolution of pit morphology during stripping may be tuned to optimize CE and cycle life. An image series of deposition within a faceted pit is shown in Figure 5.14. Consistent with previous studies, nucleation of plated Li preferentially occurred at the edges of the pit.\textsuperscript{12} It has also been previously shown that the reversibility CE of plating and stripping is influenced by the local morphology at the base of a mossy deposit, which is attributed to changes in the volume of remaining “dead Li”.\textsuperscript{12} The anisotropic pit geometries observed in this study will therefore influence the base of the plated Li deposits in the subsequent cycle, which could play a role in reversibility.

Metallurgical processing of the electrode could enable rational control of pit morphology. However, a practical challenge facing the metallurgical processing of Li is the extreme reactivity of metallic Li. Therefore, future investigations of process–structure relationships in manufacturing of Li metal batteries are needed to identify safe, scalable, and low-cost
methods to control the crystallographic and microstructural properties of Li metal. Moreover, it is important to note that the electrode surface texture will continue to evolve when Li metal has been electrodeposited. Therefore, strategies are needed to rationally control plated Li microstructure and grain orientation, including electrochemical conditions (e.g. variations in current density and charging protocol), as well as electrolyte composition.

In addition to planar electrode geometries, the findings in this study also have implications for the design of 3-D electrode architectures, which have emerged as one of the most promising approaches to achieve high reversibility in Li metal batteries. For example, the size and morphology of plated Li can be influenced by steric hinderances in porous 3-D electrodes, which can be further modified by control of surface chemistry and substrate–metal interactions. Further control of current collector geometry and surface chemistry in anode-free batteries could potentially allow for control of crystallographic texture and grain orientation, including exploration of epitaxial relationships and strain effects between the current collector and plated Li. This control, in turn, will influence stripping morphology, and thus reversibility.

The anisotropic stripping of Li metal demonstrated in this study could also play an important role in dead Li formation, which is a critical factor that influences CE and cycle life. The transition from plated Li to dead Li is thought to occur when Li is preferentially stripped from a region that results in electrical and/or electrochemical isolation from the substrate. Since Li metal dendrites have been shown to exhibit faceting and preferential growth directions, these microstructural characteristics will influence stripping along the deposited Li surface. As charge is removed from the deposit, preferential stripping can occur as a consequence of the crystallographic texture and local geometry of the deposited metal. These factors will be further influenced by preferential diffusion pathways along the plated Li surface, including surface grain boundaries. This can drive a rapid decrease in the dendrite dimensions along the specific crystallographic directions and microstructural features associated with anisotropic stripping, causing the isolation of
5.2.6 Conclusions

In conclusion, in this work, a platform for operando focus variation microscopy was introduced and used to map the morphological evolution of individual pits in 3-dimensions. Using this platform, the following insights were gained into the dynamic behavior of the Li surface during stripping:

1. Pits were observed to expand more rapidly along the surface of the Li electrode (in-plane) than into the depth of the electrode (through-plane). This anisotropic stripping produced shallow pits.

2. Pits were observed to develop faceted edges at intermediate stages of a stripping half cycle. The various polygonal shapes displayed by pits indicate that the underlying microstructure of Li plays an important role in the morphological evolution of a pit.

3. Pit morphology is impacted by surface microstructural features, including the orientation of grain boundaries and the surrounding grains. Pit expansion was observed to preferentially occur along specific surface grain boundaries. Furthermore, pits expanding into the same grains displayed similar morphologies, while pits expanding into different grains displayed distinct morphologies.

Overall, the observations listed above highlight the importance of the electrode crystallographic orientation and microstructure on cycling. These two properties both influence anisotropic expansion of pits during stripping. The results point towards a potential pathway to achieve improved performance through rational control of the electrode crystallographic orientation and microstructure, both during manufacturing and subsequent plating. Additionally, the results suggest that dead Li formation may be impacted by anisotropic stripping, which will be influenced by the crystallographic texture and surface microstructure of individual Li deposits. In the future, further analysis of the influence of cycling
conditions, electrolyte composition, and external variables will be valuable to guide strategies to rationally control pit morphology.
CHAPTER 6

Conclusions and Future Work

6.1 Conclusions

The work presented in this thesis introduces a custom platform for real-time viewing of a Li metal anode surface, provides mechanistic insight into the morphological evolution of the Li metal anode surface, and identifies the relationship between morphology and performance.

Chapter 3 introduces a custom electrochemical cell that enables imaging from a plan-view perspective of the electrode surface while simultaneously achieving a uniform current distribution across the working electrode. The design incorporates a concentric ring geometry with a height offset between the working and counter electrodes. A physical barrier is also placed between the direct line of sight of the electrodes. The combination of these features promotes a uniform current distribution along the working electrode surface. The plan-view perspective allows for quantitative analysis of nucleation/growth on a Li metal anode and for correlation of surface morphology with the electrode microstructure. The plan-view platform is not constrained to only visualizing Li metal anodes, and it can be adapted to other battery chemistries.\(^{142}\)

Chapter 4 provides mechanistic insight into the coupled relationships between nucleation, morphology and reversibility. The areal nucleation density of both dendrites and pits was quantified as a function of current density. A positive correlation was observed,
which aligns with classical nucleation theory. However, a higher areal density of pits was observed at a given current density than the corresponding areal density of dendrites at the same current density. This provided evidence that the nucleation process differs for dendrites and pits. A potential mechanism for the difference is that surface heterogeneity, including surface grain boundaries, grains, and defects, impacts the nucleation activation barrier differently for dendrites and pits. Surface grain boundaries were observed to serve as preferential nucleation sites for dendrites and pits in the first half cycle. This observation demonstrated the impact of electrode microstructure on nucleation. However, in subsequent cycles, dendrites were observed to preferentially nucleate along the edges of pits that formed in the first cycle. The edges of these initial pits served as nucleation “hot” spots into extended cycling, highlighting the importance the initial surface properties on extended cycling performance. Lastly, the size of individual dendrites were quantified during cycling. A strong correlation between the dendrite size and reversibility was not found. However, reversibility was found to improve between the first and second cycle. Furthermore, reversibility improved when larger amounts of charge were passed during cycling. These trends were attributed to the presence of pits on the electrode surface. The transition between nucleation on a pristine surface to the pit edge promoted better reversibility, and larger pits promoted an improved reversibility. These observations suggest that dead Li formation is impacted more by nucleation than growth. Overall, the results of this chapter identify the importance of pit formation, the initial surface condition, and the electrode microstructure on Li metal anode performance.

Chapter 5 demonstrates the anisotropic nature of Li metal electrodissolution. The plan-view platform was updated to perform focus variation microscopy, which is a technique that captures areal surface topography. Using this new capability, the morphological evolution of individual pits was explored. Pit expansion was observed to be highly anisotropic, where expansion occurred more rapidly along the surface of the electrode than into the depth. Furthermore, pits developed facets where the polygonal shapes varied from grain
to grain. However, pits that expanded into the same grain displayed a similar morphology. These observations suggest that the electrodissolution of Li metal is dependent on the crystal structure of the electrode. Additionally, pit expansion was observed to preferentially occur along certain surface grain boundaries. This observation highlights that the electrode microstructure also promotes stripping anisotropy. Overall this chapter highlights the impact of electrode crystallographic orientation and microstructure on Li metal anode performance.

6.2 Future Work

The work shown above has provided a better understanding of the factors governing the morphological evolution of a Li metal anode and how this relates to performance. In the future, there are numerous opportunities to expand upon the results presented.

In chapter 4, the areal nucleation density was quantified as a function of current density for both dendrites and pits. A positive correlation was observed, however the nucleation density of pits was observed to be more sensitive to current density than dendrites. The difference in nucleation density is not fully understood, and future investigations are needed to gain insight into how nucleation occurs on metallic Li. A potential factor promoting this difference is the transition time from nucleation to growth. The transition may occur faster for dendrites, given the greater exposed surface area compared to pits. There is less time for new dendrites to form, leading to a smaller nucleation density. Another contributing factor is that surface heterogeneity (grains, grain boundaries, defects) impacts the activation barrier for nucleation differently for dendrites and pits. Unfortunately, the spatial resolution required to resolve the differences in nucleation are beyond the capabilities of the plan-view optical microscopy platform. Characterization techniques, such as TEM and AFM, that provide superior spatial resolution are needed to elucidate how nucleation occurs on Li metal at smaller length scales.
Pit formation was also explored and found to influence the reversibility of dendrites. Reversibility improved when dendrite nucleation occurred at the edge of a pit compared to the pristine surface. Furthermore, reversibility was sensitive to the size of the pits. The rationalization presented for these observations is that the pit edge increases the base-to-electrode contact area, and this improves the physical/electrical contact between the dendrite and bulk electrode. Recent studies have built upon this understanding, and demonstrated that initially pitting Li electrodes improves the cycle life of a Li-Li symmetric cell. However, an important remaining question is: what is the optimal pit morphology? Exploration of this question also has implications on the design of 3-D electrode architectures, which has become a promising pathway to improve Li metal anode performance.

In chapter 5, the electrode crystallographic orientation and microstructure were observed to cause preferential stripping of Li. A bottleneck in the commercialization of rechargeable Li metal anodes is the formation of dead Li. It is possible that preferential stripping caused by the crystallographic and microstructural proprieties of the plated Li may promote the formation of dead Li. Several studies have implored the use of SEM, TEM, x-ray diffraction (XRD) and DFT to explore the impact of the electrode crystal lattice on deposition. These techniques could be applied to study the preferential stripping of plated Li as well.

Additional future work includes addressing how to rationally control the pit morphology for better performance. The results of Chapter 5 suggest that tuning the electrode crystallographic and microstructural proprieties can enable rational control of the pit morphology. However, the reactivity of metallic Li prevents safe metallurgical processing of Li. Developing methods to process the structure of Li metal would have a significant impact on Li-metal battery research.

Another promising direction to build upon this work is to further explore the preferential expansion of pits along surface grain boundaries. As shown in Chapter 5, certain surface grain boundaries caused preferential pit expansion, but not all. This may be re-
lated to the level of misorientation between adjacent grains. To further explore this behavior, complimentary electron backscatter diffraction (EBSD) measurements should be made. EBSD measurements on a Li anode would elucidate the misorientation between grains, and subsequent plan-view operando video microscopy experiments could correlate the misorientation to preferential pit expansion.

Overall, this thesis provides insight into the factors impacting Li metal anode performance. However, there are many remaining questions about the nucleation and anisotropic evolution of Li. Advanced in situ operando characterization techniques (AFM, TEM) that offer superior spatial resolution compared to the plan-view platform are needed to elucidate the morphological evolution of Li metal. Furthermore, this thesis primarily focuses on the morphological/structural heterogeneity of the electrode surface; however, spatial variations in the surface chemistry likely also play a role in the origins of dendrites and pits. To build upon this work, spectroscopic methods can be integrated with the plan-view platform to explore heterogeneity in the surface chemistry and potentially correlate chemical composition with preferential nucleation.

Lastly, the work presented above focuses on Li metal anodes, however the plan-view platform is not constrained to visualizing metallic Li. Recently, it was adapted to study the spatial heterogeneity in the state-of-charge of a graphite anode and explore how Li plating/dead Li formation occurs in Li-ion batteries. A pathway to expand upon this thesis is to implement the plan-view platform to study other metal anodes. Other metal anodes, such Aluminum, Zinc, Magnesium and Sodium have all demonstrated that dendrite formation can occur. The phenomena observed in thesis may not be unique to metallic Li, and may also be relevant to other metal anodes. For example, pitting has been observed with Mg anodes, and the pits formed in the first cycle have been shown to impact the morphological evolution of subsequent cycles, which is consistent with the observations in Chapter 4.

In summary, there are numerous avenues to expand upon the work presented in this
thesis. The insights gained highlight several critical factors that impact the performance of Li metal anodes, and can inform new strategies on how to address the poor performance of metallic Li.
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