In Situ Scanning Electron Microscopy Analysis of Li Metal Dendrite in Battery Applications

Maryam Golozar

Department of Mining and Materials Engineering McGill University Montreal, Quebec, Canada May, 2020

A thesis submitted to McGill University in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

© Maryam Golozar, 2020

Dedication

This thesis is dedicated to my parents, Mohammad Ali Golozar and Fariba Fazel Anvar

Abstract

Lithium metal is a promising anode material for Li-ion battery applications owing to its high specific capacity. Cycling Li-ion batteries with Li metal anode however, faces challenges specially when cycled at high rates. Li metal anode could undergo dendrite formation. These dendrites could short circuit the battery and result in explosions. One proposed method to hinder dendrite growth is using solid electrolytes with high shear modulus. Nevertheless dendrite formation is still observed in these batteries. The anode also undergoes volume change during cycling that deteriorates the solid electrolyte interphase protecting the Li surface. The damage to this layer results in inhomogeneous Li deposition and dissolution during charge and discharge. To be able to use Li metal as the anode, the cycling behavior of the batteries containing Li anode should be fully investigated.

Studying the morphology and chemical evolution of Li faces difficulties due to Li properties including; high reactivity, ultra-softness, low melting temperature, and low x-ray energy. Li sample preparation and handling is difficult due to the high reactivity and ultra-softness. Morphology and chemical analysis of Li is also challenging as the result of possible electron and ion beam damages and low x-ray energy detectability limitations.

In this work an *in situ* scanning electron microscopy (SEM) method is optimized and employed to monitor the behavior of all-solid-state Li-metal batteries with polymer or ceramic electrolytes. SEM images are obtained from the anode and the electrolyte surface from the beginning till the end of cycling and videos are constructed to show the sequence by which different phenomenon occurs during cycling. A windowless energy dispersive spectroscopy (EDS) detector is used to conduct chemical analysis. After cycling, the battery is transferred to a focused ion beam (FIB)-SEM to conduct further analysis and extract more information about the depth of the sample by milling different regions.

Résumé

Le lithium métallique est un matériau prometteur pour l'avenir de l'industrie des batteries au lithium-ion en raison de sa grande capacité spécifique. L'utilisation de lithium métal dans les batteries apporte néanmoins certains défis, particulièrement à fort taux de cyclage puisque la formation de dendrites peut mener à des courts-circuits et même à l'explosion des batteries. L'utilisation de matériaux avec des modules de cisaillement élevés en guise d'électrolytes entrave la formation des dendrites sans toutefois en inhiber la formation. De plus, le changement de volume au niveau de l'anode pendant les cycles de charge et de décharge compromet l'intégralité de la couche de passivation (ou interphase d'électrolyte solide (SEI)) censée protéger la surface du lithium et d'éviter sa dissolution ou la déposition inhomogène du Li lors des cycles. Ainsi, l'étude du comportement de batteries employant le lithium comme anode est d'une importance capitale en vue de sa commercialisation.

L'étude du lithium est complexe en soi en raison de nombreuses propriétés intrinsèques de celuici. La grande réactivité du lithium et sa faible dureté affectent particulièrement la préparation d'échantillons et leur manutention. De plus, la grande sensibilité du lithium aux faisceaux électroniques et ioniques entrave les analyses morphologiques et chimiques, d'autant plus que ces dernières souffrent de limites de détection en raison de la très faible énergie des rayons x émis par le lithium.

Ce travail porte sur l'optimisation d'une méthode *in situ* au microscope électronique à balayage (MEB) permettant de surveiller l'évolution de batteries tout solide avec l'emploi de différents électrolytes, polymères ou céramiques. Des images MEB des surfaces anodiques et de l'électrolyte sont obtenues du début à la fin du cyclage, permettant la construction de vidéos démontrant le déroulement de différents phénomènes durant le cyclage. Les analyses chimiques sont conduites via la spectroscopie des rayons X par dispersion d'énergie (EDS) en utilisant un détecteur sans fenêtre protectrice permettant alors la détection du lithium. Après l'expérience de cyclage *in situ*, l'assemblage est transféré dans un microscope à double faisceau comportant une sonde ionique focalisée (FIB) qui permet de découvrir plus d'information sur les phénomènes se déroulant sous la surface de l'échantillon.

Acknowledgements

I would like to acknowledge the help and support of everyone from McGill University, Hydro-Québec, and my friends and family throughout this work.

I would like to thank my supervisor Prof. Raynald Gauvin for his ongoing encouragement, candid advice, academic guidance, and for sharing his wisdom with me throughout my PhD that truly kept me motivated. He not only intrigued me to learn more every day during my studies, but prepared me for my future after graduation. I would also like to thank my co-supervisor Dr. Karim Zaghib, director of Center of Excellence in Transportation Electrification and Energy Storage at Hydro-Québec, for providing me with guidence and his scientific vision for the future of lithium ion batteries. Additional thanks to Dr. Zaghib for providing me with the opportunity to join his research group, and to conduct this work using his world class facilities and the experties of himself and his group that exposed me to the leading edge of research into lithium ion batteries.

I would like to thank Dr. Hendrix Demers for always being there for scientific brainstorming and sharing his expertise, and for helping me in every step of my studies both in academia and the industry. I would like to thank Dr. Andrea Paolella for sharing his experiences and knowledge with me, and for always supporting me. I would like to thank Dr. Pierre Hovington and Dr. Marin Lagacé for their theoretical and hands-on training that provided the foundation to my work, taught me persistence, inspired me to stay curious in my research, and for supporting me. I would also like to thank Stéphanie Bessette for not only being my colleague and classmate, and helping me with my work; but in whom I also found a valuable friendship.

I would like to acknowledge and thank Daniel Clément, Michel Roy, and Vincent Gariépy, for their technical support and training over the past years. Also many thanks to Patrick Bouchard, Julie Hamel-Pâquet, Martin Dontigny, Serge Verreault, Gabriel Girard, and Steve Collin-Martin, for providing the samples and the batteries.

I would also like to thank my fellow students and colleagues Dr. Shirin Kaboli, Rachel Lévesque-Bélanger, Pierre-Michel Jalbert, François Larouche, Éloïse Leroux, Christina Maria

Katsari, Konstantinos Korgiopoulos, and all my group members, for never-ending scientific discussions, moral support, and for making this journey memorable. I would also like to thank my lifelong friends Bahar Kazemi, Ahmad Bakhshai, Sarvin Bahar, and Amir Ali Ashrafizadeh, for their valued friendship and never-ending support.

I am grateful to my parents, without whose unconditional love and support throughout my life, this accomplish would not have been possible. I am thankful for their guidance and for providing me with a life that allowed me to pursue my goals. And heartfelt thanks to my brothers Mehdi and Matin, and my aunt Samira, for their faith in my abilities and endless encouragement in life.

Contribution of Authors

This thesis is prepared in the manuscript format in which the results and discussion section is consisted of the manuscripts that are either published (chapters 4 and 5) or are currently submitted to the journals and are under revision (chapters 6 and 7). This work was conducted in collaboration between the Materials engineering department at McGill University and Center of Excellence in Transportation Electrification and Energy Storage (CETEES) at Hydro Quebec. This work was financially supported by Hydro Québec, Natural Sciences and Engineering Research Council of Canada (NSERC), and McGill Engineering Doctoral Award (MEDA). The author of this thesis has conducted the research, and is the primary author of the manuscripts. The co-authors of the manuscripts from CETEES have provided the batteries, assisted with the interpretations of the data, and the fabrication of the in situ set up. Dr. Karim Zaghib has provided the instruments to conduct this study. Professor Raynald Gauvin and Dr. Karim Zaghib have provided insight into the conducted experiments and data analysis. The papers included in this thesis are:

M. Golozar, P. Hovington, A. Paolella, S. Bessette, M. Lagacé, P. Bouchard, H. Demers, R. Gauvin and K. Zaghib, In-situ SEM detection of carbide nature of dendrites in Li-Polymer Batteries, Nano Letters, 18(12), 7583-7589 (2018).

M. Golozar, A. Paolella, H. Demers, S. Bessette, M. Lagacé, P. Bouchard, A. Guerfi, R. Gauvin, and K. Zaghib, In situ observation of solid electrolyte interphase evolution in a lithium metal battery, Communications Chemistry, 2(1), 1-9 (2019).

M. Golozar, H. Demers, A. Paolella, R. Gauvin, and K. Zaghib, Direct Li detection and microstructure evolution of Li^o anode in all solid state battery: in situ SEM cycling observation, Microscopy and Microanalysis, (Submitted)

M. Golozar, A. Paolella, H. Demers, S. Savoie, G. Girard, N. Delaporte, R. Gauvin, A. Guerfi, H. Lorrmann and K. Zaghib, Direct observation of lithium metal dendrites with ceramic solid electrolyte, Scientific Reports, (Submitted)

The accuracy of this statement is confirmed by Professor Raynald Gauvin, the student's supervisor.

Prof. Raynald Gauvin

Table of Contents

Abstract	iii
Résumé	iv
Acknowledgements	v
Contribution of Authors	vii
List of Figures	xii
1. Chapter 1 Introduction	1
1.1 Motivation	1
1. 2 Objective	4
2. Chapter 2 Literature Review	5
2. 1 Lithium-Ion Batteries	5
2. 1. 1 Battery Failure	6
2. 1. 2 Polymer Electrolytes	
2. 1. 3 Ceramic Electrolytes	11
2. 2 In Situ Microscopy Techniques for Li-Ion Battery Studies	
2. 2. 1 In Situ Confocal and Optical Microscopy	
2. 2. 2 In Situ Transmission Electron Microscopy	15
2. 2. 3 In Situ Scanning Electron Microscopy	17
2. 3 Scanning Electron Microscopy – Focused Ion Beam	
2. 3. 1 Principles of Scanning Electron Microscopy	
2. 3. 2 Principles of Focused Ion Beam	
2. 3. 3 Challenges of Lithium Electron Microscopy Characterization	
2. 4 Chemical Analysis	
2. 4. 2 Principles of Energy Dispersive Spectroscopy	
2. 4. 1 Challenges of Lithium X-ray Detection and Quantitative Analysis	
3. Chapter 3 Methodology	
3. 1 In Situ and Ex Situ Scanning Electron Microscopy	
3. 2 All-Solid-State Li-Metal Polymer Battery Cycling	
3. 2 All-Solid-State Li-Metal Ceramic Cell Cycling	

Dendrites
40
ium Metal 62
62
63
64
64
67
67
70
72
75
01 Salid Stata
85

6. 3 Materials and Methods	
6. 3. 1 Cell preparation	
6. 3. 2 In situ cycling	
6. 4 Results and Discussion	
6. 4. 1 Morphology evolution	
6. 4. 2 Chemical evolution	
6. 5 Conclusion	
6. 6 References	
6. 7 Supplementary Information	
 Chapter 7 Direct Observation of Lithium Metal Dendrites with Cer 105 	amic Solid Electrolyte
7. 1 Abstract	
7. 2 Introduction	
7. 3 Materials and Methods	
7. 3. 1 Ceramic and symmetrical Li–LLZO–Li cell preparation	
7. 3. 2 In situ cycling and post-mortem analysis	
7. 4 Results and Discussion	
7. 4. 1 Thinning of Li electrode	
7. 4. 2 Bump and mossy morphology dendrite	
7. 4. 3 Needle morphology dendrite	
7. 4. 4 LLZO chemical analysis	
7. 5 Conclusion	
7. 6 References	
7. 7 Supplementary Information	
8. Chapter 8 Summary	
8. 1 Conclusions	
8. 2 Contributions to the Original Knowledge	
8. 3 Suggestions for Future Work	
9. References	

List of Figures

Figure 2.1 Schematic of an all-solid-state Li-metal battery showing the anode, cathode and	
electrolyte	6
Figure 2.2 Schematic showing the failure of the battery in 4 steps including: SEI damage,	
dendrite formation, Li isolation, and the resulting dead Li and porous electrode	7
Figure 2.3 Light microscopy images of a needle morphology dendrite growth obtained durin	g in
situ cycling.	15
Figure 2.4 TEM images obtained during electrodeposition of Li on gold	16
Figure 2.5 SEM images of different dendrite morphologies.	18
Figure 2.6 Schematic of the electron beam column and the beam parameters	20
Figure 2.7 Schematic of the components of a FIB column	22
Figure 2.8 Schematic showing the ion-sample interaction and the sputtering process	23
Figure 2.9 Phase diagram of Ga-Li (figure 1 of reference [28])	27
Figure 2.10 Schematic of the process of excitation of a neon atom and generation of an Auge	er
electron and an x-ray photon	29
Figure 2.11 Schematic of different parts of an EDS detector.	30
Figure 2.12 Comparison of EDS Li x-ray detection using standard electronics (red) and	
optimized electronics (yellow) (figure 1 of reference [29])	32
Figure 3.1 The two scanning electron microscopes used for <i>in situ</i> and <i>ex situ</i> studies	35
Figure 3.2 Schematic of all solid Li metal polymer battery assemblies for in situ studies (figu	ure 1
of reference [105]).	37
Figure 3.3 Schematic of the symmetrical Li cell with LLZO electrolyte (adapted from figure	3 of
reference [110])	38
Figure 4.1 Schematic of the a) cross section view and b) plane view of the batteries during in	ı-situ
experiments	42
Figure 4.2 Cross section view in-situ experiment a) Cycling curve, b, c, d and e) SEM image	es at
four different times during cycling indicated by the arrows on the cycling curve.	44
Figure 4.3 SEM images showing the morphology of deposited Li after cross section and plan	ne
view in-situ cycling:	45
Figure 4.4 Plane view <i>in-situ</i> experiment	46
Figure 4.5 SEM images showing a) dendrite on the edge of the anode, b) dendrite removed w	vith
the nanomanipulator, c) milled dendrite using FIB showing hollow morphology and d) thick	ness
of the wall of a dendrite.	47
Figure 4.6 SEM images obtained after plane view <i>in-situ</i> cycling	48
Figure 4.7 EDS of a a) needle morphology dendrite, b) mossy morphology dendrite and c)	
interior and exterior wall of a needle milled using FIB.	50

Figure 4.8 EDS of milled Li ₂ CO ₃ powder using FIB.	. 51
Figure 4.9 SEM images of the nanomanipulator	. 53
Figure 4.10 Schematic showing formation of hollow morphology	. 54
Figure S4.11. SEM image of the battery after cycling with the cross section set-up.	. 58
Figure S4.12. EDS analysis showing presence of Li, C and O inside a dendrite which was brol	ken
in the SEM.	. 58
Figure S4.13. EDS analysis showing a comparison between Li anode surface, mossy and need	lle
dendrite.	. 59
Figure S4.14. Raman spectroscopy showing a comparison between fresh SPE, SPE after cyclin	ng,
and reference graphite.	. 60
Figure S4.15Raman spectroscopy of dendrites. A peak at 1856 cm-1 related to Li_2C_2 was	
observed in SPE	. 60
Figure 5.1 SEM images of the surface of the Li anode and SPE during cycling (scale bars	
representing 200 µm).	. 65
Figure 5.2 Cycling curve and SEM images obtained during cycling (scale bars representing 10)0
μm)	. 66
Figure 5.3 SEM images of the surface of the lithium showing isles.	. 69
Figure 5.4 Map of one isle on the anode surface (scale bars representing 100 µm)	. 69
Figure 5.5 SEM images of the isles that were milled using FIB.	. 70
Figure 5.6 Map of the cross section of an isle and a schematic showing isle formation	. 72
Figure 5.7 SEM images (corresponding to Supplementary Movie 2 and Supplementary Figure	;
5.12) of the polymer and a schematic showing dendrite growth.	. 74
Figure 5.8 EDS of the morphological change observed on the SPE close to the anode edge	. 75
Supplementary Figure 5.9 Panorama images obtained by stitching together SEM images	. 81
Supplementary Figure 5.10 SEM images of the anode. SEM images showing high number of	
dendrites in the vicinity of four isles at different regions of the anode.	. 81
Supplementary Figure 5.11 Mapping of a milled region of the polymer.	. 82
Supplementary Figure 5.12 Cycling curve and SEM images obtained during cycling (scale bar	ſS
representing 100 µm).	. 83
Figure 6.1 SEM images of the anode edge and SPE during cycling showing appearance of an	
surface separation on the anode, as seen in Video S2	. 91
Figure 6.2 Relationship between the change in the average distance (blue curve) of the surface)
separation with the voltage change (red curve) over time.	. 92
Figure 6.3 SEM images obtained after the experiment showing the dendrite morphologies	
observed during cycling.	. 93
Figure 6.4 EDS point analysis of the surface separation of the anode and the anode surface at	
different times.	. 94
Figure 6.5 Schematic of the cross-section of the battery before and after cycling	. 96
Figure 6.6 Line scan of the surface separation, as observed in Video S2	. 97

Figure 6.7 Comparison of the Li content of the surface separation region showing the expansion	on
of the surface as the result of charging.	98
Figure S6.8 Schematic of the <i>in situ</i> set up	103
Figure S6.9 F-ratio of Figure 6.4f-g from the manuscript.	103
Figure S6.10 SEM images of the anode surface showing the evolution of Li during cycling	
correlating to Figure 6.6 of the manuscript	104
Figure 7.1 Obtained cell SEM images corresponding to Video S1	110
Figure 7.2 SEM images of the cell with dendrites with mossy and needle morphologies on Li	at
the bottom side of LLZO formed when applied current has negative values	111
Figure 7.3 Mapping and schematic of Li thinning	113
Figure 7.4 SEM images of the cell corresponding to Video S2 at +20 μ A	117
Figure 7.5 EDS analysis of the needle dendrite in Figure 7.4	118
Figure 7.6 SEM images of Li surface after cycling showing dendrite growth initiation from	
LLZO surface on regions where Li was consumed.	119
Figure 7.7 SEM images of one dendrite on Li surface and high magnification of its different	
regions showing growth of new arms and formation of kinks	119
Figure 7.8 a) Cross-section mapping of LLZO under the Li electrode after cycling, showing	
inhomogeneous distribution of Zr, La, and C, b) Schematic of a cross-section of the top Li an	d
LLZO before and after cycling.	121
Figure S7.9 a) EIS plots at 25 and 80 °C and b) Arrenhius plot of LLZO pellet	126
Figure S7.10 Schematic of the set up	126
Figure S7.11 Cycling curve of the cell showing the time at which the current was changed	127
Figure S7.12 SEM images of the cell surface during cycling	127
Figure S7.13 SEM images of different areas of the Li after cycling showing growth of mossy	and
needle dendrites and bumps close to the regions where Li was consumed	128
Figure S7.14 SEM images of dendrites with different morphologies showing ability of dendri	tes
2, 3, and 4 to perforate through the Li in comparison to dendrite 1 which was pushing the Li u	ıр.
	128
Figure S7.15 EDS elemental mapping of the LLZO cross section before cycling	129

Chapter 1 Introduction

1.1 Motivation

Li-ion batteries are used in various applications including most consumer electronics devices: laptops and cell phones [1, 2]. The climate change phenomenon has also led to profound interest in battery technology, as substitutes for fossil fuels are sought, particularly in electric vehicles [1].

An optimal battery is cost-effective, safe, and has long life, and high capacity [1, 3]. While Liion batteries for electric vehicles have made great strides, these vehicles are still not affordable for all and have limited driving ranges [4]. Thus, further studies and improvements are needed for these batteries to fully replace fossil fuels.

One of the key components of Li ion batteries is the anode material. Lithium is a promising anode material owing to its high specific capacity of 3860 mAh g⁻¹, compared to its competing materials such as graphitic carbon with a specific capacity of 372 mAh g⁻¹ [5]. Even though Li has attractive properties as the anode material, it could undergo dendrite formation. These dendrites could get detached from the Li surface, produce "dead Li", and subsequently lower the battery efficiency [6]. Li is also an ultra-soft, highly reactive metal with low melting temperature [7, 8]. These properties, makes Li a difficult material to prepare for battery applications and also to characterize. Due to high reactivity, a protective layer, referred to as solid electrolyte interphase (SEI), is formed on the Li [1, 9]. However this layer could get damaged during cycling of the battery and expose the Li to the electrolyte which could result in preferential deposition and dendrite formation.

Dendrites could short-circuit the battery and lead to a possible explosion [10, 11]. Dendrite formation poses an even higher safety concern when in contact with a flammable liquid electrolyte [4]. Dendrite formation and growth could cause thermal runaway of the battery. Exothermic reactions take place in the battery as the result of temperature increase which releases oxygen and further temperature increase and could cause explosion in presence of flammable liquid electrolyte [12-14]. Therefore, it is crucial to investigate the formation and growth mechanism of the dendrites, to be able to suppress them and prolong the life of the battery.

Two methods that can be used to suppress dendrite growth are: applying pressure on the battery and using solid electrolytes. These methods could potentially lower the possibility of short circuit in the battery by not allowing the dendrites to grow along the electrolyte.

Polymers and ceramics could be used as solid electrolytes. Solid electrolytes not only eliminate the flammability of the liquid electrolytes, but also provide a mechanical barrier against dendrite growth [5, 15, 16]. Solid polyethylene oxide (PEO)-based polymer was first introduced by Armand et al. [17] as solid polymer electrolyte material. In 1979, Hydro Quebec used polymer electrolytes in Li-vanadium oxide batteries and from 1992, it was continued in partnership with 3M [2]. Electricité de France and Bolloré Technologies in collaboration with Schneider Electric, also manufactured batteries with polymer electrolytes [2]. All solid-state Li metal polymer batteries (30 kWh) were used by Bolloré group for the first time in plug-in vehicles (Bluecars) that provided a range of 250 km [5, 18, 19]. One of the drawbacks of using solid polymer electrolytes (SPE) is the required operating temperature of up to 80°C [5, 15]. It has also been shown that they still suffer from dendrite growth, especially at high cycling rates [10, 20, 21].

Ceramics are another possible electrolyte materials that have gained interest due to their high shear modulus to suppress dendrite growth. $Li_7La_3Zr_2O_{12}$ (LLZO) is a favorable electrolyte material for application in all-solid-state Li-metal batteries due to properties including low reactivity with Li, high conductivity and high shear modulus [22-24]. Although LLZO has shown great potential as a solid electrolyte, failure of batteries containing this electrolyte has been reported [25, 26].

Even though studies have been able to show failure of the batteries with polymer and ceramic electrolytes, further investigation is still needed to find the root cause of dendrite growth through the electrolyte and Li dissolution and deposition related to both mechanical and electrochemical aspects of the batteries. One effective method to investigate these batteries is *in-situ* scanning electron microscopy (SEM). However, Li characterization faces many challenges due to the

mentioned properties of this metal: ultra-softness, low melting point, high reactivity, and as well as low x-ray energy [7, 8, 27, 28]. To conduct *in situ* SEM a special set up is needed to be able to cycle the batteries at high temperatures (50°C-80°C) inside the microscope. A software is also required to be able to image the battery from beginning till the end of cycling. Batteries should be prepared in a dry room or a glove box and transferred to the SEM using a transfer holder that could minimize sample contamination.

Li characterization with SEM or focused ion beam (FIB) faces difficulties as well. The possibility of contamination must be taken into account when analyzing Li. The electron and the ion beam could also result in beam damage and possible sputtering [29]. FIB ion source could also be problematic. For example the Ga source produces intermetallic phases with Li [28]. These phases not only change the surface of the under study sample but also prevents further milling.

Chemical analysis using energy dispersive spectroscopy (EDS) has difficulties as well. Li has a low x-ray energy of 52 eV [3]. This low energy x-ray could get absorbed in the window of the EDS detector and not get detected. Generating Li x-ray is also difficult due to the low fluorescence yield.

1.2 Objective

The objective of this work is to study the failure of all-solid-state Li-metal batteries, as well as to optimize an *in-situ* and *ex-situ* SEM technique to conduct this study. For this study two solid-state electrolytes of PEO-based polymer and LLZO ceramic are investigated. The objectives include:

- 1. Optimize in-situ SEM battery cycling set-up
- 2. Optimize *ex-situ* characterization techniques to study morphology and chemical change of the battery after cycling
- 3. Investigate dendrite growth and failure of an all-solid-state Li-metal battery with polymer electrolyte
- 4. Investigate the failure mechanism when using LLZO ceramic electrolyte
- 5. Propose methods to hinder dendrite growth

This work consists of 7 chapters. Chapter 2 summarizes the basics of Li-ion batteries, their failure behavior, solid electrolytes, the microscopy techniques that are used to perform these studies, basics of scanning electron microcopy and their challenges. Chapter 3 explains the methods and material preparation used for the purpose of this study. Chapter 4 presents the results on the chemical analysis of the dendrites and effect of pressure on the polymer based Li-metal battery. Chapter 5 presents the results on the overall failure mechanism of the battery including Li dissolution and deposition and the effect of salt in polymer based Li-metal battery. Chapter 6 presents the morphological and chemical evolution of the Li surface during cycling and the effect of volume change. Chapter 7 presents the results on the failure of a cell containing LLZO electrolyte and a comparison between this electrolyte and polymer electrolyte. Chapter 8 summarizes the findings of this work, the contributions to the original knowledge, and the suggested future work.

Chapter 2 Literature Review

This chapter summarizes the basics of Li-ion batteries, their causes of failure and the potential solid electrolytes. It also presents the different microscopy techniques that have been employed to conduct *in situ* studies of these batteries. Furthermore it discusses the principals of scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) and the challenges faced in case of Li characterization.

2.1 Lithium-Ion Batteries

Li-ion batteries consist of three parts: anode (negative electrode), cathode (positive electrode), and an electrolyte that is electron insulator and ionic conductor [1]. Figure 2.1 shows a schematic of an all-solid-state Li-metal battery [18]. During charging electrons and Li⁺ move from the cathode to the anode through the exterior circuit and the electrolyte respectively, and Li is deposited on the anode surface. During discharge the reverse of this behavior occurs: which is Li dissolution on the anode. During the first cycle a passivation layer is formed on the anode surface called solid electrolyte interphase (SEI) as the result of the reactions between the anode and the electrolyte which is ionic conductive and electron insulator [1, 9]. This layer consists of various compounds including Li oxides, carbides, carbonates, fluorides, and chlorides [30]. The SEI layer stabilizes and further protects the surface of the anode during cycling. However this layer is prone to damage during cycling that could result in failure of the battery. The effects of the SEI damage is further discussed in section 2. 1. 1.

The electrolytes used in Li-ion batteries can be either liquid or solid [1]. Liquid electrolytes impose safety risks due to their flammability specially in case of Li dendrite formation [1]. Lithium also has high reactivity with liquid electrolytes [31]. Thus solid electrolytes have gained

attention to increase battery efficiency and safety. Solid electrolytes have high thermal stability and high chemical stability compared to liquid electrolytes [31]. A solid electrolyte must have high mechanical properties to withstand dendrite growth and also have high ionic conductivity [18]. Below two types of polymer and ceramic solid electrolytes are described in more details.



Figure 2.1 Schematic of an all-solid-state Li-metal battery showing the anode, cathode and electrolyte. The anode is the Li metal (negative electrode), the cathode is the LiFePO4 (positive electrode), and the solid-state electrolyte is polymer. During charge the electrons and Li ions move from the cathode to the anode through the outer circuit and the electrolyte respectively. During discharge the revers occurs (from the graphical abstract of reference [18]).

2.1.1 Battery Failure

Lithium deposition and dissolution is not always homogenous. It is possible to damage the SEI layer during the cycling of the battery [32]. Preferential Li deposition in these regions could result in dendrite formation and possible short circuit of the battery which causes safety concerns [6, 32]. As cycling continues, dendrites could become hollow and thus electrochemically inactive

resulting in their detachment from the Li electrode and formation of "dead Li" [6, 33, 34]. "Dead Li" lowers the efficiency and life of the battery [6].

Figure 2.2 shows a schematic of the basics of failure of a battery in 4 steps [35]. At the beginning of cycling the Li surface is covered with a uniform SEI layer. During Li deposition, the EI layer is damaged as the result of the anode volume expansion (step 1). These regions expose the Li surface to the electrolyte and are preferential regions for further Li deposition. Li deposits in the form of dendrites as deposition continues (step 2). During dissolution, these dendrites are detached form the surface and produces "dead Li" (step 3). Further cycling of the battery causes formation of more dead Li, thicker SEI layer and a porous electrode [35].



Figure 2.2 Schematic showing the failure of the battery in 4 steps including: SEI damage, dendrite formation, Li isolation, and the resulting dead Li and porous electrode. At the beginning a uniform SEI layer is covering the Li surface. During charge and Li deposition, cracks are formed on the SEI layer due to expansion. Further deposition results in formation of dendrites. During discharge the dendrites are detached from the surface. As cycling is continued the SEI layer becomes thicker, the Li electrode becomes porous and more dendrites are detached from the surface forming dead Li (adapted from Figure 1 in reference [35]).

The main cause of inhomogeneous Li deposition in batteries with polymer electrolytes is reported to be the inhomogeneous distribution of Li ions on the electrode surface caused by polymer deformation [36, 37]. Monroe and Newman [38] introduced a stability parameter for this phenomenon. The polymer electrolyte undergoes deformation during cycling. In case of positive stability parameter, deposition is faster on the peaks than the valleys of the deformed

surface which results in unstable deposition [38]. Positive values result in high exchange current densities at the peaks which causes dendrite growth in these regions [38]. In case of negative stability parameter the revers takes place. Deposition is faster in the valleys than the peaks of the deformed surface resulting in more stable deposition [38]. Monroe and Newman have also reported that if the shear modulus of the electrolyte is more than twice of the shear modulus of Li, a negative stability parameter and thus a stable electrodeposition is achieved [38].

The SEI layer deterioration during cycling also plays an important role in the formation of the dendrites [39]. An ideal SEI layer is homogenous, elastic, and has low resistance [40-42]. The more homogenous the SEI layer, the more uniform the Li deposition during charging [41, 42]. SEI layer's elastic behavior could withstand the volume change during charge and discharge and assist in uniform deposition [41, 42]. Lower ionic resistance of the SEI layer leads to easier movement of the Li ions through the layer [41, 42]. This layer, however, could get damaged during cycling and expose the Li surface to the electrolyte and result in inhomogeneous Li deposition. SEI deterioration could occur as the result of chemical inhomogeneities in the SEI and volume change [35, 40, 43].

Steiger et al. [40] suggested a dendrite formation and growth mechanism based on the defects. They described the defects as chemical inhomogeneities in the SEI layer (possible presence of inorganic crystals), regions with thin SEI layer, and grain boundaries [40]. They proposed Li deposition to preferably occur in these regions because of the uneven local conductivity [40]. Harry et al. [43] observed preferential Li deposition at the impurities located at the Li/electrolyte interface. They assumed that this behavior was due to the SEI layer deterioration in these regions which caused current localization [43]. Kushima et al. [33] reported that the dissolution begins from the newly formed whiskers due to the fact that they have thinner SEI layer showing that inhomogeneous SEI layer affects both deposition and dissolution.

Brissot et. al. [44] studied Li dendrite formation in a symmetrical Li polymer cell and correlated Li deposition to the ionic concentration in the vicinity of the anode. They reported that accumulation of cations near the anode results in a large electric field in this region causing a local space charge which promotes dendrite growth [45].

Dendrites have been investigated in many studies and the observed morphology at different applied current densities and temperatures has been described in different ways including: mossy, needle, whisker, multi-globular, "*dense eden-like clusters*", "*dense mushroom-shaped*", and "*jagged particulates*" [20, 21, 33, 43, 46-48]. Yamaki et al. [48] introduced the term whiskers for Li dendrites as they resemble the same morphology as tin whiskers which grow from the tip or the base and have high aspect ratio [40]. A whisker is referred to "a fibrous crystal" [40, 48]. The term dendrite, however, is referred to structures resembling snowflakes that grow from the tip and results in branching as they grow [40, 49].

Dendrite growth and the resulting short circuit of the battery could result in thermal runaway which imposes high safety risks for the battery. Thermal runaway occurs when the temperature of the battery rises due to dendrite formation, overcharging, external or internal short circuits which causes passing of large currents in the battery [12, 13]. This temperature increase causes exothermic reactions in the battery [12-14]. The possible exothermal reactions include: SEI decomposition, melting of the separator, Li anode reaction with the electrolyte, electrolyte decomposition, and cathode decomposition [12, 50]. These exothermic reactions not only further increase the temperature of the battery, but release oxygen [12]. This excess heat in the battery along with the released oxygen could cause explosion if a flammable electrolyte is used in the battery [12]. Chen and Evans [14] modeling results showed that thermal runaway could occur in the case of high cycling rates and in presence of a local heat source.

One method to suppress dendrite growth and increase battery efficiency is to apply pressure on the battery. Applying pressure could control Li deposition and the morphology of the dendrites. Hirai et al. [51] observed a more uniform Li deposition as the result of applying pressure that subsequently increased the cycling efficiency. Wilkinson et al. [52] observed a difference in the dendrite morphology in presence of pressure. Presence of high stack pressure resulted in a *"closed-packed column morphology"* and low pressure resulted in different morphologies including needle morphology [52]. Gireaud et al. [53] observed suppression in dendrite formation and increase in the cycling efficiency as the result of pressure. They, however, reported that dendrite formation could not be completely eliminated because of the inner microstructure defects in the Li [53].

Another method to hinder the growth of the dendrites is to use solid electrolytes with high shear modulus to impose pressure towards dendrite growth. Monroe and Newman [38] have reported that if the shear modulus of the electrolyte is twice that of Li, dendrite growth could be hindered. Even though high shear modulus electrolytes have been suggested to suppress dendrite growth, studies have shown that even in the case of ceramics which fulfill the Monroe and Newman shear modulus criterion, short circuit of the batteries is still observed [26, 54-56]. This is an indication of the fact that just applying pressure on the battery cannot fully eliminate formation of the dendrites. These studies are further discussed in section 2.1.3.

2.1.2 Polymer Electrolytes

Using solid polymer electrolytes (SPE) was first introduced by Armand et al. [17]. To produce these electrolytes, a salt containing Li is dissolved in a polymer with high-molecular-weight [57]. Solid polymer electrolytes pose high mechanical properties compared to liquid electrolytes that could suppress dendrite growth and they also eliminate the flammability of liquid electrolytes [15, 18]. Their ability to deform also is an attractive quality since it can lower the effect of anode and cathode volume change during cycling [15]. In general an optimum polymer electrolyte must be electrochemically, chemically, and thermally stable, have Li salt solubility, and have high ionic conductivity and mechanical properties [57]. Poly(ethylene oxide) (PEO) polyether based polymers are widely used SPEs due to their low glass transition temperature, high Li salt dissolution, and high ionic conductivity at temperatures above 70°C [17, 18, 58]. The most common Li salt used in SPE is lithium bis(trifluoromethanesulfonyl)imide (Li[N(SO₂CF₃)₂], LiTFSI) [59, 60]. LiTFSI in ether solvent has high transference number which result in long battery cycle life at high currents [61]. Suo et al. [62] reported a more stabilized Li surface when using solvent–in–salt (4M LiTFSI in DME/DOL). This method, however, cannot be used in PEO:LiTFSI because of the low salt solubility.

The drawback of SPE is the fact that for them to exhibit high ionic conductivity, they need to be operated at temperatures up to 80°C [5, 15]. The conductivity of the PEO-based solid polymer electrolytes at high temperatures is from 10^{-4} to 10^{-3} S/cm [2]. Batteries containing polymer

electrolytes and Li metal should also be cycled at low C-rates in order to avoid dendrite formation [5].

Studies have shown that even though PEO-based polymers have attractive properties as solid polymer electrolytes, batteries containing polymers still could undergo dendrite formation. Rosso et al. [10] observed short circuit of a battery as the result of dendrite formation. Dolle et al. [20] and Orsini et al. [21] also showed presence of dendrite in the case of polymer electrolytes.

Other challenges facing the use of SPEs are possible salt and polymer decomposition. Eshetu et al. [59] reported two LiTFSI salt reduction mechanisms by Li. Chao et al. [63] also reported salt decomposition with x-ray photoelectron microscopy (XPS). They observed a more sever salt decomposition in the SPE in case of batteries with graphite in comparison with Li [63]. Galluzzo et al. [64] have also shown the Li dissolution and diffusion in the polymer. The resulting Li⁺ and the free electron in the polymer may result in salt reduction. Salt decomposition could result in inhomogeneous Li deposition during cycling. Commarieu et al. [65] also reported polycarbonate solid electrolytes decomposition in contact with Li.

2.1.3 Ceramic Electrolytes

Ceramics have high shear modulus that makes them great candidates as solid electrolytes for battery applications. In case of ceramic electrolytes no salt is used, that eliminates the complications related to possible salt decomposition during cycling [59]. They also have higher Li^+ transfer number than polymers [66]. An ideal ceramic material to be used as solid electrolyte in Li ion batteries should have high Li ion transfer number (close to 1), high chemical stability when in contact with the anode and the cathode, high voltage stability, low charge transfer resistance at the electrode interface, and cost effective preparation techniques [67]. Among different ceramics, $Li_7La_3Zr_2O_{12}$ (LLZO) is an attractive solid electrolyte [15]. The properties that have made LLZO a potential candidate include: its high ionic conductivity at low temperature (> 1 10⁻⁴ S/cm), high shear modulus, low reactivity with Li, and high voltage stability [22-24, 68, 69].

Based on Monroe and Newman [38] studies, for an electrolyte to be able to hinder dendrite growth, a shear modulus of twice that of Li is needed. LLZO has shear modulus of 55 GPa and Li has shear modulus of 3.4 GPa, which makes LLZO fall within the Monroe and Newman criterion [24, 36, 69]. However they still suffer from dendrite growth. Li can propagate through the grain boundaries or porosities and result in short circuit of the battery [25, 54, 56, 70]. An uneven contact between the electrodes could also result in inhomogeneous Li deposition and dissolution [71].

Porz et al. [54] reported that Li could penetrate through the defects of the electrolyte at high current densities during charging and cause short circuit of the batteries. They indicated their observations not to correlate to the Monroe and Newman shear modulus model and to be related to the morphology of the electrolyte [54]. Basappa et al. [55] studied the effect of grain boundaries of Li_{6.5}La₃Zr_{1.5}Ta_{0.5}O₁₂ (LLZT) pellet on the call short circuit and analyzed the microstructure with SEM, scanning transmission electron microscope (STEM), and EDS. They reported the pore interconnectivity to cause short circuit of the cells and showed that grain boundary modifications could enable the cells to be cycled at higher current densities [55]. Shen et al. [26] also reported the interconnected pores in LLZO to result in short circuit of the cells using synchrotron x-ray tomography. They observed that the temperature increase results in a decrease in the porosity but increases the pore connectivity [26]. Aguesse et al. [25] also indicated the collapse of batteries with LLZO electrolyte to be the result of Li metal formation in the depth of the electrolyte using SEM and solid-state NMR. Cheng et al. [56] showed the Li plating in the grain boundaries of the cross section of Li_{6.25}Al_{0.25}La₃Zr₂O₁₂ (LLZO) using SEM and FIB milling after cell short circuit which caused fracture of the grains. Marbella et al. [71] investigated the behavior of a symmetrical Li cell with Li_{6.5}La₃Zr_{1.5}Ta_{0.5}O₁₂ electrolyte using SEM and NMR. They observed inhomogeneous Li deposition and dissolution and correlated this phenomenon to the uneven contact between the electrodes [71].

To be able to effectively hinder dendrite growth both mechanical and electrochemical properties of the electrolyte must be considered [36]. To do so, Tikekar et al. [36] suggested three methods of: immobilizing the anions, using high shear modulus electrolytes, and cycling at low current densities.

Even though studies have been done on the behavior of ceramic solid electrolytes during cycling, further investigations is still needed to fully understand the failure mechanism of these batteries from the beginning of cycling until the end, including the microstructural and chemical evolution of the battery.

2. 2 In Situ Microscopy Techniques for Li-Ion Battery Studies

In situ microscopy techniques are effective methods to obtain details about the failure mechanism of Li ion batteries, and microstructure and chemical evolution during cycling. *In situ* analysis provides more information about the cycling behavior of a battery compared to ex situ studies. *In situ* microscopy is capable of showing the complete behavior of the battery from the beginning till the end of cycling. In this section the capabilities of different *in situ* microscopy techniques including: confocal and optical microscopy, transmission electron microscopy (TEM), and scanning electron microscopy (SEM), their pros and cons, and figures showing the type of results they provide during battery cycling are summarized.

2. 2. 1 In Situ Confocal and Optical Microscopy

In situ confocal and optical microscopy has provided information about the growth of dendrites, short circuit of battery, different dendrite morphologies, and the effect of temperature and applied current which will be discussed in this section [40, 46, 47, 72, 73]. These studies focus on the behavior of the cells with liquid electrolytes and dendrite formation during Li electrodeposition [40, 46, 47, 72, 73]. Steiger et al. [40] investigated the dendrite growth mechanism during Li electrodeposition on tungsten using *in situ* light microscopy. They reported formation of dendrites with needle morphologies with non-uniform tips [40]. They suggested the initiation of dendrites to be from the defects on the surface, and described these defects as regions with thin SEI layer, grain boundaries, and regions with inhomogeneous chemical composition [40]. They also suggested the growth to be the result of deposition of Li at the base,

kinks, and tip of the dendrites [40]. Figure 2.3 shows the images obtained during in situ cycling [40]. Wood et al. [72] showed the relation between voltage variations with time and "reaction pathways" and the Li deposition and dissolution in a symmetrical Li cell using *in situ* optical microscopy. They showed formation of dendrites on the electrodes and the pitting occurred in the bulk of the electrode as the result of dissolution in these regions [72]. Love et al. [47] investigated the effect of temperature on dendrite growth in a symmetrical Li⁰|Li⁰ cell using *in* situ optical microscopy. The increase in the temperature, increased the initiation dendrite formation time and decreased the number of the dendrites [47]. They also observed three dendrite morphologies of "dense mushroom-shaped", "jagged particulates", and "thin needlelike wires and films" at different temperatures [47]. Nishikawa et al. [46] observed Li electrodeposition behavior on Ni using in situ laser scanning confocal microscopy. They described the observed dendrite morphology as whiskerlike which exhibited a swinging movement during electrodeposition [46]. The residual stress at the Li and SEI layer interface was indicated as the cause for this movement [46]. Stark et al. [73] reported dendrite growth from the tip and the base and formation of the kinks with *in situ* optical microscopy. They indicated the tip growth to be the result of electrochemical reactions and the base growth to be in fact the extrusion of Li as the result of pressure buildup under the SEI layer [73]. Their observation showed greater growth from the tip compared to the walls of the dendrites [73]. They suggested that the dendrites have a crystal structure and that the kink formation in the dendrites is the result of the defects in this structure [73].



Figure 2.3 Light microscopy images of a needle morphology dendrite growth obtained during *in situ* cycling. The section of the dendrite that is illustrated with white lines stays constant during charging and growth takes place from the base. The arrows indicate formation of a kink. Images are obtained after b) 15 s, c) 180 s, and d) 450 s after image a (figure 3 from reference [40]).

The pros of *in situ* optical and confocal microscopy methods are the fact that they are relatively easier to use compared to electron microscopes and they can be used to study batteries with both liquid and solid electrolytes [74]. The cons of these methods are the low resolution (sub-µm range), the need for an optically transparent window, and no capability of conducting chemical analysis [74].

2. 2. 2 In Situ Transmission Electron Microscopy

In situ TEM has the capability of providing more details about the behavior of a Li ion battery during cycling compared to *in situ* confocal and optical microscopy due to its higher resolution and the ability to conduct chemical analysis. Kushima et al. [33] reported two morphologies of whiskers and "*dense Eden-like clusters*" using *in situ* TEM that were observed at large and small overpotentials respectively during Li electrodeposition on a gold substrate. They indicated

whisker growth from the base to be the result of accumulation and release of stress caused by Li deposition in these regions [33]. They showed the dissolution to begin from the newly formed regions of the whiskers due to the fact that they were covered with thinner SEI layers [33]. Further dissolution resulted in hollowing out of the whiskers and formation of "dead Li" [33]. Figure 2.4 shows TEM images obtained during electrodeposition of Li on gold which shows whiskers growth [33]. Ghassemi et al. [75] captured the Li fiber initiation, growth, formation of kinks in the fiber, and dead Li using *in situ* TEM as well. The growth direction was reported to be parallel to the applied electric field [75].



Figure 2.4 TEM images obtained during electrodeposition of Li on gold. Images obtained at different times during cycling showing the growth of the whiskers (figure 2a from reference [33]).

The pros of using TEM to study Li ion batteries are its high resolution, and their ability to conduct chemical analysis [74]. The cons of this technique are the difficult sample preparation procedures, the sample size limitation, and high beam damage due to high beam energies [74, 76].

2. 2. 3 In Situ Scanning Electron Microscopy

Sample preparation for *in situ* SEM studies does not face the challenges that are encountered when using TEM. In situ SEM can also provide chemical analysis unlike optical and confocal microscopy. Thus in situ SEM has been widely used to study Li ion batteries. Dolle et al. [20] investigated the effect of applied current density on the morphology of the dendrite in a Li polymer battery using in situ SEM. They observed dendrites with needle morphology at higher current density, and dendrites with mossy morphology at lower current density [20]. They also captured short circuit of the cell as the result of dendrite growth through the polymer [20]. Figure 2.5 shows the different morphologies that were reported in this study using SEM [20]. Orsini et al. [21] also reported the same correlation between the dendrite morphology and applied current density. Hovington et al. [5] observed formation of isles on the anode as well as solid polymer electrolyte bridges in an all-solid-sate Li-metal battery as the result of cycling using *in situ* SEM. They also monitored the thickness change of the anode, cathode, and polymer electrolyte during cycling. Harry et al. [43] observed formation of a "multi-globular structure" on the cross section of a symmetrical Li cell with polymer electrolytes during cycling using in situ SEM. They reported this structure to have initiated from impurities in the interface of the Li electrode and the polymer electrolyte [43]. Their growth mechanism suggested that inhomogeneity in the SEI layer where these impurities were observed resulted in the formation of these structures [43]. These structures were milled using FIB and then chemical analysis was conducted on these regions using EDS. The mapping results showed presence of electrolyte in these structures [43]. They reported the white regions of the EDS map as Li due to the fact that no signal was detected in these regions [43].



Figure 2.5 SEM images of different dendrite morphologies. (a) Mossy morphology in Li/polymer battery (b) needle morphology in Li/polymer battery, and (c) needle morphology deposited on Cu substrate (adapted from figures 3 and 4 of reference [20]).

The pros of using SEM for *in situ* analysis of batteries are its high resolution, ability to conduct chemical analysis, and study batteries with bigger sizes than the ones used for *in situ* TEM studies [74]. The cons of this method are the need for a specialized set up to study batteries with liquid electrolyte (because of the vacuum), and beam damage [74]. Even though SEM faces some challenges, it is an optimum technique to be used for *in situ* investigations of all-solid-state Li-metal batteries. Sample preparation is easy for these studies compared to the sample preparation requirements for TEM. The observed beam damage in SEM is less than TEM due to using lower beam energies [76]. It is also a more attractive technique than optical and confocal microscopy because of its capability to conduct chemical analysis and higher resolution. *In situ* SEM is used in this study to investigate all-solid-sate Li-metal batteries. Next chapter explains the principals of SEM.

2. 3 Scanning Electron Microscopy – Focused Ion Beam

Among the *in situ* techniques summarized earlier in this chapter to study Li-ion batteries, *in situ* scanning electron microscopy has shown promising capabilities and results. In this work *in situ* SEM is used to investigate the behavior of the batteries during cycling. A FIB-SEM is also used to conduct *ex situ* analysis. In this chapter principals of these two techniques and the challenges that are faced when studying samples containing Li are discussed.

2. 3. 1 Principles of Scanning Electron Microscopy

A scanning electron microscope is consisted of an electron column and a control console [77]. Figure 2.6a shows a schematic of an electron column that consists of: an electron gun, electron lenses, apertures, scan coils, and a detector [77]. The electron gun produces the electron beam with an energy in the range of 0.1 KeV to 30 KeV [77]. The electron lenses demagnify the electron beam to produce a beam with a small spot size on the sample [77]. Aperture controls the beam convergence angle which subsequently controls the lens aberrations and the scan coils deflect the beam in a way that the beam scans the sample line by line at specific points [77]. The detector converts the signals collected from the sample to "*point-by-point intensity changes*" on the screen [77].

The signals that are produced as the result of electron beam interaction with the sample are divided into the following categories: secondary electron (SE), backscattered electrons (BSE), SE2, SE3, and SE4. It is crucial to know the origin of these signals in order to better understand the information that they provide about the sample. Secondary electrons are the result of the inelastic scattering of the electrons which undergo energy loss [77]. SEs provide topographic contrast information mainly from the surface of the sample [77]. Backscattered electrons are the result of the result of the elastic scattering of the electrons which do not lose energy and provide composition

contrast information [77]. Brighter regions on the image are an indication of heavier elements in the sample due to the fact that they produce more BSEs and darker regions are an indication of lighter elements [77]. SE2 and SE3 are produced as the result of further collision of BSEs in the sample and with the chamber walls respectively, that generate SEs and SE4 are produced in the aperture of the SEM [77].

The parameters that affect the images obtained with a SEM are: accelerating voltage (V), probe current (i_p) , probe diameter (d_p) and convergence angle (α_p) (Figure 2.6b shows a schematic of these parameters) [77].



Figure 2.6 Schematic of the electron beam column and the beam parameters. a) Schematic of a SEM electron column showing the different components: an electron gun, electron lenses, apertures, scan coils, and a detector, b) schematic of beam parameters: accelerating voltage (V), probe current (i_p), probe diameter (d_p) and convergence angle (α_p) (figure 2.2 and 2.5 of reference [77]).

These parameters correlate to the imaging modes of: resolution, high-current, depth-of-focus, and low voltage modes [77]. The resolution mode correlates to the probe size: to be able to observe a feature, the probe size has to be equal or smaller than that feature [77]. The high current mode is defined through the probe current and probe size: to have a strong signal when imaging, high enough current is required. A high probe current result in more signal but

increases the probe size which lowers the resolution and Smaller probe size results in higher resolution but lowers the probe current and the signal [77]. Therefore, optimum probe current and probe size is needed to obtain enough signal, good resolution, and less noise in the image. The depth of focus mode depends on the convergence angle: smaller angles provide higher depth of focus [77]. The low voltage mode depends on the beam accelerating voltage: lower voltages provide more information about the surface of the sample compared to higher voltages [77]. Higher voltages result in higher beam penetration depth in the sample which provides information about the depth [77]. The correlation between these parameters is explained with the term brightness (β) that is shown in Equation 1 [77].

$$\beta = \frac{current}{area. solid angle} = \frac{4i_p}{\pi^2 d_p^2 \alpha_p^2}$$
 Equation 1

Brightness has a constant value for each SEM electron gun and column [77]. All these four parameters must be taken into consideration when imaging a sample according to the information that is required and the type of the sample under study.

2. 3. 2 Principles of Focused Ion Beam

A focused ion beam (FIB) is primarily used to prepare thin lamellas for TEM studies [78]. It can also be used to extract more information about the depth of the sample through milling and exposing the interior regions of the sample to further analysis or for conducting chemical analysis using Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) [79]. Figure 2.7 shows a schematic of different components of a FIB column: a liquid metal ion source (LMIS), extractor, apertures, condenser lens (lens 1), objective lens (lens 2), beam blankers, and deflection octopole [80]. LMIS produces the primary ions during analysis. The LMIS contains a reservoir with the metal source material and a tungsten (W) needle [80]. Gallium is the most popular metal source due to its properties such as: low melting temperature, viscosity, high mechanical behavior, and having a small energy spread [80]. In a FIB column, the liquid gallium wets the W needle and a "Taylor cone" shaped gallium is created as the result of the electric

field at the needle [80]. This "Taylor cone" shaped gallium is extracted by the extraction voltage and is ionized and accelerated in the column through a potential [80]. Condenser lens (lens 1) and objective lens (lens 2), form the probe and focus the beam respectively and the apertures indicate the probe size and ion currents [80]. Beam blankers deflect the beam from the column center, and the cylindrical octopole lenses control the deflection and alignment of the beam as well as the astigmatism correction, and finally the ions bombard the specimen surface and emit the secondary species from the specimen [80].



Figure 2.7 Schematic of the components of a FIB column. A liquid metal ion source (LMIS), extractor, apertures, condenser lens (lens 1), objective lens (lens 2), beam blankers, and deflection octopole (figure 3 of reference [80]).

Figure 2.8 shows the ion-sample interaction and the sputtering process that result in milling of the sample [80]. When the primary ions enter the sample, they could undergo elastic or inelastic collisions. As the result of elastic collisions, the ions could transfer their momentum to the atoms of the sample under study and provided that this kinetic energy is greater than the surface binding energy at the surface of the sample, the atom can be sputtered from the sample which could be used to produce an image or could be used for the purpose of mass analyzing when conducing chemical analysis [80]. The inelastic collisions could produce phonons, plasmons, and
secondary electrons [80]. Secondary electrons are used for imaging. The primary ion is implanted in the sample provided that it is not backscattered out [80]. FIB can be used to mill a wide range of materials with high precision in a relatively short time [78].



Figure 2.8 Schematic showing the ion-sample interaction and the sputtering process. After the primary ions enter the sample they can undergo elastic or inelastic scattering. The elastic scattering, transfers the energy of the ions to the atoms and these atoms can leave the sample if this energy is higher than the surface binding energy. The inelastic scattering results in generation of secondary electrons (figure 2-1 of reference [80]).

An electron column can be coupled with an ion column to produce a dual-beam microscope (FIB-SEM). A dual-beam microscope overcomes the challenges of using only an ion column which are: milling and imaging using the ion beam results in surface damage of the sample and also generates low resolution images [80]. Using a dual-beam microscope, the electron beam can be used to conduct the imaging and thus reduce the beam damage and produce high resolution images [80]. In a typical dual-beam system the electron and ion columns are vertical and tilted respectively [80]. For the first time, Hovington et. al. [27] used a dual-beam microscope for Li detection. This microscope is equipped with a TOF-SIMS detector (Tescan and TOFWERK) and a windowless EDS detector (Oxford Instruments NanoAnalysis). They were able to detect Li in LiFePO4 using TOF-SIMS and detect Li K peak in pure Li (Hydro-Quebec) and Li_xS_{1-x}

polysulfide using the windowless EDS detector (this EDS detector is discussed in section 2.4.1) [27].

2. 3. 3 Challenges of Lithium Electron Microscopy Characterization

Using FIB-SEM to analyze properties and behaviors of materials require an understanding of how these techniques work and the underlying process by which the data are produced. Analyzing certain materials, including Li, using these techniques however, face many challenges that could affect the characterization process. The challenges that are encountered when characterizing Li samples are summarized in this section.

Lithium sample preparation

Li is an ultra-soft material which makes it difficult to prepare Li samples for microscopy characterizations using widely used techniques such as mechanical polishing [7]. The particles used in the mechanical polishing could remain in the Li sample after polishing and affect the characterization of the samples [7]. Techniques that can be used to prepare a flat Li surface include: Ar^+ ion milling machines or FIB-SEM. Li sample preparations using these techniques still should be carried out following specific protocols to minimize melting of the sample (Li has very low melting point of 180.6 °C), contamination, or beam damage [7, 28].

Lithium electron beam damage

The effects that an electron beam could have upon impinging on the sample should be taken into account when studying different materials using electron microscopy. These effects include: *"heating, electrostatic charging, ionization damage (radiolysis), displacement damage, sputtering, and contamination*" [76]. Egerton et al. [76] classified these beam damages into two groups based on the elastic and inelastic scattering of the electrons. The elastic scattering could cause atomic displacement or surface atom sputtering. The inelastic scattering could cause radiolysis that either changes the structure or results in mass loss [76]. Atomic displacement occurs when the incident beam energy is higher than the material displacement energy and results in the displacement of the atomic nuclei and deteriorates the crystal structure and this

atomic displacement could also occur when a metal is bombarded with ions [76]. Sputtering takes place as the result of high-angle elastic scattering on the surface of the sample and causes the atoms on the surface to leave the sample and the electron-beam heating takes place when the electron beam energy is transferred to the atomic electrons as the result of their interaction which results in a local temperature increase [76]. In the case of electrically-insulating materials, electrostatic charging could take place as the result of both elastic and inelastic scattering [76]. Radiolysis or ionization damage deteriorates the sample through crystallinity or mass loss and the damage severity depends on the energy per unit volume [76, 81].

These beam related sample damages could be decreased through different techniques: to reduce the effects of radiolysis damage in the sample, the temperature of the sample holder could be lowered using liquid nitrogen, to reduce the effects of knock-on damage, a lower accelerating voltage could be used, and to reduce the local temperature increase or charging, a lower beam current could be used [81]. All the above possible beam damages must be considered when analyzing Li specimens and the obtained data to lower the damages.

Lithium contamination

Li metal has high reactivity with oxygen, hydrogen, carbon dioxide and nitrogen [8]. Therefore, in order to minimize sample contamination, Li sample preparations and characterizations must be carried out in an inert environment or under vacuum [7, 8]. The sample preparation can be conducted in a dry room or a glove box and a transfer holder is needed to minimize contamination during transferring the sample to the microscope. C and O contamination in the SEM chamber is also possible [82, 83]. C sources in the chamber are hydrocarbons in pump oils, vacuum grease, O-rings, and the sample itself [76, 84, 85]. When the electron beam impinge on the surface of the sample, it polymerizes the hydrocarbons and produces a C coating on the surface [85]. The O source in the SEM chamber is the residuals of water molecules adsorbed on the surface of the sample [85]. O contamination on Li samples could produce lithium oxide [86]. Bessette et al. [87] monitored the O and C pick up rate on the Li sample surface in the SEM chamber at different temperatures. They reported high amounts of O pick up on the surface in less than 20 min and almost no C pick up [87]. Characterization should be conducted in an ultrahigh vacuum or at cryogenic temperature in order to avoid contamination [82, 85].

Lithium characterization using gallium primary ion source FIB challenges

The implantation of the primary ions, used in FIB characterization, in the sample could damage the sample. Implantation of the ions could result in amorphization, intermetallic phase production, or microstructural change [78]. In FIB analysis, the specimen atoms produce a collision cascade when the primary ions enter the sample [80]. Provided that enough momentum is transferred to the atoms at the surface of the sample, sputtering and formation of an amorphous phase on the surface could take place [80]. Bessette et al. [88] showed the effect of amorphization when analyzing Li_xNi_yCo_wMn_zO₂ cathode using time-of-flight secondary ion mass spectrometry (TOF-SIMS) with a gallium source FIB. The FIB SE images before the analysis showed the secondary and primary grains with high contrast, whereas the FIB SE images after the analysis showed contrast loss in the primary grains [88].

Gallium source FIB could also result in formation of intermetallic phases during analysis [78]. Li characterization using gallium source FIB could result in the formation of these phases. These phases are shown in the Ga-Li phase diagram, Figure 2.9Figure 2.9 [28]. The phase diagram shows two eutectic points of: 1) Liq \leftrightarrow Ga₁₄Li₃ + Ga and 2) Liq \leftrightarrow GaLi₂ + Li [28, 89]. The first eutectic was indicated at 29°C, 0.002 at.% Li by Okamoto [28], and at 28°C, 0.001 at.% Li by Azza et. al. [89]. The second eutectic was indicated at 166°C, 0.980 at.% Li and at 164°C, 0.980 at.% Li by Okamoto and by Azza et. al. respectively [28, 89].



Figure 2.9 Phase diagram of Ga-Li (figure 1 of reference [28]).

The Ga eutectic formation during milling of the sample using FIB could change the chemistry and surface morphology and could prevent milling of the sample once this phase is formed [90, 91]. Bessette et al. [90] have shown that using FIB for Li studies at cryogenic temperature may delay the formation of the eutectic phase but cannot fully eliminate this phenomenon. Therefore, detecting Ga from TOF-SIMS analysis or EDS on the regions that have been milled using FIB for Li samples is inevitable, which must be considered when analyzing the results. In order to enhance the milling process using FIB, other primary ion sources including Ar and Xe plasma ions could be used [92].

Another challenge that is faced when using FIB is the increase in the local temperature of the sample on the region where the collision cascade has occurred which could result in melting of the sample [80, 93]. To reduce the damage and melting of the sample, the experiments could be conducted at cryogenic temperature [94].

2. 4 Chemical Analysis

Energy dispersive spectroscopy (EDS) is one of the widely used methods to conduct chemical analysis. In this work EDS is used to provide chemical information during and after battery cycling. The principals of this method and challenges faced when using EDS to analyze Li is explained in this section.

2. 4. 2 Principles of Energy Dispersive Spectroscopy

Energy dispersive spectroscopy method is based on generation of x-rays in the sample and their detection after exiting the sample. When the electron beam collides with the sample, it removes an electron from an inner shell of an atom. Subsequently an electron from an outer shell fills this vacancy and produces an x-ray that has an energy equal to the difference of the energies of these shells. There are two types of x-rays: continuous (bremsstrahlung) and characteristic [77]. The continuous x-ray is produced as the result of deceleration of the electron beam by the atoms and the characteristic x-ray is produced as the result of removing an electron from the atom and subsequent filling of the vacancy [77]. Continuous and characteristic x-rays provide the background of the spectrum and the chemical information about the sample respectively [77]. Another possibility other than the generation of an x-ray is the generation of an Auger electron. The energy difference of the two shells can also remove another electron from the outer shell and produce Auger electron [77]. The probability of production of an x-ray is given as the fluorescence yield (ω) that depends on the atomic number [77, 95]. Higher atomic numbers result in higher fluorescence yields [77, 95]. Figure 2.10 shows a schematic of the process of Auger electron and x-ray photon generation in a neon atom [77].



Figure 2.10 Schematic of the process of excitation of a neon atom and generation of an Auger electron and an x-ray photon. When the primary electron removes an electron from an inner shell of the atom, a vacancy is formed in the inner shell. As the result an electron from an outer shell fills this vacancy which could result in occurrence of two events: emission of an x-ray or an auger electron (figure 6.5 of reference [77]).

Figure 2.11 shows a schematic of different parts of an EDS detector [96]. The main components of an EDS detector are: "*the x-ray detector, the window, preamplifier, amplifier, and multichannel analyzer (MCA)*". The generated x-ray photons from the sample get absorbed by the Li-drifted silicon detector through the beryllium window during EDS analysis. Thereafter, the photoelectrons are emitted that form electron-hole pairs which create a charge pulse as the result of the applied bias. The preamplifier and the amplifier convert the charge pulse to a voltage pulse and amplifies the signal respectively. Ultimately the multichannel analyzer organizes these pulses based on their voltage [96].

To quantify the EDS results, the term k ratio (k_i) was introduced by Castaing (1951) [77], which shows the relation between the concentrations and intensities of the elements in the under study sample and a standard (Equation 2 [77]). A standard sample is described as a sample that is uniform with a specific chemical composition that is known [77].

$$\frac{C_i}{C_{(i)}} = \frac{I_i}{I_{(i)}} = k_i$$
 Equation 2

In this equation: C_i is the concentration and I_i is the intensity of element i in the sample, and $C_{(i)}$ is the concentration and $I_{(i)}$ is the intensity from the standard [77].



Figure 2.11 Schematic of different parts of an EDS detector. The x-ray detector, the window, preamplifier, amplifier, and multichannel analyzer (MCA) (figure 5.15 of reference [96]).

The matrix effects of atomic number (Z_i), x-ray absorption (A_i) and x-ray fluorescence (F_i) in the sample however, result in a deviation in the above equation and, are used to correct Equation 2 as Equation 3 [77].

$$\frac{C_i}{C_{(i)}} = [ZAF]_i \frac{I_i}{I_{(i)}} = [ZAF]_i \times k_i$$
 Equation 3

The atomic number effect is explained with two parameters of backscattering (R) and energy loss (S). A low number of x-rays are generated when the sample has a high atomic number since: when the specimen has a higher atomic number than the standard, the electrons generate BSE rather than x-rays, as well as the fact that high atomic numbers result in high electrons energy loss that produces less x-rays due to the fact that the electrons will not have enough energy to ionize the atoms [77]. If the energy of the x-ray is greater than the ionization energy of the atoms, the atoms are further ionized and thus result in x-ray absorption [77]. These secondary x-rays are referred to as x-ray fluorescence that affect the intensity of the x-rays [77].

Finding standards for all samples with the same conditions to conduct quantitative analysis is challenging. Cliff and Lorimer [97] introduced a standardless method for thin samples with no absorption and fluorescence effects. In the Cliff and Lorimer method rather than using a standard, x-rays from different elements in the specimen itself is considered [97]. Horny et al. [98] introduced a standardless method (f-ratio) for thick samples similar to the Cliff and Lorimer method. In this method the intensity of each element is normalized by the total intensities of all the elements in the sample [98].

2. 4. 1 Challenges of Lithium X-ray Detection and Quantitative Analysis

Conducting chemical analysis on Li samples using EDS faces many challenges that need to be addressed when studying these specimens. These challenges are discussed in this section.

Lithium X-ray generation

The first challenge is generating high enough signals to conduct quantitative analysis. Lithium has a low fluorescence yield of the order of 10^{-4} which is an indication of low x-ray generation probability as the result of electron beam interaction with the sample [99]. To obtain enough signals, a large beam current could be used due to the fact that only a small part of the electron beam and sample interaction produces x-rays [77]. In case of Li samples, however, a large current could damage the sample and result in sputtering as discussed in section 2. 3. 4 [29, 100]. Thus during characterization of samples containing Li, and optimum current must be used in order to minimize the beam damage and obtain enough signals.

Lithium X-ray detection

Another challenge is the ability to detect the generated Li x-rays. Li has low x-ray energy of 52 eV and cannot be detected using the standard EDS detectors due to the fact that x-rays with energies close to 55 eV are absorbed in the window of these detectors [3, 27]. To overcome this limitation, Hovington et. al. [3] used a windowless EDS detector with extreme electronics (Oxford Instruments) to detect Li K in Li binary compounds. This detector eliminates the limitation of x-ray absorption by the window [3, 101]. These detectors also have low noise

extreme electronics and optimized signal processing to increase the detection capabilities specially for low energy x-rays to be able to differentiate the low energy x-rays and the noise peak [3, 101]. Hovington et al. [29] comparison of the detection capabilities of two detectors, one with enhanced electronics and the other with the original electronics, showed a 250% more Li K peak signal in case of enhanced electronics, Figure 2.12.



Figure 2.12 Comparison of EDS Li x-ray detection using standard electronics (red) and optimized electronics (yellow) (figure 1 of reference [29]).

Lithium X-ray in compounds

Li x-ray generation is particularly difficult when studying compounds. This is due to the fact that Li has one valence electron which produces the x-ray and participates in the chemical bond of the compound as well, thus in some compounds, it might not be possible to detect Li [3, 101, 102]. To examine the possibility of Li detection in compounds, Hovington et al. [3] conducted a comparison between theoretical Li x-ray detection using Monte Carlo x-ray program in some binary compounds with the experimental data obtained using the windowless EDS detector. They reported a difference of Li K k-ratio with a factor of 3 obtained from the two methods [3]. They showed, for the first time, the detection of Li K x-rays in binary compounds using EDS.

Lithium EDS analysis accelerating voltage

Another parameter that must be chosen carefully when conducting chemical analysis on Li using EDS, is the accelerating voltage. High accelerating voltages provide more x-rays, but electron beam travels deeper in the sample and provide the x-rays from the depth of the sample [3]. Thus

the possibility of Li x-ray absorption in the sample increases [3]. Hovington et al. [3] reported accelerating voltage of 5kV for: Li, LiH, Li₂S, and LiCl to be able to detect Li x-rays.

In this work the same windowless EDS detector with extreme electronics (Oxford Instruments) used in Hovington et al. [3] work at Hydro Quebec is used to conduct chemical analysis on the batteries.

Chapter 3 Methodology

In this chapter a summary of the methodology of this work is given. The two microscopes that are used for *in situ* and *ex situ* analysis are explained along with the *in situ* set up and software. The sample handling during preparation and transferring to the microscope is also explained. Finally the battery assembly and the preparation steps of the two types of batteries with polymer or ceramic electrolyte that are investigated in this work are summarized. This chapter is the overall materials and methods sections that are explained in the manuscripts. Chapters 4, 5, and 6 show the preparation and cycling of Li-metal batteries with polymer electrolytes and chapter 7 shows the preparation and cycling of cells with a ceramic electrolyte.

3. 1 In Situ and Ex Situ Scanning Electron Microscopy

Figure 3.1 shows the set ups used for *in situ* and *ex situ* analysis of the batteries [103]. Figure 3.1a shows the *in situ* set up that consist of a SEM (TESCAN Mira 3) that is equipped with a standard EDS detector and an extreme detector (Oxford Instruments) that is used for Li detection. A cycler connected to the SEM is used for *in situ* cycling. The *in situ* set up can be set to the temperature needed for battery cycling. In order to minimize sample contamination, transfer holders were designed at Hydro-Québec. Figure 3.1b is the FIB-SEM (TESCAN Lyra 3 GT FIB-SEM) used for *ex situ* analysis. This microscope is equipped with a standard EDS detector and extreme EDS detector (Oxford Instruments), TOF-SIMS, EBSD, and gallium ion source FIB. After the *in situ* cycling is finished, the battery is transferred to the FIB-SEM that allows for more in depth analysis.

In the FIB-SEM the electron beam is normal to the sample and the ion beam has a 55° angle with the electron beam. This microscope is mainly used to mill the sample and conduct microstructural and chemical analysis on the interior regions of the sample. It is also used to lift

out dendrites and conduct chemical analysis on them. Imaging and EDS analysis are done at beam energy of 5.00 kV to minimize beam damage and gather enough signals.

Two holders were used for plane view observations and cross section observations. The plane view holder was airtight and was used to move the sample from the dry room or the glove box to the SEM. During transferring the holder used for cross section observation, the sample was flushed with Ar.



Figure 3.1 The two scanning electron microscopes used for *in situ* and *ex situ* studies. a) *In situ* set up including a SEM (TESCAN Mira 3) equipped with a standard and an extreme EDS detector, and the cycler, b) FIB-SEM used for *ex situ* analysis (TESCAN Lyra 3 GT FIB-SEM) equipped with a standard and an extreme EDS detector, TOF-SIMS, gallium ion source FIB, and EBSD (adapted from Figure 3.1 of reference [103]).

The *in situ* software was developed at Hydro-Québec that enables the user to obtain images during cycling. Images can be obtained from as many regions on the sample as desired and at different magnifications with different time intervals. Images are obtained from the beginning until the end of cycling. In order to minimize the sample exposure to the electron beam, the beam is blanked when no images are being obtained during cycling.

Chemical analysis can also be conducted during cycling. After cycling is finished, images are used to produce videos. Videos are generated using ffmpeg [104]. The videos show the correlation between morphological evolution and the voltage change with time during cycling. In

order to gather the maximum data from the battery, most of the battery surface is monitored during cycling.

3. 2 All-Solid-State Li-Metal Polymer Battery Cycling

All-solid-state Li-metal polymer batteries used in this work are consisted of Li metal (Hydro-Québec) with thickness of 34 μ m, polyether-based solid polymer electrolyte (SPE) (Hydro-Québec) with lithium trifulorosulfonimide (LiTFSI) salt, and LiFePO₄ (LFP) cathode. To prepare the cathodes, LFP and a polyether-based polymer and LiTFSI with ethylene oxide to LiTFSI ratio of approximately 20:1 were mixed. The final slurry was doctor blade coated on an aluminum carbon-coated current collector with a final loading of 7.291 mg/cm² [105-107].

To investigate the behavior of these batteries, two battery assemblies and *in situ* holders are used: cross section view and plane view. Figure 3.2 shows the two assemblies [105]. In the cross section view assembly (Figure 3.2a) the battery is held vertically between two surfaces that are connected to copper wire connectors. To apply pressure and to keep the sample vertically, these surfaces are tightened with screws. In the plane view assembly (Figure 3.2b) the battery is placed horizontally on the holder and the Li anode is facing the electron beam. To induce dendrite growth no pressure is applied on the battery and a smaller anode area than the polymer and the cathode is used (edge effect) [105].

Batteries are prepared in the glove box or the dry room and transferred to the SEM with an airtight transfer holder or by flushing Ar on the sample to minimize contamination. Cycling is conducted at 70-80 °C to have the ionic conductivity of approximately 10⁻⁴ S/cm. During cycling the cross section or the anode surface with the polymer is imaged at different time intervals and different magnifications [105-107].



Figure 3.2 Schematic of all solid Li metal polymer battery assemblies for *in situ* studies (figure 1 of reference [105]). a) Cross section view assembly of the battery with applied pressure, b) plane view assembly of the battery in absence of pressure. In this assembly a smaller anode area is used compared to the SPE to induce dendrite growth.

3. 2 All-Solid-State Li-Metal Ceramic Cell Cycling

To study the effect of ceramic electrolytes, symmetrical Li cells with Li₇La₃Zr₂O₁₂ (LLZO) solid electrolytes are prepared. Li metal electrode (Hydro-Québec) has a thickness of 34 µm. The gallium-doped LLZO electrolyte is prepared following the previous work [108, 109]. To prepare the gallium-doped LLZO, 5,92 g of Li_2CO_3 , 11,39 g of La_2O_3 , 5,77 g of ZrO_2 and 0.56 g of Ga₂O₃ are mixed in a planetary mill with ZrO₂ balls in air. Thereafter, the mixture is annealed in tubular furnace on graphite (or zirconia or alumina) boat through the process of: increasing the temperature from room temperature to 700 °C and subsequently increasing the synthesis temperature up to 950 °C for 2 hours with N₂ gas flowing and cooling down the powder at the end. The final powder is cold pressed at 100 MPa and annealed in air atmosphere at 1100°C for 10 hours. The LLZO pellet has a thickness of 1 mm and a 99% density. The ionic conductivity at room temperature and 80 °C are 6×10^{-4} S/cm and 2×10^{-3} S/cm respectively [110]. To prepare the cells, two Li-metal electrodes are pressed on both sides of the LLZO pellet. The surface of the Li electrode is covered with residuals of polyether oxide [87] used as lubricant for the thin film fabrication. To induce dendrite growth the edge effect was used by using a smaller Li electrode area of 1.33 cm² (this is the area of the Li electrode facing the electron beam and the other Li electrode has the same area as the LLZO). A copper spring was used as contact electrode and to

apply pressure on the Li film to push it on the LLZO electrolyte and to make a good contact between them. The lower Li electrode rests on the flat aluminum sample holder which acts as a contact electrode and pushes the lower Li electrode on the LLZO electrolyte [110]. The cell is assembled in the glove box and thereafter transferred to the SEM using an airtight sample holder. Figure 3.3 shows a schematic of the cell assembly used for *in situ* cycling [110].



Figure 3.3 Schematic of the symmetrical Li cell with LLZO electrolyte (adapted from figure 3 of reference [110]).

Chapter 4 *In Situ* Scanning Electron Microscopy Detection of Carbide Nature of Dendrites in Li-Polymer Batteries

Maryam Golozar^{1,2}, Pierre Hovington³, Andrea Paolella², Stéphanie Bessette^{1,2}, Marin Lagacé², Patrick Bouchard², Hendrix Demers², Raynald Gauvin¹ and Karim Zaghib*²

¹ McGill University, Department of Mining and Materials Engineering, Montréal, Quebec H3A 0C5, Canada

² Hydro-Québec's Research Institute, Center of Excellence in Transportation Electrification and Energy Storage, Varennes, Québec JOL 1N0, Canada

³ Hovington's Consulting, Boucherville, Québec, Canada

*Corresponding author: zaghib.karim@ireq.ca

Preface

This chapter shows the *in situ* cycling of all-solid-state Li-metal batteries with polymer electrolytes. This work explains the effect of pressure on the dendrite growth and the chemical analysis of the dendrites using EDS as well as the effect of dendrite growth on the polymer. This chapter was published in Nano Letters on November 21, 2018:

M. Golozar, P. Hovington, A. Paolella, S. Bessette, M. Lagacé, P. Bouchard, H. Demers, R. Gauvin, and K. Zaghib, "In situ scanning electron microscopy detection of carbide nature of dendrites in Li–polymer batteries," *Nano Lett.*, vol. 18, no. 12, pp. 7583-7589, 2018.

4.1 Abstract

Li metal batteries suffer from dendrite formation which causes short circuit of the battery. Therefore, it is important to understand the chemical composition and growth mechanism of dendrites that limit battery efficiency and cycle life. In this study, *in-situ* scanning electron microscopy was employed to monitor the cycling behavior of all-solid Li metal batteries with

LiFePO₄ cathodes. Chemical analyses of the dendrites were conducted using a windowless energy dispersive spectroscopy detector, which showed that the dendrites are not metallic lithium as universally recognized. Our results revealed the carbide nature of the dendrites with a hollow morphology and hardness greater than that of pure lithium. These carbide-based dendrites were able to perforate through the polymer, which was confirmed by milling the polymer using focused ion beam. It was also shown that applying pressure on the battery can suppress growth of the dendrites.

Keywords: in-situ, scanning electron microscope, all-solid Li metal batteries, polymer, dendrite

4.2 Introduction

Li-ion batteries are widely used in a variety of applications including electric vehicles and electronic devices such as cell phones and laptops.¹ The anodes that are used in these batteries are very critical to produce cost effective, safe and long-life batteries.² Metallic Li is an attractive anode material because of its higher specific capacity (3860 mAh g^{-1}) compared to other anode materials such as graphitic carbon, which has a capacity of 372 mAh g^{-1,3} Li metal was used as the anode in Li metal/polymer batteries by Bolloré in Bluecars with the range of 250 km.³ Even though Li has higher capacity than other anode materials, it suffers from dendrite formation that could result in short circuits during charging, which decreases the life of the battery and increases safety concerns.^{4,5} Thus, it is crucial to mitigate the formation and growth of the dendrites to limit their presence. Steiger et al.⁶ suggested a mechanism for dendrite growth where the dendrites initiate from the defects on the surface of the anode and grow from the base, tip and middle of the kinks. These defects were described as areas with a thin solid electrolyte interface (SEI), surface contamination and grain boundaries.⁶ Kushima et al.⁷ reported two morphologies of whiskers, which grow from the root and Eden-like clusters growing from the surface. Initiation of the whiskers were reported to be from the thin SEI layer areas, and growth was the result of accumulation and releasing of stress due to deposition of Li in these regions.⁷ Dolle et al.⁸ showed the dendrite behaving like a fuse in a symmetric polymer cell by scanning electron microscopy (SEM) imaging of the cross section of the cell, and the polymer appeared burnt

where the tip of the dendrite touched the polymer upon short circuiting. Harry et al.⁹ observed a multi- globular structure on the polymer/Li interface after battery cycling. They proposed a growth mechanism where these structures were initiated from inhomogeneity of the SEI layer in the regions containing impurities.⁹

In this study, *in-situ* analyses are conducted using two set-ups with cross section view or plane view of the battery during cycling. A movie is constructed from the observations to show the growth of the dendrites. Focused ion beam (FIB) is used to mill the dendrites and polymer electrolyte to extract more information about the cycling behavior of the battery after cycling. Energy dispersive spectroscopy (EDS) is also used to conduct chemical analysis.

4.3 Materials and Methods

Batteries used in this work consist of pure metallic Li anode (Hydro-Québec), polyether-based solid polymer electrolyte (SPE) with LiTFSI as salt and LiFePO₄ (LFP) cathode. The LiFePO₄ cathode was prepared by mixing LFP with PEO-based polymer and LiTFSI, with an ethylene oxide to LiTFSI ratio of around 20:1. The battery was assembled with a cathode that has a flat morphology and loading of 7.291 mg/cm². *In-situ* and *ex-situ* studies of the battery were performed by TESCAN scanning electron microscopes Mira3 and Lyra3.

4.3.1 In-situ analysis

We designed and fabricated sample holders and developed the acquisition software specifically for the *in-situ* analysis experiments. **Figure 4.1** shows schematics of the batteries prepared for *in-situ* studies. **Figure 4.1a** shows the battery assembly for cross section-view experiments where the anode, SPE and cathode have the same dimensions. In this assembly, the battery is held vertically on the sample holder so that the cross section is facing the beam. The battery is held vertically by fixing it between two surfaces, which are connected to copper wire connectors that are tightened with screws to apply pressure on the anode and cathode surfaces. **Figure 4.1b** shows the assembly for plane-view experiments in which an anode with smaller area than the cathode is used to create edge effect during cycling. The battery is placed horizontally on the

sample holder with no pressure applied and with a connector on top of the anode. This assembly induces growth of dendrites due to edge effect and absence of pressure. This battery also enables observing more regions of the anode during cycling since the surface of the anode is facing the beam rather than the cross section. For the cross section-view experiments, oxidation of the Li anode during transfer from the dry room or glove box to the microscope was mitigated by flushing the sample with Ar during transfer. For the plane view experiments, the sample holder was air tight. Polymer electrolyte-based batteries were cycled at 70°C to have an ionic conductivity around 10⁻⁴ S/cm. SEM images of various regions of the batteries were obtained at several magnifications and at different time intervals during cycling. These images were used to construct movies to show the change in the cross section or surface with time.



Figure 4.1 Schematic of the a) cross section view and b) plane view of the batteries during *in-situ* experiments.

4. 3. 2. Ex-situ analysis

A dual-beam FIB-SEM (TESCAN Lyra 3 GT FIB-SEM) was used to analyze the batteries after cycling. Chemical analysis of the dendrites was done using an extreme EDS detector (Oxford instrument).

4. 4 Results and Discussion

The battery assembly shown in **Figure 4.1a** was used to monitor the cross section, and the results are illustrated in **Figure 4.2**. **Figure 4.2a** presents the cycling curve of a LFP battery with 34 µm

thick metallic Li anode and solid polymer electrolyte. Cycling was started at a low current of 0.056 mA and then increased to 0.112 mA and 0.224 mA. The red circles indicate the open circuit voltage (OCV) that was measured at different times. Figure 4.2 also shows four SEM images corresponding to b, c, d, and e points on the cycling curve. Figure 4.2b shows the crosssection region of the battery that was imaged at the start of cycling. Figure 4.2c shows the formation of a crack on the anode. The crack could have initiated from the inhomogeneities or stress concentrated regions that were formed on the anode surface during manufacturing processes including lamination. Figure 4.2d-e shows extrusion of Li from the anode/SPE interface. The movie that was constructed from the images with time interval of 30 minutes during cycling (Movie S1) shows the formation of the crack and shifting of the anode and SPE planes away from each other. As a result, a region where no pressure is applied on the anode is created and is the location for extrusion of Li. In the set up used in this experiment pressure is applied only on two vertical side surfaces of the battery. Thus when the crack is formed on the top of the battery, an open space where no pressure is applied is formed. Due to absence of pressure Li is extruded out of this interface. Further cycling of the battery also shows growth of one needle out of this region. Several studies have been dedicated to investigating the effect of pressure on cycling efficiency.¹⁰⁻¹² Hirai et al.¹⁰ showed that applying pressure increases the cycling efficiency by enforcing a uniform Li deposition on the anode, which reduces isolation of Li during discharge. Wilkinson et al.¹¹ also reported a closed-packed column morphology is obtained by high stack pressure, whereas various morphologies including needles are observed at low pressure. Gireaud et al.¹² reported that applying pressure on the battery increases the cycling efficiency by hindering dendrite formation, but cannot fully eliminate dendrite formation due to the presence of defects on the inner microstructure of Li. In our cross-section experiment, we observed extrusion of Li from a region where no pressure is applied.



Figure 4.2 Cross section view *in-situ* experiment a) Cycling curve, b, c, d and e) SEM images at four different times during cycling indicated by the arrows on the cycling curve.

In the present work, two different dendrite morphologies were observed (Figure S4.11): mossy (Figure 4.3a) and needle (Figure 4.3b). SEM images of the needles show a different morphology at the tip than the arm of the needle. This morphology was also observed by Steiger et al.⁶, and was referred to as inoxidizable particles which were not dissolved during dissolution. These inoxidizable particles result in the presence of inhomogeneity in the SEI layer where further Li deposition occurs.⁶ The *in-situ* movie (Movie S2) shows the slow-motion growth of the needle at the end of charging. The *in-situ* movie (Movie S1) also shows that, when cycling stopped, Li

extrusion stopped as well, indicating that Li extrusion was induced electrochemically and not chemically.



Figure 4.3 SEM images showing the morphology of deposited Li after cross section and plane view *in-situ* cycling: a) mossy morphology and b) needle morphology, observed during cross section *in-situ*, and c) needle morphology observed during plane view *in-situ*.

To increase the possibility of observing dendrites during cycling, an *in-situ* experiment with a plane-view orientation was conducted where no pressure was applied on the battery with a 6 μ m thick metallic Li anode. **Figure 4.4a-e** shows the cycling curves and SEM images obtained at four different times during cycling. A current of 0.3 mA was used at the start of cycling and then increased to 0.6 mA. A low columbic efficiency was observed only for the first three charge/discharge cycles (**Figure 4.4a**). Imaging of the surface was conducted with a time interval of 15 min. The movie of one region of the battery from this experiment (Movie S3) shows the growth of two needles on the edge of the anode. **Figure 4.4b-e** shows the growth of the two needles on the edge of the anode. **Figure 4.4d-e** also illustrates movement of the two needles during cycling. The high-magnification SEM image of the needles grown on the edge of the battery after cycling (**Figure 4.3c**) shows a 90° angle between the two needles. Further investigation will be carried out to confirm if the needles have preferable crystallographic orientation.



Figure 4.4 Plane view *in-situ* experiment a) Cycling curve, b, c, d, and e) SEM images at four different times during cycling indicated by the arrows on the cycling curve.

Figure 4.5a shows the SEM image of another needle on the edge of the anode. To observe the morphology of the inside of the needle, a nanomanipulator (Omniprobe 400) was used to lift out the needle (**Figure 4.5b**). The surface of the needle was then milled using a gallium ion source-focused ion beam (**Figure 4.5c**) which showed a hollow morphology. These hollow needle structures could be residues from the SEI.^{6,7} Steiger et al.⁶ suggested that during dissolution, the Li dendrites are consumed, and SEI residues that remain are connected to an inactive tip. Kushima et al.⁷ suggested that dissolution of the whiskers begin from the newly formed regions which have a thinner SEI layer, leaving behind a hollow SEI tube which

separates the electrically inactive tip from the surface. The inactive tip is referred to as "dead Li", which later detached, suggesting that the SEI residues were brittle.^{7,13} Li et al.¹⁴ also reported growth of single-crystalline dendrites in carbonate-based electrolytes which were coated with SEI layer containing Li oxide and Li carbonate. **Figure 4.5d** shows a needle wall thickness of around 100 nm which was measured after milling.



Figure 4.5 SEM images showing a) dendrite on the edge of the anode, b) dendrite removed with the nanomanipulator, c) milled dendrite using FIB showing hollow morphology and d) thickness of the wall of a dendrite.

In another *in-situ* experiment of a battery, the plane view was used, but with a thicker anode (34 μ m) compared to the previous experiment, the battery was cycled for a longer time and at higher currents to induce dendrite formation. In this experiment, a change in the morphology of the SPE was observed due to cycling. **Figure 4.6** shows the presence of needles and the rough morphologies on the SPE surface further from the anode.



Figure 4.6 SEM images obtained after plane view *in-situ* cycling showing a) presence of dendrite on the SPE further from anode b) two milled regions using FIB (1 and 2) on the SPE, c) high magnification of milled region 1 showing two regions of attacked and not attacked, d) high magnification of milled region 2, e) SPE before cycling and f) high magnification of milled region shown by red circle in e.

To observe the effect of these needles on the SPE, two regions were milled using FIB (**Figure 4.6b**). The SEM images of the milled regions show that the SPE does not have a smooth and uniform morphology in the depth. **Figure 4.6c** shows two different morphologies in the milled area of the SPE; a smooth region and a porous region. **Figure 4.6d** also shows a milled region of the SPE that is fully attacked, in contrast to the flat and smooth morphology of the SPE before cycling (**Figure 4.6e-f**). Harry et al.⁹ also observed morphology similar to the porous region in the FIB milled cross section of the multi globular structure. Their EDS mapping of these regions showed the presence of electrolyte in these structures.⁹

Chemical analysis was conducted on the needle and mossy dendrites using EDS. Figure 4.7a show presence of Li, C and O on a needle dendrite, which could be associated with compounds of Li₂O and Li_xC_v. Different regions of the mossy Li also showed the presence of Li, C and O, with higher amounts of Li on the newly formed regions (Figure 4.7b). Figure 4.7c shows EDS results obtained from the interior and exterior wall of a needle that was removed with the nanomanipulator in the microscope and milled with FIB to observe the inside of the needles. Before milling, the needles were coated with platinum to produce a smoother milled surface. EDS spectra from inside of a needle which was broken using the nanomanipulator without FIB milling also showed Li, C, and O (Figure S4.12). The EDS spectra from our study were compared with the EDS spectra of Li_2CO_3 to determine if the CO_3^{2-} functional group is present on the dendrites. This was carried out by placing Li₂CO₃ powder on a SEM stub with silver glue and cross section milled using an Argon ion miller. The EDS of Li₂CO₃ powder (Figure 4.8) shows higher O to C ratio and higher amounts of O compared with the dendrites. Furthermore, the EDS spectra for the needle and mossy dendrites show a small Li peak, whereas no Li peak is observed on the spectrum of Li₂CO₃ powder. This could be due to the difference in fluorescence yield in Li₂CO₃ and the dendrites. Hovington et al.² showed that the fluorescence yield of Li K xray is lower in compounds than in pure Li. These observations indicate that the dendrites have different composition than Li_2CO_3 powder, and that they are not composed solely of Li_2CO_3 . Hence, the presence of pure Li_2CO_3 can be excluded.



Figure 4.7 EDS of a a) needle morphology dendrite, b) mossy morphology dendrite and c) interior and exterior wall of a needle milled using FIB.



Figure 4.8 EDS of milled Li₂CO₃ powder using FIB.

The absence of fluorine and sulfur suggests that the reduction of LiTFSI does not occur, but it can promote Li_xC_y formation, as reported by Parimalam et al.¹⁵ We believe that the reduction of SPE during cycling can produce carbon-rich species. The C and O peaks inside the needle (Figure 4.7c) shows that, even after sample preparation in the vacuum chamber of the microscope, these two elements are still present. The C and O could be due to contamination or decomposition of the polymer electrolyte. Contamination in the high vacuum chamber of the microscope is highly likely,^{16,17} with C contamination from hydrocarbons in pump oils, vacuum grease, O-rings, or the sample itself.¹⁸⁻²⁰ The electron beam in the microscope polymerizes the hydrocarbon molecules adsorbed on the surface of the sample, which result in a C coating on the surface.¹⁹ The O contamination could be due to residuals of water molecules in the chamber that are adsorbed and excited on the surface of the sample,¹⁹ which produce lithium oxide.²¹ To avoid sample contaminations in the SEM chamber; characterization should be carried out in an ultra-high vacuum or at cryo temperature.^{16,19} Even though it is possible that the C and O observed in the EDS spectra were the result of contamination, the presence of these elements may also be due to other factors since the interior of the needles were only exposed to the chamber environment for at least 2 minutes. Furthermore comparison between the composition of the mossy and needle dendrite with the anode surface using EDS shows lower C to oxygen ratio on the anode surface (Figure S4.13) which was exposed to the SEM chamber for a longer time. This suggests that not only contamination could be responsible for observing C and O on the dendrites but also other sources of C and O including polymer decomposition could be responsible. To further investigate this phenomenon, we conducted Raman spectroscopy on the SPE before and after cycling (Figure S4.14). After cycling we observe two new peaks at 1360.9

cm⁻¹ and 1601.4 cm⁻¹ on the SPE which don't observe on the SPE before cycling. These two bands may correspond to lithiated carbon.^{22,23} This observation suggests that we may have carbon reduction during cycling (reduction of polymer during charging). Observing Li₂C₂ on Li is possible.²⁴⁻²⁶ Schmitz et al.²⁴ reported presence of Li₂C₂ on deposited Li on copper using Raman spectroscopy, and concluded that Li₂C₂ is the major component of the SEI on the deposited Li.²⁴ Schmitz et al.²⁵ also showed that Li₂C₂ is observed both on the surface and the bulk of pristine battery grade metallic Li. Su et al.²⁶ also reported the bands observed in the Raman spectroscopy obtained from the dendrites formed on lithiated graphite to be related to electrolyte degradation products including $X - C \equiv C - X$ type which are the result of the reaction between Li and the electrolyte during dendrite nucleation and growth. Moreover we were able to see the Li₂C₂ band. Figure S4.15 shows the Raman spectrum of the dendrite and the peak present at 1856.0 cm⁻¹. However it is uncertain whether the measured position was exactly on the dendrite or not due to the imaging difficulty under optical microscope.

The Li_xC_y in the dendrites could explain how the needles were able to perforate through the polymer electrolyte, while pure lithium metal seems too soft and malleable. In an attempt to lift out the dendrites, the tungsten nanomanipulator was bent as the result of pushing the dendrites (**Figure 4.9a-b**). An experiment was conducted on pure Li sheets where the nanomanipulator was used to scratch the surface to obtain a qualitative comparison between the hardness of the dendrites and pure Li. In this experiment we observed accumulation of Li on the nanomanipulator rather than observing a bent (**Figure 4.9c-d**). Based on these observations, we believe that Li metal could not perforate the polymer. The presence of carbon increases the hardness of the dendrites and facilitates perforation of the solid polymer, which may produce the porous morphology observed on the SPE after cycling (**Figure 4.6**).



Figure 4.9 SEM images of the nanomanipulator a) shown by red circle before scratching the dendrite, b) after scratching the dendrite showing the bent in the nanopanuluator, c) before scratching metallic Li sheet and d) after scratching metallic Li sheet showing the accumulation of Li on the tip. Further investigation is needed to confirm the mechanism for formation of the hollow morphology. However, there are two possible growth mechanisms that could explain the hollow needles. First, the hollow morphology could be due to consumption of the Li_xC_y by oxygen and carbon artifacts and formation of Li₂O/Li_xC_yO_z (not pure Li₂CO₃, see earlier discussion). Hollow metal-oxide-based particle formation followed by an oxidation reaction is quite common, according to Peng et al.²⁷ for Fe \rightarrow Fe₃O₄, Park et al.²⁸ for Cu₂O \rightarrow CuO and Titirici et al.²⁹ for metal-organic decomposition. In addition, hollow nanowires were synthesized by β -FeOOH oxidation reaction.³⁰ Han et al.³¹ also reported the growth of nano- and micro-wires by cooling liquid Li alloys. They observed composition of Au-, Ag- or In-rich tips and LiOH walls for the wires, and reported that the wires were initially Li metal which then transformed to LiOH.³¹ Figure 4.10 shows a schematic representation of the formation of hollow morphology dendrites. Second, a possible mechanism is that the morphology is obtained by CO₂ degassing of the polymer during cycling, with formation of oxygen gas bubbles that help keep the inside of the needles hollow. Metal carbonates can promote the hollow shape, as shown by Hadiko et al.³² when CO_2 gas is bubbling with CaO.



Figure 4.10 Schematic showing formation of hollow morphology (the growth steps are higher magnification of the region shown with red dotted square). Initially the dendrites grow as filled LixCy needles. They become hollow due to consumption of the LixCy by oxygen and carbon. Further consumption of the LixCy results in hollowing of the needles and decreasing wall thickness.

4.5 Conclusion

In-situ and *ex-situ* SEM techniques were employed to study the growth of dendrites in Li metal batteries. Applying pressure on the battery can hinder growth of the dendrites. Two morphologies of mossy and hollow needles were observed. Since EDS is an elemental analysis technique, an indirect investigation method was used in an attempt to conduct chemical analysis of the dendrites. It was shown that the dendrites were not pure Li and had higher hardness than Li metal. EDS analyses of the needles showed the presence of Li, C, and O, which were attributed to Li_xC_y , Li_2O , and $Li_xC_yO_z$. C and O could be the result of contamination in SEM. However these two elements were also detected inside the dendrites after milling using FIB, where the milled surface was exposed to the SEM chamber for a limited time. Also EDS spectra from the anode surface showed lower C to O ratio than the dendrites although the anode surface was exposed to the SEM chamber for a longer time. Thus contamination cannot be the only source of detection of these elements. Polymer decomposition could be another source for observing these elements in the dendrites. Raman spectroscopy on the SPE showed two new peaks at 1360.9 cm⁻¹ and 1601.4 cm⁻¹ after cycling which was not observed on the SPE before

cycling. These two bands may correspond to lithiated carbon suggesting that we may have decomposition of the polymer during cycling. The carbide nature of the dendrites can explain the observation that the needles were able to perforate through the polymer due to its higher hardness compared to pure metallic Li. Two mechanisms were suggested for the hollow needles; consumption of the Li_xC_y by oxygen and carbon artifacts, and degassing of the polymer during cycling. More investigation will be done to confirm the growth mechanism of the dendrites.

Acknowledgement

This work was financially supported by Hydro Québec and the McGill Engineering Doctoral Award (MEDA). The authors gratefully acknowledge the work of Julie Hamel-Pâquet, Martin Dontigny and Serge Verreault in preparing the batteries and Dr.Wen Zhu, Dr. Ali Darwiche, Michele Roy, René Veillette, Daniel Clément and Vincent Gariépy for their technical support.

Additional Information

The authors declare no competing financial interest.

4.6 References

1. Kalhammer, F. R. Solid State Ionics 2000, 135, 315-323.

2. Hovington, P.; Timoshevskii, V.; Burgess, S.; Demers, H.; Statham, P.; Gauvin, R.; Zaghib, K. *Scanning* **2016**, 38, 571-578.

3. Hovington, P.; Lagacé, M.; Guerfi, A.; Bouchard, P.; Mauger, A.; Julien, C.; Armand, M.; Zaghib, K. *Nano Lett.* **2015**, 15, 2671-2678.

4. Rosso, M.; Brissot, C.; Teyssot, A.; Dolle, M.; Sannier, L.; Tarascon, J.-M.; Bouchet, R.; Lascaud, S. *Electrochim. Acta* **2006**, 51, 5334-5340.

5. Monroe, C.; Newman, J. J. Electrochem. Soc. 2003, 150, A1377-A1384.

6. Steiger, J.; Kramer, D.; Mönig, R. J. Power Sources 2014, 261, 112-119.

7. Kushima, A.; So, K. P.; Su, C.; Bai, P.; Kuriyama, N.; Maebashi, T.; Fujiwara, Y.; Bazant, M. Z.; Li, J. *Nano Energy* **2017**, 32, 271-279.

8. Dollé, M.; Sannier, L.; Beaudoin, B.; Trentin, M.; Tarascon, J.-M. *Electrochem. Solid-State Lett.* **2002**, 5, A286-A289.

9. Harry, K. J.; Liao, X.; Parkinson, D. Y.; Minor, A. M.; Balsara, N. P. J. Electrochem. Soc. 2015, 162, A2699-A2706.

10. Hirai, T.; Yoshimatsu, I.; Yamaki, J. i. J. Electrochem. Soc. 1994, 141, 611-614.

11. Wilkinson, D. P.; Blom, H.; Brandt, K.; Wainwright, D. *J. Power Sources* **1991**, 36, 517-527.

12. Gireaud, L.; Grugeon, S.; Laruelle, S.; Yrieix, B.; Tarascon, J.-M. *Electrochem. Commun.* **2006**, 8, 1639-1649.

13. Yoshimatsu, I.; Hirai, T.; Yamaki, J. i. J. Electrochem. Soc. 1988, 135, 2422-2427.

14. Li, Y.; Li, Y.; Pei, A.; Yan, K.; Sun, Y.; Wu, C.-L.; Joubert, L.-M.; Chin, R.; Koh, A. L.; Yu, Y.; Perrino, J.; Butz, B.; Chu, S.; Cui, Y. *Science* **2017**, 358, 506-510.

15. Parimalam, B. S.; Lucht, B. L. J. Electrochem. Soc. 2018, 165, A251-A255.

16. Orsay Physics. Scientific Overviews: What is UHV? http://www.orsayphysics.com/whatis-uhv (accessed Sep 7, 2018). 17. Li, Y.; Li, Y.; Sun, Y.; Butz, B.; Yan, K.; Koh, A. L.; Zhao, J.; Pei, A.; Cui, Y. Nano Lett. 2017, 17, 5171-5178.

18. Ennos, A. E. Br. J. Appl. Phys. 1954, 5, 27-31.

19. Hren, J. J., Barriers to AEM: Contamination and etching. In *Introduction to Analytical Electron Microscopy*, Hren, J. J.; Goldstein, J. I.; Joy, D. C., Eds. Springer: Boston, MA, **1979**; pp 481-505.

20. Egerton, R. F.; Li, P.; Malac, M. Micron 2004, 35, 399-409.

21. Markowitz, M. M.; Boryta, D. A. J. Chem. Eng. Data 1962, 7, 586-591.

22. Bao, W.; Wan, J.; Han, X.; Cai, X.; Zhu, H.; Kim, D.; Ma, D.; Xu, Y.; Munday, J. N.; Drew, H. D. *Nat. Commun.* **2014**, 5, 4224.

23. Sole, C.; Drewett, N. E.; Hardwick, L. J. Faraday Discuss. 2014, 172, 223-237.

24. Schmitz, R.; Mueller, R. A.; Schmitz, R. W.; Schreiner, C.; Kunze, M.; Lex-Balducci, A.; Passerini, S.; Winter, M. *J. Power Sources* **2013**, 233, 110-114.

25. Schmitz, R.; Müller, R.; Krüger, S.; Schmitz, R. W.; Nowak, S.; Passerini, S.; Winter, M.; Schreiner, C. *J. Power Sources* **2012**, 217, 98-101.

26. Su, X.; Dogan, F.; Ilavsky, J.; Maroni, V. A.; Gosztola, D. J.; Lu, W. *Chem. Mater.* **2017**, 29, 6205-6213.

27. Peng, S.; Sun, S. Angew. Chem., Int. Ed. 2007, 46, 4155-4158.

28. Park, J. C.; Kim, J.; Kwon, H.; Song, H. Adv. Mater. 2009, 21, 803-807.

29. Titirici, M.-M.; Antonietti, M.; Thomas, A. Chem. Mater. 2006, 18, 3808-3812.

30. Xiong, Y.; Li, Z.; Li, X.; Hu, B.; Xie, Y. Inorg. Chem. 2004, 43, 6540-6542.

31. Han, S. Y.; Boebinger, M. G.; Kondekar, N. P.; Worthy, T. J.; McDowell, M. T. *Nano Lett.* **2018**, 18, 4331-4337.

32. Hadiko, G.; Han, Y. S.; Fuji, M.; Takahashi, M. Mater. Lett. 2005, 59, 2519-2522.

4. 7 Supplementary Information



Figure S4.11. SEM image of the battery after cycling with the cross section set-up. SEM image of the extruded Li from the cross section of the battery after cycling indicating needle and mossy morphology dendrites from the region where the crack is formed and no pressure is applied.



Figure S4.12. EDS analysis showing presence of Li, C and O inside a dendrite which was broken in the SEM. To minimize the effect of the techniques used to conduct chemical analysis of the inside of the needles; one needle was broken from the cross section by pressing on it using the nanomanipulator rather than FIB milling.


Figure S4.13. EDS analysis showing a comparison between Li anode surface, mossy and needle dendrite. Observing C and O on the anode surface and small amount of Li indicates that presence of C and O could be due to contamination of the Li anode. However C to O ratio is lower for the anode than the dendrites, even though the anode has been exposed to SEM chamber environment for a longer time than the dendrites. This observation could suggest that contamination is partially responsible for presence of C and O in the dendrites. Polymer decomposition could be another source for these elements in the dendrites.



Figure S4.14. Raman spectroscopy showing a comparison between fresh SPE, SPE after cycling, and reference graphite. The spectrum of SPE after cycling shows two new peaks at 1360.9 cm⁻¹ and 1601.4 cm⁻¹ which is not present in the fresh SPE. These two bands may correspond to lithiated carbon. [1, 2] This observation suggests that we may have carbon reduction during cycling (reduction of polymer during charging).



Figure S4.15Raman spectroscopy of dendrites. A peak at 1856 cm-1 related to Li_2C_2 was observed in SPE

Supplementary Movies:

Movie S1. Cycling of the battery using the cross section set-up showing crack formation and extrusion of Li.

Movie S2. Slow motion of cycling the battery showing growth of a needle dendrite.

Movie S3. Cycling of the battery using the plane view set-up showing growth of needle dendrites on the edge of the anode.

References

1. Bao, W.; Wan, J.; Han, X.; Cai, X.; Zhu, H.; Kim, D.; Ma, D.; Xu, Y.; Munday, J. N.; Drew, H. D. *Nat. Commun.* **2014**, *5*, 4224.

2. Sole, C.; Drewett, N. E.; Hardwick, L. J. Faraday Discuss. 2014, 172, 223-237.

Chapter 5 In Situ Observation of Solid Electrolyte Interphase Evolution in a Lithium Metal Battery

Maryam Golozar^{1,2}, Andrea Paolella^{*1}, Hendrix Demers¹, Stéphanie Bessette², Marin Lagacé¹, Patrick Bouchard¹, Abdelbast Guerfi¹, Raynald Gauvin², and Karim Zaghib^{*1} 1 Center of Excellence in Transportation Electrification and Energy Storage, Hydro-Québec, Varennes, Québec J0L 1N0, Canada 2 Department of Mining and Materials Engineering, McGill University, Montréal, Québec H3A 0C5, Canada

*Corresponding author: paolella.andrea2@hydro.qc.ca; zaghib.karim@hydro.qc.ca;

Preface

This chapter shows the behavior of the all-solid-state Li-metal polymer battery from the beginning of cycling till the end, the effect of salt decomposition, and the SEI evolution during cycling. The change in the polymer during cycling is also observed. This chapter was published in Communications Chemistry on November 15, 2019:

M. Golozar, A. Paolella, H. Demers, S. Bessette, M. Lagacé, P. Bouchard, A. Guerfi, R. Gauvin, and K. Zaghib, "In situ observation of solid electrolyte interphase evolution in a lithium metal battery," *Commun. Chem.*, vol. 2, no. 1, p. 131, 2019.

4.1 Abstract

Lithium metal is a favorable anode material in all-solid Li-polymer batteries because of its high energy density. However, dendrite formation on lithium metal causes safety concerns. In this study, we obtain images of the Li-metal anode surface during cycling using *in situ* scanning electron microscopy and construct videos from the images, which enables us to monitor the failure mechanism of the battery. Our results show the formation of dendrites on the edge of the anode and isles composed of decomposed lithium bis(trifluoromethanesulfonyl)imide on the grain boundaries. Cycling at high rates result in the opening of the grain boundaries and depletion of lithium in the vicinity of the isles. We also observ changes in the surface morphology of the polymer close to the anode edge. Extrusion of lithium from these regions could be evidence of polymer reduction due to local increase in the temperature and thermal runaway assisting in dendrite formation.

5.2 Introduction

Lithium metal anode has a high capacity of 3860 mAh/g, which makes it a good candidate for use in Li-ion batteries¹. However, dendrite formation on lithium metal poses a safety issue due to the possibility of short circuit and explosion, especially when in contact with flammable liquid electrolytes²⁻⁴. All-solid Li-polymer batteries are safer choices since polymers are not flammable, in contrast to liquid electrolytes, and can add mechanical strength to the battery⁵. The most common electrolytes used in these batteries are poly (ethylene oxide) POLYETHER based polymers owing to their low glass transition temperature, dissolution of lithium salt, and high ionic conductivity at temperatures above 70 °C⁵⁻⁷. The main conductive salt that is used in polymer electrolytes is lithium bis(trifluoromethanesulfonyl)imide (Li[N(SO₂CF₃)₂], LiTFSI)^{8,9}. Even though all-solid Li-metal polymer batteries are great replacements for batteries with liquid electrolytes, further investigation of higher charging rate cycling should be conducted, as this can cause the formation of dendrites that can perforate through this medium due to their carbide nature¹⁰.

In this work, we investigate the failure mechanism of an all-solid Li-metal polymer battery following the evolution of a solid electrolyte interphase (SEI) using *in situ* scanning electron microscopy (SEM). Images of the surface of the battery are gathered during cycling, and videos are constructed after the experiment that shows the performance of the battery from the beginning to the end of cycling. Chemical analysis are also performed using energy dispersive spectroscopy (EDS). We follow the formation of isles and holes, which are related to the various reactions that could take place at the defects in comparison with the rest of the anode¹. Furthermore, it is also possible to observe the reduction of LiTFSI salt⁸. Electrolytes containing LiTFSI salt have been shown to increase dendritic morphology formation on copper

substrates^{8,11}. Thus, it is crucial to study the behavior of the Li-metal anode in contact with polymer electrolytes in these batteries. This study shows formation of dendrites, opening of grain boundaries, and isles, and also decomposition of the salt.

5.3 Results

5. 3. 1. In Situ Cycling Observations

In this section first an overall view of all the phenomena observed during cycling and presented in the videos are given and then each phenomena is further explained in the following sections. **Figure 5.1** shows SEM images of the surface of the anode and polymer close to the edge of the anode before cycling, after 9 days of cycling, after 13 days of cycling, and at the end of cycling. In total, the battery was cycled inside the microscope for 14 days. At the beginning of cycling, the polymer electrolyte-based battery was stabilized at 70°C in order to have a total ionic conductivity of approximately 10^{-4} S/cm; then, after 2 days of cycling, the temperature was increased to 80°C to further facilitate ionic conductivity and, thus, the reactions at the interface. Cycling started at a low current of 0.1 mA (C/12, first charge) and was increased to 0.403 mA (C/3, from 2^{nd} cycle), 0.537 mA (C/2, from 6^{th} cycle), and 1.074 mA (C/1, from 12^{th} cycle) during cycling to induce dendrite growth, and the battery failed after 14 days. Before cycling, we observed a smooth anode and polymer surface (Figure 5.1a). As we cycled the battery we generally observed: a) growth of dendrites on the edge of the anode, b) high activity on the grain boundaries, c) formation of isles on the surface of the anode, and d) depletion of lithium metal in the vicinity of these isles. These phenomena were observed on the entire anode surface (Supplementary Figure 5.9). To better understand the sequence in which these phenomena had taken place, as well as at what point during cycling, a video was constructed from the images obtained during cycling with time interval of 30 min (Supplementary Movie 1). Supplementary Movie 1 shows the correlation between the images and the cycling curve. Figure 5.2 shows the cycling curve and images from different times during cycling. At the beginning, both the anode and the polymer have a smooth surface (Figure 5.2b at 3.25 V). After a few hours of cycling, the polymer was subjected to a change close to the anode edge (Figure 5.2c at 3.43 V) where the dendrites originate (Figure 5.2d at 3.49 V). Dendrites started forming during the first charge due to unstable Li/polymer interface at the beginning of cycling where the SEI layer is not fully formed to protect the lithium surface. The fluctuations in the first charge in the cycling curve (**Figure 5.2a**) are an indication of dendrite formation. The unstable interface of the lithium and the polymer can lower the coulombic efficiency of the battery¹². After the first cycle Li/polymer interface becomes more stable with a more uniform SEI layer which is indicated by the smooth cycling curve. However; with an increase in the cycling rate, the possibility of damaging the SEI layer increases as well, which results in formation of more dendrites.

Further cycling of the battery shows further growth of dendrites on the edge and more pronounced grain boundaries (**Figure 5.2e-f** at 3.42 V after 14 cycles and at 2.93 V after 35 cycles, respectively). After 7 days of cycling, two isles start appearing: one on the surface of the anode and one close to the edge; also, a new edge starts forming on the lithium surface (**Figure 5.2g** at 3.49 V after 59 cycles). Further cycling does not show continued growth of the dendrites that appeared at the beginning of cycling but does show the formation of a new edge on the anode and lithium depletion in the vicinity of the isles (**Figure 5.2h** at 3.14 V after 75 cycles). After 14 days of cycling, we observed dendrite growth on the new edge, opening of the grain boundaries, further depletion of lithium in the vicinity of the isles, and coverage of the dendrites that were formed at the beginning of cycling by polymer (**Figure 5.2i** at 3.55 V at the end of cycling). These observations are discussed in more detail below.

The behavior of the battery observed through the cycling curve and the SEM images indicates that the electrochemical performance of the battery could possibly be enhanced provided that a stable Li/SPE interface is achieved¹².



Figure 5.1 SEM images of the surface of the Li anode and SPE during cycling (scale bars representing 200 μ m). SEM images: **a** before cycling, **b** after 9 days, **c** after 13 days and **d** after 14 days of cycling. The cycling points at which these images were obtained are indicated in Figure 2 with green arrows.



Figure 5.2 Cycling curve and SEM images obtained during cycling (scale bars representing 100 μ m). a Cycling curve showing the times at which the SEM images b-i were obtained (red circles), corresponding to Supplementary Movie 1 (straight lines indicate the times at which cycling was stopped). SEM image b at the beginning of cycling (at 3.25 V); c after 13 hours of cycling, showing a change in the SPE close to the anode edge (at 3.43 V); d after 14.5 hours of cycling, showing dendrites on the anode edge (at 3.49 V); e after 3 days of cycling, showing further growth of dendrites and more pronounced grain boundaries (at 3.42 V); f after 5 days of cycling, showing more activity on the grain boundaries (yellow dashed lines indicate the thickness of the Li consumed on the anode edge (isles) and the beginning of the formation of a new anode edge (at 3.49 V); h after 8 days, showing Li depletion in the vicinity of the isles and formation of a new anode edge and (at 3.14 V); and i after 14 days of cycling, showing dendrites on the newly formed edge, high activity at the grain boundaries and isles and the coverage of dendrites formed at the beginning by SPE (at 3.55 V).

5. 3. 2. Dendrites and New Anode Edge

During formation and growth of the dendrites on the edge of the anode, lithium metal on the edge and at the interface is consumed to produce lithium oxides, carbides, and carbonates¹³. Further growth results in the hollowing out of the dendrites, which makes them electrochemically inactive, resulting in "dead Li"^{10,14,15}. Consumption of lithium in this region could lead to a lack of lithium metal for participation in redox electrochemical processes, which results in the consumption of another lithium layer from the anode and the formation of a second anode edge layer. This observation is indicated by the yellow dotted lines in Figure 5.2, which compares the position of the original anode edge with that of the new edge. This observation is in agreement with a previous report by Yoshimatsu et al.¹⁵: using the voltage profile, they showed that the plated lithium is stripped during discharge, and some lithium is also stripped from the substrate to compensate for lithium loss as a result of "dead Li" formation¹⁵. At the end of cycling, we observed the growth of dendrites on the newly formed anode edge. This region contains fresh lithium that could participate in the formation of new dendrites due to non-uniform SEI layer or a nonhomogeneous solid-solid contact between the lithium anode and the SPE^{12,16}.

5. 3. 3. Grain Boundaries

By continuously imaging during cycling, we observed the opening of the grain boundaries, which indicates a higher activity in these regions compared to the grains. This opening occurs because grain boundaries are sites with high free energies and, thus, higher diffusion rates than the grains¹⁷⁻¹⁹.

5.3.4. Isles

Supplementary Movie 2 shows a close up of a region on the anode where an isle starts appearing. This isle starts appearing at the intersection of the grain boundaries. As lithium is consumed in this region during cycling, we start seeing an isolated region of the anode, which we

refer to as an isle. **Figure 5.3a** shows a higher magnification of one of the isles, where we see that two dendrites with needle morphology have formed. The wall of the isle contains fresh lithium metal from the interior of the anode that has not been in contact with the rest of the battery, which is more prone to dendrite formation²⁰. Supplementary Figure 5.10shows a high magnification of some of the isles that are surrounded by high numbers of dendrites in the hollow region. This phenomenon was also reported by Yu et al.²⁰. **Figure 5.3b-c** show three isles in another region of the anode after 9 and 14 days of cycling, respectively. These images show how lithium metal changes during cycling. Isles are formed where the grain boundaries meet and their surroundings become lithium content-deficient as cycling continues. Hovington et al.¹ also observed these isles in Li_{1.2}V₃O₈ (LVO) solid-state batteries after cycling. They showed that the formation of these isles is independent of the applied pressure on the battery and is related to the lithium film¹. They suggested that lithium is removed preferentially at the grain boundaries because of its high reactivity in these regions¹. We were able to show the creation of these isles and a high activity at the grain boundaries using *in situ* cycling with no applied pressure on the battery.

To investigate the depth of the depleted lithium layer in the vicinity of the isles, we conducted mapping of the surface using an extreme EDS detector (**Figure 5.4**). The mapping findings show that the region around the isle is rich in S, F, and N and does not contain lithium, which indicates that the lithium surrounding the isle is fully consumed in the depth of the anode (this finding was also confirmed by cross section mapping of the isle). High concentration of S, F, and N in the vicinity of the isle shows an exposed region of the polymer as the result of lithium consumption. To better understand why these isles are formed on the anode, the isles were milled using FIB (**Supplementary Movie 3** shows the milling of an isle using FIB). **Figure 5.5a** shows the cross section of one of the isles (lithium anode (isle), SPE, and LFP). **Figure 5.5b** shows a higher magnification image of **Figure 5.5a**, where we see the appearance of lines in the isle with a precise geometry, suggesting that the precipitate is crystalline in nature. Additionally, we observed the presence of pores on the interface of the lithium and the polymer. **Figure 5.5c** shows the cross section of another isle, where the porosity and the depletion of lithium in the vicinity of the isle are more evident.



Figure 5.3 SEM images of the surface of the lithium showing isles. SEM images a at high magnification of the isle from Figure 2h after cycling showing two needle morphology dendrites (scale bar representing 50 μ m), b of three isles on the anode after 9 days of cycling (scale bar representing 100 μ m), and c of the three isles in b after cycling (scale bar representing 100 μ m).



Figure 5.4 Map of one isle on the anode surface (scale bars representing 100 μ m). This map shows high concentration of S and F in the vicinity of the isle, indicating the consumption of lithium in these regions (dark regions indicated with white arrows are the result of a shadowing effect).



Figure 5.5 SEM images of the isles that were milled using FIB. Images show a cross section of one isle (scale bar representing 10 μ m), b higher magnification of image a showing the lines on the edge (scale bar representing 10 μ m) and, c cross section of another isle showing the porosity of the isle-SPE interface (scale bar representing 20 μ m).

5. 3. 5. LiTFSI Salt

Mapping of the cross section of an isle shows that the lines in **Figure 5.5b** are rich in N and that the isle is surrounded by S (**Figure 5.6**). This mapping also shows that the sides and bottom of the isle are rich in C, F, and some N. This distribution could be the result of LiTFSI decomposition and the probable formation of a precipitate composed of Li_3N , Li_2S , $LiF^{21,22}$. The strong C-F bond in LiTFSI should produce a small amount of pure LiF and then a different hydrolysis reaction in comparison with $LiPF_6$ or $LiBF_4$. In Figure 6 the presence of C, F, and N in the core (on the wall of the isle) and S in the shell (further away from the isle) suggests a gradual decomposition of LiTFSI by multiple reductions forming subunits such as Li_xCNF_3 and Li_ySO_X .

At first, Li₃N crystal precipitates could form, which are not soluble and do not dissolve with further cycling, thus forming the isles. Kızılaslan et al.²³ used Li₃N as a protective layer on a lithium anode to enhance the cycling of the battery. After that, further decomposition of the salt may result in the formation of Li₂S, LiC_xF_y, LiF, Li_xCNF₃, and Li_ySO_x surrounding the isle. The LiF surrounding the isle acts as a solid electrolyte interphase (SEI) layer to protect the lithium in the isle from further dissolving, as Li ion transfer in LiF is slower than that of Li₂CO₃ and

 $Li_2O^{20,24}$. Salt decomposition was also reported by Chao et al.²⁵ using X-ray photoelectron spectroscopy (XPS) where a more sever decomposition was reported on graphite/SPE interface in comparison with Li/SPE interface. **Figure 5.6** shows a schematic of isle formation and the composition of the salt surrounding the isles. The mapping results for these isles in a battery cycled with no external pressure shows that the formation of isles depends on the reactions that take place in these regions and not on the applied pressure on the battery, as suggested by Hovington et al.¹ Galluzzo et al.²⁶ has shown that lithium metal dissolves and diffuses in the POLYETHER bulk as Li⁺ and a free electron. Lithium metal may then reduce the salt in the polymer. Eshetu et al.⁸ has proposed two mechanisms for LiTFSI salt reduction by lithium in all-solid-state Li-S batteries. Our study suggests that dissolution of lithium metal in POLYETHER begins at the grain boundaries and continues with further cycling at high rates until we observe the depletion of lithium in the vicinity of the isles. The resulting lithium metal in these regions could reduce the LiTFSI salt, which explains the high concentration of S, F, and C around the isles.

Supplementary Figure 5.11 shows the mapping of a milled region of the polymer, where we observed perforation by dendrites. The mapping result shows an inhomogeneous distribution of F, C, and O, with greater F and O contents below the region where we observed dendrites and a lower C content. The inhomogeneous distribution of F shows the dependency of dendrite formation on the salt decomposition. The low C concentration underneath the region with dendrites could be due to consumption of C by Li to form dendrites¹⁰.

Generally among all the possible Li-salt, LiTFSI is considered a salt able to limit dendrite formation. As reported by Li et al.²⁷, LiTFSI in ether solvent shows the longest cycle life with highest current due to its high transference number. LiTFSI is able to keep lithium metal with a flat and dense surface. As reported by Suo et al.²⁸ solvent –in- salt configuration (4M LiTFSI in DME/DOL) can improve the stabilization of lithium metal surface although this specific configuration is not applicable on PEO:LiTFSI due to limitation of salt solubility. In the future in order to increase transfer number (and reduce dendrite formation) PEO should be replaced with another polymer.



Figure 5.6 Map of the cross section of an isle and a schematic showing isle formation. a Map of an isle milled using FIB showing the N content of the lines in the cross section and a high concentration of C and F surrounding the isle (SEM image scale bar representing 50 μ m and map results scale bar representing 25 μ m). **b** Schematic of the battery during cycling showing the appearance of the isles and the chemical composition surrounding them.

5. 3. 6. Dendrite and Polymer

Figure 5.7a-d show SEM images of the polymer close to the anode edge after 3, 7, 9, and 13 days of cycling, which corresponds to **Supplementary Movie 4** and Supplementary Figure 5.12. **Figure 5.7e-f** also show higher magnification images of this region. The sequence shows the perforation of dendrites through the polymer close to the anode edge, which was previously observed¹⁰. **Figure 5.8** shows the EDS analysis of the morphological change in the polymer close to the anode edge after half of a day. A comparison of the EDS spectra shows the extrusion of lithium from the polymer where a Li peak is observed.

As we cycle the battery, we observe a morphological change in the polymer surrounding the dendrites due to a liquefaction process. This phenomenon is probably due to a local temperature increase followed by decomposition and degassing of the polymer. As cycling is continued at high rates, dendrites that were formed in these regions are covered by the polymer (Figure 5.2h and Figure 5.7d). We suppose that the dendrite formation locally increases the temperature of the polymer to above its melting point, which could result in side reactions and a change in the state of the polymer from solid to more liquid-like. Figure 5.2 shows a schematic of this process. Thermal analysis modeling by Chen and Evans²⁹ showed that the battery temperature could increase and result in thermal runaway if the battery is cycled at high rates and there is a local heat source. A local increase in the temperature of the battery could elevate the battery temperature to the onset of thermal runaway, resulting in exothermic side reactions²⁹. The local temperature can increase as the result of exothermic reactions, such as SEI decomposition, electrolyte decomposition, or lithium reaction with the electrolyte³⁰ or due to an increase in the resistance of the area. Commarieu et al.³¹ investigation on polycarbonate solid electrolytes also shows the decomposition of this SPE in lithium metal batteries. Further studies need to be focused on decomposition of other polymers.



Figure 5.7 SEM images (corresponding to Supplementary Movie 2 and Supplementary Figure 5.12) of the polymer and a schematic showing dendrite growth. SEM images a after 3 days of cycling (scale bar representing 50 μ m), b after 7 days of cycling (scale bar representing 100 μ m), c after 9 days of cycling (scale bar representing 50 μ m), and d after 13 days of cycling (scale bar representing 20 μ m), and f high magnification of the red box in image c (scale bar representing 20 μ m), and f high magnification of the red box in image d showing the morphological change on the SPE (scale bar representing 20 μ m). The cycling points at which these images were obtained are indicated in Supplementary Figure 5.12 by blue arrows. g Schematic of the dendrite formation and the effect of SPE melting on further dendrite growth.



Figure 5.8 EDS of the morphological change observed on the SPE close to the anode edge. a SEM image showing the extrusion of lithium from the SPE after half a day (scale bar representing 100 μ m). b EDS spectra of this region.

5.4 Discussion

In this study, an *in situ* SEM analysis technique was used to study an all-solid Li-metal polymer battery. Videos were used to study the battery behavior and failure mechanism from the beginning to the end of cycling.

The formation and growth of dendrites were observed, which leads to the formation of dead lithium that does not participate in the redox electrochemical reactions. Additionally, a new lithium edge that was active in these reactions was observed. Furthermore, the interaction of the dendrites with the polymer was observed. SEM images showed a morphological change on the SPE during cycling corresponding to regions where dendrites extruded out of the polymer. This interaction leads to the decomposition of the polymer by local melting, reduction, and thermal runaway. The videos also showed an increase in activity at the grain boundaries during cycling rates. Characterization of the isles showed that the increase in activity could lead to salt decomposition and explain the formation of these isles. These isles decreased the electrochemical performance of the battery.

5.5 Methods

5. 5. 1. Battery preparation

All-solid-state POLYETHER-based Li-metal polymer batteries were used in this study. The LiFePO₄ (LFP) cathode was prepared by mixing LFP with a POLYETHER-based polymer and LiTFSI at an ethylene oxide to LiTFSI ratio of approximately 20:1. The final slurry was doctor blade coated on an aluminum carbon-coated current collector with a final loading of 7.291 mg/cm^2 . **Batteries** assembled using LiFePO₄ (LFP) cathode were а (LFP-(POLYETHER:LiTFS)), POLYETHER-based solid polymer electrolyte (SPE) (Hydro-Québec) with lithium trifulorosulfonimide (LiTFSI) salt, and a 34 µm thick lithium metal anode produced by Hydro-Québec.

The final LFP-(POLYETHER:LiTFSI)-lithium metal batteries were assembled in a glove box and then transferred to the microscope using an airtight sample holder designed and fabricated at Hydro-Québec. A plane view set up was used to conduct these experiments, where the surfaces of the anode and edges of the polymer were constantly monitored during cycling with no pressure applied to the battery. This assembly induces the growth of dendrites due to the edge effect and absence of pressure, as reported in our previous work¹⁰.

5. 5. 2. In situ cycling

In situ cycling experiments were carried out using a TESCAN scanning electron microscope, Mira 3. Different regions of the anode were imaged during cycling at different magnifications by using acquisition software developed specifically for these *in situ* experiments. Videos were constructed from these images after cycling to better understand the behavior of the battery from the beginning to the end of cycling.

To conduct *ex situ* analysis after cycling, a focused ion beam scanning electron microscope (FIB-SEM) (TESCAN Lyra 3 GT FIB-SEM) with a gallium ion source-focused ion beam was used. Chemical analysis during and after cycling was conducted by using a windowless EDS detector with extreme electronics (Oxford Instrument). This EDS detector allows for the detection of

lithium with a low X-ray energy of 52 eV, which cannot be detected with standard EDS detectors^{32,33}. This detector eliminates the absorption of low energy X-rays by the windows in standard EDS detectors and increases the detection capabilities by using low noise extreme electronics³³.

Data availability

All data used in this manuscript are available from the authors.

Acknowledgement

This work was financially supported by Hydro Québec and McGill Engineering Doctoral Award (MEDA). The authors gratefully acknowledge the work of Julie Hamel-Pâquet in preparing the batteries and Michel Roy, Daniel Clément, and Vincent Gariépy for their technical support.

Author contribution

M.G. performed the experiments, M.G., A.P. H.D., S.B., and R.G. interpreted the in situ results; M.L., P.B., A.G., K.Z. prepared the Li metal anode and set up; M.G. and A.P. wrote the manuscript with the input from all the authors.

Competing interests

The authors declare no competing interests.

5.6 References

- 1. Hovington, P. *et al.* New lithium metal polymer solid state battery for an ultrahigh energy: Nano C-LiFePO₄ versus nano Li1. 2V₃O₈. *Nano Lett.* **15**, 2671-2678 (2015).
- 2. Zhang, H. *et al.* Single lithium-ion conducting solid polymer electrolytes: advances and perspectives. *Chem. Soc. Rev.* **46**, 797-815 (2017).
- 3. Rosso, M. *et al.* Dendrite short-circuit and fuse effect on Li/polymer/Li cells. *Electrochim. Acta* **51**, 5334-5340 (2006).
- 4. Monroe, C. & Newman, J. Dendrite growth in lithium/polymer systems a propagation model for liquid electrolytes under galvanostatic conditions. *J. Electrochem. Soc.* **150**, A1377-A1384 (2003).
- 5. Mauger, A., Armand, M., Julien, C. M. & Zaghib, K. Challenges and issues facing lithium metal for solid-state rechargeable batteries. *J. Power Sources* **353**, 333-342 (2017).
- 6. Daigle, J. C. *et al.* Lithium battery with solid polymer electrolyte based on comb-like copolymers. *J. Power Sources* **279**, 372-383 (2015).
- 7. Armand, M., Chabagno, J. & Duclot, M. Fast ion transport in solids. *Electrodes and Electrolytes* **131** (1979).
- 8. Eshetu, G. G. *et al.* Ultrahigh performance all solid-state lithium sulfur batteries: salt anion's chemistry-induced anomalous synergistic effect. *J. Am. Chem. Soc.* **140**, 9921-9933 (2018).
- 9. Judez, X. *et al.* Lithium bis (fluorosulfonyl) imide/poly (ethylene oxide) polymer electrolyte for all solid-State Li–S cell. *J. Phys. Chem. Lett.* **8**, 1956-1960 (2017).
- 10. Golozar, M. *et al.* In situ scanning electron microscopy detection of carbide nature of dendrites in Li-polymer batteries. *Nano Lett.* **18**, 7583-7589 (2018).
- 11. Qian, J. *et al.* High rate and stable cycling of lithium metal anode. *Nat. Commun.* **6**, 6362 (2015).
- 12. Xin, S. *et al.* Solid-state lithium metal batteries promoted by nanotechnology: progress and prospects. *ACS Energy Lett.* **2**, 1385-1394 (2017).
- 13. Ismail, I., Noda, A., Nishimoto, A. & Watanabe, M. XPS study of lithium surface after contact with lithium-salt doped polymer electrolytes. *Electrochim. Acta* **46**, 1595-1603 (2001).

- 14. Kushima, A. *et al.* Liquid cell transmission electron microscopy observation of lithium metal growth and dissolution: Root growth, dead lithium and lithium flotsams. *Nano Energy* **32**, 271-279 (2017).
- 15. Yoshimatsu, I., Hirai, T. & Yamaki, J. i. Lithium electrode morphology during cycling in lithium cells. *J. Electrochem. Soc.* **135**, 2422-2427 (1988).
- 16. Zhao, C. Z. *et al.* Liquid phase therapy to solid electrolyte–electrode interface in solidstate Li metal batteries: A review. *Energy Storage Mater.* (2019).
- 17. Fisher, J. C. Calculation of diffusion penetration curves for surface and grain boundary diffusion. *J. Appl. Phys.* **22**, 74-77 (1951).
- 18. Park, M., Zhang, X., Chung, M., Less, G. B. & Sastry, A. M. A review of conduction phenomena in Li-ion batteries. *J. Power Sources* **195**, 7904-7929 (2010).
- 19. Porter, D. A., Easterling, K. E. & Sherif, M. *Phase Transformations in Metals and Alloys, (Revised Reprint).* (CRC press, 2009).
- 20. Yu, S.-H., Huang, X., Brock, J. D. & Abruna, H. D. Regulating key variables and visualizing lithium dendrite growth: an operando X-ray study. *Journal of the American Chemical Society* (2019).
- 21. Wang, M. *et al.* Effect of LiFSI Concentrations To Form Thickness- and Modulus-Controlled SEI Layers on Lithium Metal Anodes. *The journal of physical chemistry* **122**, 9825-9834 (2018).
- 22. Cheng, X.-B. *et al.* Implantable Solid Electrolyte Interphase in Lithium-Metal Batteries. *Chem* **2**, 258-270 (2017).
- 23. Kizilaslan, A. & Akbulut, H. Assembling All-Solid-State Lithium-Sulfur Batteries with Li3N-Protected Anodes. *ChemPlusChem* 84, 183-189 (2019).
- 24. Chen, Y. C., Ouyang, C. Y., Song, L. J. & Sun, Z. L. Electrical and lithium ion dynamics in three main components of solid electrolyte interphase from density functional theory study. *The journal of physical chemistry* **115**, 7044-7049 (2011).
- 25. Chao, X. *et al.* Interface layer formation in solid polymer electrolyte lithium batteries: an XPS study. *J. Mater. Chem. A* **2**, 7256-7264 (2014).
- 26. Galluzzo, M. D. *et al.* Dissolution of lithium metal in poly(ethylene oxide). *ACS Energy Lett.* **4**, 903-907 (2019).
- 27. Li, Y. *et al.* The effects of lithium salt and solvent on lithium metal anode performance. *Solid State Ion.* **324**, 144-149 (2018).

- 28. Suo, L., Hu, Y. S., Li, H., Armand, M. & Chen, L. A new class of solvent-in-salt electrolyte for high-energy rechargeable metallic lithium batteries. *Nat. Commun.* **4**, 1481 (2013).
- 29. Chen, Y. & Evans, J. W. Thermal analysis of lithium-ion batteries. *J. Electrochem. Soc.* 143, 2708-2712 (1996).
- 30. Spotnitz, R. & Franklin, J. Abuse behavior of high-power, lithium-ion cells. *J. Power Sources* **113**, 81-100 (2003).
- 31. Commarieu, B. *et al.* Solid-to-liquid transition of polycarbonate solid electrolytes in Limetal batteries. *J. Power Sources* **436**, 226852 (2019).
- 32. Hovington, P. *et al.* Direct and indirect observation of lithium in a scanning electron microscope; not only on pure Li! *Microsc. Microanal.* **21**, 2357 (2015).
- 33. Hovington, P. *et al.* Can we detect Li KX-ray in lithium compounds using energy dispersive spectroscopy? *Scanning* **38**, 571-578 (2016).

5.7 Supplementary Information



Supplementary Figure 5.9 Panorama images obtained by stitching together SEM images. a Left side of the battery and b right side of the battery after cycling (scale bars representing 500 μ m)



Supplementary Figure 5.10 SEM images of the anode. SEM images showing high number of dendrites in the vicinity of four isles at different regions of the anode. Scale bars representing: a 50 μ m, b 100 μ m, c 50 μ m, and d 50 μ m.



Supplementary Figure 5.11 Mapping of a milled region of the polymer. Mapping showing a morphological change on the polymer which was observed during cycling showing inhomogeneous distribution of F, C, and O (SEM image scale bar representing 50 μ m and map results scale bar representing 25 μ m).



Supplementary Figure 5.12 Cycling curve and SEM images obtained during cycling (scale bars representing 100 μ m). a Cycling curve showing the time the SEM images b-i were obtained (purple circles) corresponding to Video S2, SEM image b at the beginning of cycling (at 3.25 V); c after 12.5 hours of cycling showing dendrites on the edge of the anode (at 3.39 V); d after 15 hours of cycling showing further growth of the dendrites (at 3.52 V); e after 1 day of cycling showing change on the SPE close to the edge of the anode (at 3.39 V); f after 3 days of cycling showing change on the SPE further from the anode edge (at 3.39 V); g after 7 days of cycling showing more pronounced grain boundaries and formation of a new edge on the anode (at 3.45 V); h after 10 days of cycling showing dendrites formed on the new edge and change on the SPE (at 3.24 V); and i after 14 days of cycling showing further dendrite growth on the new edge, more activity on the grain boundary and coverage of dendrites formed at the beginning by SPE (at 3.54 V)

Description of Additional Supplementary Files

- File: Supplementary Movie 1 Movie showing in-situ cycling of the battery, correlating the SEM images to the cycling curve.
- 2. File: Supplementary Movie 2 Movie showing the close up of formation of an isle on the lithium surface during cycling.
- 3. File: Supplementary Movie 3 Movie showing milling of an isle using FIB.
- File: Supplementary Movie 4 Movie showing in-situ cycling of a different region of the battery, correlating the SEM images to the cycling curve.

Chapter 6 Direct Li Detection and Microstructure Evolution of Li^o Anode in All Solid State Battery: *In Situ* Cycling SEM Observation

Maryam Golozar^{1,2}, Hendrix Demers¹, Andrea Paolella¹, Raynald Gauvin², and Karim Zaghib^{*1} 1 Center of Excellence in Transportation Electrification and Energy Storage, Hydro-Québec, Varennes, Québec J0L 1N0, Canada 2 Department of Mining and Materials Engineering, McGill University, Montréal, Québec H3A 0C5, Canada

*Corresponding author: zaghib.karim@hydro.qc.ca

Preface

In this chapter the anode surface morphology and chemical change is monitored during cycling to investigate the deterioration and reconstruction of the SEI layer during cycling. The effect of anode volume change as the result of charge and discharge is also described. EDS line scans are also conducted on the anode surface to show the distribution of Li, C, and O during cycling. This chapter was submitted to Microscopy and Microanalysis journal on March 2020.

6.1 Abstract

Lithium is a promising anode material in Li-ion battery applications. However, Li is highly reactive and suffers from irregular plating and dendrite formation during cycling which could cause a short-circuit. A solid electrolyte interphase (SEI) layer on the anode protects the Li surface and facilitates homogeneous Li dissolution and deposition. The dissolution and deposition of Li cause volumetric stress that can damage the SEI layer. Monitoring the change in the morphology and chemical composition of the battery is challenging due to the high reactivity and low X-ray energy of Li. In this study, an *in situ* cycling in a scanning electron microscopy (SEM) technique was optimized to monitor the battery throughout its life. Videos of the anode

were prepared using the SEM images. A windowless energy-dispersive spectroscopy (EDS) detector was used to detect Li and monitor the change in the chemical composition. Line scans were conducted to study the distribution of different elements on the anode. This technique helped monitor the evolution of the SEI layer. The EDS results showed a high Li content upon SEI layer damage, which decreased while the C and O contents increased as this layer started forming again. The videos showed inhomogeneous Li deposition and dendrite growth.

Key words: In situ cycling in SEM, dendrites, Li detection, all-solid-state Li metal battery, solid electrolyte interphase

6.2 Introduction

In order to replace fossil fuels with renewable energy sources to minimize the pollution, electrical storage technologies including Li-ion batteries should be further studied and enhanced. These batteries have been used in a variety of applications, from electric vehicles to electronic devices (Goodenough & Park, 2013; Kalhammer, 2000). Li^o is the main component of next generation batteries. Li^o has gained attention for use as anode in all solid state batteries. Even though Li^o is suitable as an anode owing to its high capacity of 3861 mAh g⁻¹ (Hovington et al., 2015a), it could undergo dendrite formation, which could result in failure of the battery.

Li is highly reactive with several elements including oxygen, hydrogen, carbon, and nitrogen (Jeppson et al., 1978). During the first charge of the battery, a protective layer is formed on the surface, which is referred to as the solid electrolyte interphase (SEI) layer (Goodenough & Park, 2013; Emanuel Peled, 1979). The SEI layer is reported to contain Li oxides, carbides, carbides, fluorides, and chlorides (E Peled et al., 1997). The main qualities of an ideal SEI layer are: a) it fully covers the surface of the Li electrode to allow for uniform deposition, b) is elastic to compensate for the electrode volume change during cycling without damage, and c) has low ionic resistance to enable smooth movement of ions through the layer (Z. Li et al., 2014; Mogi et al., 2002; Steiger et al., 2014).

The SEI layer, however, does not remain constant during battery cycling as this layer could be damaged as a result of chemical inhomogeneity or volume change (Harry et al., 2015; Lin et al., 2017; Steiger et al., 2014).

If the SEI layer does not uniformly cover the surface of the Li electrode, an uneven Li layer is irregularly deposited due to the formation of dendrites (W. Li et al., 2015). Steiger et al. (Steiger et al., 2014) reported preferential Li^o deposition on the defects of the SEI layer including chemical inhomogeneities, grain boundaries, and thin SEI layers. Harry et al. (Harry et al., 2015) also reported that deposition mainly occurred on the deteriorated regions of the SEI layer which were present in the vicinity of the impurities at the Li/electrolyte interface. An inhomogeneous SEI layer also affects the dissolution of Li. Kushima et al. (Kushima et al., 2017) reported that dissolution starts from the whiskers that are covered by a thin SEI layer.

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) have been effective in studying the microstructure and chemical evolution of the battery during cycling that could lead to battery failure. In particular, the *in situ* cycling technique allows us to monitor the behavior of the battery throughout cycling. Nevertheless, analyzing Li using SEM and EDS presents several challenges. Li^o has low X-ray energy of 52 eV, which makes it undetectable with a standard EDS detector (Hovington et al., 2016). Low X-ray energies (close to 55 eV) are absorbed in the window of the standard detector (Hovington et al., 2015b; 2016). Li also has a low fluorescence yield of the order of 10^{-4} , which indicates that the probability of Li X-ray generation is low (Hubbell et al., 1994). In this case, a high beam current can be used. A high beam current, however, could cause beam damage (Hovington et al., 2017). Hovington et al. (Hovington et al., 2016) used a windowless EDS detector and detected Li K in binary compounds. This windowless detector was able to overcome the limitation of X-ray absorption that is observed in the standard EDS detectors (Hovington et al., 2016). The high-performance electronics of this detector also increase the detection capabilities of the system (Hovington et al., 2016).

In this study, an *in situ* cycling technique was used to monitor the change in the morphology of an all-solid-state Li metal battery with a polymer electrolyte and LiFePO₄ (LFP) cathode as a result of volume change during cycling with SEM. Videos were prepared using the SEM images

obtained during cycling. A windowless EDS detector was also used to monitor the chemical evolution of the anode surface. Chemical analysis was conducted using point and line scan EDS.

6.3 Materials and Methods

The method described in previous studies (Golozar et al., 2018; 2019) was used in this study. A schematic of the battery assembly in the SEM chamber is shown in **Figure S6.8** of the supplementary information. The cell preparation and *in situ* cycling technique are summarized below.

6.3.1 Cell preparation

In this study, an all-solid-state Li metal battery with a polymer electrolyte was examined. A plane-view battery assembly was used, where the Li surface faced the electron beam during cycling. In this battery assembly, inhomogeneous pressure was applied on the battery; this increased the possibility of dendrite growth. To further accelerate battery failure and dendrite formation, a smaller anode area, with respect to the cathode area, was used (Golozar et al., 2018). The battery assembly has been illustrated in a previous study (Golozar et al., 2018). The battery consisted of a Li metal anode (Hydro-Quebec) with a thickness of 39 µm, polyether-based solid polymer electrolyte (SPE) (Hydro-Quebec) with lithium trifluorosulfonimide (LiTFSI) salt, and an LFP cathode (LFP-(polyether:LiTFSI)). To prepare the cathode, LFP was mixed with a polyether-based polymer and LiTFSI salt with ethylene oxide to a LiTFSI ratio of 20:1. The final slurry was doctor-blade-coated on an aluminum current collector coated with carbon. The loading of the cathode was 7.291 mg cm⁻². The surface of the Li electrode is covered with residuals of polyether oxide (Bessette et al., 2019) used as lubricant for the thin film fabrication. A copper spring was used as contact electrode and to apply pressure on the Li film to push it on the SPE electrolyte and to make good contact between them (Golozar et al., 2018; 2019). The LFP electrode has the same area as SPE and rest on the flat aluminum sample holder, which acts as a contact electrode and pushes the LFP electrode on the SPE electrolyte. The battery was assembled in a dry room and then transferred to the SEM using an airtight sample holder. The

airtight sample holder was built at Hydro-Quebec, but it is similar to the commercial one. The airtight sample holder has a cap with an O-ring which isolated the sample during transport. The cap was removed inside of the SEM after the SEM chamber vacuum of 1×10^{-4} Pa was reached.

6. 3. 2 In situ cycling

A schematic of the battery assembly in the SEM chamber is shown in **Figure S6.8** of the supplementary information. The battery is placed horizontally on the sample holder from the cathode side and the anode side faces the electron beam. The aluminum surface of the sample holder below the cathode is one of the contact electrodes. The other contact electrode in touch with the Li is a copper spring on top of the holder. The wires forming the exterior circuit of the battery are passed through one of the ports of the chamber from the holder to a cycler outside of the microscope. The cycling parameters including the cycling currents, the charge and discharge time for each cycle and the number of cycles are fixed on the cycler software and the voltage of the battery is recorded at each time during cycling.

A heater was placed inside the sample holder to heat the cell. A thermocouple was also placed inside the holder to monitor the cell temperature. Cycling was performed with an SP-150 cycler (BioLogic Science Instruments) at an operating temperature of 80 °C (\pm 0.5 °C). The acquisition software uses Tescan SharkSEM Remote Control API to control the SEM and acquire image at specific regions of interest on the sample and time interval. For this study, the set up was used to monitor the edges of the Li surface and the polymer from the start till the end of cycling at 80 °C. Images were obtained from different regions of the battery for 7 days with a time interval of 30 min to observe the change in the morphology of the battery during charge and discharge. At the beginning of cycling 38 regions were imaged in 30 min and after 1 day, two more regions were added. As observed in the videos, no stage drift was seen during cycling. To correlate the cycling curve to the SEM images. *In situ* experiments were conducted using a TESCAN scanning electron microscope (Mira 3). Chemical analyses were carried out using Oxford Instruments windowless EDS detector (Hovington et al., 2016). Images were obtained at an accelerating

voltage of 5.00 kV and a beam intensity of 10.00 with a predicted beam current of 0.264 nA in the secondary electron (SE) mode (in chamber Everhart-Thornley detector). The image acquisition time was 1s for a 640 x 480 pixels size (pixel dwell time of $3.2 \ \mu$ s) and only 1 frame was acquired. The horizontal field of view was 160 μ m. The *in situ* software enabled to collect images during cycling from the regions that were assigned before cycling. To reduce the beam damage, the beam was blanked in the duration that imaging was not being conducted. Distances on the image were measured by the straight line tool of ImageJ software after setting the scale of the image (Analyze->Set Scale...). The EDS analyses were carried out at beam energy of 5.00 kV in order to minimize the damage and to collect enough signals. The point EDS analysis were done at acquisition time of 30 s, with the longest process time (PT 6), 2048 channel with 5 eV per channel. A dead time of less than 15% was used for both spectrum and line scan acquisition. The X-ray input counts rate was between 2.0 and 3.0 kcps. For the line scan, the distance between pixels was 52 nm.

6. 4 Results and Discussion

Video S1 shows the behavior of one edge of the anode and the SPE during cycling at low magnification. In this video, formation of a surface separation on the Li metal and a dendrite was observed. The cycling curve in the video shows a good cycling behavior for the battery for the first two cycles (4 h of cycling). The following fluctuations in the voltage indicate the beginning of the failure of the battery, probably due to a contact loss. Video S2 shows a higher magnification of the surface separation (shown in Video S1) to analyze this phenomenon in further detail. The region corresponding to Video S2 is shown with a red box in Figure 6.1a. Figure 6.1 shows the SEM images of the battery corresponding to Videos S1 and S2. Figure 6.1a shows the Li edge and SPE with an open circuit voltage (OCV) of 3.27 V. Figure 6.1b-f show the images of the red box from **Figure 6.1a** at a higher magnification. These images show the formation of a surface separation on Li during cycling. The distance of this surface separation was measured, using the software ImageJ, from three different sections to investigate the relationship between the change in the distance and voltage. The measurement of the distance of the surface separation region was done manually using the straight line feature of ImageJ. Three fixed regions of the surface separation area were used to measure the distance using 152 frames. The average of these three regions was used to monitor the distance change with time. The

voltage and time to which these images correlate to are shown through the curve in **Figure 6.2**. The Li morphology evolution and chemical analysis as a result of cycling are discussed in detail below.



Figure 6.1 SEM images of the anode edge and SPE during cycling showing appearance of an surface separation on the anode, as seen in Video S2. The width of the surface separation was measured from three different regions using ImageJ. SEM images obtained a) at the beginning of cycling (at 3.27 V) with low magnification (the red box shows the region from where images b-f were obtained from), b) after 20 h of cycling (at 3.42 V), c) after 29 h of cycling (at 3.52 V), d) after 59 h of cycling (at 2.30 V), e) after 77 h of cycling (at 3.24 V), and f) after 88 h of cycling (at 3.57 V), where this SEM image was obtained during the failure of the battery (Video S1). The time and voltage at which these images were obtained at are illustrated in Figure 6.2. These images correspond to Video S2.

6.4.1 Morphology evolution

Figure 6.2 shows the relationship between changes in the width of the surface separation (blue curve) and the voltage (red curve) during cycling. In this figure, only the region of the cycling curve that showed good cycling behavior is shown. The graph shows that the average width increased during charge and decreased during discharge. This observation is in accordance with the charge and discharge mechanism of the battery. During charge, Li was deposited on the anode which causes volume expansion. As inhomogeneous pressure was applied on the battery, the volume expansion could have caused lateral volume change. During battery discharge,

dissolution of Li occurred on the anode which resulted in closing of this region. The volume change during cycling could have damaged the SEI layer (Lin et al., 2017).



Figure 6.2 Relationship between the change in the average distance (blue curve) of the surface separation with the voltage change (red curve) over time. A comparison between the two curves shows an increase in the distance during charge and a decrease in the distance during discharge.

Other morphological changes that were observed during cycling were the presence of two dendrite morphologies of mossy and needle, as shown in **Figure 6.3**. The blue box in **Figure 6.3a** shows a needle morphology of the dendrite after cycling, and the same is shown at a higher magnification in **Figure 6.3b**. The growth of this dendrite was captured in **Video S1**. **Figure 6.3c** shows a higher magnification of the red box in **Figure 6.3a** which contains a mossy and a needle morphology dendrite located near the surface separation region on the anode. The formation of these two morphologies has also been reported in other studies (Dollé et al., 2002; Golozar et al., 2018). The dendrites with a needle morphology could have perforated through the polymer and may have caused a short circuit of the battery (Dollé et al., 2002). Dendrite growth involves two stages – initiation and propagation – and cannot be stopped once the propagation stage begins (Monroe & Newman, 2004). Rapid growth of the dendrite, shown in Video S1, could be an indication of the rapid progress of the propagation stage.



Figure 6.3 SEM images obtained after the experiment showing the dendrite morphologies observed during cycling. SEM images of a) anode edge showing two regions containing dendrites, b) high-magnification image of the blue dotted box showing a needle dendrite, and c) high-magnification image of red dotted box showing two dendrites with mossy and needle morphologies.

6.4.2 Chemical evolution

In order to analyze the morphological evolution of the Li^o anode, qualitative chemical analysis was carried out using the windowless EDS detector described earlier. Figure 6.4a-e show the SEM images of the surface separation on the anode surface and the regions where point analysis was conducted after 1, 2, 3, 4, and 7 days of cycling. Figure 6.4g shows the EDS results of the surface separation region (referred to as the fiber) during cycling. After 1 day of cycling, the fiber was found to contain a high amount of Li and low amounts of C and O. As cycling continued, the Li content decreased and C and O contents increased. Figure 6.4f shows the EDS results of the anode surface during cycling and the initiation of the surface separation. The Li content remained almost constant with time whereas the C and O contents increased with time. Figure S6.9 in the supplementary information shows the f-ratio of the Li, C, and O with time correlated to Figure 6.4g-f for easier comparison. The C and O observed on the surface of the Li metal anode at the beginning of cycling were from the SEI layer on the surface. The formation of this protective layer was the result of the chemical reactions between the anode and the electrolyte during cycling and the fabrication of the electrodes (Emanuel Peled, 1979). The properties of an SEI layer include being uniform, elastic, protecting the Li surface during cycling and resulting in a uniform deposition (Z. Li et al., 2014; Mogi et al., 2002; Steiger et al., 2014).

However, this layer could get damaged during cycling and result in a preferential deposition in the damaged regions. The surface separation region observed in this study could be a damaged region of the SEI layer as a result of the change in the volume (Lin et al., 2017). Being able to observe the deterioration of the SEI layer and detect the regions that undergo damage during cycling could help understand the underlying principles of inhomogeneous Li deposition and possible dendrite formation in batteries. A comparison of the EDS spectra showed an increase of the C and O contents on both the anode surface and the surface separation. However, the surface separation underwent a higher C increase than at the anode surface and the anode surface showed higher O increase as compared to the surface separation.



Figure 6.4 EDS point analysis of the surface separation of the anode and the anode surface at different times. SEM images show the evolution of anode surface after a) 1 day, b) 2 days, c) 3 days, d) 4 days, and e) 7 days. EDS spectra showed f) comparison of the Li, C, and O contents of the surface separation (fiber) during cycling, g) comparison of the Li, C, and O contents of the anode surface during cycling and the initiation of the surface separation. EDS results showed the presence of fresh Li on the surface separation at the beginning, which decreased with time as the C and O contents increased. Anode surface showed lower amount of Li than at the surface separation. Higher increase in the C content was observed on the fiber and a higher increase in O content was observed on the anode surface. Figure S6.9 shows the f-ratio of the Li, C, and O of the anode and the surface separation for easier comparison.

There were two sources of C and O in this system and set-up: contamination and the battery itself including the polymer and salt. C and O contamination was inevitable in the chamber of the
SEM (Bessette et al., 2019; Y. Li et al., 2017; OrsayPhysics). C contamination was the result of polymerization of the hydrocarbon molecules by the electron beam, which produced a C coating on the surface of the sample (Hren, 1979). The potential sources of these hydrocarbons are pump oils, O-rings, vacuum grease, or the sample itself (Egerton et al., 2004; Ennos, 1954; Hren, 1979). The potential source of O contamination in the SEM chamber was the residual of the water molecules (Hren, 1979). Bessette et al. (Bessette et al., 2019) investigated the C and O pick up on the Li surface in the SEM chamber by removing the passivation layer on the Li surface in the chamber and exposing the fresh Li to the SEM chamber environment. Their study showed that it was O that was mainly picked up (in less than 20 min) while the C content remained constant in the SEM chamber with time (Bessette et al., 2019). In our study, however, a large increase in the C content was observed, indicating that the increase in the C content was mainly due to cycling of the battery.

In our study, the volume change that occurred during cycling damaged the SEI layer and resulted in exposure of fresh Li on the anode surface to the SEM chamber. The increase in O content with time could be attributed to the contamination from the chamber. The increase in the C content, however, was higher than the change in the C content from contamination observed by Bessette et al. (Bessette et al., 2019). Another source of C in this study was the reactions occurring in the battery itself during cycling, including possible polymer PEO and LiTFSI salt decomposition (Commarieu et al., 2019; Eshetu et al., 2018; Golozar et al., 2019). In order to attribute the increase in the C content to the electrolyte, the surface separations should occur on both sides of the anode. Figure 6.5 shows a schematic of this phenomenon. The damage to the SEI layer occurred on both sides of the anode as the cycling continued. The expansion and reduction in the volume of the electrode resulted in the damage to the SEI layer in these regions (similar to a stretch mark), and the freshly exposed Li reacted with C and O from the electrolyte. If the cycling was to continue at high rates, it would result in the complete consumption of Li in the regions with damaged SEI layer and formation of isles (Golozar et al., 2019; Hovington et al., 2015a). Hovington et al. (Hovington et al., 2015a) have demonstrated the thinning of Li in a Li_{1.2}V₃O₈ Li metal polymer battery to the point that the polymer formed bridges between two cells stacked on top of each other. Golozar et al. (Golozar et al., 2019) also showed the initiation of these surface separations and formation of the resulting isles during cycling using *in situ*

cycling with SEM. Our study was able to show the chemical evolution of these surface separations during cycling using EDS analysis.



Figure 6.5 Schematic of the cross-section of the battery before and after cycling. Before cycling, the anode was covered with a uniform SEI layer and after cycling, the SEI layer was damaged.

Figure 6.6 shows the f-ratio of the line scan of the anode surface during cycling. Line scan analysis can show the distribution of Li on the anode surface. The f-ratio method is used to normalize the intensity of each element by the sum of the intensities of all elements (Horny et al., 2010). The SEM images and the EDS spectra showed the formation of three regions. Region 1 (Figure 6.6a) shows the initiation of the surface separation on the anode after 1 day, which contained high Li and low C and O contents. Region 2 shows a new surface separation after 2 days of cycling which again contained the highest amount of Li as compared to the surrounding regions (Figure 6.6b). Region 3 was formed after 4 days of cycling (Figure 6.6d). Formation of these regions is shown in Video S2. Figure S6.10 of the supplementary information shows the different regions as they appear to help with following the change occurring on the surface separation region. Figure 6.7 shows the comparison of the Li line scans after 1, 2, 3, 4, and 7 days of cycling and the initiation of the three regions explained earlier, to better understand the chemical evolution of Li. The 0 of the graphs after 1, 2, 3, and 4 days of cycling are shifted so that the start point of the separation region is aligned to assist in the comparison of the line scans. At the initiation of formation, each region contained fresh Li as compared to the vicinity and as cycling progressed, Li was consumed by C and O. The fresh Li observed at the beginning of the formation of each region was the result of the SEI layer damage. Formation of these regions can be observed in the videos as well. As shown in this figure, the separation in the surface is expanded with time and thus showing newly formed Li rich regions as cycling is continued. The irreversible expansion that could occur during cycling causes the increase in the length of the

separation region and thus the shift in the line scans. Deterioration of the SEI layer and exposure of fresh Li could result in an inhomogeneous deposition and possible dendrite formation (W. Li et al., 2015). The preferential Li deposition on the defects of the SEI layer could be due to uneven local conductivity and localized current (Harry et al., 2015; Steiger et al., 2014). It has also been reported that dendrites are not composed of pure Li but rather contain high amounts of C (Golozar et al., 2018). In this study, it was shown that damage to the SEI layer and the Li consumption by C could result in the formation of dendrites (as shown in **Figure 6.3**).



Figure 6.6 Line scan of the surface separation, as observed in Video S2. F-ratio of the line scan analysis showing the surface separation after a) 1 day (at the end of charge), b) 2 days (at the beginning of discharge), c) 3 days (at the beginning of discharge), d) 4 days (at the end of charge), and e) 7 days (after cycling). The surface separation region contains fresh Li and less C and O as compared to the surrounding. As cycling continued, the Li content decreased and C and O contents increased. Figure S6.10 of the supplementary information shows the different regions as they appear to help follow the change occurring on the surface separation.



Figure 6.7 Comparison of the Li content of the surface separation region showing the expansion of the surface as the result of charging. The comparison shows high Li content at the beginning and a subsequent decrease as the battery is cycled. The three marked regions show the Li content of a region on the anode that is opened up and which contained a high Li content. The fresh Li observed during the cycling is the result of the damage in the SEI layer.

6.5 Conclusion

In this study, *in situ* cycling with SEM was conducted to monitor the behavior of an all-solidstate Li metal battery with polymer electrolytes. A windowless EDS detector was used to conduct chemical analysis. The videos prepared using the SEM images showed an inhomogeneous Li deposition during cycling that included dendrite growth. Formation of a surface separation on the anode surface that was correlated to SEI layer deterioration was also observed. The correlation between the cycling curve and the change in the distance of the surface separation showed that this phenomenon was the result of change in volume during cycling. During charging, Li accumulated towards the anode surface, which induced local volume expansion and measurably increased anode surface separation. The dissolution of Li occurred during discharge, which resulted in a decrease in the distance of the surface separation. The windowless EDS detector was able to overcome the limitations of a standard EDS detector in detecting Li. The point analysis and line scan results showed exposure of fresh Li from the bulk of the anode as the result of SEI layer deterioration during cycling. As cycling continued, the C and O contents of this region increased and Li content decreased. This could be due to high reactivity of Li and restoration of the SEI layer. The increase in the C content detected in this study indicated the consumption of Li in the anode by the C that was present in the electrolyte.

Acknowledgement

This study was financially supported by Hydro Québec, Natural Sciences and Engineering Research Council of Canada (NSERC), and McGill Engineering Doctoral Award (MEDA). The authors gratefully acknowledge the work of Steve Collin-Martin in preparing the batteries and Michel Roy, Daniel Clément, and Vincent Gariépy for their technical support.

6. 6 References

Bessette, S., Hovington, P., Demers, H., Golozar, M., Bouchard, P., Gauvin, R., & Zaghib, K. (2019). In-situ characterization of lithium native passivation layer in a high vacuum scanning electron microscope. *Microsc. Microanal.*, *25*(4), 866-873.

Commarieu, B., Paolella, A., Collin-Martin, S., Gagnon, C., Vijh, A., Guerfi, A., & Zaghib, K. J. J. o. P. S. (2019). Solid-to-liquid transition of polycarbonate solid electrolytes in Li-metal batteries. *J. Power Sources*, 436, 226852.

Dollé, M., Sannier, L., Beaudoin, B., Trentin, M., & Tarascon, J. M. (2002). Live scanning electron microscope observations of dendritic growth in lithium/polymer cells. *Electrochem. Solid-State Lett.*, *5*(12), A286-A289.

Egerton, R. F., Li, P., & Malac, M. (2004). Radiation damage in the TEM and SEM. *Micron*, 35(6), 399-409.

Ennos, A. E. (1954). The sources of electron-induced contamination in kinetic vacuum systems. *Br. J. Appl. Phys.*, *5*(1), 27-31.

Eshetu, G. G., Judez, X., Li, C., Martinez-Ibañez, M., Gracia, I., Bondarchuk, O., Carrasco, J., Rodriguez-Martinez, L. M., Zhang, H., & Armand, M. (2018). Ultrahigh performance all solid-state lithium sulfur batteries: salt anion's chemistry-induced anomalous synergistic effect. *J. Am. Chem. Soc.*, *140*(31), 9921-9933.

Golozar, M., Hovington, P., Paolella, A., Bessette, S., Lagacé, M., Bouchard, P., Demers, H., Gauvin, R., & Zaghib, K. (2018). In situ scanning electron microscopy detection of carbide nature of dendrites in Li–polymer batteries. *Nano Lett.*, *18*(12), 7583-7589.

Golozar, M., Paolella, A., Demers, H., Bessette, S., Lagacé, M., Bouchard, P., Guerfi, A., Gauvin, R., & Zaghib, K. (2019). In situ observation of solid electrolyte interphase evolution in a lithium metal battery. *Commun. Chem., 2*(1), 131.

Goodenough, J. B., & Park, K. S. (2013). The Li-ion rechargeable battery: a perspective. *J. Am. Chem. Soc.*, 135(4), 1167-1176.

Harry, K. J., Liao, X., Parkinson, D. Y., Minor, A. M., & Balsara, N. P. (2015). Electrochemical deposition and stripping behavior of lithium metal across a rigid block copolymer electrolyte membrane. *J. Electrochem. Soc.*, *162*(14), A2699-A2706.

Horny, P., Lifshin, E., Campbell, H., & Gauvin, R. (2010). Development of a new quantitative X-ray microanalysis method for electron microscopy. *Microsc. Microanal.*, *16*(6), 821-830.

Hovington, P., Lagacé, M., Guerfi, A., Bouchard, P., Mauger, A., Julien, C., Armand, M., & Zaghib, K. (2015a). New lithium metal polymer solid state battery for an ultrahigh energy: Nano C-LiFePO4 versus nano Li1. 2V3O8. *Nano Lett.*, *15*(4), 2671-2678.

Hovington, P., Lagace, M., Principe, E., Burgess, S., Guerfi, A., Demers, H., Gauvin, R., & Zaghib, K. (2015b). Direct and indirect observation of lithium in a scanning electron microscope; not only on pure Li! *Microsc. Microanal.*, *21*, 2357-2358.

Hovington, P., Timoshevskii, V., Bessette, S., Burgess, S., Statham, P., Demers, H., Gauvin, R., & Zaghib, K. (2017). On the detection limits of Li K X-rays using windowless energy dispersive spectrometer (EDS). *Microsc. Microanal.*, 23(S1), 2024-2025.

Hovington, P., Timoshevskii, V., Burgess, S., Demers, H., Statham, P., Gauvin, R., & Zaghib, K. (2016). Can we detect Li KX-ray in lithium compounds using energy dispersive spectroscopy? *Scanning*, *38*(6), 571-578.

Hren, J. J. (1979). Barriers to AEM: Contamination and etching. In J. J. Hren, J. I. Goldstein, & D. C. Joy (Eds.), *Introduction to Analytical Electron Microscopy* (pp. 481-505). Boston, MA: Springer.

Hubbell, J., Trehan, P., Singh, N., Chand, B., Mehta, D., Garg, M., Garg, R., Singh, S., & Puri, S. (1994). A review, bibliography, and tabulation of K, L, and higher atomic shell x-ray fluorescence yields. *J. Phys. Chem. Ref. Data*, 23(2), 339-364.

Jeppson, D. W., Ballif, J. L., Yuan, W. W., & Chou, B. E. (1978). *Lithium literature review: lithium's properties and interactions* (No. HEDL-TME--78-15). Hanford Engineering Development Lab.

Kalhammer, F. R. (2000). Polymer electrolytes and the electric vehicle. *Solid State Ion., 135*(1), 315-323.

Kushima, A., So, K. P., Su, C., Bai, P., Kuriyama, N., Maebashi, T., Fujiwara, Y., Bazant, M. Z., & Li, J. (2017). Liquid cell transmission electron microscopy observation of lithium metal growth and dissolution: Root growth, dead lithium and lithium flotsams. *Nano Energy*, *32*, 271-279.

Li, W., Zheng, H., Chu, G., Luo, F., Zheng, J., Xiao, D., Li, X., Gu, L., Li, H., & Wei, X. (2015). Effect of electrochemical dissolution and deposition order on lithium dendrite formation: a top view investigation. *Faraday Discuss.*, *176*, 109-124.

Li, Y., Li, Y., Sun, Y., Butz, B., Yan, K., Koh, A. L., Zhao, J., Pei, A., & Cui, Y. (2017). Revealing nanoscale passivation and corrosion mechanisms of reactive battery materials in gas environments. *Nano Lett.*, *17*(8), 5171-5178.

Li, Z., Huang, J., Liaw, B. Y., Metzler, V., & Zhang, J. (2014). A review of lithium deposition in lithium-ion and lithium metal secondary batteries. *J. Power Sources, 254*, 168-182.

Lin, D., Liu, Y., & Cui, Y. (2017). Reviving the lithium metal anode for high-energy batteries. *Nat. Nanotechnol.*, *12*(3), 194-206.

Mogi, R., Inaba, M., Jeong, S. K., Iriyama, Y., Abe, T., & Ogumi, Z. (2002). Effects of some organic additives on lithium deposition in propylene carbonate. *J. Electrochem. Soc.*, *149*(12), A1578-A1583.

Monroe, C., & Newman, J. (2004). The effect of interfacial deformation on electrodeposition kinetics. *J. Electrochem. Soc.*, *151*(6), A880-A886.

OrsayPhysics. Scientific Overviews: What is UHV?

Peled, E. (1979). The electrochemical behavior of alkali and alkaline earth metals in nonaqueous battery systems—the solid electrolyte interphase model. *Journal of The Electrochemical Society*, *126*(12), 2047-2051.

Peled, E., Golodnitsky, D., & Ardel, G. (1997). Advanced model for solid electrolyte interphase electrodes in liquid and polymer electrolytes. *J. Electrochem. Soc.*, 144(8), L208-L210.

Steiger, J., Kramer, D., & Mönig, R. (2014). Mechanisms of dendritic growth investigated by in situ light microscopy during electrodeposition and dissolution of lithium. *J. Power Sources, 261*, 112-119.

6.7 Supplementary Information



Figure S6.8 Schematic of the *in situ* set up. The battery is placed horizontally on the sample holder and the anode surface is imaged during cycling.



Figure S6.9 F-ratio of Figure 6.4f-g from the manuscript. The f-ratios show the change in the Li, C, and O content of the anode surface and the surface separation (fiber) at different times during cycling. The fiber shows high amount of Li at the beginning which decreases with time and low C and O.



Figure S6.10 SEM images of the anode surface showing the evolution of Li during cycling correlating to Figure 6.6 of the manuscript. Different regions are indicated with different colors to help with following the change occurring on the surface separation (the size of the images are changed so that they would be aligned and the sizes do not represent the actual distance of the line scans).

Chapter 7 Direct Observation of Lithium Metal Dendrites with Ceramic Solid Electrolyte

Maryam Golozar^{1,2}, Andrea Paolella¹, Hendrix Demers¹, Sylvio Savoie¹, Gabriel Girard¹, Nicolas Delaporte¹, Raynald Gauvin², Abdelbast Guerfi¹, Henning Lorrmann³ and Karim Zaghib^{*1}

1 Center of Excellence in Transportation Electrification and Energy Storage, Hydro-Québec, Varennes, Québec J0L 1N0, Canada

2 Department of Mining and Materials Engineering, McGill University, Montréal, Québec H3A 0C5, Canada

3 Fraunhofer-Institut für Silicatforschung ISC, Neunerplatz 2, 97082 Würzburg, Germany

*Corresponding author: zaghib.karim@hydro.qc.ca

Preface

This chapter investigates the effect of using a solid electrolyte with a high shear modulus and to study if enhancing the mechanical properties alone could improve battery cycling behavior. To do so, an all-solid-state Li-metal cell with LLZO ceramic electrolyte that has a higher shear modulus than polymer was cycled inside a SEM. The behavior of the battery is monitored from the beginning till the end of cycling and with the aid of the videos from the SEM images and the chemical analysis conducted during cycling the failure mechanism is explained. This chapter was submitted to Scientific Reports on April 2020 and is currently under revision.

7.1 Abstract

Dendrite formation, which could cause a battery short circuit, occurs in batteries that contain lithium metal anodes. In order to suppress dendrite growth, the use of electrolytes with a high shear modulus is suggested as an ionic conductive separator in batteries. One promising candidate for this application is Li₇La₃Zr₂O₁₂ (LLZO) because it has excellent mechanical properties and chemical stability. In this work, *in situ* scanning electron microscopy (SEM) technique was employed to monitor the interface behavior between lithium metal and LLZO electrolyte during cycling with pressure. Using the obtained SEM images, videos were created that show the inhomogeneous dissolution and deposition of lithium, which induce dendrite growth. The energy dispersive spectroscopy analyses of dendrites indicate the presence of Li, C, and O elements. Moreover, the cross-section mapping comparison of the LLZO shows the inhomogeneous distribution of La, Zr, and C after cycling that was caused by lithium loss near the Li electrode and possible side reactions. This work demonstrates the morphological and chemical evolution that occurs during cycling in a symmetrical Li–Li cell that contains LLZO. Although the superior mechanical properties of LLZO make it an excellent electrolyte candidate for batteries, the further improvement of the electrochemical stabilization of the garnet–lithium metal interface is suggested.

Keywords: ceramic Garnet, LLZO, Lithium metal, solid state batteries, In situ, Dendrites

7.2 Introduction

Metallic lithium is a potential anode material for high energy density Li-ion batteries because of its high capacity (3860 mAh·g⁻¹ for the reduced form).¹ Lithium anodes, however, undergo dendrite formation during cycling that can increase the risk of battery short circuit.² To overcome this limitation, one technique is the use of solid electrolytes with a high shear modulus to withstand perforations by dendrites and thus prevent battery short circuit. Monroe and Newman³ have reported that a shear modulus that is twice that of Li can suppress dendrite growth. Recently, the use of ceramics as solid electrolytes in all-solid Li metal batteries have attracted interest because of their high shear modulus. The failure and short circuit of batteries that contain ceramic electrolytes, however, have been reported.⁴⁻⁷ One interesting electrolyte material for this application is Li₇La₃Zr₂O₁₂ (LLZO) because it has a) a high voltage stability (up to 5V), b) high conductivity at room temperature (> 1×10⁻⁴ S/cm), c) low kinetic reactivity with Li, and d) high shear modulus (approximately 55 GPa).⁸⁻¹² Although LLZO satisfies the Monroe and Newman criteria and has exhibited promising properties, the failure of batteries that contain this electrolyte has been reported. Aguesse et al.⁵ indicated the electrochemical collapse of batteries

that contain LLZO electrolytes at room temperature as a result of Li metal formation in the LLZO during cycling. It is also found that lithium metal propagation through this electrolyte occurs through the grain boundaries.⁶ Shen et al.¹³ correlated the battery short circuit to the interconnected pores in the LLZO. Basappa et al.¹⁴ solved the pore interconnectivity problem by modifying the grain boundaries.

In order to fully understand the behavior of garnet LLZO during cycling, further investigations are necessary. This work focuses on observing the failure behavior of the cell containing LLZO electrolyte including conducting chemical analysis on the dendrites. In this *in situ* study, scanning electron microscopy (SEM) is employed to monitor the behavior of Li surface and $Li_7La_3Zr_2O_{12}$ during cycling. Videos are constructed using a multitude of subsequent SEM images that exhibit the morphological evolution during cycling. Energy dispersive spectroscopy (EDS) is also employed to conduct a chemical analysis. The *set up* and the experiments of this work are designed in a way to push the cell to its limits and to observe dissolution and deposition of lithium, leading to the formation of mossy and needle morphology dendrites. The chemical analysis of dendrites shows that they are mainly composed of Li_2CO_3 and Li_xC_y , and Li_2O . The chemical comparison of the LLZO cross-sections before and after cycling also shows the inhomogeneous distribution of Zr, La, and C after cycling as a result of lithium loss reaction near the lithium metal electrode.

7.3 Materials and Methods

7.3.1 Ceramic and symmetrical Li-LLZO-Li cell preparation

Symmetrical Li cells with $Li_7La_3Zr_2O_{12}$ (LLZO) solid electrolytes were used in this study. Following our previous reports,^{15,16} the gallium-doped LLZO electrolyte is synthesized by mixing 5,92 g of Li_2CO_3 , 11,39 g of La_2O_3 , 5,77 g of ZrO_2 and 0.56 g of Ga_2O_3 in planetary mill with ZrO_2 balls under air atmosphere and then the mixture is annealed in tubular furnace on graphite (or zirconia or alumina) boat. The temperature was increased from room temperature to 700 °C and then the synthesis temperature was increased up to 950 °C and kept for 2 hours keeping N_2 gas flowing. Finally, the powder was cooled down. The final powder is cold pressed at 100 MPa and annealed in air atmosphere at 1100°C for 10 hours. The final ceramic pellet has a thickness of 1 mm and an ionic conductivity at room temperature and 80 °C of 6×10^{-4} S/cm and 2×10^{-3} S/cm respectively (see **Figure S7.9**). The LLZO pellet shows a density of 99%. A plane view cell assembly and set up were used in this work.¹⁷ Lithium metal electrodes (Hydro-Quebec) that are 34 µm thick are pressed on both sides of the electrolyte. The surface of the Li electrode is covered with residuals of polyether oxide¹⁸ used as lubricant for the thin film fabrication. To induce dendrite growth, the Li electrode facing the SEM electron beam, which is monitored during cycling, has a smaller area than the LLZO with area of 1.33 cm² that creates edge effect.¹⁷ A copper spring was used as contact electrode and to apply pressure on the Li film to push it on the LLZO electrolyte and to make good contact between them.^{17,19} The lower Li electrode has the same area as LLZO and rest on the flat aluminum sample holder, which acts as a contact electrode and push the lower Li electrode on the LLZO electrolyte. The electrodes were connected to the cycler using an electric feedthrough installed in one of the SEM port. A schematic of the set up is shown in **Figure S7.10**. The cell is assembled in the glove box and thereafter transferred to the SEM using an airtight sample holder.

7. 3. 2 In situ cycling and post-mortem analysis

A TESCAN scanning electron microscope (Mira 3) was employed to perform the *in situ* imaging of cells during cycling. *In situ* set up, transfer holder, and acquisition software were designed and developed at Hydro-Québec. Beam energy of 5.00 kV was used for imaging and analysis. Also during cycling, images were obtained every 30 min from different areas of the upper Li and LLZO and the beam was blanked during the time that no images were obtained to minimize the exposure of each region to the beam. Thereafter these images were used for constructing videos to demonstrate the behavior of the cell during Li shuttling. *Ex situ* analyses were conducted using a focused ion beam scanning electron microscope (FIB-SEM) (TESCAN Lyra 3 GT FIB-SEM) with a gallium ion source-focused ion beam. Chemical analyses were conducted using a windowless EDS detector with extreme electronics (Oxford Instrument) that enables the detection of Li.²⁰

7. 4 Results and Discussion

Figure 7.1a shows the surface of Li and LLZO before cycling. The cell is cycled in the microscope at 80 °C to reach the ionic conductivity of 2×10^{-3} S/cm. Figure S7.11 shows the

cycling curve of the cell: first, a $-7.5 \ \mu A.cm^{-2}$ current density was applied to induce Li metal deposition on the Li electrode at the bottom of LLZO that does not face the electron beam. After 1 day of cycling, the current density was changed to -15μ A.cm⁻². After 4 days, the current density was increased to $+15 \ \mu A.cm^{-2}$; Li deposition occurs on the Li electrode facing the electron beam. The increase in the current density was done to monitor the failure of the cell faster and at extreme conditions. Figure 7.2 depicts two dendrite morphologies of needle and mossy on the bottom Li electrode that were formed during Li deposition on the bottom side. These dendrites could have been initiated from the defects such as the grain boundaries, regions covered with thin solid electrolyte interphase (SEI) layer, and possible contaminations.^{21,22} The fact that these dendrites are observed in this specific region of the bottom Li electrode from the top view could be due to possible low pressure in this area that allows for further dendrite growth outwards the cell. The SEM images in Figure 7.1 correspond to those of Video S1, which demonstrates the behavior of the cell from the beginning to end of cycling. The phenomena observed during cycling include Li thinning, formation of mossy morphology dendrite, bump morphology deposition, formation of needle morphology dendrite, and change in the LLZO chemical composition. Figure 7.1b and 1c show the thickness evolution of some regions of Li after 50 and 94 h of cycling, respectively (corresponding to -7.5 µA.cm⁻², at -0.0057 V and +15 μ A.cm⁻², at -0.0018 V respectively). Figure 7.1d shows the initiation of a mossy dendrite morphology after 97 h of cycling (corresponding to $+15 \ \mu A.cm^{-2}$, at -0.0022 V). In addition, Figure 7.1e illustrates the further growth of a mossy dendrite and the formation of a bump beside it after 110 h of cycling (corresponding to +15 µA.cm⁻², at -0.0022 V). Figure 7.1f depicts an emerging needle dendrite after 119 h of cycling on the region where Li thinning was observed (corresponding to +15 μ A.cm⁻², at -0.0022 V). Figure 7.1g and 1h show the further growth of dendrites on Li after 124 and 128 h of cycling, respectively (corresponding to +15 μ A.cm⁻², at -0.0034 V and +15 μ A.cm⁻², at -0.0018 V respectively). The many spiked that are observed in the cycling curve is due to the formation of dendrites and the loss of Li as the result of thinning of Li electrode that could lower the contact between the Li and the LLZO electrodes. The goal of this work is to study the failure of the cell. Therefore the cell is push to the extreme in order to be able to collect data and images of the cell in a shorter period of time using the SEM. These phenomena are further discussed in detail below.



Figure 7.1 Obtained cell SEM images corresponding to **Video S1**; a) Li and LLZO (at -0.0036 V and $-7.5 \ \mu$ A.cm⁻²) at the beginning of cycling; b) beginning of Li thinning (at -0.0057 V and $-7.5 \ \mu$ A.cm⁻²) after 50 h cycling ; c) further Li thinning and formation of a bump on Li indicated by yellow dotted circle (at -0.0018 V and $+15 \ \mu$ A.cm⁻²) after 94 h cycling; d) initiation of the extrusion of mossy dendrite indicated by green dotted circle (at -0.0022 V and $+15 \ \mu$ A.cm⁻²) after 97 h cycling; e) further extrusion of mossy dendrite and formation of an adjacent bump morphology (at -0.0022 V and $+15 \ \mu$ A.cm⁻²) after 110 h cycling; f) mossy dendrite and initiation of needle dendrite formation indicated by red dotted circle (at -0.0022 V and $+15 \ \mu$ A.cm⁻²) after 119 h cycling; g) further growth of mossy and needle dendrites (at -0.0034 V and $+15 \ \mu$ A.cm⁻²) after 124 h cycling; h) mossy and needle dendrites and bump morphology on Li surface (at -0.0018 V and $+15 \ \mu$ A.cm⁻²) after 128 h cycling. A small shift in images was observed because of specimen drifting during cycling that can be monitored by following the yellow dotted circle.



Figure 7.2 SEM images of the cell with dendrites with mossy and needle morphologies on Li at the bottom side of LLZO formed when applied current has negative values.

7.4.1 Thinning of Li electrode

For reference, a dense Li film in theory (homogenous film dissolution) loses approximately 5 µm per 1 mAh.cm⁻² of charge. The thickness of some regions in the Li electrode facing the electron beam was significantly reduced during cycling (Figure 7.1 and Figure 7.2). Figure S4 shows three SEM images at higher magnification, focused on the thinned regions. Figure S7.12b shows the diameter and thickness of a thinned region after 4 days of cycling. This thickness reduction was correlated to Li metal dissolution, which is more uniform compared to that in Li metal polymer batteries reported by Golozar et al.¹⁸ and Hovington et al.¹. In batteries that use polymer electrolytes, a more local dissolution starting from the grain boundaries is observed.²² In the case of LLZO, however, the dissolution of Li was observed in larger areas; in some cases containing a few neighboring grains at different parts of the Li electrode. This may be because of the higher Li⁺ transfer number in the LLZO than in polymers²³ and elimination of salt decomposition reported in polymer batteries.^{22,24} Although Li dissolution was more uniform in these cells, the change in Li thickness during the dissolution was still inhomogeneous on the electrode surface. To further investigate this phenomenon, the windowless EDS detector was employed to conduct mappings of the Li surface. Lithium has an X-ray energy of 52 eV, which is too low to be detected with a standard EDS detector;^{20,25} on the contrary, a windowless detector can detect Li.

Different from a standard detector, this detector a) does not have a window, which overcomes the absorption of low energy X-ray limitations and b) it has low-noise extreme electronics, which increases its detection capabilities of low energy X-ray.²⁰

Figure 7.3a shows the mapping of one region of metallic lithium after cycling. This mapping area is divided into three regions with different thicknesses. Region 1 has the highest amount of Li, indicating the least change in thickness. In region 2, high amounts of C and O, as well as some amounts of La and Zr from the LLZO electrolyte, were detected, indicating the thinning of Li in this part. Region 3 has the highest La and Zr contents; the SEM image shows the highest dissolution of Li in this region where even the LLZO morphology can be observed. The inhomogeneous dissolution on the entire surface of Li could be related to the crystallographic orientations of different Li grains. Some crystallographic orientations could be more susceptible to Li dissolution than others.²⁶ The end of the cycling curve (**Figure S7.11**) also shows significant voltage fluctuations, indicating the consumption of Li resulting in the thinning of various regions of the Li electrode with different thicknesses is presented in **Figure 7.3b** (in this figure all electrodes are drawn with the same size to show the behavior of the cell during cycling better and easier to follow).



Figure 7.3 Mapping and schematic of Li thinning. a) Mapping of Li surface after cycling from a region where Li thinning was observed. It is divided into three regions: Region 1 shows a high Li amount where lesser thinning occurs than that in Region 2 that shows higher amounts of C, O, La, and Zr. Region 3 is the thinnest area with the highest La and Zr contents. b) Schematic of cell behavior after the dissolution. The cell cross-section shows inhomogeneous Li dissolution on different electrode regions.

7. 4. 2 Bump and mossy morphology dendrite

Observations show the inhomogeneous Li deposition in the form of mossy dendrites, needle dendrites, and bump morphology (Figure 7.1e-h). Figure S7.13 shows the SEM images of some areas on the Li surface with bump and mossy morphologies. These morphologies were mainly observed close to the regions where lithium metal becomes thinner. Inhomogeneous Li

deposition might be responsible for lowering the efficiency of the cell, damaging the Li surface, and resulting in a possible short circuit. **Figure S7.13a** and **f** show two mossy dendrites that were able to tear open the Li from the thinned region (dendrite 1) and pierce through the thinned Li (dendrite 4) where less pressure was applied. Monroe and Newman³ reported that if the separator's shear modulus is more than twice that of Li, a more uniform electrodeposition can be achieved and less roughening is observed. Lithium and LLZO have shear moduli of 3.4 GPa²⁷ and approximately 55 GPa^{11,12}, respectively, that satisfy Monroe and Newman's criterion. Local Li deposition and dendrite growth in these cells, however, are still observed. To overcome inhomogeneous deposition, the sole use of Monroe and Newman's criterion is insufficient .^{27,28} When the electrolyte is porous, it is still possible to observe dendrites .²⁸ In order to achieve a uniform lithium metal deposition both the mechanical properties of the electrolyte and the ion transport must be accomplished.²⁷ Tikekar et al.²⁷ investigated the effect of both electrochemical and mechanical properties of the electrolyte on Li electrodeposition. They suggested three methods to achieve a more uniform electrodeposition: a) immobilization of anions, b) use of electrolytes with a high shear modulus, and c) cycling at low current densities.

The main origin of inhomogeneous deposition is Li surface roughening during cycling, which results in the non-uniform current density distribution on the surface. In the case of polymer electrolytes, the polymer deformation causes variation in the concentration of lithium ions and thus ionic conductivity.^{27,29} This phenomenon alters the current density on the electrode, where regions with higher conductivities encounter higher current densities that results in local deposition in these regions.²⁷ Tikekar et al.²⁷ reported that the immobilization of anions in the electrolyte could reduce the electric field close to Li that facilitates dendritic deposition. When using polymer electrolytes, Monroe and Newman's³ model introduces a new stability parameter that describes deposition and roughness. When the stability parameter is positive, a faster deposition is observed on the peaks of the deformed surface, resulting in unstable deposition and further surface roughness.³ They also indicated that when the shear modulus of the electrolyte is greater than twice that of Li, the electrodeposition is stabilized because the parameter is negative.³ Although ceramic electrolytes satisfy the shear modulus criterion and no electrolyte deformation occurs, unstable and non-uniform deposition is still observed. This could be the result of the inhomogeneous dissolution of Li during cycling, resulting in a rough Li electrode surface. The thinned regions are similar to the valleys in Li metal polymer batteries, and the

adjacent thick regions are similar to the peaks. The exchange current density is higher near the peaks, causing a faster Li deposition. Tsai et al.¹² also reported that inhomogeneous dissolution and deposition could result in non-uniform contacts between the ceramic and Li, causing high interface resistance and high current densities, which makes these regions susceptible to dendrite growth. Marbella et al.⁷ also reported the inhomogeneous deposition and dissolution of Li to be due to inhomogeneous contact between the electrodes. In this study, although the observation of long dendrites could be correlated to the inhomogeneous pressure on the Li electrode facing the beam, inhomogeneous Li deposition and bump and mossy morphologies cannot be fully eliminated even in the presence of homogeneous pressure. This is because the foregoing are the result of inhomogeneous Li dissolution and uneven distribution of current density on the Li electrode. In fact, the bump morphologies are original Li surface regions with new Li depositions beneath them that are unable to break the surface dendrites.

7. 4. 3 Needle morphology dendrite

Figure 7.4 shows the SEM images of the growth of a needle morphology dendrite on the Li surface when $\pm 15 \ \mu$ A.cm⁻² current density was applied (**Video S2**). These images show that the tip (yellow dotted circle) and kink (green dotted circle) on the dendrite do not change during growth. The red line in **Figure 7.4** indicates the elongation of dendrite from the base. Yamaki et al.³⁰ also reported dendrite growth from the base in an organic electrolyte that was compared to tin whisker growth. The growth of dendrites towards the direction where less pressure was applied (from the Li surface outward in the SEM vacuum) could be due to the compressive stress applied at the base of the dendrite as Li deposition continues in these regions. To further investigate the dendrite, a chemical analysis was conducted using EDS. **Figure 7.5** presents the EDS analysis of the Li surface and the base and different points on the dendrite arm. The EDS analysis shows that the dendrite contains higher amount of Li than the electrode surface, which indicates the presence of fresh Li metal in the dendrite.

As indicated by the C and O contents, the dendrites are not composed of pure Li.¹⁷ The presence of C and O could be the result of both chemical reactions during cycling and contamination. Contamination is inevitable in the SEM chamber due to polymerization of hydrocarbon molecules on the surface of the sample by the electron beam and residuals of water

molecules.^{18,31,32} Bessette et al.¹⁸ investigated the rate of O and C pick up on the Li surface at different temperatures in an SEM. In their work, a high amount of O pick up was observed in less than 20 min, whereas almost no C pick up was noted. Based on their study, it can be concluded that the C content of dendrites that are observed on the battery is mainly the result of battery cycling. A second source of C and O in the battery is represented by Li₂CO₃, which is present around the LLZO particles. Based on the comparison of EDS spectra of dendrites with those of Li₂CO₃ powder¹⁷, the C–O ratio in the dendrites is higher than in the Li₂CO₃ powder. The excess C may be caused by the presence of Li carbide (Li_xC_y) in the dendrites. Lithium carbide and oxide may be the result of Li carbonate reduction during cycling. Overall, it could be concluded that the dendrites are composed of a combination of Li₂CO₃ and Li_xC_y, and Li₂O.



Figure 7.4 SEM images of the cell corresponding to Video S2 at +20 μ A after a) 93 h, b) 95 h, c) 97 h, d) 100 h, e) 104 h, f) 107 h, and g) 119 h of cycling. The red lines show the change in dendrite length from the base. The yellow and green dotted circles show the regions where no change was observed. This figure shows growth from the dendrite base.



Figure 7.5 EDS analysis of the needle dendrite in Figure 7.4. a) SEM image of the needle dendrite; b) high magnification of red dotted square in a; c) high magnification of blue dotted square in a; d) EDS analysis of Li surface and base with a high amount of Li at dendrite base; e) EDS spectra from different parts of the dendrite showing presence of C and O.

Figure 7.6 shows the SEM images of a needle morphology dendrite that is formed on the region of the electrode where Li is consumed. The high magnification SEM image of the base shows that the dendrite initiates from the LLZO surface and grows outward rather than perforating through the electrolyte. **Figure S7.14c-e** also show two dendrites (dendrites 2 and 3) that form on a thinned Li region and pierce through Li as they grow. These images show that although LLZO provides good mechanical pressure towards dendrite perforation through the electrolytes, inhomogeneous Li deposition in the form of needle and mossy dendrites that can lower the battery efficiency are still observed. Lithium propagation through the ceramic has been observed in some studies.⁴⁻⁶ Aguesse et al.⁵ detected regions containing Li metal in the cross-section of LLZO. Cheng et al.⁴ observed an opening in the cross-section of Li_{6.25}Al_{0.25}La₃Zr₂O₁₂ after cycling. They attributed this to Li propagation through the grain boundaries.⁴ Porz et al.⁶ reported Li propagation to be through the defects of Li₆La₃ZrTaO₁₂.

Dendrite formation mainly consists of two regimes—initiation and propagation.³³ Its formation, however, cannot be stopped if propagation begins.³³ In this study, inhomogeneous pressure was applied to the Li surface facing the electron beam. The variation of pressure on this Li face and

the presence of ceramic on the other face could explain the dendrite growth. The foregoing only considers the mechanical properties of the electrolyte. Considering the electrochemical properties of the electrolyte, dendrite initiation is expected to occur because of inhomogeneous Li dissolution and deposition, as discussed in Section 3.2. The suppression of dendrite propagation could prevent possible battery short circuits, but phenomena, such as local dissolution, deposition, and dendrite initiation, reduce battery efficiency. The use of LLZO ceramic electrolyte with applied homogenous pressure could suppress dendrite growth. To fully eliminate dendrite formation, however, the electrochemical properties of the battery should be further enhanced. High-magnification SEM images of a dendrite formed during cycling are shown in **Figure 7.7**. These images show that the dendrites are not formed as one continuous arm but rather contain different sections and arms. This type of dendrite growth is more stable than one continuous arm because of its lower surface free energy.



Figure 7.6 SEM images of Li surface after cycling showing dendrite growth initiation from LLZO surface on regions where Li was consumed.



Figure 7.7 SEM images of one dendrite on Li surface and high magnification of its different regions showing growth of new arms and formation of kinks.

7. 4. 4 LLZO chemical analysis

The cross-section mapping of LLZO before cycling shows a homogeneous distribution of different elements (**Figure S7.15**). **Figure 7.8a** shows the cross-section mapping of LLZO prepared using the FIB milling after cycling. Mapping results show the inhomogeneous distributions of La, Zr, and C, where the upper part of the milled region close to the Li surface contains more La and Zr and less C. This suggests the occurrence of La₂Zr₂O₇ segregation at the LLZO surface. A lower amount of C close to the LLZO surface may be the result of the consumption of C by the formation of lithium carbides. This C is from the Li₂CO₃ covering the LLZO particles. Higher amounts of La and Zr close to the Li electrode could be caused by the loss of Li in these regions of the ceramic and the formation of La₂Zr₂O₇ resulting from the side reaction with Li₂O. These phenomena may also be another cause of the inhomogeneous dissolution and deposition of Li. The C consumption by Li also results in the formation of mossy and needle dendrites.¹⁷ **Figure 7.8b** shows a schematic of the cell cross-section before and after cycling, indicating the inhomogeneous Li dissolution and deposition during cycling and the chemical compositions of LLZO before and after cycling.



Figure 7.8 a) Cross-section mapping of LLZO under the Li electrode after cycling, showing inhomogeneous distribution of Zr, La, and C, b) Schematic of a cross-section of the top Li and LLZO before and after cycling. After cycling an inhomogeneous distribution of Zr, La, and C was observed, indicating $La_2Zr_2O_7$ segregation. Close-up schematic shows one region containing bump and needle dendrite morphologies that appear close to electrode areas where Li thinning occurs.

7.5 Conclusion

In this work, *in situ* SEM is employed to analyze the LLZO/Li interface in symmetrical Li–Li cell that contains LLZO electrolyte. Dendrite growth was monitored during cycling. The dendrites cannot perforate through the LLZO electrolyte because of the mechanical force acting against their growth through this medium. However, dendrites can still form in these systems because of the presence of C as well as the inhomogeneous dissolution and deposition of Li. This results in the irreversible consumption of Li that thereby causes capacity loss during cycling. The

EDS results show that dendrites are not pure Li, and they contain C and O, which could be correlated to possible chemical compositions of Li_2CO_3 , Li_xC_y , and Li_2O . Based on the cross-section mapping of LLZO, the inhomogeneous distribution of La, Zr, and C after cycling could be caused by the Li loss close to the Li electrode and the side reaction with Li_2O . Based on this study, the key factor resulting in dendrite growth is the LLZO/Li interface. Inhomogeneous dissolution at the interface, causes uneven distribution of current and thus inhomogeneous Li deposition. The dendrites are formed near the thin Li regions. Although LLZO has excellent mechanical properties to suppress dendrite growth, the electrochemical properties of this electrolyte should be further improved to achieve homogeneous dissolution and deposition and fully eliminate dendrite formation.

Acknowledgement

This work was financially supported by Hydro Québec, Natural Sciences and Engineering Research Council of Canada (NSERC), and McGill Engineering Doctoral Award (MEDA). The authors gratefully acknowledge Michel Roy, Daniel Clément, and Vincent Gariépy for their technical support.

7.6 References

- 1 Hovington, P. *et al.* New lithium metal polymer solid state battery for an ultrahigh energy: Nano C-LiFePO4 versus nano Li1. 2V3O8. *Nano letters* **15**, 2671-2678 (2015).
- 2 Rosso, M. *et al.* Dendrite short-circuit and fuse effect on Li/polymer/Li cells. *Electrochimica Acta* **51**, 5334-5340 (2006).
- 3 Monroe, C. & Newman, J. The impact of elastic deformation on deposition kinetics at lithium/polymer interfaces. *Journal of The Electrochemical Society* **152**, A396-A404 (2005).
- 4 Cheng, E. J., Sharafi, A. & Sakamoto, J. Intergranular Li metal propagation through polycrystalline Li6. 25Al0. 25La3Zr2O12 ceramic electrolyte. *Electrochimica Acta* 223, 85-91 (2017).
- 5 Aguesse, F. *et al.* Investigating the dendritic growth during full cell cycling of garnet electrolyte in direct contact with Li metal. *ACS applied materials & interfaces* **9**, 3808-3816 (2017).
- 6 Porz, L. *et al.* Mechanism of lithium metal penetration through inorganic solid electrolytes. *Advanced Energy Materials* **7**, 1701003 (2017).
- 7 Marbella, L. E. *et al.* 7Li NMR chemical shift imaging to detect microstructural growth of lithium in all-solid-state batteries. *Chemistry of Materials* **31**, 2762-2769 (2019).
- 8 Murugan, R., Thangadurai, V. & Weppner, W. Fast lithium ion conduction in garnet-type Li7La3Zr2O12. *Angewandte Chemie International Edition* **46**, 7778-7781 (2007).
- 9 Kotobuki, M., Munakata, H., Kanamura, K., Sato, Y. & Yoshida, T. Compatibility of Li₇La₃Zr₂O₁₂ solid electrolyte to all-solid-state battery using Li metal anode. *Journal of The Electrochemical Society* **157**, A1076-A1079 (2010).
- 10 Wolfenstine, J., Allen, J. L., Read, J. & Sakamoto, J. Chemical stability of cubic Li7La3Zr2O12 with molten lithium at elevated temperature. *Journal of materials science* **48**, 5846-5851 (2013).
- 11 Ni, J. E., Case, E. D., Sakamoto, J. S., Rangasamy, E. & Wolfenstine, J. B. Room temperature elastic moduli and Vickers hardness of hot-pressed LLZO cubic garnet. *Journal of Materials Science* **47**, 7978-7985 (2012).
- 12 Tsai, C. L. *et al.* Li7La3Zr2O12 interface modification for Li dendrite prevention. *ACS applied materials & interfaces* **8**, 10617-10626 (2016).

- 13 Shen, F., Dixit, M. B., Xiao, X. & Hatzell, K. B. Effect of pore connectivity on Li dendrite propagation within LLZO electrolytes observed with synchrotron X-ray tomography. *ACS Energy Letters* **3**, 1056-1061 (2018).
- 14 Basappa, R. H. *et al.* Grain boundary modification to suppress lithium penetration through garnet-type solid electrolyte. *Journal of Power Sources* **363**, 145-152 (2017).
- 15 Paolella, A. *et al.* Discovering the influence of lithium loss on Garnet Li7La3Zr2O12 electrolyte phase stability. *ACS Applied Energy Materials* (2020).
- 16 Delaporte, N. *et al.* Facile protection of lithium metal for all-solid-state batteries. *ChemistryOpen* **8**, 192-195 (2019).
- 17 Golozar, M. *et al.* In situ scanning electron microscopy detection of carbide nature of dendrites in Li–polymer batteries. *Nano Letters* **18**, 7583-7589 (2018).
- 18 Bessette, S. *et al.* In-situ characterization of lithium native passivation layer in a high vacuum scanning electron microscope. *Microscopy and Microanalysis* **25**, 866-873 (2019).
- 19 Golozar, M. *et al.* In situ observation of solid electrolyte interphase evolution in a lithium metal battery. *Communications Chemistry* (2019).
- 20 Hovington, P. *et al.* Can we detect Li KX-ray in lithium compounds using energy dispersive spectroscopy? *Scanning* **38**, 571-578 (2016).
- 21 Steiger, J., Kramer, D. & Mönig, R. Mechanisms of dendritic growth investigated by in situ light microscopy during electrodeposition and dissolution of lithium. *J. Power Sources* **261**, 112-119 (2014).
- 22 Golozar, M. *et al.* In situ observation of solid electrolyte interphase evolution in a lithium metal battery. *Commun. Chem.* **2**, 131 (2019).
- 23 Yu, S. & Siegel, D. J. Grain boundary contributions to Li-ion transport in the solid electrolyte Li7La3Zr2O12 (LLZO). *Chemistry of Materials* **29**, 9639-9647 (2017).
- 24 Eshetu, G. G. *et al.* Ultrahigh performance all solid-state lithium sulfur batteries: salt anion's chemistry-induced anomalous synergistic effect. *Journal of the American Chemical Society* **140**, 9921-9933 (2018).
- 25 Hovington, P. *et al.* Direct and indirect observation of lithium in a scanning electron microscope; not only on pure Li! *Microscopy and Microanalysis* **21**, 2357-2358 (2015).
- 26 Shi, F. *et al.* Lithium metal stripping beneath the solid electrolyte interphase. *Proceedings of the National Academy of Sciences* **115**, 8529-8534 (2018).

- 27 Tikekar, M. D., Archer, L. A. & Koch, D. L. Stabilizing electrodeposition in elastic solid electrolytes containing immobilized anions. *Science advances* **2**, e1600320 (2016).
- 28 Yu, S. *et al.* Elastic properties of the solid electrolyte Li7La3Zr2O12 (LLZO). *Chemistry of Materials* **28**, 197-206 (2016).
- 29 Li, L., Li, S. & Lu, Y. Suppression of dendritic lithium growth in lithium metal-based batteries. *Chemical communications* **54**, 6648-6661 (2018).
- 30 Yamaki, J. I. *et al.* A consideration of the morphology of electrochemically deposited lithium in an organic electrolyte. *Journal of Power Sources* **74**, 219-227 (1998).
- 31 Hren, J. J. in *Introduction to Analytical Electron Microscopy* (eds John J Hren, Joseph I Goldstein, & David C Joy) 481-505 (Springer, 1979).
- 32 Egerton, R. F., Li, P. & Malac, M. Radiation damage in the TEM and SEM. *Micron* **35**, 399-409 (2004).
- 33 Monroe, C. & Newman, J. The effect of interfacial deformation on electrodeposition kinetics. *Journal of The Electrochemical Society* **151**, A880-A886 (2004).

7.7 Supplementary Information



Figure S7.9 a) EIS plots at 25 and 80 °C and b) Arrenhius plot of LLZO pellet.



Figure S7.10 Schematic of the set up. The top copper wire is a contact electrode and pushes the Li film on the LLZO with a spring. The lower copper wire is connected to the sample holder which serves as the other contact electrode. A smaller Li electrode is used on the top to have edge effect.



Figure S7.11 Cycling curve of the cell showing the time at which the current was changed.



Figure S7.12 SEM images of the cell surface during cycling. a) SEM image of the anode edge after 3 days of cycling showing the Li anode surface, thinned Li, Li edge, and the LLZO. The thinned region is detected by comparing the morphology of the Li surface and the LLZO, b) SEM image of the Li surface after 4 days of cycling showing the diameter and the thickness of one thinned region, and c) SEM image of the Li edge after 4 days of cycling showing a ribbon of thinned region.



Figure S7.13 SEM images of different areas of the Li after cycling showing growth of mossy and needle dendrites and bumps close to the regions where Li was consumed.



Figure S7.14 SEM images of dendrites with different morphologies showing ability of dendrites 2, 3, and 4 to perforate through the Li in comparison to dendrite 1 which was pushing the Li up.



Figure S7.15 EDS elemental mapping of the LLZO cross section before cycling.

Supplementary Videos:

Video S1: Cycling behavior of the battery showing thinning of the Li and dendrite formation and growth.

Video S2: Growth of a needle morphology dendrite on the Li surface.

Chapter 8 Summary

8.1 Conclusions

In this work the failure mechanism of all-solid-state Li-metal batteries was investigated through monitoring the battery behavior using SEM during cycling. Below are the conclusions of this work:

- An *in situ* SEM technique was optimized that enabled the monitoring of the anode surface or the cross section of the battery from the beginning till the end of cycling. Batteries were assembled in the glove box or the dry room and transferred to the SEM using an air tight transfer holder. It was possible to obtain images during cycling from different regions of the sample using the *in situ* software. After cycling videos were constructed to show the failure of the battery.
- Using the windowless EDS detector, it was possible to overcome the Li detection limitations. The change in the Li content was measured during cycling using EDS point analysis and line scan.
- 3. The effect of applying pressure on the battery was investigated using two battery assemblies. In one case the cross section of the battery was monitored and pressure was applied on the anode and the cathode. In the other case, no pressure was applied on the battery and the anode surface facing the electron beam was monitored. It was shown that pressure could suppress dendrite growth in the battery.
- 4. Two dendrite morphologies of mossy and hollow needles were observed. These dendrites were mainly observed on the regions that fresh Li was exposed.
- 5. The dendrites were not pure Li and contained C and O. They also had higher hardness than the Li metal. The presence of C in the dendrite was attributed to possible polymer
electrolyte decomposition. High hardness of the dendrite is the reason that the dendrites could perforate through the polymer.

- 6. Observing hollow morphology for the needle dendrites could be the result of the consumption of the Li_xC_y by O and C, or degassing of the polymer.
- Videos constructed from the images obtained from the plane view of the battery showed the cycling behavior from the beginning till the end of cycling. The following phenomena were observed:
 - a. Dendrite growth on the anode edge:

Dendrite formation began during the first charge due to the unstable Li/polymer interface and a not fully formed SEI layer. Higher cycling rates increased dendrite formation due to the deterioration of the SEI layer.

- b. Opening of the grain boundaries which is an indication of the higher activity on the grain boundaries than the grains.
- c. Formation of inactive isles on the anode:

As cycling was continued, isles started forming on the intersection of the grain boundaries and they start becoming isolated from the rest of the surface as Li was consumed in the vicinity of them.

- d. End of the growth of the dendrites which is an indication of the formation of dead Li. Subsequently a new anode edge was formed followed by dendrite formation on these regions that contained fresh Li.
- e. Li depletion around the isles:

With further cycling, more Li was consumed in the vicinity of the isles. Dendrites also started forming on the walls of the isles. Mapping of the cross section of the isles that were prepared using FIB showed inhomogeneous distribution of C, F, and N which suggested gradual decomposition of LiTFSI with LiF surrounding the isle.

Isle formation was the result of the reactions occurring during cycling of the battery and not the external pressure.

- f. Morphological change on the polymer and extrusion of Li from the polymer:
 The morphological change could be due to the local temperature increase followed by decomposition and degassing of the polymer
- 8. Anode surface monitoring showed the deterioration of the SEI layer during cycling. This deterioration was due to the volume change during cycling. During charge, Li was deposited on the anode which resulted in an increase in the volume and during discharge Li was dissolved from the anode resulting in a decrease in the volume.
- 9. EDS line scans showed the distribution of Li, C, and O on the anode surface during cycling which confirmed the deterioration and reconstruction of the SEI layer during charge and discharge.
- 10. To see the effect of electrolytes with higher mechanical properties, cycling behavior of a cell with LLZO ceramic electrolyte was observed with *in situ* SEM. The constructed videos showed the behavior of these cells throughout cycling. The following phenomena were observed:
 - a. Thinning of the Li electrode: an inhomogeneous Li dissolution was observed during cycling where some grains showed higher Li dissolution.
 - Formation of dendrites with bump and mossy morphology: an inhomogeneous Li deposition was observed as the result of non-uniform current density distribution on the surface.
 - c. Formation of needle morphology dendrite: the chemical analysis of these dendrites showed that they are not pure Li and contain C and O.
 - d. Chemical analysis of the cross section of the LLZO after cycling showed inhomogeneous distribution of La, Zr, and C, where the upper part of the milled region close to the Li surface contained more La and Zr and less C. Higher amounts of La and Zr close to the Li electrode could have been caused by the loss of Li in these regions of the ceramic and the formation of La₂Zr₂O₇ resulting from the side reaction with Li₂O.

- Although ceramic electrolytes satisfy the shear modulus criterion and no electrolyte deformation occurs during cycling, unstable and non-uniform deposition is still observed. Dendrite formation is also observed in these cells due to presence of C.
- 12. Even though LLZO has excellent mechanical properties to suppress dendrite growth, the electrochemical properties of this electrolyte should be further improved to achieve homogeneous dissolution and deposition and fully eliminate dendrite formation.
- 13. All in all to hinder dendrite growth: external pressure should be applied on the battery, a uniform SEI layer must be achieved on the Li surface to have uniform dissolution and deposition and to inhibit local Li consumption by C, C content of the battery should be minimized, electrochemistry aspects of the ceramic electrolytes should be enhanced.

8. 2 Contributions to the Original Knowledge

- For the first time, this work showed the ability to image and conduct chemical analysis using SEM-EDS on all-solid-state Li-metal batteries from the beginning of cycling till the failure of the battery and show the cycling behavior of the battery using videos.
- 2. This work showed the ability to detect Li during cycling using EDS point analysis, line scan, and mapping in battery applications for the first time.
- 3. This is the first work to show that the dendrites are not pure Li and have high hardness, and to show their hollow morphology using SEM.
- 4. The high activity and consumption of Li on the grain boundaries during cycling was captured using SEM images.
- 5. The changes in the morphology of the polymer during cycling and the effect of dendrite growth on the polymer electrolyte was shown.

- 6. This work showed the ability to monitor the deterioration and reconstruction of the SEI layer during cycling using SEM.
- 7. The inhomogeneous dissolution of Li in cells containing ceramic LLZO electrolyte was captured using SEM.
- 8. The inhomogeneous composition of the polymer and ceramic electrolyte after cycling was shown using EDS.

8.3 Suggestions for Future Work

- 1. Analyze the cycling behavior of cells with LLZO ceramic electrolyte in absence of C to investigate the probability of dendrite formation when there is no C in the cell. In the case of dendrite observation, conduct chemical analysis on the dendrites.
- Conduct in situ cycling on cell with thinner LLZO electrolyte to study the probability of short-circuits in these cells and to investigate if dendrite propagation would be through the grain boundaries.
- 3. Conduct chemical analysis on the dendrites using electron energy loss spectroscopy (EELS) to acquire quantitative results or use time-of-flight secondary ion mass spectrometry (TOF-SIMS) with a different primary ion source than gallium to avoid formation of intermetallic phases.
- 4. Investigate the correlation between dendrite formation and different Li-metal anode crystallographic orientations using electron backscatter diffraction (EBSD) to discover which orientations are more prone to dendrite formation.
- 5. Conduct in situ analysis on the base of a dendrite during cycling to capture the initiation of the dendrites and conduct chemical analysis on these regions as the dendrite is being formed to observe the chemical properties of the regions that undergo dendrite formation.

Even though it is shown that a non-uniform SEI layer results in dendrite formation and that dendrites initiate from defects on the surface including thin SEI layer or grain boundaries, being able to image the exact moment and region at which these dendrites are formed provide more data that could be used to hinder dendrite initiation.

References

- [1] J. B. Goodenough and K. S. Park, "The Li-ion rechargeable battery: a perspective," *J. Am. Chem. Soc.*, vol. 135, no. 4, pp. 1167-1176, 2013.
- F. R. Kalhammer, "Polymer electrolytes and the electric vehicle," *Solid State Ion.*, vol. 135, no. 1, pp. 315-323, 2000.
- [3] P. Hovington *et al.*, "Can we detect Li KX-ray in lithium compounds using energy dispersive spectroscopy?," *Scanning*, vol. 38, no. 6, pp. 571-578, 2016.
- [4] A. L. Robinson and J. Janek, "Solid-state batteries enter EV fray," *MRS Bull.*, vol. 39, no. 12, pp. 1046-1047, 2014.
- [5] P. Hovington *et al.*, "New lithium metal polymer solid state battery for an ultrahigh energy: Nano C-LiFePO4 versus nano Li1. 2V3O8," *Nano Lett.*, vol. 15, no. 4, pp. 2671-2678, 2015.
- [6] X. B. Cheng and Q. Zhang, "Dendrite-free lithium metal anodes: stable solid electrolyte interphases for high-efficiency batteries," *J. Mater. Chem. A*, vol. 3, no. 14, pp. 7207-7209, 2015.
- [7] N. Brodusch, K. Zaghib, and R. Gauvin, "Electron backscatter diffraction applied to lithium sheets prepared by broad ion beam milling," *Microsc. Res. Tech.*, vol. 78, no. 1, pp. 30-39, 2015.
- [8] D. W. Jeppson, J. L. Ballif, W. W. Yuan, and B. E. Chou, "Lithium literature review: lithium's properties and interactions," Hanford Engineering Development Lab., Richland, Wash.(USA), 1978.
- [9] E. Peled, "The electrochemical behavior of alkali and alkaline earth metals in nonaqueous battery systems—the solid electrolyte interphase model," *J. Electrochem. Soc.*, vol. 126, no. 12, pp. 2047-2051, 1979.
- [10] M. Rosso *et al.*, "Dendrite short-circuit and fuse effect on Li/polymer/Li cells," *Electrochim. Acta*, vol. 51, no. 25, pp. 5334-5340, 2006.
- [11] C. Monroe and J. Newman, "Dendrite growth in lithium/polymer systems a propagation model for liquid electrolytes under galvanostatic conditions," *J. Electrochem. Soc.*, vol. 150, no. 10, pp. A1377-A1384, 2003.

- [12] K. Liu, Y. Liu, D. Lin, A. Pei, and Y. Cui, "Materials for lithium-ion battery safety," Sci. Adv., vol. 4, no. 6, p. eaas9820, 2018.
- [13] T. M. Bandhauer, S. Garimella, and T. F. Fuller, "A critical review of thermal issues in lithium-ion batteries," *J. Electrochem. Soc.*, vol. 158, no. 3, pp. R1-R25, 2011.
- [14] Y. Chen and J. W. Evans, "Thermal analysis of lithium-ion batteries," J. Electrochem. Soc., vol. 143, no. 9, pp. 2708-2712, 1996.
- [15] J. Janek and W. G. Zeier, "A solid future for battery development," *Nat. Energy.*, vol. 1, no. 9, pp. 1-4, 2016.
- [16] A. Perea, M. Dontigny, and K. Zaghib, "Safety of solid-state Li metal battery: Solid polymer versus liquid electrolyte," J. Power Sources, vol. 359, pp. 182-185, 2017.
- [17] M. B. Armand, J. M. Chabagno, and M. J. Duclot, in *Fast ion transport in solids: electrodes and electrolytes*, P. Vashista, J. N. Mundy, and G. K. Shenoy Eds. New York: North Holland, 1979.
- [18] A. Mauger, M. Armand, C. M. Julien, and K. Zaghib, "Challenges and issues facing lithium metal for solid-state rechargeable batteries," *J. Power Sources*, vol. 353, pp. 333-342, 2017.
- [19] J. Motavalli, "Technology: A solid future," *Nature*, vol. 526, no. 7575, pp. S96-S97, 2015.
- [20] M. Dollé, L. Sannier, B. Beaudoin, M. Trentin, and J. M. Tarascon, "Live scanning electron microscope observations of dendritic growth in lithium/polymer cells," *Electrochem. Solid-State Lett.*, vol. 5, no. 12, pp. A286-A289, 2002.
- [21] F. Orsini *et al.*, "In situ SEM study of the interfaces in plastic lithium cells," J. Power Sources, vol. 81, pp. 918-921, 1999.
- [22] R. Murugan, V. Thangadurai, and W. Weppner, "Fast lithium ion conduction in garnettype Li7La3Zr2O12," *Angew. Chem. Int. Ed.*, vol. 46, no. 41, pp. 7778-7781, 2007.
- [23] M. Kotobuki, H. Munakata, K. Kanamura, Y. Sato, and T. Yoshida, "Compatibility of Li₇La₃Zr₂O₁₂ solid electrolyte to all-solid-state battery using Li metal anode," J. *Electrochem. Soc.*, vol. 157, no. 10, pp. A1076-A1079, 2010.
- [24] J. E. Ni, E. D. Case, J. S. Sakamoto, E. Rangasamy, and J. B. Wolfenstine, "Room temperature elastic moduli and Vickers hardness of hot-pressed LLZO cubic garnet," J. *Mater. Sci.*, vol. 47, no. 23, pp. 7978-7985, 2012.

- [25] F. Aguesse *et al.*, "Investigating the dendritic growth during full cell cycling of garnet electrolyte in direct contact with Li metal," *ACS Appl. Mater. Interfaces*, vol. 9, no. 4, pp. 3808-3816, 2017.
- [26] F. Shen, M. B. Dixit, X. Xiao, and K. B. Hatzell, "Effect of pore connectivity on Li dendrite propagation within LLZO electrolytes observed with synchrotron X-ray tomography," ACS Energy Lett., vol. 3, no. 4, pp. 1056-1061, 2018.
- [27] P. Hovington *et al.*, "Direct and indirect observation of lithium in a scanning electron microscope; not only on pure Li!," *Microsc. Microanal.*, vol. 21, pp. 2357-2358, 2015.
- [28] H. Okamoto, "Ga-Li (Gallium-Lithium)," J. Phase. Equilib. Diff., vol. 27, no. 2, p. 200, 2006.
- [29] P. Hovington *et al.*, "On the detection limits of Li K X-rays using windowless energy dispersive spectrometer (EDS)," *Microsc. Microanal.*, vol. 23, no. S1, pp. 2024-2025, 2017.
- [30] E. Peled, D. Golodnitsky, and G. Ardel, "Advanced model for solid electrolyte interphase electrodes in liquid and polymer electrolytes," *J. Electrochem. Soc.*, vol. 144, no. 8, pp. L208-L210, 1997.
- [31] B. Commarieu, A. Paolella, J. C. Daigle, and K. Zaghib, "Toward high lithium conduction in solid polymer and polymer-ceramic batteries," *Curr. Opin. Electrochem.*, vol. 9, pp. 56-63, 2018.
- [32] J. B. Goodenough and Y. Kim, "Challenges for rechargeable Li batteries," *Chem. Mater.*, vol. 22, no. 3, pp. 587-603, 2009.
- [33] A. Kushima *et al.*, "Liquid cell transmission electron microscopy observation of lithium metal growth and dissolution: Root growth, dead lithium and lithium flotsams," *Nano Energy*, vol. 32, pp. 271-279, 2017.
- [34] I. Yoshimatsu, T. Hirai, and J. i. Yamaki, "Lithium electrode morphology during cycling in lithium cells," *J. Electrochem. Soc.*, vol. 135, no. 10, pp. 2422-2427, 1988.
- [35] D. Lin, Y. Liu, and Y. Cui, "Reviving the lithium metal anode for high-energy batteries," *Nat. Nanotechnol.*, vol. 12, no. 3, pp. 194-206, 2017.
- [36] M. D. Tikekar, L. A. Archer, and D. L. Koch, "Stabilizing electrodeposition in elastic solid electrolytes containing immobilized anions," *Sci. Adv.*, vol. 2, no. 7, p. e1600320, 2016.

- [37] L. Li, S. Li, and Y. Lu, "Suppression of dendritic lithium growth in lithium metal-based batteries," *ChemComm*, vol. 54, no. 50, pp. 6648-6661, 2018.
- [38] C. Monroe and J. Newman, "The impact of elastic deformation on deposition kinetics at lithium/polymer interfaces," *J. Electrochem. Soc.*, vol. 152, no. 2, pp. A396-A404, 2005.
- [39] W. Li *et al.*, "Effect of electrochemical dissolution and deposition order on lithium dendrite formation: a top view investigation," *Faraday Discuss.*, vol. 176, pp. 109-124, 2015.
- [40] J. Steiger, D. Kramer, and R. Mönig, "Mechanisms of dendritic growth investigated by in situ light microscopy during electrodeposition and dissolution of lithium," *J. Power Sources*, vol. 261, pp. 112-119, 2014.
- [41] Z. Li, J. Huang, B. Y. Liaw, V. Metzler, and J. Zhang, "A review of lithium deposition in lithium-ion and lithium metal secondary batteries," *J. Power Sources*, vol. 254, pp. 168-182, 2014.
- [42] R. Mogi, M. Inaba, S. K. Jeong, Y. Iriyama, T. Abe, and Z. Ogumi, "Effects of some organic additives on lithium deposition in propylene carbonate," *J. Electrochem. Soc.*, vol. 149, no. 12, pp. A1578-A1583, 2002.
- [43] K. J. Harry, X. Liao, D. Y. Parkinson, A. M. Minor, and N. P. Balsara, "Electrochemical deposition and stripping behavior of lithium metal across a rigid block copolymer electrolyte membrane," *J. Electrochem. Soc.*, vol. 162, no. 14, pp. A2699-A2706, 2015.
- [44] C. Brissot, M. Rosso, J. N. Chazalviel, and S. Lascaud, "Dendritic growth mechanisms in lithium/polymer cells," *J. Power Sources*, vol. 81, pp. 925-929, 1999.
- [45] J. N. Chazalviel, "Electrochemical aspects of the generation of ramified metallic electrodeposits," *Phys. Rev. A*, vol. 42, no. 12, p. 7355, 1990.
- [46] K. Nishikawa, T. Mori, T. Nishida, Y. Fukunaka, M. Rosso, and T. Homma, "In situ observation of dendrite growth of electrodeposited Li metal," *J. Electrochem. Soc.*, vol. 157, no. 11, pp. A1212-A1217, 2010.
- [47] C. T. Love, O. A. Baturina, and K. E. Swider-Lyons, "Observation of lithium dendrites at ambient temperature and below," *ECS Electrochem. Lett.*, vol. 4, no. 2, pp. A24-A27, 2015.

- [48] J. I. Yamaki, S. I. Tobishima, K. Hayashi, K. Saito, Y. Nemoto, and M. Arakawa, "A consideration of the morphology of electrochemically deposited lithium in an organic electrolyte," *J. Power Sources*, vol. 74, no. 2, pp. 219-227, 1998.
- [49] G. Wranglen, "Dendrites and growth layers in the electrocrystallization of metals," *Electrochim. Acta*, vol. 2, no. 1-3, pp. 130-143, 1960.
- [50] R. Spotnitz and J. Franklin, "Abuse behavior of high-power, lithium-ion cells," J. Power Sources, vol. 113, no. 1, pp. 81-100, 2003.
- [51] T. Hirai, I. Yoshimatsu, and J. i. Yamaki, "Influence of electrolyte on lithium cycling efficiency with pressurized electrode stack," *J. Electrochem. Soc.*, vol. 141, no. 3, pp. 611-614, 1994.
- [52] D. P. Wilkinson, H. Blom, K. Brandt, and D. Wainwright, "Effects of physical constraints on Li cyclability," *J. Power Sources*, vol. 36, no. 4, pp. 517-527, 1991.
- [53] L. Gireaud, S. Grugeon, S. Laruelle, B. Yrieix, and J. M. Tarascon, "Lithium metal stripping/plating mechanisms studies: A metallurgical approach," *Electrochem. Commun.*, vol. 8, no. 10, pp. 1639-1649, 2006.
- [54] L. Porz *et al.*, "Mechanism of lithium metal penetration through inorganic solid electrolytes," *Adv. Energy Mater.*, vol. 7, no. 20, p. 1701003, 2017.
- [55] R. H. Basappa, T. Ito, T. Morimura, R. Bekarevich, K. Mitsuishi, and H. Yamada, "Grain boundary modification to suppress lithium penetration through garnet-type solid electrolyte," *J. Power Sources*, vol. 363, pp. 145-152, 2017.
- [56] E. J. Cheng, A. Sharafi, and J. Sakamoto, "Intergranular Li metal propagation through polycrystalline Li6. 25Al0. 25La3Zr2O12 ceramic electrolyte," *Electrochim. Acta*, vol. 223, pp. 85-91, 2017.
- [57] Q. Zhang, K. Liu, F. Ding, and X. Liu, "Recent advances in solid polymer electrolytes for lithium batteries," *Nano Res.*, vol. 10, no. 12, pp. 4139-4174, 2017.
- [58] J. C. Daigle *et al.*, "Lithium battery with solid polymer electrolyte based on comb-like copolymers," *J. Power Sources*, vol. 279, pp. 372-383, 2015.
- [59] G. G. Eshetu *et al.*, "Ultrahigh performance all solid-state lithium sulfur batteries: salt anion's chemistry-induced anomalous synergistic effect," *J. Am. Chem. Soc.*, vol. 140, no. 31, pp. 9921-9933, 2018.

- [60] X. Judez et al., "Lithium bis (fluorosulfonyl) imide/poly (ethylene oxide) polymer electrolyte for all solid-State Li–S cell," J. Phys. Chem. Lett., vol. 8, no. 9, pp. 1956-1960, 2017.
- [61] Y. Li *et al.*, "The effects of lithium salt and solvent on lithium metal anode performance," *Solid State Ion.*, vol. 324, pp. 144-149, 2018.
- [62] L. Suo, Y. S. Hu, H. Li, M. Armand, and L. Chen, "A new class of solvent-in-salt electrolyte for high-energy rechargeable metallic lithium batteries," *Nat. Commun.*, vol. 4, p. 1481, 2013.
- [63] X. Chao, S. Bing, G. Torbjorn, E. Kristina, B. Daniel, and H. Maria, "Interface layer formation in solid polymer electrolyte lithium batteries: an XPS study," *J. Mater. Chem. A*, vol. 2, no. 20, pp. 7256-7264, 2014.
- [64] M. D. Galluzzo, D. M. Halat, W. S. Loo, S. A. Mullin, J. A. Reimer, and N. P. Balsara,
 "Dissolution of lithium metal in poly(ethylene oxide)," *ACS Energy Lett.*, vol. 4, pp. 903-907, 2019.
- [65] B. Commarieu *et al.*, "Solid-to-liquid transition of polycarbonate solid electrolytes in Limetal batteries," *J. Power Sources*, vol. 436, p. 226852, 2019.
- [66] S. Yu and D. J. Siegel, "Grain boundary contributions to Li-ion transport in the solid electrolyte Li7La3Zr2O12 (LLZO)," *Chem. Mater.*, vol. 29, no. 22, pp. 9639-9647, 2017.
- [67] V. Thangadurai, S. Narayanan, and D. Pinzaru, "Garnet-type solid-state fast Li ion conductors for Li batteries: critical review," *Chem. Soc. Rev.*, vol. 43, no. 13, pp. 4714-4727, 2014.
- [68] J. Wolfenstine, J. L. Allen, J. Read, and J. Sakamoto, "Chemical stability of cubic Li7La3Zr2O12 with molten lithium at elevated temperature," J. Mater. Sci., vol. 48, no. 17, pp. 5846-5851, 2013.
- [69] C. L. Tsai *et al.*, "Li7La3Zr2O12 interface modification for Li dendrite prevention," ACS Appl. Mater. Interfaces, vol. 8, no. 16, pp. 10617-10626, 2016.
- [70] S. Yu *et al.*, "Elastic properties of the solid electrolyte Li7La3Zr2O12 (LLZO)," *Chem. Mater.*, vol. 28, no. 1, pp. 197-206, 2016.
- [71] L. E. Marbella, S. Zekoll, J. Kasemchainan, S. P. Emge, P. G. Bruce, and C. P. Grey,
 "7Li NMR chemical shift imaging to detect microstructural growth of lithium in all-solidstate batteries," *Chem. Mater.*, vol. 31, no. 8, pp. 2762-2769, 2019.

- [72] K. N. Wood *et al.*, "Dendrites and Pits: Untangling the Complex Behavior of Lithium Metal Anodes through Operando Video Microscopy," *ACS Cent. Sci.*, vol. 2, no. 11, pp. 790-801, 2016.
- [73] J. K. Stark, Y. Ding, and P. A. Kohl, "Nucleation of electrodeposited lithium metal: dendritic growth and the effect of co-deposited sodium," *J. Electrochem. Soc.*, vol. 160, no. 9, pp. D337-D342, 2013.
- [74] J. Conder, C. Marino, P. Novák, and C. Villevieille, "Do imaging techniques add real value to the development of better post-Li-ion batteries?," *J. Mater. Chem. A*, vol. 6, no. 8, pp. 3304-3327, 2018.
- [75] H. Ghassemi, M. Au, N. Chen, P. A. Heiden, and R. S. Yassar, "Real-time observation of lithium fibers growth inside a nanoscale lithium-ion battery," *Appl. Phys. Lett.*, vol. 99, no. 12, p. 123113, 2011.
- [76] R. F. Egerton, P. Li, and M. Malac, "Radiation damage in the TEM and SEM," *Micron*, vol. 35, no. 6, pp. 399-409, 2004.
- [77] J. Goldstein *et al.*, *Scanning Electron Microscopy and X-ray Microanalysis*, Third ed. Springer Science and Business Media, 2003.
- [78] J. Mayer, L. A. Giannuzzi, T. Kamino, and J. Michael, "TEM sample preparation and FIB-induced damage," *MRS Bull.*, vol. 32, no. 5, pp. 400-407, 2007.
- [79] F. A. Stevie, Secondary Ion Mass Spectrometry: Applications for Depth Profiling and Surface Characterization. New York: Momentum Press, 2016.
- [80] L. A. Giannuzzi and F. A. Stevie, *Introduction to focused ion beams: instrumentation, theory, techniques and practice.* Springer Science & Business Media, 2005.
- [81] R. Egerton, "Mechanisms of radiation damage in beam-sensitive specimens, for TEM accelerating voltages between 10 and 300 kV," *Microsc. Res. Tech.*, vol. 75, no. 11, pp. 1550-1556, 2012.
- [82] OrsayPhysics. "Scientific Overviews: What is UHV?" http://www.orsayphysics.com/what-is-uhv
- [83] Y. Li *et al.*, "Revealing nanoscale passivation and corrosion mechanisms of reactive battery materials in gas environments," *Nano Lett.*, vol. 17, no. 8, pp. 5171-5178, 2017.
- [84] A. E. Ennos, "The sources of electron-induced contamination in kinetic vacuum systems," Br. J. Appl. Phys., vol. 5, no. 1, pp. 27-31, 1954.

- [85] J. J. Hren, "Barriers to AEM: Contamination and etching," in *Introduction to Analytical Electron Microscopy*, J. J. Hren, J. I. Goldstein, and D. C. Joy Eds. Boston, MA: Springer, 1979, pp. 481-505.
- [86] M. M. Markowitz and D. A. Boryta, "Lithium Metal-Gas Reactions," J. Chem. Eng. Data, vol. 7, no. 4, pp. 586-591, 1962.
- [87] S. Bessette *et al.*, "In-situ characterization of lithium native passivation layer in a high vacuum scanning electron microscope," *Microsc. Microanal.*, vol. 25, no. 4, pp. 866-873, 2019.
- [88] S. Bessette *et al.*, "Nanoscale Lithium Quantification in Li X Ni y Co w Mn ZO 2 as Cathode for Rechargeable Batteries," *Sci. Rep.*, vol. 8, no. 1, pp. 1-9, 2018.
- [89] H. Azza, N. Selhaoui, A. Iddaoudi, and L. Bouirden, "Thermodynamic Reassessment of the Gallium–Lithium Phase Diagram," *J. Phase. Equilib. Diff.*, vol. 38, no. 5, pp. 788-795, 2017.
- [90] S. Bessette, M. Golozar, P. Hovington, R. Gauvin, and K. Zaghib, "Ga FIB/TOF-SIMS Analysis of Lithium Materials," in *European Microbeam Analysis Society - 16th European workshop on modern developments and applications in microbeam analysis*, Trondheim, Norway, 2019.
- [91] J. D. Casey Jr et al., "Copper device editing: Strategy for focused ion beam milling of copper," J. Vac. Sci. Technol. B: Microelectronics Nanometer Structures Processing, Measurement, Phenomena, vol. 20, no. 6, pp. 2682-2685, 2002.
- [92] F. Stevie, L. Sedlacek, P. Babor, J. Jiruse, E. Principe, and K. Klosova, "FIB-SIMS quantification using TOF-SIMS with Ar and Xe plasma sources," *Surf. Interface Anal.*, vol. 46, no. S1, pp. 285-287, 2014.
- [93] N. Antoniou, A. Graham, C. Hartfield, and G. Amador, "Failure analysis of electronic material using cryogenic FIB-SEM," in *Conf. Proc. 38th Int. Symp. Testing and Failure Analysis, Phoenix, AZ*, 2012, pp. 399-405.
- [94] M. Hayles, D. Stokes, D. Phifer, and K. Findlay, "A technique for improved focused ion beam milling of cryo-prepared life science specimens," *J. Microsc.*, vol. 226, no. 3, pp. 263-269, 2007.
- [95] D. B. Williams and C. B. Carter, Transmission Electron Microscopy: A Textbook for Materials Science, Second ed. Springer, 2009.

- [96] J. Goldstein, D. E. Newbury, P. Echlin, D. C. Joy, C. Fiori, and E. Lifshin, Scanning Electron Microscopy and X-Ray Microanalysis: A Text for Biologists, Materials Scientists, and Geologists, First ed. Plenum press. new york and london, 1981.
- [97] G. Cliff and G. W. Lorimer, "The quantitative analysis of thin specimens," J. Microsc., vol. 103, no. 2, pp. 203-207, 1975.
- [98] P. Horny, E. Lifshin, H. Campbell, and R. Gauvin, "Development of a new quantitative X-ray microanalysis method for electron microscopy," *Microsc. Microanal.*, vol. 16, no. 6, pp. 821-830, 2010.
- [99] J. Hubbell *et al.*, "A review, bibliography, and tabulation of K, L, and higher atomic shell x-ray fluorescence yields," *J. Phys. Chem. Ref. Data*, vol. 23, no. 2, pp. 339-364, 1994.
- [100] P. Hovington *et al.*, "Towards Li quantification at high spatial resolution using EDS," in *Microsc. Microanal.*, 2016, vol. 22, no. S3, pp. 84-85.
- [101] S. Burgess, J. Sagar, J. Holland, X. Li, and F. Bauer, "Ultra-low kV EDS-a new approach to improved spatial resolution, surface sensitivity, and light element compositional imaging and analysis in the SEM," *Microscopy Today*, vol. 25, no. 2, pp. 20-29, 2017.
- [102] T. Sui, B. Song, J. Dluhos, L. Lu, and A. M. Korsunsky, "Nanoscale chemical mapping of Li-ion battery cathode material by FIB-SEM and TOF-SIMS multi-modal microscopy," *Nano Energy*, vol. 17, pp. 254-260, 2015.
- [103] S. Bessette, "Development of Quantitative Techniques for Lithium Compounds for Next Generation Batteries with Focused Ion Beam Scanning Electron Microscopy," Masters of Engineering, Department of Mining and Materials Engineering, McGill University, McGill Library, 2018.
- [104] FFmpegDevelopers. "ffmpeg tool [Software]." http://ffmpeg.org/
- [105] M. Golozar *et al.*, "In situ scanning electron microscopy detection of carbide nature of dendrites in Li–polymer batteries," *Nano Lett.*, vol. 18, no. 12, pp. 7583-7589, 2018.
- [106] M. Golozar *et al.*, "In situ observation of solid electrolyte interphase evolution in a lithium metal battery," *Commun. Chem.*, vol. 2, no. 1, p. 131, 2019.
- [107] M. Golozar, H. Demers, A. Paolella, R. Gauvin, and K. Zaghib, "Direct Li detection and microstructure evolution of Li^o anode in all solid state battery: in situ SEM cycling observation "*Microsc. Microanal.*, vol. Submitted, 2020.

- [108] A. Paolella *et al.*, "Discovering the influence of lithium loss on Garnet Li7La3Zr2O12 electrolyte phase stability," ACS Appl. Energy Mater., 2020.
- [109] N. Delaporte, A. Guerfi, H. Demers, H. Lorrmann, A. Paolella, and K. Zaghib, "Facile protection of lithium metal for all-solid-state batteries," *ChemistryOpen*, vol. 8, no. 2, pp. 192-195, 2019.
- [110] M. Golozar *et al.*, "Direct observation of lithium metal dendrites with ceramic solid electrolyte," *Sci. Rep.*, vol. Currently Under Revision, 2020.