INTERROGATING BURIED ELECTROCHEMICAL INTERFACES

by

Deepti Tewari

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THE PURDUE UNIVERSITY GRADUATE SCHOOL STATEMENT OF COMMITTEE APPROVAL

Dr. Partha P. Mukherjee, Chair

School of Mechanical Engineering

Dr. Ivan Christov School of Mechanical Engineering

Dr. Vikas Tomar School of Aeronautics and Astronautics

> **Dr. Guang Lin** Department of Mathematics

Approved by:

Dr. Nicole Key

I dedicate this dissertation to my grandmothers, Khatirani and Dalgira.

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ABSTRACT

Lithium is a very attractive material for batteries. It has low redox potential (-3.04V vs SHE) and high theoretical capacity of 3860 mAh g-1. So, lithium batteries would have high energy density. During charging and discharging of the batteries, the interface between electrode and electrolyte changes as lithium is deposited or dissolved. If the deposition is dendritic, it can short circuit and cause failure of the battery. During dissolution of lithium from the electrode, pits can form on the surface and some part of lithium is detached. It is called dead lithium since it is not electrochemically active. Solid electrolyte and lithium metal interfaces are characterized by high interfacial resistance. The interface between electrode and electrolyte is critical to the safety and performance of lithium batteries. The aim of this research is to understand the evolution of interfaces are considered, interface formed between intercalation anode and liquid electrolyte, interface of metal anode and liquid electrolyte and interface between metal anode and solid electrolyte.

Stringent performance and operational requirements in electric vehicles can push lithiumion batteries toward unsafe conditions. Electroplating and possible dendritic growth are a cause for safety concern as well as performance deterioration in such intercalation chemistry-based energy storage systems. There is a need for better understanding of the morphology evolution due to electrodeposition of lithium on graphite anode surface, and the interplay between material properties and operating conditions. In this work, a mesoscale analysis of the underlying multimodal interactions is presented to study the evolution of morphology due to lithium deposition on typical graphite electrode surfaces. It is found that electrodeposition is a complex interplay between the rate of reduction of Li ion and the intercalation of Li in the graphite anode. The morphology of the electrodeposited film changes from dendritic to mossy structures due to the surface diffusion of lithium on the electrodeposited film.

Dendritic deposition on lithium metal anode during charging poses a safety concern. During discharging, formation of dead lithium results in low Coulombic efficiency. In this work, a comprehensive understanding of the interface evolution leading to the formation of dead lithium is presented based on a mechanism-driven probabilistic analysis. Non-dendritic interface morphology is obtained under reaction controlled scenarios. Otherwise, this may evolve into a mossy, dendritic, whisker or needle-like structures with the main characteristic being the propensity for undesirable vertical growth. During discharging, pitted interface may be formed along with bulk dissolution. Surface diffusion is a key determinant controlling the extent of dead lithium formation, including a higher probability of the same when the effect of surface diffusion is comparable to that of ionic diffusion in the electrolyte and interface reaction.

One of the biggest advantages of solid electrolyte over liquid electrolyte is its mechanical rigidity which provides resistance to dendritic deposition. The electrodeposition at the interface of solid electrolyte and lithium metal anode will be affected by the nature of the interface formed between solid electrolyte and lithium metal, i.e. coherent, semi-coherent or incoherent depending on the misfit between the two crystal lattices. A coupled energetics and deposition mesoscale model is developed to investigate the nature of deposition and surface roughness of the deposition. The strength of interaction between metal anode surface and solid electrolyte surface at the interface is key in determining the roughness of the morphology during deposition. The energy is localized to region near the interface. With surface diffusion at the interface, the roughness of the interface as well as the energy near the interfacial region decreases.

1. INTRODUCTION

1.1 Background

Renewable energy needs to be scaled up to meet the greenhouse gases targets and to limit the extent of pollution in densely populated urban areas. One of the main limitations of the renewable energy is interrupted nature of the available energy, for example, daily and seasonal variations in the amount of the sunshine available or the wind energy available to drive the wind turbines. If energy storage is coupled with the renewable energy technology, then this limitation is voided^{1–3}. In densely populated urban centers, particulate emission and noxious fumes from vehicles is a hazard to public health. Chronic exposure can lead to breathing difficulties, risk to heart and children and other vulnerable sections of population are particularly at risk. Use of electric vehicles and hybrid vehicles will reduce the concentration of these harmful matter and increase the wellness of the population. So, there is strong impetus to develop safe and low cost rechargeable batteries.

1.2 Lithium batteries and their significance

Lithium is one of the lightest element in the periodic table. It has high redox potential (-3.04V vs SHE). Lithium metal anodes offer theoretical capacity of 3860 mAh/g⁴. So, lithium is light weight and has high theoretical capacity. Lithium-ion batteries (LIB) are the most successful commercial batteries. They are widely used in electronics like laptops, wireless cell phones, microbatteries⁵ like flexible wearable technologies, health monitoring devices, applications in transport sector like electric and hybrid electric vehicle. Safety, life, performance and cost of the battery are important considerations in all these applications. However, lithium ion batteries replaced the previous generation of batteries like lead-acid and nickel metal hydride because of higher energy density. Energy density of a rechargeable battery is contributed by two factors, the operational voltage of anode and cathode of the battery and the specific capacity⁶. The energy density requirements of the applications like electric vehicle has pushed towards development of next generation of lithium batteries⁷. The current status of lithium ion batteries and possible improvements with particular focus on use in automotive industry is discussed by Blomgren⁸.



Figure 1-1 Possible anode and cathode materials to achieve high energy density in relation to energy density of current batteries (adapted from Aurbach and co-workers)⁹.

The current generation of LIB use graphite anode as intercalating material and a variety of hosts like LCO (lithium cobalt oxide), LiFePO₄, LiMnPO₄ as cathode materials. The capacity of the battery is limited by the specific capacity of graphite anode (372mAh/g) and oxide cathode (100-400 mAh/g)¹⁰. Intercalation based materials like graphite have a limited number of sites where lithium can be accommodated. This limits the energy density of the battery. Figure 1-1 shows the capacity and potential for different anode and cathode materials and path to achieve high density battery by combination of anode and cathode.

To meet the demands for higher energy density, new chemistries and active materials in electrochemical storage like lithium-sulfur, lithium-air, lithium-bromine, lithium metal, silicon as anode etc. are being developed. These are marked changing from intercalation of lithium to conversion reactions or alloying reactions 6,11 . Sulfur has theoretical capacity of 1672 mAh/g sulfur

is one of the most abundant materials and is cheap. However, Li-S batteries are challenged by large volume change, soluble polysulfides that migrate to anode (shuttle effect) and insulating nature of sulfur and lithium sulfide¹². Lithium-air batteries offer theoretical capacity of 3500 Wh/kg ¹³ but the underlying electrochemistry is not fully understood. Silicon as an anode material ¹⁴ is very promising because the theoretical specific capacity is greater than 4000 mAh/g. Silicon forms alloy with lithium during charging and dealloys during discharging. The most challenging aspect is the accompanying volumetric change (~300%) during alloying/dealloying of the silicon anode.

Another approach is to use nanostructured materials to improve the life and safety of the lithium batteries^{10,15}. The aim is to stabilize the fracture or deposition by use of nano-architecture of active material. To mitigate the effect of fracture of silicon anodes, a highly elastic polymer binder or self-healing polymeric binder is used to keep the pulverized fragments together and improve the life of the battery ¹⁶⁻¹⁹. Xu et al ²⁰ used densely compacted Si/C microspheres to alleviate the issue of fracture of silicon active material. In silicon anodes, the main idea is to add an interface comprising of flexible elastic material and silicon, which can absorb the damage due to fracture or reduce the size of silicon particle and force contact and agglomeration through binder. In lithium metal anodes, to ensure uniform deposition with successive cycling, structure or framework in the form of graphene network or lithium coated polymer matrix is provided in which lithium deposition occurs ^{21,22}. Another approach to obtain uniform lithium deposition was to use nanoscale carbon encapsulation ^{23,24} or mesoporous structure of CoCO₃ hollow sphere ²⁵. Kozen et al ²⁶ improved the performance of lithium metal anode by depositing Al₂O₃ using atomic layer deposition. Heine et al ²⁷ used coated lithium powder (CLiP) to improve the performance of the battery. Lee et al ²⁸ used fibrous metal felt as a scaffold to improve e the performance of lithium metal batteries. Liu et al ²⁹ used nanochannel to ensure uniform lithium flux to obtain uniform deposition of lithium on lithium metal anodes. The introduction of additional interfaces between lithium and framework or host which is lithiophilic in nature (good wettability of lithium) causes stable deposition of lithium.

Development of solid electrolyte is focus of intense research because it offers significant advantages of electrochemical and thermal stability and safety over liquid electrolytes³⁰. Solid electrolytes are of two kinds, in organic or polymeric ³¹. Different architecture of batteries are possible with the use of solid electrolyte ³⁰.

Lithium as an electrode material is very attractive because of high theoretical capacity. There are several issues related to the next generation of lithium ion batteries and it is focus of intense research.

1.3 Issues with Lithium batteries

Lithium is one of the most reactive element. It reacts with the liquid organic electrolyte and the resultant products form a deposit on the anode surface referred to as solid electrolyte interphase (SEI) ³². The SEI is ionically conducting but are electronically insulators. A stable SEI film provides protection against further consumption of Li in irreversible capacity losses. However, the SEI is composed of many different reaction products and is prone to fracture ^{32,33}. If the SEI film cracks due to irregular deposition of lithium during charging, more lithium is consumed in forming the new SEI layer. The properties of the SEI also change with ageing ³³. Also, the non-uniform thickness of SEI film leads to local inhomogeneity in the diffusion of lithium ion which can be an important factor in non-uniform plating or stripping ³⁴. Roder et al ³⁵ developed a multiscale model to simulate the growth of SEI on graphite electrodes. The model links atomic configuration effects of the SEI film on surface reactivity and macroscopic overpotential and current rates that affect the growth rates of SEI film.

Another issue with lithium batteries is formation of dendrites on lithium metal anodes during charging. These dendritic growth punctures the separator and short-circuits the battery resulting in catastrophic failure. Dendritic growth during charging has been an issue for lithium metal anodes for a long time ³⁶. Dendritic deposition on lithium metal anode can encompass different film morphology like whiskers, needles, mossy and dendrites. Peng et al ³⁷ performed experiments to study lithium growth mechanisms and concluded that lithium growth changes from mossy to dendritic which would penetrate the separator and cause short circuit due to limitation of electrolyte diffusion.

During discharging of lithium metal electrode, some fragments of lithium are detached from the electrode. This lithium is not electrochemically active, and it is called "dead" lithium. Formation of dead lithium reduces the Coulombic efficiency of the battery. The other feature observed is the formation of pits at the electrode-electrolyte interface during stripping ^{38–40}. The presence of dead lithium in liquid electrolyte also changes the transport characteristics of the lithium ion in electrolyte. It has been proposed that dead lithium is formed when lithium is stripped

from the root of dendrite like structure during discharging ^{34,41,42}. So even though dendrite formation and resultant short-circuit are more dangerous for safety of the battery, the performance with successive cycling is affected by the nature and morphology of lithium deposition and morphology and the amount of dead lithium formed during stripping. Sun et al ⁴³ observed the porous structure developed at the electrode and the cleavage of the separator due to lithium microstructure during stripping and plating using phase contrast x-ray tomography. Rong et al ⁴⁴ developed batteries using liquid electrolyte where they could observe plating and stripping of lithium metal anodes in-situ using scanning electron microscopy. They observed formation of mossy lithium deposition during charging and evidence of dead lithium during discharging. Gireaud et al ⁴⁵ observed that at very discharge currents during stripping, lithium was dissolved along grain boundaries, while at low currents, general pitting was observed. The surface roughness created during stripping served as nucleating sites for dendrite formation during charging. The formation of dendrites was suppressed by application of compressive stress to the cell.

Lithium ion batteries use graphite as anode and a variety of cathode materials like lithium cobalt oxide (LCO), LiFePO₄ etc. During charging, lithium ion is reduced at the anode surface and subsequently lithium intercalates inside the graphite anode. Li is deposited at the anode surface at high rates of charging or at low temperatures ⁴⁶. This is called lithium plating on the graphite anode surface. The plated lithium can grow to short-circuit and battery failure. Even if catastrophic failure does not occur, lithium is consumed in forming new SEI layers over plated lithium. Uhlmann et al ⁴⁷ found a characteristic voltage signature in the voltage during charging due to plating and a plateau in the voltage curve during relaxation attributing it to intercalation of some of the plated lithium from the surface to graphite. Both these signatures in voltage was more pronounced if higher value of charging pulse was used. The SEM images showed plated lithium on graphite and smaller amount of plated lithium on graphite anode surface after prolonged relaxation.

The main advantage of solid electrolyte over liquid electrolyte is its high modulus can prevent penetration of lithium dendrites and causing short-circuit. Monroe and Newman concluded that if the shear modulus of the solid electrolyte is more than two times than shear modulus of lithium metal, then irregularities in lithium deposition would be suppressed. Solid electrolytes are discussed in greater detail below.

1.3.1 Comparison of solid electrolyte with liquid electrolyte

Liquid electrolytes offer excellent wetting of the electrode and have high ionic conductivity compared to solid electrolytes. Liquid electrolytes are organic compounds and are volatile and flammable. They also suffer from poor ion selectivity, inadequate chemical and electrochemical stability and poor safety ^{30,48,49}. The main attraction of solid electrolyte is it offers high modulus to stop the propagation of lithium dendrite during charging. However, the ionic conductivity of lithium ion is low in solid electrolytes, particularly at room temperature ³⁰. Another critical problem is high interfacial resistance and lack of good contact at the solid electrolyte and electrode interface. To reduce the interfacial resistance, a thin layer of Al2O3 was deposited at the interface of lithium and solid electrolyte by using atomic layer deposition ^{26,50} or a thin layer of amorphous silicon using plasma enhanced chemical vapor deposition ⁵¹. The chemical and electrochemical stability of solid electrolytes is a topic of further research ^{52,53}.

1.3.2 Types of solid electrolyte and different architecture of batteries

There are primarily two kinds of electrolyte, inorganic and polymer. Inorganic or ceramic solid electrolytes. Figure 1-2 lists the main kind of solid electrolytes and the conductivity value ³⁰. The ionic conductivity of liquid electrolytes is 0.01 S cm^{-1 54}. To improve the interfacial contact between solid electrolyte and electrolyte, two approaches are taken, and these electrodes are called hybrid electrolytes. One approach is to fabricate composite electrolyte using ceramic and polymer electrolyte with the overall aim to improve contact at the interface ^{17,30}. The other approach is to use inorganic electrolytes with pores filled with gel electrolyte to improve ionic conductivity ^{4,17,32}. Solid electrolyte also enables different architecture of batteries, all solid batteries, gaseous or liquid cathodes (lithium-air, lithium-sulfur, and lithium-bromine) and mediator ion batteries ³⁰.

Inorganic solid electrolyte suffer from high contact resistance at the electrolyte and lithium metal interface. It has been reported that lithium penetrates the inorganic solid electrolyte LZZO across the grain boundary and other existing defects in the solid electrolyte ⁴⁸. Harry et al ⁵⁵ found that initially, the bulk of the dendritic structure was beneath the polymer electrolyte-lithium interface. This structure was created at the crystalline impurities in the lithium electrode and short-circuit is caused as the dendrites grow with cycling. Brissot et al ⁵⁶ observed dendritic growth in lithium metal battery with polymer PEO electrolyte at high rates of charging. They found that at

low rates of charging, thin needle like lithium deposits was formed while at high rates tree like dendrites was formed. They also observed a global motion of the electrolyte due to concentration changes at the electrodes. Brissot et al ⁵⁷ performed another series of experiment on Li/PEO/Li symmetric cells and calculated the ionic concentration of lithium and correlated the dendritic growth to the concentration gradient of lithium ions.

Туре	Materials	Conductivity (S cm ⁻¹)	Advantages	Disadvantages
Oxide	$\begin{array}{l} Perovskite \\ Li_{3,3}La_{0,56}TiO_3, \\ NASICON LiTi_2(PO_4)_3, \\ LISICON Li_{14}Zn(GeO_4)_4 \\ and garnet Li_7La_3Zr_2O_{12} \end{array}$	10-5-10-3	 High chemical and electrochemical stability High mechanical strength High electrochemical oxidation voltage 	 Non-flexible Expensive large-scale production
Sulfide	Li ₂ S–P ₂ S ₅ , Li ₂ S–P ₂ S ₅ –MS _x	10-7-10-3	 High conductivity Good mechanical strength and mechanical flexibility Low grain-boundary resistance 	 Low oxidation stability Sensitive to moisture Poor compatibility with cathode materials
Hydride	$ LiBH_4, LiBH_4-LiX \\ (X = Cl, Br or I), LiBH_4- \\ LiNH_2, LiNH_2, Li_3AlH_6 \\ and Li_2NH $	10-7-10-4	 Low grain-boundary resistance Stable with lithium metal Good mechanical strength and mechanical flexibility 	 Sensitive to moisture Poor compatibility with cathode materials
Halide	Lil, spinel Li₂Znl₄ and anti-perovskite Li₃OCl	10-8-10-5	 Stable with lithium metal Good mechanical strength and mechanical flexibility 	 Sensitive to moisture Low oxidation voltage Low conductivity
Borate or phosphate	$\begin{array}{l} \text{Li}_2\text{B}_4\text{O}_7, \text{Li}_3\text{PO}_4 \text{ and} \\ \text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5 \end{array}$	10-7-10-6	 Facile manufacturing process Good manufacturing reproducibility Good durability 	 Relatively low conductivity
Thin film	Lipon	10-6	 Stable with lithium metal Stable with cathode materials 	 Expensive large-scale production
Polymer	PEO	10 ⁻⁴ (65–78 °C)	 Stable with lithium metal Flexible Easy to produce a large-area membrane Low shear modulus 	 Limited thermal stability Low oxidation voltage (<4 V)

LiPON, lithium phosphorus oxynitride; LISICON, lithium superionic conductor; NASICON, sodium superionic conductor; PEO, poly(ethylene oxide).

Figure 1-2 Summary of solid electrolytes and their key features ³⁰

There are several challenges associated with the lithium ion batteries and lithium metal batteries using liquid electrolytes or solid electrolytes. In the next section, the interface between electrode and electrolyte and their importance is discussed.

1.4 Role of interfaces and challenges

Interfaces between electrode and electrolyte is and its behavior is key in determining the performance of the battery. The electrochemical reaction occurs on the interface and modifying or applying surface engineering to the interface has been able to improve the electrochemical performance. Wang el al ⁵⁸ discuss some of the ways in which electrode surface is modified, one of which is decreasing the size of active particles, which increases the area available for electrochemical reactions. The electrochemical and chemical stability of the electrolyte at the electrode and electrolyte interface is very important. Gauthier et al ⁵⁹ discuss the criterion for stability of electrolyte and the current mosaic theory of SEI formation and the unanswered question in the formation of SEI on graphite anode in LIB. The electrochemical stability of the interfaces between solid electrolyte and lithium metal and the decomposition products formed at the interface is focus of these two studies ^{52,53}.

The interface is dynamically evolving due to deposition or dissolution of metal from the electrode. If the interface becomes unstable, resulting in formation of dendrites, thermal runaway and failure of the battery occurs. Tikekar et al ⁶⁰ have taken a holistic approach to designing the interface between electrode and electrolyte. They recommend following avenues to suppress dendrite formation are regulating the ion flux, mechanical strength of the electrolyte and forming a stable and passive SEI or an artificial SEI layer.

Plating or formation of dendrite leads to increased surface area available for electrochemical reactions. Similarly, the pitting or other features formed due to dissolution of lithium from electrode during the discharging modify the interface between the electrode and electrolyte and the electrochemical reaction kinetics. This research thesis is focused on the evolution of the interface during charging or discharging. The formation and effect of SEI is not considered. The evolution of the interface is solely due to electrodeposition or electrodissolution of lithium.

In the next section, different kinds of interfaces studied in this thesis and challenges associated with them are discussed.

1.5 Kinds of interfaces and particular challenges

This study focuses on three different kind of interfaces. These interfaces as well as the issues related to them are described below.

1.5.1 Intercalation anodes

This interface is formed between liquid electrolyte and graphite anode. During charging, lithium ion is reduced at the interface and lithium atoms subsequently intercalate inside the anode. However, at high charging rates or low temperatures, deposits of lithium is found at the anode surface. This is called "plating" on the anode. If adversely affects the efficiency of the battery and if the lithium deposit grows and puncture the separator, the battery short-circuits.

1.5.2 Lithium metal anodes

During discharging, lithium deposition on lithium metal anodes tends to be unstable and different kind of morphology like needles, whiskers, mossy and dendrites are formed. If lithium growth penetrates the separator, failure of the battery occurs. During discharging, pits are formed on the interface. In addition, some of the lithium gets detached from the electrode. This is called "dead" lithium since it is no longer electrochemically active.

1.5.3 Solid electrolyte

Solid electrolyte and lithium metal interface are characterized by high interfacial resistance. The contact at the interface is an issue. The lithium deposits at the heterophase interface under a diffusive flux. The mechanical properties of the solid electrolyte is important. Monroe et al ^{61,62} suggested that if the shear modulus of the solid electrolyte is twice than that of lithium, unstable electrodeposition of lithium is suppressed. The evolution of the interface as lithium is electrodeposited has not been studied.

1.6 Mesoscale modeling

Atomistic calculations using ab-initio or first principles are limited by the size of the computational domain that can be resolved as well as the simulation time. However, using coarse

grained techniques (reduce the number of variables to capture the physics of interest), physical phenomena can be captured for longer length and time scales. These models are referred to as mesoscale models and are particularly useful in multiscale materials modeling ^{63–68}. Figure 1-3 shows the capability of different computational methods and capability in terms of length and time scales. Urban et al ⁶⁹ describe the use of DFT calculations in materials relevant to lithium ion batteries and use of coarse grained models to extend the length and time scales. Different physical length scales associated with electrochemical processes and multiscale simulations are discussed here ^{65,70–72}.



Figure 1-3 Capability of modeling technique to capture appropriate length and time scale ⁷³.

Monte Carlo and Kinetic Monte Carlo (KMC) is a versatile modeling technique. An introduction to KMC method ⁷⁴ by Arthur Voter is very useful. Heath et al ⁷⁵ provide a useful review of the KMC method used in various electrochemical problems. KMC is particularly useful in studying the morphology of deposition ^{76–83}, grain boundaries ^{84–87}, phase segregation at grain

boundaries ⁸⁸, evolving surfaces ⁸⁹, sink strength of interfaces ⁹⁰ and ionic transport in cathode ⁹¹ and solid electrolytes ^{92–99}. In general, KMC deposition studies, the effect of strain due to lattice mismatch between substrate and material being deposited is not explicitly accounted for. However, the strain effects can induce the formation of dislocation to relieve energy or islands or pits or other deposition characteristics. Subramanian et al ¹⁰⁰ has developed KMC method to account for arbitrary strains in KMC simulations. KMC models including the effects of strain energy has been used to study heteroepitaxial deposition ^{101–103}, growth of islands ^{104–109}, formation of dislocations ^{110,111} and growth of thin films ^{112–114}. Multi-scale simulations in which KMC and finite element methods are coupled to study the electrochemical reactivity ¹¹⁵ and heterogeneous surface film growth ³⁵.

In this research work, Kinetic Monte Carlo (KMC) method is used to study deposition characteristics at the buried interface.

1.7 Objective and organization of thesis

The interface between electrode and electrolyte is critical to the safety and performance of lithium batteries. In this research, mesoscale modeling technique has been used to evolution of interface during charging and discharging. The evolution of interface between electrode and electrolyte as charging or discharging occurs is the focus of this research. The scope is limited to electrodeposition or electrodissolution of lithium and formation of SEI layer is not considered. Three kinds of interfaces are considered, interface formed between intercalation anode and liquid electrolyte, interface of metal anode and liquid electrolyte and interface between metal anode and solid electrolyte.

1.7.1 Interface of intercalation anode and Liquid electrolyte

Kinetic Monte Carlo method is used to study whether plating occurs or not on the graphite anode surface during charging. There are two different electrochemical reactions that can occur, reduction of lithium ion on the graphite surface or reduction of the lithium ion on the plated lithium surface. The reduced lithium can intercalate into the graphite anode. Plating or deposition of lithium on graphite surface will depend upon the balance of kinetics of electrochemical reactions and kinetics of intercalation of lithium inside the graphite anode. The following factors affecting plating and the extent of plating are studied

- 1. Operating conditions (overpotential, temperature and state of charge)
- 2. Effect of concentration of lithium ions in the electrolyte
- 3. Diffusion of lithium ions in electrolyte
- 4. Diffusion of lithium atoms in the graphite anode
- 5. Surface diffusion of lithium on graphite surface and lithium surface

1.7.2 Interface of metal anode and liquid electrolyte

During charging, deposition at lithium metal anode is likely to be dendritic. If the dendrites grow, they can penetrate the separator and cause short-circuit and failure. Lithium is irreversibly consumed as new SEI layer is formed over the newly created surface during deposition. During discharging, lithium dissolution is not uniform and there is pitting on the anode surface. Also, some part of lithium is detached from the electrode during discharging. This is referred to as "dead" lithium as it is no longer attached to the electrode and is not electrochemically active. The formation of dead lithium reduces the Coulombic efficiency of the battery.

In this research work, generalized probability based KMC model has been developed to study plating and stripping during charging and discharging of a metal electrode. Plating and stripping are studied in tandem to gain a better understanding of issues related to metal electrodes. The KMC model includes diffusion of metal ion, diffusion on metallic surface and reaction (reduction or oxidation). The KMC model allows for formation of dead metal during discharging. The morphology and electrode interface area is studied during and discharging as described below

Charging

- 1. Effect of reaction rate, ion diffusion and surface diffusion on morphology
- 2. Number of layers deposited and the average height of the deposition
- 3. The evolution of surface formed at the interface during charging

Discharging

1. Effect of reaction rate, ion diffusion and surface diffusion on morphology

- 2. Number of layers of metal dissolved and layers of "dead" metal formed
- 3. The evolution of surface formed at the interface during discharging

The issue of dead lithium is further investigated and the functional trend of increase in dead lithium with operating conditions, temperature and applied voltage is studied using mesoscale method and experimental image analysis of the interface.

1.7.3 Interface of metal anode and solid electrolyte

One of the biggest advantage of solid electrolyte over liquid electrolyte is its mechanical rigidity which provides resistance to dendritic deposition apart from thermal stability and electrochemical and chemical stability ³⁰. However, solid electrolytes have high ionic resistance compared to liquid electrolyte. While the liquid electrolyte has excellent wetting of the lithium anode, solid electrolytes have issues of imperfect contact with the lithium electrode and suffer from high interfacial resistance.

The electrodeposition at the interface of solid electrolyte and lithium metal anode will be affected by the nature of the interface formed between solid electrolyte and lithium metal, i.e. the orientation of the lithium crystal and the solid electrolyte and the misfit of the crystal lattices. The mechanical properties of the solid electrolyte is also expected to play a key role. This study develops a generalized coupled energetics and deposition model to study deposition at the buried metal and solid state electrolyte. The effect of strength of interaction between metal surface and solid state electrolyte surface at the interface on morphology of deposition is investigated. Diffusion of metal atoms on the surface is also considered and the average distance and roughness of the interface is characterized.

The thesis is organized in the following manner. Chapter 1 provides the background information about the importance of lithium batteries and challenges associated with it, why better understanding of interface between electrode and electrolyte is important for safety and better performance of battery, the mesoscale model used in this work and the scope and the objective of this research thesis.

Chapter 2 deals specifically with the issue of electrodeposition at intercalation anodes. It offers the background and previous research with respect to plating at intercalation anodes, the

computational model and discussion of results. Appendix A offers the KMC algorithmic details and the effect of computational domain size.

Chapter 3 describes in detail the plating and stripping at a metal electrode. The relevant literature and background of deposition and stripping of a metal anode is discussed in the introduction section. The computational model and the morphology and the evolving interface during plating and stripping is discussed. Appendix B provides detailed description of the KMC algorithm and effect of computational domain size.

Chapter 4 deals specifically with lithium metal anode and liquid electrolyte and formation of dead lithium. The relevant background about dead lithium is given. The amount of dead lithium formed with changing operating conditions of the battery is studies using mesoscale method and analyzing the lithium interface after performing experiments on battery in glovebox. Appendix C gives details of KMC parameters and image analysis procedure.

Chapter 5 provides background on lithium metal and solid state electrolyte and issues. A coupled energetics and deposition model is used to study deposition at the interface. Appendix D provides with detailed algorithmic details of the coupled energetics and deposition model and the computational domain size.

Chapter 6 focuses on the effect of surface diffusion on the morphology of deposition at the solid state electrolyte and metal interface. The background information relevant to solid state electrolyte and lithium metal and modeling efforts is given. The morphology and energy distribution near the interface with progression of deposition is discussed.

Chapter 7 briefly summarizes the key findings of this research work and outlook for this line of study.

2. INTERCALATION ANODE AND LIQUID ELECTROLYTE INTERFACE

Relevant Publications and/or Working Papers

1. **Deepti Tewari**, Zhixiao Liu, Perla B. Balbuena and Partha P. Mukherjee, Mesoscale understanding of lithium electrodeposition from intercalation electrodes. Journal of Physical Chemistry C, 2018, 122, 21097-21107

2.1 Introduction

Rechargeable lithium-ion batteries are used extensively in electronics, telecommunication, transportation and many other application ^{7,116}. Energy storage devices are the critical component in renewable energy revolution and in promoting electric vehicles which are less polluting. The challenge for the next generation of Lithium-ion batteries is to deliver higher specific energy density and power density while maintaining safety and performance standards. However, Lithium electrodeposition can occur on the anode during charging if the operating conditions are extreme like fast charging or low temperatures ^{40,46,117,118}. Electrodeposition of Li on anode or plating is a safety concern and it also degrades the battery performance. Accumulation of Li atoms on the anode surface is thought to occur because of disparity between the rate of the electrochemical reduction reaction occurring on the anode and the rate of intercalation of Li atoms inside the graphite anode.

Continuum models ¹¹⁹ for Li electrodeposition on Li-ion batteries use two critical criteria for deposition of Li atoms on the electrode, the first criterion proposed by Purushothaman and Landau ¹²⁰ is based on concentration. If the diffusion of Li atoms inside the electrode is smaller than the rate of reduction of Li ions on electrode, Li atoms would accumulate on the surface of the electrode and if the concentration reaches a saturation level, plating occurs. The second is the overpotential criterion developed by Arora and Doyle. If the net overpotential $\eta_{(Li/Li+)}$ for Li deposition in the Butler Volmer equation is negative, Li plating occurs on the electrode surface ¹²¹.

The models for dendrite formation and growth on metal substrate consist of a surface tension based continuum model initially proposed by Barton and Bockris, phase field model ¹²², Brownian motion based statistical models, and the Chazalviel electromigration limited model ^{119,123}. Barton

and Bockris model contains two stages, the initiation stage and the propagation stage of the dendrite. In the initiation stage, the tip formed its own spherical diffusion layer within the global diffusion layer. In the propagation stage, the velocity of propagation depends upon overpotential, concentration of adatoms in solution, and temperature. These theories for studying formation and growth of dendrite formation are general and are applicable to solidification processes by undercooling of melt, chemical vapor deposition or electrodeposition.

The Brownian statistical models ¹²⁴ are modified from the classical diffusion limited aggregation model ^{125,126} and they are useful in studies of morphological evolution of deposited atoms. When the adatoms (reduced metal atom) reach the electrode surface, the probability of deposition, Ps reflects the balance between the rate of electrochemical reaction and the bulk diffusion. The probability is 1 for the diffusion-limited aggregation model. The value of P_s depends upon many parameters like overpotential, exchange current density, and bulk electrolyte concentration. If the probability is low, the deposited morphology is dense. On the other hand, if the probability is high, the deposited structure is more diffuse and there is more chance of dendritic growth. The difficulty in using this model is to accurately link the probability of deposition to the parameters affecting it like overpotential, exchange current density and temperature. Also, it does not account for the presence of a porous anode (intercalation of Li atoms in graphite anode) which would change the nature of electrodeposition.

Kinetic Monte Carlo (KMC) is a versatile statistical mechanics based technique. A broad overview of utility of KMC techniques in electrochemical systems is presented by Turner et al ⁷⁵. Although KMC method has been used to study different aspects of batteries like electrochemical impedance of solid oxide fuel cell electrolyte ¹²⁷, formation and growth of Solid Electrolyte Interphase ^{128,129}, formation of passivation layer on Li-Sulfur cathode ¹³⁰, it is particularly useful for studying the morphology of deposition.

Electrodeposition and the resulting morphology has been the focus of several studies. Guo et al ¹³¹ studied the kinetics of nucleation and growth by specifying the attachment probability of metal on metal and metal on substrate deposition. Several electrodeposition studies of copper ^{77,132,133} have used deposition rates based on specified overpotential. Dendritic growth on Lithium metal anode has been studied by Aryanfar et al ^{134–136}. One commonality between all these studies is that the deposition is occurring on a metal substrate. If the substrate is porous like an intercalating

anode, it is questionable whether deposition on the anode surface would take place and if it does, what is the morphology of the deposition.

In the present work, the Kinetic Monte Carlo technique is used to study the morphology of Lithium electrodeposition on a graphite anode which allows for intercalation of Li atoms inside it. This is a mesoscale model since the length and time scales of the simulations are in between the atomic/molecular scales and continuum scales, which also allow for a physical scale bridging description. Diffusion of Li atoms in to the bulk graphite anode is expected to modify the nature of electrodeposition of the Li ion on the anode surface. Diffusion of Li atoms on the deposited Li surface has been modeled. The kinetics is explicitly modeled in terms of operating conditions and material properties. It is found that the morphology of the electrodeposited film changes from dendritic to mossy due to surface diffusion of Li atoms on the film. The amount of film deposited on the anode surface correlates strongly to the current rate. If the diffusion of Li⁺ ions in the electrolyte is fast, there is more electrodeposition. This study shows that surface diffusion of Li atoms on the film.

2.2 Computational Model

A two-dimensional coarse-grained lattice KMC model was developed to study electrodeposition during the charging process. The following assumptions were made (i) Solid electrolyte interphase is not included (ii) solvation structure of Li⁺ ion is not modeled (iii) only the anode is included the model.

There are two kinds of events; the electrochemical reduction reaction modeled using Butler-Volmer relation and a Brownian diffusive motion. A description of the KMC events shown in Figure 2-1 is provided below:



Figure 2-1 Schematic of the physical events included in the two-dimensional Kinetic Monte Carlo model. The empty circles indicate Li ions in electrolyte solution while the filled circles indicate Li atoms.

- 1. Diffusion of Li^+ ion in the electrolyte
- 2. Electrochemical reduction of Li⁺ ion on the graphite anode surface
- 3. Diffusion of Li atom on the anode surface
- 4. Diffusion of Li atom from the anode surface into the bulk anode
- 5. Diffusion of Li atoms on the electrodeposited Li film
- 6. Electrochemical reduction of Li^+ ion on the Li film
- 7. Diffusion of Li atom in inside the anode

The computational domain is periodically repeated in the x direction as shown in Figure 2-1.
The rate of diffusion events is modeled using the Arrhenius equation

$$k = v \exp\left(\frac{-\Delta E}{K_B T}\right) \tag{1}$$

Here, $\mathbf{v} = 2K_BT/h$ is the jump frequency, ΔE is the activation energy, K_B is the Boltzmann constant and T is the temperature in Kelvin and h is Planck's constant. Table 2-1 lists a description of rates of KMC events. To calculate the diffusive rates, k_e , k_b , k_s and k_f , pertinent activation energy ΔE_e , ΔE_b , ΔE_s and ΔE_f listed in Table 2-2 are used respectively in equation 1.

The rate of the electrochemical reaction is modeled using the Butler-Volmer relation. The potential on the anode surface is constant because of the high conductivity of graphite and lithium. As a first approximation, the influence of the geometric irregularity due to electrodeposition on the anode surface potential, although minimal, is not considered in this study. The rate of electrochemical reduction reaction, k_{rs} is for the reduction reaction $Li^+ + e^- + 6C \rightarrow LiC_6$ on graphite anode surface. It is determined from the current density j_1 as follows

$$k_{rs} = \frac{j_1 a_0^2}{e} \tag{2}$$

In the above equation, e is the electronic charge, a_0 is the characteristic lattice distance. j_1 is determined using Butler-Volmer relation,

$$j_{1} = j_{01} \left\{ \exp\left(\frac{\alpha_{a,1}F\eta_{1}}{RT}\right) - \exp\left(\frac{-\alpha_{c,1}F\eta_{1}}{RT}\right) \right\}$$
(3)

Here j_1 is the current density, j_{01} is the exchange current density, $\alpha_{a,1} = 0.5$ and $\alpha_{c,1} = 0.5$ are the transfer coefficients for oxidation and reduction respectively, F is the Faraday constant and R is the universal gas constant. η_1 is defined as,

$$\eta_{\rm l} = \varphi_{electrode} - \varphi_{electrolyte} - U_{e,\rm l} \tag{4}$$

Here $\varphi_{electrode} - \varphi_{electrolyte}$ is the potential difference and $U_{e,1}$ is the equilibrium potential for reduction reaction. j_{01} is defined as ¹¹⁷,

$$j_{01} = Fk_{10} \exp\left[\frac{E_1}{R}\left(\frac{1}{298} - \frac{1}{T}\right)\right]$$
(5)

Here, F is the Faraday constant, R is the universal gas constant, E₁ and k₁₀ are listed in Table 2-2. The rate of electrochemical reduction reaction, k_{rLi} is for reduction reaction Li⁺ + e⁻ \rightarrow Li on deposited Li film.

$$k_{rLi} = \frac{j_2 a_0^2}{e}$$
(6)

$$j_{2} = \min\left\{0, j_{02}\left[\exp\left(\frac{\alpha_{a,2}F\eta}{RT}\right) - \exp\left(\frac{-\alpha_{c,2}F\eta}{RT}\right)\right]\right\}$$
(7)

Here, j_2 is the current density, j_{02} is the exchange current density, $\alpha_{a,2} = 0.3$ and $\alpha_{c,2} = 0.7$ ^{117,121} are the transfer coefficients for oxidation and reduction respectively, F is the Faraday constant and R is the universal gas constant. η is defined as,

$$\eta = \varphi_{electrode} - \varphi_{electrlyte} - U_{e,2} \tag{8}$$

Here, $\varphi_{electrode} - \varphi_{electrolyte}$ is the potential difference and $U_{e,2}$ is the equilibrium potential for reduction reaction. j_{02} is defined as ¹¹⁷

$$j_{02} = Fk_{20} \exp\left[\frac{E_2}{R} \left(\frac{1}{298} - \frac{1}{T}\right)\right]$$
(9)

Here, F is the Faraday constant, R is the universal gas constant, E_2 and k_{20} are listed in Table 2-2. Equations 5 and 9 are modified from the equations presented in ¹¹⁷, where there is no need to include the concentration of Li⁺ ions as it is explicitly modeled in the KMC model through Li⁺ ion diffusion in the electrolyte. The constants k_{10} , k_{20} , E_1 and E_2 were adjusted until similar trends in the plating current versus the intercalating current ¹¹⁷, was obtained.

In the current KMC model, domain size of 175×200 lattice sites is used. The area of one square lattice grid is a_0^2 . In the x direction, $N_x = 175$ lattice sites while in the y direction $N_y = 200$ is used. The one hundredth layer in the y direction marks the interface between electrolyte and anode. Periodicity in the x direction is enforced. For the boundary in the y direction, at the base of the electrode (y=0), the Li atoms cannot diffuse in the –y direction and at the top of the domain (y=N_y), the Li ions cannot diffuse in the +y direction. To begin with the normalized concentration of Li⁺ ions in electrolyte is 0.1, i.e., ten percent of the lattice sites in the electrolyte region are occupied by Li⁺ ions. This would approximately be about 1M Li⁺ ion concentration. This value of concentration of Li⁺ ions is in the range of reported value 0.1M to 3.3M ^{137,138}. The total number

of Li atoms and Li⁺ ions is constant in the current implementation of KMC algorithm. A different way to implement the boundary condition would be to maintain the number density of Li⁺ ions in the electrolyte to be constant, such that a new Li⁺ ion is introduced when a Li⁺ ion is reduced at the anode surface or lithium surface. Although this implementation would allow for longer simulation time, it would not affect if plating has occurred on the anode surface or not. The KMC simulations were performed at room temperature and low temperatures because of the concern that plating is more likely to occur at low temperature because of mismatch between electrochemical reaction and slow diffusive intercalation at low temperature. Therefore, we focus our efforts on conditions when plating is more likely to occur.

In our two dimensional model, the xy plane is a slice through cathode-electrolyte-anode of which a small section of anode and electrolyte interface is modeled using KMC technique. In the xz plane, there is no driving force or potential to influence the motion of Li+ ion or Li atom. So, the particle motion on xz plane is independent of direction.

In three-dimension, if the applied overpotential is low, there might not be any Li deposition on anode surface or if there were small amount of electrodeposition, it would be irregular on the anode surface similar to results from two dimensional study presented in our manuscript. At negative overpotential with respect to Li⁺/Li, electrochemical reaction will occur on both graphite anode as well as Li surface. Since the electrochemical reactions are surface driven, in threedimension, the surface area of dendritic Li deposition would be larger. Therefore, there are more opportunities for electrochemical reaction as well as rearrangement of Li electrodeposit through diffusion of Li atoms on surface. If surface diffusion of Li atoms on Li surface is not allowed, the resulting morphology will be three-dimensional dendrite similar to the shapes of tree branches. If surface diffusion of Li atoms on Li surface is allowed, the resulting morphology would be mossy. The detailed KMC algorithm is described in Appendix A.

To analyze the results, the following quantities are defined. The number density of electrodeposited film is defined as the ratio of number of Li atoms on or above the anode surface to the possible sites for Li deposition in the x direction. A higher value of number density would indicate greater amount of electrodeposition.

Number density =
$$\frac{\sum_{i} Li \text{ atoms on or above the anode surface}}{N_x}$$
 (10)

The electrodeposition rate is defined as the slope of the number density with respect to time

$$Electrodeposition \ rate = \frac{d \left(Number \ density\right)}{dt}$$
(11)

Table 2-1 Description of the physical and electrochemical reaction rate terms

Rate	Description		
ke	Rate of diffusion of Li ⁺ ion in electrolyte		
kb	Rate of diffusion of Li atom in bulk anode		
ks	Rate of diffusion of Li atom on anode surface		
kf	Rate of diffusion of Li atom on electrodeposited Li film		
krs	Rate of electrochemical reduction of Li ⁺ ion on anode surface		
krLi	Rate of electrochemical reduction of Li ⁺ ion on electrodeposited Li film		

Symbol	Description	Value	Unit
ΔE_e	Activation energy for diffusion of the Li ⁺ ion in	0.206 139	eV
	the electrolyte		
ΔE_b	Activation energy for diffusion of the Li atom in	0.218 140	eV
	the graphite anode		
ΔE_s	Activation energy for diffusion of the Li atom on	0.16 141,142	eV
	the graphite anode surface		
ΔE_{f}	Activation energy for diffusion of the Li atom on	0.09 143	eV
	Li (100) plane		
a ₀	Lattice constant for graphite	2.46E-10	m
U _{e,1}	Equilibrium potential for reduction of Li ⁺ ion on	-2.84	Volts
	graphite		
U _{e,2}	Equilibrium potential for reduction of Li ⁺ ion on	-3.04	Volts
	Li		
k ₁₀	Reaction rate constant	5.0E-9	$1/(\text{sec } \text{m}^2)$
k ₂₀	Reaction rate constant	1.60E-9	$1/(\sec m^2)$
E ₁	Activation energy	2.5E4	J/mol
E ₂	Activation energy	1.0E4	J/mol

Table 2-2 Parameters used in KMC model

2.3 Results and Discussion

2.3.1 Dependence of Li deposition morphology on modeling complexity and rate of reduction of Li ion on Li surface

The morphology of Lithium electrodeposition on the anode surface is quite different if diffusion of Li atom into the anode is allowed. Similarly, different results are expected if surface diffusion of Li atoms on Li surface is allowed. The following four cases are proposed to systematically study how the morphology changes including these modeling features

Case 1. Diffusion of Li atom into the bulk anode is not allowed. There is no surface diffusion of Li atoms on the anode surface. There is also no diffusion of Li atoms on the Li film deposited above the anode surface ($k_f = 0, k_s = 0, k_b = 0$).

Case 2. Diffusion of Li atoms into the bulk anode is permitted. No surface diffusion of Li atom on the anode surface and Li film is allowed ($k_f = 0$, $k_s = 0$).

Case 3. Diffusion of Li atom into the bulk anode and on the anode surface is allowed. No surface diffusion of Li atoms on the Li film is allowed ($k_f = 0$).

Case 4. Diffusion of Li atom in the bulk anode as well as the diffusion of Li atom on the anode surface and on the deposited Li surface are allowed.

Figure 2-2 shows the morphology of electrodeposition for the four cases in a columnar format. The first row of pictures corresponds to rate of electrochemical reduction of Li ion on graphite anode surface, k_{rs} and rate of reduction of Li ion on Li surface, k_{rLi} when value of applied potential, $\mathbf{\eta}$ is -0.1 V. The ratio of k_{rLi}/k_{rs} is very small, i.e., the probability of electrochemical reaction on graphite anode surface is a lot higher than electrochemical reaction on Li film. The value of k_{rLi} has been increased by a factor of 10 successively from labels (a) to (e). So for row (e) k_{rLi} is 10,000 times that for row (a).

Figure 2-2, (a) to (e) show the morphology of Li deposition for case 1. If the $k_{rs} << k_{rLi}$, it would imply that probability of electrochemical reaction occurring at anode surface is very large compared to electrochemical reaction on the deposited Li film. The electrodeposition is a layer of thin film. As the value of k_{rLi} is similar to k_{rs} , there is equal probability of electrochemical reaction on anode surface as well as deposited Li film. The resulting morphology is rougher and a couple of layers thick. If $k_{rs} << k_{rLi}$, electrochemical reaction occurs overwhelmingly on deposited Li. The resulting morphology is dendrite or tree like structure. There is clear transition from reaction

control to diffusion control as we progress from image (a) to (e). There is comprehensive discussion of electrodeposition on impermeable substrate by ¹²³.

If diffusion of Li into bulk anode is allowed, if $k_{rs} \gg k_{rLi}$, there is almost no Li deposition on the anode surface. If k_{rs} and k_{rLi} are comparable, the film is not regularly deposited on the surface (compare 2(c) to 1(c) in figure 2-1). If $k_{rLi} \gg k_{rs}$, $(k_{rLi}/k_{rs} > 10^3)$ diffusion of Li atom in the anode is immaterial. The resulting morphology is dendritic. The morphology does not appear any different for case 3 from that of case 2. Surface diffusion of Li atom on anode surface does not seem to be a factor in the morphology of electrodeposition. One explanation may be that, in this 2-dimension problem set up, the diffusion of Li atoms on anode surface is a line and therefore in the KMC implementation, there are very few occasions when surface diffusion of Li atom on anode is triggered. The morphology of the Li film changes significantly if diffusion of Li atom on deposited film is included in the KMC model as in case 4. If $k_{rs} \gg k_{rLi}$, $(k_{rLi}/k_{rs} > 10^{-3})$ Li atoms form cluster on the surface. If $k_{rs} << k_{rLi}$, Li electrodeposition look like clump or mossy in appearance compared to the case 1, 2, and 3 where dendritic morphology is obtained. Including surface diffusion of Li atoms on Li surface as electrodeposition is occurring dramatically changes the morphology from dendritic to mossy.

Figure 2-3 shows plots of time evolution of number density with time for cases 1, 2, 3 and 4 for different values of k_{rLi} multiplied by scaling factor of 10 successively from (a) to (e). These plots correspond to the morphology of Li deposits shown in Figure 2-2. In Figure 2-3(a), the number density approaches a value of 1, indicating one layer of Li atoms deposited on the anode surface for case 1 as seen in Figure 2-2,1(a). Because electrochemical reaction is preferential on graphite surface, once a layer of Li atoms is formed, it acts a passivation layer. For cases 2 and 3, there is almost no accumulation of Li on the anode surface, so the number density is almost zero with small fluctuations to account for the net increase due to electrochemical reduction or decrease due to Li atom diffusing in to anode. For case 4, the number density is almost linear it overtakes the number density for case 1 at large time. In Figure 2-3(b), k_{rLi} is 10 times larger than that for 3(a) and the number density is larger than for case 1 when diffusion into bulk anode is prohibited. Still the number density for case 4 is larger than those for case 2 and case 3. This is the trend for Figure 2-3(c) as well. For large values of k_{rLi} , the value of number density is the same for all four cases as seen in Figure 2-3(e). Even though numerically, the value of the number density is the same, the resulting morphology is very different for case 4 than for the other three cases. The

number density curves are same because of depletion of Li^+ ions in electrolyte and therefore the electrochemical reaction is conditional on diffusion of Li^+ ion to the electrodeposited Li surface.

Based on Figures 2-2 and 2-3, it can be concluded that surface diffusion of Li atoms on changing Li surface as electrodeposition progresses is a key property because the morphology of the film changes from dendrite to mossy if surface diffusion is included. If the rate of electrochemical reaction on the Li surface is very large compared to that on the anode surface, electrodeposition is a certainty, despite the diffusion of Li atoms into the anode.

2.3.2 Relaxation

Here we would like to investigate for a Li film that has been deposited on anode surface and is allowed to relax, if the number density for the film would decrease as the Li atoms are given chance to diffuse into the anode in the absence of any electrochemical reaction. In Figure 2-4, results of such a study are presented. To begin with, the Li film structure from Figure 2-2, labels 2(c), 3(c) and 4(c) are used as initial configuration. They are subsequently allowed to relax, i.e., no electrochemical reaction event is permitted, only diffusion events are allowed. Diffusion into anode is allowed for all three simulations. When diffusion of Li atoms on the anode surface and on the Li film are not allowed, there is no change in the number density as shown by the blue lines in Figure 2-4. The morphology of the film at the end of simulation is the same. If diffusion of Li atoms on the anode surface is allowed but not the diffusion of Li atoms on the film, the number density remains unchanged as seem from the green line in Figure 2-4, and so does the morphology of the Li film. If both kinds of surface diffusion are allowed, the number density for the film decreases after a long time. This can also be seen from snapshots of the electrodeposited film at the beginning and at the end of simulation. Smaller sized deposits are relatively easier for rearrangement and subsequent diffusion into the anode than larger sized deposits. This series of calculations was done at room temperature; at lower temperature, the rate of diffusion will be slower, so the result will be less marked. Also, if the anode is nearly filled with Li atoms, the Li film will not show any decay or relaxation. At the core, the relaxation is only possible due to rearrangement of Li atoms on the film due to surface diffusion.



Figure 2-2 Effect of modeling complexity and rate of reduction of Li ions on Li surface. The rate of reduction of Li ions on Li surface, krLi is increased successively by a scaling factor of 10 from (a) till (e). Modeling complexity increases between cases 1 to 4. KMC calculations are done for $\eta = -0.1$ V (vs Li+/Li) and temperature of 298 K. Green is used for Li ions in electrolyte, red for Li atoms on the anode surface or above the anode surface while blue is used for Li atoms residing inside the anode. The pictures of Li electrodeposition film were taken at 90 nanoseconds.



Figure 2-3 Lithium film deposition on the anode surface as a function of modeling complexity and rate of reduction of Li ions on the Li surface. Figure 2-3(a) corresponds to Li film deposition corresponding to conditions shown in Figure 2-2, 1(a), 2(a), 3(a) and 4(a). Similarly, Figures 2-3(b), (c), (d) and (e) correspond to row of Figures 2-2 (b), (c), (d) and (e).



Figure 2-4 Relaxation of deposited Li film with no electrochemical reaction. The evolution of amount of Li film deposited as a function of time for deposited film structure corresponding to Figure 2-2 2(c), 2-3(c) and 2-4(c). The Li film deposited on the anode surface evolves due to diffusive events, in the absence of electrochemical reduction events. The KMC simulations are performed at 298K.

2.3.3 Overpotential, temperature, and state of charge effects

Figure 2-5, (a), (b) and (c) show the total current as a function of time at temperatures 298, 273 and 248 K and applied overpotential of 0.1, 0.0 and -0.1 V (vs Li⁺/Li) while (d), (e) and (f) show the number density for the Li film. There is no electrodeposition when the applied overpotential, η is 0.1 V. The value for the current is small. At this value of η , there is no Li⁺/Li reduction reaction. Electrochemical reaction occurs only on graphite and the ratio of rate of diffusion of Li atom in to anode and rate of electrochemical reaction on anode surface ranges between 400 to 500 at 248K to 298K. Therefore, Li atoms diffuse faster into anode and there is no accumulation of Li atoms on the anode surface.

At η of 0.0 V, the value of current is larger, even though the current is caused only due to reduction of Li⁺ on anode surface. But the value of current is larger and there is deposition on the anode surface even though it is slow. The ratio of k_b/k_{rs} is about 35 at 248K and 70 at 298K. Compared to η of 0.1V, this ratio is about 7 to 10 times smaller. The Li⁺ ions are reduced at a faster rate than diffusion into anode with net accumulation on the anode surface.

At η of -0.1V, the electrochemical reaction occurs on both the anode surface and the Li film surface. The resulting value of the current is high, and the electrodeposition occurs almost from the beginning.

At larger temperature, the value of the current is greater, and the number density of electrodeposition correlates strongly with the current. Electrodeposition is more sensitive to applied overpotential than to temperature because the current changes at a faster rate with changing overpotential than with temperature. The overall effect is greater electrodeposition at greater current irrespective of the cause for increased value of current.

Figure 2-6(a) shows contours of electrodeposition rate on graphite anode as function of temperature and overpotential. The electrodeposition rate is zero at 0.0 V and 0.05 V. The electrodeposition rate is largest at 298 K and -0.1 V.

Figures 2-6(b), (c) and (d) show the change of number density of electrodeposited film with time at η of 0.0 V, -0.05 V and -0.1 V respectively. It is important to note that there is almost no film deposited for about 500 nanoseconds for applied η of 0.0 V, about 100 nanoseconds for η of -0.05 V and about 50 nanoseconds for η of -0.1 V. There is no electrodeposition for η of 0.05 V and 0.1 V.

The activation energy for diffusion of Li atoms in the graphite anode varies for dilute and non-dilute limits ¹⁴⁰. If the in-plane Li concentration in graphite increases, so does the activation energy required for diffusion of Li. In a practical sense, this corresponds to the state of the charge of battery. Figure 2-7 shows the results for electrodeposition if the activation energy for diffusion of Li atoms in graphite anode is increased from 0.22 eV to 0.3 eV. This range corresponds to the activation barrier calculated using first principle calculations by Persson *et al.*¹⁴⁰ for dilute and non-dilute limits of Li in graphite. Figure 2-7(a) shows contour of electrodeposition rate for **η** and temperature. Compared to Figure 2-6(a) the electrodeposition rate is greater than zero for the entire range of applied **η** and temperature. The overall electrodeposition rate is about 2.5 times larger than when activation energy is smaller. Apart from higher numerical value and absence of any region in the operational domain where the electrodeposition rate is zero, the pattern of the contour in the bottom half of Figure 2-7(a) is like Figure 2-6(a). Figures 2-7(b), (c) and (d) show the number density of electrodeposited film as function of time at **η** of 0.1 V, 0.05 V and 0.0 V respectively. The number density of film increases sharply after about 120 ns, 100 ns and about 80 ns for **η** of 0.1, 0.05, and 0.0 V respectively.

Pulse charging is used a means to mitigate the issue of electrodeposition on anode surface ^{119,144}. The pulse is characterized by the amplitude of current and duration of charge and rest. The number density plots in Figure 2-6 and Figure 2-7 show that electrodeposition on anode does not occur for some time and then it grows rapidly. If the pulse duration of charging corresponded to this time and then some rest period is allowed where only diffusive events are permitted, the small electrodeposited nucleus on anode surface would dissolve and intercalate inside the anode.

It has been proposed in the pulse charging technique that either the amplitude of charging current is reduced, or the duration of rest increased towards the end of charging process when the state of charge in the anode is high to avoid electrodeposition on anode surface. From Figure 2-6 and Figure 2-7, it can be concluded that the time to build up electrodeposited film is larger if the current is smaller (the more positive overpotential results in lower current and lower number density of electrodeposited film) or the anode is empty. Towards the end of the pulse charging process, if the amplitude of current is reduced, the time before electrodeposited film starts to grow, is larger and electrodeposition can be avoided. On the other hand, if duration of pulse for rest is increased, it gives larger time for dissolution of electrodeposited clusters on the anode to dissolve and intercalate inside the anode. In Figure 2-4, it can be seen that for greater time allowed for

relaxation when no electrochemical reaction occurs, more the number density of the electrodeposited film decreases. So, both of these modifications to pulse charging method at the end of the cycling process would work to reduce the problem of electrodeposition of Li atoms on anode.

2.3.4 Effect of normalized concentration of Li ions in electrolyte

Figure 2-8(a) shows that the electrodeposition rate increases linearly as the normalized concentration of Li^+ ions in the electrolyte increases from 0.05 to 0.25. Figure 2-8(b) shows that the current density also increases linearly with the normalized concentration of Li^+ ions while the plating current density increases non-linearly with concentration. With the increase in concentration of Li^+ ions, the average distance traversed by Li^+ to reach a site for electrochemical reaction decreases. Therefore, both current density and electrodeposition rate increase. The plating current density increases quickly at larger concentration because with higher electrodeposition rate, the surface area of the film provides sites for electrochemical reduction of Li^+ on the Li surface.

2.3.5 Effect of rate of diffusion of Li⁺ ions in electrolyte

Electrolytes play a critical role in the optimal performance of battery. The electrolyte is generally a mixture of organic solvents to obtain desired values of solvent viscosity, dielectric constant and melting temperature ^{118,139}. Recent reports have shown that some combinations of electrolyte mixtures perform better than others with regards to electrodeposition. To study the effect of Li diffusion in the electrolyte, KMC simulations at $\mathbf{\eta}$ of -0.1V, temperature of 248 K and three different values for rate of Li diffusion in the electrolyte, ke/10, ke and 10ke were used. Figure 2-9(a) shows the variation of the current density with time for three different values of rate of Li diffusions at about 500 nanoseconds. With increasing Li diffusion in the electrolyte, higher current density is obtained and greater electrodeposition on the anode surface.



Figure 2-5 Current density and number density of film deposited on anode surface at different applied overpotential and temperature. (a) current density at applied overpotential of 0.1 V (Li+/Li); (b) current density at applied overpotential of 0.0 V (Li+/Li); (c) current density at applied overpotential of -0.1 V (Li+/Li); (d) number density at applied overpotential of 0.1 V (Li+/Li); (e) number density at applied overpotential of 0.0 V (Li+/Li) (f) number density at applied overpotential of -0.1 V (Li+/Li); (e) number density at applied overpotential of -0.1 V (Li+/Li); (f) number density at applied overpotential of -0.1 V (Li+/Li); (f) number density at applied overpotential of -0.1 V (Li+/Li).



Figure 2-6 Electrodeposition rate and number density of film as function to time. (a) Contour of electrodeposition rate as function of applied overpotential and temperature; (b) Number density of film deposited at applied overpotential of 0.0 V (Li+/Li); (c) Number density of film deposited at applied overpotential of -0.05 V (Li+/Li); (d) Number density of film deposited at applied overpotential of -0.1 V (Li+/Li).



Figure 2-7 Electrodeposition rate and number density of film as function to time when activation energy for diffusion of Li atoms in bulk is 0.3eV. (a) Contour of electrodeposition rate as function of applied overpotential and temperature; (b) Number density of film deposited at applied overpotential of 0.1 V (Li+/Li); (c) Number density of film deposited at applied overpotential of 0.05 V (Li+/Li); (d) Number density of film deposited at applied overpotential of 0.0 V (Li+/Li).



Figure 2-8 Effect of Li ion concentration of in the electrolyte. (a) Rate of growth of deposited film; (b) current density and plating current density as function of concentration of Li ions in electrolyte solution.



Figure 2-9 Effect of the Li ion diffusion rate in the electrolyte, ke. (a) Current density and time profile for 1/10 ke, ke and 10 ke; (b) Plating current density and time profile for 1/10 ke, ke and 10 ke; (c) Number density of film deposited as function of time.

2.3.6 Effect of rate of diffusion of Li atoms on electrodeposited Li surface

Diffusion of Li atoms on the electrodeposited Lithium film changes the morphology of the film as well as the number density of the film. To understand the sensitivity of morphology of Li film with the rate of surface diffusion of Li atom on film, a series of KMC calculations were done. The value of rate of diffusion of Li atom on film was changed from 10^{-4} k_{f0} to 10 k_{f0}, where k_{f0} is the rate of diffusion calculated using activation energy of Li diffusion on (100) plane. Figure 2-10 shows the rate of electrolyte diffusion with respect to ratio k_f/k_{f0} as well as picture of Li film at

about 1700 nanoseconds. There are two distinct regimes of electrodeposition with respect to k_f . At smaller surface diffusion, nearly regular flat film is formed, and the rate of electrodeposition is small. With lower rate of surface diffusion of Li atoms on Li surface, there are fewer instances of Li surface diffusion and there is less likelihood of rearrangement of Li atoms to generate vertical structures from the horizontal film which is formed at the beginning of electrodeposition process. Flat or nearly flat film facilitates the intercalation of Li atoms inside the graphite anode because Li atoms located at the edge of the film can intercalate inside the graphite anode.

At larger values of Li surface diffusion, the rate of electrodeposition is higher and the height of the Li film in the vertical direction is large. Consider two extreme cases, one in which a layer of Li atoms is aligned to anode surface, another in which it is perpendicular to the surface. If the rate of surface diffusion is very high, then the frequency of occurrence of these two realizations is high. When the layer is aligned to the surface, Li atoms from the edges can intercalate into the anode, so the likelihood of their survival decreases, while the layer aligned vertically survive and grow. This vertical growth of Li film at high rate of surface diffusion is of more concern because large vertical growth can puncture the separator of the battery and lead to catastrophic failure.

2.3.7 Effect of rate of electrochemical reaction of Li⁺ ions on electrodeposited Li surface

In Figure 2-11, the electrodeposition rate is plotted against the ratio k_{rLi}/k_{rLi0} , where k_{rLi0} is the reference value of rate of electrochemical reaction used in KMC simulations and k_{rLi} the rate obtained by scaling k_{rLi0} by 10 successively. The red line shows the rate of electrodeposition at the beginning when the film has just started to grow while the green line shows the electrodeposition rate at the end of the KMC simulation. At smaller value of k_{rLi} , the value of electrodeposition rate is small because the surface area of the film is small and therefore there are fewer sites for the electrochemical reaction. Towards the end of simulation, the electrodeposition rate is higher because the surface area of film has grown and therefore the green line is above the red at smaller value of k_{rLi} . There is a cross-over in the green and red lines at about k_{rLi}/k_{rLi0} value of 1000. When k_{rLi} is large, the rate of electrodeposition rate is larger at the beginning of film formation compared rate of growth at the end of the simulation. Because k_{rLi} is large, the surface area of electrodeposited film increases quickly, consuming the Li⁺ ions in its neighborhood, and creating a Li⁺ ion depleted region. Thus, the electrodeposition rate slows down towards the end.



Figure 2-10 Effect of Li diffusion rate on the electrodeposition and morphology of deposited film.



Figure 2-11 Effect of Li ion reduction rate on electrodeposition. Profile of electrodeposition rate and krLi/ krLi0 at the beginning when film starts to grow and at the end of KMC simulation.

2.4 Conclusions

During the charging process, electrodeposition of Lithium atoms on the graphite anode becomes a safety issue. In this work, a mesoscale Kinetic Monte Carlo model was developed linking rates of reduction of Lithium ions and diffusion of Li atoms into the anode and electrolyte and surface diffusion to operating conditions and material properties. The critical events determining whether electrodeposition will happen or not, occur at the anode-electrolyte interface. If the rate of diffusion of Li atoms into the anode is about the same order as the rate of reduction of Li ions on the anode surface, Li atoms accumulate on the anode surface as a film. There are two electrochemical reactions occurring on the anode surface, reduction on the graphite anode and reduction on the deposited Li film. For graphite anode, the rate of reduction on graphite anode is large compared to the reduction on the Li surface. In the absence of surface diffusion of Li atoms on the electrodeposited film, if the reduction reaction on the graphite anode dominates compared to the reaction on the Li film deposited film deposited is that of a uniform layer. On the other hand, if the reduction reaction on the Li film dominates, a dendritic morphology is obtained. If the diffusion of the Li atoms on film is included, the morphology of the electrodeposited film changes from dendritic to columnar or mossy. Surface diffusion is a key component in the morphology of the electrodeposited film. The effect of the rate of surface diffusion was investigated over several orders of magnitude: if the rate of diffusion is small, the film is irregular due to diffusion, the film growth is mostly vertical.

3. METAL ANODE AND LIQUID ELECTROLYTE INTERFACE: MECHANISTIC UNDERSTANDING OF ELECTROCHEMICAL PLATING AND STRIPPING OF METAL ELECTRODES

Relevant Publications and/or Working Papers

1. Deepti Tewari and Partha P. Mukherjee. Mechanistic Understanding of Electrochemical Plating and Stripping of Metal Electrodes. Journal of Materials Chemistry A 2019, 7, 4668–4688.

3.1 Introduction

Rechargeable lithium batteries are ubiquitous in our technological society. They are used in electronic appliances, particularly cell phones, laptops, in transportation like hybrid vehicles, power sector and many other applications. Lithium-ion batteries have been a great commercial success. However, the graphite that acts as a host for intercalating Li is extra weight. Li is one of the lightest element (534 kg/m³) and has high redox potential (-3.04V vs SHE). The Li metal electrodes are promising because of lightweight and high energy density. The issue with Li metal anode is the propensity for dendritic morphology during charging which can cause short circuit and catastrophic failure. In addition, Li is consumed in creating solid electrolyte interphase on the newly created surface on dendrite. During discharging, there is detachment of some Li from the metallic electrode. This detached Li is referred to as dead Li since it is not electrochemically active. This dead Li reduces the Coulombic efficiency of the battery.

A continuum model was developed by Barton and Bockris¹⁴⁵ to study dendritic deposition on a metal substrate. A dendrite would grow faster because it would experience spherical diffusion compared to global linear diffusion. The surface tension was the driving force for dendrite propagation. Subsequently, Diggle *et al.*.¹⁴⁶ incorporated overpotential by using Butler-Volmer kinetic relation and Monroe and Newman⁶¹ modeled dendritic growth between parallel electrodes with transient concentration and potential profiles. In all of these models, viscous and mechanical forces are not considered. Monroe and Newman¹⁴⁷ developed a model to include mechanical forces and its effect on exchange current densities and potentials at roughening interfaces. Another approach to model dendritic growth is through continuum phase field modeling¹⁴⁸.

Dissolution has been a topic of study in different fields like mineral dissolution^{149–151}, evolution of etch pits due to presence of screw dislocation and other defects^{124,152}, preferential

etching of crystallographic planes¹⁵³, particularly, etching of Silicon to create surface features^{154,155}. The kinetics of reaction is influenced by local environment, for example, in the terrace-ledge-kink (TLK) model, reaction rates are different because of difference in the coordination number. Lasaga and Luttge proposed stepwave dissolution model, which describes both bulk dissolution and local etching of pits¹⁵⁶.

It is observed in Li metal electrodes that during discharging, some Lithium is detached from the electrode. Since it is electronically isolated, it does not participate in further electrochemical reaction and is called dead Li. Formation of dead Li is intrinsically linked to the nature of the electrodeposition during the previous charging cycle. Experimental studies^{34,37,41} using TEM and SEM show that whiskers grow from root and since newly formed SEI is thinner and facilitates Li ion diffusion, during discharging, the roots of whiskers is dissolved at a faster rate leading to disconnection from the electrode. It can subsequently break away and float in the electrolyte or be connected to the electrode through the support of the SEI layer. Gireaud et al.45 observed that dendrites originated on the pits formed during the discharge cycle. Several studies ^{38,39,157} by Dasgupata research group have correlated the voltage profile with the morphology of deposition or dissolution of Li symmetric cells with cycling. They attributed the change from peaking voltage profile during initial cycling to arcing voltage profile towards the end of cycling to the gradual buildup of dead Li. Aryanfar et al.¹⁵⁸ quantified the amount of dead Li based on images of electrode and dead Li during discharging and concluded that amount of dead Li is reduced if the cycling period is shortened. Yoon *et al.*¹⁵⁹ studied the continuum behavior of plating and stripping of Li metal and found that the amount of dead Li is less when the discharge rate is high.

Kinetic Monte Carlo (KMC) is a statistical technique and it is particularly useful in studying the morphology during deposition or dissolution. Shvab *et al.*⁸⁴ studied different precipitation mechanism of nanoparticle aggregation. Trigueros *et al.*¹⁶⁰ studied diffusion controlled electrodeposition. Electrodeposition and associated morphology of the deposits were studied by Guo *et al.*¹³¹ by specifying the relative probability of attachment of metal on the substrate or metal on metal. Drews *et al.*⁷⁷ and Liu¹³³ studied electrodeposition of copper and linked the reaction kinetics to the overpotential. KMC modeling was used to study plating on intercalation anode ⁷⁸, formation of solid electrolyte interphase (SEI) ¹²⁹, dendrite formation on metal anodes ⁸² and dendrite-SEI interactions ¹⁶¹. Dissolution has also been studied by using KMC. Porous structures through dealloying were studied by Haldar¹⁶² and Erlbacher¹⁶³. KMC was used to investigate the

surface roughness¹⁵³ and dissolution of crystal^{164,165} and amorphous glass¹⁶⁶. Since KMC can only resolve small length and time scales, multi-paradigm studies have used coupled KMC and continuum scale transport to bypass these limitations^{35,115,167}.

There are many applications¹⁶⁸ where controlled deposition or plating is achieved by electrodeposition, for example, thin coating of surface deposition in solar panels .There are also many instances where stripping or electrodissolution is used to obtain the desired feature, for example etching of Silicon to obtain microchannel. The batteries are more challenging because of cyclic plating and stripping of an electrode. Therefore, studying plating and stripping in concert would give better understanding of the issues related to Li metal electrodes. In the current work, a generalized probability based KMC model has been developed to study plating and stripping during charging and discharging. The KMC model includes diffusion of metal ion, diffusion on metallic surface and reaction (reduction or oxidation). The KMC model allows for formation of dead metal during discharging. A wide variety of morphology of deposition is seen during charging. During discharging, a pitted electrode-electrolyte interface evolves along with steady bulk dissolution. Surface diffusion is key factor in the evolution of morphology. During charging, mossy deposition is obtained due to surface diffusion. During discharging, greater amount of dead metal is formed when the probability of surface diffusion is commensurate with the probabilities of oxidation reaction and ion diffusion. Since in batteries, the probability of reaction can be changed through applied overpotential, charging at slow reduction kinetics and discharging at fast oxidation kinetics will result in flat deposition during charging and minimize the amount of dead metal formation during discharging.

3.2 Computational Model

A two dimensional lattice Kinetic Monte Carlo model was developed to model plating and stripping during charging and discharging process. During the charging process, following three events can occur as shown in Figure 3-1 (a)

- 1. Diffusion of metal ion, M⁺ in the liquid electrolyte
- 2. Electrochemical reduction of M⁺ ion at the interface between electrode and electrolyte
- 3. Diffusion of metal atom M on the surface

During discharging, following three events are included in the KMC model as seen in Figure 3-1 (b)

- 1. Diffusion of the metal ion, M^+ in the liquid electrolyte
- 2. Oxidation of metal atom on the interface between electrode and electrolyte
- 3. Diffusion of metal atom, M on the surface.

If a metal atom is the only connecting link between a group of atoms and the electrode and it is oxidized, the group of atoms become detached from the electrode as seen in Figure 3-1 (b). This group of atoms cannot participate in further electrochemical reactions and are referred to as "dead" metal.



Figure 3-1 Schematic of the KMC model (a) transition events modeled in charging process (b) transition events for discharging process (c) probability space of transition events modeled during charging and discharging (d) determining surface ratio by counting N, number of metal atoms on the electrode surface and N1, the number of lattice sites on the enveloping surface

The reaction rates of the three processes during charging and discharging are assigned directly in terms of probabilities of three processes included in the KMC model. During the charging process, P_{red} is the probability of reduction of M^+ ion at the interface, P_e is the probability of diffusion of M^+ ion in electrolyte and P_f is the probability of surface diffusion of M atom on surface. During discharging process, P_{ox} is the probability of oxidation of a metal atom in to M^+ ion. P_e and P_f have the same definition as charging. Figure 3-1 (c) shows the probability space used in the KMC simulations. Since P_e and P_{red} or P_{ox} have to be non-zero for charging or discharging to occur, the minimum value for P_{red}/P_{ox} and P_e is 0.001. The maximum value that P_e and P_{red}/P_{ox} can take is 0.999. Since sum of probabilities is 1, P_f is not independent. The diagonal line shown in Figure 3-1 (c) is $P_e+P_{red}=1$ for charging or $P_e+P_{ox}=1$ for discharging and surface diffusion P_f is zero. The dotted line shown is for $P_e=P_{red}$ or $P_e=P_{red}$ line towards origin, implies larger value of P_f . Therefore, the diagonal line is a limiting case where there is no surface diffusion and moving towards origin implies very large value of P_f . For example, at $P_e=0.001$, $P_{red}=0.001$, $P_f=0.998$.

The electrochemical reactions occur at the interface of electrode and electrolyte. With plating or stripping, the interface changes and so does the surface area. To characterize the surface area, count the number of metal atoms on the actual interface, N. Next, find the unique set of all the lattice points, which are first neighbor of the atoms belonging to the interface and not occupied by metal atoms. Let this surface be referred to as the enveloping surface. Let N_1 be the sum of all the points belonging to the enveloping surface.

Define

Surface Ratio =
$$\frac{N}{N_1}$$
 (1)

Figure 3-1 (d) shows the schematic of determining the surface ratio. Consider a concave surface, the actual surface is shown as red while the enveloping surface is shown in blue. Since the perimeter of the enveloping surface is smaller than the actual surface, the surface ratio is greater than one. On the other hand, for convex surface, the perimeter of the enveloping surface is larger than the actual surface and hence the surface ratio is less than one. For a flat surface, the length of actual interface and the enveloping surface are same and the surface ratio is 1. Surface ratio is a tool to characterize the overall nature of the interface during plating or stripping. During plating, the nucleation phase or whiskers deposition or dendritic deposition, perimeter of the enveloping

surface is larger than the actual interface surface ratio would be less than 1. During discharging or stripping, the interface becomes pitted and the length of the enveloping surface is smaller than the actual surface and therefore, the surface ratio is greater than 1. In case of porosity, the surface ratio would be greater than one. Having information about the enveloping surface could be useful. If a reaction occurs at the interface, it will be when a site on the enveloping surface is occupied by the reacting agent. N₁ gives an estimate about the number of sites available for the reaction. Example, for catalytic activity, surface ratio < 1 would be preferred. Surface ratio provides information about how the interface is evolving with plating and stripping, and perhaps it could be useful in describing the updated reaction rate on interface in continuum descriptions.

Define following parameters for analyzing the results of KMC simulations

No. of layers deposited =
$$\frac{No. of reduction reactions}{N_x}$$
 (2)

$$AverageHeight = \frac{\sum_{i=1}^{M} y_i}{M}$$
(3)

No. of layers dissolved =
$$\frac{No. of oxidation reactions}{N_x}$$
 (4)

No. of layers of "dead" metal =
$$\frac{No. of "dead" metal atoms}{N_x}$$
 (5)

In equations 2, 4 and 5, N_x is the number of lattice points in the horizontal direction. To calculate average height in equation 3, y_i is the vertical distance from the bottom boundary and M is the total number of atoms in the deposit.

In the two-dimensional KMC model, a small segment of the electrode-electrolyte interface is modeled. The lattice grid is $(N_x \times N_y) = 175 \times 100$ sites, where 175 lattice points are in the horizontal direction and 100 lattice points are in the vertical direction. Periodicity is enforced in the horizontal direction. During the charging process, the first layer is comprised of metal atoms on which further deposition occurs. This boundary at the bottom is fixed, no surface diffusion is allowed. At the beginning, the fraction of lattice sites occupied by M⁺ ions is 0.1. As deposition progresses, whenever an ion is reduced, another ion is introduced at the top boundary, such that the number of M^+ ion remains constant during simulation. The M^+ ions at the top boundary cannot diffuse up in the vertical direction. During discharging process, at the beginning, there are 50 layers of stacked metal atoms. Ten percent of the empty lattice sites is occupied by M^+ ions. During dissolution, a metal atom is oxidized and an M^+ ion is introduced. When this happens, an ion is removed such that the total concentration of the metal ions remain constant during the course of simulation. The other boundaries are same as in the charging process. The details of the KMC algorithm is given in Appendix B.

3.3 Results and Discussion

3.3.1 Charging

Dependence of morphology on reaction rate, ion diffusion and surface diffusion

The morphology of deposition for different probabilities of reduction reaction, P_{red} , surface diffusion, P_f and ion diffusion P_e is shown in Figure 3-2. Pictures labeled 0-3 lie on 0-degree line with respect to P_{red} axis with $P_e=0.001$. Pictures labeled 0,4,5,6 line on 30-degree line, pictures labeled 0,7,8,9 line on 45-degree line while pictures labeled 0,10,11,12 lie on 60-degree line with respect to P_{red} axis. Pictures labeled 0,13,14,15 line on 90-degree line with respect to P_{red} axis with $P_{red}=0.001$. All points are equally spaced on a line.

Consider pictures labeled 0-3. This is a diffusion control scenario, P_e is very small and the value of probability of reduction increases on moving along the P_{red} axis while probability of surface diffusion, P_f decreases. Since, the deposition is limited by the diffusion of ions to the metal surface, there is not much difference in terms of number of reduction reactions that occur with increasing value of Pred. However, the morphology of deposition changes from whiskers to needle like with increasing P_{red} and decreasing P_f . With greater probability of surface diffusion, there is rearrangement of metal atoms and the vertical realizations are favored because of access to metal ions. If surface diffusion is zero, newly reduced ions attach at the point of the metal surface where the reaction took place, which results in a fine needle deposition as seen in picture 3. Arakawa *et al.* ¹⁶⁹ observed needle morphology of lithium deposition at high charge density.



Figure 3-2 Morphology of deposition during charging. Pictures marked 0, 1, 2 and 3 use
Pe=0.001 and Pred increasing from 0.001 to 0.999. Pictures labeled 0, 13, 14 and 15 use constant
Pred= 0.001 and Pe increasing from 0.001 to 0.999. Pictures labeled 4, 5 and 6 lie on 30-degree line with respect to Pred axis. Pictures 7, 8 and 9 show the morphology for Pe=Pred. Pictures labeled 10, 11 and 12 lie on 60-degree line with respect to Pred axis. Pictures labeled 4 is at time 5000, 5 is at time 1500 and 6 is at 1500. Pictures labeled 7, 8 and 9 are obtained at time 2700, 2600 and 1500 respectively. Pictures labeled 10, 11 and 12 are obtained at time 4100, 2000 and 1500 respectively.

Consider the 90-degree line with respect to P_{red} axis, where $P_{red}=0.001$. This is the reaction control region. Moving along this line, as P_e increases, P_f decreases. The deposition is limited by the number of reduction reaction that occur. When P_e is low and P_f is high, very few reactions occur and morphology is whiskers. As the probability of diffusion of ions, P_e increases, the morphology gradually changes from rough, non-uniform deposition to flat uniform deposit as seen in picture labeled 15. Langenhuizen ¹⁷⁰ reported that smooth deposition of lithium on Nickel substrate was obtained when the mass transport was increased by rotating electrodes.

On the diagonal line, $P_e+P_{red}=0$, the surface diffusion is zero. Pictures labeled 3,6,9,12 and 15 show the resulting morphology with zero surface diffusion. The morphology changes from needle like (picture 3) when the response limited by diffusion of ions to dendritic (picture 6,9,12) where P_e and P_{red} are comparable to uniform deposition (picture 15) where reaction kinetics determines the morphology.

The morphology of deposits is mossy in transition between these limiting scenarios. The morphology of the deposition is a complex interplay between probabilities of reaction, ion diffusion and surface diffusion. During charging, a flat surface or uniform deposition is desired. Uniform deposition is obtained only for very large probability of ion diffusion.

Number of layers and average height of deposition

The number of layers deposited on metal electrode is shown in Figure 3-3(a) as a function of time for five cases shown as dots on the probability space in the inset figure. The rate of deposition is nearly same for ($P_{red}=0.999$, $P_e=0.001$) and ($P_{red}=0.001$, $P_e=0.000$) even though the morphology is very different as seen in Figure 3-2. There are more layers deposited for higher ion diffusion ($P_{red}=0.001$, $P_e=0.999$). The fastest deposition occurred for $P_e=P_{red}=0.5$, with no surface diffusion. For both, $P_{red}=P_e=0.167$ and $P_{red}=P_e=0.5$, the slope of the curve of number of layers deposited with respect to time is very steep, indicating that likely dendritic deposition is occurring. However, the same information cannot be inferred form the other three curves.



Figure 3-3 Plating as a function of time (a) Number of layers of metal atoms deposited due to reduction (b) Average height of deposition. The inset triangle shows the value of Pe and Pred on probability space for the five curves plotted.



Figure 3-4 Contour of number of layers deposited with respect to probability of reduction, Pred and probability of diffusion of M+ ion in electrolyte, Pe (a) at time = 100 (b) at time = 1250



Figure 3-5 Contour of average height of deposition with respect to probability of reduction, Pred and probability of diffusion of M+ ion in electrolyte, Pe (a) at time = 100 (b) at time = 1250

The average height of the deposit with respect to time is shown in Figure 3-3(b) for five different cases as shown in the inset figure. The average height of the deposit increases very rapidly for $P_{red}=P_e=0.5$ and $P_{red}=P_e=0.167$ which is due to dendritic deposition. In Figure 3-3(a) the number of layers deposited for $P_{red}=0.001$, $P_e=0.009$, black curve is larger than $P_{red}=0.009$, $P_e=0.001$, while in Figure 3-3(b) the average height of the deposit is same for both cases. For the black curve, the morphology of deposit is flat or uniform, while the red curve is for needle like deposit. So even though, more layers are deposited for P_{red}=0.001, P_e=0.009, the average height low compared to the needle like deposition for $P_{red}=0.999$, $P_e=0.001$ where fewer layers are deposited, but the average height is relatively larger. The average height for P_{red}=0.001, P_e=0.001 increases after time=20,000. Even though, the number of layers deposited is same as P_{red}=0.999, P_e=0.001. The morphology is whisker like and because of very high surface diffusion; the average height fluctuates and increases after some time due to rearrangements of atoms in the vertical direction. An important point to note is the different time scales of deposition for different kind of morphology. For dendritic and mossy morphology, where P_{red} and P_e are both high and are of the same order, the time before number of layers of deposition grow very rapidly is $\sim 10^3$, while for extreme cases, when the deposition is constrained by reduction reaction or ion diffusion, the time to observe the morphology is 10^4 or larger.

Figure 3-4 (a) and (b) shows the contour plot of number of layers deposited with respect to probability of reduction, P_{red} and probability of diffusion of ion, P_e at time =100 and time=1250 respectively. At time=100, fewer layers are deposited when either the probability of reduction reaction, P_{red} is very small (marked as reaction limited in Figure 3-4(a)) or the probability of diffusion of ions, P_e is very small (marked as diffusion limited). In the mixed region, where diffusion of ions and reaction are in play, maximum number of reduction events occur and the number of layers deposited is highest. However, as deposition progresses, the region in probability in which the maximum number of reduction reactions and hence the highest number of layers deposited moves up as seen in Figure 3-4(b). The highest number of reactions occur when P_e/P_{red} is larger than 2.

The contour plot of average height of deposition with respect to probability of reduction, P_{red} and probability of ion diffusion, P_e at time=100 and time=1250 is shown in Figure 3-5 (a) and (b) respectively. The average height is very small in diffusion limited and reaction limited regions. In Figure 3-5 (a), the average height is maximum for mixed (reaction and diffusion control) region
and this corresponds to the largest number of reduction reaction occurring as seen Figure 3-4(a). However at time =1250, there are two distinct regions for which the average height of deposition is large as seen Figure 3-5(b). The region corresponding to larger P_{red} and smaller P_e ($P_e/P_{red} <1$), has greater value for average height of deposit because of nature of morphology. Dendrites are formed for these combinations of P_{red} and P_e as seen from Figure 3-2. The region corresponding to $P_{red} < P_e$ ($P_e/P_{red} > 1$) has greater value of average height because maximum number of reduction reactions occur in that region as seen in Figure 3-4(b).



Figure 3-6 Contour of surface ratio of the interface between electrode and electrolyte with respect to probability of reduction, Pred and probability of diffusion of M+ ion in electrolyte, Pe (a) at time = 100 (b) at time = 500 (c) at time = 750 (d) at time = 1250



Figure 3-7 Evolution of electrodeposited surface with time for Pf=0 and different values of Pred (Pe=1-Pred). (a) Surface ratio (b) Microstructure for Pred = 0.9999 at time = 25000 (c)
Microstructure for Pred = 0.8 at time = 2000 (d) Microstructure for Pred = 0.5 at time = 1500 (e)
Microstructure for Pred = 0.2 at time = 1700 (f) Microstructure for Pred = 0.05 at time = 4500 (g) Microstructure for Pred = 0.001 at time = 25000



Figure 3-8 Evolution of electrodeposited surface with time for Pred =Pe and Pf = 1-2×Pred. (a) Surface ratio (b) Microstructure for Pred=Pe=0.5 at time=1500 (c) Microstructure for Pred=Pe=0.4 at time=2300 (d) Microstructure for Pred=Pe=0.3333 at time=2600 (e) Microstructure for Pred=Pe=0.2 at time=5000 (f) Microstructure for Pred= Pe=0.05 at time=15000 (g) Microstructure for Pred = Pe =0.001 at time=25000

Evolution of surface formed at the interface between electrode and electrolyte

The contour plots of surface ratio with respect to probability of reduction, P_{red} and probability of diffusion of M^+ ions, P_e at time = 100, 500, 750 and 1250 is shown in Figure 3-6 (a) to (d). At time 100, across the entire P_{red} - P_e space, the surface ratio is less than one. In the reaction-controlled region, the surface ratio is close to 1 because the interface is nearly flat due to very few reduction reactions. In the mixed reaction and diffusion regime, there are more layers deposited and the surface ratio is lowest. In Figure 3-6 (b), the surface ratio is 1 for very high ion diffusion in electrolyte and small reaction rates. In (c), at the very tip, where P_e is 0.999, the interface is flat, however at slightly larger values of P_{red} , the surface ratio is greater than 1 indicating rough deposit. Meanwhile, the surface ratio is less than 1 for majority of space. In (d), the region in which surface ratio is greater than 1 has grown, For larger reaction rates, more rough deposition occurs while at the very tip, the surface ratio is 1. It is important to note that there is transition in the value of surface ratio in the region of uniform deposition, from slightly less than one to greater than one. In the region where there is dendritic growth, there is not significant change in the value of surface ratio. Flat or uniform deposition is obtained when ion diffusion is about three orders of magnitude greater than reaction rate.

Figure 3-7 shows the evolution of surface ratio and the corresponding morphology for different reaction rates P_{red} and ion diffusion P_e combinations and probability of surface diffusion is zero. The inset picture in Figure 3-7 (a) shows that value of P_{red} ranging from 0.001 to 0.999 on the diagonal line with no surface diffusion. Figure 3-7 (b)-(g) show the corresponding morphology. While the value of P_{red} decreases from 0.999 to 0.001, the value of P_e increases from 0.001 to 0.999. From (b) to (g), the trend goes from needle like deposit to dendritic to more bushy branch like deposit to rough deposit with pores to more uniform deposit. One common feature for the surface ratio curves is that all of them have value less than one (due to nucleation, which is a convex geometric feature). For P_{red} =0.05 and 0.001, there is crossover from less than one to greater than one. For P_{red} =0.05, rate at which deposition occurs is faster and the crossover at smaller time. Since the morphology shows many pores, the value of surface ratio is high. For P_e =0.001, the crossover occurs after a very long time and the surface ratio is close to one. For other cases, surface ratio is less than one, although it approaches a steady value after some time.

Figure 3-8 shows the evolution of surface ratio for equal probability of reduction and ion diffusion ($P_{red}=P_e$) and the corresponding morphology. Surface diffusion increases from 0 at

 $P_{red}=0.5$ to 0.998 at $P_{red}=0.001$. The inset picture in Figure 3-8 (a) shows the values of P_{red} used on the $P_{red}=P_e$ line. The surface ratio for the entire range of P_{red} is less than one, which is corroborated by the morphology of deposit shown in (b), to (g). The morphology changes from dendritic as seen in (b) when there is no surface diffusion to mossy (c)-(d), thick pillars (f) and whiskers (g) as P_{red} decreases and probability of surface diffusion increases. The surface ratio is lowest for zero surface diffusion and $P_{red}=0.5$ and highest for $P_{red}=0.001$. There are fluctuations in surface ratio when surface diffusion is allowed because of rearrangement to atoms on the surface.

The average surface at the interface is convex in nature when the morphology of deposition is any other than flat or non-uniform deposit. The envelope of the surface is about 2 times larger than actual surface for dendritic deposit. This might be useful in updating the surface activity term in the reaction rate calculations.

3.3.2 Discharging

Dependence of morphology on reaction rate, ion diffusion and surface diffusion

The morphology of dissolution or stripping with different probabilities of oxidation, ion diffusion and surface diffusion is shown in Figure 3-9. The distribution of pictures marked 0 to 15 with respect to P_{ox} and P_e is same as described during charging. On 0-degree line with respect to P_{ox} axis, at very high P_{ox} , the layer is oxidized very quickly, but the diffusion of ions is so low that it acts as a kind of passivating layer and inhibits further reaction. In pictures labeled 1 and 2, some pits are formed and because of higher probability of surface diffusion, some of the electrolyte is trapped. Picture 0 shows a porous structure due to high frequency of surface diffusion and very few reactions.

On 90-degree line with respect to P_{ox} axis, very few oxidation reactions occur, and as probability of surface diffusion decreases, so does the porosity of the microstructure. Consider the diagonal line, where there is no surface diffusion, the interface between electrode and electrolyte look almost same for pictures 6, 9 and 12, however the amount of dead metal is higher for picture 12. This is the region of mixed control where reaction and ion diffusion are both important. If surface diffusion is allowed, the quantity of dead metal formed is significantly higher than zero surface diffusion. Surface diffusion is a critical factor that affects the amount of dead metal.



Figure 3-9 Morphology during discharging. Pictures marked 0, 1, 2 and 3 use Pe=0.001 and Pox increasing from 0.001 to 0.999. Pictures labeled 0, 13, 14 and 15 use constant Pox= 0.001 and Pe increasing from 0.001 to 0.999. Pictures labeled 4, 5 and 6 lie on 30-degree line with respect to Pox axis. Pictures 7, 8 and 9 show the morphology for Pe=Pox. Pictures labeled 10, 11 and 12 lie on 60-degree line with respect to Pox axis. All the pictures are obtained at time=100.

The mixed control region is where maximum dissolution of metal occurs. This is similar to charging process, where maximum deposition occurs in the mixed control regime. The dissolution results in pitted interface, however when probability of surface diffusion is high, there are trapped ions in some deeper pits. Pitting is observed on the lithium metal electrode surface during stripping ^{39,40}. Gireaud el al ⁴⁵ observed pitting of the lithium electrode at both high and low

current density. At high current density, the dissolution of lithium occurred along the slip planes ⁴⁵. It can be concluded surface diffusion is a key parameter in reducing the amount of dead metal formed. When the ion diffusion is slow, there is high concentration of ions near the interface.



Figure 3-10 Striping as a function of time (a) Number of layers of metal dissolved due to oxidation reactions (b) Number of layers of "dead" metal. The inset triangle shows the value of Pe and Pox on probability space for the five curves plotted.



Figure 3-11 Contours with respect to probability of oxidation, Pox and probability of diffusion of M+ ion in electrolyte at time=100. (a) Number of layers dissolved (b) Number of layers of "dead" metal (c) ratio of "dead" metal and number of oxidation events

Number of layers dissolved and layers of "dead" metal

Figure 3-10 shows the number of layers dissolved and number of layers of "dead" metal formed during the discharging process. The inset picture marks the five (P_{ox},P_e) pairs as dots on input probability space. In Figure 3-10 (a), the number of layers dissolved is same for two cases when $P_{ox}=P_e=0.5$ and $P_{ox}=P_e=0.167$. Very few layers are dissolved when the system is constrained by either diffusion or oxidation reactions. The number of layers dissolved is linear with time for all five cases, although the slope vary. This is in contrast to the charging process, when number of layers deposited rose very sharply when (P_{ox},P_e) was equal to (0.5,0.5) and (0.167,0.167) respectively. When $P_{ox}=0.999$ and Pe=0.001, the number of layers dissolved is 1 and it is same throughout the discharge process. The ions formed during discharge cover the interface due to slow ionic diffusion and act as a passivating layer.

Figure 3-10 (b) shows the number of layers of dead "metal" with time. For the three cases, where P_e or P_{ox} or both of them are very low (the three corner points on the inset picture), no "dead" metal is formed. The number of layers of dead metal increases linearly with time indicating that cluster of atoms are detaching from electrode as the oxidation progresses. Almost five times more dead metal is formed between blue and green curves. Between these two cases, surface diffusion is the differentiating factor. With surface diffusion, rearrangement of atoms lead to situations where an atom is the lynchpin between a group of atoms and the rest of the electrode. If this particular atom is oxidized, the group of atoms are electrically detached from the electrode and contribute to "dead" metal. Surface diffusion strongly affects the magnitude of "dead" metal formed during discharging. It has been experimentally observed that particulate like lithium deposits were uniformly stripped while needle like lithium deposits resulted in dead lithium 42 . Kushima et al 34 observed the formation of dead lithium due to preferential dissolution of lithium whiskers at the root.

The contour plots of number of layers dissolved, the number of layers of dead metal formed and the ratio of number of dead metal and number of oxidation events with respect to probability of oxidation and probability of diffusion of ion in electrolyte is shown in Figure 3-11. In the diffusion limited and reaction-limited regions, very few layers are dissolved as seen in Figure 3-11 (a) while in the mixed control region, where both reaction and ion diffusion are equally likely, maximum number of layers are dissolved. The number of layers of dead metal formed is maximum in two regions. In one region, the maximum in dead metal coincides with the highest number of oxidation reactions in (a). In the other region of maximum dead metal results due to high surface diffusion despite fewer oxidation reactions in comparison. Figure 3-11 (c) shows the number of dead metal per oxidation reaction. The number of dead metal formed is about 20 percent of the total oxidation reactions in the mixed control region. For efficient discharge, high P_{ox} and low P_e or vice-versa is preferable. In lithium batteries, Coulombic efficiency measures the irreversible loss of cycling capacity. Formation of dead lithium leads to loss in Coulombic efficiency. The Coulombic efficiency of 80 percent to 90 percent for discharging is reported for lithium metal electrodes by Langenhuizen ¹⁷⁰ while Steiger et al ⁴¹ report about 30 percent capacity loss due to undissolved lithium. Experimentally, the loss in Coulombic efficiency is due to loss of electroactive lithium as well as formation of solid electrolyte interphase (SEI) and other irreversible side reactions.

Evolution of surface formed at the interface between electrode and electrolyte

In Figure 3-12, the surface ratio of the interface during electrodissolution and the corresponding microstructure is shown when there is no surface diffusion. The inset picture in Figure 3-12 (a) shows that value of P_{ox} ranging from 0.001 to 0.999 on the diagonal line with no surface diffusion. The value of P_e varies from 0.999 to 0.001. In Figure 3-12 (a), the surface ratio the surface ratio for three curves for $P_{ox}=0.8$, 0.5 and 0.2 fluctuate because the rate of oxidation is high and when some dead metal is detached the value of surface ratio changes suddenly. The average surface ratio is about 0.95 for these curves. When P_{ox} is 0.001, there are very few oxidations and the surface ratio increases linearly from 1 to 1.05. When P_{ox} is 0.999, the surface ratio is nearly 1. Discharging along the diagonal line where the probability of surface diffusion is zero, the surface ratio is close to 1 and the interface is flat or nearly flat with small pits as seen in Figure 3-12 (b) to (f).



Figure 3-12 Evolution of the electrodissoluted surface with time for Pf=0 and different values of Pox, (Pe=1-Pox). (a) Surface ratio (b) Microstructure for Pox=0.999 (c) Microstructure for Pox=0.8 (d) Microstructure for Pox=0.5 (e) Microstructure for Pox=0.2 (f) Microstructure for Pox=0.001



Figure 3-13 Evolution of the electrodissoluted surface with time for Pox=Pe and Pf=1-2×Pox. (a) Surface ratio (b) Microstructure for Pox=Pe=0.5 (c) Microstructure for Pox=Pe=0.4 (d) Microstructure for Pox=Pe=0.333 (e) Microstructure for Pox=Pe=0.2 (f) Microstructure for Pox=Pe=0.05 (g) Microstructure for Pox=Pe=0.001



Figure 3-14 Contour of surface ratio of the interface between electrode and electrolyte with respect to probability of reduction, Pox and probability of diffusion of M+ ion in electrolyte, Pe at time = 100

Figure 3-13 shows the evolution of surface ratio for equal probability of reduction and ion diffusion $(P_{ox}=P_e)$ and the corresponding morphology. Surface diffusion increases from 0 at $P_{ox}=0.5$ to 0.998 at $P_{ox}=0.001$. The inset picture in Figure 3-13 (a) shows the values of P_{ox} used on the $P_{ox}=P_e$ line. The interface between electrode and electrolyte is nearly flat when $P_{ox}=0.5$ during the entire duration of discharge. As the P_{ox} decreases and P_f increases, the value of surface ratio increases. Looking at microstructure in (b) to (e), the depth of pitting as well as trapped electrolyte has increased as the probability of surface diffusion has increased. In (f), whisker like features can be seen above the average interface with a porosity and trapped electrolyte. This is due to large probability of surface diffusion and slow oxidation and ion diffusion. In (g), when the surface diffusion is 0.998 while P_{ox} and P_e are orders of magnitude lower, the microstructure evolves to a very porous structure. One important point to note is that surface ratio evolves to a steady value after some initial time.



Figure 3-15 Evolution of surface ratio of the interface between electrode and electrolyte for Pox=0.211, Pe=0.122 and Pf=0.667. (a) Surface ratio as function of time (b) Microstructure at time=4 (c) Microstructure at time=8 (d) Microstructure at time=40 (e) Microstructure at time=80 (f) Microstructure at time=92

The contour of surface ratio of the interface between electrode and electrolyte with probability of oxidation, P_{ox} and probability of ion diffusion, P_e is shown in Figure 3-14. Across the entire space, the value of surface ratio is close to 1 or higher than 1 indicating that the interface contains pits or in the case of low P_{ox} and about 10^3 times P_f , a very porous microstructure. Flat interface is obtained in two regions, one where $P_{ox} >> P_e$ and P_f is close to zero and in the other region, $P_e >> P_{ox}$ and P_f is close to zero. Interface with pits is obtained when oxidation, ion diffusion and surface diffusion are equally.

Figure 3-15 shows the evolution of surface ratio of the interface for $P_{ox}=0.211$, $P_e=0.122$ and $P_f=0.667$ (this point lies on 30-degree line with respect to P_{ox} axis) and the corresponding microstructure. The surface ratio is always greater than one. The surface ratio is characterized by a series of minima and maxima. Figure 3-15 (b) correspond the maxima peak at time=4. During the start of discharge, as the first few layers are oxidized, small pits are formed and they occur frequently on the surface. Figure 3-15 (c) corresponds to the microstructure at the minima of surface ratio at time=8. The surface is characterized by pores and deeper pits than before, however the frequency of the pits is smaller than (b). Figure (d) corresponds to the maximum in surface ratio at time=40. The pits are now deeper and wider. Figure (e) corresponds to the minima in surface ratio at time=80. The surface is not as deeply pitted as before, but there are many pores just below the interface. Figure (f) corresponds to the maxima in surface ratio at time=92. The network of pores has been reduced compared to the previous microstructure. The amount of electrolyte trapped has increased with the progression of discharge.

An important thing to note is that the pits during discharging do not get deeper and deeper with progression of discharge. The diffusion of ions is restricted in a pit and they act as passivating layer, preventing further oxidation. This facilitates the oxidation of the top layer of the interface. This process leads to a leveling effect during discharge and the height of the average surface decreases steadily. This is similar to the global or bulk dissolution of crystal in which overall height of the crystal is reduced along with the formation of pits ¹⁵⁶.

3.4 Charge and Discharge

It is important to note that the rate at which number of layers are dissolved is faster during discharging than the rate at which number of layers are deposited during charging. This effect is specially marked when probability of reaction (either oxidation or reduction) and probability of

ion diffusion is commensurate. During charging, the deposition is constrained by the arrival of ion at the interface, which is slow because of two factors, concentration of ions (about ten percent of lattice sites are occupied by ions and probability of diffusion of ions is less than one. During discharge, the only restriction on dissolution of the first layer is the assigned probability of oxidation. After that if the ions at the interface diffuse away, the next series of oxidations can occur. Therefore, the limit is on or two hops of the ions away from the interface for discharging while several hops are of ions towards the interface are required for charging process. This is consistent with the different time scales observed during charging and discharging¹⁶⁷.

For safe and efficient operation of battery, during charging uniform deposition is desirable and during discharging, minimum amount of dead metal would be preferable. For charging, this would imply restricting the battery operation to a limited range of P_{red} and P_e ($P_{red} << P_e$). For discharging, there are two regions in which fewer dead metal per oxidation reaction is formed as seen in Figure 3-11 (c). In one region, $P_{ox} << P_e$ and surface diffusion is very close to zero. In the other region, $P_{ox} >> P_e$ and surface diffusion is close to zero. The size of the second region is bigger than region one. In electrochemical systems like batteries, the probabilities can be adjusted by changing the overpotential during charging or discharging. Therefore, during charging, small overpotential and therefore small P_{red} is recommended. During discharging, high overpotential and thus high P_{ox} would be preferable because the associated region seen in Figure 3-11 (c) is larger. Arakawa *et al.*¹⁶⁹ observed improved performance of lithium metal anode when discharging at high current density. Yoon et al ¹⁵⁹ report that formation of dead lithium is facilitated if the lithium electrode is discharged at low current density using a continuum mechanics formulation.

Batteries also entail cycling of charge and discharge processes. In this study, at the start of charging and discharging, the interface was flat. In the scenario, that charging happens first and then discharging, if the morphology is mossy or dendritic deposition, more dead metal will be formed because there are many arrangements in which a cluster of atoms is connected to the substrate through a linchpin atom. If this particular linchpin atom is oxidized, the cluster of atoms are separated from electrode and are counted as dead metal. If discharge occurs first and then charge, if there is dead metal near the electrode, the mass transport of ions near the electrode will be reduced because the dead metal will act as obstacle to ion diffusion. Smaller ion diffusion would lead to dendritic deposition.

3.5 Conclusions

A wide range of microstructure during charging process, needles, whiskers, mossy, dendrite, non-uniform and uniform deposition depending upon the combination of probability of reduction, ion diffusion in electrolyte or surface diffusion on metallic surface. In contrast, during discharging, the microstructure is either porous for large surface diffusion, pitted or pitted with trapped electrolyte. During charging, the number of layers deposited, and the average height of the deposition can increase very sharply when P_{red} and P_e are similar in value. During discharging, the number of layers dissolved increases linearly with time.

The surface ratio of the interface between electrode and electrolyte has a crossover during charging. During the initial phase of charging, the surface ratio is less than one for the entire P_{red} - P_e space. However, for P_{red} <P_e, the surface ratio becomes greater than or equal to one with the progression of the charging process. In the rest of the P_{red} - P_e space, the surface ratio is less than one. For discharging, the surface ratio is about one when surface diffusion is not allowed, or greater than one for the entire P_{ox} - P_e range. The nature of the interface is either flat surface or convex surface depending upon P_{red} and P_e combination during charging while during discharging, the interface can be approximated as concave surface. The surface ratio evolve to a steady value during both charging and discharging and can be useful in updating the surface activity in reaction rates during continuum studies.

Surface diffusion is key in determining the morphology during charging. High surface diffusion and low reduction results in whiskers and comparable surface diffusion and reduction result in mossy deposition. During discharging, higher surface diffusion results in greater amount of dead metal.

4. METAL ANODE AND LIQUID ELECTROLYTE INTERFACE: MESOSCALE ANATOMY OF DEAD LITHIUM FORMATION

Relevant Publications and/or Working Papers

Deepti Tewari, Sobana P. Rangarajan, Perla B. Balbuena, Yevgen Barsukov and Partha P. Mukherjee. Mesoscale Anatomy of Dead Lithium Formation. Journal of Physical Chemistry C 2020, 124 (12), 6502–6511. <u>https://doi.org/10.1021/acs.jpcc.9b11563</u>.

<u>Comment:</u> The experimental work described in this chapter was performed by Sobana P. Rnagarajan.

Energy storage is a key enabler for electric mobility and renewable energy integration into the grid. Greater demands on energy density require moving beyond the lithium-ion batteries and especially focusing on lithium metal electrodes. Lithium is one of the lightest elements in the periodic table, with low redox potential (-3.04V vs SHE). The theoretical capacity of lithium metal anodes is 3860 mAh/g, with the promise to offer high energy density. However, during plating, lithium interface suffers from morphological instabilities and results in dendritic deposition ^{4,36,38}. The growth and formation of high aspect-ratio dendrites may penetrate through the separator and result in short circuit and catastrophic failure. Understanding and finding means to mitigate the formation of dendritic deposition of lithium has been a focus of intense research ^{28,82,83,147,161,171,172}. However, during discharging or stripping of lithium metal electrodes, small parts of lithium get detached from the electrode ^{40,159}. Since this lithium does not participate in further electrochemical reaction, it is called dead lithium. Dead lithium is the irreversible loss of lithium and lowers the Coulombic efficiency. The presence of dead lithium debris in the liquid electrolyte may also affect the mass transport characteristics. The problem of dead lithium is relatively unexplored because the failure and loss in performance is gradual ¹⁷³ and not catastrophic as in the case of dendritic deposition during plating.

Formation of dead or electrochemically inactive material during cycling of batteries causes irreversible loss of active material and results in lower Coulombic efficiency. Electrochemically inactive dead material during stripping has been observed for lithium ^{39,40,42,169,170} and sodium ¹⁷⁴ metal anodes. Earliest research on dead lithium by Yoshimatsu *et al.*⁴² observed that during stripping or electrochemical dissolution of lithium metal electrodes, the mossy deposits of lithium

were dissolved, while thin needle-like structures remained on top of electrode and the amount of dead lithium was cumulative with cycling. Arakawa *et al.* ¹⁶⁹ found that the amount of remanant dead lithium increased with decreasing discharge current, and the life cycle of the cell improved at higher discharge current rates. In these studies, the morphology of the electrode-electrolyte interface was critical in the formation of the dead lithium. Irregular and thin morphologies, such as whiskers and needles, dissolve at the roots during stripping and lead to dead lithium, which accumulate with cycling leading to lower Columbic efficiency and poor cycling performance.

Recent studies on dead lithium have sought to find the interconnection between interface morphology, transport and macroscopic battery response. Chen *et al.* ³⁹ observed that the voltage profile during stripping changed due to increased resistance to lithium ion transport because of gradual accumulation of dead lithium. Wood *et al.* ⁴⁰ observed that the electrode surface became pitted during stripping and dissolution of lithium from dendrites occurred first, followed by stripping of the bulk electrodes and the dead lithium appeared black in color. Gireaud *et al.* ⁴⁵ reported that at high discharge current density, the dissolution of lithium occurred preferentailly along the grain boundary while at low discharge current density, the electrode surface appears pitted in a pinhole like pattern .

In-stiu studies have been used to monitor the interfacial evolution and track how dead lithium is formed. Steiger *et al.* ⁴¹ and Kushima *et al.* ³⁴ performed *in-situ* microscopy during stripping and found that the whiskers growing from the root were more susceptible to detachment, because of faster lithium ion diffusion through the newly created solid electrolyte interphase (SEI). In some instances, although the lithium whisker is detached from the electrode, it is still connected to the electrode by the rigidity of the SEI structure. Several studies ^{43,175,176} have used X-Ray tomography to study the interface during stripping and observed dead lithium when porous interconnected microstructures was formed. Recently, Fang et al ¹⁷⁷ have developed a new technique to distinguish between unreacted metallic lithium (dead lithium) and the lithium ion in the solid electrolyte interphase (SEI). Aryanfar *et al.* ¹⁵⁸ quantified the amount of dead lithium formed by analyzing the digital image and found that for the same amount of charge through the battery, the amount of dead lithium decreased with decreasing time period of the cycle.

Computational methods has also been used to investigate the formation of dead lithium. Yoon *et al.* ¹⁵⁹ reported that lower discharge rates yield more dead lithium compared to high rate of discharge based on a continuum mechanics model, which is in agreement with cycling results reported by Yoshimatsu *et al.*⁴². Tewari *et al.*⁷⁹ conducted a probability based mechanistic study of stripping and observed that the amount of dead metal formed during discharge of a metal anode is largest when the magnitude of the probability of oxidation reaction, diffusion of ion in the electrolyte and the solid surface diffusion are of the same order.

Understanding the mechanisms of lithium stripping or electrochemical dissolution is critical, with analogous interplays prevalent in other systems. For example, dissolution and the resulting structure has been investigated for porous rocks due to mineral dissolution ^{150,151,162}, dissolution of crystals ^{152,153,165}, and etching of silicon surfaces ^{154,155}. The reaction kinetics vary spatially due to difference in local environment, scuh as in the presence of point defects or dislocations or differences in the coordination number as the interface is evolving ^{164,165}. The stepwave model proposed by Lusge and Luttka ¹⁵⁶ postulates stepwaves emanating from local etch pits and the global dissolution (decrease in height with respect to reference height). Using stochastic method, such as monte carlo and kinetic monte carlo approach, is useful for studying dissolution and the evolution of the interface. However, many of these studies ^{124,149,150,155} use the solid-on-solid model and can not capture the fragment detachment from the rest of the solid.

In this research work, we limit our focus to stripping of lithium electrodes and evaluating the amount of dead lithium with changing operating conditions (temperature and overpotential). We use mesoscale computational model and experiments to study the evolution of electrode-electrolyte interface and relate the interface evolution to the amount of dead lithium formed during stripping.

4.1 Methods

Since dead lithium or isolation of lithium from the electrode occurs only during dissolution ^{34,40,41,159}, we limit our study to discharge or stripping only. The dead lithium is formed because of dissolution of a part of electrode which is narrow at the base. This precondition for dead lithium formation can be due to (i) stripping of electrodes with dendritic morphology (ii) stripping of pristine interface where morphology of the interface evolves to thin narrow structures. In case (i), the cycling history of the electrode cannot be decoupled from the processes occurring during the stripping. While there are several studies linking the electrodeposition morphology and operating conditions during charging ^{78,82,178}, there is dearth of studies focusing on discharging morphology and dead lithium formation. Also, stripping of pristine electrode, gives a common basis for

comparing experimental and computational results. In this study, we decouple the effect of history on the formation of dead lithium and focus on the stripping of pristine electrodes and the effects of operating conditions on the amount of dead lithium. The mesoscale model and experiments corroborate the trends in dead lithium formation with operating conditions and fill in the gap about the mechanistic origin of electrode evolution during stripping. The mesoscale computational model and experimental details is provided below.

4.1.1 Computational Method

The physical mechanisms responsible for the formation of dead lithium, and considered in the mesoscale model, are elucidated schematically in Figure 4-1 (a). Three processes are included in the model, the diffusion of lithium ions in electrolyte, surface diffusion of lithium on the interface and oxidation of lithium at the interface. If a narrow region connecting a part of lithium and rest of the electrode is oxidized, this small part of lithium is disconnected from the rest of the electrode and is called dead lithium. Lattice Kinetic Monte Carlo (KMC) model is used to study the stripping of lithium electrode. The current density for the oxidation reaction (Li \rightarrow Li⁺ + e⁻) is described by Butler-Volmer relation ¹⁷⁹

$$j = j_0 \left\{ \exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(-\frac{\alpha_c F \eta}{RT}\right) \right\}$$
(1)

Where j is the current density, j_0 is the exchange current density, α_a and α_c are charge transfer coefficients, F is the Faraday's constant, η is the overpotential, R is the universal gas constant and T is the temperature.

The prescribed rate of oxidation at the lithium electrode-electrolyte interface is given by ⁷⁸

$$k_o = \frac{ja^2}{\rho} \tag{2}$$

Where k_0 is the rate of oxidation, a is the lattice constant of lithium and e is the electronic charge. However, the oxidation rate at a particular lattice site, A, on the interface will depend upon the local environment of A. If the nearest neighbor sites of A, are occupied, then oxidation rate of A will be zero, otherwise, it would be k_0 . The oxidation rate at the dead lithium interface is set to zero because it is disconnected from the electrode.

The rate of diffusion of lithium ion in electrolyte is described as

$$k_e = \upsilon \exp\left(\frac{-\Delta E_e}{K_b T}\right)$$
(3)

Where ΔE_e is the activation barrier for ionic diffusion, K_b is the Boltzman constant and T is the temperature. The activation energy is calculated using the approach described by Urban *et al.* ⁶⁹ and using the diffusion coefficients reported by molecular dynamics studies ^{139,180–182}. The concentration of lithium ions at the interface depends on rate of oxidation and rate of ionic diffusion. Example, if the oxidation rate is very high but ionic diffusion is slow, lithium ions would accumulate at the interface. In the opposite scenario, if the oxidation rate is slow, but the ionic diffusion is fast, the concentration of ions at the interface is low. At high applied overpotential, lithium ions accumulate on the interface, forming a passivating layer. No further oxidation takes place and cell shuts down.

The rate for self-diffusion of lithium atom on the solid electrode-electrolyte interface, ks is

$$k_{s} = \upsilon \exp\left(\frac{-\Delta E_{s}}{K_{b}T}\right)$$
(4)

Where ΔE_s is the activation barrier for surface diffusion ¹⁸³. Since lithium atom is diffusing on lithium surface, it is also referred to as self-diffusion. In the two dimensional KMC model, the lattice grid is $(N_x \times N_y)$ is (150×100) where N_x is the number of lattice points in the horizontal direction and N_y is the number of lattice points in the y direction. Periodic boundary condition is applied in the horizontal direction. In the vertical direction, at the bottom, the first layer is static, i.e., no diffusion or oxidation of the first layer. The top boundary in the vertical direction does not allow ions to diffuse outside the computational domain. Initially, 50 layers ($0 \le N_y \le 50$) is designated as lithium layers and the rest as electrolyte ($51 \le N_y \le 100$). Ten percent of the electrolyte sites are occupied by lithium ions. During oxidation, lithium ions are injected in to the electrolyte solution as stripping progresses at the interface. To maintain the same fraction of occupancy sites of lithium ion during the entire simulation, an ion farthest from the interface is removed. The effect of electromigration on diffusion of lithium ions is not considered. The values of the parameters used in kinetic rate equations are listed in Table C.1 in Appendix C. Surface ratio ⁷⁹ has been used to characterize the interface between lithium electrode and electrolyte.

If the value of surface ratio is less than one, then the interface is convex, if it is equal to one, the interface flat and if it is greater than one, the interface is concave. A schematic description of how to calculate surface ratio is given in the Appendix C.



Figure 4-1 Schematic representation of the method used to study lithium metal electrode stripping and dead lithium formation. (a) Mesoscale computational model. Physical processes considered in the mesoscale KMC model include diffusion of lithium ion in the electrolyte, surface diffusion of lithium atom on solid lithium, and oxidation reaction of lithium at the interface. (b) Experimental method workflow. (i) Electrochemical signature of voltage and current during lithium metal electrode stripping from Li-Li symmetric coin cell experiments; (ii) Original image of the electrode after stripping acquired from the optical microscope embedded in the glovebox; (iii) Dead lithium area fraction calculation from binarized image and (iv) Surface morphology or topography reconstruction based on pixel luminance.

4.1.2 Experimental method

Symmetric, Li/Li coin cells were constructed with pure lithium foil (14 mm diameter and 0.75mm thick) as working electrode and counter electrode in an argon-filled glove box. 1M Lithium hexafluorophosphate (LiPF₆ in 1:1 of EC: EMC) was used as the electrolyte in the cells. The electrochemical measurements were made at room temperature (20°C), low temperature (-20°C) and high temperature (40 °C) in a Maccor temperature chamber. Identical cells were assembled and discharged for three hours at 1 mA/cm² and 2 mA/cm² and at different temperatures (-20°C, 20°C and 40°C). In order to isolate the effect of stripping on dead lithium formation, the cells were subjected to a single discharge at a particular value of current density. The discharge profile of the cell at 2 mA/cm² at 20°C is shown in Figure 4-1b (i).

The stripped lithium metal electrodes were extracted after disassembling the cells in the glovebox. High resolution images of the stripped lithium electrode after galvanostatic discharge were captured using the Leica S90 microscope embedded in the glovebox as shown in Figure 4-1(b) (ii). Given the 2D nature of the images, the area fraction of the dead lithium relative to the total electrode area is used to estimate the amount of dead lithium formed. It has been reported in previous studies ^{40,42,158,169} that the dead lithium particles appear black compared to gray lithium electrode. An array of image analysis techniques was used for quantifying dead lithium and characterize the electrode surface. The dead lithium particles are limited to a specific range of pixel values. Therefore, the electrode image is thresholded and binarized based on the pixel color values to demarcate the dead lithium particles in the electrode.

The binarized image has a number of dead lithium clusters as shown schematically in Figure 4-1(b) (iii). The percentage of dead lithium area fraction was calculated using the following equation.

% Dead lithium Area Fraction =
$$\sum_{i=1}^{n} \frac{A_m}{A_{electrod}} * 100$$

Where A_m denotes the area of dead lithium cluster and $A_{electrode}$ denotes the total electrode area and '*n*' denotes the number of dead lithium particle clusters.

The morphology of the electrode surface was reconstructed using a luminescence based surface plot. The surface of the electrode reflects light based on its topography. The sharp peaks on the surface reflect specular light, while the smoother peaks reflect diffuse light. The light gets diffracted at edges of pits and hence the pits are less luminescent than the average surface. A section of the electrode, 200 x 200 pixels was used to create the surface plot with the pixel color values based on the luminescence of the image, as demonstrated later in the Results and Discussion section. Figure 4-1(iv) representatively shows the surface topography of the electrode. Details about image analysis is given in Appendix C.

4.2 **Results and Discussion**

4.2.1 Effect of overpotential and temperature on dead lithium

We explore the effect of temperature and current density/overpotential on the amount of dead lithium formed during stripping using both experiments and computational simulations. In Figure 4-2(a), the experimental results show that the amount of dead lithium increases almost linearly with increasing temperature. More dead lithium is observed at 1mA/cm² compared to $2mA/cm^2$. In Figure 4-2(b), the amount of dead lithium increases with increasing temperature and decreasing overpotential. The trends in the amount of dead lithium is same using experiment and computational method. Increasing the temperature yields more dead lithium. Increase in current density or overpotential decreases the amount of dead lithium formed during stripping. The concentration of lithium ions at the interface is higher during stripping ¹⁸⁴. The concentration of lithium ions at the interface depends upon both the rate of oxidation as well as how quickly the newly created ions diffuse away from the interface. If the applied overpotential is high, the concentration of lithium ions at the interface is larger, which slows down the further oxidation at the interface, leading to low dead lithium. If the temperature is high, the mobility of lithium ions away from the interface is higher and the next layer of lithium atoms at the interface can then be oxidized. Another effect of temperature is the heightened self-diffusion of lithium atoms at the interface, which might lead to narrow structures whose dissolution yield dead lithium.

To gain a deeper insight into the dependence of overpotential and temperature on the relative magnitude of dead lithium formation, a series of mesoscale (KMC) simulations over the overpotential range of (0.01V to 0.125V) and temperature range of (-25 °C to 50 °C) using three different values of ionic diffusion barrier (0.1 eV, 0.15 eV and 0.2 eV, respectively) are performed. In Figure 4-3(a), the number of dissolved layers increase with increase in temperature or overpotential. Since the ionic diffusion barrier is low, the lithium ions at the interface move away

into the bulk electrolyte easily and the next layer of lithium atoms at the interface can be oxidized. Increase in temperature aids in this process. In this scenario, the stripping is limited by reaction kinetics. In Figure 4-3(b), the number of dissolved layers is insensitive to the applied overpotential and increases with temperature. Since the ionic diffusion barrier is higher compared to (a), more lithium ions are accumulated at the interface and increase in temperature facilitates in ionic transport away from the interface. If the ionic diffusion barrier is high, dissolution trends seen in Figure 4-3(c) are opposite to Figure 4-3(a) in terms of overpotential. In this scenario, the stripping is limited by diffusion kinetics. The accumulation of lithium ions at the electrode interface acts as a passivating layer and constrains further oxidation 79 . Figure 4-3(a) – 4-3(c) show that increase in temperature leads to more layers of dissolution, while the effect of overpotential is coupled with the ionic diffusion barrier of the system.

More dead lithium is formed if the ionic diffusion barrier is low as seen in Figure 4-3(d) in comparison to Figure 4-3(f) where the ionic diffusion barrier is high. The contour lines of amount of dead lithium show parabolic trend for (d) to (f) for applied overpotential. At low overpotential, very few oxidation reactions occur and the amount of dead lithium formed is very small. At high overpotential, the accumulation of lithium ions at the interface becomes a limiting factor. Yoshimatsu *et al.* ⁴² and Arakawa *et al.* ¹⁶⁹ observed that the amount of dead lithium increased with decreasing discharge current. With the increase in ionic diffusion barrier, the parabola becomes sharper and offsets towards the lower overpotential values. All three contour plots show that increase in temperature yields more dead lithium.

The number of oxidation reactions or the amount of dead lithium in isolation is not a meaningful descriptor by itself. The ratio of dead lithium to the number of oxidation reactions conveys the irreversible loss of lithium. It is preferable to have this ratio as small as possible. The value of this ratio is highest when the ionic diffusion barrier is lowest as seen in Figure 4-3(g). Figure 4-3(g) - (i) show similar trends in the ratio of dead lithium to oxidation reactions with respect to overpotential and temperature. This ratio is high in a conical region corresponding to low overpotential and high temperature shown by dashed lines in the figure. The effect of temperature is straightforward, increase in temperature results in more dead lithium. The correlation between dead lithium and overpotential is more complex. It depends upon the operating range and ionic diffusion barrier.

The length and time scales in experimental and computational study are very different, so numerical correspondence in the amount of dead lithium is not possible. However, functional dependence of dead lithium on temperature and overpotential (current density) is similar using both methods. It is important to note the mechanistic underpinnings (reaction kinetics vs ionic diffusion limitation) of dead lithium formation from the mesoscale modeling and corroboration thereof with the experimental data, which is an important highlight of this study.

4.2.2 Evolution of the lithium metal electrode interface during stripping

The extent of dissolution and formation of dead lithium depends upon the morphology of the interface. It has been experimentally observed that dead lithium is formed when the morphology of the lithium interface is narrow at the root ^{34,41}. When lithium is dissolved at the root, the lithium at the top is disconnected. The evolution of electrode interface is characterized by means of luminescence mapping of electrode surface obtained after the stripping experiment, and in terms of the average surface ratio obtained from the mesoscale modeling.

Figure 4-4(a)-(f) shows the topographical map of the stripped electrode from the experiment, at different current densities and temperatures. Figure 4-4(g) shows the color bar for height of the interface. Peaks are depicted in warm colors (red) and pits in cool colors (blue). The average surface is depicted in white. Pits are a prominent feature at the electrode during stripping and can be observed at both high and low current densities. It is however more interesting to note the presence of peaks at low current density and high temperature seen in Figure 4-4(c). The presence of peaks is significant to our study as their dissolution leads to formation of dead lithium.

Figure 4-5 shows the contour plot of average surface ratio of the interface in (a), (b) and (c) for ionic diffusion barrier of 0.1 eV, 0.15 eV and 0.2 eV respectively. If average surface ratio is less than one, it implies that the average surface is convex, if it is equal to one, the surface is flat and if it is greater than one, the average surface is concave. Details about surface ratio is provided in the Appendix C. The contour for three ionic diffusion barriers show a common trend. The average surface ratio is close to one at high overpotential and low temperature, indicating that overall, the interface is flat or pitted during stripping. This is consistent with pitting observed during stripping 39,40,45 . Porous or interconnected ligament features at the electrode give higher value of surface ratio, as seen in Figure 4-5(a)-(c) at lower overpotential and higher temperature.



Figure 4-2 (a) Percentage of dead lithium area fraction determined from experiments as a function of temperature and current density from Li/Li symmetric cells; (b) Effect of temperature on the number of layers of dead lithium at different overpotential and operating temperatures from the mesoscale computational model. Ionic diffusion barrier of 0.15eV and surface diffusion barrier of 0.14 eV are used. The amount of dead lithium increases with increasing temperature and with decreasing current density or overpotential.



Figure 4-3 Characterizing dead lithium with variation in applied overpotential and operating temperature. (a), (b) and (c) show contours of the number of dissolved layers. (d), (e) and (f) show the number of layers of dead lithium formed. (g), (h) and (i) show the contour of ratio of number of layers of dead lithium and number of dissolved layers. The ionic diffusion barrier for (a), (d) and (g) is 0.1 eV, (b), (e) and (h) is 0.15 eV and (c), (f) and (i) is 0.2 eV. The surface diffusion barrier is 0.14 eV. Smaller values of dead lithium per oxidation reaction is obtained at higher overpotential and lower temperature for all the three values of ionic diffusion barriers.

The topography maps of electrodes from experiment show the top view of the electrode. The morphology pictures seen in Figure 4-5(i) to (ix) show the cross section of the electrode/electrolyte interface from computational simulations. Microstructure 5(i), (iv) and (vii) show the interface at similar operating conditions but different ionic diffusion barrier. The interface is characterized by thin and narrow interconnected structures. Figure 4-5(ii), (v) and (viii) lack the thin and narrow structures, rather the interface is highly pitted with some porosity. Figure 4-5(ii), (v) and (viii) show similar interfacial features, however they show different extent of dissolution. Figure 4-5(iii), (vi) and (ix) show nearly flat or slightly pitted interface at high overpotential and low temperature. There is more dissolution in Figure 4-5(iii) at lower ionic diffusion barrier.

The morphology of the interface is the missing link between operating conditions and the amount of dead lithium formed. Examination of the interface using both experiments and computational model reveal that the interface has peaks or thin interconnected structures at lower overpotential and higher temperature. When the roots of these structures is dissolved, they disconnect from the electrode and dead lithium is formed. Yoshimatsu *et al.* ⁴² and Kushima *et al.* ³⁴ observed that the dead lithium is formed due to dissolution of the root of the thin structures like whiskers or needles. It should be noted that the interface does not become unstable during stripping, unlike the morphology of the interface during plating. This is in agreement with the linear stability analysis of the interface during discharging by Aogaki *et al.* ¹⁸⁵



Figure 4-4 Luminance based surface topography plot of the stripped lithium electrode (top view): at current density 1 mA/cm2 at (a) -20o C, (b) 20o C, (c) 40o C, and at current density 2 mA/cm2 at (d) -20o C, (e) 20o C, (f) 40o C. (g) The average surface is depicted in white, peaks are shown in warmer colors (green to red) and pits are shown in cooler colors (blue to violet). Each image shows 530×530 µm (200×200 pixels) representative region of the stripped electrode. An increase in temperature results in needle-like protrusions in the surface, leading to higher dead lithium formation. Fewer peaks are formed at higher current density and the interface is mostly pitted.

Ionic diffusion barrier = 0.1 eV

Ionic diffusion barrier = 0.15 eV

Ionic diffusion barrier = 0.2 eV



Figure 4-5 Average surface ratio with changing overpotential and temperature for different ionic diffusion barriers. (a) Contour of average surface ratio for ionic diffusion barrier = 0.1 eV; (b) Contour of average surface ratio for ionic diffusion barrier = 0.15 eV; (c) Contour of average surface ratio for ionic diffusion barrier = 0.2 eV. (i), (ii) and (iii) show microstructure corresponding to three white dots shown on contour plot (a). (iv), (v) and (vi) show microstructure corresponding to three white dots shown on contour plot (b). (vii), (viii) and (ix) show microstructure corresponding to three white dots shown on contour plot (c). (i) to (ix) show the cross-section of the electrode-electrolyte interface. The surface diffusion barrier is 0.14 eV for all simulations. At higher overpotential and lower temperatures, the interface is mostly pitted. Thin, interconnected structures are formed at the interface at lower overpotential and higher temperatures, leading to formation of more dead lithium.

4.2.3 Effect of ionic diffusion barrier and surface diffusion barrier on the formation of dead lithium

The amount of dead lithium depends on the ionic diffusion barrier as seen in Figure 4-3. The self-diffusion of lithium atoms at the solid lithium interface influences the evolution of morphology of the interface, hence, the amount of dead lithium. To evaluate the relative importance of these two diffusive processes, computational simulations were performed for two cases, (1) high temperature and low overpotential (0.05 V, 50 °C), (2) low temperature and high overpotential (0.125V, -25 °C). These operating conditions were chosen for contrast, case 1 yields largest amount of dead lithium while case 2 the smallest amount. For these two cases, the ionic and self-diffusion barrier is varied and the results are shown in Figure 4-6. For case 1, the number of dissolved layers increases with smaller ionic and self-diffusion barrier as seen in Figure 4-6(a). The amount of dead lithium and the ratio of dead lithium to number of oxidation reactions also increase if the ionic and self-diffusion barrier is decreased as seen in Figure 4-6(b) and 6(c). Both the diffusion mechanisms are operative at these conditions. For case (2), the number of dissolved layers depends mostly on the ionic diffusion barrier as seen in Figure 4-6(d). Figure 4-6(e) shown the amount of dead lithium is higher at smaller values of ionic and self-diffusion barrier. Although the magnitude of dead lithium for case 2 is smaller than case 1, the contour lines are similar for the two cases.

Figure 4-6(f) plots the contour of ratio of dead lithium per oxidation reaction. Numerically, case 2 shows smaller values compared to case 1, but decreasing the ionic and self-diffusion barrier results in higher value of this ratio for both case 1 and 2. To conclude, both ionic and self-diffusion processes are significant in determining the irreversible loss of dead lithium per oxidation reaction. However, the slope of the contour lines in Figure 4-6(c) and (f) is greater than 135 degrees with respect to ionic diffusion barrier axis, indicating that the formation of dead lithium is more sensitive to surface diffusion than ionic diffusion.



Figure 4-6 Dead lithium with changing ionic and surface diffusion barriers. (a) Number of dissolved layers (b) number of layers of dead lithium (c) ratio of number of dead lithium and number of dissolved layers (d) number of dissolved layers (e) number of layers of dead lithium (f) ratio of number of dead lithium and number of dissolved layers. (a), (b), (c) use overpotential of 0.05 V and temperature of 50 oC while (d), (e) and (f) use overpotential of 0.125 V and temperature of -25 oC. Smaller activation barriers for ionic and surface diffusive processes result in greater amounts of dead lithium.

4.3 Conclusion

The presence of dead lithium may not cause instant failure or safety concerns as in the case of lithium dendritic growth for lithium metal batteries. However, the accumulation of dead lithium with cycling causes irreversible loss of active material, leading to lower Coulombic efficiency. Also, the presence of dead lithium near the electrode/electrolyte interface introduces additional resistance to the mass transport characteristics of the electrolyte. This would indirectly affect the deposition characteristics during charging and ionic diffusion limitations which would lead to dendritic deposition. Therefore, it is important to understand the fundamental mechanisms that underlie formation of dead lithium, the morphological evolution of the interface, and quantification of the amount of dead lithium with respect to the operating conditions (overpotential or current density and temperature). In this study, we present the mesoscale underpinnings of dead lithium formation via a synergistic computational and experimental approach.

The evolution of the interface morphology during stripping directly impacts the amount of dead lithium formed. When the interfacial morphology consists of thinly connected ligaments or peaked structures above the height of the average interface, greater amount of dead lithium is formed. On the other hand, when the interfacial morphology is nearly flat or pitted, smaller amount of dead lithium is formed. The optical imaging of the lithium metal electrode inside the glovebox after electrochemical stripping experiment and the mesoscale computational model both reveal this connection between interfacial morphological feature and the amount of dead lithium.

The mesoscale computational model is used to study the physical mechanism affecting the formation of dead lithium. The ionic diffusion of lithium in electrolyte, the self-diffusion of lithium at the solid interface and the lithium oxidation electrochemical reaction at the interface is considered. More dead lithium is formed at higher temperature and lower overpotential. Changing the overpotential modifies the rate of oxidation reactions, while changing the temperature modifies the diffusion kinetics of ions in the electrolyte and lithium self-diffusion at the solid interface. So, the diffusive processes play a key role in the amount of dead lithium formed near the interface. Further studies reveal that between the two diffusive processes, the self-diffusion of lithium at the solid interface is more significant than ionic diffusion towards formation of dead lithium.

Our study provides a link between the physical mechanisms (ionic and self-diffusion and oxidation reaction) active near the interface and evolution of morphology of the interface and the amount of dead lithium formed. To minimize the amount of dead lithium, the stripping or

discharging of the electrode should occur at low temperature and higher overpotential or higher current density. This is in stark opposition to the recommended operating conditions of high temperature and low current density during plating or charging of the battery to reduce the likelihood of dendritic deposition at the lithium metal anode.
5. SOLID STATE ELECTROLYTE AND METAL INTERFACE: A MESOSCALE STUDY OF DEPOSITION AT THE SOLID STATE ELECTROLYTE/METAL BURIED INTERFACE

Relevant Publications and/or Working Papers

1. Deepti Tewari and Partha P. Mukherjee. A Mesoscale Study of Deposition at the Solid State Electrolyte/Metal Buried Interface.

Higher demand for energy and power density from rechargeable batteries has made use of lithium as a metal anode an attractive option ^{186,187}. Lithium has high energy density of 3860 mAhg⁻¹ and lowest redox potential of -3.04V vs SHE. However, lithium metal batteries with liquid electrolytes face a range of issues, consumption of lithium in parasitic side reactions in formation of Solid Electrolyte Interphase (SEI), deposition in the form of dendrites which can lead to internal short circuit, dead lithium which are remnants of active lithium detached from the anode and thermal safety issues related to volatility and flammability of liquid electrolytes ^{4,6,36,79,80,188,189}.

Monroe and Newman ^{147,184} proposed that solid state electrolyte (SSE) and lithium interface is stable if the shear modulus of the SSE is greater than two times the shear modulus of lithium metal. The rigidity of the SSE offers a barrier to the propagation of dendrites. The key properties required for working SSE is ionic conductivity, chemical and electrochemical stability, mechanical properties like high elastic modulus and fracture toughness and stability over a wide range of temperature ^{30,48,53,190}. There are different kind of SSE, inorganic SSE, polymer SSE, composite and gel SSE and thin film SSE like LIPON. The ionic conductivity of SSE in general in smaller than liquid electrolyte at room temperature ³⁰. However, there has been impetus to understand the mechanism for ionic transport in SSE and develop SSE with ionic transport comparable to liquid electrolyte at room temperature ^{191–194}.

The SSE/lithium interface is characterized by high impedance particularly for inorganic SSE due to lack of conformal interface. Polymer SSE offer better contact at the interface but have lower ionic conductivity compared to ceramic SSE as well as smaller elastic modulus ^{30,195}. The poor contact at interface affects rate capability and cyclic performance.

Recently, all solid state batteries (ASSB) using LLZO as SSE were reported to fail due to short by lithium propagation through SSE. Since the shear modulus of LLZE ^{196,197} is more than

ten times greater than lithium ¹⁹⁸, several theories have been proposed to explain the presence of dendrite inside the LLZO. Yue *et al* ¹⁹⁹ and Song *et al* ²⁰⁰ concluded that the electronic conductivity at the grain boundaries of polycrystalline LLZO was sufficient to reduce the lithium ions to metallic lithium. Other research work has focused on the Griffith like crack in the ceramic LLZO and propagation of lithium through these cracks leading to failure ²⁰¹. Co-sintering of cathode and SSE particles is the preferred method to manufacture ASSB. This ensures good interfacial contact between cathode and SSE ¹⁹⁵. However, the volumetric changes with insertion and de-insertion of lithium in cathode is a source of stress for the composite SSE and cathode structure. With cycling, flaws or defects in ceramic SSE would enlarge resulting in crack growth. Yan et al ²⁰² have characterized the critical crack distribution, growth and length in LLZO.

The chemical and electrochemical stability of lithium and SSE interface plays significant role in whether short through lithium propagation would occur. He *et al* ¹⁹⁵ characterized the interface in three categories, SSE and Li interface is thermodynamically stable and reaction interphase is absent at the interface, SSE and Li reaction interphase is electronically and ionically conducting (example LATP, LAGP) and SSE and Li reaction interphase is ionically conductor but electronic insulator (example, cubic LLZO forms a thin layer of tetragonal LLZO with lower ionic conductivity compared to the cubic crystal at the interface). The third kind of interface would require larger operating voltages to drive the current. One effect of larger operating voltage is the increase of electronic conductivity at the grain boundaries of SSE which may result in lithium deposition at the grain boundary.

The coupled electro-chemo-mechanical picture of SSE/Li interface is incredibly complex. Recently, in-situ observation techniques has been used to study the lithium deposition at the SSE/Li interface ²⁰³. Porz *et al* ²⁰⁴ used in-situ optical microscopy and observed lithium penetration at existing flaws above a certain current density in garnet LLZO and other SSE. He *et al* ²⁰⁵ used in-situ ETEM to observe formation and growth of a whisker under stress. The initial deposition was a single crystal Li with no preferential growth direction and subsequent morphology was dependent upon lithium transport at the surface ²⁰⁵. Li et al ²⁰⁶ used neutron depth profiling to see generation of cracks after initial lithium deposition. Stress generated during plating exacerbated the damage and aided in dendrite propagation ²⁰⁶.

The most notable theoretical analysis of the coupled electrochemical and mechanical SSE/Li interface is by Newman and Monroe concluding that the roughness at the interface is

dampened if the shear modulus of SSE is twice of that of lithium. Ahmad *et al* ²⁰⁷ proposed that interfacial stability depends on shear modulus, Poisson's ratio as well as molar volume ratio. They also extended the model to include the anisotropic effects at solid-solid interfaces ²⁰⁸. Barai *et al* ²⁰⁹ used relaxed SSE/Li interface instead of rough interface by Monroe and found that the effect of current distribution was important in determining mechanical forces to prevent dendrite growth. Recently, Li *et al* ²¹⁰ have developed an electrochemical/mechanical coupling in space charge layer to explain dendrites in ceramic SSE. Bucci *et al* ¹⁹⁰ have used a continuum model to study electrodeposition of lithium at ceramic SSE/Li interface in presence of defects. The model studied the concentration of current in the presence of cracks in the SSE during lithium deposition.

The SSE/Li is a heterointerface and it is essential to understand how cyclic deposition and dissolution would change the interface. A conformal SSE/Li interface is preferred for low interfacial resistance in battery operation and avoiding current concentration at points of contact. The aim of this research work is to study the deposition at the heterointerface of SSE and metal using stochastic Kinetic Monte Carlo method (KMC) incorporating the effect of mechanical interaction between SSE/metal interface. If the strength of interaction between SSE and metal is very small compared to interaction between metal, a rough interface is observed with the progression of deposition. A flat interface is possible for strong interaction between SSE and metal.

5.1 Computational Model

The interface between SSE and lithium is a heterointerface (between two dissimilar materials). Since the lattice size of two materials are different, three different kinds of interfaces can occur based on the value of misfit between two lattices, coherent, semi-coherent or incoherent interface ²¹¹. Misfit is defined as ²¹²

$$Misfit = \frac{2(a_1 - a_2)}{a_1 + a_2}$$
(1)

An interface is coherent if the misfit is less than 0.1. A coherent interface has correspondence or continuity of atomic planes across two materials. A semi-coherent interface results if misfit is between 0.1 and 0.2. The discrepancy in the lattice size is accommodated by periodic array of dislocations called misfit dislocations in a semi-coherent interface. If the misfit is greater than 0.2, an incoherent interface is formed where there is no correspondence between

atoms and planes of two materials ²¹². Incoherent interfaces have high energy and low work of separation because of weak interaction between the atoms across the interface ²¹².

Crystalline SSE have coordinated polyhedra which provide the framework for diffusion pathways for mobile ions ²¹³. Figure 5-1 shows the misfit for different kinds of crystalline lithium SSE with respect to lithium. The lattice constant of lithium is 3.5Å ²¹⁴ and shear modulus of 3.83GPa ¹⁹⁸. The lattice constants of different lithium SSE shown in Figure 5-1 as well as shear modulus is provided in Table 5-1. It can be seen in Figure 5-1 that misfit is greater than 0.2 for most of the lithium SSE and lithium and the interface formed between SSE and lithium will be incoherent.

Kinetic Monte Carlo (KMC) has been used in studying the morphology evolution during charging of batteries ^{78,82}, epitaxial thin film deposition ²¹⁵ and heteroepitaxial growth ^{105,216,217}. In this work, a KMC model is developed which incorporates the mechanistic interactions at the interface. This is 2-dimensional deposition model at a general SSE and metal interface. Figure 5-2(a) shows the schematic of the energy description of the system. Since the elastic modulus of the SSE ^{218–226} is large compared to the lithium metal (except for LGPS which is glassy inorganic SSE ^{227,228}), the SSE in our model is treated as rigid, while atomic position of the metal may vary to minimize energy of the system. Since the interface between lithium SSE and lithium is incoherent, there is no pattern or periodicity to the interface, so in our model, the solid electrolyte and metal interface is assumed to be isotropic.

Although this research work is motivated by lithium and lithium SSE, this coupled mechanics and deposition model can also be applied to sodium batteries ^{54,229–233}. The misfit between sodium ²³⁴ and sodium SSE ^{54,235–239} is greater than 0.2 except for antiperovskite Na₃OBr. The elastic modulus of ceramic sodium SSE ¹⁹⁶ is several times larger than elastic modulus of sodium ²⁴⁰.

The interaction between SSE and metal atoms is described by harmonic potential characterized by stiffness k_0 and equilibrium distance a_0 as shown in Figure 5-2(a). The interaction between metal atoms is given by harmonic potential with stiffness constant k and equilibrium distance a. If k_0 is small compared to k, there is weak interaction between the SSE and metal surface at the interface. Conversely, if k_0 is large compared to k, there is strong interaction at the interface. After a certain number of layers in the vertical direction from the interface (shown as faded blue in Figure 5-2(a)), it is assumed that there is no relative displacement between the atoms

and bulk response is obtained. As the deposition occurs at the interface, the bulk metal is displaced upwards. However, since relative displacement between atoms in the bulk is zero, there is no contribution to energy of the system. The energy of the system is given by

$$E(r) = \sum_{i=1}^{N_{atoms}} \sum_{j>i}^{N_{atoms}} \frac{1}{2} k(r_{ij} - a)^2 + \sum_{i=1}^{N_{int\,erface}} \frac{1}{2} k_0 (r_{is} - a_0)^2$$
(2)
where, $r = \begin{cases} x_1 & x_2 & x_3 \\ y_1 & y_2 & y_3 \end{cases}$...}

Where r is the set of x and y position of all metal atoms, r_{ij} is the distance between ith and jth metal atoms. The first term on right hand side of equation 2 is the contribution of the metal atoms due to deviation from equilibrium distance a and the second term is due to interaction between metal atom and SSE interface. In this energetic description, there are two ratios which describe the system

stiffness ratio =
$$\frac{k_0}{k}$$
 and equilibrium distance ratio = $\frac{a_0}{a}$ (3)

Figure 5-2(b) and (c) describe the deposition at the interface where the rate of deposition is dependent upon the energy of the system. Figure 5-2(b) show the SSE/metal interface at an instance, the gray atoms at the interface interact with the SSE. The energy of the total system is E_{old} . When an atom is deposited at the interface as shown in Figure 5-2(c), the position of all the atoms in the computational domain is relaxed to obtain the minimum energy of the system E_{new} . The rate of deposition at the particular interface site is given by equation 4.

$$k_{deposition} = p_{deposition} \left(\frac{-(E_{new} - E_{old})}{E_{old}} \right)$$
(4)

Since deposition is the only process being considered, $p_{deposition}$ is 1. The rate of deposition depends on evolution of energy of the system, the energy and kinetics of deposition are coupled in this model.

In the two dimensional KMC model, eleven layers from the SSE interface is included in the computational model. Periodic boundary condition is imposed in the horizontal direction. The number of lattice points in the x directions, N_x , is 150. The details of the KMC algorithm and the computational domain size is provided in the Appendix D.



Figure 5-1 Misfit between Li and Li solid electrolyte.

Table 5-1 Details of cr	stal structures o	of lithium solid	l electrolytes	featured in Figur	e 5-1
			_	0	

Solid Electrolyte	Lattice Constant a (Å)	Lattice Constant b (Å)	Lattice Constant c (Å)	Crystal Structure	Space Group	Shear Modulus (GPa)
Antiperovskite Li3OCl	3.91	3.91	3.91	Cubic	Pm3m ²⁴¹	41.5 ¹⁹⁶
Perovskite Lio.3Lao.57TiO3	7.73	7.73	7.74	Orthorhombic	Cmmm ²⁴²	104 ¹⁹⁶
NASICON like LiTi2(PO4)3	8.51	8.51	20.85	Rhombohedral	R-3c ¹⁹¹	57.6 ¹⁹⁶
LISICON like Li10GeP2S12	8.69	8.69	12.6	Tetragonal	P4 ₂ /nmc ²⁴³	7.9 ¹⁹⁶
Garnet Li7La2Zr2O12	12.98	12.98	12.98	Cubic	Ia-3d ²⁴⁴	68.9 ¹⁹⁶



Figure 5-2 Description of the model (a) Energy of the system as sum of metal-metal interaction and SSE/metal interface interaction. (b) SSE/metal interface at an instant. The energy of the system is Eold. (c) A new atom is deposited at the interface. Position of metal atoms are relaxed to obtain minimum energy of the system Enew. The KMC rate of deposition at the interface depends on the evolution of energy of the system with deposition.

5.2 Results and Discussion

5.2.1 Morphology of interface with stiffness ratio

The morphology of the buried SSE/metal interface after two layers have been deposited is shown in Figure 5-3. The equilibrium distance ratio (a0/a) is 1 for all the cases (a) to (e) in Figure 5-3. If the stiffness ratio, k_0/k is small, the interaction between metal atoms and SSE is small compared to the interaction between metal-metal atoms and the contribution due to interfacial interactions is small to the total energy of the system. At small stiffness ratio of 0.01, the interface on the metal side is rough as seen in Figure 5-3(a). Distortion of atomic distances in metal is energetically more expensive than deviating from the equilibrium distance, a_0 at the interface between metal and SSE. Small value of stiffness ratio should mimic the behavior of liquid electrolytes and the resulting morphology is rough as expected in Figure 5-3(a). The deposition morphology shown in Figure 5-3(a) is similar to morphology obtained for ballistic deposition 245 , since only deposition is occurring and surface diffusion process is not included and the mechanical interaction at the SSE/metal interface is weak.

As stiffness ratio increases to 0.1, the interface is less rough as seen in Figure 5-3(b). However, the metal atoms near the interface are compressed together and the distance between metal atoms is shortened compared to equilibrium metal-metal distance. The interface is nearly flat if the stiffness ratio is 1 as seen in Figure 5-3(c). However, the degree of compression of newly deposited atoms is higher compared to Figure 5-3(b).

At higher stiffness ratio, k_0/k , the energetic contribution from SSE/metal interaction is considerably higher than metal-metal interaction. Although the deposition at the buried interface is stochastic, energy is minimized if distance between metal atoms and SSE is equilibrium distance a_0 and deformation is limited to metal side of the interface. As seen in Figure 5-3(d) and (e), the interface is flat when the stiffness ratio is 10 and 100 respectively. However, the deformed region, a couple of layers thick near the interface is seen in (d) and (e). In this deformed region, there are alternate regions of compressed and dilated metal atoms. It is important to note that the distortion in the metal lattice increases as the stiffness ratio increases, however, this distorted region is limited to only a couple of layers in the metal near the interface. There is no distortion in the metal five or six layers away from the interface and the behavior is like bulk. One of the issues with lithium SSE and lithium is the high contact resistance at the interface. Krauskopf *et al* ²⁴⁶ report that constriction resistance at small contact spots between LLZO/Li interface is responsible for high resistance at the interface and applying pressure reduces interfacial impedance. If the stiffness ratio is small, the interface is rough as seen in Figure 5-3(a) and there is poor contact between SSE and metal. If external pressure is applied to the bulk metal, average distance between metal and SSE would be reduced, providing better contact. Another approach to address the high interfacial impedance due to poor contact at the lithium SSE/lithium interface is to deposit an alloying element like aluminum to LLZO ²⁴⁷, lithium-aluminum alloy was formed at the interface leading to more than ten times less interfacial impedance. Polishing or cleaning of the SSE also decreases the interfacial impedance ²¹³. These surface modifications alter the strength of interaction between SSE/lithium. These results qualitatively support the morphology shown in Figure 5-3. With higher stiffness ratio (stronger interaction between SSE and metal), the interface changes from rough to flat leading to better contact at the interface.

5.2.2 Energy distribution at the SSE/metal interface

To map the energy distribution in the system, the energy contribution from atomic pair interaction is halved to each atom. The energy map of the system is shown in Figure 5-4 for different values of stiffness ratio after two layers have been deposited at the buried interface. The equilibrium distance ratio is 1 for all the cases. Since the energy is described in terms of nondimensional stiffness ratio and equilibrium distance ratio, the color bar at the top of figure 5-4 represents non-dimensional energy. The energy distribution shown in Figure 5-4 correspond to the morphologies shown in Figure 5-3. When the stiffness ratio is small, $k_0/k=0.01$, there is negligible energy in the entire system, there is very small amount of energy at the interface as seen in Figure 5-4(a). As the stiffness ratio increases to 0.1, there is not a significant increase in the energy of the system, although the metal atoms at the interface have higher energy as seen in Figure 5-4(b). When the stiffness ratio is 1, a couple of layers at the interface has high energy, but the energy distribution in the bulk is negligible as seen in Figure 5-4(c). As the stiffness ratio increases to 10 and 100, the value of energy of atoms at the interface is higher as seen in Figure 5-4(d) and (e). The high energy of atoms extends to about a third of the domain near the interface. As the stiffness ratio increases, the total energy of the system increases. As seen in Figure 5-3, with high stiffness ratio, the interface was flat after deposition of two layers, however the area near the interface has

high energy. The bulk of the system has negligible energy for all values of stiffness ratio. This shows that changes to the interface due to deposition is local. The extent of penetration at the interface depends upon the value of stiffness ratio. Our model does not consider any relaxation mode, such as interfacial diffusion, but it would be an interesting topic to explore in future research, particularly for high energy interfaces generated for large stiffness ratio.

5.2.3 Interface distance

The average distance between SSE and metal surfaces at the interface is a_0 as shown in Figure 5-2(a), before the deposition occurs. As the deposition progresses, the metallic surface becomes rough and the average distance between the SSE and metal changes. The fractional change in average distance, $\Delta D_{interface}$, between the SSE and metal surface at the interface is defined by

$$\Delta D_{\text{int erface}} = \frac{1}{a_0} \left(\frac{\sum_{i \in Interface} y_i}{N_x} - a_0 \right)$$
(5)

Where i is a lattice site at the metal surface at the interface, y_i is the vertical position of the ith interfacial atom and N_x is the total number of lattice sites in the horizontal direction. $\Delta D_{interface}$ indicates that how far apart the SSE and metal surfaces at the interface at any instant during deposition.

There are two parameters which affect the mechanistic aspect of deposition at the SSE/metal interface. One parameter is stiffness ratio, the other is the equilibrium distance ratio. As seen in Figure 5-3, with smaller stiffness ratio, the metal surface at the interface is rough while flat interface is possible with high stiffness ratio. In Figure 5-5, the change in average distance between SSE and metal surfaces at the interface is plotted for different stiffness ratio and equilibrium distance ratio. There are some common trends seen in all three plots in Figure 5-5. $\Delta D_{interface}$ is positive for all values of stiffness ratio and equilibrium distance ratio. The $\Delta D_{interface}$ is compared to the ratio of the value of $\Delta D_{interface}$ is smaller. As seen in Figure 5-3, for higher stiffness ratio, the interface is nearly flat, indicating that $\Delta D_{interface}$ is zero.

With increasing equilibrium distance ratio, a_0/a , $\Delta D_{interface}$ is smaller. The values of $\Delta D_{interface}$ is highest for $a_0/a = 0.5$ as seen in Figure 5-5(a) and smallest for $a_0/a = 1.5$ in Figure 5-5(c). Both stiffness ratio and equilibrium distance ratio determine the separation at the interface.



Figure 5-3 Morphology of interface after two layers of deposition. The equilibrium distance ratio, a0/a is 1 (a) k0/k = 0.01 (b) k0/k = 0.1 (c) k0/k = 1 (d) k0/k = 10 (e) k0/k = 100



Figure 5-4 Energy distribution in the system after two layers of deposition. The equilibrium distance ratio, a0/a is 1 (a) k0/k = 0.01 (b) k0/k = 0.1 (c) k0/k = 1 (d) k0/k = 10 (e) k0/k = 100



Figure 5-5 Fractional change in the average distance between the SSE/metal interface after two layers of deposition (a) The equilibrium distance ratio, a0/a is 0.5 (b) The equilibrium distance ratio, a0/a is 1.5

5.2.4 Surface Roughness at the interface

All solid state batteries suffer from imperfect contact at the lithium/SSE interface leading to high resistance and issues with performance. Evolution of surface roughness at the SSE/metal interface with deposition is shown in Figure 5-6. Surface roughness is calculated as

Surface Roughness =
$$\left(\frac{\sum_{i \in Interface} (y_i - D_{interface})^2}{N_x}\right)^{\frac{1}{2}}$$

$$D_{interface} = \sum_{i \in Interface} \frac{y_i}{N_x}$$
(6)
(7)

Where i a lattice site at the metal surface at the interface, N_x is the total number of lattice sites in the horizontal direction and $D_{interface}$ is the average distance between SSE and metal surface at the interface.

There are some common observations for between three plots for different equilibrium distance ratio in Figure 5-6(a), (b) and (c). There is a sharp increase in surface roughness initially for stiffness ratio less than one. The increase in surface roughness slows down after further deposition. For stiffness ratio greater than one, the increase in surface ratio is almost linear with increase in number of layers of deposition. With increasing stiffness ratio, the value of surface roughness decreases.

The value of surface roughness is higher with increasing equilibrium distance ratio as seen in Figure 5-6(a), (b) and (c). This is opposite to the trend observed in the fractional change in average distance, $\Delta D_{interface}$ in Figure 5-6. With increasing equilibrium distance ratio, the value of $\Delta D_{interface}$ decreases while surface roughness increases. For high values of stiffness ratio, the interface is flat seen in Figure 5-3, and $\Delta D_{interface}$ is close to zero but surface roughness is non-zero. The difference in surface roughness values with increasing a_0/a ratio is small but change in $\Delta D_{interface}$ is more significant.



Figure 5-6 Surface roughness of the interface after deposition of two layers (a) The equilibrium distance ratio, a0/a is 0.5 (b) The equilibrium distance ratio, a0/a is 1.0 (c) The equilibrium distance ratio, a0/a is 1.5

In Figure 5-7(a), the contour plot of fractional change in average distance between SSE and metal surface at the interface, $\Delta D_{interface}$, with changing stiffness ratio and equilibrium distance ratio after deposition of two layers at the buried interface is shown. $\Delta D_{interface}$ is very small if stiffness ratio is greater than 1. For stiffness ratio less than one, $\Delta D_{interface}$ depends both on stiffness ratio and equilibrium distance ratio and equilibrium distance ratio. The contour plots show radial pattern, with decreasing k₀/k and a₀/a values leading to higher magnitude of $\Delta D_{interface}$.

In Figure 5-7(b), the contour plot of surface roughness of SSE/metal interface with changing stiffness and equilibrium distance ratio is shown. The surface roughness value is small for stiffness ratio greater than 1. For stiffness ratio less than 1, the surface roughness is higher with increasing a_0/a ratio and decreasing k_0/k ratio. The contour trend for surface ratio and $\Delta D_{interface}$ with stiffness ratio less than one is opposite for a_0/a ratio.

In Figure 5-7(c), the contour plot of total energy of the system with changing stiffness ratio and equilibrium distance ratio is shown. The energy of the system is independent of the equilibrium distance ratio and increases with increasing stiffness ratio.

These contour plots show that at higher stiffness ratio, the equilibrium distance ratio is immaterial to the morphology of the interface during deposition. The response is more nuanced for stiffness ratio less than one. Now, both stiffness ratio and equilibrium distance ratio and important. The response of varying equilibrium distance ratio is opposite for $\Delta D_{interface}$ and surface roughness of the evolving metal surface at the interface.

In this study we explicitly model the interaction at the interface between SSE and metal and the morphology depends upon stiffness ratio. In our study, the SSE is treated as rigid (the elastic modulus is infinite compared to the modulus of metal). Still rough interface with deposition is possible for weakly interacting interfaces. Changing the nature of interfacial interactions might be a way forward to reduce surface roughness during deposition.



Figure 5-7 Contour plots after deposition of two layers at the metal/solid electrolyte interface (a) Fractional change in average distance between the SSE/metal interface (b) Surface roughness (c) Total energy of the system. The horizontal axis is stiffness ratio, k0/k and the vertical axis is equilibrium distance ratio, a0/a.

5.3 Conclusion

In this research work, we developed a coupled mechanics and deposition model to study deposition at the buried SSE/metal incoherent interface. The rate of deposition is dependent on the energetics of the morphology of interface. A rough interfacial morphology is obtained for a weak interaction between SSE and metal surfaces at the interface. If the interaction between SSE and metal surfaces at the interface is obtained after deposition of two layers. Even though the metallic surface is flat, near the interface region, alternate domains of compressed and dilated material is found in the metal. The energy of the system is localized near the interfacial region and the bulk of the metal is not distorted and has negligible energy.

The average distance between SSE and metal surface increases with deposition. The separation is lager for weakly interacting SSE/metal interface and smaller for strongly interacting interface. The surface roughness of the metal at the interface follows the same trend. Understanding the morphology of the SSE/lithium interface is crucial for improving the performance of all solid state batteries. In this research work we show that not only elastic modulus

of the SSE is critical, but the strength of interaction between SSE and lithium surface. Further efforts should be directed towards understanding formation of voids, inhomogeneity, delamination and other interfacial defects during deposition and dissolution and effects on cycling performance.

6. SOLID STATE ELECTROLYTE AND METAL INTERFACE: EFFECT OF SURFACE DIFFUSION ON MORPHOLOGY OF DEPOSITION AT SOLID STATE ELECTROLYTE/METAL BURIED INTERFACE

Relevant Publications and/or Working Papers

1. Deepti Tewari and Partha P. Mukherjee. Effect of surface diffusion on morphology of deposition at Solid State Electrolyte/Metal Buried Interface: A mesoscale study

Batteries as energy storage devices are ubiquitous, from cell phones and computers to electric vehicles, sensors, storage from solar and other renewable power generation and other applications ^{3,5,248}. The volumetric and gravimetric energy density of the batteries is one of the key design criteria ^{6,187,249,250}. To improve upon these criteria, lithium as anode material ^{4,189} is being considered instead of graphite intercalation anode ²⁵¹ which is used commercially. However, there are several issues with using lithium metal as anode in combination with liquid electrolyte, formation of dendrites on the lithium anode during charging which penetrate the separator causing internal short-circuit, formation of solid electrolyte interphase (SEI) due to parasitic side reactions, dead lithium which causes irreversible loss of lithium with each cycle ^{39,79,80,252–254}. One of the proposed solutions is to replace the liquid electrolyte with solid state electrolyte (SSE) ^{32,49}. Since liquid electrolytes are organic and volatile chemicals, the solid electrolytes are preferable in terms of fire safety. One major push towards exploring use of SSE in combination with lithium as anode material was the research work by Monroe and Newman ^{62,184}. They proposed that if the shear modulus of the SSE is twice that of lithium metal, the perturbations in the interface due to electrodeposition would die out and the interface would remain stable with electrodeposition.

Several kinds of SSE have been designed and explored for lithium ion as the mobile carrier. Broadly, they fall in to two categories, inorganic SSE and polymer SSE ^{30,31,213,255}. In the inorganic SSE categories, it can be crystalline or amorphous SSE. The SSE are required to have chemical and electrochemical stability with lithium metal, high ionic conductivity through the SSE and mechanical strength ^{53,256,257}. In terms of ionic conductivity, the SSE in general have lower conductivity compared to the liquid electrolyte, particularly at room temperature. It has also been reported that the impedance due to SSE and metal interface is very high ^{48,194,258}.

One of the most attractive features about SSE, particularly the inorganic ceramic SSE was their high elastic modulus (most of ceramic SSE ¹⁹⁶ have elastic modulus more than ten times greater than that of lithium ¹⁹⁸) which would offer mechanical rigidity to growth and penetration of lithium dendrites during charging of the battery. Recently, several studies have reported the presence of dendrite propagation through LLZO ^{206,210,259} which is a ceramic SSE with shear modulus of about 64 GPa¹⁹⁷ compared with lithium with shear modulus of 2.8 GPa¹⁹⁸. Several avenues have been explored to explain this discrepancy. One of them is the electronic conductivity of the SSE ²⁶⁰. Yue et al ¹⁹⁹ found that the electronic conductivity of LLZO and LPS was high enough to reduce the lithium ion inside the SSE. Song et al ²⁰⁰ compared the electronic conductivity within the grain and grain boundary of LLZO and concluded that the electronic conductivity in the grain boundary is large enough to reduce the mobile lithium ion carrier inside the SSE. Grain boundaries are found to have smaller elastic modulus and aid in lithium dendrite penetration ²⁶¹. Another mechanism which has been explored to explain the propagation of dendrites inside the SSE is the presence of cracks in the SSE ²⁰¹. To address the issue of insufficient contact between cathode and SSE, a method called co-sintering is used. However, the volumetric change in cathode to insertion and de-insertion of lithium generated cracks in the ceramic SSE ¹⁹⁵. The deposition of lithium inside the cracks during charging causes the cracks to grow and propagate.

In terms of theoretical models of the interface, Newman and Monroe model has been most influential. It predicted a stable interface between lithium and SSE with deposition if shear modulus of SSE is twice that of lithium. Ahmad et al ²⁰⁷ extended this stability analysis to distinguish two different regime of stability, pressure driven stability at high molar volume ratio and density driven stability at low molar volume ratio. Ahmad et al ²⁰⁸ also analyzed the effect of anisotropy on interface stability during deposition and concluded that crystallographic orientation in creating the interface plays a role in the stability of the interface. Recently, Barai et al ²⁰⁹ made a distinction between initially rough interface used in Monroe and Newman model and relaxed interface and found that it is important to include the effect of current distribution in finding the mechanical forces required for suppression of dendritic growth. Barai et al ²⁶² also concluded that for polymer SSE, increasing the elastic modulus and yield strength reduces dendritic propagation during charging. Li et al ²¹⁰ investigate the critical current above which dendrites propagate in LLZO using chemomechanics principles. Bucci et al ¹⁹⁰ study the effect of geometry and interfacial resistance of cracks in lithium deposition using coupled electromechanics continuum model and

concluded that controlling the defects at the interface and resistance at interface is crucial to the performance of the battery.

The SSE and metal interface present a complex picture, particularly the morphology evolution with deposition. The average separation and contact length would affect the impedance during charging or discharging of the battery. Several research studies have noted that SSE and lithium have imperfect contact at the interface and high impedance. Studies have also reported that higher applied voltage is required when the interfacial impedance is large. The electronic conductivity of the SSE increases with increase in applied voltage ²¹⁰. This would change whether dendritic deposits would occur at the SSE and lithium interface.

In our current research work, we have developed a coupled energetics and deposition model using Kinetic Monte Carlo (KMC) method to study the deposition at a generalized SSE and metal interface. KMC method is particularly useful in investigating deposition characteristics like three dimensional island formation ²⁶³, dislocations in heteroepitaxial growth ²⁶⁴ and strained heteroepitaxial deposition ^{108,265}.

In our coupled model, the rate of deposition or diffusion at the interface of SSE and metal depend on the energetics of the evolving morphology of the interface. If the interaction between the SSE and metal surface is weak, the morphology of deposition is rough. With increasing surface diffusion at the interface, the roughness of morphology decreases. At higher interaction between SSE and metal surface, flat deposition morphology is achieved. However, with increasing surface diffusion at the interface, there is less energy near the interface region. The morphology of deposition and energy distribution near the interface depend strongly on the strength of interaction between metal and SSE surfaces as well as surface diffusion at the interface.

6.1 Computational Model

In the coupled energetics and Kinetics Monte Carlo (KMC) model, two processes are considered, deposition and diffusion at the interface. With the evolution of the interface because of deposition and diffusion at the interface, the energy of the system changes. The rates of deposition and diffusion depend upon the change in the energy of the system due to either event. The energetics and KMC processes are described in detail below.

6.1.1 Energetics of the system

The interface formed between SSE and metal is heterointerface. Depending on misfit between the two lattices, the interface can be characterized as coherent, semi-coherent or incoherent. The misfit is defined as ²¹²

$$Misfit = \frac{2(a_1 - a_2)}{a_1 + a_2}$$
(1)

Where a_1 and a_2 are the lattice size of two materials. If the misfit < 0.1, the interface is coherent and there is continuity of atomic planes across the two crystal systems. If 0.1<misfit<0.2, the interface is called semi-coherent. The difference in the lattice of two materials is accommodated by the presence of periodic dislocations called misfit dislocations. If the misfit > 0.2, the interface is incoherent and there is no correspondence between atomic planes of two materials at the interface.

The lattice size of lithium inorganic SSE is in the range of about (4 to 13 Å) ^{191,241–244}. The lattice size of lithium is 3.5 Å ²¹⁴. The misfit between lithium and inorganic lithium SSE is greater than 0.2. In general, the inorganic SSE and lithium form incoherent heterointerface and there is no pattern between SSE and metal surface. Therefore, this heterointerface between a generalized SSE and metal in our model is treated as isotropic. The elastic modulus of inorganic ceramic SSE ¹⁹⁶ is more than ten times than that of lithium ¹⁹⁸. Therefore, in our model, the SSE is treated as rigid and the atomic positions of SSE is not included in the energy minimization.

Figure 1(a) schematically describes the energetics of the system. Since the elastic modulus of inorganic lithium SSE and sodium SSE is several times larger than lithium or sodium, in our model, the SSE is assumed to be rigid. In 1(a), the metal atoms at the interface are shown in grey and the computational domain, i.e., the number of layers included in simulation is shown in red. The interaction between metal atoms is described by harmonic potential characterized by stiffness constant k and equilibrium distance a as shown in Figure 1(a). The interaction between metal atoms at the interface and SSE surface is described by another harmonic potential characterized by stiffness k₀ and equilibrium distance a₀. The total energy of the system is given by

$$E(r) = \sum_{i=1}^{N_{atoms}} \sum_{j>i}^{N_{atoms}} \frac{1}{2} k(r_{ij} - a)^2 + \sum_{i=1}^{N_{interface}} \frac{1}{2} k_0 (r_{is} - a_0)^2$$
(2)
where, $r = \begin{cases} x_1 & x_2 & x_3 \\ y_1 & y_2 & y_3 & \cdots \end{cases}$

Where r is the set of atomic positions of all the metal atoms, r_{ij} is the distance between neighboring ith and jth metal atoms and r_{is} is the distance in the vertical direction between SSE and metal atom at the interface.

The deposition occurs at the buried interface between SSE surface and metal surface. When a new atom is added, the position of all the metal atoms is relaxed such that the total energy of the system is minimized. As deposition progresses, the bulk metal is displaced in the vertical direction as shown in Figure 1(a). As the deposition is occurring at the interface, the atomic positions near the deposition will change more compared to many layers away from the interface. After certain layers of metal atoms away from the interface, the relative positions between neighboring atoms do not change and beyond this domain, there is no contribution to energy. The determination of the required number of layers in the computational domain is discussed in the Appendix D.

The total energy of the system can be described in terms of ratio k_0/k , referred to as stiffness ratio and a_0/a , referred to as equilibrium distance ratio. High stiffness ratio implies that contribution from interaction between metal atoms at the interface and SSE towards total energy is high compared to metal-metal energy contribution. This scenario is referred to as strongly interacting interface. On the other hand, low stiffness ratio implies that that contribution of metal atoms at the interface and SSE interaction at the interface towards total energy is much less compared to metal-metal atoms interface. This scenario is referred to as strongly interacting interface and SSE interaction. This scenario is referred to metal-metal atoms at the interface towards total energy is much less compared to metal-metal atoms interaction. This scenario is referred to as weakly interacting interface.

6.1.2 Kinetic Monte Carlo (KMC) Model

In the two dimensional KMC method, two processes are considered, deposition at the interface and diffusion at the interface. Bulk diffusion is not allowed and diffusion at the interface occurs only at a step. Step up or step down diffusion is not allowed. The probability of deposition is P_{dep} and probability of diffusion is P_{diff} . Since, only two process are allowed, $P_{dep} + P_{diff} = 1$. This means that if P_{dep} increases, P_{diff} decreases. P_{diff} can be zero, but P_{dep} has to be greater than

zero so that deposition at the interface can commence. In batteries, the probability of deposition can change depending on the applied voltage or current density.

Figure 1(b) and (c) schematically describe the energetic description of kinetic rates of deposition and diffusion. Figure 1(b) shows the SSE/metal system at an instance. The energy of the total system is E_{old} after minimizing the energy with respect to atomic positions. In Figure 1(c), if a new atom is added at site i of the interface, the new energy of the system, E_{new} , is calculated such that it is minimum with respect to all the atoms in and the newly added atom. The rate of deposition k_{dep} is given by,

$$k_{dep}^{i} = P_{dep} \exp\left(\frac{-(E_{new} - E_{old})}{E_{old}}\right)$$
⁽³⁾

Diffusion only occurs at a step, which is shown in Figure 6-1(b). In Figure 6-1(c), diffusion of a metal atom at the interface towards right on a step is shown. To calculate the rate of diffusion, k_{diff} at ith site at the interface, the atomic positions of the updated system after diffusion is relaxed to obtain the new total energy, E_{new} , of the system.

$$k_{diff}^{i} = P_{diff} \exp\left(\frac{-(E_{new} - E_{old})}{E_{old}}\right)$$
⁽⁴⁾

The rate of deposition and diffusion depend on the how the total energy of the system evolves due to diffusion of deposition at that particular site of the interface. Periodic boundary conditions are imposed in the horizontal direction. The number of lattice sites in the horizontal direction, N_x is 150. The amount of deposition is reported in terms of number of layers, which is number of atoms added divided by N_x . The equilibrium distance ratio, $a_0/a = 1$ for all the simulations in this research work. The stiffness ratio, k_0/k varies in the range of 0.01 to 100. The probability of deposition, P_{dep} varies in the range of 0.005 to 1. If $P_{dep} = 0.005$, it means that probability of diffusion, $P_{diff} = 0.995$. If $P_{dep} = 1$, the probability of diffusion, P_{diff} is zero. At the beginning of the simulation, 11 layers from the interface is included in the computational domain. Details of KMC algorithm and computational domain is provided in the Appendix D.



Figure 6-1 Description of the model (a) Energy of the system as sum of metal-metal interaction and metal-interface interaction. Two processes are considered in the Kinetic Monte Carlo model, diffusion and deposition at the metal surface at the SSE/metal interface (b) Energy, Eold of the system at an instance, depends on the local interfacial morphology (c) With either diffusive event or deposition event at the interface, the energy of the system is Enew after relaxation of atomic positions to minimize energy of the system.

6.2 Results and Discussion

6.2.1 Morphology of deposition

The morphology of the SSE/metal interface after deposition of two layers of metal atoms is shown in Figure 6-2 for different values of stiffness ratio, k_0/k and probability of deposition, P_{dep} . If the metal surface and SSE surfaces have weak interaction, the k_0 term in the harmonic potential shown in equation 2 will be small and the non-dimensional stiffness ratio, k_0/k will be small. Figure 6-2(a1) and (a2) show the morphology for small k0/k ratio and deposition probability, P_{dep} of 0.005 and 1 respectively. The morphology in Figure 6-2(a1) is characterized by the presence of steps, since diffusion occurs only at steps at the interface and diffusion across steps is not permitted. The morphology in (a1) is smoother compared to (a2) where there is only deposition and no diffusion. Still the morphology in (a1) is not flat due to stochastic nature of deposition. In both (a1) and (a2), there is no appreciable distortion of distance between metal atoms at the interface, since it is more favorable to energetically to change the distance between metal atoms and SSE at the interface because k_0 is very small compared to k. The effect of diffusion on the morphology is to reduce the roughness with deposition.

The morphology for higher stiffness ratio, $k_0/k=1$ is shown in Figure 6-2(b1) and (b2) for P_{dep} equal to 0.005 and 1 respectively. The interface is nearly flat for both the cases, although there are slight differences. When the probability of diffusion is high (b1), steps can be seen. There are regions near the interface where metal atoms are close together in (b1) and (b2). However, in (b1) where probability of diffusion on steps is high, these compressed regions are farther apart compared to (b2) where there is no diffusion.

If the stiffness ratio is very large, it is more favorable energetically to accommodate distortion in the metal atoms compared to interfacial distance between metal atoms and SSE surface. The morphology of the interface after deposition of two layers for stiffness ratio of 100 is shown in Figure 6-2(c1) and (c2) for P_{dep} of 0.005 and 1 respectively. The interface is flat for both the cases and there are adjacent compressed and dilated regions of metal atoms at the interface for both the cases. However, if diffusion is high (c1), the size of compressed and dilated regions is larger compared to (c2), where there is no diffusion. Also, the number of layers to which accommodate distortion near the interface is higher in (c1) compared to (c2).

In Figure 6-2, for all the scenarios presented, the distortion at the interface due to deposition is local and there is no distortion after five or six layers away from the interface. The predominant effect in determining whether the morphology is flat or rough is the stiffness ratio. The effect of diffusion is more subtle, particularly for high stiffness ratio. For smaller stiffness ratio, the effect of diffusion is to reduce the roughness due to deposition. For larger stiffness ratio, the effect of diffusion at the interface is to permeate the distortion to a larger number of layers near the interface and to increase the size of contiguous compressed and dilated regions near the interface.

The morphology of deposition strongly depends on the strength of interaction between metal and SSE surface. There is little atomic restructuring between ceramic and metal atoms and the work of adhesion for incoherent surfaces is generally small, implying that they are weakly interacting interfaces in terms of discussion presented above. Rough morphology obtained for weakly interacting interfaces in our study is in line with the reports of imperfect contact and high impedance between lithium and lithium SSE. Modifying the interface by forming lithium metal alloy ^{266,267} and changing the nature of interface improves the contact at the interface. Modifying the strength of interaction would decrease the roughness of deposition at the buried interface.

6.2.2 Evolution of energy of the system during deposition

Since the energetics and deposition are coupled, it is interesting to study the distribution of energy near the interface with deposition. In Figure 6-3, the energy distribution after two layers of deposition, corresponding to the morphology shown in Figure 6-2 is plotted. Half of the energy computed to a pair of atoms is assigned to each atom to create this map. The energetics of the system is described in terms of non-dimensional stiffness ratio and equilibrium distance ratio and the colorbar at the top of the figure represents the non-dimensional energy. When the stiffness ratio is small (k0/k = 0.01), the magnitude of energy is small and localized to interface as seen in Figure 6-3(a1) and (a2). Diffusion at the interface does not seem to be reflected in the energy map of the system since (a1) and (a2) look very similar. Figure 6-3(b1) and (b2) show the energy map for stiffness ratio of 1 and P_{dep} = 0.005 and P_{dep} = 1 respectively. Energy is localized near the interface. When the probability of diffusion is high (b1), there is less energy in the interfacial region compared to (b2) with zero probability of diffusion. This trend is more pronounced when the stiffness ratio is 100. The energy near the interface is significantly smaller in Figure 6-3(c1) compared to Figure 6-3(c2).



Figure 6-2 Morphology of the SSE/metal interface after deposition of two layers at the buried interface. (a1) stiffness ratio, k0/k = 0.01 and probability of deposition, Pdep = 0.005 (a2) stiffness ratio, k0/k = 0.01 and probability of deposition, Pdep = 1.0 (b1) stiffness ratio, k0/k = 1.0 and probability of deposition, Pdep = 0.005 (b2) stiffness ratio, k0/k = 1.0 and probability of deposition, Pdep = 0.005 (c2) stiffness ratio, k0/k = 100 and probability of deposition, Pdep = 0.005 (c2) stiffness ratio, k0/k = 100 and probability of deposition, Pdep = 1.0

The energy of the system is localized to the interfacial region as seen in Figure 6-3. The total energy of the system increases with increasing stiffness ratio and increasing probability of deposition. The effect of diffusion at the interface is not reflected in the energy map because the scale of energy is low, however the morphology is less rough as seen in Figure 6-2(a1). At high stiffness ratio, diffusion at the interface does not change the morphology as seen in Figure 6-2, but there is significant impact of interfacial diffusion on the energy map. With diffusion, there is less energy in the interfacial region.

Figure 6-4 shows the contour plot of total energy of the system with varying stiffness ratio, k_0/k and probability of deposition, P_{dep} at different stages of deposition. Figure 6-4(a) shows the energy contour when 0.25 layer has been deposited at the interface. Increasing the value of stiffness ratio leads to higher value of total energy of the system. There is slight decrease in energy with decrease in P_{dep} for stiffness ratio less than one. The decrease in total energy if more pronounced for stiffness values greater than one. Decreasing P_{dep} or increasing probability of diffusion at the interface results in lower values of the total energy. In Figure 6-4(b), the contour of total energy is plotted after depositing 1 layer at the interface. The trend is similar to that in Figure 6-4(a). The decrease in total energy with decreasing P_{dep} is more pronounced at higher values of stiffness ratio. Figure 6-4(c) shows the contour of energy after deposition of two layers at the interface. The trend that increasing stiffness ratio results is higher total energy of the system is consistent with that observed in (a) and (b), but the effect of decreasing P_{dep} and higher stiffness ratio is not as pronounced as in (a) and (b). From the three plots, it can be concluded that the effect of diffusion at the interface on total energy of the system is greater at smaller amounts of deposition. Since, diffusion is only allowed across the step, the chance for diffusion decreases with progression of deposition, as several steps form as new atoms are randomly deposited. The effect of diffusion at the interface is rearrangement such that energy of the system is lowest. With progressive deposition, the opportunities for diffusion are reduced because of formation of several discontinuous steps. Therefore, in Figure 6-4(c), the effect of diffusion is considerably smaller than in Figure 6-4(a)and (b).



Figure 6-3 Energy distribution of SSE/metal interface after deposition of two layers at the buried interface. (a1) stiffness ratio, k0/k = 0.01 and probability of deposition, Pdep = 0.005 (a2) stiffness ratio, k0/k = 0.01 and probability of deposition, Pdep = 1.0 (b1) stiffness ratio, k0/k = 1.0 and probability of deposition, Pdep = 0.005 (b2) stiffness ratio, k0/k = 1.0 and probability of deposition, Pdep = 1.0 (c1) stiffness ratio, k0/k = 100 and probability of deposition, Pdep = 0.005 (c2) stiffness ratio, k0/k = 100 and probability of deposition, Pdep = 1.0. The colorbar at the top of the figure indicates the non-dimensionalized energy of the total system.



Figure 6-4 Contour plots of total energy of the system with varying stiffness ratio, k0/k and probability of deposition, Pdep at the SSE/metal interface at different stages of deposition at the buried interface. (a) 0.25 layers of deposition (b) 1.0 layer of deposition (c) 2.0 layer of deposition.

6.2.3 Characterizing the interface

Fractional change in average distance between metal surface and SSE surface at the interface

Figure 6-5(a) schematically shows the average distance between SSE and metal surface at the interface, D. At the beginning of the simulation, D is equal to a_0 . As deposition progresses, the average distance, D, changes. To characterize the interface, $\Delta D_{interafce}$, the fractional change in average distance between SSE and metal surface at the interface is defined,

$$\Delta D_{\text{interface}} = \frac{1}{a_0} \left(\frac{\sum_{i \in Interface} y_i}{N_x} - a_0 \right)$$
(5)

Where a_0 is the equilibrium distance between SSE and metal atom in the harmonic energy term described in equation (), i is a site at the interface, y_i is the vertical distance of the i_{th} metal atom at the interface and N_x is the number of lattice sites in the horizontal direction.

Figure 6-5(b) shows plot of $\Delta D_{interface}$ with layers of deposition at the interface for stiffness ratio, k₀/k=0.01 for different values of probability of deposition, P_{dep.} With increasing number of layers deposited at the interface, $\Delta D_{interface}$ increases. Looking at the five different plots for P_{dep} ranging from 0.005 to 1, $\Delta D_{interface}$ decreases with increasing probability of deposition. At smaller value of P_{dep} or high probability of diffusion at the interface, steps are formed at the interface as seen in Figure 6-2(a1) and the morphology is smoother compared to $P_{dep}=1$ case in Figure 6-2(a2). The average distance between metal surface and the SSE surface is larger when steps are formed at the metal surface during deposition. Figure 6-5(c) shows $\Delta D_{\text{interface}}$ for stiffness ratio, $k_0/k=1$ for different values of P_{dep} with increasing number of layers deposited. The overall increase in $\Delta D_{interface}$ for the entire range of P_{dep} is smaller compared to Figure 6-5(b). $\Delta D_{interface}$ is greater than zero for all values of P_{dep} in Figure 6-5(c), although there is not much difference between plots for different values of P_{dep} . In Figure 6-5(d), $\Delta D_{interface}$ with number of layers deposited for different values of P_{dep} is shown for stiffness ratio of 100. The value of $\Delta D_{interface}$ is nearly zero for all values of P_{dep} , although there are more fluctuations in $\Delta D_{interface}$ after 1.5 layers of deposition. With increasing stiffness ratio, $\Delta D_{interface}$ is decreasing. The effect of diffusion at the interface on $\Delta D_{interface}$ is seen at smaller values of stiffness ratio.

Figure 6-6 shows the contour plot of $\Delta D_{interface}$ with varying stiffness ratio, k₀/k and P_{dep} at different stages of deposition at the interface. In Figure 6-6(a), the contour plot of $\Delta D_{interface}$ is after

deposition of 0.25 layers at the interface. For stiffness ratio greater than one, $\Delta D_{interface}$ is close to zero. For smaller values of stiffness ratio, $\Delta D_{interface}$ increases with decreasing P_{dep} and decreasing stiffness ratio. Contour plot of $\Delta D_{interface}$ after deposition of one layer is shown in Figure 6-6(b). $\Delta D_{interface}$ is very small for stiffness ratio greater than one. For stiffness ratio less than one, decrease in stiffness ratio and P_{dep} results in larger values of $\Delta D_{interface}$ although the effect of P_{dep} is not as pronounced as in Figure 6-6(a). Figure 6-6(c) shows the contour plot of $\Delta D_{interface}$ after deposition of two layers. The effect of P_{dep} on $\Delta D_{interafce}$, is almost absent in this contour plot. With decreasing stiffness ratio, $\Delta D_{interface}$ increases in Figure 6-6(c). There is almost no variation in $\Delta D_{interface}$ with changing P_{dep}. The effect of probability of deposition on morphology is significant in the initial stages of deposition. During initial deposition, there is one continuous step and there are more sites for diffusion. With progressive deposition, several discontinuous steps are formed. Since diffusion across steps is not permitted, there are fewer opportunities for diffusion. Hence, at the end of two layers of deposition, $\Delta D_{interface}$ depends only on stiffness ratio.

Fractional change in length of metal surface at the SSE/metal interface

The interface comprises of metal surface and the SSE surface. As deposition occurs at the interface and new atoms are added to the metal surface at the interface, its morphology changes. One way to characterize the roughness of the metal surface at the interface is by tracking the length of the metal surface with deposition. In Figure 6-7(a), the length L of the metal surface at the interface is shown schematically. The fractional change in length, $\Delta L_{interface}$, is defined as

$$\Delta L_{\text{interface}} = \frac{1}{L_0} \left(\sum_{\substack{i,j \in Interface\\i=[0,N_x-1], j=i+1}} r_{ij} - L_0 \right)$$
(6)

Where, L_0 is the length at the start of the simulation ($L_0=N_x-1$), i and j are neighboring lattice points at the interface, r_{ij} is the distance between ith and jth lattice point and N_x is the number of lattice points in the horizontal direction.



(c)

(d)

Figure 6-5 The fractional change in average distance, Δ Dinterface between metal surface and SSE surface at the interface for three different values of stiffness ratio, k0/k with the progression of deposition (a) schematic description of Δ Dinterface (b) k0/k = 0.01 (c) k0/k = 1.0 (d) k0/k = 100.0



Figure 6-6 Contour plots of fractional change in average distance between metal and SSE surface at the interface, Δ Dinterface with varying stiffness ratio, k0/k and probability of deposition, Pdep at different stages of deposition at the buried interface. (a) 0.25 layers of deposition (b) 1.0 layer of deposition (c) 2.0 layer of deposition.

Figure 6-7(b) shows the plot of $\Delta L_{interface}$ with number of layers of deposition at the interface for different values of probability of deposition, P_{dep} . The results shown in Figure 6-7(b) use stiffness ratio of 0.01. The value of $\Delta L_{interface}$ increases with increasing deposition. The increase in $\Delta L_{interface}$ is largest for $P_{red}=1$ and decreases with smaller values of P_{red} . Figure 6-7(c) plots $\Delta L_{interface}$ for stiffness ratio of 1. The trend in $\Delta L_{interface}$ is similar to that observed in Figure 6-7(b), $\Delta L_{interface}$ increases with increasing deposition and change in $\Delta L_{interface}$ is largest for $P_{dep}=1$ and decreases with smaller values of $P_{dep}=1$ and decreases with smaller values of $P_{dep}=1$ and the decreases with smaller values of $P_{dep}=1$ and values of P_{dep} . In Figure 6-7(d), plot of $\Delta L_{interface}$ is close to zero for all values of P_{dep} for this stiffness ratio.

From Figure 6-7, it can be concluded that $\Delta L_{interface}$ increases with the number of layers of deposition. $\Delta L_{interface}$ depends on both the stiffness ratio and P_{dep}. $\Delta L_{interface}$ decreases with increasing stiffness ratio and decreasing P_{dep}. This matches with the deposition morphology shown in Figure 6-2. With increasing diffusion or smaller values of Pd_{ep}, the interface is less rough, indicated in the value of $\Delta L_{interface}$ seen in Figure 6-7(b) and (c). At large stiffness ratio, the morphology does not seem to depend upon diffusion, but the energy at the interface is lower with higher diffusion as seen in Figure 6-3.

Figure 6-8(a), (b) and (c) shows the contour plot of $\Delta L_{interface}$ with varying stiffness ratio and probability of deposition, P_{dep} after 0.25, 1 and 2 layers of deposition at the interface respectively. All three contour plots show similar trend in $\Delta L_{interface}$. There is negligible change in $\Delta L_{interface}$ for stiffness ratio greater than 1 in all the three plots. For stiffness ratio less than one, $\Delta L_{interface}$ increases with increasing P_{dep} and decreasing stiffness ratio. Weaker interaction or smaller value of stiffness ratio results in rougher morphology. Similarly, higher value of P_{dep} or smaller chance of diffusion at the interface results in rougher diffusion.

The interface is characterized by average distance between SSE and metal surface and the length of the metal surface as deposition progresses. The contour plots in Figure 6-6 for $\Delta D_{interface}$ and Figure 6-8 for $\Delta L_{interface}$ show different trends with respect to P_{dep} . $\Delta D_{interface}$ is dependent on P_{dep} for 0.25 and 1 layer of deposition but not when 2 layers have been deposited. So, on average separation, D, probability of deposition or diffusion at the interface is relevant at the beginning stage of deposition but not at higher deposition. The roughness as indicated by the length of the metal surface depends on P_{dep} or probability of diffusion for the entire range of deposition. Lower P_{dep} or higher diffusion at the interface results in less rough deposition.


Figure 6-7 The fractional change length of metal surface, Δ Linterface at the SSE/metal interface for three different values of stiffness ratio, k0/k with the progression of deposition (a) schematic description of Δ Linterface (b) k0/k = 0.01 (c) k0/k = 1.0 (d) k0/k = 100.0



Figure 6-8 Contour plots of fractional change in length of the metal surface, ΔLinterface at SSE/metal interface with varying stiffness ratio, k0/k and probability of deposition, Pdep at different stages of deposition at the buried interface. (a) 0.25 layers of deposition (b) 1.0 layer of deposition (c) 2.0 layer of deposition.

6.2.4 Displacement of the bulk metal

One feature of metal anodes is volumetric expansion during electrodeposition unlike intercalation anodes or host anodes where volumetric change due to deposition is not significant. In our model, due to deposition at the buried interface, the bulk of the metal would be displaced in the vertical direction with reference to Figure 6-1. In Figure 6-9, the contour plots of bulk displacement with varying stiffness ratio (k_0/k) and P_{dep} is shown for deposition of 0.25, 1 and 2 layers of deposition in (a), (b) and (c) respectively. With 0.25 layers of deposition, if the bulk displacement is less than 0.25 layers, it is labeled as bulk contraction in the contour plot. If the bulk displacement is greater than 0.25 layers, it is labeled as bulk dilation in the contour plot. In Figure 6-9(a), it can be seen that displacement of bulk is greater than 0.25 for a narrow region with loser stiffness ratio and small P_{dep}. When 1 layer has been deposited, the bulk dilation region as seen in Figure 6-9(b) has expanded compared to Figure 6-9(a). After 2 layers have been deposited, the bulk dilation is in narrow region with low stiffness ratio as seen in Figure 6-9(c) and the amount of dilation and contraction is independent of P_{dep} and depends only on the stiffness ratio. The overall trend is that for higher stiffness ratio, the displacement of the bulk metal is less than the number of layers deposited at the buried interface. For smaller stiffness ratio, contraction or dilation depends upon the amount of deposition, P_{dep} and the stiffness ratio.

6.3 Conclusion

In this research work, we have used coupled energetics and KMC model to study the morphology of the buried interface as deposition progresses. The interfacial interaction between SSE and metal is weak if the stiffness ratio (k_0/k) is small and strong if stiffness ratio is large. Figure 6-10 shows the map of energetics and morphology with respect to diffusion at the interface and interfacial interaction. If the interfacial interaction is weak, the morphology of deposition is rough. For strong interfacial interaction, the morphology of deposition is flat. The effect of diffusion on the morphology is more pronounced in the weaker interfacial interaction region. With increasing probability of diffusion at the interface, the morphology is less rough. There is not much change in the energy distribution of the system, since the energy contribution due to interfacial interaction is small compared to the total energy of the system.



Figure 6-9 Contour plot of bulk displacement of the metal with varying stiffness ratio, k0/k and probability of deposition, Pdep at different stages of deposition at the buried interface. (a) 0.25 layers of deposition (b) 1.0 layer of deposition (c) 2.0 layer of deposition.



Interfacial interaction

Figure 6-10 Map of the morphology and energetics of the system with respect to interaction between metal and SSE surfaces at the interface (k0/k ratio) and surface diffusion of metal atoms at the interface.

For stronger interfacial interaction, where the morphology of the deposition is flat, changing the probability of diffusion at the interface does not change the appearance (flatness) of the interface. However, the energy near the interfacial region decreases. Due to interfacial diffusion, the rearrangement of atoms at the interface with progression of deposition results in lower energy in the metal region near the interface.

The strength of interaction between metal surface and solid state electrolyte is critical in determining the morphology of deposition at the buried interface. Higher interfacial interaction leads to flat deposition. Diffusion at the interface results in smoother deposition for weak interfacial interaction and lower energy in the interfacial region for strong interfacial interaction.

7. SUMMARY AND OUTLOOK

The electrode and electrolyte interface is critical to performance and safety of the batteries. As deposition or dissolution progresses, the area of the interface changes. Since electrochemical reactions occur at the interface, change in area influences the rate of deposition or dissolution as well as any parasitic reactions. Enhanced kinetics of these electrochemical reactions can result in increased temperature, degradation of battery components and decay in performance over long time. In this research, the morphology of different class of electrode and electrolyte has been studied and the degree of stability of interface has been analyzed using mesoscale methods. The interfaces under investigation are graphite intercalation anode and liquid electrode, lithium metal anode and liquid electrolyte and lithium metal anode and solid state electrolyte. Lithium ion batteries which use graphite anodes are the commercial batteries which are used in portable electronics, electric vehicles and numerous other applications. Lithium metal batteries (LMB) use lithium as anode material in combination with liquid electrolyte. Lithium metal batteries suffer from several performance and safety issues and are still a topic of research. All solid state batteries (ASSB) use lithium metal as anode in combination with solid state electrolyte and solid cathode. Research on ASSB with regards to materials for solid electrolytes and cathode and interfacial behavior is ongoing. The only commercial solid electrolyte in ASSB is LIPON, which is a thin film solid electrolyte. The LIPON ASSBs have lower energy density. In this research, the interfacial morphology and stability for three different electrode and electrolyte interfaces which range from current commercial use to research and development is analyzed.

7.1 Summary of key findings

7.1.1 Intercalation anode and liquid electrolyte

In this work, a mesoscale analysis of the underlying multimodal interactions is presented to study the evolution of morphology due to lithium deposition on typical graphite electrode surfaces. It is found that electrodeposition is a complex interplay between the rate of reduction of Li ions and the intercalation of Li in the graphite anodes. The morphology of the electrodeposited film changes from dendritic to mossy structures because of the surface diffusion of lithium on the electrodeposited film.

7.1.2 Metal anode and liquid electrolyte

There are two aspects presented in this work, one is focused on plating and stripping of a generalized metal. The other is specific to lithium, find the functional dependence of dead lithium on operating conditions, temperature and overpotential using experimental and mesoscale analysis synergistically.

A non-dendritic interface morphology is obtained while plating on a metal anode under reaction and ionic transport controlled scenarios. Otherwise, this may evolve into mossy, dendritic, whisker or needle-like structures with the main characteristic being the propensity for undesirable vertical growth. During discharging, a pitted interface may be formed along with bulk dissolution. Surface diffusion is a key determinant controlling the extent of dead lithium formation, including a higher probability of the same when the effect of surface diffusion is comparable to that of ionic diffusion in the electrolyte and interface reaction.

Dead lithium is the fragment of lithium that is detached from the lithium electrode during electrodissolution or stripping. In this study, the mesoscale underpinnings of dead lithium formation via a synergistic computational and experimental approach are presented. The mechanistic focus centers on the morphological evolution of the lithium electrode–electrolyte interface and the relative quantification of dead lithium formation under a range of operating temperatures and currents. This study reveals that the amount of dead lithium formed during stripping increases with decreasing current and increasing temperatures. This finding is in direct contrast to the operating conditions that lead to dendritic deposition during charging, i.e., at higher currents and lower temperatures. During stripping, more dead lithium is formed when the interface has thin narrow structures. The ionic diffusion and self-diffusion of lithium at the interface play a key role in the evolution of narrow structures at the interface. Therefore, more dead lithium is formed when diffusive processes are facilitated compared to the oxidative reaction at the interface.

7.1.3 Metal anode and solid electrolyte

Solid state electrolytes (SSE) is a promising avenue towards utilizing lithium metal as anode material with high specific capacity and low redox potential. The SSEs provide mechanical barrier to dendrite growth of lithium during charging of batteries. Monroe and Newman model suggested that if the shear modulus of the solid electrolyte is greater than two times the shear modulus of lithium metal, the amplitude of roughness at the interface would decay. However, dendrite penetration though solid state electrolytes has been reported. In this work, we develop a coupled mechanics and deposition model at SSE /metal incoherent interface to study the morphology during initial stages of deposition at the buried interface. If the interaction between SSE and metal surfaces at the interface is weak, the morphology of the metal surface is rough after deposition. Conversely, for strongly interacting interface, flat interface is obtained. The energy of the total system is limited to a small region near the interface and the bulk of the metal away from the interface is distortion free and has negligible energy. The strength of interaction between SSE and metal surface at the interface is a key property in determining the morphology of the interface during deposition. Rough morphology is obtained for weak interaction and flat morphology is obtained for strong interaction. Increasing surface diffusion at the interface reduces the roughness of deposition for weakly interacting interface but does not change the morphology for strongly interacting interface. However, the energy near the interfacial region decreases with surface diffusion for strongly interacting interface.

7.2 Outlook

7.2.1 Machine learning in design of solid state electrolytes

Solid electrolytes are very promising towards safely utilizing lithium as metal anodes. There is urgency in creating solid state electrolytes with higher ionic conductivity and stable electrochemical and chemical properties with respect to lithium. Machine learning or artificial learning in conjunction with atomistic calculations is a likely avenue to speed up the design and development of new solid electrolytes (substitutional elements and respective fractions)^{268–271}. This design approach would also apply in search for new cathode materials.

7.2.2 "Cradle to death" accounting for footprint of batteries

Researchers and scientists are motivated to work on the problems and issues related to batteries as energy storage medium because of the belief that it would hail the renewable revolution. The footprint or green impact of batteries need to consider the cost in energy and environmental impact from mining and synthesizing the raw materials, intermediate processing as well as disposal of the batteries.

7.2.3 Recycle, reuse and maintenance of batteries and parts

One way to reduce the environmental footprint of batteries is to study and develop strategies for recycling the batteries or components of batteries. Economic studies of servicing or maintaining batteries is desirable. Since the proliferation of batteries in everyday use, throwing them away would cause loss of expensive and rare metals and degrade the environment.

APPENDIX A. INTERCALATION ANODES

Implementation of Transition events in Kinetic Monte Carlo Algorithm

A rejection free, partitioned search strategy KMC algorithm was used 74,130,272 . A two dimensional coarse-grained lattice grained model is used. The computational domain is periodic in x direction. At the anode and electrolyte interface, electrochemical reduction of Li⁺ ion occurs. The Li atom can subsequently diffuse into the graphite anode or it might reside on the anode surface. After some time, the Li atoms on the anode surface might form an aggregate. Two events are possible in this scenario. A Li⁺ ion might approach this deposit and an electrochemical reduction occurs or a Li atom belonging to the film might diffuse to its nearest neighbor location such that the integrity of the deposited film is maintained. At the anode and electrolyte interface, a single Li atom might diffuse on the graphite surface. Also, the Li atoms which are located at the interface and are situated at the edges of film might intercalate inside the graphite anode.

An occupancy matrix is maintained to indicate whether a particular lattice site is empty or occupied by a Li^+ ion or a Li atom. A matrix that stores rates for each ion or atom is calculated and updated after each KMC step. The steps for KMC algorithm are as follows

Calculate the total rate

(i) The total rate for diffusion of Li atoms inside graphite anode

$$\Omega_{diff_anode} = \sum_{i=1}^{N} R^{i}_{diff_anode}$$
(1)

(ii) The total rate for diffusion of Li ions in electrolyte

$$\Omega_{diff_electrolyte} = \sum_{i=1}^{N} R^{i}_{diff_electrolyte}$$
(2)

(iii) The total rate of diffusion of Li atoms on electrodeposited Li surface

$$\Omega_{diff_Li_surface} = \sum_{i=1}^{N} R^{i}_{diff_Li_surface}$$
(3)

(iv) The total rate of diffusion of Li atoms on graphite anode surface

$$\Omega_{diff_anode_surface} = \sum_{i=1}^{N} R^{i}_{diff_anode_surface}$$
(4)

(v) The total rate of electrochemical reduction rate on graphite anode surface

$$\Omega_{rxn_anode} = \sum_{i=1}^{N} R^{i}_{rxn_anode}$$
⁽⁵⁾

(vi) The total rate of electrochemical reduction rate on electrodeposited Li surface

$$\Omega_{rxn_Li_surface} = \sum_{i=1}^{N} R^{i}_{rxn_Li_surface}$$
(6)

The total rate is calculated as

$$\Omega_{tot} = \Omega_{diff_anode} + \Omega_{diff_electrolyte} + \Omega_{diff_Li_surface} + \Omega_{diff_anode_surface} + \Omega_{rxn_anode} + \Omega_{rxn_Li_surface}$$
(7)

Select the transition event

This requires two steps, first the class of event is selected (example diffusion of Li ion in electrolyte or reduction of Li⁺ ion on anode surface) and secondly, the location or identity of atom/ion on which this class of transition event is implemented. Figure A.1 shows a schematic where Ω_{tot} is the cumulative sum of different class of KMC events (for example diffusion of Li⁺ ion in electrolyte). To select the transition event to implement, generate a random number, γ_1 uniformly distributed on (0,1). The example in figure A.1 shows that

$$\Omega_{diff_anode} + \Omega_{diff_electrolyte} < \gamma_1 \Omega_{tot} \le \Omega_{diff_anode} + \Omega_{diff_electrolyte} + \Omega_{diff_Li_surface}$$
(8)

Therefore, diffusion of Li atom on electrodeposited Li film is selected.



Figure A.1 Schematic showing how to select the class of transition event.

To continue the example described above, the next task is to select the Li atoms that will diffuse on the surface of the electrodeposited film. Figure A.2 shows the schematic for how to select the particular Li that will diffuse to new lattice position. Generate a random number, γ_2 uniformly distributed on (0, 1). Select atom i such that



Figure A.2 Schematic showing how to select the position or entity at which transition event occurs.

Update structure and time

After the transition event in implemented, the matrix containing rates for all the processes and for all the lattice positions is updated for the first and the second nearest neighbors of the atom/ion.

To update time, a random number, γ_3 on (0, 1) is generated. The time increment is given by,

$$\delta t = \frac{-\ln(\gamma_3)}{\Omega_{tot}} \tag{10}$$

Computational Domain

To study the effect of domain size, the number of lattice points, N_x was varied from 25 to 225 at applied overpotential, η of -0.1V (vs. Li⁺/Li) and temperature of 248K and KMC simulation was repeated three times for each data set. The electrodeposition rate is the y axis and number of lattice points is the x axis. The electrodeposition rate is nearly constant if N_x is greater than 150 as seen in Figure A.3. N_x equal to 175 was used is all KMC simulations in our study. In the current KMC model, domain size of 175×200 lattice sites is used. The area of one square lattice grid is a_0^2 , where a0 = 2.46 Angstrom, is the lattice constant for graphite. So, the total domain size is about 43 nanometers in x direction and 49 nanometers in y direction.



Figure A.3 Effect of computational domain size on electrodeposition rate. The KMC simulations are performed at overpotential $\eta = -0.1$ V (vs Li+/Li) and temperature 248K.

APPENDIX B. PLATING AND STRIPPING AT METAL ANODE

Implementation of Transition events in the Mesoscale Kinetic Monte Carlo (KMC) Algorithm

Three processes that are included in the mesoscale Kinetic Monte Carlo (KMC) model during charging and discharging. Diffusion of metal ion in liquid electrolyte, diffusion of metal atom on the surface and reduction or oxidation for charging or discharging respectively. The probabilities for different processes are assigned to kinetic rates. A two dimensional lattice based KMC model is developed. A rejection free, partition search KMC algorithm is used^{74,78,272}. The computational domain is periodic in horizontal direction. N_x is the number of lattice points in the horizontal direction.

During charging, two set of matrices are maintained and updated. One is the occupancy matrix, which keeps track of the lattice sites that are occupied or empty. The other matrix is the charge matrix which keeps track whether an entity is a metal ion or a metal atom.

During discharging process, three set of matrices are maintained and updated. The occupancy and the charge matrix have the same definition as during the charging process. In addition, a connectivity matrix is created to keep track of metal atoms that are connected to the electrode and metal atoms that are disconnected to the substrate. A metal atom can be oxidized if it is connected to the electrode. Metal atoms not connected to the electrode are counted as dead metal.

For both charge and discharge process, the matrix containing the rate of all the processes is maintained and updated with each transition event.

The KMC algorithm involves the following steps.

Calculate the total rate

The total rate for diffusion of Li ions in electrolyte

$$\Omega_{ion_diffusion} = \sum_{i=1}^{N} R^{i}_{ion_diffusion}$$
(1)

The total rate for diffusion of Li atoms on surface

$$\Omega_{surface_diffusion} = \sum_{i=1}^{N} R^{i}_{surface_diffusion}$$
(2)

Total rate of reduction or oxidation for charging or discharging

$$\Omega_{reduction / oxidation} = \sum_{i=1}^{N} R^{i}_{reduction / oxidation}$$
(3)

N is the number of atoms and ions. Superscript i denotes the rate for a particular atom or an ion. The total rate is calculated as

$$\Omega_{total} = \Omega_{ion_diffusion} + \Omega_{surface_diffusion} + \Omega_{reduction / oxidation}$$
⁽⁴⁾

Selection of the transition event

A partial search strategy is used to select the transition event. A random number γ_1 uniformly distributed on (0,1) is generated. If $0 < \gamma_1 \Omega_{total} \leq \Omega_{ion_diffusion}$, then ion diffusion is selected. If $\Omega_{ion_diffusion} < \gamma_1 \Omega_{total} \leq \Omega_{ion_diffusion} + \Omega_{surface_diffusion}$, then surface diffusion is selected. If $\Omega_{ion_diffusion} + \Omega_{surface_diffusion} < \gamma_1 \Omega_{total} \leq \Omega_{total}$, then reduction or oxidation is selected depending on whether it is charging or discharging. Figure B.1 depicts this selection of the type of event schematically. In the example shown in Figure B.1, diffusion of metal atom on surface is selected.



Figure B.1 Schematic showing selection of type of the transition event.

The next step is to select the entity (specific ion or atom) for transition. In the example shown in Figure B.1, surface diffusion is selected. Figure B.2 shows schematically how to select the specific atom that will diffuse. Generate another random number γ_2 uniformly distributed on (0, 1). Surface diffusion of the ith atom is enacted.

$$\sum_{j=1}^{i-1} R_{surface_diffusion}^{j} < \gamma_{2} \Omega_{surface_diffusion} \leq \sum_{j=1}^{i} R_{surface_diffusion}^{j}$$

$$i = 1 \qquad i \qquad i = N$$

$$R_{surface_diffusion}^{i}$$

$$\gamma_{2} \Omega_{surface_diffusion} \qquad \Omega_{surface_diffusion}$$

Figure B.2 Schematic showing the selection of surface diffusion of the ith atom.

Update structure and time

After the implementation of the transition event, the occupancy and the charge matrix is updated. The rate matrix is updated for the first and second neighbor of the entity (ion or atom) undergoing transition. If a reduction reaction occurs, another ion is introduced such that the number of ions in the KMC computational domain remains constant. Then the occupancy and charge matrix are modified to account for the additional ion. The matrix containing rates is also updated for the additional ion and its first and second neighbors. If an oxidation event occurs during discharging process, the occupancy and charge matrices are updated as well as the rates of first and second neighbors of the atom that is oxidized. In addition, the connectivity matrix is updated to check if any new group of atoms have become detached from the electrode. Upon oxidation, an ion is removed from the computational domain so the number of ions remain constant throughout the discharge process. When an ion is removed, the occupation and charge matrices are updated.

To update time, a random number, γ_3 on (0, 1) is generated. The time increment δt is calculated as,

$$\delta t = \frac{-\ln(\gamma_3)}{\Omega_{tot}} \tag{S6}$$

Computational Domain

The two dimensional computational domain comprises of lattice grid of $(N_x \times N_y)$ sites where N_x is the number of lattice sites in horizontal direction and N_y is the number of lattice sites in vertical direction. To study the effect of domain size, N_y=100 is kept constant while N_x is varied. Figure B.3 shows the effect of domain size N_x for charging. Rate of reduction is the average slope of the number of reduction reactions with time. Rate of height is the average slope of height of deposition with time. N_x=175 is used in all KMC simulations based on the results shown in Figure B.3.

Figure B.4 shows the effect of computational domain during discharging. In Figure B.4 (a), the rate of oxidation is the average slope of number of oxidation reactions with time and in Figure B.4 (b), the rate of dead metal formation is the average slope of the number of dead metal with time. $N_x=175$ is used in all KMC simulations.



Figure B.3 Effect of the KMC domain size during charging. (a) Rate of reduction as the number of lattice points in horizontal direction, Nx is increased (b) Rate of height of deposition with Nx. The KMC simulations were performed at Pred=0.1, Pe=0.8 and Pf=0.1.



Figure B.4 Effect of the KMC domain size during discharging. (a) Rate of oxidation as the number of lattice points in horizontal direction, Nx is increased (b) Rate of dead metal formation with Nx. The KMC simulations were performed at Pox=0.5, Pe=0.4 and Pf=0.1.

APPENDIX C. EVALUATION OF DEAD LITHIUM AT LITHIUM AND LIQUID ELECTROLYTE INTERFACE

Transition events in Kinetic Monte Carlo Algorithm

The KMC model includes three processes, the diffusion of lithium ions in the electrolyte, the electrochemical oxidation of lithium at the electrode-electrolyte interface and diffusion of lithium at solid electrode interface. A rejection free and partial search KMC algorithm is used ^{74,75,272}. A detailed description of the algorithm is given in ⁷⁹.

The value of the parameters used in describing the three rates given by equation 2, 3 and 4 in Chapter 4 is listed in Table C.1. The local overpotential and temperature values are typical of battery operations. The range for ionic diffusion barrier is based on different molecular dynamics studies for different electrolyte composition. The activation energy for surface diffusion of lithium on (100) plane is 0.14 eV and 0.41 eV on (111) plane for hopping mechanism ¹⁸³. In the two dimensional KMC model, surface diffusion barrier values ranging from 0.14 eV to 0.25 eV is used to study the effect of surface diffusion on the process of formation of dead lithium. This range of surface diffusion barriers is sufficient to show that surface diffusion is one of the key factors in formation of dead lithium.

Symbol	Description	Value	Units
η	Overpotential	0.01 to 0.125	Volts
Т	Temperature	-25 to 50	°C
jo	Exchange current density	2 179	mA/cm ²
α _a	Anode charge transfer coefficient	0.3 117,179	
α_{c}	Cathode charge transfer coefficient	0.7 117,179	
a	Lattice constant for lithium	3.5 ×10 ⁻¹⁰	m
ΔE_{e}	Activation energy barrier for diffusion of	0.1 to 0.2	eV
	lithium ion in the electrolyte	139,180–182	
ΔE_s	Activation energy barrier for diffusion of	0.14 to 0.25 ¹⁸³	eV
	lithium atom on solid surface of the interface		

Table C.1 Parameters used in KMC model

Calculation of Surface Ratio

The surface ratio is used to characterize the average nature of the interface ⁴. Figure C.1 describes the procedure to calculate the surface ratio. If N1 is the number of lattice points on the envelope of the interface and N is the number of lattice points on the actual interface, then the surface ratio is defined as the ratio of N and N1. If the surface ratio is less than one, the interface is convex, if it is equal to one, the interface is flat, if it is greater than one, the interface is concave.



Figure C.1 Schematic describing how to calculate the surface ratio.

Computational Domain

In the two dimensional lattice based KMC model, N_x is the number of lattice points in the horizontal direction and N_y is the lattice points in the vertical direction. Initially, 50 layers are lithium, $(0 \le N_y \le 50)$ is lithium electrode and the rest is lithium ions distributed in electrolyte. The computational domain is periodic in horizontal direction. To study the effect of domain size, the number of lattice points in the horizontal direction is increased from 25 to 200 while the number of layers of lithium and the lattice points in the vertical direction is kept constant. In Figure C.2(a), the number of dissolved layers is plotted with increasing N_x and in (b), the number of layers of layers of lithium is plotted with increasing N_x . It can be seen that there is not strong dependence on the size of the computational domain. Based on the plots shown in (a) and (b), N_x =150 has been used in all KMC simulations.



Figure C.2 Domain size during stripping of lithium electrode. (a) Number of dissolved layers with increasing domain size Nx (b) Number of layers of dead lithium with increasing Nx. These studies were performed using overpotential of 0.01 V and temperature of 25 oC.

Experimental Details

All materials were handled in an Argon-filled glovebox (MBraun), with water and moisture levels below 0.5 ppm. A typical electrolyte with 1 M LiPF6 in 1:1 (volume ratio) ethylene carbonate/ethyl methyl carbonate (EC/EMC) (BASF) and lithium chips of 14 mm diameter and 0.75 mm thick (MTI) were used in this work. Celgard 2500 polypropylene separators were used in between two lithium electrodes. All the electrodes were assembled in CR2032 type coin cells. The stripped electrodes were harvested from the cells after discharge at 1 mA/cm2 and 2 mA/cm2. The stripped lithium metal electrode was examined and imaged under a Leica S9i Microscope. For each current density, three identical cells were assembled and cycled at three different temperatures, i.e. at -20°C, 20 °C and 40 °C respectively.

Image analysis

The amount of dead lithium is quantified based on the pixel intensity values. As the color of the lithium varies with passivation with electrolyte as well as the texture, we used a histogram based method to identify the threshold value instead of setting a manual threshold.

In addition to this, the imaging conditions may affect the outcomes significantly. In order to avoid this, all imaging conditions such as the sample orientation, working distance and the level of light were same for all the electrode images.

Image color thresholding was used to select the dead lithium particles by choosing a specific pixel color value as the threshold. The dead lithium particles exhibit particular range of pixel color values. The range is identified by calculating the mode from the histograms of dead lithium crystals. Figure C.3 shows the different thresholding algorithms applied for segmentation of the image. We use minimum method for threshold as it effectively helps us avoid errors caused by continuous structures such as ridges, pits in the electrode as well as the occasional dullness of the surface caused by the passivation of lithium with electrolyte from the dead lithium particles shown in the highlighted box in Figure C.3.



Figure C.3 (1) Original image of stripped electrode; (2) Binary Image after applying different thresholding algorithms on original image shown in (1) (a) Default Algorithm (b) Huang Algorithm (c) Intermodes Algorithm (d) IsoData Algorithm (e) Li Algorithm (f) MaxEntropy Algorithm (g) Mean Algorithm (h) MinError(I) Algorithm (i) Minimum Algorithm (j) Moments Algorithm (k) Otsu Algorithm (l) Percentile Algorithm (m) RenyEntropy Algorithm (n) Shanbhag Algorithm (o) Triangle Algorithm (p)Yen Algorithm. The minimum algorithm shown in (i) shows the binary image where the threshold is not affected by the surface roughness factor or dullness.

Once the threshold is set, the pixels with values greater than the threshold value will be discounted as the background. Only the pixels with values less than or equal to the threshold will remain. In our case, these pixels represent dead lithium particles. The image is binarized after

thresholding process for particle analysis. The black regions indicate dead lithium particles. The area of each particle is calculated by the product of the estimated number of pixels in the particle and area of a pixel. Figure C.4 (a), (b) and (c) illustrate the flowchart of image analysis for dead lithium quantification.

In order to map the surface morphology of the stripped electrode, a luminescence based surface plot is obtained using the hue, brightness and saturation of each pixel in the image. Based on the surface topography, the amount of light reflected by the surface varies. The pixel values range from 0-255, where zero represents black and 255 represents white. Point tips reflect specular light and hence appear white with pixel values around 255. Pits absorbs and diffracts light and hence appear dark, closer to pixel values around zero. Based on this, the surface of the electrode is reconstructed as shown in Figure C.4 (d) and (e).



Figure C.4 (a) Original image of stripped electrode; (b) Image after thresholding based on pixel values, black particles represent the pixels with values less than the threshold, the green part represents the pixel values above the threshold; (c) Binarization of thresholded image, black particles represent dead lithium crystals; (d) Image of stripped electrode with intense pitting of size 530×530 µm (200×200 pixels); and (e) Image reconstructed as surface plot based on the luminescence values of pixels.

The voltage and current profile of the Li-Li symmetric cells at different temperatures during the three-hour discharge is shown in Figure C.5(a) and (b) at 1mA/cm^2 and 2 mA/cm^2 .



Figure C.5 Voltage profile of a Li-Li symmetric cell cycled (a) at 1 mA cm2, (b) at 2 mA/cm2



Figure C.6 Original images of stripped lithium electrode (top view): at current density 1 mA/cm2 at (a) -200 C, (b) 200 C, (c) 400 C, and at current density 2 mA/cm2 at (d) -200 C, (e) 200 C, (f) 400C.

APPENDIX D. COUPLED ENERGETICS AND DEPOSITION MODEL FOR SOLID STATE ELECTROLYTE AND METAL INTERFACE

Figure D.1 describes the flow of the algorithm for coupled energetics and deposition KMC model. Following data is generated and maintained throughout the simulation, the occupancy matrix L (the entries in this matrix distinguish is a lattice site is occupied by a metal atom and whether it belongs to the interface), the variable matrix V (which records the row number of variables in the column vector X, corresponding to occupancy matrix L) and position vector X (x and y locations of all metal atoms).

The total transition rate, Ω_{total} is sum of total deposition rate, $\Omega_{\text{deposition}}$ and total diffusion rate at the metal surface at the interface, $\Omega_{\text{diffusion}}$. Procedure to calculate energy dependent deposition and diffusion transition rate is described schematically in Figure D.2. The energy of the total system which is obtained after minimization of current atomic positions, X is calculated and stored and is referred to as E_{old} in Figure D.1 and D.2. To calculate the diffusion rate of deposition rate at ith site at the interface, temporary copies of occupancy matrix, L, the variable matrix, V and position vector X is created with updated structure for either deposition or diffusion event. Energy minimization on the temporary vector X is performed and the minimum energy of the system in the updated configuration, E_{new} is calculated. The transition rate for deposition or diffusion at ith site is calculate based on E_{old} and E_{new} as shown in Figure D.2. The rest of the KMC algorithm is standard.

To minimize the total energy of the system, energy and energy gradient as function of atomic positions is formulated. Non-linear conjugate energy minimization algorithm with Polak-Ribiere varient is used ²⁷³. The line search algorithm in the conjugate gradient scheme uses Brent algorithm ²⁷³.



Figure D.1 Schematic of KMC process for deposition at the metal/solid electrolyte interface



Details of calculating deposition transition rates

Figure D.2 Details of calculating transition rates for diffusion and deposition processes

Computational domain

In our model, there are two variables which define the computational size of the problem, the number of lattice sites in the horizontal direction, N_x and the number of layers in the vertical direction, N_{layer} with respect to the interface. As the deposition at the interface occurs, the atoms near the newly deposited atoms are displaced to minimize the energy. The average distance between adjacent layers would change from the equilibrium lattice distance. However, far from the interface, this relative displacement between layers would decay. If there is no relative change in distance between layers, they do not contribute to the total energy of the system. To determine

 N_{layer} , 0.5 layer is added to the interface and energy minimization is performed. The number of layers is increased from 5 to 15 in increments of 2. The number of lattice sites in the horizontal direction, N_x is set to 100. The average distance of ith layer with respect to interface d_i is calculated. In Figure D.3, the difference in (d_i-d_i-1) is plotted with respect to number of layers, N_{layer} included in simulations. As bulk behavior is realized, (d_i-d_i-1) will become equal to a, the equilibrium lattice distance. The stiffness ratio, k₀/k is equal to 0.5 and equilibrium distance ratio a₀/a is 1.5 in these set of calculations. Based on the plots in Figure D.3, $N_{layer} = 11$ has been used in all subsequent calculations.

To determine the number of lattice sites in the horizontal direction, two layers were deposited at the interface. $N_{layer} = 11$ was fixed and N_x values were varied from 25 to 175 with increment of 25. The stiffness ratio, k_0/k is equal to 0.5 and equilibrium distance ratio a_0/a is 1.5 in these set of calculations. The probability of deposition is 0.5 in all these calculations. In Figure D.4, the time required to deposit two layers at the interface is shown and $N_x = 150$ is used for all KMC simulations.



Figure D.3 Number of layers required to obtain bulk behavior



Figure D.4 Time required to deposit two layers at the interface of metal/solid electrolyte interface as the number of lattice points in the horizontal direction, Nx is increased. The probability of reduction Pred is 0.5 in all the simulations. The stiffness ratio, k0/k is 0.5 and equilibrium distance ratio, a0/a is 1.5. Nx=150 is used all calculations.

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