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Local Investigations into the Nucleation and Growth of Lithium Dendrites using Scanning
Probe Microscopy

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Abstract

There is considerable technical interest in the improvement of battery technology, as it would allow for the enhancement and realization of many different applications, including the continued miniaturization of portable computational devices, plug-in electric vehicles, and intermittent power storage. Lithium metal represents a theoretical limit on the anode energy density of lithium-ion batteries, currently being considered for many of the aforementioned applications due for their relatively high power and energy density, however lithium metal is not used in rechargeable (“secondary”) batteries because it has the tendency to form dendrites that compromise the stability and rechargeability of the batteries in question. The currently used alternative lithium-ion anode, graphite, entails a modestly reduced cell voltage and approximately one tenth of the specific capacity (charge stored per unit mass of electrode material) compared with Li metal.

In this thesis, several behaviors of lithium metal battery-relevant materials are examined, and where applicable, the effects of cycling are examined in the low-current limit. Dendrite formation at higher current is relatively well understood in terms of electrolyte depletion leading to large deposition overpotential and nonuniform/inhomogeneous deposition as a result. Using highly local methods, such as those of Scanning Probe Microscopy, investigations of dendrite nucleation and the elucidation of local properties of battery materials that promote dendrite formation on relevant length scales have been performed. These experiments have previously been highly challenging to perform and examine in battery-relevant conditions over a significant

area. The understanding of these properties and the impact they have on dendrite formation will inform future attempts at battery design not just with lithium metal, but with other battery chemistries that can result in dendrite nucleation under applied electric field.

Acknowledgements

I'll admit this still doesn't feel entirely real, but this dissertation marks the conclusion of my doctoral studies. It's been quite a journey and while it seems far steadier when I look back on it, the route I took was not always certain. In a technical sense this is the easiest section to write, but this is also the one I am least prepared to write: I've received aid, counsel, and comfort from many people over the course of my studies, and condensing five years of gratitude onto a few pages seems daunting, to put it mildly.

Many things do until they're done, though, so I'd like to start by thanking my direct advisors: Dr. Charudatta Phatak and Dr. Seungbum Hong.

I learned to use the Scanning Probe Microscope that I would use to perform most of the research in this thesis from Dr. Hong, so in quite a literal sense I would not be writing this thesis today without his help. He was upbeat, attentive, and patient as I learned more about the instrument and the literature context of the first project I would undertake in my research at Argonne. I'm sure his students at KAIST are in capable hands, and expect I will hear of more exciting research by his group in the future.

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Chapter 1: Introduction

1.1 Batteries as electrochemical systems

Batteries are compact, isolated, electrochemical systems powered by a spatially separated reduction-oxidation (redox) reaction. All the precursors and reagents for this reaction are contained within the housing of the battery, and ideally their only interface with the outside environment or the devices they power is through an electrical contact at each electrode. An example diagram is shown below in figure 1-1, for the case of cation-mobile batteries such as all lithium-ion

cells:

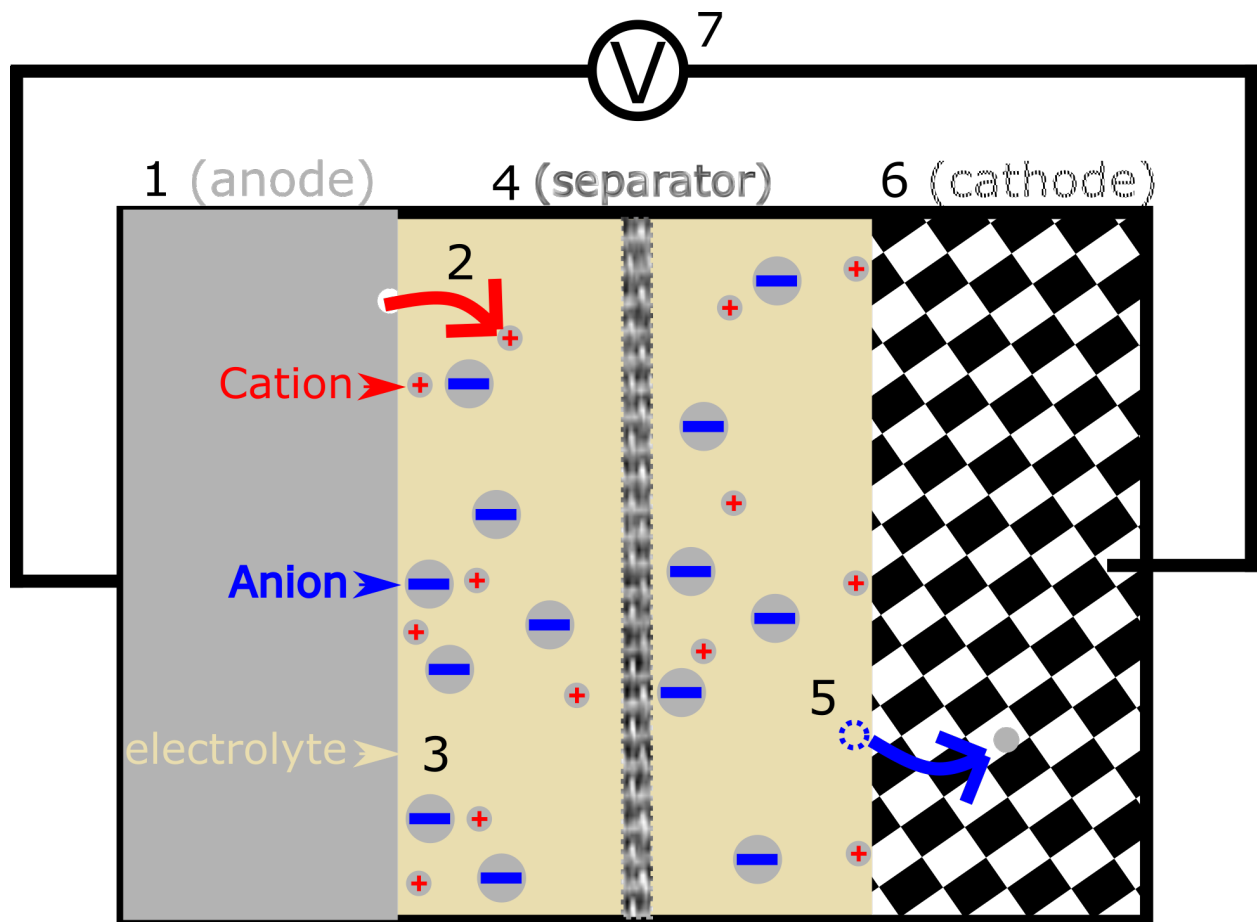
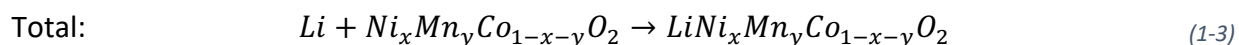
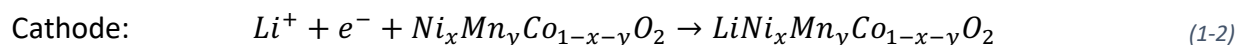
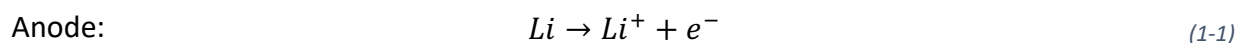


Figure 1-1: Example schematic of a Li-ion battery

The anode (1) performs an oxidation reaction (2) to produce a cation. This cation is conducted to the other electrode through the electrolyte (3) by diffusion, across a porous but insulating separator (4) whose purpose is to keep the conductive electrodes separate to prevent electrical short-circuiting. This cation is consumed by a reduction reaction (5), at the cathode (6), generating a pair of charges between the electrodes resulting in an electrical potential difference (7). The half reactions for this example lithium cell are as follows:



NMC is commonly chosen for its high reduction potential vs Li and relatively high current capacity. NMC has a layered oxide structure, where lithium intercalates into specific atomic planes, illustrated here by the checkered pattern of the cathode. This intercalation chemistry is a common feature of lithium ion batteries, as this behavior is also shared with the current most commonly used anode: graphite. In practice, intercalation into NMC can lead to large internal stress, so the particles are often milled to small size and mixed with an electrically and ionically conductive binder to improve cycle lifetimes and reduce capacity loss, necessarily at the cost of theoretical maximum energy density.

The chemical reaction inside a battery is spontaneous, but the separation of cathode and anode materials largely prevents their reaction until the terminals of the battery are electrically connected, and without the ability to discharge the potential forming at these terminals the half-reactions occurring at one or more terminal stall as they approach the electrochemical

equilibrium of their respective half-reactions at their respective electrodes. When the terminals are connected, the electric potential that developed previously to impede the half reaction occurring at each electrode is removed, and the reaction becomes spontaneous again. This reference to chemical spontaneity is not incidental: since the most stable battery processes occur close to equilibrium and/or in steady-state conditions, Gibb's free energy can be used to predict the theoretical maximum performance of a given battery chemistry based on the reaction occurring and the valence of the charged species that is exchanged in the reaction. More specifically:

$$V = \frac{-\Delta G}{nF} \quad (1-4)$$

Where V is the Electrical Potential Difference produced by the cell (in Volts), if ΔG is the molar free energy change of the reaction occurring (in J/mol), n is the number of electrons exchanged in the two half-reactions that make up the total reaction occurring, and F is Faraday's constant (the charge, in coulombs, of one mol of electrons).

Batteries are technologically interesting because they occupy a relatively unique niche in portable electrical power delivery. This is illustrated with a plot known as a Ragone plot, a log-log plot of the power density vs the energy density of various devices that can supply electrical power (ex: batteries, fuel cells, and capacitors), examples thereof are found occasionally in comparative reports on power sources¹. Of note in these graphs is the ability to draw equally spaced straight parallel lines that represent characteristic discharge times. The unique niche batteries fill is a discharge time between several minutes, and several hours. Current capacitor technology would find it exceedingly difficult to discharge for much longer than one minute, and current fuel cell

technology has somewhat lower specific power than batteries do but considerably higher energy density that is promising for large installations like grid scale power storage, but difficulties associated with instability and/or low power at room temperature have presented barriers to the adoption of fuel cells.

1.2 Applications and associated concerns of batteries

Within this niche of portable electrical power, for most applications the relevant properties of a battery are the volume taken up by the battery, the power supplied by the battery, and the mass of the battery, each evaluated at the amount of energy storage required for the application in question. Lithium-ion chemistry (that is, a battery reaction where the species conducted through the electrolyte and involved at both half-reactions is lithium) is well-suited to many of these for several reasons. Firstly, lithium reduction chemistry is relatively energetic: a table of standard reduction potentials will indicate a lithium ion reduction potential of -3.04 V vs the Standard Hydrogen Electrode², making it the lowest negative reduction potential of any single element. Although this only explicitly applies to a lithium metal battery, many other commercially used lithium ion electrode compounds make good use of this: Nickel Manganese Cobalt oxide (NMC) is a common rechargeable battery cathode whose peak cell voltage is in excess of 4 V vs Li/Li⁺, and graphite functions as an anode with a lithiation voltage of ~0.15 V vs Li (approx. one tenth of a volt lower energy as an anode)^{3,4,5}.

While a battery's thermodynamic maximum energy output may be fixed by Gibb's free energy, as addressed previously, the power output of a battery is strongly dependent on how quickly the electrochemical processes that supply current to the terminals can occur. It is at this

point that a discussion of the kinetic losses in batteries becomes important. The battery will produce as much current as it can under a given load but producing more current comes at a penalty to the cell voltage: some amount of energy is required to cause the reaction to proceed under finite current conditions. Because these losses are associated with energy required to move charged species, they're often expressed as "overpotentials": an energy expended per unit charge that permits the reaction to proceed under conditions that aren't the infinitely slow thermodynamic limit. These are often illustrated in polarization curves, such as the one on the following page. Total cell voltage as a function of applied current is indicated by the thick curve, color-coded by the largest contributing overpotential of the three indicated by the thin curves: activation losses associated with the biasing of the electrochemical reactions at both electrodes as described by the Butler-Volmer equation, ohmic losses due to various cell conductivities (both ionic and electronic), or losses associated with the changing concentration at each electrode in the steady state limit that result from diffusion and the ionic current required to produce the current density below in figure 1-3.

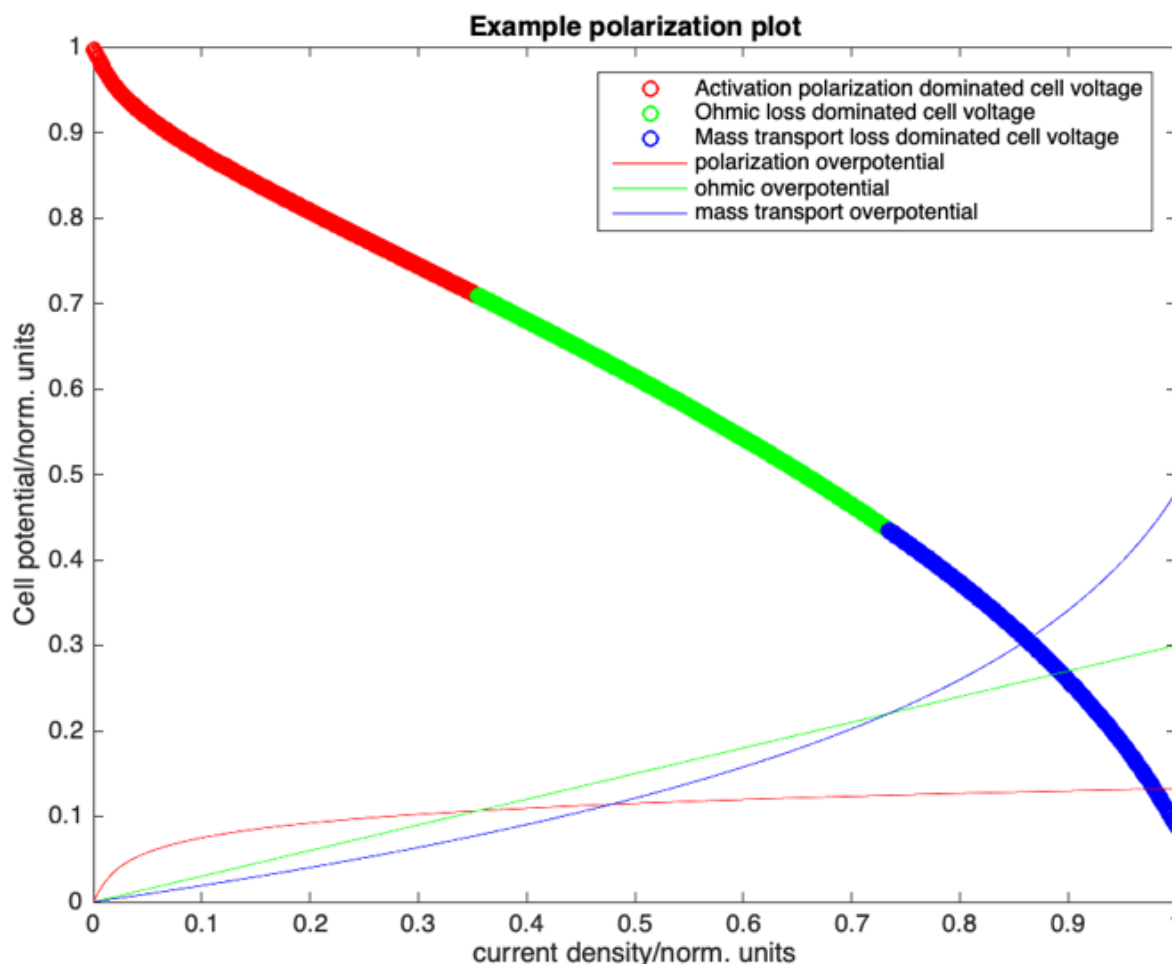


Figure 1-2: Example plot of overpotential sources in an electrochemical cell

From a scaling factor argument, in order from least to greatest current, the dominant source of cell resistance and thus energy losses come from: (i) activation losses due to biasing the electrode such that the electrochemical reaction proceeds at the interface between electrolyte and electrode, which scales logarithmically with current in the Tafel (high-current) limit (a more detailed description of the Tafel equation, from which this limit gets its name, follows below); (ii) ohmic losses that relate to many processes in the battery, including energy lost to allow a net conduction of ionic species from one side of the electrode to another, maintaining a concentration gradient in the salt electrolyte, and pure ionic and electronic

conductivity concerns at the electrodes. As the name suggests, these overpotentials scale linearly with current; (iii) and mass-transport losses due to effects associated with the changing concentration of charged species at the electrode surface; when the current demand on the cell is so high that thermal diffusion cannot maintain a significant concentration of salt species at one electrode, this scales as $\log((j_L - j)^{-1})$, where j is the current density the battery is being operated at, and j_L is the “limiting current density”. This overpotential diverges as current density approaches a limiting current value defined by the maximum steady-state ionic current achievable from thermal diffusion in the electrolyte. These sources of overpotential will be discussed in further detail in the following section.

Activation losses are thusly named because the resulting overpotential is used to cause the chemical reaction occurring at each electrode to proceed. At the electrode, both the forward and reverse reactions are occurring, and so the net current that flows can be expressed as the difference in these reaction rates. Each reaction’s rate can be expressed in the Arrhenius form, a brief description of which can be found on pages 360 and 361 of “Molecular Driving Forces”⁶:

$$r_1 = Ae^{\frac{E_A}{RT}} \quad (1-5)$$

The above phrasing of the Arrhenius equation allows you to express the rate at which a reaction occurs, r_1 , as the product of a proportionality constant sometimes called an “attack frequency” A , and a Boltzmann factor. This Boltzmann factor is expressed above in molar quantities, or more explicitly as Euler’s number raised to the power expressed by the ratio of the molar activation energy of the reaction (E_A) and the product RT of the gas constant R and the absolute temperature T .

Because the reaction necessarily occurs at the interface between electrode and electrolyte, we can state that this is proportional to current density, or more specifically, when defined by a reference state at equilibrium, the forward (j_+) and reverse (j_-) current densities may be expressed as:

$$j_+ = j_0 e^{\frac{E_A}{RT}} \quad (1-6)$$

$$j_- = j_0 e^{\frac{E_A}{RT}} \quad (1-7)$$

When the reference state is defined at equilibrium, the forward and reverse reaction rates are equal, so the preexponential factor is the same in both cases (j_0 here is referred to as “exchange current density” for this reason: it expresses the baseline rate at which the reaction occurs). It is useful to express this equation in terms of the effect that overpotential has on the reaction rate: because one of these reactions produces a charged species, the difference between initial and final states is offset by the electrical energy supplied by the overpotential. This change in activation energy is expressed in molar quantities as the following:

$$\Delta E_A = nF\eta \quad (1-8)$$

Where n is the valence of the charged species produced, F is Faraday’s constant, η is the overpotential supplied to this part of the reaction, and ΔE_A is the change in activation energy of the reaction. While this difference is due to the existence of a charged species in the reaction, in practice not all of this free energy difference is applied to change the magnitude of the activation barrier on the side of the reaction containing the charged species. This is accounted for in a parameter between zero and one known as the charge transfer coefficient (α)², which expresses

what fraction of the overpotential applied is allocated to raise/lower the activation barrier on one side of the reaction vs lowering/raising the other. Applying this form of the activation energy and noting: 1. that the charge transfer coefficient for the forward reaction must be opposite that of the reverse reaction due to the opposite pathway involved, and 2. that the applied overpotential is effectively reversed for the reverse reaction when compared with the forward reaction, and then expressing the net current density in these terms yields an equation for the behavior of current density produced at an electrode as a function of overpotential applied to the reaction. The equation is known as the Butler-Volmer equation, given in this form on page 90 of O'Hayre's text²:

$$j = j_0 \left(e^{\frac{\alpha n F \eta}{RT}} - e^{-\frac{(1-\alpha) n F \eta}{RT}} \right) \quad (1-9)$$

Where, as previously, j is the current density produced by the electrode, j_0 is the exchange current density, RT is the product of the gas constant R and absolute temperature T , α is the charge transfer coefficient for the reaction, n is the valence of the exchanged species, F is Faraday's constant, η is the applied overpotential to this electrode, and e is Euler's number.

Similarly, in the case of relatively large forward-biased activation overpotential, one can imagine that the reverse current density approaches zero. Assuming the overpotential is sufficiently large that the second term in this equation is negligible and taking the logarithm of both sides of this equation produces what is known as the Tafel equation², an approximation to the Butler-Volmer equation sometimes used in the case of high current density. A similar form of this equation is shown in O'Hayre's text on page 98.

$$\ln(j) = \ln(j_0) + \frac{\alpha n F \eta}{RT} \quad (1-10)$$

Where the terms in this equation (j , j_0 , R , T , α , η , n , and F) are the same as the previous equation. This equation illustrates the asymptotically logarithmic dependence of current density on overpotential at the electrode. It should be noted that this equation and the Butler-Volmer equation (and consequently, the Tafel equation) only address the reaction occurring at one electrode. The reaction occurring at the other electrode may have vastly different parameters based on the different reaction occurring there, but electrostatic equilibrium requires that the current produced at one electrode be consumed at the other, so the net current densities at the electrodes are such that the total currents produced at each electrode are equal in magnitude and opposite in direction.

Ohmic losses are thusly named because they obey Ohm's law. Both electronic and ionic conductivity under bias can result in this. In cases of composite cathodes, such as the NMC in the model cell at the start of this chapter, conductivity can be improved by adding more conductive binder (at the cost of energy and power density) or milling finer particles of active material (up to a point, and at the penalty of increased manufacturing cost).

Mass transport losses occur because when the cell is being operated, a concentration gradient in the conducted species forms. This provides the ionic current between electrodes that allows the reaction to proceed, like in the case of steady state diffusion by Fick's diffusion law, but because the concentrations of species in the electrolyte are different from equilibrium this has two effects: the first being to reduce the exchange current density at one electrode (because

fewer species are there to react per unit area), and the second is to reduce the free energy of the half-reaction occurring at both electrodes (because the concentration is higher than equilibrium where the conducted species is produced, and lower than equilibrium where it is consumed). More specifically in the first case, the exchange current density j_0 scales linearly with concentration. Because the steady state concentration gradients for Fick's diffusion law are linear, one can define a limiting current j_L above which Fick's diffusion law cannot supply the ionic current consumed at one electrode continuously based on the diffusion constant of the electrolyte, the bulk average concentration of salt species, and the distance separating the electrodes. This has the following form, as derived in O'Hayre's "Fuel Cell Fundamentals"² on page 175.

$$j_L = nFD \frac{c_R^0}{\delta} \quad (1-11)$$

Where j_L is the limiting current, n is the valence of the conducted species, F is Faraday's constant, D is the diffusion constant of the electrolyte (assumed to be constant w.r.t. salt concentration, an assumption that can be invalid in the case of Li-ion battery electrolyte⁷), δ is the separation of the electrodes and c_R^0 is the bulk average concentration of the electrolyte. The full derivation of this overpotential from these sources is too long to reproduce here, but can be derived from: the Butler-Volmer equation, the variation in chemical potential of a species as a function of concentration, and the linear dependence of exchange current on reactant concentration. The overpotential due to these losses takes the following form as illustrated in the aforementioned text on page 178²:

$$\eta = \left(1 + \frac{1}{\alpha}\right) \frac{RT}{nF} \ln \left(\frac{j_L}{j_L - j}\right) \quad (1-12)$$

Where the terms in this equation (j , j_L , R , T , α , η , n , and F) are as defined previously in equations 1-5, and 1-7.

It should be noted that lithium ion chemistry is exceptional in terms of both energy and power density⁸. The diffusive properties of the commonly used LiPF₆/carbonate based electrolyte leave something to be desired when compared with the potassium hydroxide electrolytes commonly used in single use alkaline batteries and rechargeable cells such as Nickel metal hydride. The carbonate based electrolyte displays poorer performance both in terms of absolute ionic conductivity and in terms of the fraction of mass transport overpotential used to move the species that participates in the electrochemical reaction rather than its counter-ion (a quantity referred to as “transference number”)^{7,9,10,11}. In practice, however, the cells and relevant separators that prevent electrode contact can be made with total widths as low as tens of microns thick, so that the effects this has on power output are mitigated¹². The exchange current densities are on the same order of magnitude at room temperature: approx. 3 mA/cm² for a lithium ion battery, and varying between 2.15 and 3.314 mA/cm² for a nickel metal hydride cell^{13,14,15}. Differences in these application-relevant properties, then, come down to differences in the cell voltage, cell construction, and the specific and gravimetric capacities of the limiting electrodes (~100 – 200 mAh/g for high voltage Li-ion cathodes⁴, and 200 - 300 mAh/g for either electrode of a NiMH cell^{16,17}).

Having illustrated the unique benefits and technological relevance of the lithium ion battery, and the potential that lithium metal has to improve it, the current state of research of these materials should be examined.

1.3 Complications to lithium metal

Lithium metal was the original choice for use in a lithium ion battery, but it was never useable as a secondary (rechargeable) battery in a commercial setting due to its tendency for dendrite formation and associated cell failure by short-circuit, capacity loss, or thermal runaway. Attempts have been made since then to understand why lithium performs thusly, and if possible, find ways to limit or reduce this behavior. Of interest are both the physical and chemical variations of the anode surface that occur under cycling, as inhomogeneities in the Solid-Electrolyte Interphase (SEI) that forms on the surface of lithium under cycling conditions can impact the diffusion of lithium to and from the surface. Because lithium is a relatively light element, sensitive to ambient atmosphere (such as moisture and, to a lesser degree, nitrogen), and prone to dynamics on a scale less than 1 μm it has been relatively difficult to characterize. Before introducing the previous work performed to examine this system in full detail, the unique features of Li (and to a lesser degree, Li-ion) batteries must be introduced.

1.3.1 Solid Electrolyte Interphase

One difference between Lithium batteries and several competing battery chemistries is the tendency of lithium to react with its electrolyte, forming SEI. The electrical potential differences at which these cells operate span a significant electron energy range, often in excess of the electrochemical stability window of the electrolyte species. If the potential difference

between electrodes is larger than this stability window, one or both electrodes will undergo a reaction with the electrolyte in some form, subject to either an oxidation or reduction process depending on the conditions inside the cell. While it is related, it should be noted that this electrochemical stability window is often different from the HOMO-LUMO gap, as the latter is purely an electronic structure calculation for the molecule and the former involves the possibility of chemical reactions and the rearrangement of the chemical species involved¹⁸. For the most commonly used electrolytes in lithium ion cells though, this process is self-limiting: the reaction between electrode and electrolyte forms an interphase that prevents further reaction, passivating the surface as illustrated in figure 1-4 (a figure from an investigation of the electrochemical evolution of carbon-based Li-ion cells)¹⁹. As discussed in this source and others^{20,21,22,23}, a similar process can occur at the cathode where the operating voltage of the battery causes reaction between the electrolyte and other components of the cathode, but it is usually less relevant than anode SEI due to the latter's effect on the possibility of dendrite formation.

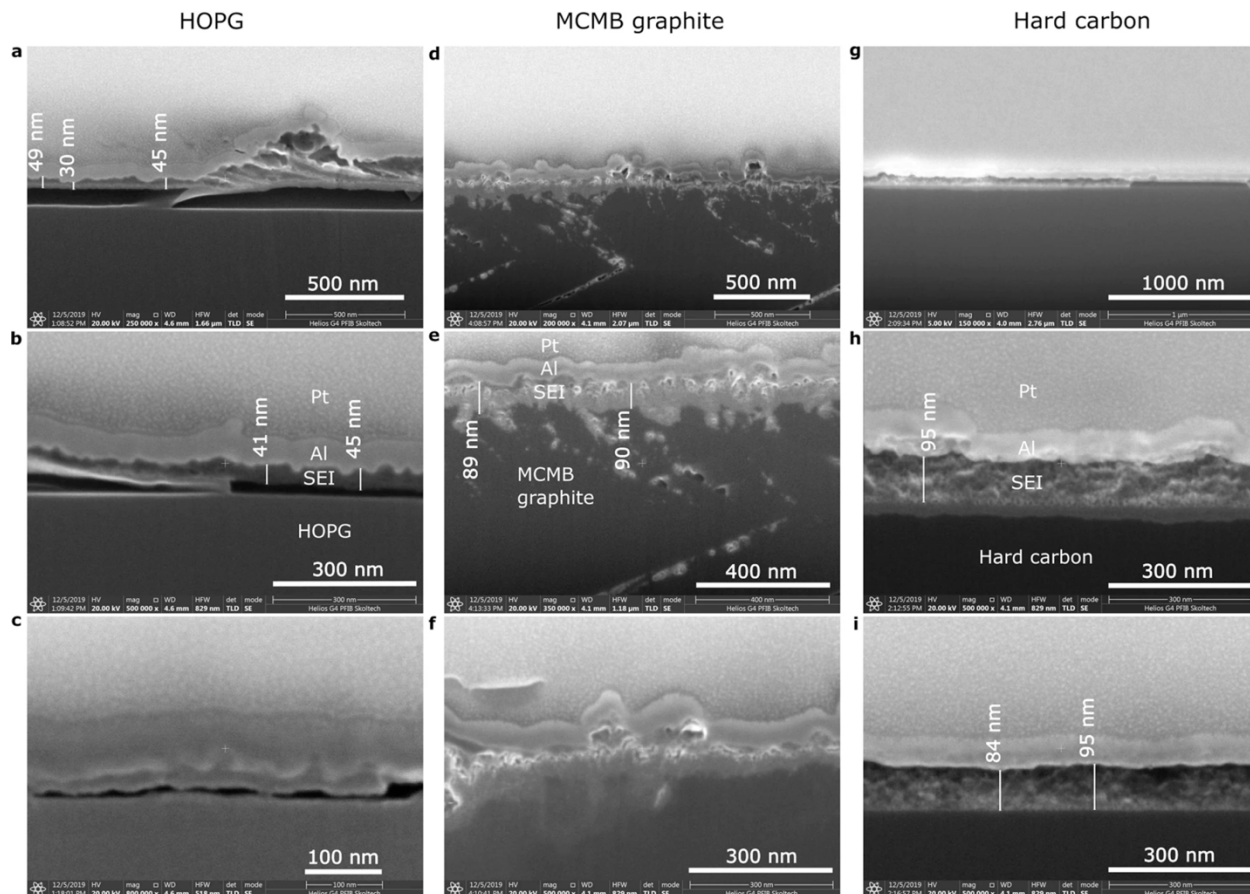


Figure 1-3: SEM image of carbon anode surface with SEI accumulation, from reference¹⁹ shared under Creative Commons Attribution 4.0 International License

Because this layer forms the interface between the electrolyte and the anode and has a significant effect on the mechanism by which lithium deposits on the surface of the anode, numerous attempts have been made to optimize the behavior of the electrolyte under bias^{24,25} the stability of the electrolyte against the electrodes in the conditions of cycling^{26,27,28,29,30} and even making chemical changes to the solvent through the additions of additives whose functions range from modifying the composition of the SEI that forms to tuning the stability of other compounds and modifying the solution behavior of ions in the electrolyte^{31,32,33}, or to substitute the native SEI entirely with an engineered protective layer^{34,35}.

1.3.2 Dendrites

As mentioned in section 1.3, the formation of dendrites is problematic for rechargeable battery applications. Dendrites are branching structures of deposited material, which are problematic for a number of reasons, including the increased surface area that consumes more of the electrolyte (a point illustrated elsewhere in literature³⁶, but to be discussed later in this thesis) resulting in reduced capacity and lower conductivity, and the possibility of such a conductive metallic structure causing short-circuits inside the cell, which has resulted in fire and explosion hazards previously³⁷. One example of which is shown in figure 1-5 below (upper row), with comparison to a tin alloy supported lithium anode (lower row) in the same cycling conditions. Though this demonstrates considerable success in cycle lifetime, the reported results fall somewhat short of the approximately 1500 cycles that would correspond to a daily recharge cycle with use for 5 years, a common target for mobile electronics and a lower bound for electric vehicle applications³⁸.

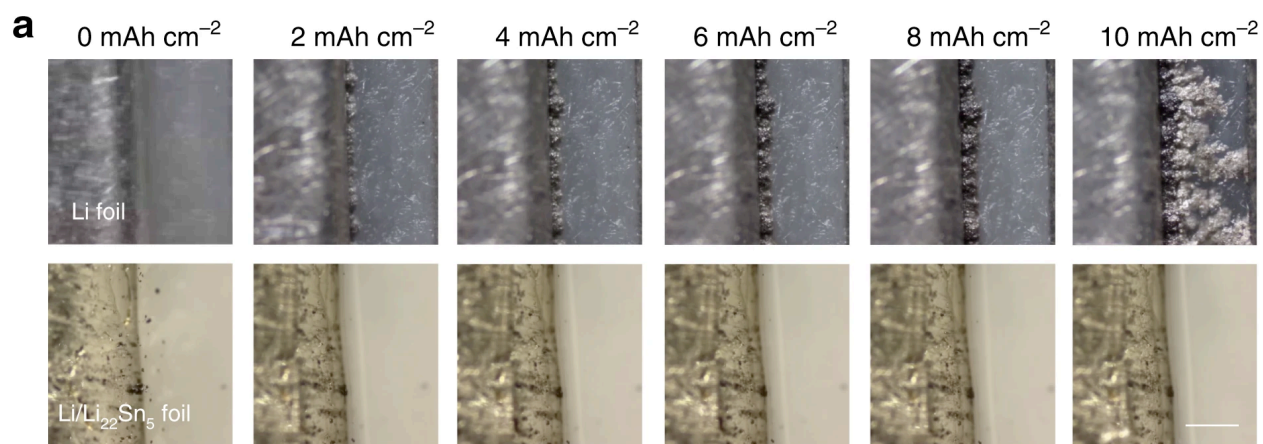


Figure 1-4: Optical microscopy illustration of lithium dendrites, from reference³⁸ shared under Creative Commons Attribution 4.0 International License (scale bar: 50μm)

Dendrites in this system are different from, but share their name with a similar feature seen to form in alloy structures, one discussion of which can be seen in “Phase Transformations in Metals and Alloys” on pages 215 – 220³⁹. Unlike the alloys discussed in this work, dendrites as they occur in batteries form under an electrical potential gradient that supplies the spatial variation in the free energy of solid deposition. One interesting difference noted between electrochemical dendrites and the dendrites that form by constitutional supercooling is that rather than pure diffusion, the concentration profile in batteries is subject to electrical interactions. As a system involving charged species and interfaces, batteries form an electric double layer (EDL), where local concentrations are not determined exclusively by diffusive properties, but also by the presence of local electric potential. A simple discussion of this is included on pages 456-461 in “Molecular Driving Forces”⁶, and a more complete one that addresses the conditions in lithium ion batteries can be found in literature⁴⁰. This is glossed over in the derivation of the Butler-Volmer equation under the assumptions of transition state theory, but has relevance to the differences in the mechanisms of dendrite formation between the two systems.

In alloys, dendritic formation occurs in relatively periodic cellular structures. This is theorized to occur because the alloy solidification case of dendrites involves a modification to the concentration of the solution in the areas surrounding a growing dendrite that significantly affects the free energy of solidification in the surrounding areas³⁹. Rather than a simple solution structure, the electrolyte in batteries often involves relatively tightly coordinated solvated complexes, which must be broken or formed as ions exchange between the inner and outer

Helmholtz layers of the EDL^{40,41}. If a local excess of deposition were to occur in steady state battery conditions, it would not induce dissolution without a significant disruption to the electric double layer, and even if that were the case the un-deposited ions would be adhered to the surface electrostatically until a solvation shell could form for them^{41,42}, providing a further barrier preventing these ions from affecting the local concentration of ions in solution. This inability to eject local concentration excesses to the surrounding solution, owing to the formation of a double-layer structure and the necessity of solvating ionic species in solution, precludes dendrite formation in batteries under steady state conditions from occurring by the same mechanisms that occur in alloys.

Conditions analogous to those of alloy dendrites can be achieved in these systems under certain conditions, and indeed fractal structures have been observed, but these require biases in excess of what thermal (as opposed to drift-) diffusion can maintain in a steady state⁴³. This departure from steady state conditions of mass balance prevents the regeneration of the EDL, resulting in a growing space charge region; this is described through the use of a critical current density required to exceed the limits of thermal diffusion, and a time at which the electrolyte near the anode is depleted of salt species (known as Sand's time)^{44,45}. Indeed while in some cases it is possible to reproduce well-oriented dendrites, even ones with apparent crystalline anisotropy behavior, this is not seen in the cases of sufficiently large electrolyte salt concentration (as is common in batteries to improve their conductivity)⁴⁶. Furthermore, while the Chazalviel model of electrolyte depletion accurately predicts the formation of dendrites in

certain conditions, and the speed at which these dendrites grow, it is not sufficient to describe inhomogeneous lithium deposition in all conditions^{47,48,49}.

The Chazalviel model predicts dendrite formation only for current densities in excess of a limiting value, and after a certain time required to deplete the electrolyte concentration at the electrode. This is not the only limitation of this model: the Chazalviel model, as well as the constitutional supercooling model of dendritic solidification, propose tip-growing dendrite formation but the dendrites that form in batteries appear to experience root-growing behavior at first, with ancillary deposition and possible densification of dendritic structures occurring afterward in cases where cell failure is not immediate^{47,48,50}.

1.4 Previous approaches to Li metal battery research

The original work that is the subject of this thesis primarily uses Scanning Probe Microscopy to examine the nucleation of dendrites and the evolution of the lithium anode, and in the following section I will review previous efforts to characterize the behavior of lithium under electrochemically relevant conditions, and explain why AFM was an appropriate technique to examine this phenomenon, with comparison to standard Optical Microscopy, X-ray measurements, Electron Microscopy methods, and computational methods.

1.4.1 Optical Microscopy

Optical microscopy is of course limited by the Raleigh criterion. The finest details resolvable with this method are on the scale of the wavelength of light used to examine it: In the visible spectrum, this corresponds to a wavelength of between ~300 nm and 800 nm. This is usually sufficient to observe large mossy structures, with diameters on the order of a micron, but

the smallest dendrites have diameters on the order of 100 nm. Importantly, any characterization of the surface of said dendrite must necessarily resolve even smaller features than that. Despite these limitations, previous work³⁶ with optical microscopy has been used to illustrate a concept known as Sand's time, specifically in this case referring to the time at which dendrites begin to form because the consumption of conducted species by the lithium anode exceeds the maximum rate at which thermal (as opposed to drift-) diffusion can supply lithium ions to the surface. When this happens, a space-charge region forms near the surface of the electrode, causing thin dendritic deposits of lithium to form under large overpotential, which in turn will also consume the electrolyte⁴⁴. This optical microscopy work illustrates that the consumption of electrolyte species by SEI formation has an appreciable effect on the maximum sustainable current of the cell, above which uncontrolled dendritic formation occurs after Sand's time.

1.4.2 X-ray methods

X-ray diffraction and tangentially related chemical characterization techniques are of interest to analyze many solid materials, but lithium is one of the lightest chemical elements. As such, it is not possible to observe chemical contrast by X-ray analysis (eg: Energy Dispersive X-ray Spectroscopy (EDXS or EDS)) in most cases, as its small nucleus has a relatively low X-ray cross-section and at an energy that would be blocked by the detector-protecting window of most setups (commonly, these windows are made of the slightly heavier beryllium). Nevertheless, attempts have been made to examine the formation of lithium dendrites on electrode surfaces by diffractive properties under high-intensity sources such as synchrotrons⁵¹. This relatively recent work⁵¹ showcased X-ray microtomography images of cycled symmetric lithium cells with

a polymer electrolyte, and highlights a possible source of dendrites in lithium: a subsurface structure that forms shortly after the cell is initially cycled. It is unknown whether these formations are generic to lithium metal, or unique to the polymer electrolyte used in their experiment; or whether they are a consequence of impurities/preconditioning or whether they form randomly under charging conditions, although the authors suggest that trace contaminations of LiN_3 that were present in the source material might be responsible. What is known about them is that there appears to be a crystalline material formed at the subsurface “root” of the dendrites observed, that was not identifiable in images before the material was cycled. What is known, based on subsequent tomography work⁵² is that dendrite formation by this so-called defect-driven failure mode is dependent on current density. Below a cycling current density of 0.08 mA/cm^{-2} some cells did not suffer from local deposition failure, lasting approximately 18x as long on average compared with those that did suffer failure from either dendritic or globular deposits of lithium before failing due to preferential deposition at a thin spot in the electrolyte. Below 0.04 mA/cm^{-2} none of them suffered local deposition failure (that is, shorting due to dendrites or globular depositions that span the thickness of the electrolyte).

1.4.3 Electron Microscopy

Electron microscopy methods provide contrast based on material interaction with an electron beam, either with relatively low energy backscattered and secondary electrons being reemitted from the surface as is the case with Scanning Electron Microscopy (SEM), or based on the diffraction pattern of a coherent electron beam that passes through the sample as a deBroglie matter wave as is the case with Transmission Electron Microscopy (TEM). SEM is useable to

obtain information about the morphology of cycled lithium, as was illustrated in several of the previously cited works, but the sample vacuum conditions usually require that the sample be removed from electrolyte and placed under vacuum, a change that may be damaging to important structures such as the SEI that forms on the surface. While lithium's electron interaction is much more readily accessible in a lab setting than its interaction with X-rays is, the relatively light nucleus results in a K-alpha line of 55 eV⁵³, meaning its signal is difficult to observe in most cases and impossible to observe on detectors that have a beryllium window.

While transmission electron microscopy is useable on lithium metal, it is hard to extract quantitative information from lithium beyond its morphology. Interaction cross section and detector issues as mentioned previously stymied the use of X-ray spectroscopy methods in TEM, but Electron Energy Loss Spectroscopy (EELS), is also confounded: The edge corresponding to lithium rests at ~55 eV, which is close to the plasmon peak of the material and also somewhat easily confounded by the presence of heavier elements, such as the transition metals used in lithium ion battery cathodes such as NMC. While the complications stemming from the presence of heavy metals can be avoided by using a symmetric cell (which would not contain these transition metal compounds), because the lithium edge rests so close to the plasmon peak quantitative analysis of this edge is confounded by surface information in the exposed area. While many sample preparatory methods are either difficult or incompatible with lithium metal, recent work by Yi Cui et al. developed a technique by which the lithium is deposited on a conductive TEM grid under bias, then removed from the electrolyte with the grid itself and

submerged in liquid N₂ to preserve its structure and prevent beam damage during the acquisition of high resolution images²².

1.4.4 Computational Methods

Computational methods allow for the examination of dynamics in a system that would be next to impossible to examine by experimental means with any significant certainty. Dendrite formation, as illustrated in the previous works, generally starts on the scale of microns, placing this firmly within the realm of mesoscale computation, and thus likely to take significant amounts of computation time to examine in significant detail. Additionally, until relatively recently it was difficult to simulate atomistic chemical interactions appropriately in even moderately sized simulations⁵⁴, a problem confounded further by the diversity of chemical species, and the variable and still somewhat uncertain chemical makeup of the passivating SEI layer that forms on the surface of lithium when exposed to electrolyte. Nevertheless, atomistic interactions can be simulated, and from the ability to simulate these chemical interactions some insight may yet be gained as modelling efforts improve⁵⁵. Even without the ability to accurately simulate chemical reactivity on significant time and length scales, previous computational works have modelled Li and Mg behaviors on the atomic scale in an attempt to reveal the physical mechanisms behind the more uniform deposition behavior observed in magnesium when compared with lithium⁵⁶. The conclusions in this paper suggest a thermodynamic origin for the dendritic failure of lithium: because Li has an insufficiently large surface energy, it is possible for dendritic structures to form (as compared with magnesium, where this behavior is absent). It should be noted that it is still thermodynamically favorable to form “bulk” Li over “surface” Li, and as such the formation of

dendrites is a non-equilibrium process. In contrast, a paper published subsequently⁵⁷ argues from cohesive energy calculations (GGA DFT) and coordination numbers that Mg-Mg bonds are not stronger than Li-Li bonds (it should be noted that 2nd nearest neighbor interactions were significant in Li modelling in the EAM used in the previous paper⁵⁶, bringing the total coordination number of Li to 14 in order to accurately model it, which suggests that the concept of simple atomic bond strength might not be meaningful in this context), and that instead the differences result from significant differences in homoepitaxial adsorbed atom (adatom) interactions: Mg has a significantly larger attractive interaction energy between two adjacent adatoms when compared with Li, and this interaction was better sustained over next-nearest-neighbor adatom locations. This, coupled with a reduced barrier to surface diffusion along the lowest energy surface, is what the authors conclude contribute to the difference in dendrite formation properties in magnesium as compared with lithium.

1.4.5 Scanning Probe Microscopy

Scanning Probe Microscopy (SPM, also referred to as Atomic Force Microscopy or AFM), use a sharp physical probe, frequently with a nominal end-radius less than 100 nm in size, to probe sample properties in a highly local manner. AFM probes are usually made of silicon, etched and ion-beam milled from a well oriented silicon wafer. This probe is situated at the end of a long ($\sim 100\text{ }\mu\text{m}$), thin ($\sim 5\text{ }\mu\text{m}$) cantilever, whose height above the sample is controlled to nanometer precision with piezoelectric actuators. Under various conditions of operation, the tip's position is measured by shining a laser spot on the back of this cantilever, and observing the position of the laser spot when it is reflected onto a photodiode array, as illustrated in figure 1-5.

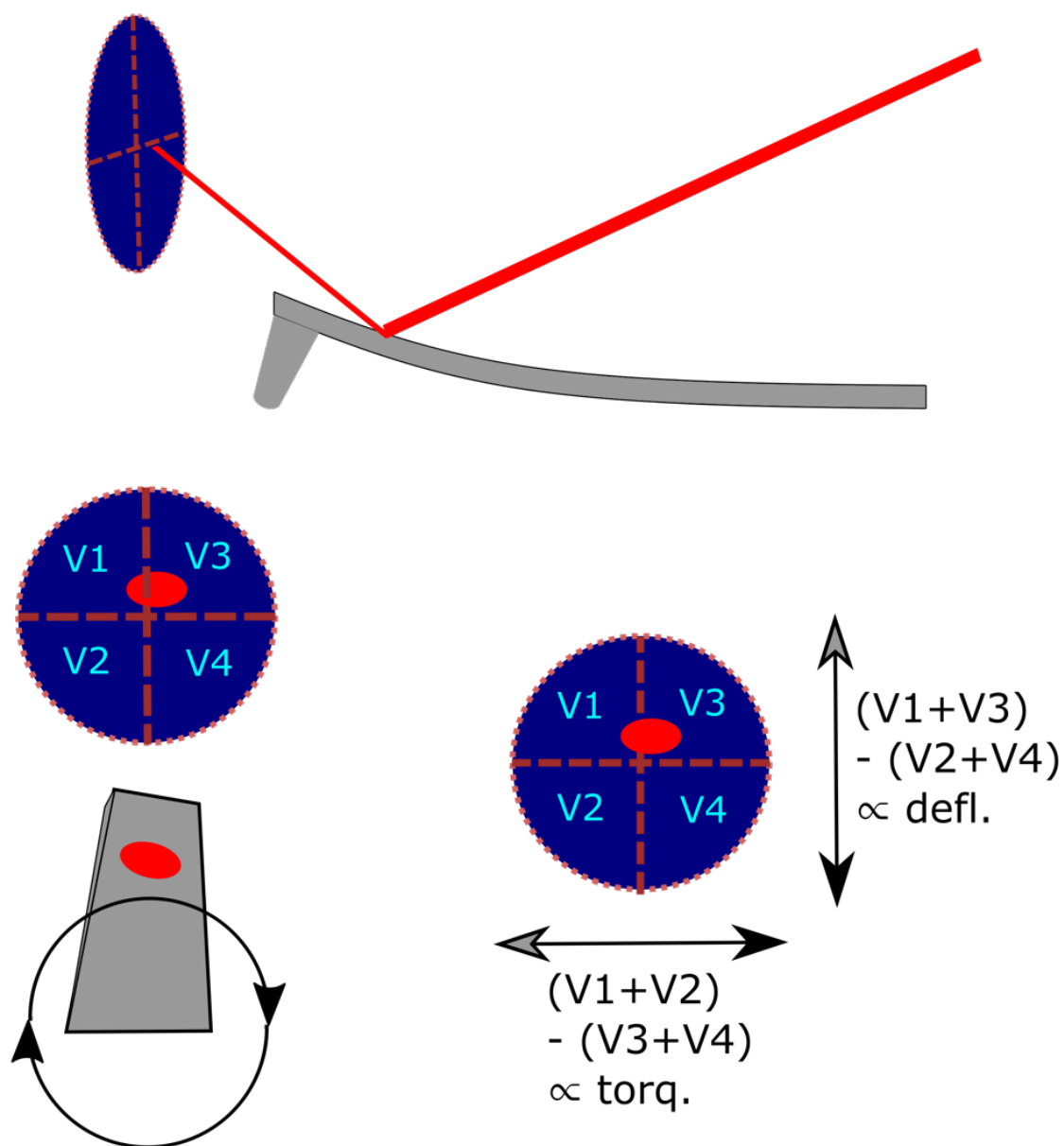


Figure 1-5: Illustration of the measurement mechanism of a scanning probe microscope

As illustrated in figure 1-5, the reflected laser spot reflects off of the back of the cantilever onto a photodiode setup, shown here in a quadrant array that also allows the measurement of the torque (torq.) acting on the tip in the plane perpendicular to the length of the cantilever. When this light hits the photodiode array, it produces a voltage proportional to the amount of

light hitting it. The macroscopic distance (on the order of centimeters) between photodiode and tip allows for even small ($\sim$ nm) deflections (defl.) of the tip to produce appreciable motion in the location of the laser spot on the photodiode, and so the sum and difference of the photodiode voltages in different combinations tells you about the position of the end of the tip. In addition to mechanical stimulus, useful for indentation or elastic properties measurement⁵⁸ AFM probes can be designed to be sensitive to local electric⁵⁹ and magnetic^{60,61} fields, surface potentials^{62,63} and, with a proper setup, chemical contrast through localized Raman spectroscopy⁶⁴.

1.4.6 Electrode Topography Modification

The above methods in sections 1.4.1 through 1.4.5 have discussed various methods and techniques of examining the physical responses of the system. The subject of this section, on the other hand, is more closely related to improving the function of battery systems directly.

There has been previous research dedicated to the patterning of anode surfaces for the deposition of Li metal in a significantly different pattern than the planar morphology commonly used^{65,66, 67, 68}. One of the motivating advantages of this is the decreased local current density: because these micropatterned anodes have a non-flat surface, their total surface area that can react is increased, allowing them to provide larger currents in the same footprint, with the same materials, at the same overpotential (and assuming conductivity is limited by the electrode reaction rate). This is often discussed in terms of dendrite suppression in part because the overpotential applied is positively related to the current produced (as illustrated in the concept of overpotential discussed earlier in this chapter) and negatively related to the lifetime of the battery (as can be seen in measurements of capacity vs C rate, the charging rate of the battery

relative to the rate that would fully charge it in one hour^{65–68}). The data in these works suggests that mechanical surface modification results in improved cycle life and capacity retention when compared with untreated metal, which suggests (counter to the expectations of increased surface area) that this method suppresses the consumption of active material and the formation of excess SEI. While the use of structured electrodes is not without precedent^{38,69,70,71,72,73,74}, the mechanism by which this occurs is not well determined. The use of mechanical patterning methods appears to disrupt a surface layer that forms on lithium which could contribute to the improved interfacial reaction properties associated with dendrites and SEI formation independently of any effects associated of the surface area of the electrode⁷⁵. Alternatively, the improved performance of these surface-patterned anodes could instead be related to the suppression of high activity sites and asperities on the surface, as one might expect from applying mechanical pressure to a surface, but in practice the reverse could also be beneficial: the presence of multiple sites at which dendrites can easily grow from necessarily reduces the amount by which they grow under a given supplied current leading to more homogeneous deposition. The latter is seen in several works involving the seeded growth of lithium on high activity sites^{76,77,78,79} and in works illustrating the effect of overpotential on electrodeposition⁸⁰. There is even work that suggests that local mechanical stress can contribute to deposition overpotential⁸¹, which will be discussed later in this work.

Chapter 2: Experimental Techniques

The work discussed herein will involve a technical understanding of the mechanics of certain scanning probe microscopy techniques, including Kelvin probe force microscopy (KPFM, also referred to as Scanning Kelvin Probe Microscopy or SKPM), Electrostatic Force Microscopy (EFM), Force-curve based local elastic modulus measurement, and understanding of the experimental setup used for certain cycling experiments. These will be discussed in detail below, starting with local elastic modulus measurements.

2.1 Hertz Indentation:

Hertz contact model measurements are performed in AFM by slowly approaching the tip to the surface and measuring the deflected distance that results from contact. This generates a data set relating tip deflection, which is proportional to the force acting on the tip, to the distance travelled by the cantilever. These curves are commonly called “Force distance curves” or, as may occasionally be abbreviated in this thesis, Hertz F/d. Because the tip is in mechanical equilibrium with the sample, the distance by which this indents into the sample reflects not only the spring constant of the AFM tip’s cantilever, but also the mutual elastic properties of the tip and sample. Originally, the models of elastic contact were derived by Hertz based on the deformations of optical lenses that were brought into contact, and the interference fringes resulting therefrom^{82,83}. One important consequence of this is the derivation of an equation relating the normal force applied to and depth of elastic indentation of an elastic spherical indenter into an elastic half-space to the elastic modulus of such a space. The Hertz indentation model has four assumptions: That the interface between the two surfaces be frictionless, that the only

deformations occurring be elastic, that the surfaces were non-conforming (so that contact started at a single point grew only due to elastic deformation), and more specifically to the application in AFM, that the indented body be representable as an elastic half-space (i.e: that the deformation properties of the sample are uniform over the load-bearing area of the sample). This model was extended as the Derjaguin-Muller-Toporev (DMT) model to include relatively weak short-range forces, such as electrostatic attractive interactions between the two bodies⁸⁴. These derivations are applicable to the contact of rounded AFM tips with the flat surface of the sample in question, and serve as the basis not only for this method, but for many advanced methods of AFM-based elastic property measurements such as contact resonance AFM and bimodal AC AFM. The Hertz relation is given according to equation 2-1 for an elastic sphere in perpendicular contact with the flat surface of an elastic volume:

$$\frac{F}{d^{3/2}} = \frac{4}{3} E^* \sqrt{R} \quad (2-1)$$

Where F is the normal force applied to the spherical indenter, d is the depth that the indenter indents into the sample, R is the radius of this spherical indenter, and E* is the reduced elastic modulus: an effective elastic parameter defined by the elastic properties of both the indenter and the indented surface. The reduced elastic modulus is defined as follows:

$$\frac{1}{E^*} = \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \quad (2-2)$$

Where E* is the reduced elastic modulus, subscripts 1 and 2 denote the indenter and indented material, E denotes the elastic (Young's) modulus and ν denotes Poisson's ratio. This analysis may be complicated by significant crystalline anisotropy due to the assumption of a

single value of Poisson's ratio, but where applicable this has significant utility in characterizing the elastic behavior of materials.

The tip is approached to the sample, its indentation into the sample measured in response to the motion of the AFM cantilever holder above the sample, and then withdrawn. The known distance deflected by the tip in response to the tip being lowered into contact with the sample is based on the calibration of the photodiode signal against the piezoelectric actuators that raise and lower the cantilever. This is expressed as a quantity known as the Inverse Optical Lever Sensitivity (InvOLS), which is calculated as the ratio of the change in the height of the cantilever holder above the sample to the corresponding change in photodiode voltage when the tip is brought into contact with a stiff sample. This is illustrated in figure 2-1:

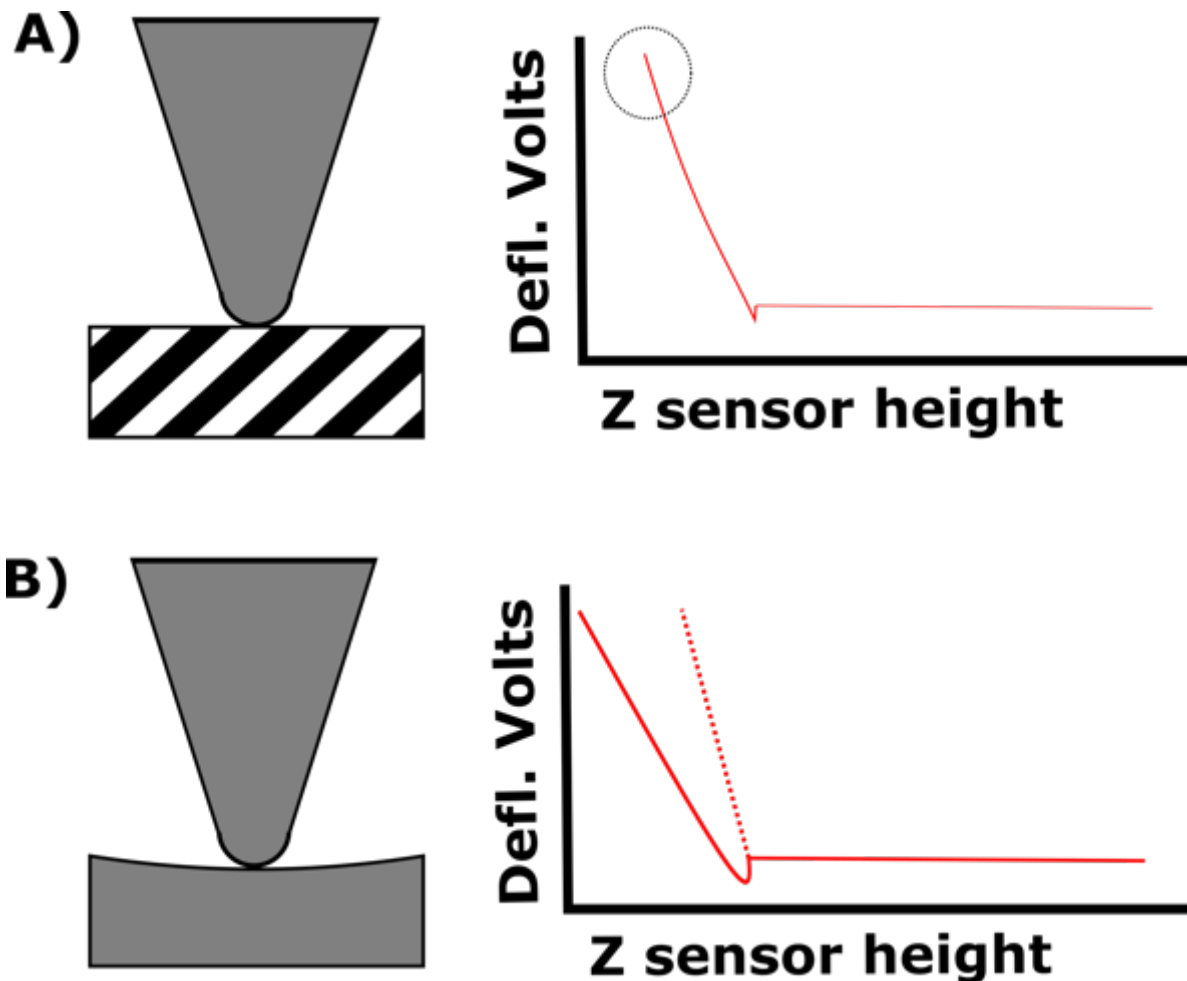


Figure 2-1: Illustration of InvOLS and subsequent hertz F/d measurement.

Figure 2-1 illustrates the measurement of the inverse optical lever sensitivity, and its use in AFM Hertz F/d measurements. In 2-1 A), the tip is brought into contact with a stiff sample, its deflection recorded, and the linear slope taken in the limit of high deflection on this sample is used to express the optical lever sensitivity. During indentation on a softer sample, as in 2-1 B), the measured deflection curve on the soft sample (solid line) is compared with the inverse optical lever sensitivity (dotted line), and a curve expressing indentation into the sample (“d”, in equation 2-1) can be calculated.

While this quantity of InvOLS can be measured in multiple ways, the most commonly used method is by calibration on a stiff sample. This ratio is used as the definition of zero indentation for the cantilever: if the cantilever deflects by less than this under a given change in tip height, the interpretation is that the cantilever had indented into the sample by the difference in these values. While this is trivial for soft samples, for stiffer ones care must be taken to use a standard much harder than the sample to be tested, and to use cantilevers that are stiff enough that their indentation into the sample is significant enough to be consistently measured. Despite these limitations, this technique has found use in the characterization of local mechanical properties in a wide variety of samples and contexts, ranging from biological samples to hard materials^{85,86,87,58}.

2.2 Kelvin Probe Force Microscopy:

Based on the Kelvin probe parallel plate method of determining surface potential, this method assumes the electrostatic interaction between the AFM tip and a sample can be modeled as a parallel plate capacitor, thusly named after early macroscopic experiments by William Thomson, Lord Kelvin^{88,89}. When two materials are brought into close proximity, the differences in their respective surface potentials produces an electric field between the two as their Fermi levels equalize (more specifically, this surface potential is the difference between the vacuum energy level for electrons in the two materials when the fermi levels are equalized). Where early methods of attempting to determine the fermi level of materials, such as the photoelectric effect, are dependent on the ability to measure miniscule currents, require vacuum conditions, and are stymied by nontrivial band structures as is the case of semiconductors (photoelectric emission

would occur from conduction band, not fermi level), the kelvin probe method suffers none of these problems (although, the necessity of a conductive probe can cause band-bending in semiconductor samples, rendering it less useful in measuring the effects of dopants on fermi level^{90,91}). Applying this phenomenon to AFM, the tip and the sample form two electrodes of a kelvin probe, and by applying both a DC and AC bias to the tip in such a close approach to the sample that the contact potential difference produces an electric field, the electric force between tip and sample can be probed in the Z direction by measuring the deflection of the cantilever with great precision. More specifically, the electric force acting on the cantilever and tip should take the following form:

$$F_z = -\frac{dU}{dz} = -\frac{d\left(\frac{1}{2}CV^2\right)}{dz} \quad (2-3)$$

$$= -\frac{1}{2}\left(V_{sp} + V_{DC} + V_{AC}\sin(\omega t)\right)^2 \frac{dC}{dz}$$

Where V_{DC} is the DC bias applied to the sample, V_{AC} is the magnitude of the AC bias applied on top of that DC bias, and V_{sp} is the surface potential (this is also referred to as contact potential, or Volta potential) difference between the probe and the sample. If the force acting on the tip is decomposed into specific frequency responses, the force acting on the tip at frequency ω is then:

$$F_z(\omega) = (V_{sp} + V_{DC})V_{AC} \frac{dC}{dz} \quad (2-4)$$

This quantity is zero when $V_{sp} + V_{DC} = 0$, so the DC bias that offsets the surface potential can be determined by finding the DC bias that minimizes of the mechanical response of the tip at the frequency at which the AC bias is applied. If the AC bias frequency ω is chosen to

correspond to the fundamental resonance frequency of the cantilever, the AFM can be very sensitive this force, and thus determine the minimum with high precision. This method has been used in the analysis of local chemical properties in such varied cases as metals, semiconductors, biological samples, and electrochemical materials^{92,93,62,94}.

One additional note should be made regarding the use of KPFM in this thesis: The kelvin probe microscopy method used in this work is the amplitude modulation kelvin probe microscopy method (AM-KPFM), wherein the tip's amplitude response to an AC bias at constant frequency is used as the feedback parameter to determine the contact potential difference between tip and sample.

2.3 Electrostatic force microscopy:

Electrostatic force microscopy is a technique based on the mechanics of tapping mode AFM, in which the tip is mechanically driven, and the properties (usually amplitude and phase) of its oscillating deflection signal are measured while the tip is either very close to or intermittently contacting the sample. Unlike in normal tapping mode topography AFM where forces are localized to a small region near contact, though, the long-range electrostatic interaction between a biased tip and sample can be probed when the tip is lifted from the sample a significant distance ($\sim >100$ nm) and applies over the entire range of oscillation (in the case of these experiments, the sample was always set to 0 V, that is, experimental ground). This effectively eliminates the effect of short-range forces, like adhesion. One consequence of this is that where in tapping mode, the amplitude is largely invariant w.r.t. the tip phase (it's fixed by the height of the sample, and often used as a feedback parameter to maintain a constant tip-

sample separation, just like deflection is used in contact mode AFM). In EFM, the amount of energy imparted to the tip by even a small electrostatic force is significant, and this causes the tip amplitude and phase to no longer serve as independent sources of information.

One example of this is a contrast inversion in amplitude signal when the tip is near resonance. A simulated AC sweep of the frequency at which an AFM tip is driven is shown in figure 2-2, with constant amplitude of driving force. The response amplitude of the tip and the phase lag between the driving signal and the tip's response are shown in red and blue respectively. Note that the peak of the amplitude oscillation occurs when the phase response is 90 degrees, after which the amplitude response of the tip. The units in this figure are arbitrary, and this is included only to illustrate the relations between these variables.

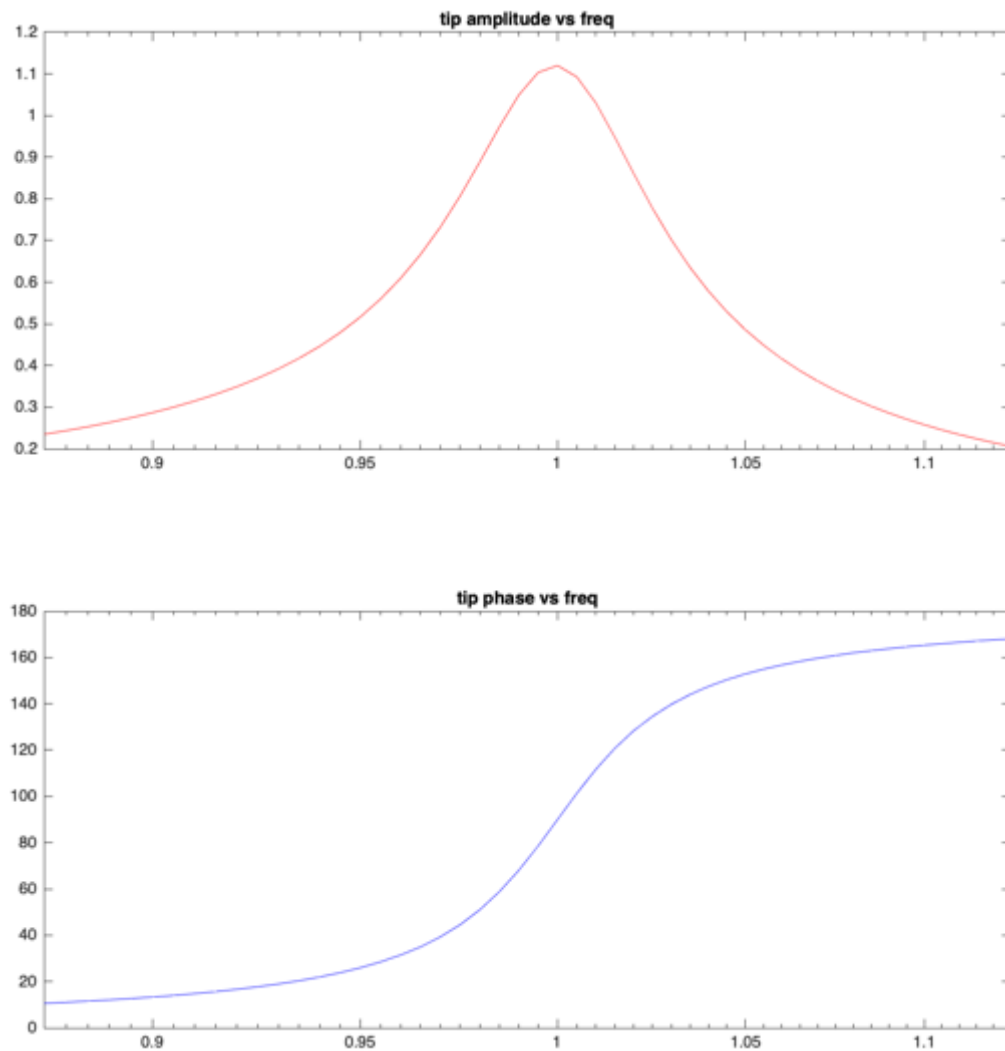


Figure 2-2: simulated frequency sweep of tip amplitude responses above a sample

Compare the relation between phase and amplitude in the figure 2-2 with that in the following figure 2-3: A simulated approach of the tip to the sample under conditions of EFM, which include a tip-sample bias. Note that the force between tip and sample must necessarily be increasing as the tip approaches the sample, as is reflected by the monotonic phase relation before contact, but at some point before contact, the EFM amplitude reaches a peak. This will be elaborated upon in later sections.

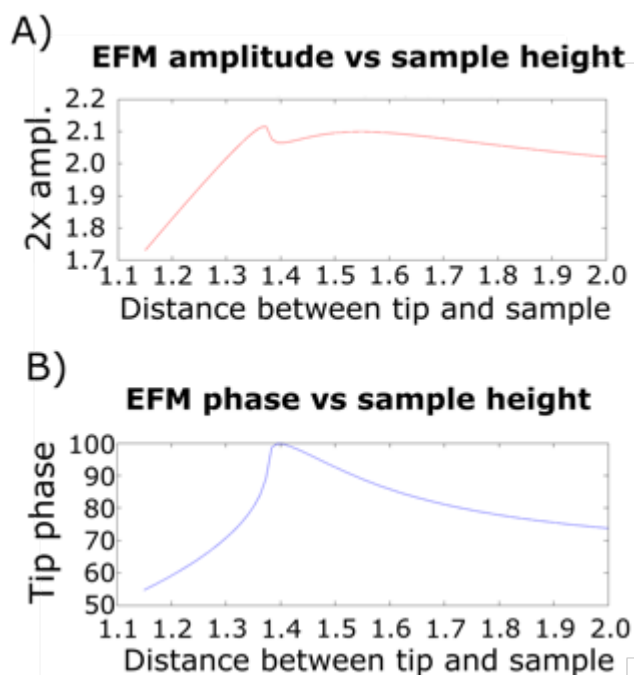


Figure 2-3: Simulated EFM AC responses as a function of distance from the sample

EFM has been used previously to illustrate variations in local dielectric properties and tip-sample capacitance, and has been shown to be sensitive to features underneath a dielectric material, with recent efforts suggesting applicability to the characterization of dynamic processes such as ionic transport^{95,96,97}.

2.4 SEM & TEM

In addition to AFM experiments on cycled electrodes, electron microscopy experiments were performed in-situ using a liquid-compatible TEM chip (see image in figure 2-4), and the Hummingbird Scientific Liquid Flow TEM Holder. The samples were cycled using a potentiostat/galvanostat and subsequently characterized ex-situ using a Phenom ProX desktop SEM. Analogous experiments had been performed previously, and the intention of this research endeavor was to visualize the formation of SEI as a function of overpotential and total deposition,

to gain insight into any effects this current dependent formation might have on dendrite growth⁹⁸.

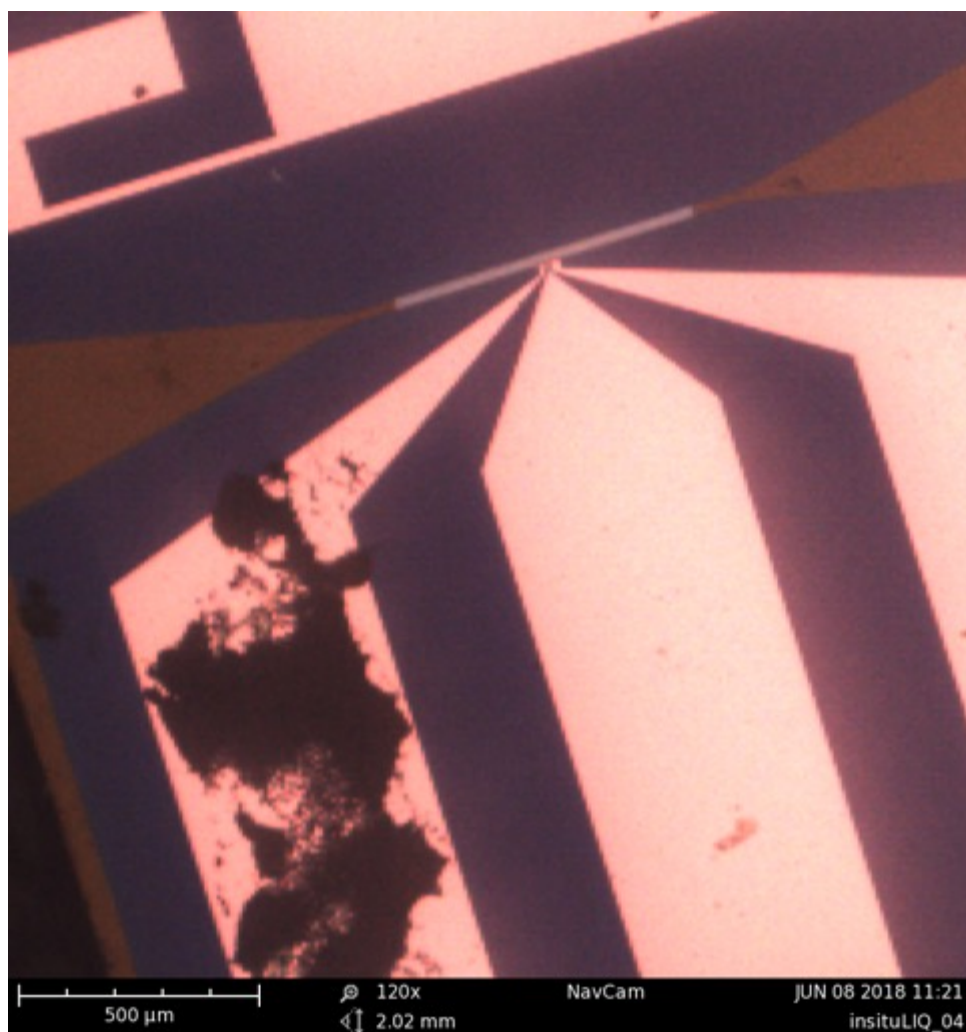


Figure 2-4: TEM cycling chip

A small amount of active material (NMC532 ($\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ electrode slurry, prepared with a polyvinylidene fluoride/conductive carbon binder) was placed on one electrode outside of the TEM viewing window of the chip, and then the chip was sealed. A volume of electrolyte was flowed into the cell at run-time, and cycling was performed at 50 pA. Lithium would first be plated from the NMC electrode onto the copper working electrode, then the current would be reversed

to observe the deposition/stripping behavior of Li periodically during cycling. After cycling, the TEM windows were separated by submerging the chip in acetone, before the bottom section of the chip was reloaded to observe the resulting deposits that formed.

Early experiments were performed using a potentiostat (CHI600E), and frequently resulted of parts of the chip interface breaking that necessitated the chip be withdrawn and that experiment discontinued, but interesting behavior was still observed after cycling. One example thereof is shown below in figure 2-5, with Counter electrode (CE, the electrode containing NMC), Reference electrode (RE) and Working electrode (WE, the electrode on which lithium was deposited) labelled.

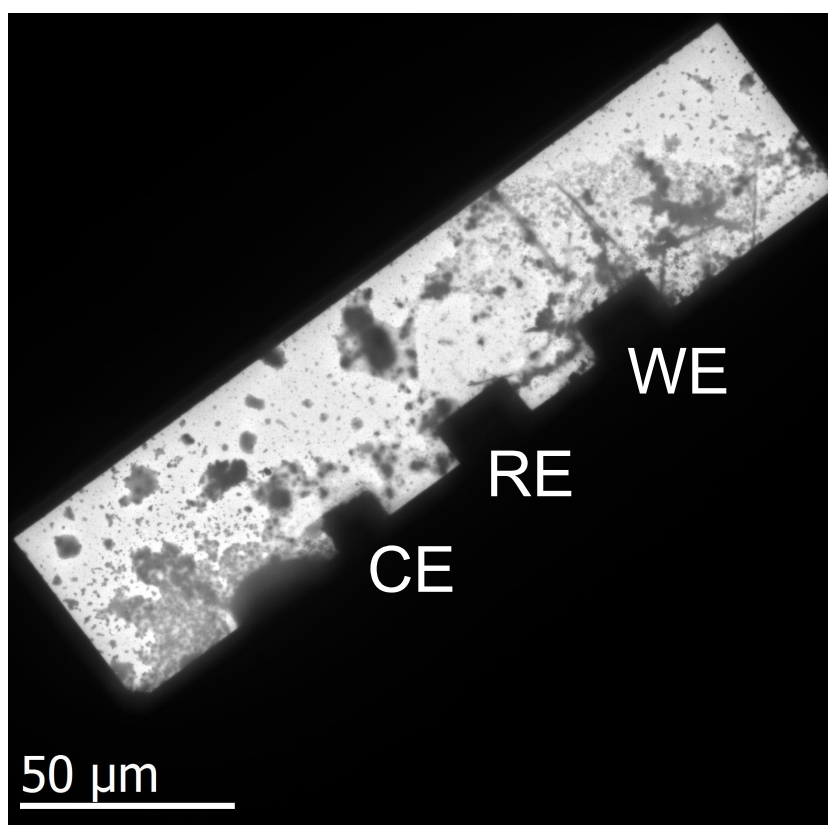


Figure 2-5: TEM chip, after cycling in electrolyte and draining said electrolyte.

This run was examined in detail afterwards. A closeup (see figure 2-6) of the counter electrode before and after the fluid containing TEM chip was separated indicate that there are structures formed that were sturdy enough to survive chip separation, and that ex-situ characterization allowed for greater resolution. Part of the cell in the “Before” image is occluded by the edge of the top window of the TEM chip.

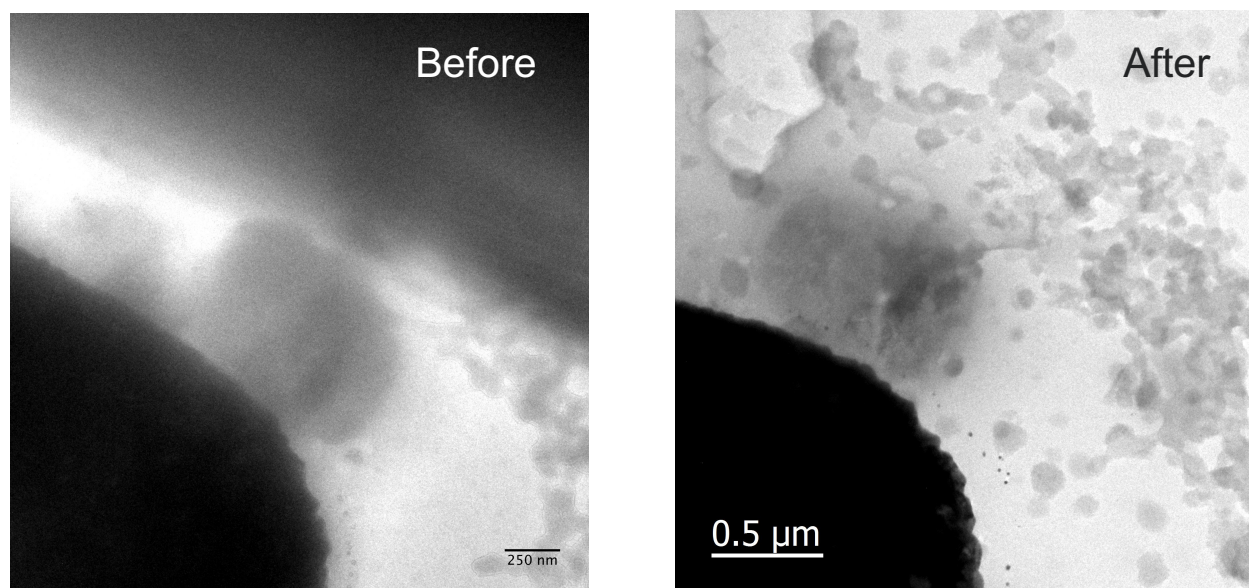


Figure 2-6: closeup of counter electrode before and after removal of electrolyte.

Additionally, dendrite-like structures were observed after the chips were separated, a bright-field TEM image of which is shown in figure 2-7. Selected area diffraction was also performed on this dendrite, but the diffuse rings thereof suggest this dendrite-like structure is not significantly crystalline.

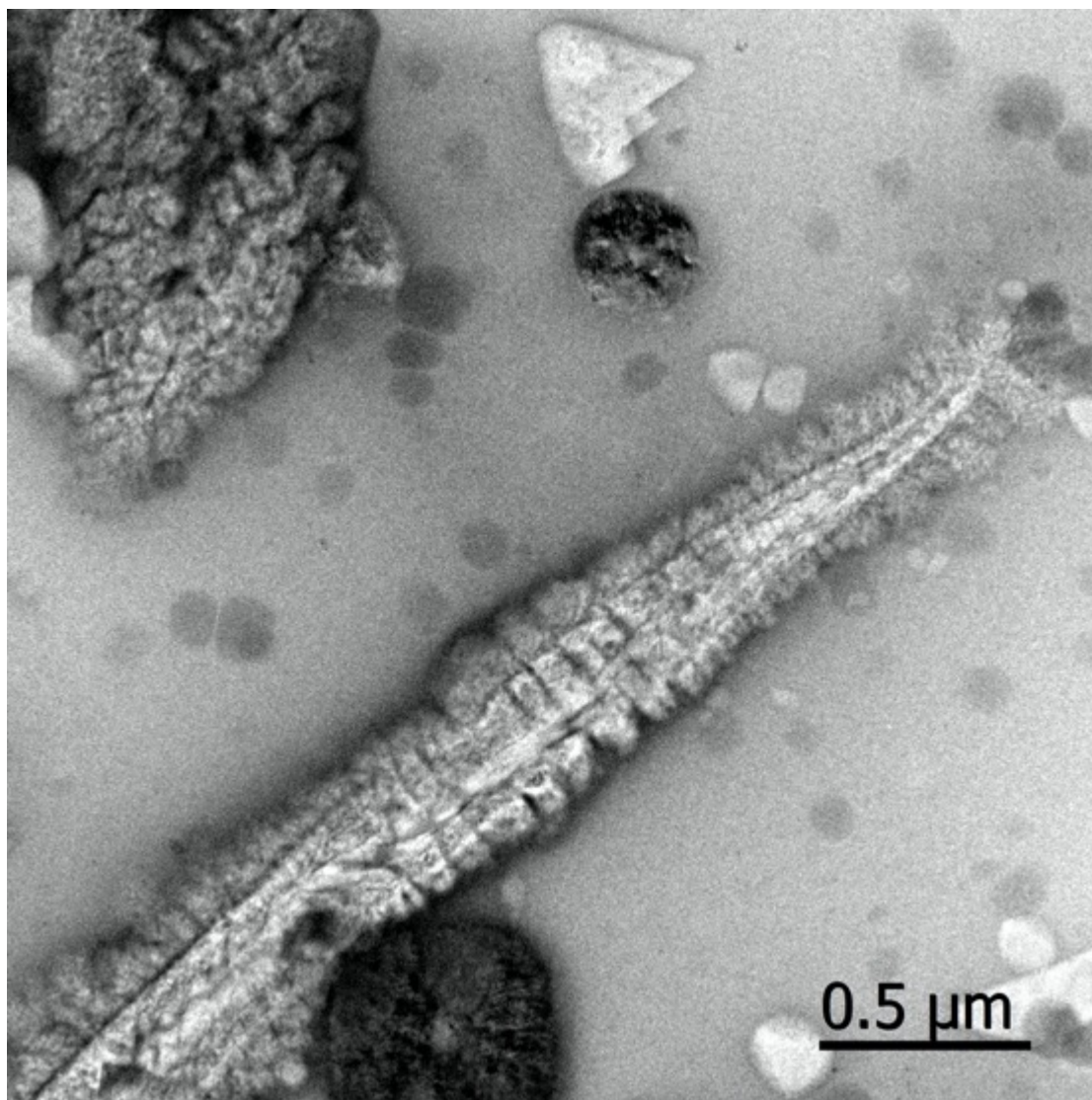


Figure 2-7: Dendrite-like structure observed in TEM

The dark crystallite in the lower left of this image was found to be highly crystalline, and comparison of the diffraction pattern of this crystallite and subsequent EDX analysis thereof suggested this to be crystallized LiPF_6 salt. This is plausible, given that the electrolyte would have evaporated quickly when the spacer window broke on this TEM chip, and finished evaporating when the chip was separated.

Followup experiments used a Keithly 6430 Sourcemeter, and a galvanostat current of 50 pA for cycling. At this current, we are able to see the differences in SEI formation that occur with subsequent plating and stripping of lithium. The location of the working electrode is indicated by the red box in each image.

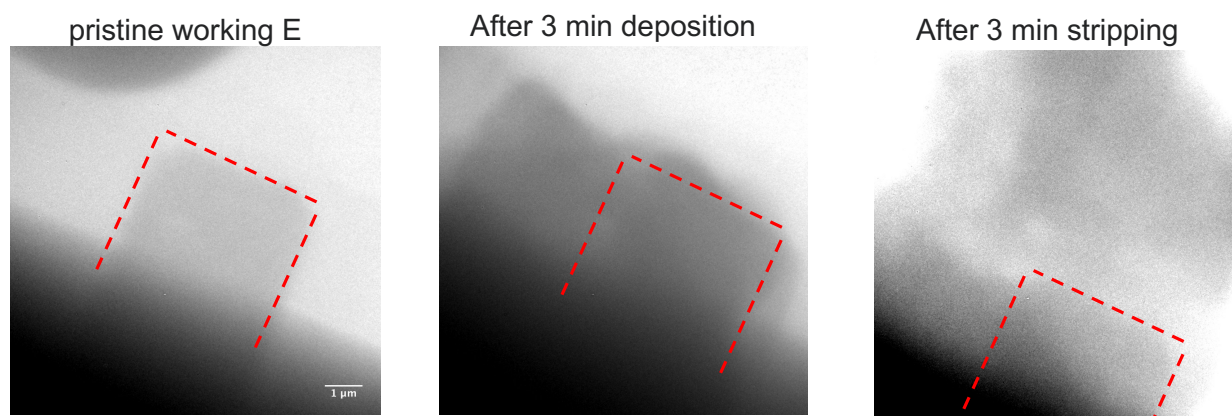


Figure 2-8: in-situ galvanostatic cycling effect on electrode

Despite the increased galvanostatic control, the voltage on stripping spikes significantly initially, to a value of approximately ~ 3.3 V upon the initiation of Li stripping from the formerly bare electrode after deposition. After ~ 7 min of stripping and plating, damage to the working electrode was noted. Some of these electrodes were characterized afterwards in SEM, noting significant damage to the working electrode (see figure 2-9).

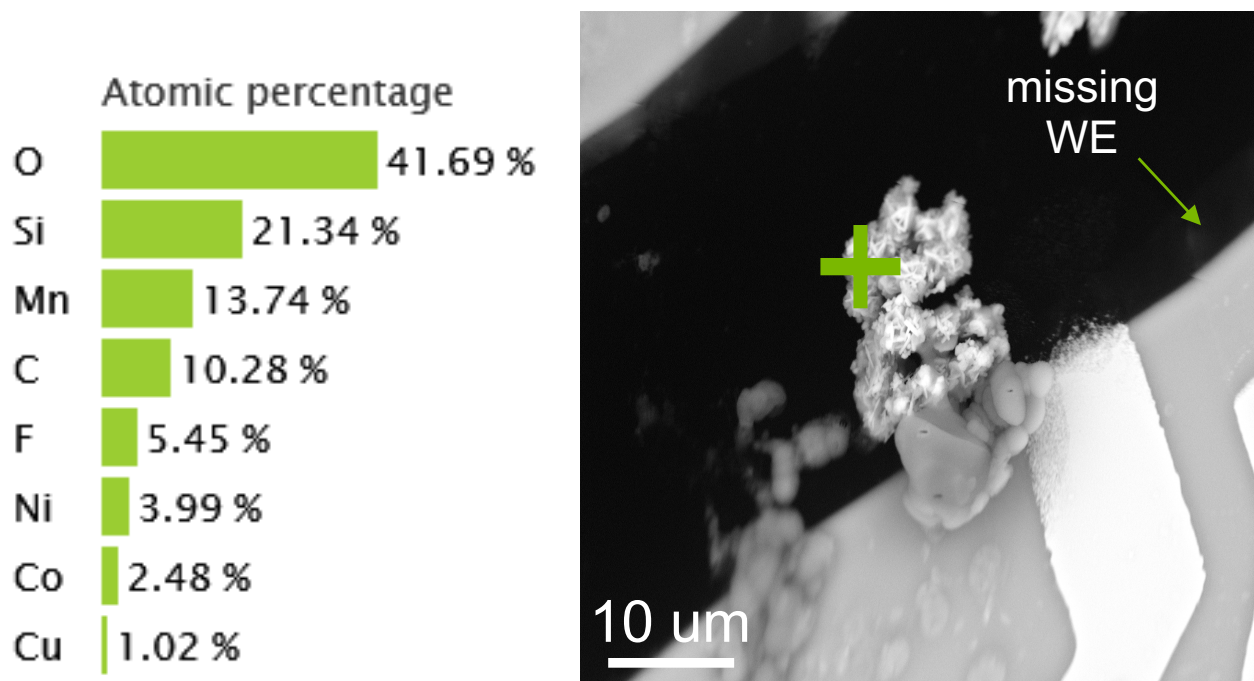


Figure 2-9: forensic analysis of galvanostatically cycled electrode in SEM

In addition to topographic analysis permitted in the Phenom SEM, local Energy Dispersive X-ray spectroscopy (EDX) could be performed and was performed at the point indicated by the green cross in the image. The presence of copper in the NMC electrode material suggests that this voltage was significant enough for copper to participate in the electrochemistry occurring here, and that future experiments would require compliance voltages to restrict the electrochemistry occurring to exclusively those reactions involving lithium.

2.5 Electrochemical cycling procedures

In an analogous experiment on a macroscopic sample, galvanostatic cycling experiments were performed using the Asylum Electrochemical cell, in a setup shown in figure 2-10:

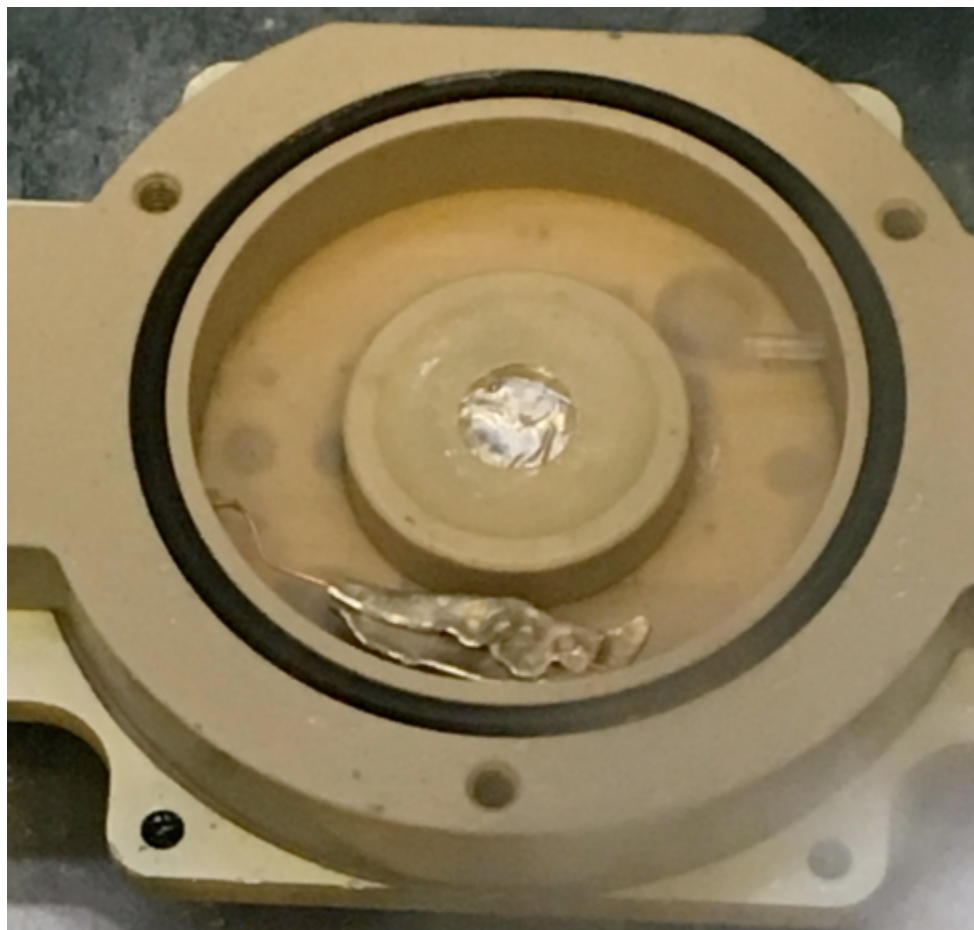


Figure 2-10: Asylum Electrochemical Cell

This cell would be assembled before and disassembled after each run in an Argon atmosphere glove box with a chamber atmosphere filter maintaining <1 ppm O_2 and H_2O . In this cell, a large lithium counter electrode is attached to a copper wire, fed through one of the fluid ports on the side of the instrument, with a length exposed on the outside surface for biasing. In the center of this cell is a 0.7 cm diameter working electrode. The fluid ports are secured with a PTFE jacket to prevent leakage, and the cell body is composed of PEEK. During operation, the black O-ring shown above seals against an elastomer membrane creating an airtight seal. Both of these parts are composed of perfluoroelastomer (FFKM), which was necessary for chemical

compatibility with the electrolyte used in our experiments (3 parts Ethylene Carbonate to 7 parts Ethyl Methyl Carbonate, with a 1.15 M LiPF_6 Electrolyte). This electrolyte would be fed into the cell through the tube in the upper right of this cell image. Electrolyte was administered using a tipless syringe with a “Luertight” fitting, and this syringe was left attached to the tube during the experiment to prevent the exposure of electrolyte to the external lab atmosphere. In this manner, the cell could be biased using an external source (potentiostat/galvanostat) and the active components of the cell could be kept isolated from the lab atmosphere while the cell was being biased. After the cell was cycled, it could be drained of electrolyte and disassembled without disturbing the active surface of the anode. Because the electrolyte used in our experiments was volatile, an acetonitrile rinse was used to dissolve any residual salt that condensed on the surface of the electrode after the electrolyte was drained. This compound was chosen based on the shared chemical properties that permit with the electrolyte that permit its use in the glove box: it is a polar, aprotic solvent. It is not expected to disturb the solid electrolyte interphase that forms on the surface of the cycled material because such an SEI cannot readily dissolve in the electrolyte that formed it. The similar properties of acetonitrile and the carbonate solvent in question suggest the SEI cannot dissolve, and the cyanide group in acetonitrile does not dissociate readily, so it is not expected to react with the SEI either. Additionally, the compound is quite volatile, so it does not leave liquid droplets on samples that would otherwise confound scanning probe microscopy measurements.

After rinsing in the above fashion, the cycled electrode could then be moved to the Asylum Electrical closed fluid cell (see figure 2-11).

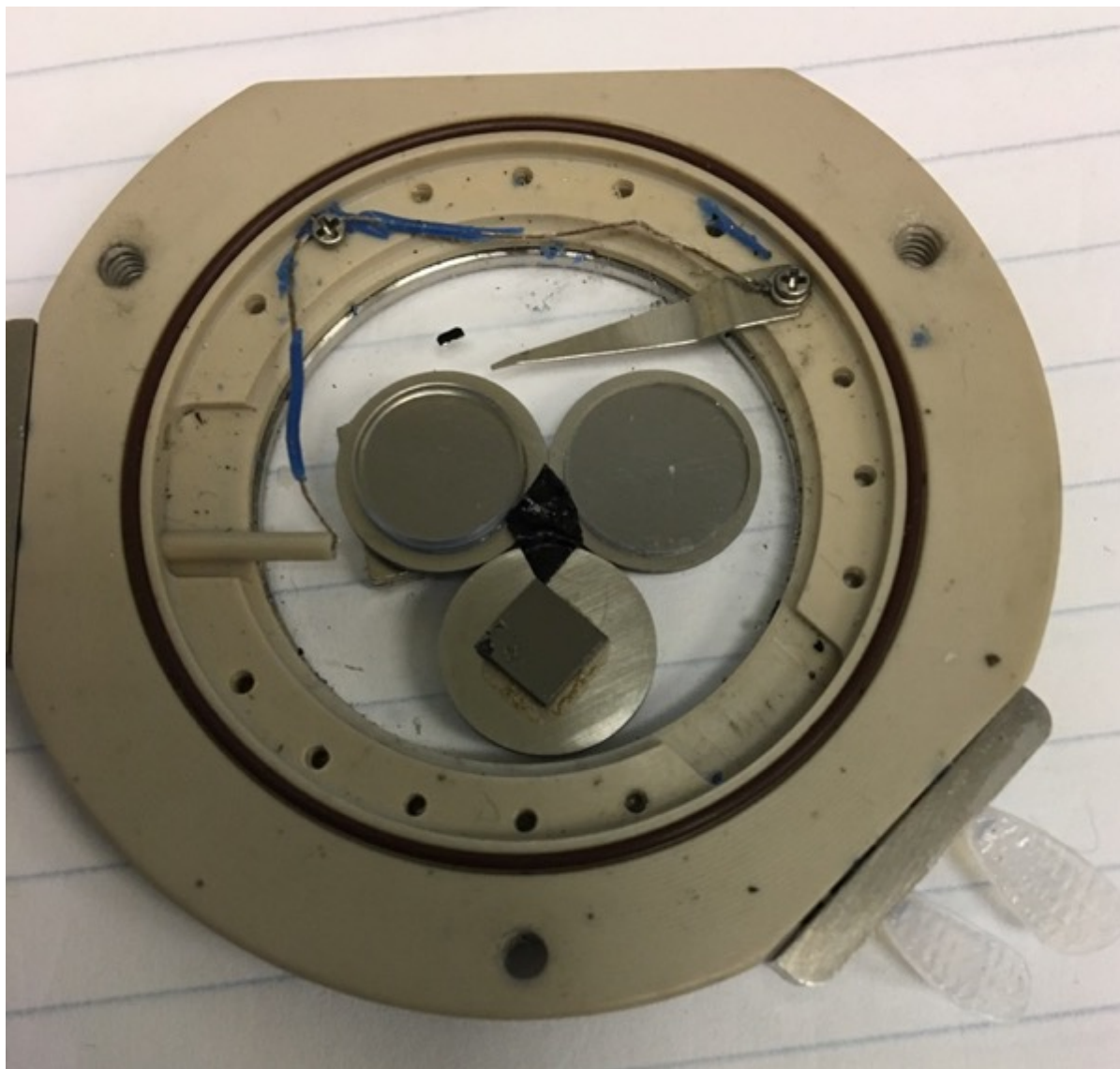


Figure 2-11: Asylum electrical closed fluid cell

This cell seals in an identical fashion to the Electrochemical cell, but without a local sample mount. While there remains the option to fill this cell with liquid, in practice this was never done. This cell was used as a hermetically sealed cell containing a sample-biasing lead, allowing for the performance of EFM and SKPM. Samples are frequently mounted on iron AFM sample disks, in

which case a small magnet can be used to hold the sample in place by placing it on the outside of the quartz window that forms the bottom of this cell during the loading process.

Chapter 3: Deposition Behavior of Lithium on Anodes

3.1 Background

As mentioned in Chapter 1, the electrochemical behavior of the anode and the consumption of electrolyte species to form SEI are closely related to the overpotential at the anode surface. Previous work^{76,80} suggests that the deposition overpotential is closely related to how lithium is distributed on the surface by electrodeposition, but the mechanism by which this results in cell failure from the inhomogeneous deposition of Li in practice is somewhat unclear. Many properties affect local overpotential variations including SEI composition and thickness, and local changes in electrolyte composition³⁰ and conductivity⁹⁹ can result in a change in the amount of salt near the surface which in turn could affect the deposition overpotential required to sustain the reaction occurring at the interface; even independent of overpotential variations local electrode topographic features produce a non-uniform electric field that can contribute to inhomogeneous deposition. These local variations in current density and overpotential have the potential to influence the SEI that forms on the surface, and its composition. To better understand the consequences of local variations in Li deposition behavior, Li depositions on various patterned anode materials were performed, and the variations in the SEI and deposition behavior observed were measured using scanning probe microscopy techniques.

3.2 Overview

As part of the investigation of the nucleation behavior of lithium metal, a comparative study of lithium deposition on various anode materials was performed. As discussed in previous

work^{80,100,76}, the deposition behavior of lithium is strongly dependent upon the nucleation overpotential required to deposit it, in a manner that can be exploited to encourage selective local deposition of lithium. The goal of the following work (publication pending) was to use this variation in deposition overpotential to learn more about the formation of SEI in lithium metal/carbonate electrolyte, and to elucidate the physical mechanisms which can lead to dendrite formation in patterned anodes. Copper, gold, and lithium were chosen due to their varied overpotential behavior and similarities: because copper forms no solid alloy with lithium at room temperature, deposition of lithium on the surface is required to occur by nucleation of lithium at the surface, resulting in a significant deposition overpotential⁷⁶, but identical chemical interactions with electrolyte. Lithium by definition has identical chemical interactions in the electrolyte to lithium metal and no thermodynamically necessary deposition overpotential because no new metal phase has to be nucleated. Gold represents an intermediate case between these two: there are a number of alloy phases that form between gold and lithium, but the final alloy phase coexists with pure lithium metal without the need for nucleation of a second phase. In practice, this has a smaller series of overpotentials to start, but similar deposition kinetics to the case of lithium metal should occur as the deposition of lithium continues. Because no lithium was present originally, the interactions with electrolyte prior to cycling may be different, representing a contrast between the Li and Au anode cases whose effects, if any, could be observed on the cycling behavior of Au.

The preparation of these anodes occurred as follows: A copper anode, cut from an approximately 1 mm thick copper sheet, and polished to both remove any surface

contamination/oxide and to produce a topographic variation that would be identifiable in the AFM. After preparation in this manner, macroscopic scratches were applied with a diamond stylus to aid in the identification of areas before and after cycling. These diamond stylus scratches served only as landmarks, and were not included in the scratched areas sampled before/after biasing. A gold anode was also prepared by depositing 300 nm of Au by sputter deposition onto a copper section prepared as described above. Lastly, a flat lithium anode was prepared by folding a thin copper-backed lithium foil around an iron AFM disk. This was done to ensure a proper seal and electrical contact could be made with the working electrode section of the electrical closed fluid cell, which was necessary to ensure that only the exposed area could react and be designated as a working electrode. Because the lithium foil was so thin ($\sim 10\ \mu\text{m}$ of lithium on the copper foil), single After cycling, the electrodes were rinsed with acetonitrile to remove residual salt.

3.3 Electrochemical Cycling

For the cycling of these anodes, the electrochemical cell was prepared as described in the experimental techniques chapter (with a typical electrode separation distance of 1.3 cm), filled with 1.15 M LiPF_6 electrolyte (3:7 Ethylene Carbonate : Ethyl Methyl Carbonate), and removed from the glove box. The lithium and gold electrodes were cycled using a Keithley 6430 power supply, but due to the significant overpotential required to deposit copper it would quickly (over ~ 20 sec) saturate to the compliance voltage set, originally 3 V vs Li. In light of this, a different power supply (Gamry Reference 600+ potentiostat/galvanostat) was used so that automated cutoffs and changes in cycling behavior could be performed without human error in

the timing thereof. All cells were cycled with a specified galvanostatic current of 19.242 μA , chosen because it corresponds to a specific current density of 0.05 mA/cm^2 . This exceedingly low current density was chosen to ensure the electrolyte would not deplete to produce dendrites directly, as this behavior is understood already by the Chazalviel model⁴⁴. As an additional buffer against this behavior, galvanostatic deposition was performed only for 5 minutes at a time, after which the electrolyte was allowed to relax under open circuit conditions for 5 minutes. Compared with the nominal Sand's time for this configuration, which is in excess of 1000 hours, and a current density that is nominally below the limiting current density for this cell, and the excess of electrolyte in the cell that should reduce the effect of electrolyte depletion that was illustrated in the optical microscopy paper mentioned previously³⁶, the conditions of uniform deposition should never allow the electrode to deplete the electrolyte to the extent that dendrites form via the Chazalviel model. This is "nominal" because it is subject to the limited applicability of the Sand's time derivation: these electrodes are not set up in a strictly planar configuration (which may worsen electrolyte depletion), there is electrolyte outside of the space between these two that could affect the concentration gradient that forms when the cell is biased (which should forestall electrolyte depletion), and in fact current understanding is that the ambipolar diffusivity of LiPF_6 in its electrolyte increases by a factor of about 2 as it depletes from 1.15 M at room temperature⁷, which means that the nominal diffusion constant for this electrolyte produces an underestimation of the current at which it depletes fully¹⁷.

3.4 Results

3.4.1 Deposition on Cu anodes

The first galvanostatic deposition experiments on copper were performed with voltage limits set between 0 V and 3 V vs lithium (the counter electrode), the change in surface potential that results from this is shown below in figure 3-1 for the anode before and after cycling.

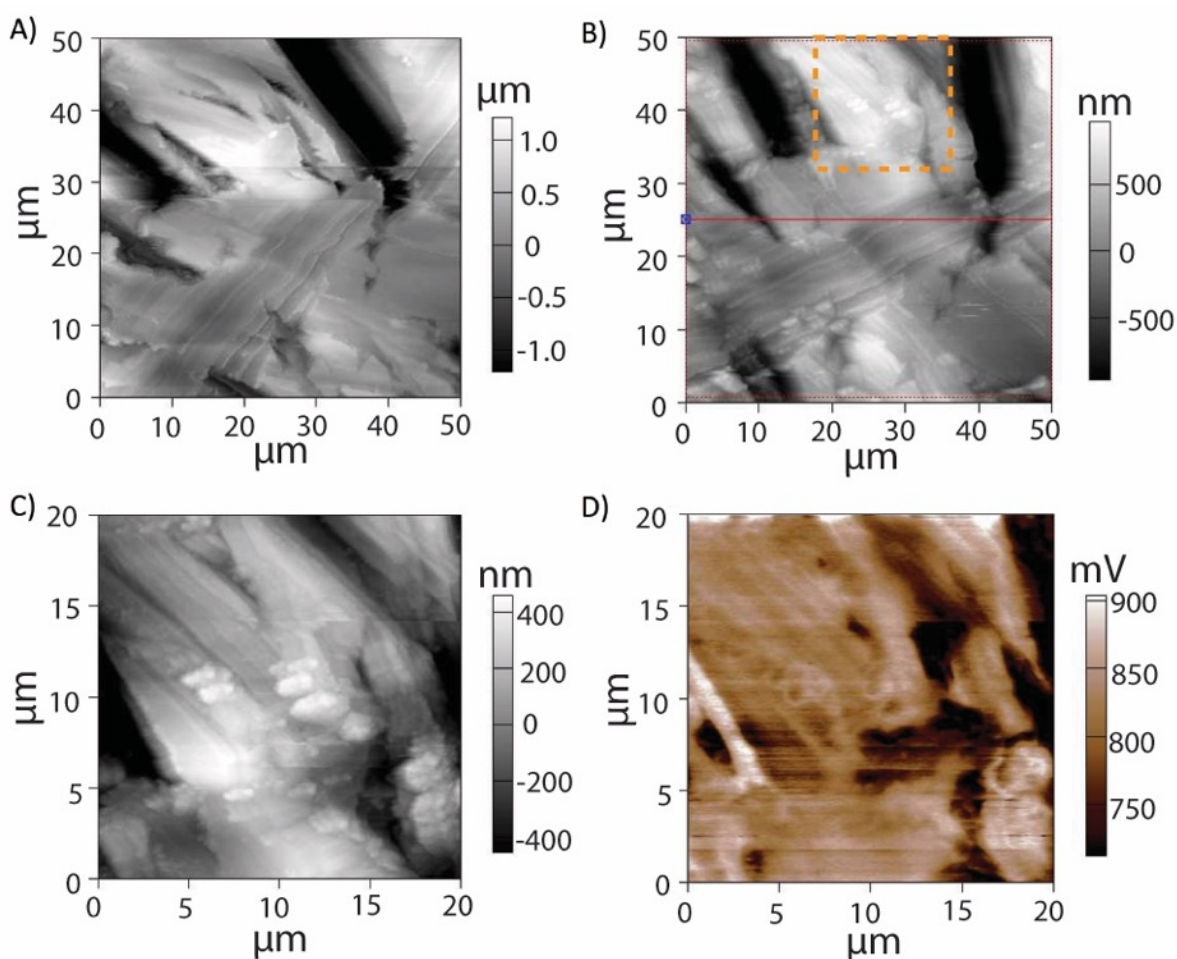


Figure 3-1: Topography and Surface potential of Copper anode

Figure 3-1 A) shows the topography of the copper anode before cycling, 3-1 B) shows the topography of the same region after cycling, with an orange dotted line rectangle indicating a

region that would be subject to further analysis. 3-1 C) indicates a closer look at the cycled anode in a region in which surface potential measurements were performed, as indicated by the aforementioned orange dotted line rectangle, and 3-1 D) indicates the corresponding surface potential variations in the region shown in image C).

In most of the regions in this sample whose topography was examined before cycling, little change was observed. Some features of surface potential in this region appear to indicate contrast based on local curvature, such as that of the rings in surface potential in image D), corresponding to small deposits at approximately 5 μm on the X axis and 12 μm on the Y axis in image C), whereas others appear to correlate with slope, such as the bright section in the left side of this image. Others still appear to indicate poor tracking due to surface roughness, such as the region in the lower right of image D). To better examine the possible factors contributing to surface potential contrast here, Pearson correlation analysis was performed comparing several topographic features with the surface potential seen in the image.

Pearson correlation analysis compares the variations in ordered pairs of data, and expresses the degree to which these two variables follow a linear relationship as a real number between 1 and -1. -1 refers to a perfect negatively sloped linear correlation (of any slope), 1 refers to a perfect positively sloped linear correlation (of any slope), and a Pearson correlation coefficient value of 0 would suggest that values are linearly uncorrelated. Mathematically, the Pearson correlation coefficient is calculated as follows, and further explanation of which can be found on page 146 of the text "Continuous Bivariate Distributions"¹⁰¹:

$$P(X, Y) = \frac{Cov(X, Y)}{\sigma_x \sigma_y} \quad (3-1)$$

Where P is the Pearson correlation coefficient, X and Y are the two variables being examined, σ_x and σ_y are the standard deviations in these variables, and $Cov(X, Y)$ is the covariance of these variables, defined as follows:

$$Cov(X, Y) = \overline{(X - \bar{X})(Y - \bar{Y})} \quad (3-2)$$

Where the overline denotes an expected value of the quantity. Pearson correlation analysis is subject to confounding by a third variable, i.e: a function defined by linear relations to two or more uncorrelated variables will not have a perfect linear correlation with any of the variables that define it due to the effects that any of the other variables have on its value. Nevertheless, it can be used to illustrate the relative strength of the dependence of a given measurement on other variables.

As applied to experimentally measured data, Pearson covariance analysis was used to express how strongly the surface potential signal depended upon topographic factors. Namely, these were local curvature (because this appeared to explain the contrast around the deposits noted earlier), fast-scan derivative (because this could be an indication of imperfect topography tracking, which can have a significant effect on KPFM signal), and sample height. The last covariance measurement is included as a baseline: KPFM is a local measurement, and because a feedback loop is used to keep the tip's height above the sample at its location constant, it cannot be significantly linked to KPFM signal. Therefore, significant correlations with this surface potential must have a higher correlation coefficient than that of height with surface potential.

Because KPFM has a lower resolution than the AC-AFM topography methods used to map the surface, a blurring effect was applied to these data sets before its Pearson covariance with surface potential was analyzed. This averaging blur was chosen such that it maximized the resulting covariance, and this blur that resulted in maximal correlation coefficient was the same for all data sets. A figure detailing these results is shown below.

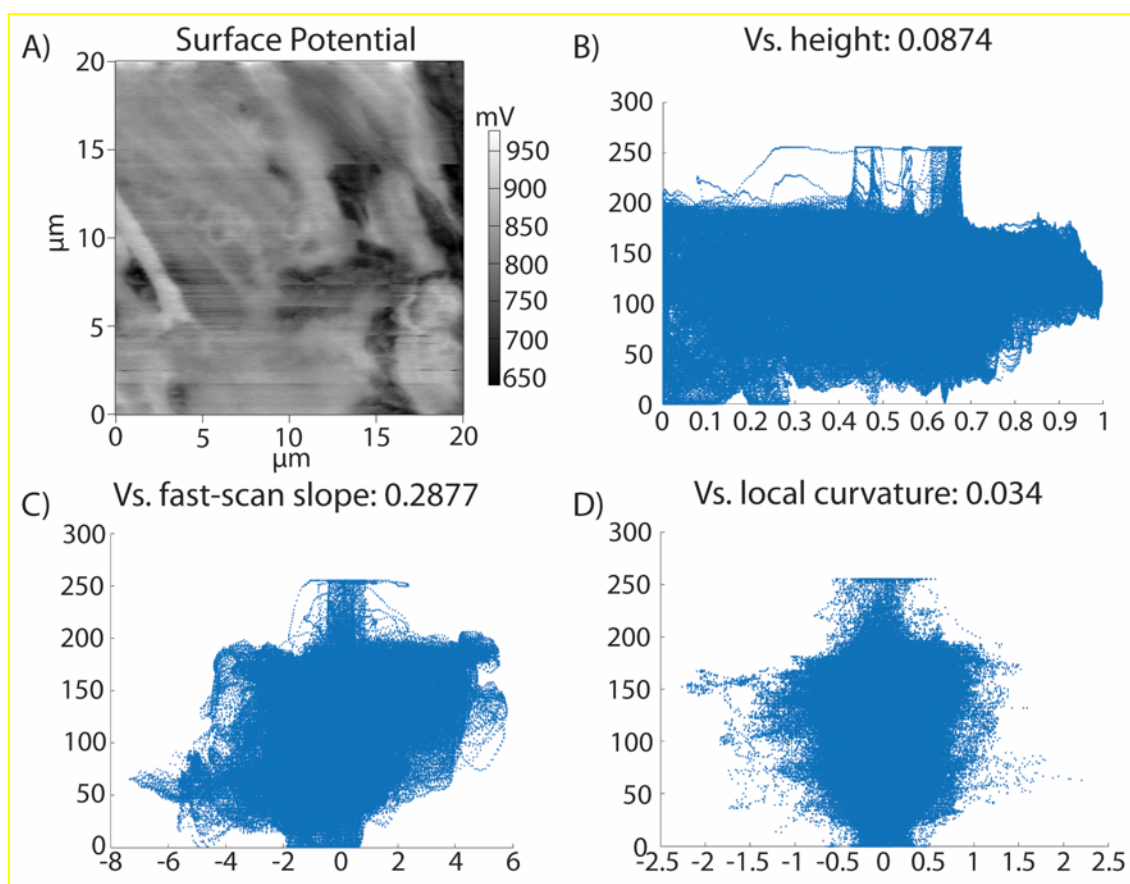


Figure 3-2: Pearson correlation maps of surface potential vs topographic variables

Where figure 3-2 A) is a replotting of the Surface Potential, and 3-2 images B) – D) are scatter plots of the surface potential at each pixel vs the titular variables (local curvature, height, and fast-scan slope) after the aforementioned blurring. The values of each of these axes are given in arbitrary units (for instance, the surface potential was taken from the grayscale image A) as a

0-255 value of pixel brightness), but because the magnitude of the Pearson correlation is independent of linear transformations of the data this has no effect on the values thereof, which are given in the title. Using topographic height as a baseline, we conclude that of those topographic variables examined here only fast-scan slope was a significant contribution to the signal in this image.

Given previous concerns from on-chip cycling experiments regarding the possibility of copper participating in the cell's electrochemistry, the experiment was performed on a new copper anode, prepared in the same fashion as this one was, but with cycling limits reduced to between 0.5 and 2.5 V vs Li, the results of which are discussed below.

3.4.2 Cu KPFM

After cycling the copper anode with more restrictive compliance voltage limits, most regions of the sample that were characterized before cycling showed little if any change after cycling, but one region of the sample was noted where significant deposition appeared to have occurred. An image taken from the AFM's camera is shown in figure 3-3, indicating the deposit noted. For scale, the width of the AFM tip is approximately 30 μm .

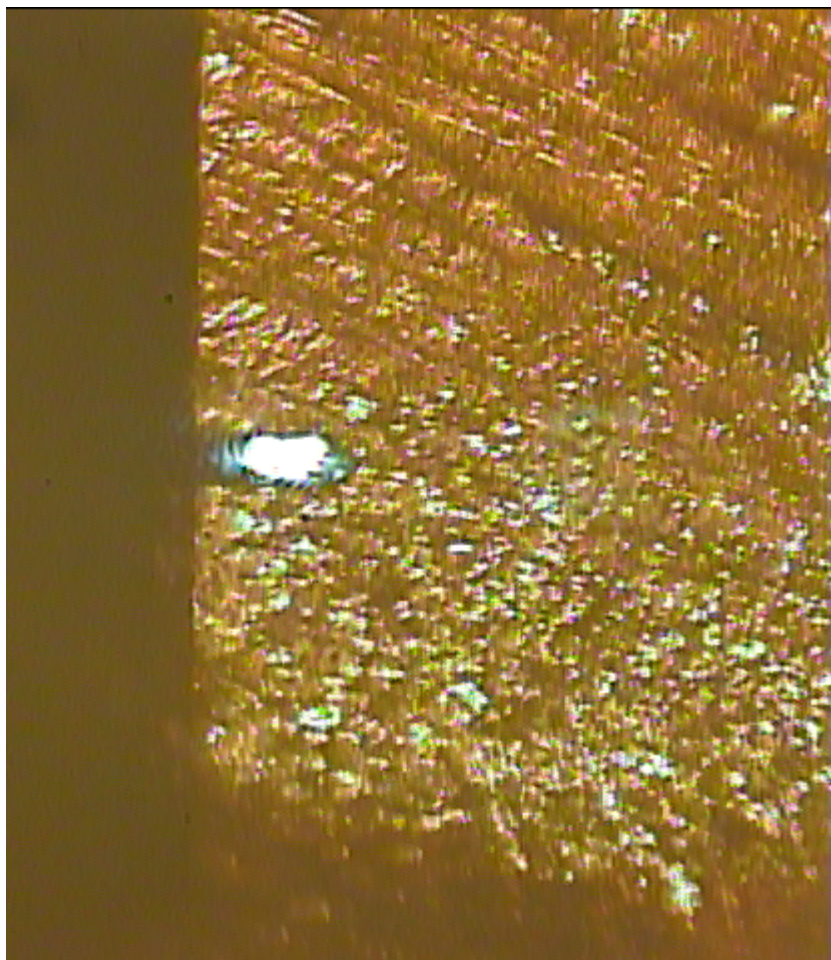


Figure 3-3: Camera image of Cu anode after cycling

This was the only region of deposit noted in this sample. Kelvin probe microscopy was performed at this location, and the scans of this area indicated features in surface potential that were consistent between scans, which are discussed in the following figure 3-4.

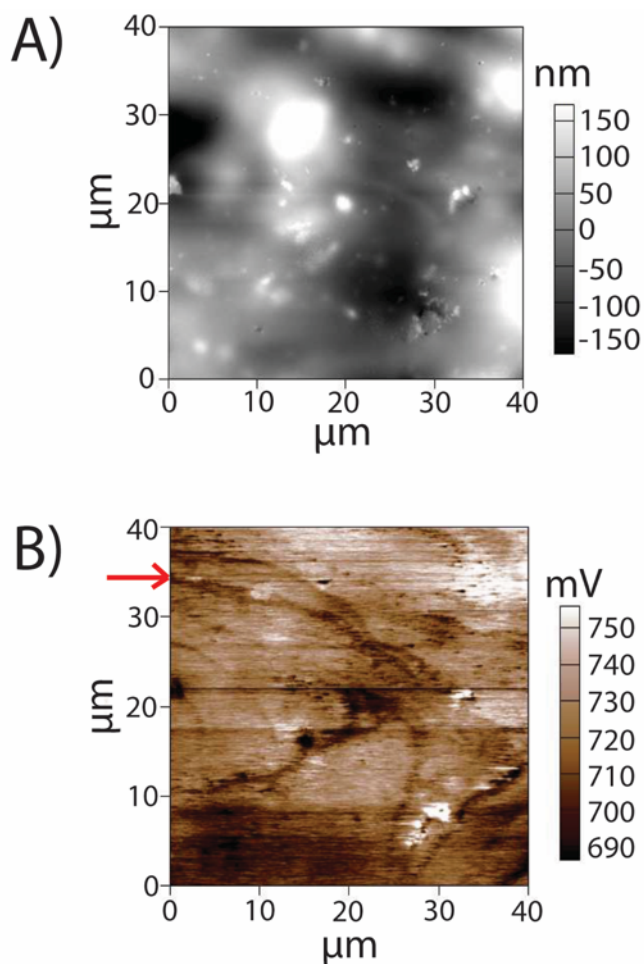


Figure 3-4: Topography and Surface potential of Cu anode in a region of significant deposition

In regions where a significant amount of lithium did deposit, not only was the topography significantly flatter than the underlying electrode, but it displayed contours in surface potential (one of which is indicated by the red arrow in image B) that were not clearly correlated with topography or phase information, the latter of which would include information about tip attractive force and the mechanical properties of the surface, a feature illustrated by the following section containing two figures of unpublished data related to these experiments.

3.4.3 Au KPFM

After cycling, KPFM was performed on the gold anode, the results of which are shown in figure 3-7 below.

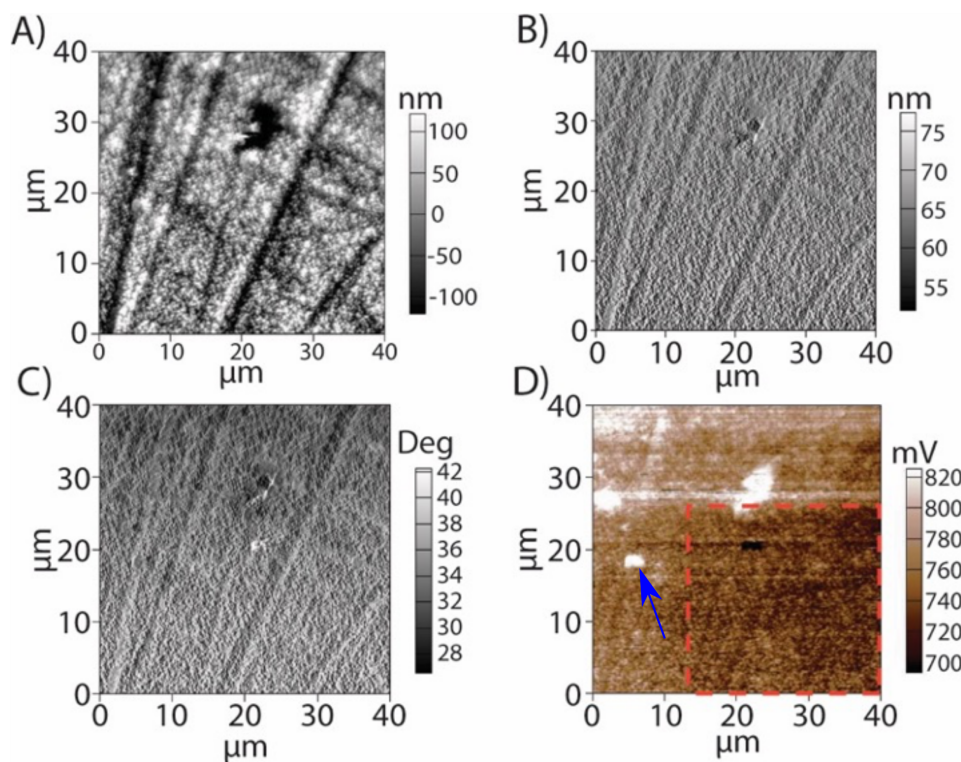


Figure 3-5: Gold anode topographic features and surface potential after cycling

Due to the small size of deposits, and the resulting nonflat topography thereof, kelvin probe microscopy could not provide information with spatial resolution on the scale of individual deposits. Some larger regions with surface potential contrast were observed, such as the white region labelled with the blue arrow, and the low potential region indicated by the red dotted line box.

3.4.4 Au EFM

In addition to kelvin probe microscopy, attempts were made to garner information about the thickness and dielectric properties of the electrolyte using electrostatic force microscopy, as shown below in figure 3-8.

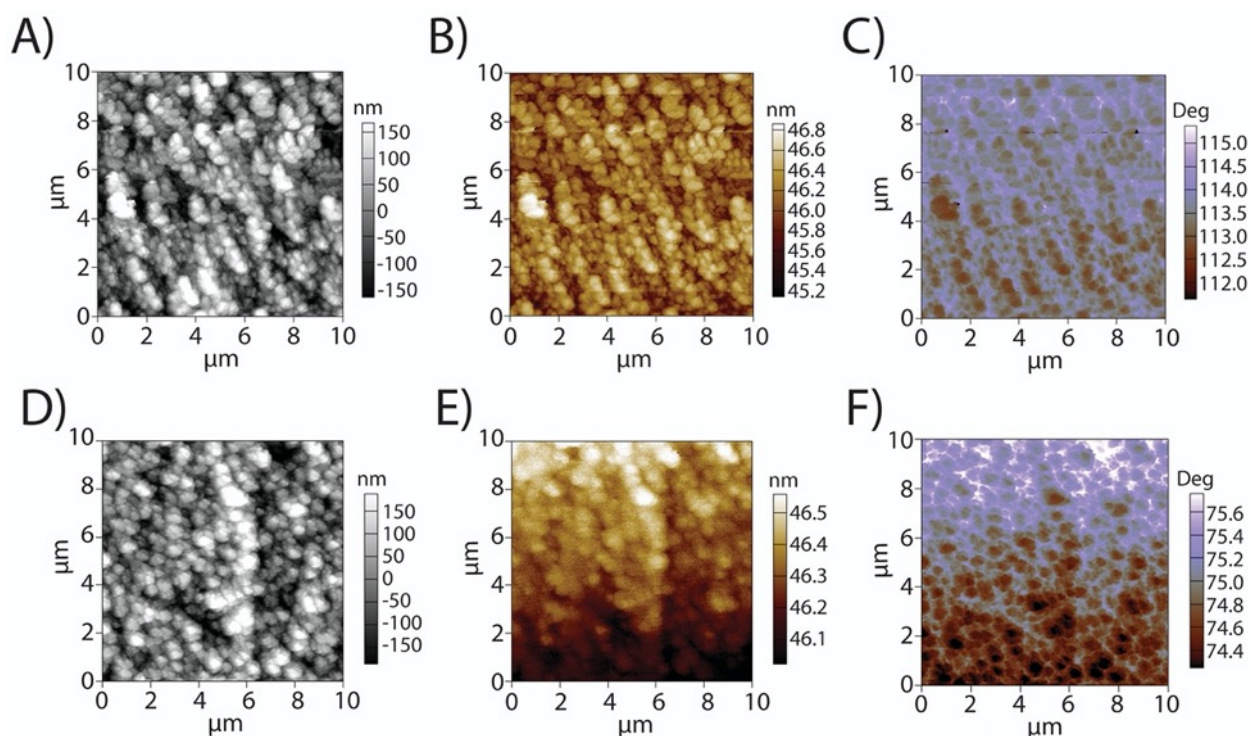


Figure 3-6: EFM of cycled Au electrode, with tip driven above and below resonance

Figure 3-8 shows topography (A) and D)), EFM amplitude (B) and E)), and EFM Phase response (C) and F)) of a tip driven at a frequency above (A)–C)) and below (D)–F)) resonance, observed on a gold sample subjected to Li deposition. This illustrates that better contrast is obtained with frequencies above resonance, and that local variations in amplitude appear to be inversely correlated with local variations in phase (the latter of which is highly sensitive to forces acting on the AFM tip in non-contact conditions). To aid in the interpretation of this data a simulated EFM force-distance curve is included in figure 3-9, which illustrates the effect that

varying electrostatic attractive force, as expressed here through varying tip-sample separation, has on the amplitude and phase response of the electrically biased tip as it moves above the sample.

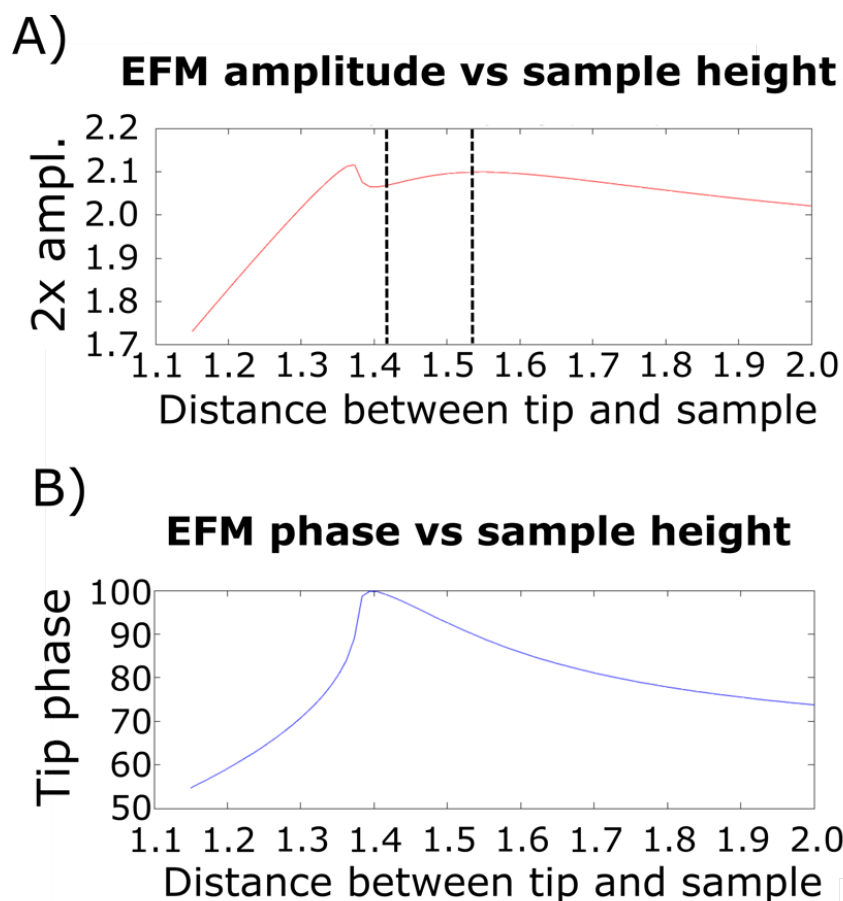


Figure 3-7: Simulated EFM force distance curve

The above figure 3-9 is an example of an AC-AFM force distance curve: a measure of the response of the tip's oscillation to the continued approach of the tip to the sample. This simulation was performed assuming the tip follows the behavior of a driven and damped harmonic oscillator, with additional force terms acting upon it in the form of a $1/r^2$ long range electrostatic interaction (as might be felt by the tip during EFM), and a shorter-ranged 12-6

(Lennard-Jones) sample interaction potential to simulate contact forces. As such, the attractive force felt by the tip increases as the separation between tip and sample decreases.

Figure 3-9 illustrates that tip interaction phase increases with increasing electrostatic attractive force acting on the tip when the tip is far from the sample. Applying this finding to figures 3-8 C) and F), we find that less force is acting on the tip in the peaks on the sample versus the valleys, consistent with either a uniform SEI and significant topographic contribution, or the formation of an insulating and weakly dielectric SEI on the peaks in this region.

Figure 3-9 is an example of an AFM tip tuned to a frequency below resonance, as indicated by the tip phase response below 90 degrees with respect to driving waveform in the limit of large separation from the sample. As the tip approaches the sample and the attractive electrostatic force acting on it over the entire range of its oscillation increases, the phase lag between the tip's oscillation and its driving force slowly increases toward resonance conditions. Consequently, the tip's amplitude response increases as the tip-sample system approaches resonance, but starts to decrease again as the forces acting on the tip increase to the point that the resonance frequency of the tip-sample system changes further still and starts to increase the difference between the constant driving frequency applied to the tip and the resonance of the tip-sample system. The result is a region where the amplitude response to changing force acting on the tip is virtually flat in a region around resonance. This explains the low amplitude contrast seen on the left shoulder tune in the previous figure's image E). Had the tip experienced more electrostatic force from the sample in this region, or been tuned to a slightly higher frequency, it could have experienced a contrast inversion in amplitude signal, where increasing electrostatic force acting on the tip

instead results in decreasing EFM amplitude, as is indicated between the dotted lines in image A).

Applying the above observations of increasing phase occurring in response to increasing attractive force to the data in figure 3-8, it may be concluded that the reduced amplitude contrast in left shoulder measurements occurs in part due to a contrast inversion in EFM amplitude that occurs with tips tuned on the left shoulder (frequencies below resonance). As the tip approaches the sample, the response of the AFM tip to its driving force changes, resulting in conditions where even significant changes in the electrostatic force acting on it may result in little to no change in the tip's amplitude signal. This flatness of response occurs as the tip approaches its peak amplitude response. This peak amplitude response normally occurs in conditions such that the tip's phase signal is at 90 degrees with respect to its driving force, but an offset occurs here in part due to a sample-based contribution to the damping experienced by the tip (this will be illustrated later). The contrast inversion indicated between the dotted lines in figure 3-9 A) was observed in further AFM data on this sample, at phase significantly offset from 90 degrees.

An example of the aforementioned offset of contrast inversion is shown below, in figure 3-10.

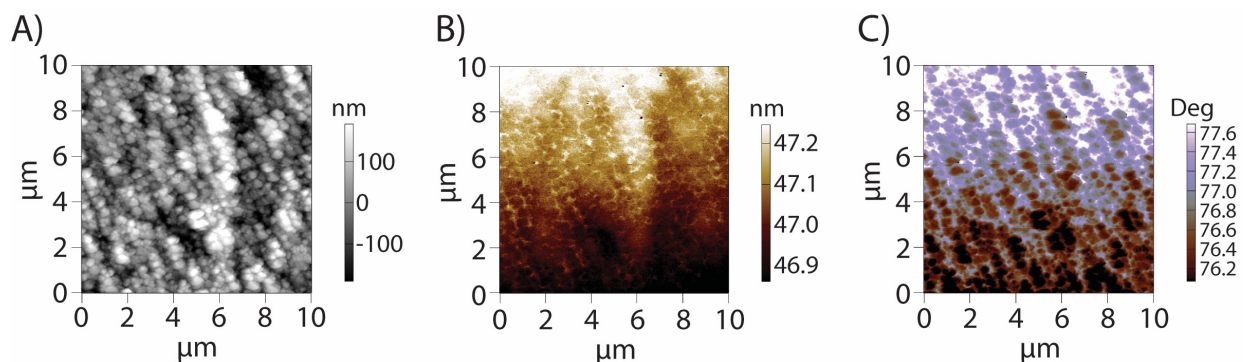


Figure 3-8: Au EFM displaying amplitude contrast inversion

Figure 3-10 A)-C) show the topography, EFM amplitude response, and EFM phase response of the tip on a gold anode sample after Li deposition when the tip is tuned to a frequency below its free-air resonance. While the contrast inversion in the simulated EFM curve in figure 3-9 B) occurs when the phase response suggests the tip is near resonance, the data here shows contrast inversion in amplitude while phase is relatively far from the 90 degree resonance condition. This is observed in simulations with a variation in the damping parameter of the tip's oscillation as a function of height above the sample, a phenomenon illustrated in figure 3-11.

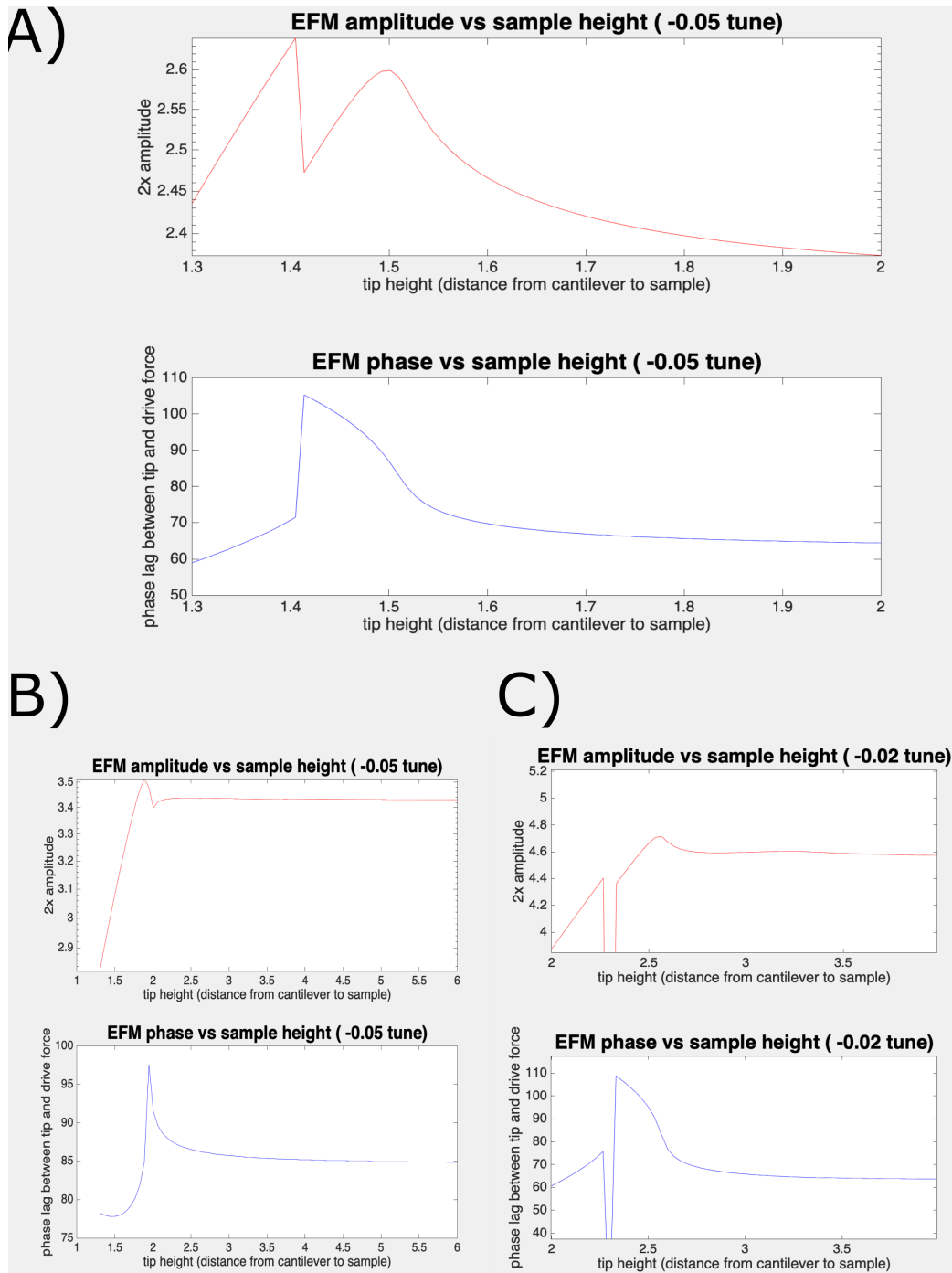


Figure 3-9: Simulated EFM responses with A) low damping, B) high damping, C) low static damping, but an additional damping parameter that increases as the tip approaches the sample.

In the above figure 3-11, the effect of varying damping parameter on the simulated EFM force curve is illustrated, with driving force adjusted to maintain similar amplitudes in all cases.

In figure 3-11 C) specifically, an amplitude contrast inversion is observed at a significant offset from the conditions of 90 degrees phase lag, a feature observed in experiments and only occurring in simulations that use a damping parameter that increases as the tip approaches the sample. Local increases in tip damping parameter based on the oscillation of a charged tip during EFM and evidence of a corresponding current induced locally in the sample by this oscillation have been observed previously^{102,103}. The presence of a significant signal corresponding to induced current suggests that image contrast could be attained by a localized scanning non-contact impedance microscopy measurements.

3.4.5 Au deposit statistical analysis

Below is figure 3-12, which details the procedure by which statistical analysis of the largest deposits that occurred in a given region of the gold anode were examined, compared with the locations of scratch edges in the underlying topography.

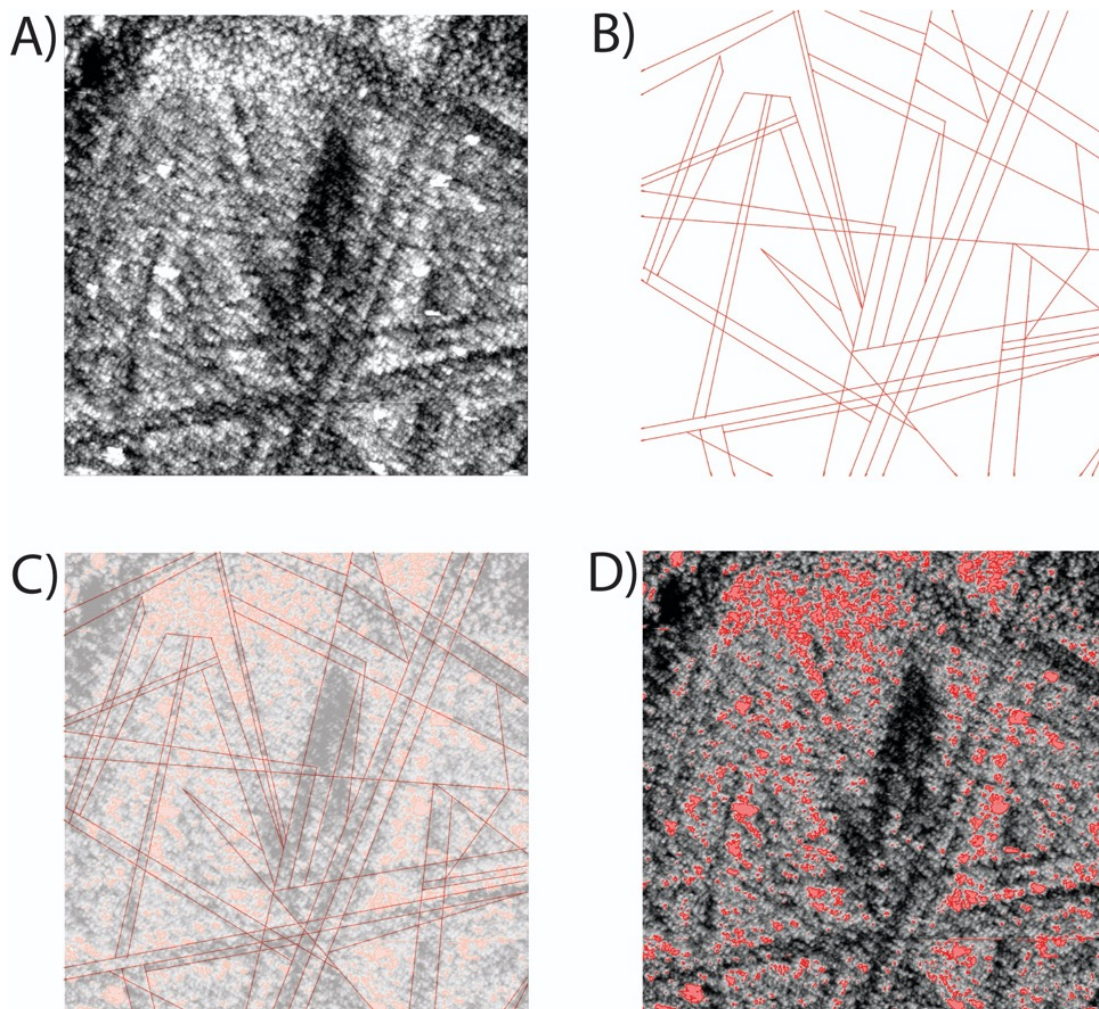


Figure 3-10: Illustration of the scratch correlation process for statistical analysis on gold anode

Because the scratches made in the gold and copper anodes are made by polishing with sandpaper, they are relatively long and straight on the scale of $40\ \mu\text{m}$ (as is the case in the topography image in A). Attempts were made to fit the straight edges of scratches in the scratched region with straight lines that terminate only on the edges of the image, and other scratches. An example of these fits is shown in B and C. In the image in D), the topography image was masked to highlight in red all pixels where the sample height exceeded 100 nm above the sample. This serves to highlight regions where significant deposition occurred. This scratch

template was compared with the highlighted image D), and a histogram of the distance of highlighted pixels to their nearest scratch edge was made, shown below with a similar histogram comparing the same data for an identical number of randomly distributed points on this scratch fit:

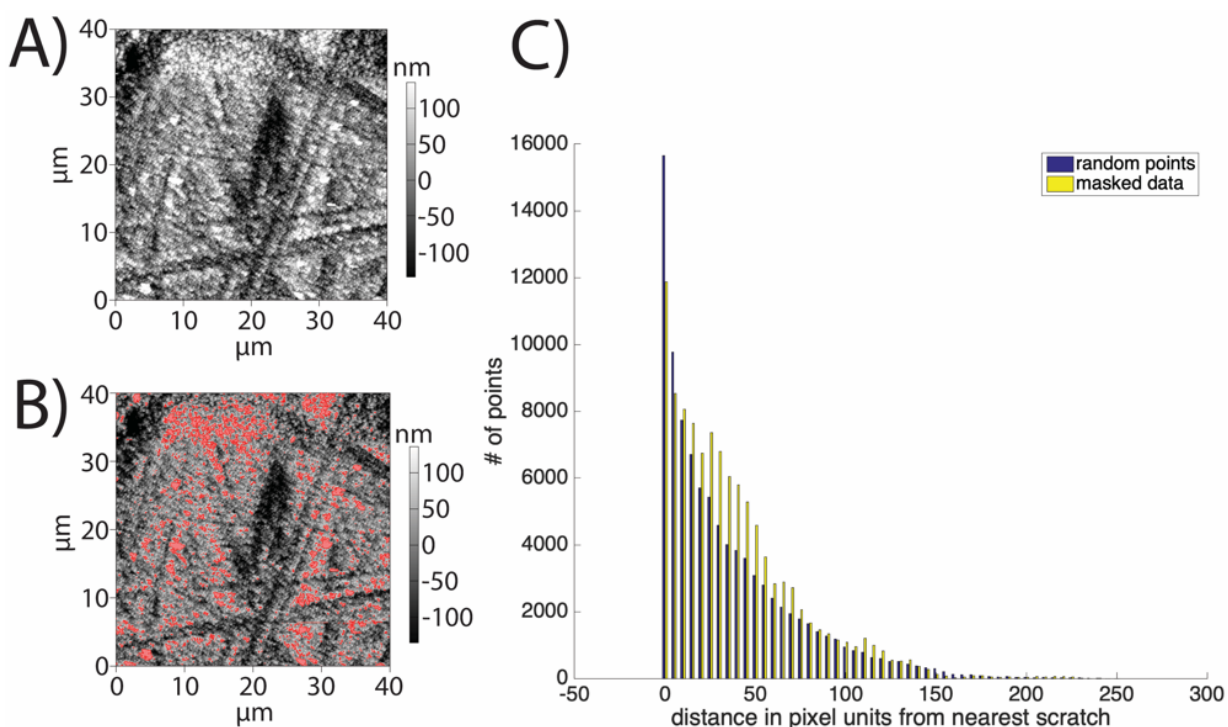


Figure 3-11: Results of Au deposit statistical analysis, including histogram of deposit locations as a function of distance from the nearest scratched region, with comparison to random distributions on the same map.

Notable in this is the comparison with randomly distributed pixels. Comparison of the masked regions with random locations in the image suggests that large deposits (in excess of 100 nm height above the image baseline) preferentially form in a region between 15 and approximately 50 pixels in this 1024 x 1024 image of a 40 μm by 40 μm region of the sample. This preferential nucleation range occurs between 600 nm and 2.4 μm from the nearest scratch edge. A similar trend was observed for other regions of this sample selected for analysis, with all

samples reporting a mean and median distance from each highlighted pixel to the nearest scratch edge that was significantly larger than that of the randomly distributed data. In every image characterized in this manner, a preferential deposition in a range of between 600 nm and 1.6 μm distance from the nearest scratch edge was observed. With a characteristic size of between 200 and 500 nm for these deposits, this suggests that deposition does not preferentially nucleate directly on top of the scratch, which suggests that deposition due to enhanced local electric field does not explain the observed behavior.

This could be explained if conditions within the scratch were unfavorable to lithium deposition, such that an excess of electrolyte within the scratch would diffuse to the surrounding anode surface and deposit there. This could be tested by subsequent experiments with varying electrolyte properties and scratch topographies. For example: if this is the case, it is expected that the preferential deposition region's upper bound increase with increasing electrolyte diffusivity and constant electrolyte concentration (as the excess would diffuse further), increase with increasing electrolyte concentration and constant diffusivity (as the excess would not deplete as quickly), and both the region's upper and lower bound distance from the nearest scratch edge decrease with increasing overpotential/galvanostatic current density (as the excess would deplete more quickly, and the nuclei that deposit would be smaller). With regards to varying scratch topography to examine this behavior, deeper scratches with the same "footprint" on the surface would carry more electrolyte and thus increase the size of nuclei within the preferential deposition region (as there is a greater excess of electrolyte salt that diffuses along

the same paths as the prior cases), assuming the effects of plastic deformation on the material and the resulting scratch topography could be neglected, or alleviated in some way.

3.4.6 Double current lithium cycling:

Initial work on this paper strived to compare the effect of varying overpotential on these deposits as well, but the response of some of these electrode materials proved difficult to measure in AFM. Below (figure 3-5) is a topography and phase image of a lithium anode after patterning with an AFM tip and before cycling:

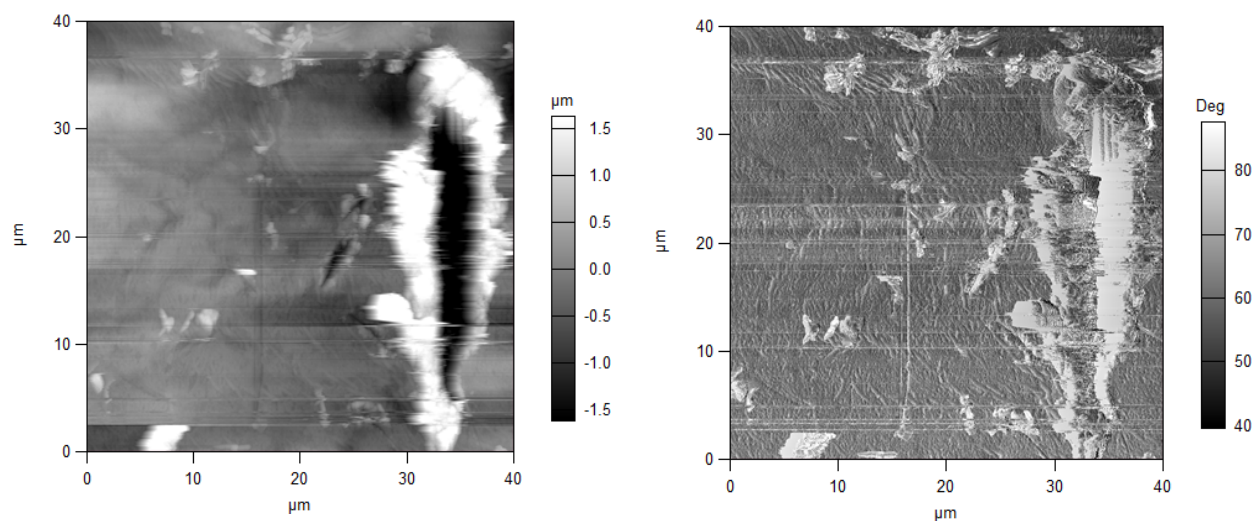


Figure 3-12: Freshly scratched lithium foil anode before double-current cycling

And on the following page figure 3-6 is the same lithium anode after biasing at 38.484 μA ($\sim 100 \mu\text{A}/\text{cm}^2$):

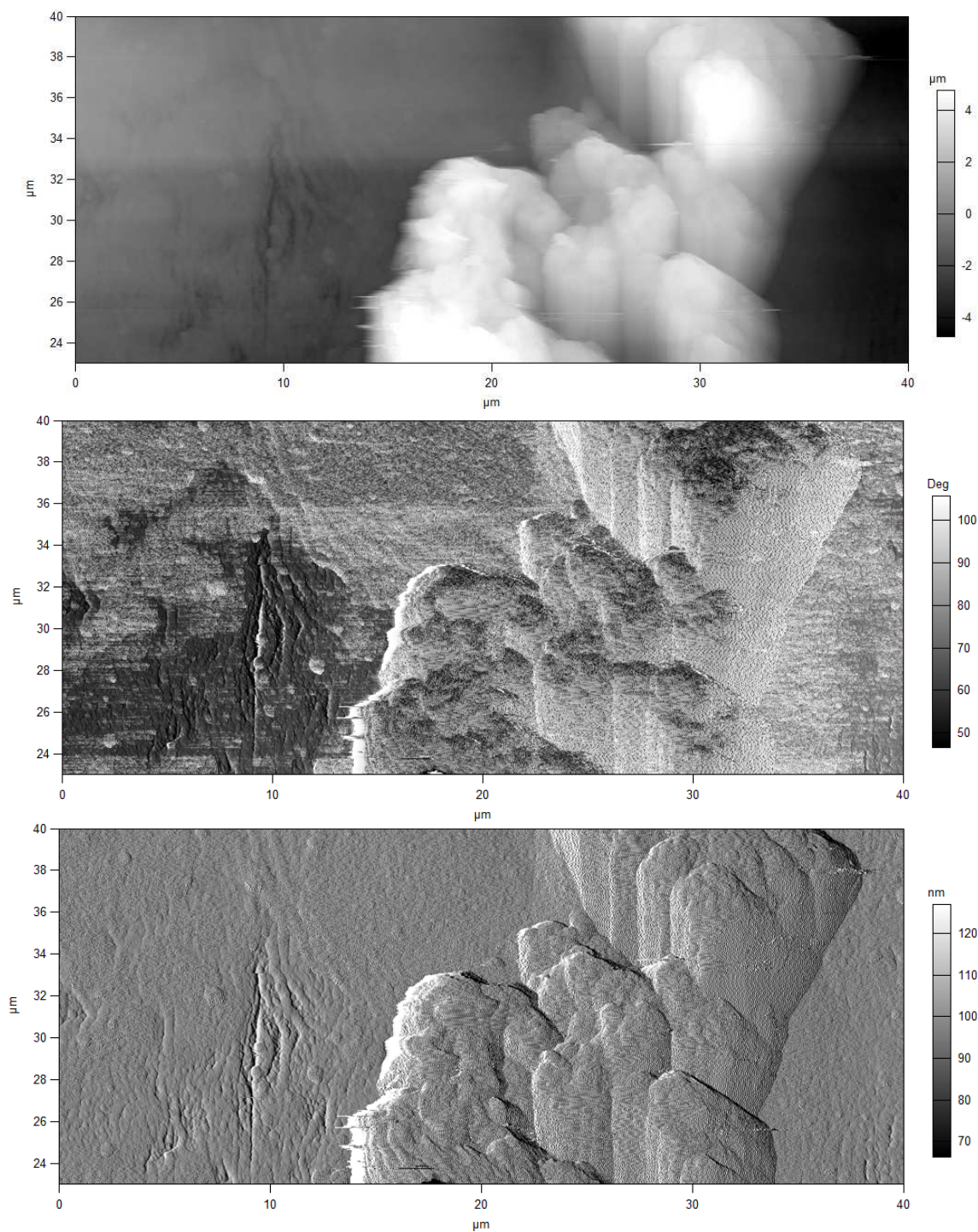


Figure 3-13: Lithium foil anode after double current cycling

This scan was stopped early because it was close to exceeding the height limits of the AFM's Z-piezo. What is notable here is that significant growth occurred in the scratched region, and that significant phase contrast was obtained between different flat regions where relatively little deposition occurred. This suggests that, if significant contrast in the properties of an SEI were present, the response of the tip could detect it.

3.4.7 Li EFM

Below in figure 3-14 is the data from an EFM session on lithium metal after deposition.

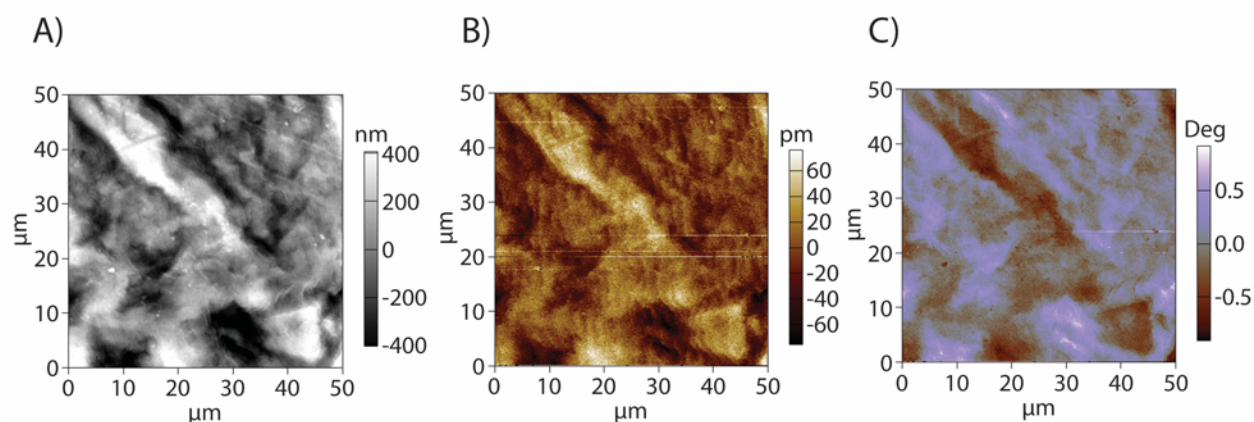


Figure 3-14: EFM performed on cycled Li electrode in an unpatterned region with sparse deposition

Shown in figure 3-14 is A) the topography, B) the EFM amplitude, and C) the EFM phase observed on a cycled lithium foil sample in a region that was not pre-patterned, and with a tip tuned to a frequency below resonance. The latter two have had a linear fit to their signal removed, in order to remove the effects of drifting tip resonance on the image. Notable in the topography (and to a lesser degree, the EFM phase image), are a number of relatively tall, narrow deposits. These regions also correlate with a low phase, suggesting that the tip experiences less electrostatic force due to its bias relative to the sample when it's above these points than when

it is above the sample area. Due to the steep topographic change, it is impossible to say whether this is due to the properties of the local SEI, or simply the fact that it is well elevated above the rest of the electrode. The rest of the phase image very uniformly follows the topography, suggesting a very thin or very uniform SEI.

3.4.8 Li KPFM

After deposition, a significant deposit was noted on the right side of a prefabricated scratch in lithium metal, and the SKPM measurements performed upon this area are detailed below in figure 3-15.

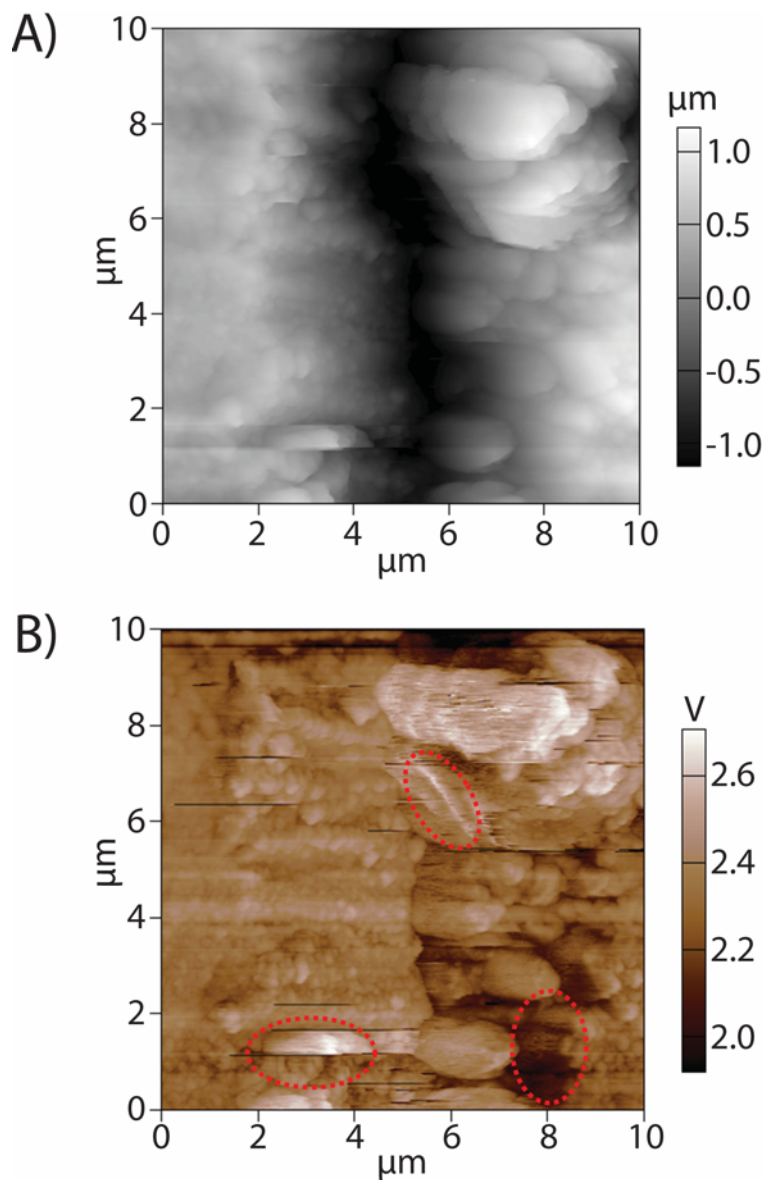


Figure 3-15: SKPM on Li anode in a scratched region

Figure 3-15 shows A) the topography and B) the surface potential observed in a scratched region after cycling. Because this sample is not flat, contributions from topography can be seen from features such as edges (uppermost dotted ellipse), and some slope contrast (lower right dotted ellipse). In the absence of this significant surface potential contrast is noted in the large deposit in the upper right of this image. This surface potential variation suggests that the SEI that

forms on large deposits of lithium is not the same as that which forms on most of the lithium surface when exposed to electrolyte. Additionally, a topographic discontinuity can be seen in the lower right of this image, suggesting that these deposits were fragile enough to be disturbed by the AFM tip, a behavior seen in similar dendritic deposits.

3.5 Conclusions

Based on the SPM studies detailed in this chapter, the following may be concluded about the deposition behavior of lithium:

The SEI that forms on lithium under electrochemical cycling conditions is not chemically homogeneous, with variations in surface potential that occur on top of large deposits of lithium as reflected in Scanning Kelvin Probe Microscopy data on copper and lithium anodes. This suggests chemical contrast within the SEI. Furthermore, EFM data on Au and Cu suggests that the SEI that forms on lithium deposits is either uniform, or significantly thicker on top of lithium deposits than in the surrounding area, and that it is neither conductive nor strongly dielectric (conditions that would allow the propagation of the electric field to the surface of the deposit from the conductive anode underneath nearly unimpeded). Additionally, a variation in the EFM phase signal seen in EFM data on the gold sample was investigated through the modelling of the AC response of the AFM tip to forces acting on it, which suggested significant tip-damping effects that likely come from induced current in the sample occurred. If a significant contribution to the tip's AC signal comes from damping that occurs as a result of induced current, it suggests that contrast could be observed with scanning impedance microscopy measurements, suggesting another technique that may prove useful for future measurements on this system.

Additionally, statistical analysis of the large number of discrete deposits that formed on the gold anode suggests that preferential deposition occurs in the vicinity of sharp topographic features in a manner that could be related to electrolyte polarization behavior, a hypothesis that could be confirmed by further measurements on samples with varying scratch topography, electrolyte conductivity, and electrolyte salt concentration.

3.6 Funding acknowledgement

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Chapter 4: Mechanical Properties of Battery Materials

4.1 Motivation

Theoretical work^{104,105} has demonstrated that the presence of mechanical stress at the anode surface can result in an overpotential that affects deposition behavior, because it contributes to the free energy of the reaction that is occurring. If this stress were localized in a lithium anode, similarly local variations in the deposition behavior of lithium metal would occur, resulting in the local enhancement/suppression of dendrite formation. Due to the constraints of mechanical equilibrium, this mechanical overpotential is not solely dependent upon the geometry and conditions of the anode, but also that of any materials in contact with it, which means this behavior is also of interest where the development of a solid electrolyte is concerned, especially where the mechanical properties of said solid electrolytes vary significantly. The original work discussed herein investigates the local mechanical properties of a lithium metal sample before and after patterning using the techniques of Scanning Probe Microscopy, and details early experiments pertaining to the variation of mechanical properties of a solid electrolyte. This work will also be discussed in its broader context in literature.

4.2 Background

Because work is being performed involving the structuring of electrode materials, and that has been demonstrated to improve cycle lifetimes and result in selective deposition, it is of interest to understand the more general consequences of applying these methods to battery materials^{106,107,65,108}. Patterning by mechanical stamp causes plastic deformation, and thus induces some amount of residual stress in the material. If this mechanical stress were localized,

it could affect local deposition behavior to either promote or suppress dendrite formation, as suggested in theoretical studies of dendrite formation and observed directly in corrosion studies on shot-peened material^{104,109,110}. To investigate this behavior in lithium metal, a lithium metal anode was scratched using an AFM tip, and its mechanical response was measured. This scratching behavior offers insight into the deformation behavior of lithium metal.

4.3 Methods

The work described below on lithium metal scratching has been published as “Effect of nanopatterning on mechanical properties of lithium anode”¹¹¹. This scratching was performed in two regimes: one above the limit of plastic deformation (“high force scratching”), and one at or below it (“low force scratching”). These two regimes of scratching allowed for the differentiation of the highly deformed hardness of Li metal (which should correspond to the maximum residual stress state of lithium), and the unworked hardness of lithium metal (i.e: the onset of plastic deformation). The tip could be measured before and after patterning using a transmission electron microscope as shown below in figure 4-1, so its diameter could be known.

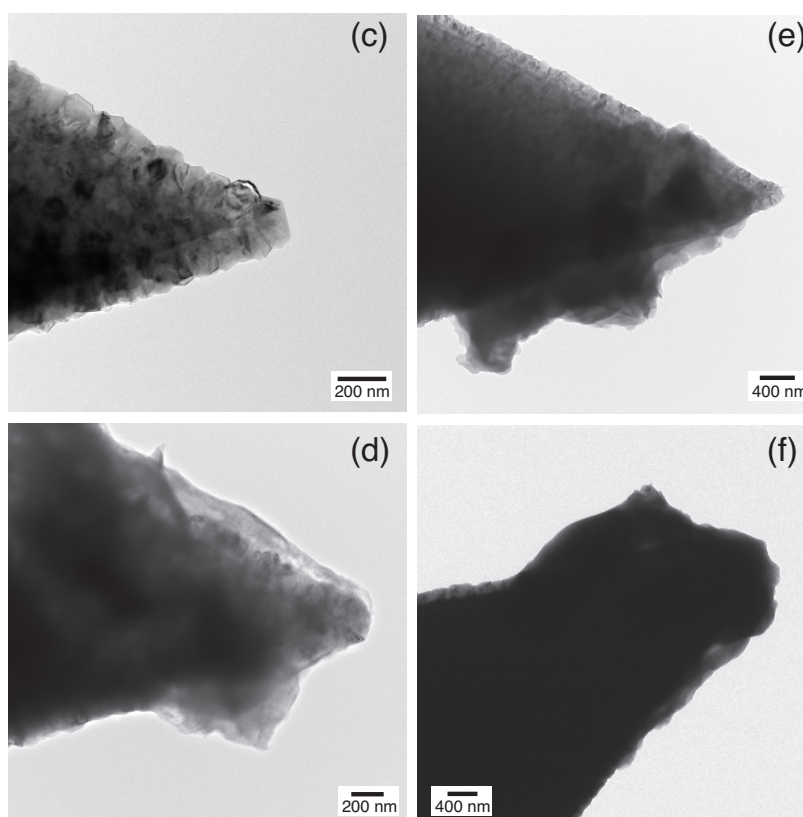


Figure 4-1: examples of AFM tip before and after different scratching protocols

The figure above illustrates tip deformation in various stages of use in the scratching experiments performed. Figure 4-1 (c) shows an AFM tip imaged prior to any use, figure 4-1 (e) shows a different such tip after one session of low force scratching, note that while debris has accumulated on the tip, its end radius does not appear to have been blunted. Figure 4-1 (d) shows the tip after a single session of high-force scratching, where significant debris has accumulated over the diamond coated AFM tip which has blunted slightly. Figure 4-1 (f) shows such a tip after two experiments with high-force scratching. Because high force scratching has the capacity to damage the tip, only one session was ever performed with a given tip, and where the radius was

concerned the tip radius was linearly interpolated in the associated hardness calculations between its initial and final values as successive scratches were performed.

Because these scratch features are necessarily on the scale of the tip (as the tip was used to scratch them), the measurements of the scratched areas are subject to significant convolution with the probe shape. Both of these hardness measurements required an accurate measure of the width of the scratch, so corrections due to the finite radius of the tip end (commonly referred to as “rolling ball” corrections, such probe-size based corrections have been performed in various fields before^{112,113}) were performed. As illustrated in Figure 4-2, these corrections occur because the region of the tip that makes contact with the sample changes as the angle of contact of the tip with the sample changes, resulting in a mismeasurement of lateral distance on the order of the size of the tip’s end radius.

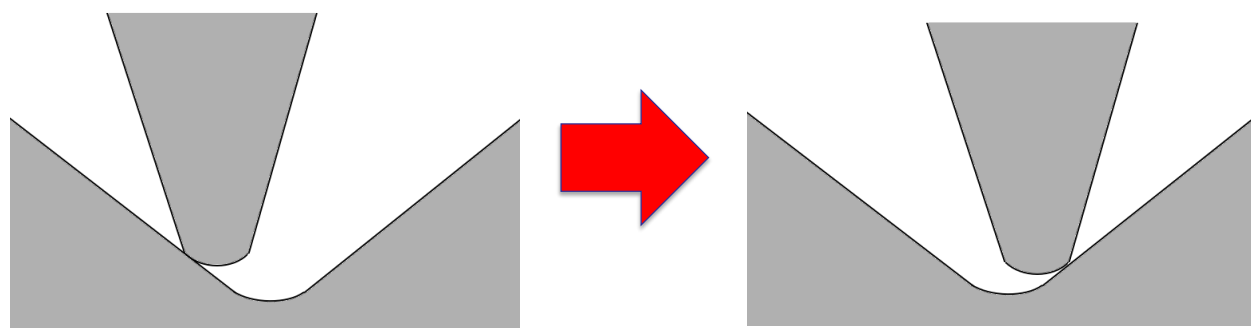


Figure 4-2: Illustration of rolling ball corrections as relevant for AFM

4.3.1 Elastic modulus measurement protocol

With the known tip radius, local elastic modulus measurements could also be performed. These measurements were performed after low-force scratching experiments, as the micrographs in figure 1 suggest that low force scratching does not result in damage to the tip.

Due to the limited space in the cell and uncertain chemical compatibility with a common hard standard (i.e: Lithium could react with a plain silicon chip, as silicon is also a proposed anode for lithium ion cells) the inverse optical lever sensitivity of the tip was calibrated by high force indentation into the lithium sample. This occasionally proved inadequate, but due to the nature of the measurements the inverse optical lever sensitivity could be corrected based on the deformation behavior of lithium. The tips used to perform these measurements, as well as the low force scratching measurement, were CDT-FMR tips from Asylum research: conductive, diamond-coated tips with a nominal spring constant of 10 N/m.

4.3.2 Low force scratching protocol

The low force scratching experiments were performed to investigate the unworked hardness of lithium. Whereas high force scratching experiments removed a significant amount of lithium in a single pass, low force scratching produced a wear groove in the surface with minimal force by passing the tip back and forth across the scratched area repeatedly at 1 Hz for 512 passes over this area. After scratching, the topography of the scratch was measured by a scan of the worn area. Because the surface was uneven, the criteria for the tip scratching the surface was whether the tip produced a scratch of sufficient depth to accommodate the rounded end of the tip over a significant length, applied quantitatively in this experiment as an averaging the depth of the scratch at its deepest point over 30 scan lines perpendicular to the scratch direction, and comparing this depth with the depth at which the tip end ceased to be well approximated by a sphere. If the scratch depth at a given force exceeded this depth of tip spherical character, the applied force was said to be sufficient to scratch the surface, and the minimum force used to

scratch the surface was used to calculate the unworked hardness of the surface. This methodology was necessary to know the contact area that occurred during scratching: if a lesser depth was assumed, it was possible that the tip would not be well approximated by a spherical capping sector in the small region of contact. If a larger depth was chosen, this would not have measured the point at which plastic deformation begins to occur, a point that this methodology can only approximate because some amount of plastic deformation is required to make this wear pattern in the sample.

The quantitative value of tip contact area for these low force scratching measurements was approximated as one quarter of the area of the spherical sector that comprises the end of the tip. This measurement is performed in sliding contact, so the trailing half of the tip is likely not significantly involved in load-bearing. Additionally, the upper parts of the rounded end of the tip would not be in contact with the sample until it came into contact with the end of the scratched region, except for those on the side of the tip which would be in contact with the sides of the scratch, which have already conformed to the profile of the tip. The minimum force required to produce a scratch in the sample, divided by this contact area, was considered the unworked hardness of lithium metal.

4.3.3 Highly deformed hardness calculation

Previous work¹¹⁴ on the mechanical and tribological properties of materials established a relation between the response of a material to loading and scratching by an indenter, and its mechanical properties. This work assumed the form of the cross-section of the indented bottom of the scratch took the form of a semicircle whose radius is equal to that of the indenter. As the

TEM images in figure 4-1 suggest, this is not necessarily the case as the tip does not always end in a hemisphere, but can instead end in a spherical sector (that is, the smaller shape that would be made by dividing a sphere with a plane that did not run through the sphere's center). In the original work discussed here, we generalize this previously established relation between the scratch cross section, indenter parameters, and material properties to include a tip shape contribution to the scratch cross-section in the form of a sector of a circle, and apply that to the equation in Zum Gahr's work which relates the grooving (scratching) wear of the material under a diamond indenter to the material's elastic properties.

The derivation of this relation starts by assuming the following form of scratch shape, as illustrated in the corresponding original research that is the subject of this section of this thesis¹¹¹, and found in figure 5.3 b) on page 138 of Zum Gahr's work¹¹⁴.

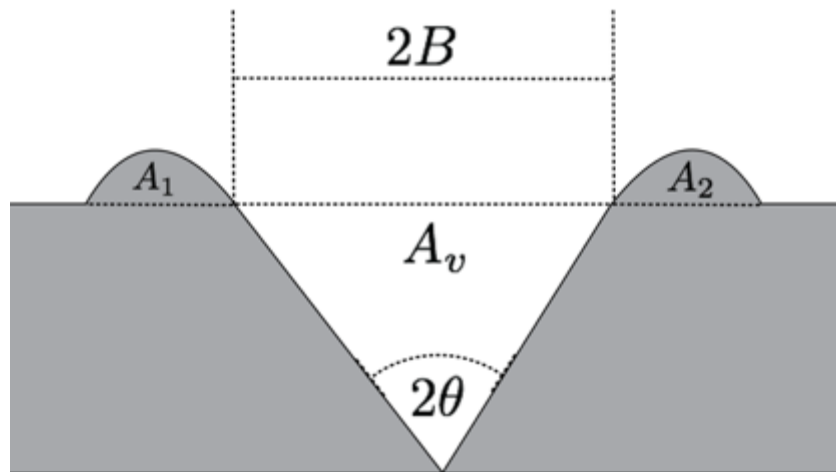


Figure 4-3: Definition of parameters of scratched area, including wear area and scratch width

Where B describes the width of the scratch, A_v is the cross sectional area of the scratch, areas A_1 and A_2 are the cross sectional area of the raised edges of the scratch, caused by material being displaced from the scratch area, and θ is the convergence angle of the scratch.

The wear area A_v is assumed to take the form of a trapezoid whose smaller parallel surface is capped by a hemispherical region that matches the radius of the spherical indenter; this relation takes the following form, from page 148 of K. H. Zum Gahr's work¹¹⁴:

$$A_v = \frac{B^2 - R^2}{\tan(\theta)} + \frac{\pi R^2}{2} \quad (4-1)$$

Where θ , B , and A_v are defined as illustrated in figure 4-3, and R is the assumed circular radius of the largest cross section of the assumed spherical tip.

However, the bottom of the scratch must conform to the profile of the tip, which in this case is not necessarily hemispherical. These tips have a radius that is a significant fraction of the scratch width ($2B$), and as such the error in wear volume (and consequently, material hardness) associated with this is large. Instead of assuming the bottom of the scratch is hemispherical, the height of the circular sector representing the tip's impression in the bottom of the scratch can be expressed using the known radius of the tip, and the slopes of the scratch topography on either side, as is shown in figure 4-4:

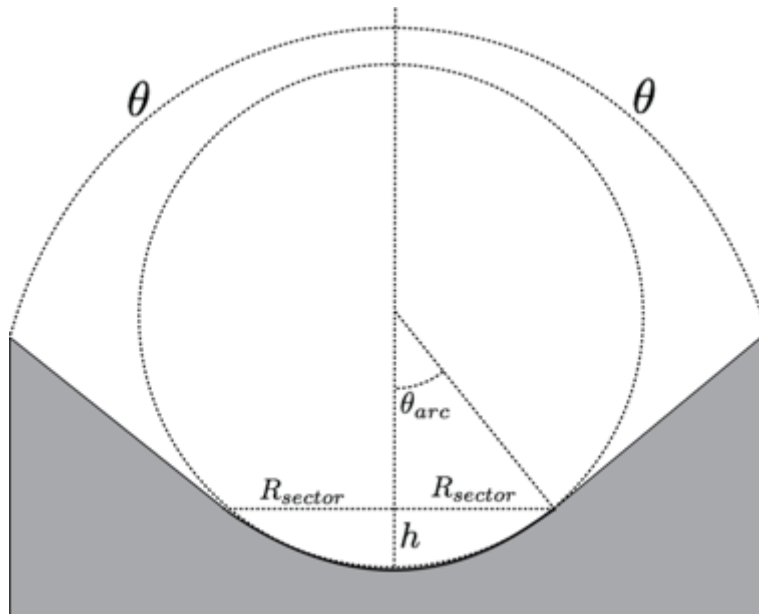


Figure 4-4: Definition of parameters concerning scratch floor defined by spherical sector

Where the radius R_{sector} of the circular sector that defines the upper limit in height of the tip conformed bottom of the scratch, θ is the scratch convergence angle, h is the height of the scratch, and θ_{arc} is the subtended angle of the circle of the tip-conformed width defined by R_{sector} . As illustrated in figure 4-4 R_{sector} can be defined according to the sine of θ_{arc} and the known tip radius, θ_{arc} can be defined geometrically from the above as the complement of angle θ . The area below the line segments of length R_{sector} is a cross sectional area of the scratch which more accurately represents the wear caused by the rounded end of the tip than the hemispherical assumption does. This area is defined as A_{sector} , and may be defined from the parameters in figure 4-4 by doubling the area calculated by subtracting the area of the right triangle (shown in dotted lines) containing the angle θ_{arc} from the area of the circle subtended by the angle θ_{arc} . This quantity may be calculated as follows:

$$A_{sector} = 2 \left[\frac{R^2}{2} (\theta_{arc} - \sin(\theta_{arc}) \cos(\theta_{arc})) \right] \quad (4-2)$$

The scratch half-width can be related to the material properties using the empirical relation for the scratch half-width formed by a diamond indenter at a 90 degree angle with the surface scratching across the surface of a material, which is given in “Microstructure and Wear of Materials”, page 139¹¹⁴:

$$B^2 = \frac{F_N \tan(\theta)}{CH} \sqrt{1 + 10\mu^2} \quad (4-3)$$

Where B is as defined in figure 4-3, F_N is the normal force applied to the grooving body, θ is as defined in figures 4-3 and 4-4, H is the hardness of the material, μ is the coefficient of friction for this material in contact with the indenter under scratching conditions, and C is a parameter that expresses the degree of work hardening experienced by the sample as follows, given on page 140 of Zum Gahr’s text¹¹⁴:

$$C = 5 \frac{H_{def}}{H} \quad (4-4)$$

Where H_{def} and H refer to the hardness of material when highly deformed and the hardness of the material in a pristine state, respectively.

The coefficient of friction μ in equation 4-3 includes both an adhesive component and a coefficient of grooving wear. The latter is generally much larger than the former and expresses the amount of work required to plastically deform all the material worn away by the tip in a single scratch. Its form is indicated in equation 4-5 (this is also given on page 149 of Zum Gahr’s text).

$$\mu \approx \mu_g = \frac{A\tau_c}{F_N} \quad (4-5)$$

Where τ_c is the critical shear stress of the material, A is the area of contact with the indenter, and F_N is again the normal loading force. τ_c can in turn be related to the hardness of the deformed material as is given on page 149 of Zum Gahr's text:

$$\tau_c \approx \frac{H_{def}}{K} \quad (4-6)$$

Where K in equation six depends on the number of slip systems of the material. 24 was chosen for these calculations based on the 48 possible slip systems available to BCC metals, and the resolution of stress along a given direction.

Replacing the semicircular wear area expressed in the second term of equation 4-1 with equation 4-2 and replacing the length R in the trapezoidal area expression of equation 4-1 with R_{sector} produces an expression for A_v that is corrected for the non-hemispherical tip profile observed in these experiments. Inserting the definition of B in terms of hardness, loading force, and grooving friction coefficient given equation 4-3 into the modified form of equation 4-1 that accounts for a non-hemispherical tip conformal cross-section, and dividing the result by tip contact area A gives the following:

$$\begin{aligned}
& \frac{A_v}{A} \\
&= \frac{F_N}{5AH_{def}} \sqrt{1 + 10 \left(\frac{AH_{def}}{KF_N} \right)^2} \\
&+ \frac{R_{sector}^2}{A \tan(\theta)} \left(\frac{\left(\frac{R}{R_{sector}} \right)^2 (2\theta_{arc} - \sin(2\theta_{arc})) \tan(\theta)}{2} - 1 \right)
\end{aligned} \tag{4-7}$$

Tip contact area A can be defined as half the surface area of the spherical sector cap of the tip evaluated with a height equal to the depth of the scratch. Essentially, the front surface of the tip is assumed to have ploughed the material of the scratch area aside. In this way, a known nondimensional wear area A_v/A can be related to a nondimensional hardness $H_{def} A/F_N$, a plot of which for various values of scratch convergence angle θ (as defined in figures 4-3 and 4-4) is shown in figure 4-5.

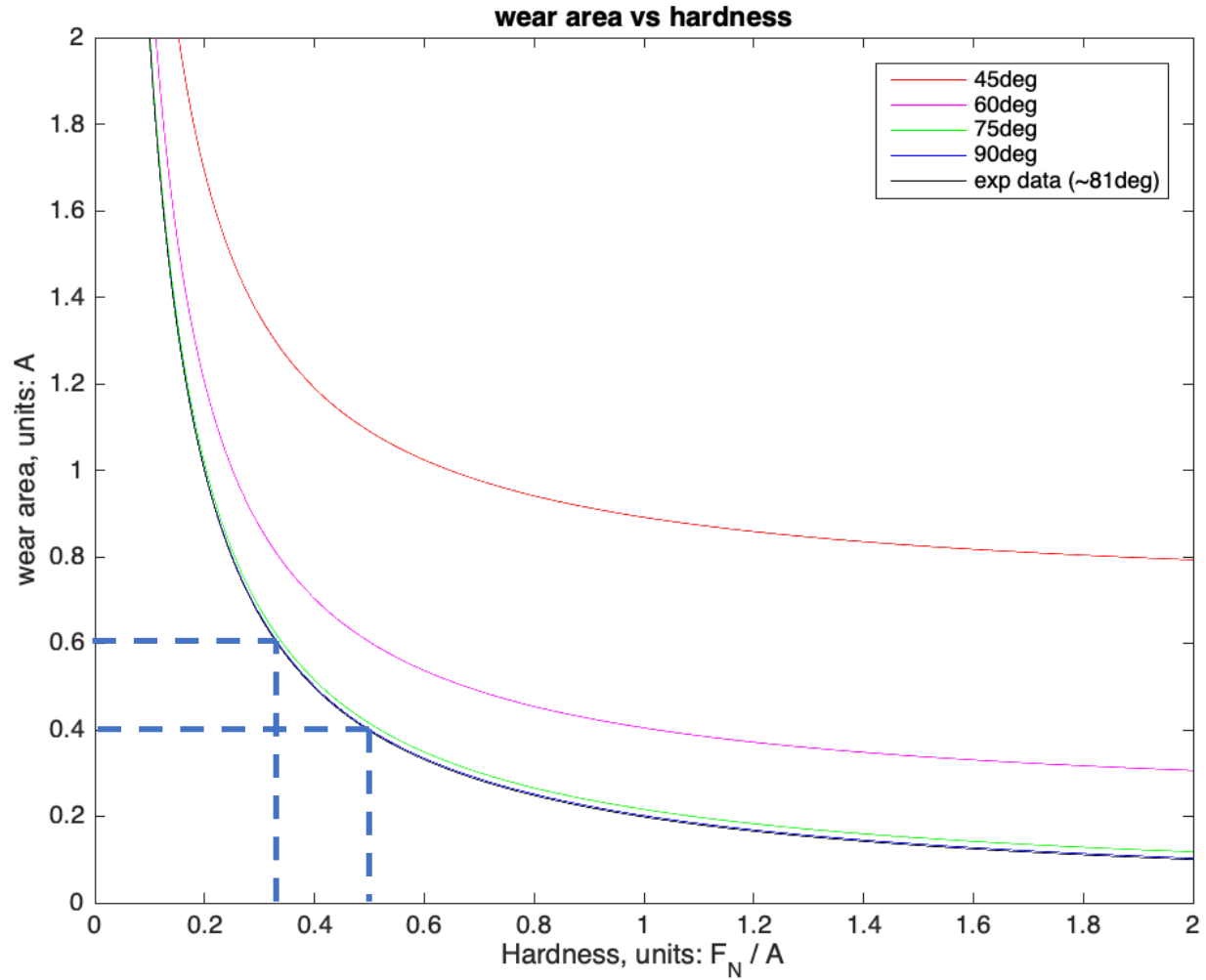


Figure 4-5: plot of nondimensional wear area A_v vs nondimensional highly deformed hardness H_{def} for various values of scratch convergence angle θ (and the corresponding variations in its complement θ_{arc})

The dotted blue lines in the above chart indicate the range of wear areas commonly seen in experimental data, and the corresponding hardness values. For reference, F_N/A was often close to 500 MPa in these experiments, and θ was on the order of 70-80 degrees ($\sim 0.4\pi - 0.45\pi$).

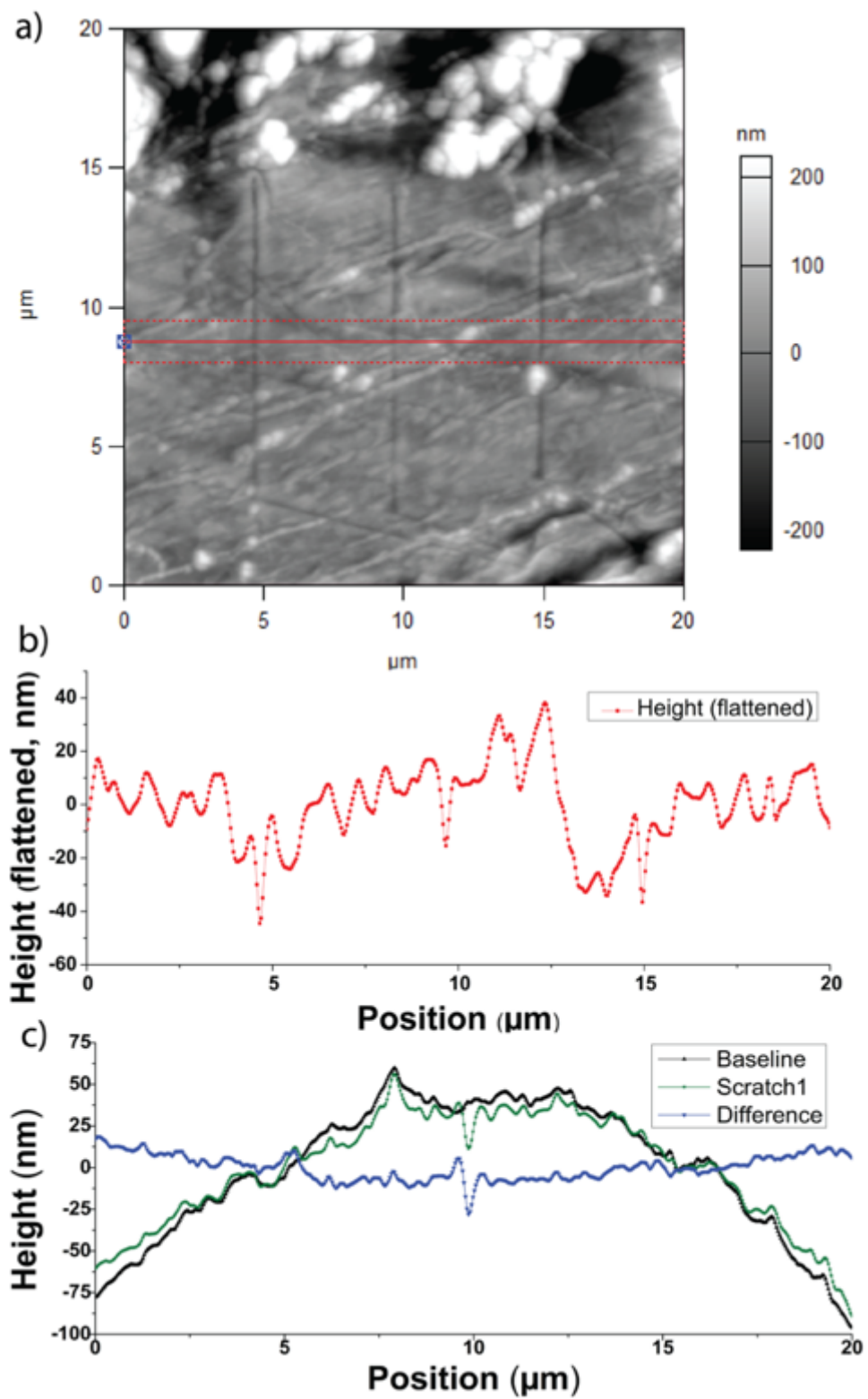
4.3.4 High force scratching protocol

Because the above derivation for the relation between high-force scratching and the highly deformed hardness of a material requires the work done by a single pass of the AFM tip, the AFM had to be manually stopped to avoid the tip tracing back along an already scratched

region. A slow scan rate of 0.1 Hz was chosen not only for this reason, but also to minimize the effect of local heating due to plastic deformation. That said, local heating errors would oppose errors associated with the roundness of the AFM tip, although no mention was made in the sections of Zum Gahr's work cited above about the end radius of the scratch diamonds used, so it is uncertain as to what degree this concern is significant in light of the empirical validity of the equation given in Zum Gahr's work.

4.4 Results

An illustration of the background subtraction performed in AFM to ensure accurate scratch profiles were measured is visible on the following page in figure 4-6.



The figure 4-6 illustrates the background subtraction performed in to ensure an accurate measurement of the scratch width occurred after a single pass of high-force scratching. After each high-force scratch was performed, the surface topography was scanned, and a region was selected for analysis based on identifiable landmarks. In this case a linear height profile, shown in figure 4-6 b), was generated from a) where the height at each point from left to right on the red line in a), is the average of the heights of all points in figure 4-6 a) between the dotted red lines that lie on a line perpendicular to the solid red line at a given length along the solid red line. This was performed after each scan, and the “height” of the scratch was taken as the difference between the linear height profile generated from the scan performed before and that from the scan performed after the scratch was made (illustrated in figure 4-6 c)). As an additional note, the AFM does not by default scan only in one direction, so the measurement had to be manually stopped. This resulted in some measurements where the tip started to trace backwards along its path (visible above the top dotted red line in figure 4-6 a)), and these regions were avoided, as the data in this region could not be used to calculate the hardness of lithium, as that calculation requires that the scratch be performed in a single pass of the indenter over the scratched material.

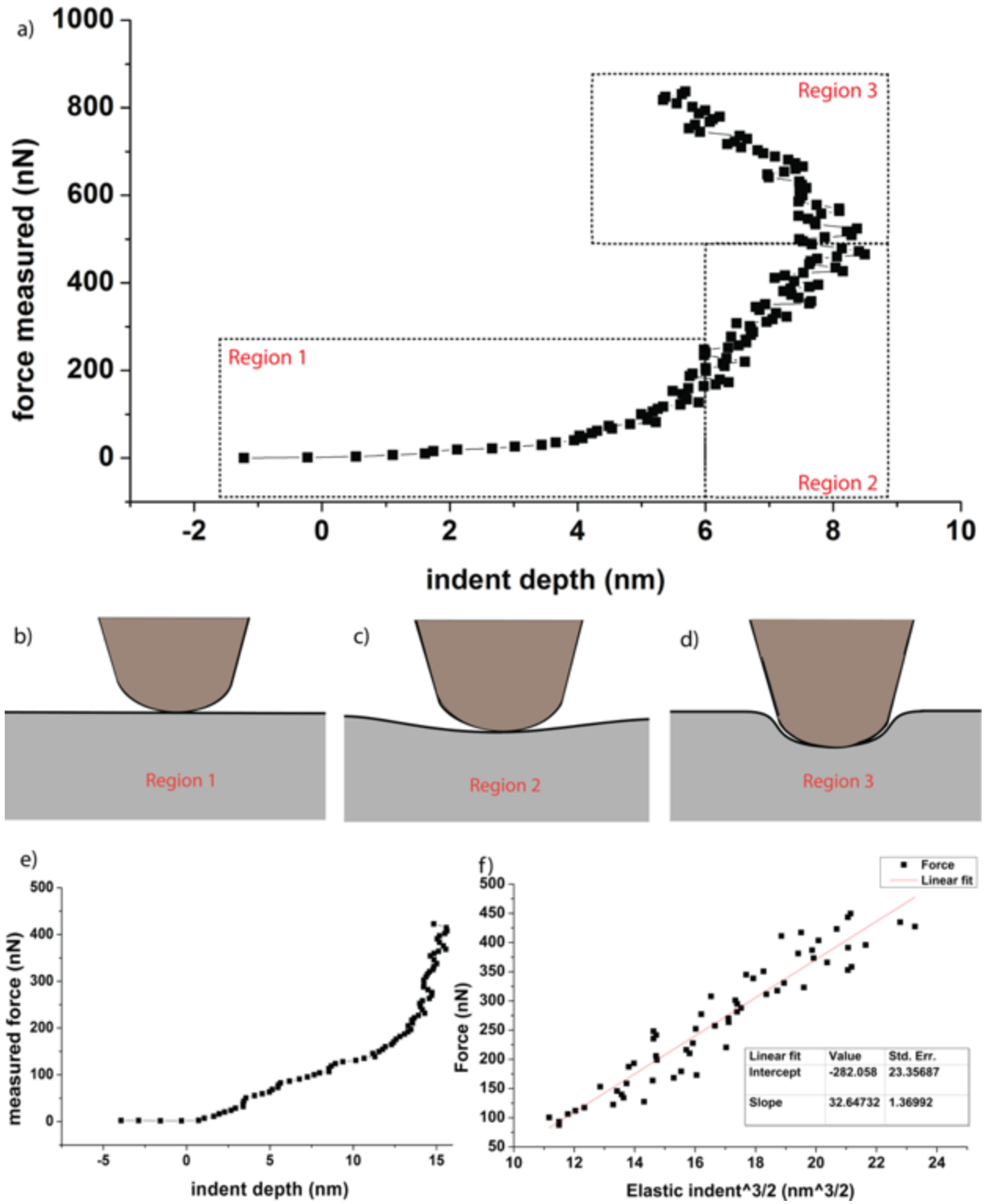


Figure 4-7: illustration of elastic modulus measurement, and the identification of various regimes of indentation behavior

The above figure, figure 4-7, illustrates the results of the elastic modulus measurement performed. An example curve of force vs indent is noted in figure 4-7 a), with regions of the curve labelled, corresponding to figures 4-7 b)-d). Figure 4-7 e) contains the section of the data in 4-7 a) that does not contain data from region 3, and figure 4-7 f) shows a replotting of that data with the x axis rescaled, the slope of this graph can be used to calculate the reduced elastic modulus, and from this, the elastic modulus of lithium may be calculated. In region one, the contact area is especially small, and as such, the tip may not be uniformly spherical in this region, as can be seen by the multiple jumps between 0 and ~8 nm indent in figure 4-7 e). In region 2, the contact force increases with increasing indentation depth as is expected of Hertz's equation for the force experienced by a spherical indenter indenting a solid surface, so the slope of this region can be used to calculate the elastic modulus of the indented material using the known elastic properties of the diamond coated tip and the value of poisson's ratio for lithium from literature. The apparent inflection observed in region 3, where the tip appears to decrease its indentation depth (retract from the sample) as its deflection increases, is due to an imperfect inverse optical lever sensitivity calibration. Without the ability to place a silicon chip in the cell to serve as a calibration standard, the inverse optical lever sensitivity was calibrated with a high force indentation into lithium metal. This overestimation of the inverse optical lever sensitivity (that is, an underestimation of the amount that the tip deflects when in contact with an infinitely stiff surface) results in the overestimation of the tip deflection distance when in the tip comes into contact with stiff regions of the sample. This can happen in cases where the tip plastically deforms the sample: under plastic deformation, the region under the tip becomes tip-conformal, and a

larger area of the material begins to resist the force applied by the tip. This increase in load bearing area causes the sample to appear stiffer to the tip. This explanation of the observed region 3 is further supported by the observed low-force scratching data, an example of which is shown below in figure 4-8:

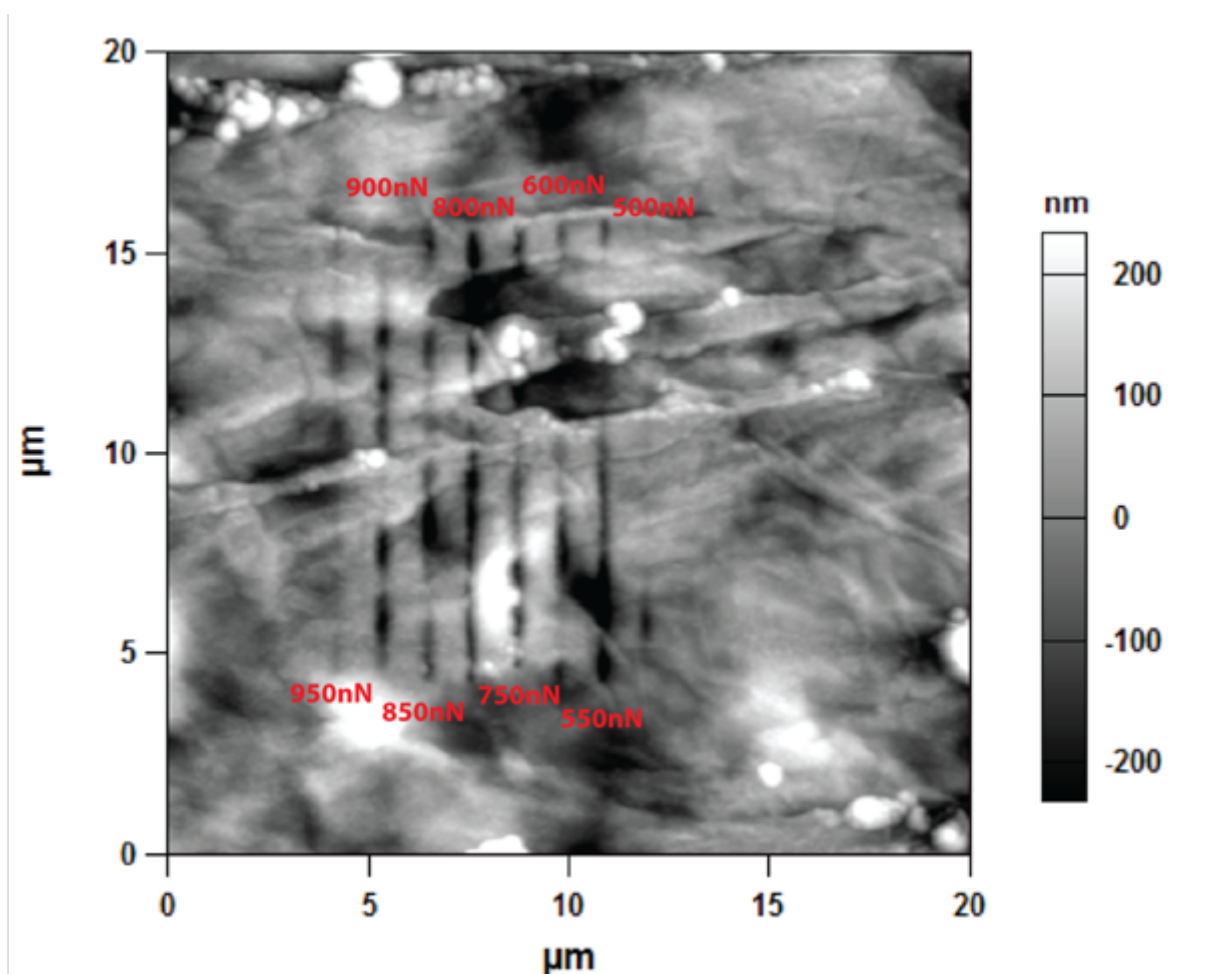


Figure 4-8: low force scratching profile, with applied forces appended in red

Figure 4-8 shows an example of the low force scratching data, with the force applied to make these scratches appended in red text. This data was taken in the same session as the elastic modulus data in figure 4-7. The last scratching force applied (500 nN) failed to scratch the surface consistently, so we conclude that the force required to cause plastic deformation in lithium with

this tip (and thus, the force used to calculate the unworked hardness of Li metal) is between 500 and 550 nN. That this is also the force at which the transition between region 2 and region 3 occurs supports this conclusion about the source of the inflection at the start of region 3 in figure 4-7. Having established this, this inflection can be corrected by adjusting the inverse optical lever sensitivity after the fact, since the raw deflection signal can be obtained from the force curves in the instrument. This was done for curves that showed evidence of plastic deformation in this way.

4.4.1 Conclusions of Li metal work

Using the above methodology, the elastic modulus measured was 1.17 ± 0.55 GPa. The significant error in this measurement is likely a result of the insufficient calibration choices, but this value is still anomalously low for the elastic lithium metal. Better calibration in the future, and the use of stiffer tips, for whom noise and error in the inverse optical lever sensitivity calibration will be less impactful, will likely yield better measurements. Other sources of error include a sampling bias in Li grain orientation, as Li is significantly anisotropic¹¹⁵, so it would be impossible to tell from the force curve whether an anomalously stiff region is just “stiffer” or “tip conformed/concave”, and force curves from those regions may have been neglected.

Figure 4-9, below, shows the highly deformed hardness measurement and unworked hardness of lithium metal.

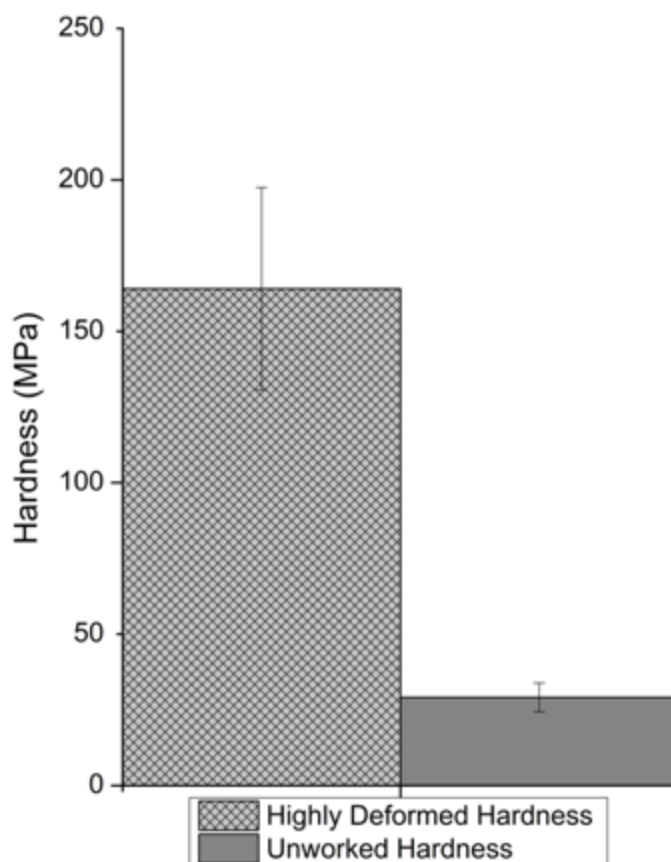


Figure 4-9: Comparison of measured hardness values

In the above figure 4-9, the unworked hardness of lithium metal is 29.1 ± 4.74 MPa, and the highly deformed hardness of lithium is 164 ± 33 MPa. Results comparing the highly deformed hardness with the unworked hardness measurement suggest that lithium hardens significantly. This presence of significant residual compressive stress suggested that lithium metal could be preconditioned by the mechanical stamping process used to produce periodic deformations in

the Li metal surface, but it should be noted that both of these measurements were performed on the scale of seconds, and thus could not observe longer scale dynamics.

4.5 Reception of Li metal work

Following this publication, a paper was published in the Journal of the Electrochemical Society in 2019¹¹⁶. The work in this paper includes bulk mechanical loading experiments on lithium film in a controlled atmosphere and temperature glove box, where the deformation of the lithium sample could be tracked without interfering with the sample directly using a Digital Image Correlation method to measure the true strain in the sample as a function of time. More specifically, it demonstrates the relaxation behavior of lithium metal under stress, and shows that for low strain rates (below 1% / sec) and moderate temperatures (above 248 K) the deformation of Lithium metal is dominated by material creep, and the parameters of this power law creep model were calculated.

The presence of this material creep suggests that it is not possible to precondition the stress in lithium metal in such a way that the deposition behavior of lithium is affected. However, in the case of solid or polymer electrolytes, the ongoing local deposition of lithium results in a local displacement of the surface, and thus an ongoing accumulation of stress proportional to the rate of deposition of lithium metal, which the authors suggest has relevance for ceramic electrolytes, such as Lithium Lanthanum Zirconate (LLZO) upon which further work was conducted in this thesis.

4.6 LLZO Work Motivation

Currently, work is being performed to measure the local elastic modulus of LLZO, a solid state electrolyte proposed for use in lithium ion batteries. They are of interest for several reasons, many of which involve avoiding the issues of liquid electrolytes such as continuous SEI formation and lithium depletion, while maintaining a high lithium transference number^{117,118}. This is especially of interest because there is a theoretical complication involving garnet type electrolytes such as LLZO: a shear modulus in excess of twice that of lithium should result in elastic behavior that suppresses dendrite formation by producing a mechanical energy penalty to deposition on the peaks of dendrites (i.e: a mechanical overpotential)⁸¹. In addition to the bulk reduction potential differences, in practice the deposition of material on the anode involves the formation of additional surface area, and the creation of material that may be subject to mechanical stress conditions, and the work required to form these must be supplied by the reaction occurring at the anode. Indeed, with recent experiments it is possible to experimentally demonstrate the use of compressive stress as an impediment to lithium deposition under applied voltage, and then to increase said applied voltage to then overcome that limit¹¹⁹.

The shear modulus of LLZO has been measured well in excess of this limit¹²⁰, but evidence of metallic lithium has been found inside the solid electrolyte after cycling^{121,122}, suggesting that these bulk mechanical properties are not sufficient to prevent dendrite formation. One theory about why this theoretical model may have been insufficient to predict the behavior of LLZO involves a relative softness of the grain boundaries in the solid electrolyte material. Previous work in other ceramics reports that the measured elastic modulus decreases with decreasing grain

size, and it has been suggested that this is due to a lower elastic modulus at the grain boundaries which results from local disorder^{123,124}. This on its own could in theory permit dendrite formation, but recent theoretical work¹⁰⁵ suggests that this local softness could result in current focusing at the grain boundaries even when significant conductivity variations would oppose it. Scanning probe microscopy is one of the only techniques that would allow the probing of mechanical properties on such a small scale, and to this end, local elastic property measurements of LLZO have been attempted.

4.7 Methods

4.7.1 Sample Prep

LLZO samples were stored in an argon atmosphere glovebox that maintains less than 1 ppm O₂ and H₂O. Nevertheless, evidence suggests that this preparation does not maintain them in stable condition for more than a day with even trace amounts of atmosphere containing CO₂ or H₂O¹²⁵. To avoid this concern, samples were polished with SiC polishing paper immediately before assembly in the closed fluid cell and subsequent measurement in the AFM. The polishing protocol proceeded in the following order: 23.6 μm , 12.6 μm , 5 μm , 3 μm , 1 μm , 500 nm, 100 nm. To demonstrate the sufficiency of this polishing protocol, a sample was prepared for SEM measurement in the glove box, removed with exposure to lab atmosphere for the ~10 seconds it took to move the sample from the glove box to the sample chamber of the SEM, and perform measurements of the polished surface, an example of which is shown in figure 10, note the grain contrast observable.

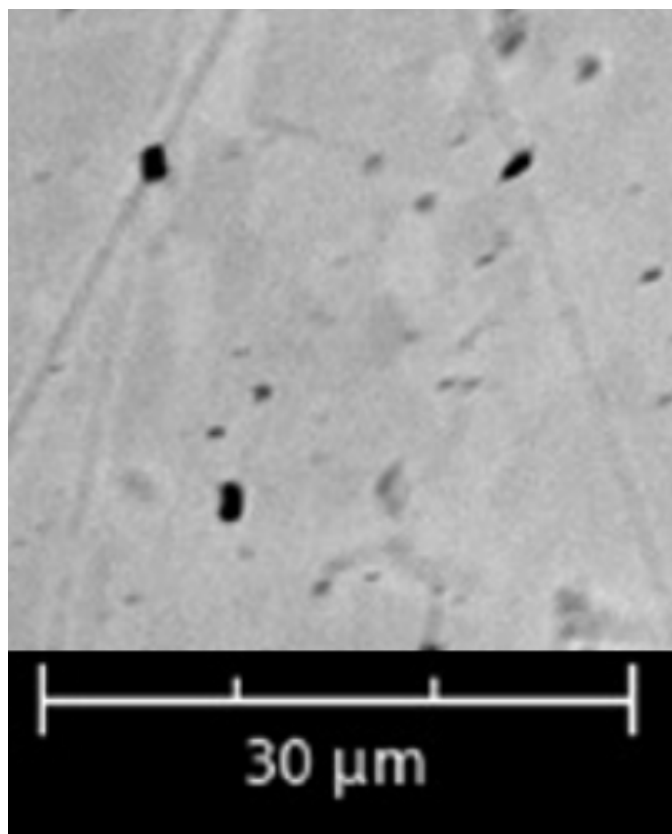


Figure 4-10: Post-polishing 15kV SEM image of LLZO sample with visible grain contrast

The above figure also confirms that the sample polishing protocol does not significantly affect the nominal grain size of the sample surface: reported originally as being between approximately 5 μm and 8 μm .

4.7.2 Initial attempts

Initial attempts at measuring the inverse optical lever sensitivity were made using “biosphere” tips: silicon tips with a nominal spring constant of 40 N/m and a sphere of deposited diamond like carbon with radius of 50 nm. Initial measurements taken with an assumed nominal tip radius yielded highly inaccurate elastic modulus values, but were successful in demonstrating coherent variations in local properties on the scale of grain boundaries, as shown in Figure 4-11.

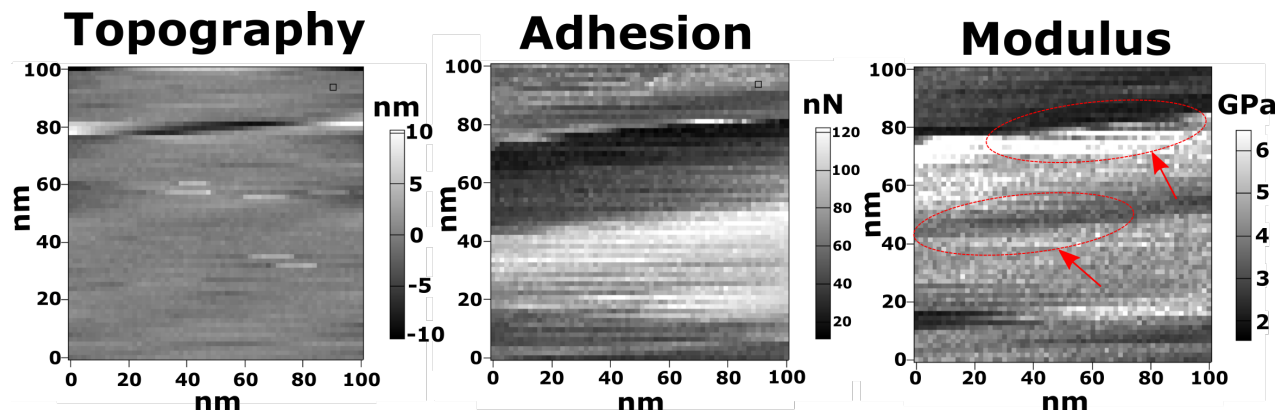


Figure 4-11: Topography (left), adhesive force (middle), and nominal measured elastic modulus (right) on LLZO.

Figure 4-11 shows a 100 nm by 100 nm force map performed on LLZO using a nominal tip radius value. While these elastic modulus results are not numerically accurate, these variations, such as the band observed in the lower circled feature, or the sharp change noted below the apparent scratch in the upper circled feature, appear to be coherent and should relate monotonically to the actual values of elastic modulus in that region. This map spans 100 nm and has 64 sampling points on each side, so the width and height of each pixel is approximately 2 nm. Features 5 pixels in width, then, correspond to a nominal feature size of 10 nm, which corresponds reasonably well to the range of sizes given for a grain boundary in LLZO¹²⁶.

Post-analysis of these tips in TEM failed to show the sphere of carbon for which they were advertised, so to avoid any uncertainty associated with these tips, CDT-NCHR tips were used: Tips with a uniform diamond-like carbon (DLC) coating, a nominal spring constant of 40 N/m, and a tip radius on the order of 100 nm. To avoid the possible complications of using an electron microscope to measure the tip radii before every run a relative calibration method was chosen: Hertz F/d measurements would be performed on a relatively soft sample of known modulus, and this would be used to measure the tip radius from the known values of loading force, indentation,

and the reduced elastic modulus (which is derived from the known elastic properties of the tip and the standard sample). This DLC tip would subsequently be used to measure the elastic modulus of a different sample of unknown modulus (LLZO). Because this measurement required that the tip radius be the same between the initial calibration and the elastic modulus measurement, scanning of the surface was minimal and only ever performed in AC mode. This was done to select a flat region from which valid data could be acquired. Figure 2-10 in chapter 2 shows a photograph of this type of experiment setup, wherein three samples were loaded: Highly Oriented Pyrolytic Graphite (HOPG) was used as a known modulus standard (bottom), Fused silica was used as an unknown modulus sample (top right), and a sapphire standard (500 GPa elastic modulus) was included for inverse optical lever sensitivity calibration (top left).

Calibration on Fused silica (nominal elastic modulus 73 GPa), failed to produce valid results with these tips (elastic modulus between 80 and 120 GPa measured on LLZO), with the values of tip radii that replicated the known elastic modulus of fused silica being physically unrealistic. This is due to the combination of the bluntness and stiffness of these tips: the indentation of the tip is very small over a large range of deflection voltage, so the measurement is exceptionally sensitive to the inverse optical lever sensitivity calibration performed at the beginning of these experiments. This can only be known to within approximately 1 nm/V, with successive tests on the diamond standard varying in their reported InvOLS by approximately this much. Although previous work with AFM on other materials was able to be performed using tips with spring constants of 40 N/m to measure elastic constants in the range of LLZO's nominal 160 GPa, these were much narrower silicon tips⁸⁵. Decreased sensitivity to this source of error can be

achieved by using stiffer tips or by using tips with a smaller end radius, both of which work to reduce the dependence of the elastic modulus measurement on InvOLS by increasing the amount of elastic indentation into the sample that occurs per given unit of tip deflection.

4.7.3 HOPG and Fused Silica

Following these experiments, the decision was made to start experiments on a Bruker Dimension FastScan Scanning Probe Microscope, to which there was easier access. With the change in instrument, new tips were required, and to that end Bruker's RTESPA-525 tips were chosen for preliminary experiments with HOPG and Fused Silica. These tips have a larger nominal spring constant of 200 N/m, are made of uncoated silicon, and come to a nominal tip radius of 8 nm. The goal of these experiments was to demonstrate that this methodology could be performed with the available equipment, and develop an experimental protocol for working with the LLZO sample. In addition to this, due to the significant compliance of the tip that could be involved with these high force samples, this presented an opportunity to examine some of the assumptions of force curve behavior inherent in scanning probe microscope measurements using the Hertz model.

Illustrated in figure 12 is an example of a force - distance curve performed to calibrate InvOLS. The inverse optical lever sensitivity is assumed to be a constant, but as is visible from the image below this appears not to be the case: the slope in the contact region appears to vary as the deflection setpoint is increased (as the tip is pressed harder into the sample).

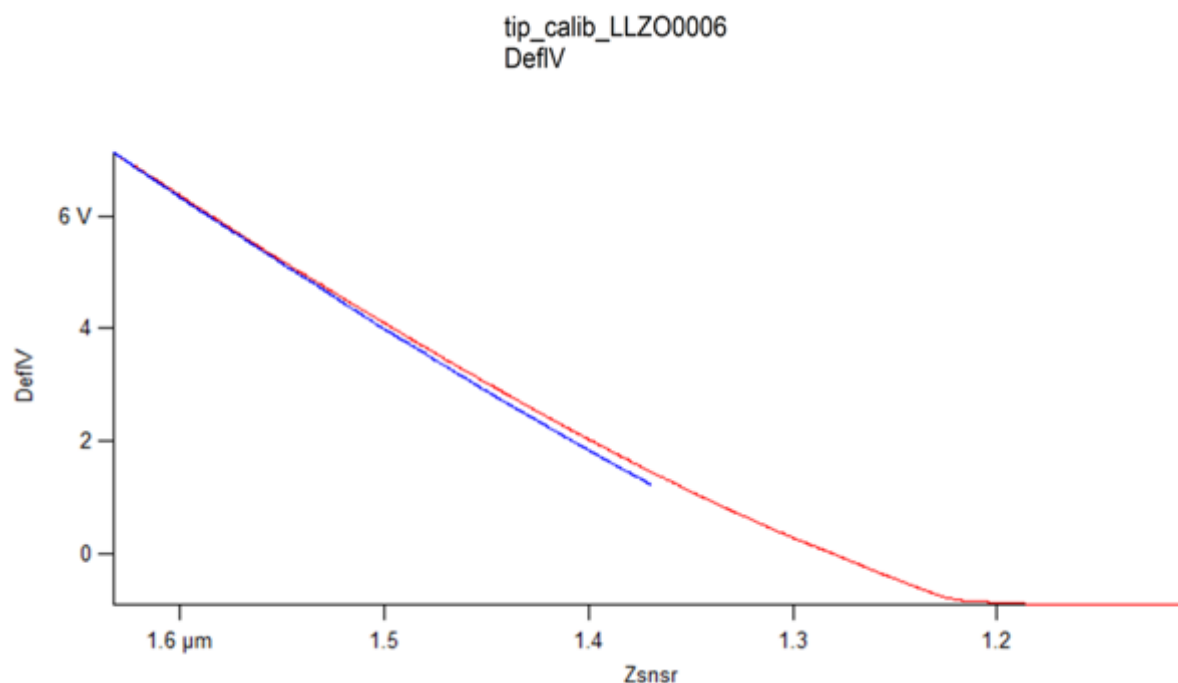


Figure 4-12: High force force-distance curve for InvOLS calibration

This behavior is also observed on the sapphire calibration standard, and is important because it illustrates a theoretical approximation involved in AFM that may be relevant to the measurement of elastic moduli on stiff samples: While the Inverse optical lever sensitivity is assumed to be a function only of the cantilever upon which the probe rests, the manner in which it is measured is not. There will always be some amount of probe compliance involved in these measurements, the consequences of which are illustrated below in figure 4-13.

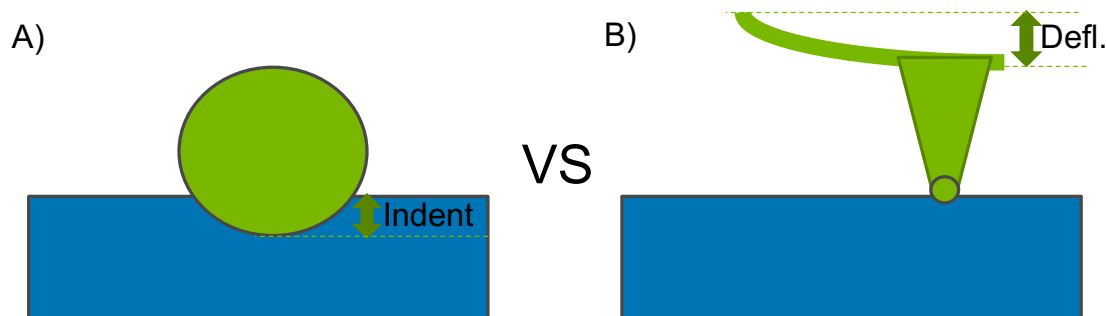


Figure 4-13: Illustration of conditions described by A) Hertz contact mechanics, and B) the conditions seen in AFM based measurements.

Where the equations of Hertz contact mechanics that are used to describe most AFM contact models express a relation between the indentation into the surface and the loading force, AFMs can only measure the deflection of the tip and the height of the cantilever above the sample, and use that to attempt to calculate indentation into the sample. This suggests that for measurements where a precise InvOLS is especially important (such as measurement on stiff samples), accounting for probe compliance might be significant.

To examine this possibility, these measurements on HOPG and FS were used to test a dynamic inverse optical lever sensitivity measurement. The optical lever sensitivity calibrated multiple times at several different deflection voltages on the Bruker AFM using the sapphire standard, an example of which is shown below in figure 14. This data would later be used to compare the efficacy of a linear regression of InvOLS as a function of loading force (dynamic InvOLS) and the use of the InvOLS value corresponding to the peak force applied to the tip (static InvOLS).

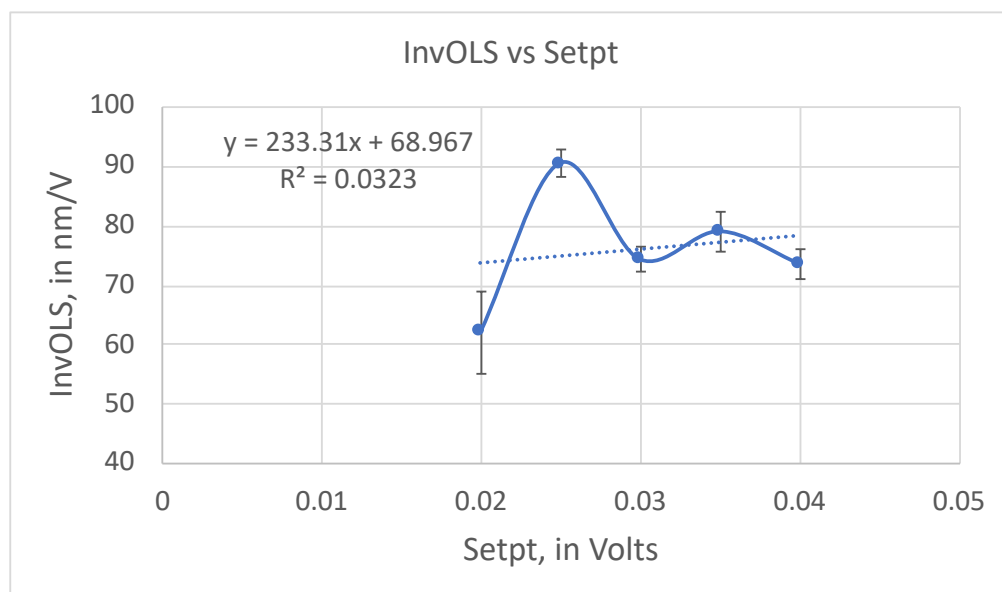


Figure 4-14: InvOLS vs deflection setpoint on sapphire standard

Even with multiple measurements, consistent contact is hard to maintain at exceptionally low force. Several maps of force distance measurements were taken at different setpoints after this data, starting on HOPG and then moving to Fused Silica. Because the calculations involving dynamic Inverse optical lever sensitivity had to be performed manually after the measurements, individual points were selected for analysis from force maps like those shown below in figure 15.

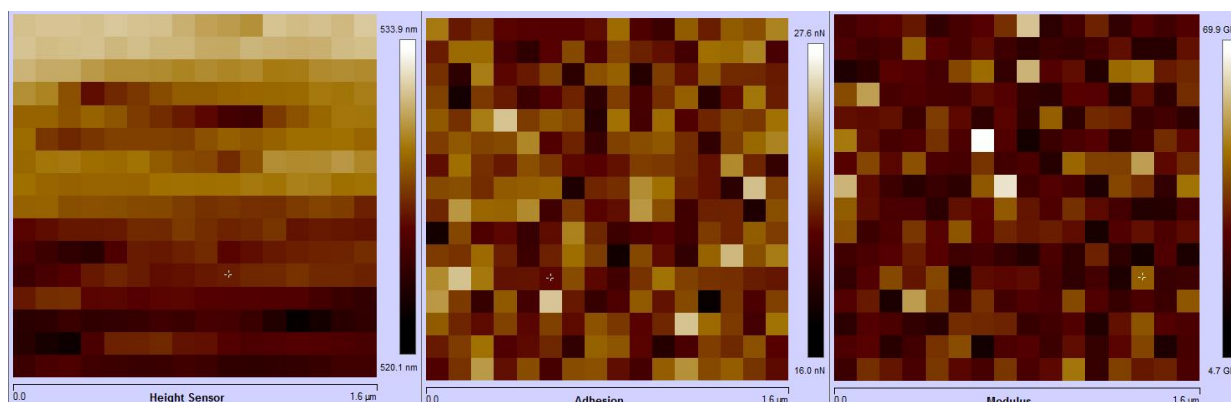


Figure 4-15: force map data on HOPG detailing A) topography B) adhesive force on the tip and C) uncalibrated modulus data.

All points were chosen for analysis based on locally flat topography (to ensure local roughness is not affecting my measurement), and low adhesive force (to ensure the measurement is not significantly affected by surface contamination in some form, despite having freshly peeled the HOPG before use). Because of the apparent shelf structure on this sampled region, two regions were chosen from each set of force map data, one above the middle and one below. Additionally, from each region, three points were chosen: one with an elastic modulus in the highest 20% of moduli values reported in the image, one with a median modulus value, and one with an elastic modulus value in the lowest 20% of values reported in the image. This was done to attempt to adjust for any statistical biases in the measurement. The preliminary results of this analysis are shown in figure 16, wherein analysis of the hardest 20% of moduli measured yielded values within range of those seen in literature for these materials. Values were calculated from an average of 8 curves in the case of HOPG, and 6 in the case of Fused Silica, each selected as described at the start of this paragraph.

0.02 V defl. setpt., dyn. InvOLS	Reduced Elastic Modulus (GPa)	Error (Gpa)
HOPG	33.0 (calibration)	± 3.37
Fused Silica	53.2	± 7.66
0.02 V defl. setpt., static InvOLS	Reduced Elastic Modulus (GPa)	Error (GPa)
HOPG	33.0 (calibration)	± 2.59
Fused Silica	50.7	± 5.93
InvOLS calculation method	Fused Silica Elastic Mod- ulus (GPa)	Error (GPa)
static InvOLS	77	± 14.2
dynamic InvOLS	84	± 19.5

Figure 4-16: Results of dynamic invols calculation on FS/HOPG, including static invols calculation and observed standard error in measurements.

For the known quantities used in the above calculation, the Elastic modulus of the silicon tip used here is that of <100> silicon (130 GPa)¹²⁷, as silicon AFM tips are etched from wafers oriented in this manner. The elastic modulus of HOPG was taken as ~41.5 GPa, cited from a recent paper that demonstrated these measurements in an AFM, with agreement across multiple types of tips and methodologies for measuring elastic moduli¹²⁸.

Both measures appear to be within one standard deviation of the literature value of the Elastic modulus of pristine silica (approximately 73 GPa)¹²⁹. Because the force applied in these experiments was nominally less than 100 nN, a contact area on the order of single square nanometers would be necessary to result in densification as suggested in the above paper. Contact areas under the elastic indentation depth in this experiment are approximated at 80 nm² using the nominal 8 nm tip radius suggested by the manufacturer, which likely overestimates the sharpness of the tip under working conditions. This, combined with the fact that densification in the previous paper occurred over the course of 24 hours, whereas the duration for which these samples experienced load was less than one second, suggests that the pristine elastic modulus of Fused Silica is appropriate. While more work is needed to examine the effectiveness of this method properly, and to reduce the error seen in these measurements by increasing the number of force curves analyzed, the work here was sufficient to demonstrate that this methodology can produce valid data on hard samples at least when selecting for the stiffest 20% of moduli that could be repeatedly measured on both modulus calibration reference and experimental sample. Further experiments are expected to follow on LLZO using PDNISP-HS single crystal diamond tips with nominal spring constant of ~400 N/m and a nominal tip radius of 40 nm.

4.8 Conclusions

From the aforementioned original research on the mechanical properties of battery materials, the following findings may be affirmatively concluded:

The techniques of Scanning Probe Microscopy are sufficient to measure the mechanical properties of battery materials on the scales relevant for dendrite and other nonhomogeneous electrodepositions of Li metal. Additionally, it was observed in lithium metal that the hardness on these scales is significantly higher than the bulk values thereof, which suggests that the bulk properties of Li metal do not adequately model the effect of mechanical stresses on dendrite formation. Attempts to measure local elastic moduli directly may be complicated by tip compliances, to the extent that critical examinations of data in the measured area and longer acquisition times may be required to ensure statistically significant results.

These in turn suggest the following: Improvements in scanning probe microscopy techniques that indirectly measure elastic properties, such as Contact Resonance microscopy, may be better able to acquire statistically significant data for the purposes of characterizing the properties of solid electrolytes, something that will be explored more in the discussion of future work on the subject.

4.9 Funding acknowledgement

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Chapter 5: Future work

5.1 Summarized conclusions

The work in this thesis details my contributions to the analysis of inhomogeneous lithium deposition in electrochemical systems, primarily using the techniques of scanning probe microscopy. The resulting conclusions illustrate a substantial scale-dependence of the mechanical properties involved in dendrite formation and suppression, further illustrate a nonuniform chemical composition of the SEI that has relevance to dendrite nucleation in liquid electrolytes, and illustrate the applicability of Scanning Probe Microscopy techniques to future attempts to measure these properties in the conditions in which they are relevant to battery materials. While this is significant, the field as a whole is more complicated, and this chapter will be devoted to examining the recent developments in this field, considering what more experiments would be beneficial to perform, and where current understanding is lacking as applied to Li-ion batteries.

5.2 Mechanical properties

5.2.1 Scale dependent hardness

Recent meta-analysis has demonstrated consistent reports of scale-dependent hardness in lithium metal features below a size of approximately 100 μm in diameter¹³⁰. This scale dependence has significant relevance for the mechanical stability of solid garnet-type electrolytes¹⁰⁵. As hardness is related to the stress required to cause plastic deformation, a scale dependence of this parameter is somewhat unusual, but has been discussed previously¹³¹.

One explanation of the reports of stress dependent hardness is given by Jackson in his work is strain gradient plasticity as was introduced by Nix and Gao: the idea that the deforming material results in geometrically necessary dislocations associated with its deformation that contribute significantly to its hardness^{131,132}. Significant variations and corrections for this equation exist in literature for models with various “indenter” geometries and accounting for surface properties^{133,134}, suggesting that greater understanding of the environment in which the dendrite forms is required to explain this phenomenon. Specifically to LLZO, this occurs in the grain boundaries, so understanding the interaction properties of lithium with the grain boundaries of LLZO becomes important¹²². As these grain boundary properties can change with dopant properties in the material, this represents a significant body of work to be performed, while the previous work’s mentioned temperature dependence of the current at which preferential growth along grain boundaries occurs suggests a dependence on the relative activation energies of lithium conduction and lithium nucleation, suggesting that further investigation of the local energies of LLZO/Li surfaces may offer insight into more stable solid electrolytes.

5.2.2 Lithium Metal

Recent work in with a combined setup of an Atomic Force Microscope and an Environmental Transmission Electron Microscope has produced real-time evaluation of the mechanical properties of lithium whiskers in which lithium whiskers could be nucleated under a voltage applied at the tip, and grown under applied bias^{135,119}. While there remains some question about to what degree this reflects the deposition conditions that might be observed in

a liquid electrolyte (He et. al. demonstrated that similar morphology occurs in a poisoned electrolyte, but the degree of crystallinity reported by Zhang et. al. in their similar setup might not be replicated with lithium in a liquid electrolyte), analogous behavior could conceivably happen in a solid electrolyte. This is especially underscored by the presence of lithium carbonate on the surface of the lithium sample, which both of these sources credit as acting as a solid electrolyte; lithium carbonate is known to form on the surface of LLZO in even trace atmosphere, and often to its detriment as a solid electrolyte for lithium^{125,136,137}.

In addition to providing an experimental demonstration of stress induced overpotential, these methods are able to resolve Li whiskers based on growth direction. These methods should be able to measure the relevant mechanical properties of lithium metal on the relevant length scales for dendrite formation, with future work focused around investigating the strain rate dependence in such an experimental setup, which the authors of the 2020 paper cited here suggest may have been relatively large compared with the strain rates observed in batteries¹¹⁹. Similar work to that performed by LePage and Dasgupta might also be performed, to examine whether similar strain rate dependence is observed in these (sub-) micron scale lithium whiskers¹¹⁶. Ideally, one might also attempt a similar experiment in liquid electrolyte to observe the effects if any that SEI formation has on the properties of these lithium whiskers.

5.2.3 Solid Electrolytes

While experiments on solid electrolytes have been performed, measurement of local mechanical properties on the scale relevant for lithium dendrite formation is still lacking^{120,138}. This is confounded further by the possibility of locally nonflat surfaces, where the simple Hertz

contact mechanics model may not apply; while it is not trivial to do so, efforts have been made to correct for such contact-area variations, which for example are detailed in this paper involving corrections made in the case of contact with the tip at multiple points when performing the Contact Resonance AFM technique¹³⁹. Additionally, for some instruments bimodal AC AFM may be appropriate for the purposes of these measurements¹⁴⁰, which would make the acquisition of measurements over a significant area significantly faster, although it is unknown how accurately the intermittent contact of an AFM tip will measure the elastic modulus of LLZO if there is a thin layer of lithium carbonate on the surface, for example.

5.3 Local Chemical Variations

Recent work involving the use of AFM and Time-of-Flight Secondary Ion Mass Spectroscopy (ToF SIMS), demonstrates local chemical variations in the SEI that correlate strongly with lithium deposition, suggesting that local chemical variations in the SEI can result in inhomogeneous growth¹⁴¹. By comparison of untreated, mechanically smoothed, and freshly machined lithium from an ingot in an argon glove box, the authors of this paper credit this local variation to inhomogeneities in the SEI caused by chemical inhomogeneities in the lithium surface under manufacturing conditions rather than topographic concerns. These measurements are on the scale of the lithium growths, and chemically resolved, which suggests that these measurements should be sufficient to address the formation of dendrites.

These conclusions (that SEI inhomogeneity is the cause of dendrite formation below limiting current density), suggest that further improvements of lithium metal cells using liquid electrolyte may either involve ways to better homogenize the lithium surface at the

manufacturing stage, or as was suggested in their paper and demonstrated in similar work regarding the selective nucleation of lithium on precious metals: to precondition the lithium surface with so many favorable deposition spots that no one location dominates in such a way as to cause dendritic failure^{141,76}. While these methods appreciably forestall catastrophic failure, the inhomogeneous growth will still result in some amount of electrolyte depletion, and a concurrent reduction in the maximum current the cell can supply without reaching a limiting current condition due to the decreasing salt concentration in the electrolyte³⁶. For lithium cells to be viable for long cycle lifetimes, some method of replenishing the electrolyte, or at least forestalling its consumption, must be developed. Some success has been reported with pulsed charging protocols, wherein the battery is allowed to charge in intervals and equilibrate in between charging periods in a manner that alleviates concentration polarization, but the cost of implementing such control processes is a barrier to the implementation thereof^{f142,143}.

Further advancements that help alleviate dendrite formation due to chemical inhomogeneities would be aided by similar analyses to the work performed by Ozhabes et. al. regarding the simulated surface energies and diffusion barriers of SEI materials¹⁴⁴, considering the possible reduction products that may form at the Li metal anode surface and examining their relative surface energies and diffusion process barriers with lithium and the electrolytic medium, in whatever form the latter takes.

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