MODELING DEGRADATION MECHANISMS IN RECHARGEABLE LITHIUM-ION BATTERIES

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▷ to base-controlled growth data and ▶ to tip-controlled growth data as reported by Orsini and coworkers [98], \diamond to electrodeposit growth experiments as reported by Cui *et al.* [100], □ to base-controlled growth data and ■ to tip-controlled growth data as reported by Li and coworkers [101]. 47

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- 3.10 Regimes of lithium growth dynamics as a function of normalized electrodeposit size and stress, for selected overpotentials: (a) $\hat{\eta} = 0.01 \ (-0.442)$ mV), (b) $\hat{\eta} = 0.5 \ (-22.1 \text{ mV})$, and (c) $\hat{\eta} = 50 \ (-2210 \text{ mV})$. The thermodynamic suppression regime, below the blue curve, is where no growth is expected; the *incubation regime*, above the blue curve and below the black curve where metastable nuclei grow as a result of local dendrite-dendrite electrochemical and chemomechanical interactions; to the left of the green curve and above the black curve, you will find the *tip-controlled growth regime*, where growth is dominated by electrodeposition; above the black curve and below the red curve you will find the base-controlled growth regime, where growth is dominated by plastic deformation of lithium; and finally between the red and the green curve you will find the *mixed growth regime*, where both electrodeposition and plastic deformation compete to define the growth of the electrodeposit. To the right of the black line and below the blue line is where large stresses mechanically suppress dendritic growth. The dashed gray line indicates a minimum in the growth rate. The analysis demonstrates that high overpotentials delay the onset of base*controlled growth.* •corresponds to experimental data as reported by Brissot and coworkers [96], \triangle to experiments as performed by Crowther and West [48], \triangleleft to base-controlled growth experiments and \triangleleft to tip-controlled growth experiments as reported by Dolle *et al.* [97], \triangleright to base-controlled growth data and \triangleright to tip-controlled growth data as reported by Orsini and coworkers [98], \Diamond to experiments as reported by Cui *et al.* |100|. \Box to base-controlled growth data, and \blacksquare to tip-controlled growth data as

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- 4.1 \bigcirc corresponds to hemispherical lithium nuclei electrodeposited on top of a copper layer at $0.1 \,\mathrm{mA/cm^2}$ for 1 hour, as performed by Pei, Cui and coworkers [100]. \triangleright corresponds to columnar growth of lithium on a copper substrate under a hollow carbon layer after 50 charge/discharge cycles at $1 \,\mathrm{mA/cm^2}$, as shown by Zheng, Cui and coworkers [143]. \Box corresponds to mossy lithium electrodeposition on a copper substrate at $2.61 \,\mathrm{mA/cm^2}$ for 0.5 hour in a liquid electrolyte column, as shown in experiments by Bazant *et al.* [94]. \diamondsuit corresponds to branched lithium dendrites electrodeposited on a lithium substrate from a gel-based electrolyte at $3 \,\mathrm{mA/cm^2}$ for 1 hour, as performed by Tatsuma, Taguchi, and Oyama [136]. Catalog of experimental lithium electrodeposit microstructures demonstrates the effect of current density on dendrite morphology, as different driving forces compete to reduce lithium.
- 4.2 Summary of simulation setups. Inset (a) shows the setup for the galvanostatic electrodeposition simulations. A fixed current density is applied from the top. The bottom edge is electrically grounded and mechanically constrained. The electrodeposit is hemispherical at t = 0. The area visualized in the analysis herein is highlighted by the dashed box. Inset (b) shows the half-cell setup used for mass and charge conservation validation. h_{ξ}° corresponds to the initial lithium metal anode thickness (in orange). The gray region represents the liquid electrolyte. Inset (c) shows the plasticity validation setup. Solid metallic lithium is pushed horizontally through a funnel-shaped section at a fixed applied velocity from the left edge. The top and the bottom edges are mechanically constrained.
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- 4.7 Normalized lithium concentration for a high current density, 10 mA/cm^2 , at four selected instants: (a) 300 s ($\sim t_{\text{Sand}}$), (b) 600 s, (c) 1200, and (d) 2600 s, in agreement with Bazant *et al.* [94]. The branched structure is a result of the combined effects of the localized stress distribution at the dendrite tip and the concentration depletion at the tip for $t > t_{\text{Sand}} = 292$ s. Localized elastic energy at the tip induces microstructural perturbations and results in the growth of thin and elongated dendrite branches. Repeated bifurcations of the initial hemispherical electrodeposit cause the growth of secondary, tertiary, and higher order dendrite arms. Darker regions highlight locations where overpotential and stress-induced electrodeposition dominate the kinetics.
- 4.8 Electric field distribution for a current density of 10 mA/cm² at four selected times: (a) 300 s, (b) 600 s, (c) 1200 s, and (d) 2600 s. Electric fields are highest at the dendrite branch tips (see inset (a)). As the dendrite grows, the metallic electrodeposit is shielded near the base regions (see insets (a) and (b)). The formation of secondary dendrite arms redistributes the electric field: the branch tips experience even higher electric fields while the electrolyte between the branches induce alternating regions of high and low electrical fields, which in turn results in preferential electrodeposition and electrodissolution regions. The shielded inner regions grow through electrochemically induced plastic flow.
- Lithium electrodeposition and electrodissolution rates for a current den-4.9sity of $10 \,\mathrm{mA/cm^2}$ at four selected times: (a) 300 s, (b) 600 s, (c) 1200 s, and (d) 2600 s. Inset (a) shows that the electrodeposition rate at the tip decreases due to diffusion limitations as specified by Sand's time (t_{Sand} = 292 s). Once the hemispherical electrodeposit splits into branches, the electrically shielded region becomes electrically and mechanically insulated (see inset (b)). Faces of the branch that are oriented away from the electric field are shielded. However, if they extend laterally, opposite overpotentials induce electrodissolution, as shown by the green regions in inset (c). Local mass transfer results due to electrodeposition and electrodissolution between adjoining secondary branches. Here, the externally exposed surfaces of the dendrite undergo slow electrodeposition on the sides (see inset (c)) until the dendrite branches fully develop (inset (d)). Similarly, the base of the dendrite is either electrochemically shielded or displays weak electrodissolution as a result of the dendrite contact area being in a compressive state of stress (see inset (d)).

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- 4.10 Effect of applied current density on lithium growth for a total charge of 2600 C for three selected current densities: $0.1 \,\mathrm{mA/cm^2}$ (left column), $1 \,\mathrm{mA/cm^2}$ (middle column), and $10 \,\mathrm{mA/cm^2}$ (right column). The top row shows the lithium microstructure and the stress tensor distribution. The bottom row shows the plastic flow rate. For all three current densities, base-controlled growth dominates the initial stages of deposition. For very low current densities $(0.1 \,\mathrm{mA/cm^2})$, stresses relax faster than the rate of electrodeposition and thus a planar electrodeposit is favored [95, 143]. For intermediate current densities (1 mA/cm^2) , surficial mechanical energy density localizes, suppresses local electrodeposition, and promotes dendrite branches [94, 136]. For high current densities $(10 \,\mathrm{mA/cm^2})$, the system becomes diffusion limited, inducing large concentration depletion gradients in front of the dendrite tip that result in tip-controlled growth. Stress accumulation results in elongated branches, which in turn promotes further dendrite branching. 4.11 Electrochemical interactions of a multiple dendrite system for an applied current density of $10 \,\mathrm{mA/cm^2}$. First column shows the microstructure, second column shows the electrical field, and third column shows the elec-

- 4.12 Mechanical interactions of a multiple dendrite system for an applied current density of 10 mA/cm². First column shows the stress distribution, second column shows the hydrostatic stress, and third column shows the von Mises stress. Initial electrodeposit sizes are selected from the experimental lithium electrodeposit size distribution, as reported by Cui and coworkers [100]. Stresses are visualized in terms of Lamé's ellipses. Ellipse orientation denotes the principal stress direction. A pure hydrostatic stress is represented by a circle. Compressive regions are in blue and tensile regions are in red. At initial times, all electrodeposits are under large compressive stress. Initially high von Mises stress push the electrodeposits towards the counter electrode until stresses at the base are relaxed. Peripheral regions of the electrodeposits are under compressive stresses are relaxed. Smaller dendrites, electrically shielded, grow through the base-controlled mechanism until stresses are relaxed.
- 4.13 Roadmap of lithium dendrite growth regimes as a function of electrodeposit size and applied current density. The black line denotes the kinetic limit of electrodeposit growth, and the blue line denotes the thermodynamic line for the stability of a hemispherical lithium nucleus. To the left of the red line and above the black line is the *base-controlled regime* where growth is driven by plastic flow of lithium. To the right of the orange line is the Sand's regime, where diffusion limitations at current densities, $\hat{i} = (z^2 \mathcal{F}^2 D_l C_{\circ} / \Delta g \Omega \kappa_i) \left(\frac{i_{\text{app}}}{i_{\text{lim}}}\right) > 2.5 \times 10^5$ result in the formation of branched dendritic structures. To the right of the green line is the tip-controlled regime, characterized by interfacial electrodeposition at the tip. Between the red, green and orange lines is the *mixed regime*, with contributions from the both the base and the tip. The dashed gray line denotes the onset of lithium plastic flow. Below the yield stress, elastic energy localized at the electrodeposit tips results in suppression of the electrodeposition rate and branching of the electrodeposit at sub-limiting current densities. Above the yielding limit, plasticity at the tips modifies, bends, or kinks the dendrite branches. In practical lithium battery operations, lithium grows mostly through the mixed-mode of growth, as denoted by the markers corresponding to experimental microstructures shown in Figure 4.1, which are compared with those simulated from the proposed framework.

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- 5.1 Simulated separator cross-section. A hemispherical lithium nucleus (in orange) is shown at the bottom surface at t = 0. An array of circles (in dark gray) denotes the polymer fibers of the separator. The light gray background denotes the electrolyte. A constant current density, I, is imposed on the top boundary (cathode side). The substrate (anode side) is electrically grounded. θ is the angle of inclination of the separator channel. x is the horizontal distance between centers of two neighboring fibers, and h is the vertical distance between the two horizontal center lines through the centers of the fibers in two consecutive layers. a is the pore radius, and r is the radius of the inclined channel. $\ldots \ldots \ldots \ldots$.

- 5.4Effect of current density on dendrite growth. (a) shows that a dendrite is fully arrested for $I = 0.09 \,\mathrm{mA/cm^2} < I_c$. Inset (i) shows that dendrite morphology is a result of the dynamic balance between electrodeposition that occurs in the pore space between the polyethylene fibers and the electrodissolution that is induced by the curvature of the lithium growth and the energy barrier imposed by the fiber. (b) shows that a critical current $I_c = 0.10 \,\mathrm{mA/cm^2}$ exists at which the dendrite penetrates the first row of polyethylene fibers, but is arrested by the next layer. (*ii*) shows that the localized increase of electrodeposition rate is balanced in the central branch by lateral electrodeposition, surface tension driving forces, and symmetry of the separator geometry. The symmetry is broken in the side branches because of self-shielding effects. (c) shows that for a higher current density, $I = 0.11 \,\mathrm{mA/cm^2} > I_c$, the dendrite fully penetrates the separator that might cause a short-circuit. (*iii*) shows that the tip of the dendrite favors local lithium plating, while the length of the dendrite is subjected to localized electrochemical dissolution events as a result of the local electrochemical interactions with the polyethylene fibers.
- Predicted regimes of dendrite behavior in a porous separator: the sup-5.5pression regime, below the blue curve, highlights the loci of pore sizes and recharge rates that are thermodynamically unfavorable for dendrites to grow; the *permeable regime*, below the black line, where dendrites cannot penetrate more than the very surface of the separator (the first laver of fibers); the *penetration regime*, between the red and the black line where dendrites rely on electrochemical shielding to find a thermodynamically stable pore to persist inside the separator; and finally, the *short-circuit* regime, to the right of the red line, where a combination of electrochemical enhancement at the dendrite tip and lateral shielding favors a subpopulation of electrodeposit branches to traverse the entire width of a separator to reach the counter electrode and cause a short-circuit. A fifth regime, delineated by the gray dotted line highlights the stability of the dendrite inside the inclined channels. Insets show predicted morphologies at representative locations.

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- 5.7 Dendrite detachment and apparent motion process, for $\hat{a} = 0.2$, $\hat{I} = 11$. (a) captures dendrite dissolution rate at the region of detachment at t = 2.30 h. (b) shows that at t = 2.68 h, an electrodeposit detaches from the main dendrite arm. (c) shows that the detached electrodeposit has moved towards the cathode at t = 3.09 h. The surface of the electrodeposit that faces the cathode undergoes deposition due to a positive overpotential, whereas the surface facing the anode, undergoes electrodissolution due to a negative overpotential. Concurrent deposition and dissolution on two opposite faces creates an apparent motion of the detached electrodeposit debris towards the cathode. This electrodeposit shields the electric field in the region below it as seen from the decrease in the deposition rates on the right branch of the main dendrite in (b) and (c), and causes it to retreat.105

SYMBOLS

power law creep prefactor
Dorn's constant
area
stress anisotropy factor
Burger's vector
right Cauchy-Green deformation tensor
stiffness tensor
normalized concentration of salt in electrolyte
normalized bulk concentration of salt
in electrolyte
rate of deformation tensor
effective diffusivity
diffusivity prefactor
diffusivity of electrolyte salt
self-diffusivity of solid metal
Green-Lagrange strain tensor
electric field
total deformation gradient
chemical deformation gradient
elastic deformation gradient
plastic deformation gradient
Faraday's constant
total free energy
effective bulk free energy density

- g_s bulk free energy density of solid
- g_l bulk free energy density of liquid
- Δg free energy of transformation to solid
 - from dissolved electrolyte
- $\stackrel{\leftrightarrow}{I}$ identity tensor
- i_{\circ} exchange current density
- $i_{\rm app}$ applied current density
- $i_{\rm lim}$ limiting current density
- J Jacobian of motion
- j_{\circ} molar exchange current density
- \mathcal{K} curvature
- $\stackrel{\leftrightarrow}{L}$ velocity gradient tensor
- L_{si} ith order regular solution coefficient of solid
- L_{li} ith order regular solution coefficient of liquid
- M_c effective mobility of species
- M_{ξ} mobility of solid-liquid interface
- M_{ρ} effective charge mobility
- n power law creep exponent
- Q diffusion activation energy
- r electrodeposit radius
- r_{\circ} initial electrodeposit radius
- r^* critical thermodynamic electrodeposit radius
- $\stackrel{\leftrightarrow}{S}$ 2nd Piola-Kirchhoff (PK2) stress tensor
- $T_l^{\rm m}$ melting point of electrolyte solvent
- T_s^{m} melting point of electrodeposited metal
- \vec{u} displacement vector
- V volume
- \vec{v}_p plastic velocity
- $\stackrel{\leftrightarrow}{W}$ spin tensor

- $W_{\mathcal{E}}$ energy barrier for solid-liquid interface
- \vec{X} position vector in Lagrangian frame
- \vec{x} position vector in Eulerian frame
- valence of metal ion z
- charge transfer coefficient α
- β Vegard coefficient
- $\vec{\Gamma}$ molar electrodeposition flux
- metal-electrolyte interfacial energy γ
- $\vec{\delta}_{\xi}$ width of metal-electrolyte interface
- $\begin{array}{c} & & \\ & & \\ \varepsilon \\ & & \\ \varepsilon \\ & \\ \varepsilon \\ & \\ \varepsilon \\ \end{array}^{e} \\ & \\ \varepsilon \\ \end{array}$ total strain tensor
- elastic strain tensor
- chemical strain tensor
- $\overset{\leftrightarrow}{\varepsilon^p}$ plastic strain tensor
- ζ_l^2 gradient energy coefficient of liquid
- ζ_s^2 gradient energy coefficient of solid
- ζ_{ξ}^2 gradient energy coefficient of solid-liquid interface
- overpotential η
- effective electrical conductivity κ
- interfacial conductivity κ_i
- electrical conductivity of liquid κ_l
- electrical conductivity of solid κ_s
- λ Lagrange multiplier
- $\stackrel{\leftrightarrow}{\sigma}$ Cauchy stress tensor
- von Mises stress $\sigma_{\rm s}$
- yield stress σ_y
- ϕ electrostatic potential
- Ω_l molar volume of liquid
- Ω_s molar volume of solid

ABBREVIATIONS

- AM active material
- BMS battery management system
- DMC dimethyl carbonate
- EC ethyl carbonate
- EMC ethyl methyl carbonate
- EV electric vehicle
- LIB lithium ion battery
- ${\rm NMC} \quad {\rm LiNi}_x {\rm Mn}_y {\rm Co}_z {\rm O}_2$
- SEI solid electrolyte interphase
- SOC state of charge

ABSTRACT

Jana, Aniruddha Ph.D., Purdue University, May 2019. Modeling Degradation Mechanisms in Rechargeable Lithium-Ion Batteries. Major Professor: R. Edwin García

A physics-based, multiscale framework is presented to describe the degradation in rechargeable lithium-ion batteries. The framework goes beyond traditional (empirical) coulomb-counting approaches and enables the identification of different degradation regimes of behavior. Macroscopically, five degradation mechanisms: (i) solid electrolyte interphase (SEI) growth on the anode, (ii) electrolyte oxidation on the cathode, (iii) anode active material loss and (iv) cathode active material loss due to chemomechanical fracture, and (v) dendrite growth were identified and modeled. Great emphasis was placed on describing the physics of lithium dendrite growth in order to demonstrate five distinguishable regimes: thermodynamic suppression regime, incubation regime, tip-controlled growth regime, base-controlled growth regime, and mixed growth regime. Mesoscopically, three local dendrite growth mechanisms are identified: 1) electrochemical shielding, where there is practically no electrodeposition/electrodissolution, 2) stress-induced electrodissolution and electrodeposition on those interfaces directly facing each other, generating a self-sustained overpotential that pushes the dendrites towards the counter electrode, and 3) lateral plastic extrusion in those side branches experiencing non-hydrostatic stresses. Overall, the experimentally validated theoretical framework allows to fundamentally understand battery degradation and sets the stage to design high energy density and fast charging rechargeable batteries.

1. INTRODUCTION

1.1 Battery Technology and Market

A rechargeable battery is an electrochemical system that stores electrical energy as part of a reversible interfacial chemical reaction, shuttling ions between the anode and the cathode, while enabling electrons through an external circuit. In practice, however, irreversible side reactions occur along with the desired electrochemical reaction, consume active lithium, result in capacity loss of the cell, and in few occasions, through catastrophic failures. Advances in electrochemical energy storage technology and improved electrode chemistries and microstructures have made lithium-based batteries the most popular and viable choice for a wide variety of applications, ranging from portable electronics to electric vehicles [1-6]. As a result of this technological progress and recent legislative support to decrease environmental pollution [7], hybrid and battery electric vehicles are becoming increasingly popular in the US and the Europe [8]. Electric vehicles are at an early adoption stage and showed a dramatic increase of 130% in 2018 yearly sales and 210% in 2018 Q4 sales [9]. Predictions indicate 50% market share by 2045 and 90% market share by 2060 [10]. Recent surveys of cathode materials reveal that $\text{LiMn}_x \text{Ni}_y \text{Co}_z \text{O}_2$ (NMC) is one of the most promising cathode chemistries, due to its high energy and power density, and lithium metal anode, the most promising anode chemistry due to its highest theoretical energy density (3800 Wh/kg) [4,5] and lowest electrochemical potential. A 2017 report, [6], showed that eight out of fourteen battery electric vehicles and every fourteen hybrid electric vehicle from major automobile manufacturers have commercialized the use of NMCbased cathodes. The rapid rise of NMC-based cathodes will continue through 2025, as predicted by Pillot [11]. Lithium metal anode suffers safety issues and results in catastrophic fires and accidents. Commercial Li-ion cell anodes are thus based on lower capacity (400 Wh/kg) [4,5], but safer graphite.

1.2 Battery Degradation Mechanisms

Despite rapid improvements on rechargeable cells and invention of new electrode chemistries, electrochemical degradation or capacity loss, however, remains a major concern to fulfill the aim to place electric vehicles at par with internal combustion engine vehicles, mostly in terms of safety, long term performance, and total cost of ownership [12, 13]. In both, electric vehicles and portable electronic applications, the underlying capacity loss, *i.e.*, the gradual and sometimes abrupt decrease in the battery capacity, remains a prime challenge in the modern energy storage industry. In this thesis, progress was made to describe the main degradation mechanisms in LIBs, including: solid electrolyte interphase (SEI) growth, electrolyte oxidation, chemomechanical degradation of active material, and lithium dendrite growth.

1.2.1 SEI Growth

The formation of the solid electrolyte interphase (SEI) on the surface of the anode particles consumes a large amount of lithium during both storage and cycling, and is considered to be a major mechanism of capacity fade in all graphite-based anode batteries with organic liquid electrolytes, which are unstable at the negative electrode [14]. The SEI has been widely shown to grow continuously, as a result of the reduction products of the electrolyte salt and the solvent [15, 16]. Typically the SEI consists of a dense inner layer and a porous outer layer, and comprises Li_2CO_3 , LiF, ROLi, ROCO₂Li [17]. These products consume active lithium during as a result of the SEI reaction, and result in capacity loss of the cell in both storage and cycling conditions [17]. The SEI layer thickness follows a parabolic growth law with time [18], increases with the cell state of charge [16], and temperature [19].

1.2.2 Electrolyte Oxidation

For Mn-based cathodes, electrolyte oxidation and Mn dissolution are two of the most well-known degradation mechanisms [20]. Electrolyte oxidation occurs at voltages higher than the stable voltage window of organic electrolytes, namely EC and EMC [21]. LiPF_6 salt is widely known to undergo direct oxidation in the 4.35to 5.5 V range [21]. For example, the oxidation potential for 1 M ${\rm LiPF}_6$ in a mixture of EC:EMC (3:7 by weight) is 4.6 V [22]. Ideally, for commercial cells with 4.2 V upper cutoff, there should be no loss of lithium due to electrolyte oxidation. Recent reports from Amine [22–24] and Dahn [25–28] demonstrate slow electrolyte oxidation below 4.2 V, measured in the form of leakage currents [22] and parasitic heat flow [26], in agreement with capacity fade reports for commercial automotive cells [27]. Electrolyte additives such as vinylene carbonate (VC), prop-1-ene-1,3sultone (PES) tris(trimethylsilyl)phophite (TTSPi), and methylene methanedisulfonate (MMDS) [28], have been used to suppress electrolyte oxidation and the subsequent migration and reduction of the oxidized products at the anode surface [29]. The onset voltage for electrolyte oxidation on metals such as aluminum, gold, and platinum was measured earlier by Moshkovich and Aurbach [30] and occurs in the 3.4 - 3.8 V range, much lower than the ~ 4.5 V electrolyte oxidation potential. For aluminum, sub-4 V electrolyte oxidation is assisted by the chemical corrosion of the current collector, as recently reported by Amine and coworkers [22, 24]. The catalytic role of the aluminum current collector on electrolyte oxidation has also been attributed in the recent work by Gasteiger *et al.* [31] and in the review by Xu [32]. The onset voltage was found to lie between 3.4 and 4.3 V [30].

Specifically, NMC cathodes lose additional capacity due to Mn dissolution into the electrolyte. Mn undergoes a disproportionation reaction, $2 \text{ Mn}^{3+} \longrightarrow \text{Mn}^{4+} + \text{Mn}^{2+}$ [20, 33, 34]. The reaction is accelerated under acidic environments, as a result of HF formed as a byproduct of the electrolyte oxidation reaction [35]. Mn²⁺ loss distorts the NMC lattice, dissolves in the electrolyte, and gets reduced on the graphite surface. Each Mn^{2+} ion consumes ~100 Li⁺ ions during codeposition on graphite [36]. However, Mn dissolution occurs above 4.2 V [37], and does not contribute to capacity losses in commercial NMC-graphite cells with 4.2 V upper cutoff.

1.2.3 Chemomechanical degradation

Chemomechanical degradation of the electrode particles is a major cause of capacity fade during cycling [38]. Lithium intercalation and deintercalation in and out of the host electrode particles result in chemomechanical stress inhomogeneities, and thereby induce chemomechanical fatigue and fracture [39]. In graphite, lithium intercalation results in 10% Vegard expansion and 300% increase in Young's modulus [40], while fractured graphite particles expose new sites for additional SEI growth and further consume available lithium. Repeated particle expansion and contraction result in particle rearrangement [41], change in electrode porosity and tortuosity [42], binder degradation [33], and finally, isolation of particles from the electrochemically active network [43].

Deintercalation in NMC111 and NMC811 cathodes results in 1.2% and 5.1% increase in volumetric strains [44]. The fracture toughness of NMC532 was reported to drop by 50% over 100 cycles at a C/20 charge-discharge rate [45]. Non-monotonic dependence of the lattice parameters on lithium content induces anisotropic Vegard strains in both NMC111 [46] and NMC811 [44], and results in Jahn-Teller distortions, degeneration of the Li-O bonds, and microcracks [45]. Further, high Ni content in NMC cathodes increases the energy density but decreases mechanical stability [47].

1.2.4 Dendrite Growth

Dendrites are undesired elongated metallic nanostructures that form on the anode during fast charging. Upon battery cycling, they grow towards the cathode causing short-circuits and other catastrophic failures (including fires) in portable electronic devices and electric vehicles. Dendritic growth thus results in safety issues and is a major bottleneck in the implementation of metallic lithium anodes, which have ten times higher energy density than commercial graphite anodes. Experiments in literature consistently reported the growth of different electrodeposit morphologies as a function of the charging current. Elongated, classic dendritic structures grow from the top at high current densities (tip-controlled mechanism) and mossy structures grow from the base under low current densities (base-controlled mechanism) [48]. Tip-controlled growth has been well explained for lithium and common electrodeposition systems of Ag, Cu, and Zn. Base-controlled growth under low currents, however, had no clear explanation and was hypothesized to be induced by localized stress relaxation at the base.

1.2.5 Dendrite Growth Through LIB Separator

The complexity of the dendrite growth problem increases further due to its heterogeneous interactions with the porous separator. Separators provide electronic insulation between the cathode and the anode layers and thus force electrons into the external resistive load. In addition, separators provide mechanical rigidity to prevent the growth of the dendrites towards the counter electrode. Commercial separator layers are on the order of 25 μ m of thickness, with porosities ranging between 20 and 80%, and pore sizes ranging from 0.1 to 2.2 μ m [49–55]. Separators comprise one to three layers of polyethylene and polypropylene entangled fibers. Extrusion of the polymer in a single direction generates elongated pores, whereas biaxial elongation gives rise to near-isotropic pores (see Figure 1.1). The pore structure of the separator determines its permeability and tortuosity. According to Zhang et al., separators with uniform permeability increase the life of the battery, whereas variations in permeability result in a non-uniform distribution of the current density that promote dendritic growth [56]. Increased thickness and poor conductivity of the separator increases the impedance of the cell by four to five times [56]; therefore, separators with low thickness and higher electrical conductivity values are commercially favored [57]. The electrical conductivity of the separator is usually characterized in terms of the MacMullin number (= $\sigma_{\circ}/\sigma_{eff}$, where σ_{\circ} is the conductivity of the electrolyte, and σ_{eff} is the combined conductivity of the electrolyte plus separator system). MacMullin numbers of some commercial separators, such as Celgard[®] and Solupor[®] range between 5 and 16, and are reported in the work by Djian and co-workers [50]. High MacMullin numbers are attributed to poor electrical conductivity of the polymeric material, high tortuosity of the structure, and low affinity of the electrolyte-polymer interface. Hence, besides the polymeric material, the processing technique that directs the separator morphology is a key factor for separator performance. According to the United States Advanced Battery Consortium in 2006, the maximum recommended MacMullin number for electric propulsion vehicles is 11 [58]. Besides low MacMullin numbers, separators must have mechanical, chemical, and thermal stability at the range of operating conditions of the battery. Detailed morphological and electrical properties of commercial separators are found in literature [50, 57, 59].



Figure 1.1.: Example SEM micrographs of commercial porous separators. (a) Celgard $2500^{\text{(B)}}$ separator, and (b) Solupor $10P05A^{\text{(B)}}$ separator show different arrangement and size distribution of pores. (a) shows elongated pores due to dry unidirectional stretching, and (b) shows equiaxed pore structure as a result of wet bidirectional stretching [50]. The pore structure determines the tortuosity and porosity that affect transport pathways for Li⁺ ions and growth of dendrites.

Attempts to arrest dendrites in the separator have focused on the use of selective phase transformation reactions that block the pore [60], or through the addition of impermeable ceramic nonporous layers [61]. However, even though the large elastic moduli helps in the suppression of dendrite formation, their internal porosity, brittleness and difficulty of processability currently make ceramics-based separators unviable. Similarly, polymer-based separators, display very low shear moduli and are more prone to dendrite growth [62].

1.3 Thesis Organization

In spite of the great commercial demand of higher density and fast charging batteries and wide experimental evidence of battery degradation, there is no fundamental theoretical framework that explains the complex electrochemomechanical mechanisms that lead to battery degradation. In this context, this dissertation proposes mutually consistent physical frameworks to demonstrate the contribution of each degradation mechanism to the overall battery degradation. Specifically, Chapter 2 proposes a physics-based degradation model to describe storage and cycling capacity loss kinetics for commercial $\text{LiNi}_{x}\text{Mn}_{y}\text{Co}_{z}\text{O}_{2}$ -graphite cells. The degradation mechanisms include: (i) SEI growth on the anode, and (ii) electrolyte oxidation, (iii) active material loss on the anode, and (iv) active materials loss on the cathode. In addition to these four mechanisms that lead to capacity loss, a fifth mechanism, the growth of lithium dendrites, is responsible for catastrophic cell failures. Chapters 3–5 present analytical and phase field frameworks to macroscopically and mesoscopically decouple the complex, heterogeneous driving forces that lead to dendrite growth. Specifically, Chapter 3 describes an analytical framework to rationalize the macroscopic thermodynamic and kinetic boundaries of lithium dendrite growth. With a macroscropic understanding of dendrite growth from Chapter 3, Chapter 4 extends it to a position-dependent phase field framework to mesoscopically couple lithium electrodeposition kinetics on the anode with the inherent mechanical behavior of metallic lithium. The framework provides detailed insight on the time-dependent, spatially heterogeneous electrochemomechanical driving forces during electrodeposition that are otherwise difficult to visualize through experiments. Chapter 5 extends the phase
field framework described in Chapter 4 to further rationalize the interactions of the lithium dendrite with the porous polymer separator, and predicts regimes of current densities and separator pore sizes to suppress dendrite growth and avoid catastrophic failures. Finally, Chapter 6 defines follow up challenges and opportunities aligned with what the long term goals of the battery research community and industry foresee in the next ten years.

2. CAPACITY LOSS MECHANISMS

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2.1 Introduction

Recent surveys of cathode materials reveal that $\text{LiMn}_x \text{Ni}_y \text{Co}_z \text{O}_2$ (NMC) is one of the most promising chemistries, due to its high energy and power density [6]. A physics-based, reduced order model was developed to describe the capacity degradation in LiNiMnCoO₂-graphite cells. By starting from fundamental principles, the model captures the effects of four degradation mechanisms: (i) SEI growth on the anode, (ii) electrolyte oxidation on the cathode, (iii) anode active material loss, and (iv) cathode active material loss, the last two due to chemomechanical fracture. The model is computationally efficient ($\sim 1 \text{ ms/cycle}$) and enables physical, real-time, capacity loss calculations for automotive applications. Results demonstrate that under storage conditions, SEI growth and electrolyte oxidation are the major degradation mechanisms, in agreement with experiments. In contrast, batteries subjected to electric currents of a wide amplitude, close to the upper cutoff voltage, electrolyte oxidation contributes $\sim 50\%$ of all the degradation mechanisms, consistent with recent experiments in the literature. Chemomechanically induced active material losses are maximal in the anode at high states of charge and maximal in the cathode at low states of charge. Results quantify the contribution to degradation from each individual mechanism, highlighting, for the first time, the need of physics-based, on-the-fly descriptions that go beyond traditional coulomb counting approaches. Finally, the identification of the individual degradation contributions enables the possibility of tailoring the charge/discharge sequence to extend battery life. A summary of the degradation mechanisms considered herein is shown in Figure 2.1.



Figure 2.1.: Degradation mechanisms of NMC-graphite cells with 4.2 V upper cutoff voltage. A schematic NMC-graphite cell is shown in inset (a). Four degradation mechanisms are modeled herein and contribute to overall loss of lithium: (i) SEI growth, and (ii) graphite fracture on the anode side; and (iii) electrolyte oxidation in the presence of the Al current collector, and (iv) NMC particle fracture on the cathode side. Pristine graphite flakes are shown in inset (b) and SEI covered flakes after one C/10 cycle is shown in inset (c) [17]. Pristine graphite particles are shown in inset (d) [63] and fractured particles after cycling are shown in inset (e) [64]. Inset (f) [65] shows pristine NMC particles and (g) [66] shows electrolyte oxidation products (in green) on the NMC particles after cycling. Insets (h) and (i) [45] show NMC particles before and after fracture.

2.2 Theoretical Framework

2.2.1 The SEI layer

A reduced order model for SEI growth on graphite anodes recently published [67] considers the irreversible formation of SEI products [17] from the electrolyte:

$$S + 2Li^{+} + 2e^{-} \longrightarrow P, \qquad (2.1)$$

where, S denotes all electrolyte solvent molecules and P denotes the organic and inorganic products that comprise the SEI layer. The rate of lithium ions consumed due to SEI growth at the graphite-electrolyte interface is given by the interfacial reaction kinetics:

$$i_s = n\mathcal{F}k_sC_s(x=0,t)\exp\left(-\frac{\alpha_c n\mathcal{F}}{RT}\eta_s\right)$$
(2.2)

where k_s is the reaction constant, $C_s(x, t)$ is the concentration of S across the SEI layer, x = 0 corresponds to the graphite-SEI interface, and η_s is the surficial overpotential given by:

$$\eta_s = \eta_k + \phi^a - \phi^s. \tag{2.3}$$

 $\phi^s = 0.4$ V is the electrolyte solvent reduction potential [68,69] versus Li⁺/Li and ϕ^a is the anode open circuit potential [70]. η_k is the kinetic overpotential [71].

The SEI growth model considers the coupled reaction-diffusion kinetics, wherein the diffusion of the electrolyte solvent, S, through the SEI layer limits the rate of the SEI formation reaction, in agreement with several accounts [68,71,72]. The diffusion kinetics of the solvent, S, and the product, P, are thus given by:

$$\begin{split} \frac{\partial C_{\rm S}}{\partial t} &= D_{\rm S} \frac{\partial^2 C_{\rm S}(x,t)}{\partial x^2} \\ \frac{\partial C_{\rm P}}{\partial t} &= D_{\rm P} \frac{\partial^2 C_{\rm P}(x,t)}{\partial x^2} \end{split}$$

The reactant and the product diffusion fluxes at the interface (x = 0) are related to the SEI growth kinetics as follows:

$$D_{\rm S} \frac{\partial C_{\rm S}(x,t)}{\partial x} \bigg|_{x=0} = D_{\rm P} \frac{\partial C_{\rm P}(x,t)}{\partial x} \bigg|_{x=0} = -\frac{i_s}{n\mathcal{F}}$$
(2.4)

 $C_{\rm S}$ and $C_{\rm P}$ are solved by using Laplace transforms, and then inverted, leading to $i_s(t) = n\mathcal{F}C_{\rm S}^*\sqrt{D_{\rm S}}/(\sqrt{\pi t}(1+\lambda\theta))$, where, $\lambda = \frac{C_{\rm S}^*\sqrt{D_{\rm S}}}{C_{\rm P}^*\sqrt{D_{\rm P}}}$ and $\theta = \frac{C_{\rm S}(0,t)}{C_{\rm P}(0,t)} = \exp\left[\frac{n\mathcal{F}}{RT}\left(\eta_k + \phi^a - \phi^s\right)\right]$ [67]. The capacity loss due to SEI growth is given by:

$$Q_{\rm SEI} = \int_0^t i_s A dt = \int_0^t \frac{n \mathcal{F} A C_{\rm S}^* \sqrt{D_{\rm S}}}{\sqrt{\pi t} (1 + \lambda \theta)} dt$$
(2.5)

By expressing the diffusivity in Arrhenius form, $D_{\rm S} = D_{\rm S}^{\circ} \exp\left(-\frac{E_{\rm S}}{RT}\right)$, and substituting into Equation 2.5, the SEI growth capacity loss is:

$$Q_{\rm SEI} = \int_0^t i_s A dt = \int_0^t \frac{k_{\rm SEI}}{2(1+\lambda\theta)} \exp\left(-\frac{E_{\rm SEI}}{RT}\right) dt$$
(2.6)

where, $k_{\rm SEI} = 2n \mathcal{F} A C_{\rm S}^* \sqrt{D_{\rm S}^{\circ}} / \sqrt{\pi}$ and $E_{\rm SEI} = E_{\rm S} / 2$.

2.2.2 Chemomechanically induced fracture

Lithium intercalation in active material particles induces chemomechanical deformation and electrochemical isolation from its surroundings, as the electrode particle fractures and the surrounding electrolyte and the binder fail to fill the crevices of the crack(s). The probability of crack nucleation and growth increases with current density [73]. In addition, the probability to induce electrode particle cracking increases with local lithium content deviations from the stress-free state of charge, SOC_{\circ} , *i.e.*, with respect to $\Delta SOC = SOC - SOC_{\circ}$ for the anode and with respect to $\Delta SOC = [1 - (SOC - SOC_{\circ})]$ for the cathode. Thus, in qualitative agreement with Jin [67] and Kalupson [71], the rate of lithium lost due to graphite particle fracture proposed herein is:

$$\frac{dQ^a_{\rm AM}}{dt} = \frac{d\varepsilon^a_{\rm AM}}{dt} \cdot (SOC - SOC_{\circ}) \cdot V_{\rm r} \cdot C_{\rm Li,max}$$
(2.7)

$$\frac{d\epsilon_{\rm AM}^a}{dt} = -k^a(T) \left\| I \right\| \tag{2.8}$$

 $k^{a}(T) = k_{\rm AM}^{a} \exp\left(-\frac{E_{\rm AM}^{a}}{RT}\right)$, and $\varepsilon_{\rm AM}^{a}$ is the volume fraction of active material in the anode. Similar rate equations hold for the NMC particles on the cathode. Thus, the amount of capacity loss due to active material loss in each electrode is:

$$Q_{\rm AM}^a = \int_0^t k_{\rm AM}^a \exp\left(-\frac{E_{\rm AM}^a}{RT}\right) \left(SOC - SOC_\circ\right) \|I\| \, dt, \,\,\text{(anode)}$$
(2.9)

$$Q_{\rm AM}^{c} = \int_{0}^{t} k_{\rm AM}^{c} \exp\left(-\frac{E_{\rm AM}^{c}}{RT}\right) \left[1 - (SOC - SOC_{\circ})\right] \|I\| \, dt, \,\,(\text{cathode}) \tag{2.10}$$

2.2.3 Electrolyte oxidation in presence of Al current collector

Amine [22–24] and Kostecki [74] demonstrated that electrolyte solvent, ethylene carbonate (EC), undergoes a slow oxidation reaction in the presence of the aluminum current collector [24, 74]:

$$EC \xrightarrow[\eta]{\text{oxidation}} EC^+ + e \tag{2.11}$$

Simultaneously, HF is produced [22, 74]:

$$\begin{array}{c} {\rm LiPF}_6 \rightleftharpoons {\rm LiF} + {\rm PF}_5 \\ \\ {\rm PF}_5 + {\rm H}_2 {\rm O} \ ({\rm trace}) \rightleftharpoons 2 \, {\rm HF} + {\rm POF}_3 \end{array} \end{array} \hspace{0.5cm} {\rm with \ moisture} \\ \\ \\ {\rm EC}^+ \rightarrow {\rm H}^+ \\ \\ {\rm H}^+ + {\rm LiPF}_6^- \longrightarrow {\rm HF} + {\rm PF}_5 \end{array} \Biggr\} \hspace{0.5cm} {\rm without \ moisture}$$

The second concurrently occurring reaction is the corrosion of the aluminum current collector. The passivating Al_2O_3 layer on the aluminum current collector gets corroded with HF:

$$6 \operatorname{HF} + \operatorname{Al}_2 \operatorname{O}_3 \xrightarrow{\text{chemical}} 2 \operatorname{AlF}_3 + 3 \operatorname{H}_2 \operatorname{O}$$
(2.12)

In presence of the aluminum current collector, define ΔG as the chemical energy barrier for the forward, purely chemical, current collector corrosion reaction and $\alpha z \mathcal{F} \eta$ as the electrochemical driving force for the electrolyte oxidation reaction. Thus, $\Delta G - \alpha z \mathcal{F} \eta$ is the overall energy barrier for the coupled reaction. Thus, in agreement with Bard [75]:

$$i_{\rm eox} = i_{\circ,\rm eox} \exp\left(-\frac{\Delta G - \alpha z \mathcal{F} \eta}{RT}\right)$$
 (2.13)

In the absence of overpotential, Equation 2.13 reduces to the chemical kinetics of the corrosion reaction, in agreement with Amine and coworkers [23]:

$$i_{\rm eox} = i_{\circ,\rm eox} \exp\left(-\frac{\Delta G}{RT}\right)$$
 (2.14)

Similarly, in the absence of the current collector corrosion, Equation 2.13 reduces to the purely electrochemical, electrolyte oxidation reaction, in agreement with Amine and coworkers [23]:

$$i_{\rm eox} = i_{\circ,\rm eox} \exp\left(\frac{\alpha z \mathcal{F} \eta}{RT}\right)$$
 (2.15)

where, $\eta = \phi^c - \phi^c_{\circ,eox}$ is the local overpotential, ϕ^c is the cathode half cell potential and $\phi^c_{\circ,eox}$ is the equilibrium oxidation potential for the electrolyte solvent.

Equation 2.13 thus physically defines that the Al corrosion assists the overall reaction through a decrease in the free energy of the coupled reaction, following Le Chaterlier's principle [76] and Bard [75]. Thus, capacity loss due to electrolyte oxidation is:

$$Q_{\text{eox}} = \int_0^t i_{\text{eox}} A dt = \int_0^t I_{\circ,\text{eox}} \exp\left(-\frac{\Delta G - \alpha z \mathcal{F} \eta}{RT}\right) dt$$
(2.16)

2.3 Numerical Implementation

The model parameters obtained from experimental data are summarized in Table 2.1. In Equation 2.13, the free energy, ΔG , corresponding to the chemical corrosion of the Al current collector is obtained from the experiments by Amine and

Parameter	Value	Reference
$E^a_{\rm AM}$	39500 J/mol	[67]
$E^c_{ m AM}$	10000 J/mol	*
$E_{\rm SEI}$	39146 J/mol	[67]
$i_{\rm eox}$ (cycling)	6 A	*
$i_{\rm eox}$ (storage)	$7 \times 10^{-6} \mathrm{A}$	*
ΔG	26344 J/mol	[23]
SOC_{\circ}	0	_
$\phi_{\circ,\mathrm{eox}}$	3.6 V	[26]
$\phi^c_{\circ,\mathrm{eox}}$	3.76 V	[26]

Table 2.1.: Physical parameters used in developed model.

* fitted from experiment

coworkers [22,23]. The equilibrium oxidation potential, *i.e.*, the onset potential for the electrolyte oxidation, is obtained from the parasitic heat flow experiments by Dahn and coworkers [26]: the half cell potential is, $\phi_{o,\text{eox}}^c = 3.76$ V and the corresponding full cell potential is, $\phi_{o,\text{eox}} = 3.6$ V. The exchange current, $I_{o,\text{eox}}$, is fitted to capacity loss experiments for Sanyo UR18650 NMC111-graphite cell reported by Ecker and coworkers [77]. Anode degradation mechanisms were readily parameterized for a graphite anode and validated for an LFP-graphite cell [67]. Electrolyte oxidation for stored and galvanically cycled conditions were calibrated from experimental data as reported by Ecker *et al.* [77]. The 70% SOC, 50°C condition was used as the storage reference and 0–100% SOC, 1 C (2.05 A) charge-discharge cycle at 35°C was used as the cycling loss reference. Cycles were normalized with respect to the 0–100% SOC cycle, known as one equivalent full cycle. The cathode active material loss was calibrated for 47.5–52.5% SOC cycle, in which electrolyte oxidation was absent. In the absence of any coupled effects, the total lithium lost is defined as the linear contribution from each mechanism:

$$Q_{\text{total}} = \begin{cases} Q_{\text{SEI}} + Q_{\text{eox}}, & \|I\| = 0\\ Q_{\text{SEI}} + Q_{\text{eox}} + Q_{\text{AM}}^{a} + Q_{\text{AM}}^{c}, & \|I\| \neq 0 \end{cases}$$
(2.17)

The developed model was validated against capacity fade experiments of NMCgraphite 18650 cells of three different makes: Sanyo, Molicel, and Sony, as performed by Ecker *et al.* [77], Shuster *et al.* [78], and Schmitt *et al.* [79]. The upper cutoff voltage was set to 4.2 V, following cells used in the experiments. The lower cutoff voltage spans in the 2 to 2.5 V range. Experimental data used in this work is summarized in Table 2.2.

				Sto	rage		Cycling	
Cell [Ref.]	Capacity	Lower Cutoff	Upper Cutoff	Temp.	SOC	Temp.	Charge, Discharge Bate	Cycle Depth
	(Ah)	(V)	(V)	(°C)	(%)	(°C)	(C)	(%)
Sanyo UR- 18650E [77]	2.05	2.5	4.2	50 35	$\begin{array}{cccc} 10, & 30, \\ 50, & 70, \\ 80, & 85, \\ 90, & 95, \\ 100 \\ 50 \end{array}$	35	1, 1	$\begin{array}{c} 0\text{-}100,\ 10\text{-}90,\\ 20\text{-}80,\ 25\text{-}75,\\ 40\text{-}60,\ 45\text{-}55,\\ 47.5\text{-}52.5;\\ 90\text{-}100,\ 85\text{-}95\\ 70\text{-}80,\ 45\text{-}55, \end{array}$
Molicel IHR 18650A [78]	1.95	2.0	4.2	-	-	35 25, 35, 50	0.5, 1	$\begin{array}{c} 20-30, \ 5-15\\ \hline 1-99,\\ 3-97,\\ 6-94,\\ 13-87\\ 3-\\ 97,13-\\ 87\end{array}$
Sony US- 18650V3 [79]	2.15	2.5	4.2	0 20 45	$\begin{array}{c} 50,100\\ 25,50,\\ 75,100\\ 50,100\end{array}$	_	_	_

Table 2.2.: Summary of degradation experiments on commercial NMC-graphite cells.

Calculations are on the order of 1 ms/cycle on a single Intel Core i5 processor. Each of the four degradation mechanism in a Python program consume ~ 50 kB of memory when measured with Python's memory profiler [80], and can be further lowered in machine language used in the battery managment system (BMS). Typical BMS programs consume ~ 3 kB memory [81]. Thus, this model enables battery manufacturers to estimate and anticipate the contributions to degradation from each mechanism in real time, make corrections, and recalibrate, on the fly.

2.4 Results and Discussion

2.4.1 Effect of long term storage (||I(t)|| = 0) on capacity degradation

2.4.1.1. Sanyo UR18650E NMC-graphite cell

Figure 2.2 shows the capacity loss predictions for a Sanyo UR18650 NMCgraphite cell when stored for ~ 1 year at 50°C for selected SOCs. Discrete data (circles) denote the experimental results from Ecker *et al.* [77]. Results demonstrate that the dominant contribution to capacity loss is from lithium consumed during SEI formation, in agreement with Dubarry and Liaw [14]. As the open circuit potential increases above 3.6 V, the SOC of the cell increases above 50%, the electrolyte oxidizes slowly in presence of the aluminum current collector, and consumes active Li ions. Thus for $\phi > \phi_{\circ,\text{eox}} = 3.6 \text{ V}$, two degradation mechanisms contribute to overall storage loss: SEI growth on the anode and electrolyte oxidation on the cathode. However, unlike electrolyte oxidation, lithium loss due to SEI growth occurs in the entire voltage window of the cell, *i.e.*, from 2.5 to 4.2 V, and increases with open circuit potential value. For a cell stored with full charge the overall capacity fade is maximal. Towards the end of life of the cell, rapid capacity loss occurs due to complex, heterogeneous microstructural effects: (i) kinetic hindrance in lithium intercalation due to debris deposition at the anode [25], (ii) lithium plating at low temperatures [78], and (iii) electrolyte drying [25, 78], in agreement with recent experiments from Dubarry and coworkers [82].



Figure 2.2.: Effect of SOC on capacity loss during long term storage of a Sanyo UR18650E NMC111-graphite cell with 4.2 V upper cutoff, at 50°C at selected SOCs: (a) 50%, (b) 60%, (c) 70%, (d) 80%, (e) 90%, and (f) 100%. White circles denote experimental data from Ecker and coworkers [77]. Two degradation mechanisms, SEI growth on the anode-electrolyte interface and electrolyte oxidation on the cathode-electrolyte interface, contribute to the overall capacity fade. The major lithium loss is due to SEI growth, in agreement with Dubarry and coworkers [14]. Electrolyte oxidation in the presence of the aluminum collector occurs above $\phi_{o,eox} = 3.6$ V and thus its contribution to overall degradation increases when the cell is stored at higher SOCs. The pink region (not included in this model) denotes abrupt losses due to microstructural mechanisms, such as kinetic hindrance of lithium intercalation at the anode, debris deposition, lithium plating, and electrolyte drying [78].

2.4.1.2. Sony US18650V3 NMC-graphite cell

Figure 2.3 shows the effect of temperature on the capacity loss for ~ 500 days of storage for a Sony US18650V3 NMC-graphite cell with a 4.2 V upper cutoff voltage. Experimental conditions reported by Schmitt and coworkers [79] are simulated. Losses due to both SEI growth and electrolyte oxidation increase with temperature and follow Arrhenius kinetics. Results show that degradation in the Sony cell is more sensitive to temperature than the Sanyo cell. Further, in both cells, results demonstrate that SEI loss is more sensitive to the temperature while electrolyte oxidation is more sensitive to the cell open circuit potential, in agreement with experiments by Dahn and coworkers [27]. For SOC $\leq 50\%$, the contributions to capacity loss from electrolyte oxidation are inexistent. At low temperatures and high SOCs (see Figure 2.3(b)), electrolyte oxidation and SEI growth contributions are nearly equal. However, for high temperatures and high SOCs (see Figure 2.3(h)), SEI growth dominates the degradation kinetics of the system.



Figure 2.3.: Effect of temperature on capacity loss during long term storage for a Sony US18650V3 NMC-graphite cell with 4.2 V upper cutoff, for selected SOCs and temperatures: (a) 50% SOC at 0°C, (b) 100% SOC at 0°C, (c) 25% SOC at 20°C, (d) 50% SOC at 20°C, (e) 75% SOC at 20°C, (f) 100% SOC at 20°C, (g) 50% SOC at 45°C, and (h) 100% SOC at 45°C. White circles denote experimental data from Schmitt and coworkers [79]. Both SEI growth and electrolyte oxidation increase with SOC and temperature. Electrolyte oxidation is negligible for SOCs \leq 50%. A cell stored at high temperature and high SOC thus suffers maximum capacity loss from SEI growth and additional losses due to electrolyte oxidation. Model parameters were calibrated for the Sanyo cell and reused here for the Sony cell.

2.4.2.1. Sanyo UR18650E NMC-graphite cell

Figure 2.4 demonstrates the effect of resting time at high electrostatic potentials. Electrolyte oxidation dominates capacity loss when the cell is subjected to open circuit potentials higher than 3.6 V.



Figure 2.4.: Effect of cycle depth for symmetrical charge(1 C)-discharge(1 C = 2.05 A) cycling about 50% average SOC on capacity loss for a Sanyo UR18650E NMC111-graphite cell with 4.2 V upper cutoff, at 35°C, for selected cycle depths: (a) 0–100%, (b) 10–90%, (c) 25–75%, (d) 40–60%, (e) 45–55%, and (f) 47.5–52.5%. Degradation increases with cycle depth, even for fixed charge throughput. For cases in which the cell spends more time above ~50% SOC (insets (a), (b), and (c)), electrolyte oxidation contributes most to the overall degradation. Similarly, the contribution of SEI growth increases as the cell spends more time at higher potentials. Losses due to complex microstructural mechanisms (not included in this model) are shown schematically in pink [78].

The remaining degradation mechanisms occur through the entire voltage range of the cell and thus scale with charge throughput. Since electrolyte oxidation occurs only at higher SOCs (> 50%), the total capacity fade does not scale with charge throughput. Figure 2.5 shows the effect of average SOC on capacity loss. A Sanyo UR18650 cell cycled at 1 C charge-discharge rate (1 C = 2.05 A) at 35°C, with a fixed 10% cycle depth for selected average SOCs is considered.



Figure 2.5.: Effect of average SOC of charge-discharge cycle on capacity loss for a fixed 10% cycle depth for a Sanyo UR18650E NMC111-graphite cell with 4.2 V upper cutoff, at 35°C, for 1 C charge-discharge rates (1 C = 2.05 A) and selected cycles: (a) 90–100%, (b) 85–95%, (c) 70–80%, (d) 45–55%, (e) 20–30%, (f) 5–15%. Degradation is maximal when the cell spends more time close to ~100% SOC, due to increased contribution from electrolyte oxidation and SEI growth. For low SOCs, lithium content in the cathode is high and thus cathode particle fracture is favored. Thus, cathode active material loss increases from inset (a) to inset (f). Similarly, active material loss on the anode as a result of chemomechanically-induced fracture is shown in insets (a) to (f).

Results demonstrate that maximum degradation occurs when the cell spends more time at SOCs close to 100%, independently of the total charge throughput, as shown in Figure 2.5(a). In agreement with Figure 2.4, capacity fade at higher SOCs is largely due to electrolyte oxidation. Electrolyte oxidation is negligible or absent below $\sim 50\%$ SOC, as shown in Figure 2.5(d), (e), and (f). Further, at higher SOCs, the active material loss due to particle fracture for the graphite anode lithium content inhomogeneously expands the lattice. Similarly, at lower SOCs, degradation is a result of cathode active material chemomechanical fracture, as shown in Figure 2.5(f). The gap between experimental and predicted results for low SOCs (see Figure 2.5(f)) is specific to underlying microstructural details which induces localized degradation. These degradation mechanisms lead to rapid capacity losses of the porous electrochemical device.

2.4.2.2. Molicel IHR18650A NMC-graphite cell

Figure 2.6 shows the effect of asymmetry in charge-discharge rates on battery degradation. A C/2 charge rate and a 1 C discharge rate (1 C = 1.95 A) with a fixed 50% average SOC at 35°C is applied to a Molicel IHR18650A NMC-graphite cell with a 4.2 V upper cutoff. A twenty-minute rest period is followed after each discharge cycle, as reported by Shuster and coworkers [78]. Results demonstrate that electrolyte oxidation is the highest contributor to the total degradation for large cycle depths, similar to the Sanyo cell. However, at C/2 charge rate, the cell spent longer time above 3.6 V, and thus underwent more electrolyte oxidation than in 1 C charging. Further, similar to the Sanyo cell, the anode and cathode active material losses remain unchanged in each inset for fixed charge throughput.



Figure 2.6.: Effect of asymmetrical charge(C/2)-discharge(1 C = 1.95 A) cycling about 50% average SOC on capacity loss for Molicel IHR18650A NMC-graphite cell with 4.2 V upper cutoff, at 35°C, and for selected cycle depths: (a) 1–99%, (b) 3– 97%, (c) 6–94%, and (d) 13–87%. Twenty minutes rest period after each discharge cycle was simulated, to emulate experimental conditions as reported by Shuster and coworkers [78]. Parameter values are unchanged and reused from the Sanyo cell. Degradation increases with cycle depth, even for fixed charge throughput. For all cases, the cell spends a large fraction of time above 50% SOC and hence electrolyte oxidation contributes most to the overall degradation. Electrolyte oxidation also increases due to the slow charging rate, as the cell spends more time in the 3.6–4.2 V range. The overprediction in the electrolyte oxidation arises from the parameter values that were set for the Sanyo cell and reused in this figure for the Molicel cell.

Figure 2.7 shows the effect of temperature on capacity loss under large chargedischarge cycles and thus electrolyte oxidation is the major contributor to capacity loss. Further, on comparison of the fixed cycle depth (3–97%) for the three temperatures (see Figure 2.7(a), (b), and (d)), results demonstrate that while the fraction of electrolyte oxidation contribution remains almost constant, and the largest fraction to degradation for all cases, the SEI growth, increases with temperature.



Figure 2.7.: Effect of temperature on charge-discharge cycling loss for a Molicel IHR18650A NMC-graphite cell with 4.2 V upper cutoff, for C/2 charge-1 C discharge rates (1 C = 2.15 A) with a 50% average SOC, and selected temperatures and cycle depths: (a) 3–97% at 25°C, (b) 3–97% at 35°C, (c) 13–87% at 35°C, (d) 3–97% at 50°C, and (e) 13–87% at 50°C. Degradation increases with cycle depth for fixed total cycled charge. The contributions from all four degradation mechanisms increase with temperature due to Arrhenius thermal-dependence. Results demonstrate that degradation is dominated by SEI growth and electrolyte oxidation.

2.5 Summary and Conclusions

A physical, full cell, capacity fade model for state-of-the-art NMC-graphite cells has been developed and applied to quantify the underlying degradation mechanisms of three commercial cells with 4.2 V upper cutoff. Four degradation mechanisms were considered: (i) SEI growth on the anode, (ii) electrolyte oxidation on the cathode, (iii) lithium loss in graphite particle fracture in the anode, and (iv) lithium loss in NMC particle fracture in the cathode. Electrolyte oxidation in presence of the Al current collector has been rationalized into a physical model for the first time. Results demonstrate that present approaches that use empirical charge throughput are inapplicable to accurately describe degradation in NMC-graphite cells and heralds the development of physics-based descriptions as the one proposed herein.

Further, results show that SEI growth is sensitive to temperature, while electrolyte oxidation is sensitive to the cell potential, as experimentally reported [27]. Chemomechanically-induced fracture of active material is maximal in the anode at high potentials, and maximal in the cathode at low potentials. Thus, results suggest that cells should be stored at the lowest possible SOC, and cycled close to 50% SOC at ~25°C in order to minimize degradation. Further, results show that lithium loss due to fracture of electrode particles remains fixed for a fixed charge throughput.

For the same single set of specified material parameters, the model was compared against eighteen experiments of stored cells and against twenty four experiments of galvanically cycled cells, across a range of SOCs and in the 0–50°C temperature range. Results suggest that electrolyte additives that suppress electrolyte oxidation for NMC-based cathodes [27,29] are necessary in order to extend the practical voltage range of degradation-free NMC-based cells.

A comparison of available degradation models shows that physics-based models have great accuracy with less than 10% error but are computationally intensive [83]. Regression-based models are fast but show 70% error when tested for conditions outside their datasets [83]. Thus, the degradation framework developed herein allows a physical, fast evaluation of the lifetime of a commercial cell by enabling on-board capacity loss calculations in electrified technologies.

3. ANALYTICAL MODELING OF LITHIUM DENDRITE GROWTH KINETICS

A version of this chapter has been published as: A. Jana, R. E. García. "Lithium dendrite growth mechanisms in liquid electrolytes." Nano Energy, 41, 552–565, 2017, DOI:10.1016/j.nanoen.2017.08.056, and adapted here for non-commercial use only.

3.1 Introduction

The growth of metallic lithium deposits, broadly referred to as "dendrites," is a major roadblock in the commercialization of high power and energy lithium-ion batteries [1,84], as well as the emergence of lithium anode-based and lithium-air batteries [85,86]. For currently used commercial graphitic anodes in lithium-ion batteries, dendrites pose a serious safety concern and have resulted in catastrophic failures, particularly at high current densities [87]. In all cases, the safety and performance of existing and emergent rechargeable batteries will determine their success tied to the survival of nascent markets of electricity-based technologies, such as of electric vehicles [88], which would greatly benefit from lithium metal anodes, and the possibility to reduce the charging time from the present 4 and 36 hours to 10 minutes [89,90]. While there has been significant progress in the fast-charging infrastructure, the dendrite growth problem remains the primary bottleneck to implement high energy, fast charging batteries. In this context, thin film (3 μ m) lithium anode batteries have been developed; however, to make them dendrite-free, alternate approaches are required to bring this technology to the main stream [91–93].

Fundamentally, the problem of dendrite growth remains largely unsolved due to the fact that, unlike copper or zinc electrodeposition, lithium grows at current densities one hundred times lower than the limiting current density, and shifts between, what appears to be, multiple growth mechanisms reported over a wide variety of time and length scales [94]. The inherent electrochemical instability of lithium metal in organic liquid electrolytes, combined with the underlying multiphysical and microstructural complexity of the local environment that each dendrite is subjected to, contributes a great deal of complexities that demand a basic science identification of the individual mechanisms that control its stability and kinetics. These mechanisms result in different lithium morphologies that determine whether the sandwiched separator will be able to arrest the dendrite, or if the dendrite will dissolve back into the electrolyte.

Figure 3.1 shows a catalog of electrodeposition experiments, where the dendrite was reported to grow either as *tip-controlled* or *base-controlled*. For example, Brissot and Chazalviel reported two regimes of lithium growth, (see \bullet in Figure 3.1): needlelike at low current densities $(0.05 \,\mathrm{mA/cm^2})$ after 38 hours [95], and "arborescent" for high current densities $(0.7 \,\mathrm{mA/cm^2})$ after 2300 s [96]. Dolle *et al.* (see \triangleleft and \triangleleft in Figure 3.1) reported that a single charge cycle at $0.22 \,\mathrm{mA/cm^2}$ produced mossy deposits, while a single charge cycle at $0.5 \,\mathrm{mA/cm^2}$ resulted in elongated dendrite-like microstructures [97]. Orsini et al. demonstrated the growth of lithium microstructures on lithium, copper, and graphite substrates [98]. It was reported that on both lithium and copper, mossy growth was observed for low C-rates $(C/5, 0.45 \text{ mA/cm}^2)$, while dendritic growth was observed at high C-rates (C, $2.2 \,\mathrm{mA/cm^2}$). However, for graphite anodes, high C-rates (2 C, 0.1 mA/cm²) only roughened the anode surface. Arakawa and coworkers were the first to propose that lithium "extrudes" from the base [99]. Experimentally, it was observed that lithium pushes out towards the counter electrode from the base, where the morphology of the tip remains largely unchanged. The authors predicted different morphologies as a function of the Laplace pressure on the electrodeposit and its surface tension.



Figure 3.1.: Catalog of different dendrite microstructures. Experimental results illustrate two main growth mechanisms: tip-controlled growth and base-controlled growth of lithium electrodeposits, as reported in scientific literature: • corresponds to experimental data of "bush-like" and "tree-like" dendritic growth for two different applied current densities, as reported by Brissot and coworkers [96]; \triangle corresponds to experiments as performed by Crowther and West [48], where the dendrite is initially *tip-controlled* and transitions to *base-controlled growth* at later times; \blacktriangleleft corresponds to base-controlled growth experiments and \triangleleft to tip-controlled growth experiments as reported by Dolle *et al.* [97]; \triangleright corresponds to *base-controlled growth* data and ▶ to tip-controlled growth data as reported by Orsini and coworkers [98]; \Diamond corresponds to electrodeposit growth experiments for different applied current densities as reported by Cui et al. [100]; \Box corresponds to base-controlled growth data and to tip-controlled growth data as reported by Li and coworkers [101]. Finally, bottom right inset shows a schematic representation of a representative hemispherical capshaped nucleus, N, deposited on a flat substrate, S, immersed in a liquid electrolyte, E.

Hollenkamp and coworkers used Raman spectroscopy to distinguish growth at the tip and from the base and demonstrated that the tip morphology remains unchanged during *base-controlled growth* [102]. Seminal experiments by Crowther and West (see \triangle in Figure 3.1) showed the transition from *tip-controlled* to *base-controlled* in a single galvanostatic recharge cycle [48], where the growth rate was shown to be proportional to the Butler-Volmer current density, consistent with Monroe and Newman [103]. Recent experiments by Cui and coworkers [100] (see \Diamond in Figure 3.1) confirmed the observations as well as predictions by Ely [104], and most recently by Bazant, Li and coworkers [94, 101] (see \blacksquare and \square in Figure 3.1). Transitions between experimentally reported growth mechanisms from *base-controlled* to *tip-controlled* [94] or from *tip-controlled* to *base-controlled* [48], clearly outline that the mechanisms for growth are a function of the underlying time-dependent conditions that dendrites are subjected to. Also, additional driving forces are at play during dendrite growth due to the lightning rod-like shielding effects of a highly conductive elongated metallic electrodeposit [105].

The first dendrite growth model was developed by Barton and Bockris, who proposed that ion transport in front of the dendrite tip is limited by diffusion [106]. The authors demonstrated the existence of a critical overpotential and described the growth of silver dendrites in liquid electrolytes. Diggie and Bockris further extended the model for higher overpotentials and showed transitions between spongy and dendritic morphologies as the overpotential increased [107]. Aogaki and Makino followed a Mullins-Sekerka type description to show dendrite growth due to the electrochemical instability at the electrode interface for diffusion-limited electrodeposition [108, 109]. Chazalviel, Fleury, and Rosso demonstrated that dendrites formed due to deviations from electroneutrality at the electrochemical interface [110–112]. Dendrite propagation velocity was shown to be equal to the anion velocity and proportional to the electric field in the electroneutral region of the electrolyte. Dendritic growth was attributed to depletion of ions near the anode interface at current densities higher than the limiting current density. At lower and battery-relevant current densities, Monroe and Newman predicted the dendrite tip velocity and extended the Butler-Volmer relation to incorporate elastic deformation to assess the separator stiffness necessary to block dendrite penetration [103, 113]. Newman also demonstrated the effect of elastic energy on the electrochemical interface to hinder dendrite growth. Ferrese and Newman further incorporated the effects of plastic deformation of lithium and examined lithium movement on the anode during charge-discharge cycles [114–116]. Ely and García rationalized the contributions from these apparently disconnected mechanisms and unified its description into a generalized electrochemical analytical framework that identified three regimes of dendrite stability and growth [104]. Srinivasan and coworkers recently resolved tensile and compressive stresses and assessed the propensity of dendrite penetration under elastic deformation [117].

In spite of the great deal of experimental evidence highlighting the unequivocal existence of *tip*- and *base-controlled growth* of lithium, there is no fundamental framework that explains clearly the observations. In this context, a generalized electrochemical and chemomechanical theory of dendrite growth kinetics is presented herein that quantitatively identifies the different regimes of lithium growth. Predicted regimes and time-dependent growth behavior are in excellent agreement with experiments that have reported *tip-controlled* and *base-controlled growth*, and the conditions that lead an isolated dendrite to switch from one mechanism to the other one are explained.

3.2 Theory

Define the total Gibbs free energy of transformation of a hemispherical electrodeposit that forms on an electrically charged mechanically stressed substrate, with a contact angle of 90° as shown in the bottom right inset in Figure 3.1. Here, the chemical, electrical, and mechanical contributions to the bulk free energy of transformation are embodied by the expression:

$$\Delta G_{\rm T} = \frac{2\pi}{3} \left(\Delta G_{\rm f} + \frac{z\mathcal{F}\eta}{\Omega} + \frac{1}{2} \stackrel{\leftrightarrow}{\sigma} \stackrel{\leftrightarrow}{\varepsilon} \right) r^3 + 2\pi\gamma r^2 \tag{3.1}$$

The state of stress of such an electrodeposit is described by a symmetric rank two tensor, which for a hemispherically symmetric cap is simplified in the diagonalized reference system as,

$$\overset{\leftrightarrow}{\sigma} = \begin{bmatrix} \sigma & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & a\sigma \end{bmatrix}$$
 (3.2)

a defines stress anisotropy and together with the principal (eigenstress) direction(s) uniquely quantifies the mechanical state of the dendrite. In general, the electrodeposit

is subjected to multiple sources of stress: those induced by the SEI, whose stiffness induces an inhomogeneous compressive effect [17], the adjoining electrodeposits, whose differential molar volume expansion contributions induce shear stresses [118], the separator, which pushes down the dendrite as a means to suppress its growth into the counter electrode [116], and the metallic casing of the battery, which hydrostatically compresses the battery stack [119, 120]. For $\sigma < 0$, and a < 0, Equation 3.2 shows that the electrodeposit is pushed laterally inwards while extruded upwards, and thus promotes the growth of the electrodeposit. Substitution of Equation 3.2 into Equation 3.1 leads to:

$$\Delta G_{\rm T} = \frac{2\pi}{3} \left(\Delta G_{\rm f} + \frac{z\mathcal{F}\eta}{\Omega} + \frac{1}{2E} (a^2 + 2)\sigma^2 \right) r^3 + 2\pi\gamma r^2 \tag{3.3}$$

The critical radius to form a thermodynamically stable, mechanically stressed electrodeposit, *i.e.*, for $d\Delta G_{\rm T}/dr = 0$, is:

$$r_{\rm c}^* = -\frac{2\gamma\Omega}{z\mathcal{F}\eta + \Delta G_{\rm f}\Omega + (a^2 + 2)\Omega\sigma^2/2E}$$
(3.4)

Dividing by $-2\gamma/\Delta G_{\rm f}$ on both sides of Equation 3.4, the dimensionless form of the critical thermodynamic radius is defined as:

$$\hat{r}_{\rm c}^* = \frac{1}{1 + \hat{\eta} - \hat{\sigma}^2} \tag{3.5}$$

Here, $\hat{r} = r/r_{\circ}$, where $r_{\circ} = -2\gamma/\Delta G_{\rm f}$ is the critical thermodynamic radius to form a stable nucleus in the absence of any overpotential and stress. For lithium, $r_{\circ} = 10.46 \,\mathrm{nm}$, in agreement with [100]. $\hat{\eta} = \eta/\eta_{\circ}$, where $\eta_{\circ} = \Delta G_{\rm f} \Omega/z \mathcal{F}$ is the characteristic or critical overpotential. For lithium, $\eta_{\circ} = -44 \,\mathrm{mV}$, in agreement with experiments [100, 121, 122]. $\hat{\sigma} = \sigma/\sigma_{\circ}$, where $\sigma_{\circ} = \pm \sqrt{\frac{-2E\Delta G_{\rm f}}{a^2+2}}$ is the critical thermodynamic stress. For lithium, $\sigma_{\circ} = \pm 732 \,\mathrm{MPa}$, in agreement with [123]. The electrodeposition dynamics for a stressed dendrite are formulated through a modified Butler-Volmer relation, in agreement with Newman and coworkers [113, 116,124]:

$$\Gamma = j_{\circ} \exp\left(-\frac{\Omega}{2RT} \overleftrightarrow{\sigma} \cdot \overleftrightarrow{\varepsilon}\right) \left(\exp\left[\frac{(1-\alpha)}{RT} \left(z\mathcal{F}\eta + \frac{\Omega}{2} \overleftrightarrow{\sigma} \cdot \overleftrightarrow{\varepsilon} + \frac{2\gamma\Omega}{r}\right)\right] - \exp\left[\frac{-\alpha}{RT} \left(z\mathcal{F}\eta + \frac{\Omega}{2} \overleftrightarrow{\sigma} \cdot \overleftrightarrow{\varepsilon} + \frac{2\gamma\Omega}{r}\right)\right]\right)$$
(3.6)

which reduces to

$$\Gamma = j_{\circ} \exp\left(-\frac{(a^2+2)\Omega\sigma^2}{2ERT}\right) \left(\exp\left[\frac{(1-\alpha)}{RT}\left(z\mathcal{F}\eta + \frac{(a^2+2)\Omega\sigma^2}{2E} + \frac{2\gamma\Omega}{r}\right)\right] - \exp\left[\frac{-\alpha}{RT}\left(z\mathcal{F}\eta + \frac{(a^2+2)\Omega\sigma^2}{2E} + \frac{2\gamma\Omega}{r}\right)\right]\right) \quad (3.7)$$

upon substituting Equation 3.2. Here, $j_{\circ} = i_{\circ}/z\mathcal{F}$ is the molar exchange current density and α is the transfer coefficient.

In the absence of stresses, Equation 3.7 reduces to the classical Butler-Volmer relation for a planar deposit, $\Gamma = j_{\circ} \left(\exp \left[(1 - \alpha) z \mathcal{F} \eta / RT \right] - \exp \left[-\alpha z \mathcal{F} \eta / RT \right] \right)$, in agreement with the existing scientific literature [103, 104].

For a symmetric electrode position reaction, *i.e.*, $\alpha = 1/2$, Equation 3.7 reduces to:

$$\Gamma = 2j_{\circ} \exp\left(-\frac{(a^2+2)\Omega\sigma^2}{2ERT}\right) \sinh\left[\frac{1}{2RT}\left(z\mathcal{F}\eta + \frac{(a^2+2)\Omega\sigma^2}{2E} + \frac{2\gamma\Omega}{r}\right)\right]$$
(3.8)

The elastic energy term contributes an additional energy barrier for electrodeposition, in agreement with [124, 125]. Thus, the state of stress, dictated by the stress anisotropy, a, will determine the extent of suppression of the Butler-Volmer electrodeposition kinetics. In addition, the elastic energy induces a shift in the critical overpotential required for electrodeposition, *i.e.*, for stressed dendrites, higher overpotentials are required to start electrodeposition, and in the absence of curvature or overpotential contributions, the stress will induce dendrite electrodissolution.

Plastic deformation of lithium, a well known phenomenon [101,114,115,118,119, 126–128], is described herein by a power law creep model [129,130], as denoted by $\dot{\varepsilon}_{\rm s} = A\sigma_{\rm s}^n$. The von Mises stress is $\sigma_{\rm s} = \left[\frac{1}{2}\left((\sigma - \sigma)^2 + (\sigma - a\sigma)^2 + (a\sigma - \sigma)^2\right)\right]^{1/2} = \|(a - 1)\sigma\|$. a = 1 indicates a pure hydrostatic state, and will suppress plastic deformation. $A = A_{\circ}D\mu^{1-n}b/kT$, where A_{\circ} is Dorn's constant, $D = D_{\circ}\exp\left(-Q/RT\right)$ is the lithium diffusion coefficient, and b is the Burgers vector [130]. Dorn's constant is a phenomenological parameter, and has been reported to scale with the power law creep exponent, n [130]. The diffusion coefficient, D, accounts for the microstructurally averaged contributions from point defects, dislocations, and grain boundaries to the stress induced transport of lithium [131]. Thus, the plastic deformation rate is given by $dr/dt = rA\sigma_{\rm s}^n$, and corresponds to the non-elastic vertical elongation of the dendrite as a result of an arbitrarily imposed state of stress.

For an isolated hemispherical nucleus, the growth rate is denoted as $dr/dt = \Gamma \Omega$, thus the combined vertical growth rate due to electrodeposition and plastic deformation is defined as:

$$\frac{dr}{dt} = 2j_{\circ}\Omega \exp\left(-\frac{(a^2+2)\Omega\sigma^2}{2ERT}\right) \sinh\left[\frac{1}{2RT}\left(z\mathcal{F}\eta + \frac{(a^2+2)\Omega\sigma^2}{2E} + \frac{2\gamma\Omega}{r}\right)\right] + \operatorname{sgn}\left(a\sigma\right)rA\left\|(a-1)\sigma\right\|^n$$
(3.9)

The function, sgn(x), is defined as sgn(x) = 1 for $x \ge 0$, and sgn(x) = -1 for x < 0. Used material parameters are listed in Table 3.1.

Symbol	Value	Units	Refs.
A_{\circ}	2.9×10^6	_	[127]
b	3.04×10^{-10}	m	[127]
D_{\circ}	10^{-5}	$\mathrm{m}^2\mathrm{s}^{-1}$	[127]
E	4.9	GPa	[128]
${\cal F}$	96485.33	$ m Cmol^{-1}$	_
i_{\circ}	30	${\rm A}{\rm m}^{-2}$	[103]
k	1.38×10^{-23}	$ m JK^{-1}$	2 5
n	6.4	_	[127]
Q	$5.61 imes 10^4$	$\rm Jmol^{-1}$	[127]
R	8.314	$\mathrm{JK^{-1}mol^{-1}}$	
T	300	Κ	—
z	1	_	_
α	0.5	_	[75]
$\Delta G_{\rm f}$	-3.28×10^8	$\mathrm{Jm^{-3}}$	[100]
Ω	1.3×10^{-5}	${ m m}^3{ m mol}^{-1}$	[132]
γ	1.716	$\mathrm{Jm^{-2}}$	[103]
μ	$\mu = \frac{E}{2(1+\nu)} = 3$	GPa	[127]
$\sigma_{ m y}$	0.56	MPa	[128]

Table 3.1.: Values of physical parameters used in calculations.

For small deviations from equilibrium, *i.e.*, $\left[\frac{1}{2RT}\left(z\mathcal{F}\eta + \frac{(a^2+2)\Omega\sigma^2}{2E} + \frac{2\gamma\Omega}{r}\right)\right] \ll$ 1, Equation 3.9 reduces to:

$$\frac{dr}{dt} = \frac{j_{\circ}\Omega}{RT} \left(1 - \frac{(a^2 + 2)\Omega\sigma^2}{2ERT} \right) \left(z\mathcal{F}\eta + \frac{(a^2 + 2)\Omega\sigma^2}{2E} + 2\Omega\gamma/r \right) + \operatorname{sgn}\left(a\sigma\right)rA \left\| (a-1)\sigma \right\|^n$$
(3.10)

Dividing both sides by $j_{\circ}\Omega^2 \Delta G_f/RT$, and using $\operatorname{sgn}(ab) = \operatorname{sgn}(a) \operatorname{sgn}(b)$, the resultant dimensionless growth rate is:

$$\frac{d\hat{r}}{d\hat{t}} = \left(1 - \Pi_1 \hat{\sigma}^2\right) \left[\hat{\eta} - \hat{\sigma}^2 - \frac{1}{\hat{r}}\right] + \operatorname{sgn}\left(-a\hat{\sigma}\right) \frac{\Pi_2}{\Pi_1^2} \hat{r}\hat{\sigma}^n \tag{3.11}$$

 $\hat{t} = t/t_{\circ}$, where $t_{\circ} = -2\gamma RT/j_{\circ}\Omega^2 \Delta G_{\rm f}^2$, denotes the *characteristic deposition time*, in agreement with Ely [104]. For dendrites whose size are in the vicinity of the critical size for thermodynamic stability, coarsening kinetics govern the growth of the electrodeposit. High interfacial energies and low Gibbs free energies of transformation will delay the onset of dendritic growth. For lithium, $t_{\circ} = 1.514$ s, in agreement with previous work [104].

The two resultant dimensionless numbers are defined as:

$$\Pi_1 = -\Omega \Delta G_{\rm f}/RT \tag{3.12}$$

$$\Pi_{2} = A\left(\frac{-2\gamma}{j_{\circ}RT}\right) \left[-2E\Delta G_{\rm f}\frac{(a-1)^{2}}{(a^{2}+2)}\right]^{n/2}$$
(3.13)

 Π_1 denotes the normalized electrodeposition driving force, and is the ratio of the chemical free energy of transformation to thermal energy. Here, lower temperatures will favor better suppression of dendritic growth by increasing the value of Π_1 . For lithium, at room temperature, $\Pi_1 = 1.709$. Π_2 is proportional to the ratio of electrodeposition time and the plastic deformation time, $\Pi_2 = \frac{t_0}{t_\sigma} \Pi_1^2 \hat{\sigma}^{-n}$, *i.e.*, $t_\sigma = \frac{\Pi_1^2}{\Pi_2} \hat{\sigma}^{-n} t_o$, and thus by substituting the expressions of Π_1 , Π_2 , and t_o , and simplifying, $t_\sigma = \frac{1}{A} \left[\frac{-(a^2+2)}{2E\Delta G_f(a-1)^2 \hat{\sigma}^2} \right]^{n/2} = 1/[A \parallel (a-1)\sigma \parallel^n]$. Thus, for a 5 MPa stress, $t_\sigma = 323t_o$, and for higher stresses (~ 50 MPa), $t_\sigma \sim 10^{-4}t_o$. See Table 3.2 for a list of characteristic parameters and dimensionless numbers for lithium.

Table 3.2.: Calculated characteristic parameters and dimensionless numbers of lithium.

Parameter	Calculated value	Experimental value	Refs.
r_{\circ}	10.46 nm	$10.46{\rm nm},71.42{\rm nm}$	[100, 101]
t_{\circ}	$1.514\mathrm{s}$	$3.84 \mathrm{\ s}$	[101]
t_{σ}	$9.61 \times 10^6 \mathrm{s} (0.1 \mathrm{MPa}),$	—	_
	$507 \mathrm{s} (5 \mathrm{MPa})$	$420 \mathrm{\ s}$	[48]
η_{\circ}	$-44.2\mathrm{mV}$	$-44.2\mathrm{mV}, -33\mathrm{mV}$	[100, 121]
σ_{\circ}	$\pm 732\mathrm{MPa}$	$> 3.45\mathrm{MPa}$	[123]
Π_1	1.709	—	—
Π_2	6.54×10^{11}	—	_

For large electrodeposits, $\hat{r} > 100 \ (\sim 1\mu\text{m})$, small Laplace pressures, and very small stresses, $\hat{\sigma} < 10^{-4} \ (\sim -0.1 \text{ MPa})$, Equation 3.11 reduces to $\frac{d\hat{r}}{d\hat{t}} \approx \hat{\eta}$, whose solution is $\hat{r}(\hat{t}) = \hat{r}_{\circ} + \hat{\eta}\hat{t}$, in agreement with the classical literature [103]. For small applied overpotentials, $\hat{\eta} < 0.01 \ (-0.44 \text{ mV})$, large electrodeposits, small Laplace pressures, and high stresses, $\hat{\sigma} > 5 \times 10^{-3} \ (\sim -5 \text{ MPa})$, Equation 3.11 reduces to $\frac{d\hat{r}}{d\hat{t}} \approx \frac{\Pi_2}{\Pi_1^2} \hat{r} \hat{\sigma}^n$, whose solution is $\hat{r}(\hat{t}) = \hat{r}_{\circ} \exp(\frac{\Pi_2}{\Pi_1^2} \hat{\sigma}^n \hat{t})$. In the absence of stress, Equation 3.11 reduces to $d\hat{r}/d\hat{t} = \hat{\eta} - 1/\hat{r}$, which for the case $d\hat{r}/d\hat{t} = 0$, results on $\hat{r}_{k,\sigma=0} = 1/\hat{\eta}$, *i.e.*, the kinetic growth radius, in agreement with Ely [104].

In this context, the *tip-controlled growth regime* corresponds to the combination of equilibrium and kinetic parameters where the contribution from the growth rate from the applied overpotential, concentrated at the dendrite tip, is at least ten times greater than the growth rate due to plastic flow. Similarly, *base-controlled growth regime* is identified herein whenever the time-dependent morphological changes induced by the dendrite's plastic deformation is at least ten times higher than contributions from electrodeposition. The *mixed growth regime* is thus defined when *tip-controlled growth* and *base-controlled growth* contributions are both active. The growth rate is defined to reach a minimum as a function of the applied stress when $\frac{\partial}{\partial \hat{\sigma}} \left(\frac{\partial \hat{r}}{\partial t}\right) = 0.$

3.3 Results and Discussion

Figure 3.2 summarizes five regimes of growth behavior as a function of electrodeposit size and local overpotential, for a fixed stress tensor. The blue curve denotes the limit of thermodynamic stability, as defined in Equation 3.5. Lithium dendrites that are larger than the critical thermodynamic size are energetically favorable (above the blue curve). Similarly, lithium embryos in the *thermodynamic suppression regime* (below the blue curve) are energetically unfavorable, and will dissolve back into the electrolyte. Thus, dendritic growth will safely be avoided by choosing overpotentials and sizes that are in the *thermodynamic suppression regime*, as reported in earlier work [104], and experimentally verified by Cui [100].



Figure 3.2.: Predicted lithium electrodeposition dynamics regimes as a function of normalized electrodeposit size and overpotential, for two selected values of stress magnitude: (a) $-\sigma = 0.1 \text{ MPa} (\hat{\sigma} = 1.36 \times 10^{-4})$, and (b) $-\sigma = 5 \text{ MPa} (\hat{\sigma} = 6.8 \times 10^{-3})$. Five regimes of behavior are identified: below the blue curve is the *thermodynamic* suppression regime, where an electrodeposit is thermodynamically unstable; between the blue and the black curve is the dendrite *incubation regime*, where a population of metastable nuclei grow as a result of the local dendrite-dendrite electrochemical interactions, in agreement with previous work [104]. Above the black curve are three growth regimes: below the green curve and above the black curve you will find the tip-controlled growth regime, where growth is dominated by electrodeposition; above the black curve and to the left of red curve you will find the base-controlled growth regime, where growth is dominated by irreversible mechanical, *i.e.*, plastic, deformation; above the black line, and between the red and the green lines you will find the mixed growth regime, where both electrodeposition and plastic deformation have nontrivial contributions. In addition, the dashed gray line indicates a local minimum in the growth rate as a result of the competition of the electrochemical, chemomechanical, and surface energy contributions. The solid gray line highlights the kinetic growth line in the absence of applied stresses, as reported in the scientific literature [104]. • corresponds to experimental data as reported by Brissot and coworkers [96], Δ to experiments as performed by Crowther and West [48], \triangleleft to base-controlled growth experiments and \triangleleft to *tip-controlled growth* experiments as reported by Dolle *et al.* [97], \triangleright to base-controlled growth data and \triangleright to tip-controlled growth data as reported by Orsini and coworkers [98], \diamond to electrodeposit growth experiments as reported by Cui et al. [100], \Box to base-controlled growth data and \blacksquare to tip-controlled growth data as reported by Li and coworkers [101].

The *incubation regime*, between the blue and the black curves, is where thermodynamically stable electrodeposits grow through coarsening, following incubation kinetics [100, 104]. The black line embodies the kinetic limit, where thermally stable isolated nuclei will grow. Three additional growth regimes are identified: the *tip-controlled growth regime*, to the right of the green line, where electrodeposits subjected to large overpotentials grow into whisker-like structures; the *base-controlled growth regime*, to the left of the red line, where hemispherical electrodeposits subjected to small overpotentials deform into elongated structures, in agreement with the numerical work by Arakawa and coworkers [133]; and the *mixed growth regime*, between the *tip-controlled* and the *base-controlled growth regimes*, where lithium kinetics is governed by the contributions of plastic deformation and surface energy, dendrite growth is possible, both through the base and the tip, in agreement with Steiger and coworkers [134, 135].

Results shows no appreciable *base-controlled* growth for $-\sigma < 0.1$ MPa, thus this stress value corresponds to the worst case scenario to observe *tip-control* growth. Similarly, $-\sigma \sim 5$ MPa was the stress value that delivered the best match between the experimental results and the performed calculations. In addition, if the stress on the electrodeposit increases, e.g., from $-\sigma = 0.1$ to 5 MPa (see Figures 3.2(a) and (b)), the extent of the *incubation regime* shrinks, while the extent of the *base-controlled growth* regime expands. For dendrities in this regime, the stress that accumulates at the base induces an outwardly directed stress that pushes the dendrite towards the counter electrode. A direct comparison against electrodeposit size as a function of overpotential experimental data [48, 96–98, 100, 101] (see example micrographs in Figure 3.1), shows that for a stress, $-\sigma = 0.1$ MPa, lower than the yield stress, dendrites grow according to the *tip-controlled growth regime* (see Figure 3.2(a)). Electrodeposits at the onset of *tip-controlled growth regime* lie just above the black line, in agreement with experiments performed by Cui and coworkers [100]. Dendritic or whisker like growth, in the *tip-controlled growth regime*, at high current densities are in agreement with experiments by Orsini et al. (2.2 mA/cm^2) [98], Brissot et al. (1.3 mA/cm^2) [96], and Dolle et al. $(0.5 \,\mathrm{mA/cm^2})$ [97]. The present analysis further asserts that early stages of lithium growth are in agreement with experimental observations of *tip-controlled*

growth by Crowther and West [48]. Potentiostatic lithium electrodeposition experiments under high applied voltages (-4.5 V) as reported by Li and coworkers [101] are also captured in the *tip-controlled growth regime*. For a stress above the yield point, e.g., $-\sigma = 5$ MPa, a comparison against experiments [48, 96, 97, 100, 101], shows that, in general, dendrite growth occurs as a combination of electrodeposition and plasticity-induced growth, *i.e.*, in the *mixed growth regime*. Only a subset of experiments by Orsini and coworkers [98] at a low current density $(0.45 \,\mathrm{mA/cm^2})$ are found to lie in the predicted *base-controlled growth regime*. Calculations further show that for stresses much larger than the yield stress, the black line shifts downward. For example, at $-\sigma = 14$ MPa, the kinetic (black) and thermodynamic (blue) line overlap, thus completely altering the coarsening dynamics. Thus, the dendrite incubation mechanism changes from electrochemically-controlled to plasticity-controlled. For $-\sigma > 14$ MPa, the kinetic line shifts below the thermodynamic line; therefore, the thermodynamic stability of a lithium nucleus becomes dominated by elastic energy, and becomes kinetically dominated by plastic flow. For these conditions, large hydrostatic elastic energy contributions will fully suppress the dendrite nucleation and growth process, in agreement with experiments [119, 120, 136]. However, large deviatoric stresses will enable the plastic flow along directions specified by the principal directions of the local stress tensor. Overall, the growth direction of the electrodeposit will be determined by the combined contributions of the local electrochemical gradients (*tip-controlled*), and the principal directions (eigenvectors) of the local stress tensor (base-controlled). The growth direction will be additionally influenced by the formation of kinks in the electrodeposit [101], or by convective flow in the liquid electrolyte [48].

Results show that a minimum in the growth rate (gray dashed line in Figure 3.2) exists just below the yield stress, $-\sigma < \sigma_y = 0.56$ MPa. Physically, as the stress increases in a lithium deposit, the energy barrier for electrodeposition increases exponentially, thus suppressing growth; however, as non-hydrostatic stress accumulates on the dendrite, the nuclei will plastically yield, favoring growth. The contribution

of plastic deformation to *base-controlled growth* is proportional to the dimensionless number, Π_2 , which in turn is a direct function of the anisotropy of the stress tensor, see Figure 3.3.



Figure 3.3.: Effect of the stress anisotropy factor, a, on the plastic deformation of the electrodeposit. The dimensionless number, Π_2 , controls plastic deformation and the rate at which plastic flow will dominate the microstructural kinetics of the dendrite. As experimentally expected, in the absence of any shear stress, plastic flow will be completely suppressed for a = 1 *i.e.*, $\sigma_s = ||(a-1)\sigma|| = 0$, [119, 120, 136]. The case $a \leq 0$ physically corresponds to the case where a dendrite is vertically extruded away from the deposition substrate. a = -2, *i.e.*, $\sigma_h = (a+2)\sigma = 0$ corresponds to the worst case scenario, where *base-controlled growth* is maximized.

Calculations show that for $\sigma < 0$, if a < 0, dendrites will be promoted to grow towards the counter electrode in a manner analogous to toothpaste being squeezed out of its tube. This effect is maximal for a = -2, which favors vertical *base-controlled* growth. Deviations from this maximum value will favor dendrite growth at an angle determined by the principal directions of the stress tensor and qualitatively in agreement with experimental observations that detail the change of dendrite growth direction [48,97,101]. Here, the time evolution of the local anisotropy of the stress tensor (a = a(t) < 0), will lead to the formation of nanostructures that curl on themselves [97], and eventually slow down or change growth mechanism [48,94,96], as a result of stress relaxation and dendrite-dendrite electrochemical and chemomechanical interactions. In contrast, if a > 0, the dendrite will be pushed downwards, kinetically canceling *base-controlled growth*, in the limit of a = 1. Values much greater than unity will plastically smear the nucleus on the plating substrate.

Overall, because the *mixed growth regime* defines a region where both, electrodeposition and plasticity, contribute to dendrite growth in comparable amounts, the development of electrochemical or mechanical heterogeneities can locally induce the development of specific dendrite morphologies not accounted for in the current theory. For example, Steiger *et al.*, [134,135], experimentally observed lithium growth from the tip, the base, and between kinks, and as a result a whole new set of morophologies was identified. In general, the strength of each of the contributions to growth will locally impact some regions, and can easily leave other regions completely isolated [134, 135].

Figure 3.4 shows the time-dependent growth behavior for zero or low stresses, $-\sigma = 0.1$ MPa for the case a = -2, the worst case scenario (*i.e.*, highest lithium growth rate) for selected values of initial dendrite sizes and applied overpotentials.



Figure 3.4.: Normalized electrodeposit size as a function of time at a fixed stress, $-\sigma = 0.1 \text{ MPa} \ (\hat{\sigma} = 1.36 \times 10^{-4})$, for three selected normalized overpotentials: (a) $\hat{\eta} = 0.01 \ (-0.442 \text{ mV})$, (b) $\hat{\eta} = 0.5 \ (-22.1 \text{ mV})$, and (c) $\hat{\eta} = 50 \ (-2210 \text{ mV})$. The black line denotes an initial electrodeposit radius equal to the critical kinetic radius, \hat{r}_k^* , and hence shows no growth. The green curve above the black line denotes an initial radius, $\hat{r}_o = 2\hat{r}_k^*$, and below the black line denotes $\hat{r}_o = \hat{r}_k^*/2$. Similarly, the blue curve above the black line corresponds to $4\hat{r}_k^*$, and below the black line corresponds to $\hat{r}_k^*/4$; the red curve above the black line corresponds to $8\hat{r}_k^*$ and below the black line is a result of tip-controlled growth. \bullet corresponds to experimental data as reported by [96]. Similarly, \triangle corresponds to [48], \blacktriangleleft corresponds to [97], \blacktriangleright correspond to [98], \Diamond corresponds to [100], and \square corresponds to [101].

Results demonstrate that in the limit of small overpotentials, the forming nucleus must spend 10 to 10^5 times the dendrite characteristic deposition time, $t_o = 1.514$ s, in order to appreciably grow, and is thus dominated by coarsening kinetics [104]. However, those dendrites whose size is smaller than the kinetic critical radius, $r < \hat{r}_k$, will shrink and dissolve back into the electrolyte [101, 104, 137]. In addition, calculations show that applied overpotentials that are comparable to or higher than η_o are necessary to experimentally observe time-dependent linear growth in time scales that are comparable to t_o , in agreement with experiments [48, 121, 137]. Finally, for large overpotentials, stress-free dendrites will develop quickly, in agreement with [6], and will deviate from the spherical approximation after a few instants, [105, 138].

Figure 3.5 shows the time-dependent dendrite size for stress values that are comparable or larger than the yield stress, e.g., $-\sigma = 5$ MPa. For small overpotentials (see Figure 3.5(a)), plasticity dominates the morphological evolution of the
electrodeposit, as highlighted by its exponential growth for those nuclei that are larger than the critical kinetic radius. The structure is dominated by *base-controlled growth* after a characteristic time, $t_{\sigma} = 323t_{\circ}$. Note that the larger the initial dendrite size the sooner plastic deformation will become evident, in agreement with *base-controlled* growth experiments as reported by Orsini and coworkers [98].

For those dendrites that are comparable in size with the kinetic radius, if the overpotential is comparable in magnitude to the critical value (see Figure 3.5(b)), the growth rate will be dominated by surface energy contributions. As dendrites become larger, growth shifts to be dominated by the *base-controlled* mechanism after the nucleus has evolved for $t_{\sigma} \sim 3000$ s. Figure 3.5(b) also demonstrates that dendrites will undergo transitions in growth modes as they shift into and out of the *mixed growth* regime, and accelerate its growth, even for cases where stress and overpotential remain constant, in qualitative agreement with Crowther and West [48] and Brissot and coworkers [95]. Figure 3.5(c) further demonstrates that individual dendrites will transition between multiple growth mechanisms. Thus, dendrites start its growth dominated by the *tip-controlled* mechanism, but are slowed down by surface energy forces. As they become bigger in size, dendrites grow in accordance to the *tip-controlled* growth regime, but will ultimately grow through the base-controlled mechanism, as the electrodeposit overcomes the characteristic plasticity time, t_{σ} . Such transitions in growth regimes explain the switch from *tip-controlled* to *base-controlled*, at the same applied current density, as observed in the experiments reported by Crowther and West [48].



Figure 3.5.: Normalized electrodeposit size as a function of time at a fixed stress, $-\sigma = 5 \text{ MPa}$ ($\hat{\sigma} = 6.8 \times 10^{-3}$) for three selected overpotentials: (a) $\hat{\eta} = 0.01$ (-0.442 mV), (b) $\hat{\eta} = 0.5$ (-22.1 mV), and (c) $\hat{\eta} = 50$ (-2210 mV). The black line denotes an initial electrodeposit radius equal to the critical kinetic radius, \hat{r}_k^* . The green curve above the black line denotes a normalized initial radius, $\hat{r}_{\circ} = 2r_k^*$, and below the black line denotes $\hat{r}_{\circ} = \hat{r}_k^*/2$. Similarly, the blue curve above the black line corresponds to $4\hat{r}_k^*$, and below the black line corresponds to $\hat{r}_k^*/4$; the red curve above the black line corresponds to $8\hat{r}_k^*$, and below the black line corresponds to $\hat{r}_k^*/8$. Exponential behavior indicates *base-controlled growth*, as shown in (a), *i.e.*, for high stresses and low overpotentials. Linear behavior is a result of *tip-controlled growth*, as shown in (c) for very high overpotentials. Deviations from linearity indicate mixed contributions from both tip and base, as shown in (b). \bullet corresponds to experimental data as reported by [96], Similarly, \triangle corresponds to [48], \blacktriangleleft corresponds to [97], \triangleright corresponds to [98], \diamondsuit corresponds to [100], and \Box corresponds to [101].

Figure 3.6 summarizes the five regimes of growth as a function of local overpotential and stress and depicts the shift in growth regimes as the electrodeposit size increases. In agreement with Figure 3.2, below the blue curve you will find the *thermodynamic suppression regime* where an hemispherical electrodeposit is thermodynamically unstable due to surface energy, low overpotentials, or large stresses; between the blue and the black curve you will find the *incubation regime*, where growth is thermodynamically favored, but dominated by local dendrite-dendrite electrochemical and chemomechanical interactions. Above the black and the blue curves you will find three growth regimes: i) to the right of the red curve you will find the *base-controlled growth regime*, ii) to the left of the green curve you will find the *tip-controlled growth regime*, and iii) between the red and the green curves you will find the *mixed growth regime*. Isolated hemispherical nuclei that are comparable in size to the kinetic critical radius (see Figure 3.6(a)), will require overpotentials that are greater than the critical overpotential to grow through the *tip-controlled mechanism*, and on the order of a tenth of the yield stress to grow through the *base-controlled mechanism*. For low overpotentials $(10^{-5} < \hat{\eta} < 0.01, i.e., 4.4 \times 10^{-4} \text{ mV} < -\eta < 0.44 \text{ mV})$, high elastic energies corresponding to large stresses $(10^{-3} < \hat{\sigma} < 0.1, i.e., 0.73 \text{ MPa} < -\sigma < 73 \text{ MPa})$, will fully suppress lithium growth (right of the black line and below the blue line in Figure 3.6(a)). For interacting populations of lithium nuclei, those dendrites below the black line and above the blue line will be dominated by electrochemical driving forces and the Gibbs-Thomson effect that lead to electrochemically-induced coarsening kinetics [104]; however, calculations demonstrate that for large stresses, plasticity will dominate the coarsening process, when the kinetic line shifts below the thermodynamic stability line.

Dendrites that have reached much larger sizes (e.g., see Figure 3.6(b)), will be dominated by the *base-controlled growth mechanism* across a much wider range of overpotentials and applied stresses. Also, for electrodeposits whose radius of curvature contributions are negligible compared to the applied overpotential and mechanical stresses (see Figure 3.6(c)), such as those experimentally observed in lithium-only anodes, dendrite growth will be dominated by *base-controlled growth*, thus suggesting that the growth of flat layers will be morphologically unstable. In this context, the present analysis suggests that a great deal of electrochemical and mechanical constraints will be necessary to suppress dendrite growth in practical designs (see supplemental information for other dendrite sizes).



Figure 3.6.: Regimes of lithium electrodeposition dynamics as a function of normalized overpotential and stress, for three selected values of electrodeposit sizes: (a) $\hat{r} = 1 (0.01 \ \mu \text{m}), (b) \ \hat{r} = 100 (1.05 \ \mu \text{m}), \text{ and } (c) \ \hat{r} = 10^4 (0.1 \ \text{mm}).$ Below the blue curve you will find the *thermodynamic suppression regime*, where dendrites are thermodynamically unstable; above the blue curve and below the black curve you will find the *incubation regime*, to the left of the green curve and above the black curve you will find the *tip-controlled growth regime*, where growth is dominated by electrodeposition; above the black curve and below the red curve you will find the base-controlled growth regime, where irreversible mechanical deformation, *i.e.*, plastic deformation of lithium dominates the growth dynamics; and finally, between the red and the green curves you will find the *mixed growth regime*, where both electrodeposition and plastic deformation have non-trivial contributions to dendrite growth. To the right of the black line and below the blue line, low overpotentials and very large stresses on relatively small electrodeposits lead to thermodynamic dendrite suppression (see inset (a)). The dashed gray line indicates a minimum in the total growth rate as a result of the contributions from electrochemical, chemomechanical and surface energy contributions. Base-controlled growth is dominant for larger electrodeposits (see inset (c)) due to higher contribution from plastic deformation. \bullet corresponds to experimental data as reported by Brissot and coworkers [96], Δ to experiments as performed by Crowther and West [48], \triangleleft to base-controlled growth experiments and ◀ to tip-controlled growth experiments as reported by Dolle et al. [97], \triangleright to basecontrolled growth data and \triangleright to tip-controlled growth data as reported by Orsini and coworkers [98], \Diamond to electrodeposit growth experiments as reported by Cui et al. [100], \Box to base-controlled growth data and \blacksquare to tip-controlled growth data as reported by Li and coworkers [101].

Figure 3.7 shows the time-dependent growth behavior for a = -2 and very small electrodeposits, as compared to the characteristic electrodeposit size, $\hat{r}_{\circ} = 1$ (0.01 µm). For large overpotentials, a hundred times the critical value (see Figure 3.7(a)) and stresses up to yield point, there is a higher contribution from the tip in the early stages of growth, as depicted by the linearity of the gray and green curves. At later stages, growth is either in the *mixed growth regime*, or entirely in the base-controlled growth regime. For overpotentials close to the critical value (see Figure 3.7(b)), the dendrite grows from the tip for a short amount of time, and starts to grow from the base after $t \sim t_{\sigma}$. For overpotentials ten times smaller than the critical value (see Figure 3.7(c)), small lithium electrodeposits ($\hat{r} < \hat{r}_k$) dissolve back to the electrolyte. However, calculations predict that for very large shear stresses, $-\sigma \sim 50$ MPa (red curve in Figure 3.7(c)), lithium electrodeposits will deform and will push the electrodeposit towards the counter electrode, even in the absence of overpotentials. Predicted growth behavior is in agreement with early stage lithium nucleation and growth experiments as performed by Cui and coworkers [100].



Figure 3.7.: Normalized electrodeposit size as a function of time for a fixed normalized initial radius, $\hat{r}_{\circ} = 1 \ (0.01 \ \mu\text{m})$ at selected locations in Figure 3.6(a). Inset (a) shows $\hat{\eta} = 100 \ (-4420 \ \text{mV})$, (b) $\hat{\eta} = 2 \ (-88.4 \ \text{mV})$, and (c) $\hat{\eta} = 0.1 \ (-4.42 \ \text{mV})$. Gray curve corresponds to normalized stress, $\hat{\sigma} = 5 \times 10^{-4} \ (-0.366 \ \text{MPa})$, green curve corresponds to $\hat{\sigma} = 10^{-3} \ (-0.732 \ \text{MPa})$, blue curve corresponds to $\hat{\sigma} = 5 \times 10^{-3} \ (-3.66 \ \text{MPa})$, and red curve corresponds to $\hat{\sigma} = 0.05 \ (-36.6 \ \text{MPa})$. Linear behavior indicates *tip-controlled growth* (gray curves in insets (a) and (b)). Mixed growth regime is described by the curves which are linear initially, but deviate from linearity at later stages (green and blue curves in insets (a) and (b)). Base-controlled growth is characterized by exponential nature of $\hat{r}(\hat{t})$, as depicted by the red curve in all three insets. Thus, in the absence or under very low overpotentials (red curve in inset (c)), lithium electrodeposits are expected to grow due to plastic flow. However, in the absence or under very low stresses and overpotentials, *i.e.*, electrodeposits in the suppression regime will shrink, as depicted by the blue curve in inset (c). \diamond corresponds to experimental data as reported by Cui and coworkers [100].

Figure 3.8 demonstrates the time-dependent growth behavior for an initial electrodeposit size of ~ 1 μ m, *i.e.*, a hundred times the characteristic electrodeposit size. Electrodeposits under large overpotentials, at about ten times the critical value (see Figure 3.8(a)) and low stresses ($-\sigma < \sigma_y$) grow from the tip for a very long time. For electrodeposits under moderate overpotentials on the order of the critical value (see Figure 3.8(b)), there is a very short time where growth is either in the *tip-controlled* or in the *mixed growth regime*, and switches to *base-controlled growth regime*, in agreement with the work from Li and coworkers [101], and from Crowther and West [48]. For smaller overpotentials, *e.g.*, on the order of 1/100th of the critical overpotential (see Figure 3.8(c)), moderately sized electrodeposits will undergo *base-controlled growth* under moderate to high stresses (5 to 50 MPa).



Figure 3.8.: Normalized electrodeposit size as a function of time for a fixed initial normalized radius, $\hat{r}_{\circ} = 100 (1.04 \ \mu\text{m})$ at selected locations in Figure 3.6(b). Inset (a) shows $\hat{\eta} = 10 (-442 \text{ mV})$, (b) $\hat{\eta} = 0.2 (-8.84 \text{ mV})$, and (c) $\hat{\eta} = 0.002 (-0.0088 \text{ mV})$. Gray curve corresponds to normalized stress, $\hat{\sigma} = 5 \times 10^{-4} (-0.366 \text{ MPa})$, green curve corresponds to $\hat{\sigma} = 10^{-3} (-0.732 \text{ MPa})$, blue curve corresponds to $\hat{\sigma} = 5 \times 10^{-3} (-3.66 \text{ MPa})$, and red curve corresponds to $\hat{\sigma} = 0.05 (-36.6 \text{ MPa})$. Linear behavior signals *tip-controlled growth* (gray curves in insets (a) and (b)). Blue curves in insets (a), (b) and (c), and green curves in insets (a) and (b) demonstrate mixed growth regime because the curves are initially linear, but deviate from linearity at later times. Exponential behavior demonstrates *base-controlled growth*, as depicted by the red curves in all three insets and blue curve in inset (c). Results show that larger initial electrodeposit size favors *base-controlled growth*, even in the absence of an applied overpotential. \triangle represents *base-controlled growth* data as reported by Crowther and West [48], and \Box corresponds to *base-controlled growth* data as reported by Li and coworkers [101].

Figure 3.9 shows the time-dependent growth behavior for very large initial electrodeposit sizes, about 10^4 times the kinetic characteristic size. For high overpotentials, on the order of a hundred times the critical overpotential value (see Figure 3.9(a)) and under low stresses ($-\sigma \sim 0.1$ MPa), growth is *tip-controlled* for a very long time. For stresses at the yield point ($-\sigma \sim 0.56$ MPa), growth is *base-controlled*. For moderate overpotentials, on the order of the critical value (see Figure 3.9(b)), and moderate stresses, the *tip-controlled* contribution is negligible, in agreement with experiments from Brissot and coworkers [96]. For very small overpotentials, on the order of 10^{-5} times the critical overpotential (see Figure 3.9(c)), and moderate to high stresses ($-\sigma > \sigma_y$), growth is entirely *base-controlled*. However, electrodeposits under smaller stresses ($-\sigma \sim 0.1$ MPa) will shrink back to the electrolyte (see gray curve).



Figure 3.9.: Normalized electrodeposit size as a function of time for a fixed initial radius, $\hat{r}_{\circ} = 10^4$ at selected locations in Figure 3.6(c). Inset (a) shows $\hat{\eta} = 10$ (-442 mV), (b) $\hat{\eta} = 0.1$ (-4.42 mV), and (c) $\hat{\eta} = 10^{-5}$ (-4.4 × 10⁻⁴ mV). Gray curve corresponds to normalized stress, $\hat{\sigma} = 5 \times 10^{-4}$ (-0.366 MPa), green curve corresponds to $\hat{\sigma} = 10^{-3}$ (-0.732 MPa), blue curve corresponds to $\hat{\sigma} = 5 \times 10^{-3}$ (-3.66 MPa), and red curve corresponds to $\hat{\sigma} = 0.05$ (-36.6 MPa). Linear behavior signals *tip-controlled growth* (gray curves in insets (a) and (b)). Non-linear indicate mixed growth regime (green and blue curves in insets (a) and (b)). Exponential growth signals *base-controlled growth* (red curve in all three insets). Results demonstrate that for larger electrodeposits, growth changes from *tip-controlled* to *base-controlled* with decreasing overpotentials. • corresponds to *base-controlled* data as reported by Brissot and coworkers [96].

Figure 3.10 describes the growth regimes as a function of electrodeposit size and stress, for a fixed overpotential. Below the blue curve you will find the *thermodynamic* suppression regime, where dendrites are thermodynamically unstable. Above the blue line and below the black line you will find the *incubation regime*. Above the blue and the black lines are three growth regimes: i) to the left of the green curve and above the black curve you will find the *tip-controlled growth regime*, where growth is dominated by electrodeposition, *ii*) above the blue and the black curves and to the right of the red curve you will find the *base-controlled growth regime*, where irreversible mechanical deformation, *i.e.*, plastic deformation of lithium, dominates the growth dynamics; and finally *iii*), between the red and the green curves you will find the *mixed growth regime*, where both electrodeposition and plastic deformation have comparable contributions to dendrite growth. To the right of the black line and below the blue line, very large stresses will mechanically suppress dendritic growth. The dashed gray line indicates a minimum in the total growth rate as a result of the contributions from electrochemical, chemomechanical and surface energy contributions. Calculations demonstrate that for small overpotentials (see Figure 3.10(a)), the *tip-controlled mechanism* dominates the microstructural evolution of dendrites, only in a very narrow range of thermodynamic parameters that includes very small and compressive stresses, and very large sizes. For larger stresses $-\sigma > \sigma_y$, calculations predict that *base-controlled mode* growth dominates the kinetics, in agreement with experiments under low current densities $(0.45 \,\mathrm{mA/cm^2})$ as reported by Orsini and coworkers [98].



Figure 3.10.: Regimes of lithium growth dynamics as a function of normalized electrodeposit size and stress, for selected overpotentials: (a) $\hat{\eta} = 0.01 \ (-0.442 \ \text{mV})$, (b) $\hat{\eta} = 0.5 \ (-22.1 \text{ mV}), \text{ and (c)} \ \hat{\eta} = 50 \ (-2210 \text{ mV}).$ The thermodynamic suppression *regime*, below the blue curve, is where no growth is expected: the *incubation regime*. above the blue curve and below the black curve where metastable nuclei grow as a result of local dendrite-dendrite electrochemical and chemomechanical interactions; to the left of the green curve and above the black curve, you will find the *tip-controlled growth regime*, where growth is dominated by electrodeposition; above the black curve and below the red curve you will find the *base-controlled growth regime*, where growth is dominated by plastic deformation of lithium; and finally between the red and the green curve you will find the *mixed growth regime*, where both electrodeposition and plastic deformation compete to define the growth of the electrodeposit. To the right of the black line and below the blue line is where large stresses mechanically suppress dendritic growth. The dashed gray line indicates a minimum in the growth rate. The analysis demonstrates that high overpotentials delay the onset of *base-controlled growth.* \bullet corresponds to experimental data as reported by Brissot and coworkers [96], \triangle to experiments as performed by Crowther and West [48], \triangleleft to base-controlled growth experiments and \triangleleft to tip-controlled growth experiments as reported by Dolle et al. [97], \triangleright to base-controlled growth data and \triangleright to tip-controlled growth data as reported by Orsini and coworkers [98], \Diamond to experiments as reported by Cui et al. [100], \Box to base-controlled growth data, and \blacksquare to tip-controlled growth data as reported by Li and coworkers [101].

For overpotentials that are comparable to the critical value (see Figure 3.10(b)), the edge of the *base-controlled growth regime* shifts by an order of magnitude. Thus, dendrites that are subjected to mechanical stresses smaller than the yield point will grow through the *tip-controlled mechanism* and will eventually shift to the *mixed* growth regime. Experimentally reported results [48,95,97,101] are found to lie within the *mixed growth regime*, except those by Orsini *et al.* [98]. Finally, for very large overpotentials (see Figure 3.10(c)), calculations show that the electrodeposit will grow mostly by adding lithium at the tip, in agreement with experiments from Li and coworkers [101]. Overall, these calculations demonstrate that as the overpotential increases, dendrites are more likely to transition from *tip-controlled* to *base-controlled* growth regimes, and to spend a significant window of time in the mixed growth regime.

Figure 3.11(a) highlights the effect of stress on the time-dependent growth rate, for fixed initial size and applied overpotential. Note that for small stresses, large dendrites require to overcome a long characteristic deposition time, t_{\circ} . As the stress increases, the characteristic deposition time is dominated by power law creep. Dendrites that start at a size one hundred times smaller, display the same characteristic deposition time when subjected to the same stresses (see Figure 3.11(b)). Finally, for dendrites that are marginally above the critical kinetic radius, the effect of stresses become much more pronounced as they transition directly from *tip-controlled* to *basecontrolled growth*, without displaying appreciable *mixed growth regime* behavior (see Figure 3.11(c)).



Figure 3.11.: Normalized electrodeposit size as a function of time for a fixed overpotential, $\hat{\eta} = 0.01 \ (-0.442 \text{ mV})$ at selected locations in Figure 3.10(a). Inset (a) shows $\hat{r}_{\circ} = 10^5 \ (1000 \ \mu\text{m})$, (b) $\hat{r}_{\circ} = 10^3 \ (10 \ \mu\text{m})$, and (c) $\hat{r}_{\circ} = 110 \ (1.1 \ \mu\text{m})$. Gray curve corresponds to normalized stress, $\hat{\sigma} = 5 \times 10^{-4} \ (-0.366 \text{ MPa})$, green curve corresponds to $\hat{\sigma} = 10^{-3} \ (-0.732 \text{ MPa})$, blue curve corresponds to $\hat{\sigma} = 5 \times 10^{-3} \ (-3.66 \text{ MPa})$, and red curve corresponds to $\hat{\sigma} = 0.05 \ (-36.6 \text{ MPa})$. Gray curves lie within the *tip-controlled growth* regime. Calculations demonstrate that for small overpotentials, as the applied stresses increase, the electrodeposit will transition from *tip-controlled* growth to base-controlled growth (e.g., green curve, inset (c)). \triangleright corresponds to basecontrolled growth data as reported by Orsini and coworkers [98].

Figure 3.12 demonstrates the growth behavior for fixed initial dendrite sizes and constant overpotentials that are comparable to the critical value, $\hat{\eta} = 0.5$ (-22.1 mV). For large initial dendrite sizes, growth is either *tip-controlled* or *mixed* (see Figure 3.12(a)). For dendrites that start one hundred times smaller, display the same characteristic deposition time when subjected to large stresses, but display a transition from *tip-controlled* to *base-controlled* growth for small stress values (see Figure 3.12(b)). Finally, dendrites whose initial size is on the same order of magnitude as the critical kinetic size will prefer to shrink in the absence of local electrochemical interactions, unless their growth rate is solely promoted by the *base-controlled growth mechanism* (see Figure 3.12(c)). Calculations show that under the application of very large stresses ($-\sigma \sim 36$ MPa), even small electrodeposits will grow through the *base-controlled mechanism*, in the absence of any charging overpotential.



Figure 3.12.: Normalized electrodeposit size as a function of time for a fixed overpotential, $\hat{\eta} = 0.5 \ (-22.1 \text{ mV})$ at selected locations in Figure 3.10(b). Inset (a) shows $\hat{r}_{\circ} = 10^4 \ (100 \ \mu\text{m})$, (b) $\hat{r}_{\circ} = 500 \ (5 \ \mu\text{m})$, and (c) $\hat{r}_{\circ} = 0.8 \ (1 \ \mu\text{m})$. Gray curve corresponds to normalized stress, $\hat{\sigma} = 5 \times 10^{-4} \ (-0.366 \text{ MPa})$, green curve corresponds to $\hat{\sigma} = 10^{-3} \ (-0.732 \text{ MPa})$, blue curve corresponds to $\hat{\sigma} = 5 \times 10^{-3} \ (-3.66 \text{ MPa})$, and red curve corresponds to $\hat{\sigma} = 0.05 \ (-36.6 \text{ MPa})$. Analytical calculations demonstrate that for low overpotentials and intermediate or low stresses, dendrites will grow through the *tip-controlled mechanism*, and will take longer to transition to the *base-controlled growth mechanism*. Very small dendrites will only grow through the application of large stresses.

Figure 3.13 shows the growth behavior for fixed initial dendrite sizes and constant applied overpotentials that are fifty times the critical kinetic value. For very large initial dendrite sizes, the growth of the electrodeposit has contributions from both *tip* and *base-controlled growth mechanisms*, thus the system evolves in the *mixed* growth regime for very long periods of time (see Figure 3.13(a)). For dendrites that are only 2000 times the critical kinetic radius, the effect of electrodeposition becomes more evident, and the lithium nuclei take a long time to transition from *tip-controlled* to *base-controlled growth* (see Figure 3.13(b)). Finally, for dendrites that are on the order of ten times the kinetic radius, calculations show that a very large amount of stress, or a large characteristic plasticity time is necessary to bring the dendrite into the *base-controlled growth* regime.



Figure 3.13.: Normalized electrodeposit size as a function of time for a fixed overpotential, $\hat{\eta} = 50 \ (-2210 \text{ mV})$ at selected locations in Figure 3.10(c). Inset (a) shows $\hat{r}_{\circ} = 5 \times 10^4 \ (523 \ \mu\text{m})$, (b) $\hat{r}_{\circ} = 20 \ (0.21 \ \mu\text{m})$, and (c) $\hat{r}_{\circ} = 0.1 \ (0.0014 \ \mu\text{m})$. Gray curve corresponds to normalized stress, $\hat{\sigma} = 5 \times 10^{-4} \ (-0.366 \text{ MPa})$, green curve corresponds to $\hat{\sigma} = 10^{-3} \ (-0.732 \text{ MPa})$, blue curve corresponds to $\hat{\sigma} = 5 \times 10^{-3} \ (-3.66 \text{ MPa})$, and red curve corresponds to $\hat{\sigma} = 0.05 \ (-36.6 \text{ MPa})$. Results show that large overpotentials enable the nucleation and growth of dendrites through the *tip-controlled mechanism*, for very long periods of time. The growth of large dendrites are dominated by the *base-controlled mechanism*, upon the accumulation of large plastic deformation $(t_{\sigma} \geq t_{\circ})$.

3.4 Conclusions

An analytical framework has been developed to rationalize the major experimentally identified mechanisms for dendrite growth in a liquid electrolyte. Contributions from electrodeposition, surface energy, and elastic and plastic deformation are assessed through a thermodynamically consistent growth theory in order to understand the driving forces controlling its dynamics. Specifically, five regimes of dendrite growth behavior have been identified: i) thermodynamic suppression regime, ii) incubation regime, *iii*) tip-controlled growth regime, *iv*) base-controlled growth regime, and v) mixed growth regime. For a single, isolated hemispherical lithium electrodeposit, linear growth signals *tip-controlled growth*, and exponential growth signals base-controlled growth. Further, the necessary electrochemical and chemomechanical conditions to minimize growth have been identified, namely by maximizing the hydrostatic contribution to stresses, and minimizing the deviatoric contribution. The predicted regimes of growth are in excellent agreement with experimental reports of tip-controlled growth and base-controlled growth, and suggest the additional existence of a *mixed growth regime*. The theory readily explains the time-dependent transition between one growth regime to the another, as reported in the experimental scientific literature [48, 94–97, 101]. Two characteristic times have been identified: the characteristic deposition time, t_{\circ} , corresponding to overpotential driven growth, and the characteristic plasticity time, t_{σ} , corresponding to plastic flow induced growth. For very large overpotentials, electrodeposits spend a short amount of time on coarsening, before *tip-controlled growth* starts. After the accumulation of stresses for a long time, $(\sim t_{\sigma})$ in the mixed growth regime, growth transitions to the base-controlled mecha*nism*, where plasticity dominates. Two key dimensionless numbers are identified: Π_1 , the ratio of the chemical free energy of transformation to the thermal energy of an isolated lithium electrodeposit, and Π_2 the weighted ratio of the deposition time to the plasticity time.

The proposed theory provides an additional degree of freedom to supress the formation of lithium dendrites, as proposed by Zhang and coworkers [139]. Following Ely *et al.*, [104], and by using the Gibbs-Duhem equation, $0 = SdT + Nd\mu_c + Ad\gamma + qd\eta + \overleftrightarrow{\varepsilon} \cdot d \overleftrightarrow{\sigma}$, for an isothermal system with fixed applied overpotential and stress, $\gamma = \gamma_{\circ} - \int_{0}^{\mu_{e}} \chi d\mu_{e}$, where γ_{\circ} is the surfactant-free, nucleus-electrolyte interfacial free energy; χ is the surface concentration; $\mu_{e} = \mu_{c} + zF\eta/\Omega + \sigma^{2}/2E$, the electrochemicomechanical potential; and μ_{c} the traditional chemical potential of the interface. Thus, the addition of a surfactant on a mechanically stressed interface can be used to suppress the nucleation of lithium embryos.

Results suggest that mechanical stresses can both suppress or promote dendrite growth. Specifically, the performed analysis suggests that through the use of existing technology such as pulse charging [140–142], dendrites can be suppressed by minimizing the possibility of nucleation and growth, as suggested by Ely [104]; however, for already existing dendrites, the period of the pulses, τ , should be shorter than t_{\circ} to minimize *tip-controlled growth*, and simultaneously shorter than t_{σ} to minimize *base-controlled growth*. Historically, it is well known that the application of large compressive hydrostatic stresses has resulted in the full suppression of dendrites [113, 116, 117, 120, 123, 124]. This analysis suggests an additional dendrite suppression design variable through the application of compressive stresses, $\sigma > \sigma_{\circ}$, such that $a = a(t) \geq 1$ for $t \gg t_{\sigma}$.

4. PHASE FIELD MODELING OF LITHIUM DENDRITE GROWTH KINETICS

A version of this chapter is currently under review for journal publication as: A. Jana, S.-I. Woo, K.S.N. Vikrant, R. E. García. "Electrochemomechanics of Lithium Dendrite Growth."

4.1 Introduction

The growth of elongated, branched structures, commonly referred to as "dendrites," is an inherent problem in the development of advanced rechargeable lithiumion batteries, has been classically attributed to long-range diffusion limitations in the electrolyte [110], poses serious safety issues [87], and has been one of the major bottlenecks in their commercialization. The problem of lithium dendrite growth remains mostly unsolved due to the contribution of multiple, apparently competing, growth mechanisms. It has been widely observed in several independent experimental reports that lithium grows from the tip at high applied currents densities and from the base at low current densities [94, 95, 101]. Arakawa [133] first proposed that lithium "extrudes" from the base at low current densities, while the tip morphology remains unchanged. Crowther and West [48] demonstrated the transition of "tip-controlled growth" to "base-controlled growth" after ~ 420 s of galvanostatic electrodeposition of lithium metal on a copper substrate at a current density of $2 \,\mathrm{mA/cm^2}$. Recently, Cui et al. [100] showed the nucleation of hemispherical electrodeposits for a range of current densities (see \bigcirc in Figure 4.1), and confirmed Ely and García 's analytical predictions [104]. Cui and coworkers [143] also demonstrated the growth of non-dendritic, columnar Li electrodeposits under a hollow carbon laver (see \triangleright in Figure 4.1). Bazant, Li, and coworkers [94] reported experimental observations of transitions between distinguishable growth mechanisms, from a base-controlled, mossy microstructure, to a tip-controlled, diffusion-limited dendritic microstructure (see \Box in Figure 4.1). Highly branched and symmetrical dendritic patterns (see \Diamond in Figure 4.1) were experimentally reported by Tatsuma and coworkers [136] for Li electrodeposited on a Cu substrate at 3 mA/cm^2 for one hour from a gel-based electrolyte.



Figure 4.1.: \bigcirc corresponds to hemispherical lithium nuclei electrodeposited on top of a copper layer at 0.1 mA/cm^2 for 1 hour, as performed by Pei, Cui and coworkers [100]. \triangleright corresponds to columnar growth of lithium on a copper substrate under a hollow carbon layer after 50 charge/discharge cycles at 1 mA/cm^2 , as shown by Zheng, Cui and coworkers [143]. \Box corresponds to mossy lithium electrodeposition on a copper substrate at 2.61 mA/cm^2 for 0.5 hour in a liquid electrolyte column, as shown in experiments by Bazant *et al.* [94]. \diamondsuit corresponds to branched lithium dendrites electrodeposited on a lithium substrate from a gel-based electrolyte at 3 mA/cm^2 for 1 hour, as performed by Tatsuma, Taguchi, and Oyama [136]. Catalog of experimental lithium electrodeposit microstructures demonstrates the effect of current density on dendrite morphology, as different driving forces compete to reduce lithium.

Three timescales of lithium dendrite growth are identified in the literature: (i) a characteristic deposition time, $t_{\circ} = -2\gamma RT/j_{\circ}\Omega^2 \Delta G_{\rm f}^2 \sim 1$ s, required to overcome the initial electrochemical energy barrier for electrodeposition, as proposed by Ely [104], (ii) Sand's time, $t_{\rm Sand} = \pi D \left(\frac{zc\mathcal{F}}{i_{\rm app}t_{\rm a}}\right)^2 \sim 300$ s (for $10 \,\mathrm{mA/cm^2}$), required for the onset of diffusion limitations in the electrolyte, as recently reported by Bazant and coworkers [94], and (iii) a characteristic plasticity time, $t_{\sigma} = \frac{1}{A} \left[\frac{-(a^2+2)}{2E\Delta G_{\rm f}(a-1)^2 \hat{\sigma}^2}\right]^{n/2} = 1/[A \parallel (a-1)\sigma \parallel^n] \sim 323$ s (for ~5 MPa stress), required for initial stresses to relax through plastic flow of lithium, as proposed in previous work [144]. Bazant *et al.* [94, 101] further defined a critical electrodeposited charge, the Sand's capacity, $Q = it_{\rm Sand}$,

to define the regime boundary of dendritic and non-dendritic growth and hypothesized a stress driven base- or "root growth" mechanism. Recent analytical work [144] rationalized for the first time the contribution of lithium plasticity [101, 114, 115, 118, 119, 126–128] to base-controlled growth and further identified the existence of a mixed mode regime, where contributions from both the tip and the base induce dendrite growth [144].

Bockris and coworkers proposed the first analytical model for dendritic growth for electrodeposition of silver [106] and zinc [107]. They considered ion diffusion limitations at the dendrite tip, calculated a critical overpotential, and predicted the growth velocity for low and high exchange current densities. Diggie and Bockris further extended the model to show transitions between spongy and dendritic zinc electrodeposits under very high overpotentials [107]. Aogaki and Makino [108] first studied instabilities at the electrochemical interface, showed the existence of an "induction time," before electrodeposits form, and a "transition time" (or Sand's time) when the ions at the interface deplete to zero concentration. Chazalviel, Fleury, and Rosso established dendrite growth models for dilute electrolytes under large electric fields at the dendrite tip [110, 111]. Dendritic patterns were attributed to deviations from the electroneutrality condition at the electrochemical interface. Electrodeposition models specifically for rechargeable batteries were put forward by Monroe and Newman [103], who showed that the kinetics of electrodeposit growth was governed by the Butler-Volmer equation for sub-limiting current densities, a phenomenon that has been repeatedly observed experimentally [94, 100]. Ferrese and Newman further extended the model to account for elastic [116] and elasto-plastic deformation [114] in order to predict: (a) the effect of elastic deformation on reaction kinetics, and (b) the thickness of lithium that was redistributed to plastic flow due to a stiff separator. Recent analytical descriptions identified the thermodynamic and kinetic regimes of lithium electrodeposition and dissolution for non-stressed [104] and stressed electrodeposits under elastic and plastic deformation [144].

Thermodynamically consistent variational principles to describe transport and phase transformation kinetics in electrochemical systems were pioneered by Bishop and García [145, 146]. Guyer and coworkers [147] proposed a variational formulation for a multicomponent electrochemical system. A phase field model of electrodeposition by Okajima, Shibuta, and Suzuki [148] integrated Butler-Volmer kinetics and simulated the growth of an electrodeposit for a very short time (~ 1 s). The morphology of the electrodeposit was influenced through a chosen anisotropic interfacial energy. Recent electrodeposition phase field models by Chen and coworkers [149], Ely [138], and most recently by Cogswell [150] demonstrated the interfacial velocity to be a combination of total free energy minimization kinetics and Butler-Volmer electrodeposition kinetics. Recently, Jokisaari and coworkers [151] proposed the only phase field description that includes elastic energy contributions to demonstrate the shape evolution of an elastically constrained precipitate with anisotropic stiffness coefficients.

In spite of the current progress, a fundamental understanding that explains the different experimentally reported lithium dendrite morphologies is missing. In this context, a thermodynamically consistent variational framework is developed herein to rationalize the effects of concurrently occurring electrochemistry and large deformation plasticity on the lithium electrodeposition thermodynamics and kinetics. Lithium morphologies predicted herein are in excellent agreement with experimental results, demonstrate the underlying driving forces, and are summarized in dendrite growth maps as a function of the relevant dimensionless quantities.

4.2 Theoretical Framework

4.2.1 Thermodynamic Principle

Consider a multicomponent electrochemical system comprised of N charged species, z_i is the valence of each species and Ω_i is its molar volume. The concentration set is described through the notation, $\{c\} = \{c_1, c_2, c_3, \ldots, c_N\}$, as proposed by Steinbach [152] and later by Cogswell [153]. ξ is a non-conserved order parameter equal to one in the electrodeposit phase and equal to zero in the liquid electrolyte phase and defines the location in the anode where lithium has been reduced into its solid form. ρ is the local charge density and ϕ is the local electrostatic potential. $\stackrel{\leftrightarrow}{\sigma}$ is the local stress tensor and $\stackrel{\leftrightarrow}{\varepsilon}^{e}$ is the local elastic strain tensor. The total Gibbs free energy of the system is defined as:

$$G[\xi, \{c\}, \rho, \vec{u}; T] = \int_{V} \left[g(\xi, \{c\}, T) + W_{\xi} h(\xi) + \frac{\zeta_{\xi}^{2}}{2} (\nabla \xi)^{2} + \sum_{i=1}^{N} \sum_{j=1}^{i} \frac{\zeta_{ij}^{2}}{2} \nabla c_{i} \cdot \nabla c_{j} + \rho \phi + \frac{1}{2} \overleftrightarrow{\sigma} \cdot \overleftrightarrow{\varepsilon}^{e} \right] dV + \int_{V} \lambda \left(\rho - \sum_{i=1}^{N} \frac{z_{i} \mathcal{F} c_{i}}{\Omega_{i}} \right) dV$$

$$(4.1)$$

Equation 4.1 is in agreement with earlier descriptions by Guyer [147], Okajima [148], Chen [154], García [138, 146], and Cogswell [150]. Here, $g(\{c\}, \xi, T) =$ $g_s(\{c\}, T) p(\xi) + g_l(\{c\}, T) (1 - p(\xi))$ is the volumetric chemical free energy density of mixing, where $g_s({c}, T)$ is the volumetric chemical free energy density of mixing of the solid electrodeposit and $g_l(\{c\}, T)$ is that of the liquid electrolyte. The spatial contributions in each phase are specified through the interpolating function, $p(\xi) = \xi^3 (10 - 15\xi + 6\xi^2)$, where p(0) = 0 and p(1) = 1. The free energy density of mixing is described through a Redlich-Kister free energy model, where, $g_m = \sum_{i=1}^{N} \frac{RT}{\Omega_i} c_i \ln c_i + \sum_{i< j=1}^{N} \sum_{\nu=0}^{k} (c_i - c_j)^{\nu} L_{ij,\nu}$ is the ν^{th} order Redlich-Kister coefficient [155] and embodies the enthalpic contributions to the free energy of the electrochemically active material. $h(\xi) = \xi^2 (1-\xi)^2$ and defines minima at $\xi = 0$ and $\xi = 1$. W_{ξ} is the height of the energy barrier. The term, $\frac{\zeta_{\xi}^2}{2}$, modulates the energy penalty for the creation of an electrodeposit-electrolyte interface. Similarly, the term, $\frac{\zeta_{ij}^2}{2}$, penalizes the formation of sharp interfaces between two chemical species. The second row in the right side of Equation 4.1 corresponds to the energy penalty to satisfy $\rho = \sum_{i=1}^{N} z_i \mathcal{F} c_i / \Omega_i$.

Local equilibrium is governed by the resultant variational derivatives:

$$\frac{\delta G}{\delta \xi} = \frac{\partial g}{\partial \xi} + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{i} \frac{\partial \zeta_{ij}^{2}}{\partial \xi} \nabla c_{i} \cdot \nabla c_{j} - \zeta_{\xi}^{2} \nabla^{2} \xi + W_{\xi} \frac{\partial h}{\partial \xi} + \frac{1}{2} \frac{\partial \overleftrightarrow{\sigma}}{\partial \xi} \cdot \overleftrightarrow{\varepsilon}^{e}$$

$$= \left[\Delta g(\{c\}, T) + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{i} (\zeta_{s}^{2} - \zeta_{l}^{2}) \nabla c_{i} \cdot \nabla c_{j} \right] \frac{\partial p}{\partial \xi} - \zeta_{\xi}^{2} \nabla^{2} \xi$$

$$+ W_{\xi} \frac{\partial h}{\partial \xi} + \frac{1}{2} \frac{\partial \overleftrightarrow{\sigma}}{\partial \xi} \cdot \overleftrightarrow{\varepsilon}^{e}$$

$$\mu_{i} = \frac{\delta G}{\delta c_{i}} = \frac{\partial g}{\partial c_{i}} - \sum_{i=1}^{N} \sum_{j=1}^{i} \zeta_{ij}^{2} \nabla^{2} c_{j} - \frac{\lambda z_{i} \mathcal{F}}{\Omega_{i}}$$

$$\frac{\delta G}{\delta \rho} = \phi + \lambda$$

$$\frac{\delta G}{\delta u} = \nabla \cdot \overleftrightarrow{\sigma} = \vec{0}$$

$$(4.2)$$

At equilibrium, the first three rows of Equation Set 4.2 show that the electrochemical state of a lithium deposit is determined by the structural, electrical, chemical, and mechanical properties of the electrodeposit. The fourth row is identified as the electrochemical potential, and includes interfacial energy effects as a result of any potential phase separation. The fifth row corresponds to the electrostatic deviations from equilibrium, as contributed by the spatially varying Lagrange multiplier, λ . Finally, the last row corresponds to the mechanical equilibrium equation, in response to the local accumulation of elastic energy density. Thus, the local stress directly influences the equilibrium state and the resultant morphology of the electrodeposit.

4.2.2 Mechanics

Physically, the encapsulating SEI [17, 101, 156, 157], the adjoining electrodeposits [118], the separator [116], and the casing of the cell [119, 120] are well known sources of mechanical stress in lithium dendrites. In addition, local volumetric changes are induced during lithium electrodeposition from the liquid electrolyte in the presence of mechanical constraints, as demonstrated experimentally by Cui [85] and Aurbach [158]. Thus, the mechanical state of stress of an electrodeposit is determined by solving the mechanical equilibrium equation, as described in Equation Set 4.2 for small strains, *i.e.*, for $\|\nabla \vec{u}\| \ll 1$ and using $\sigma_{ij} = C_{ijkl} \varepsilon_{kl}^e$. Physically, C_{ijkl} is the local phase-dependent stiffness tensor and is given by $C_{ijkl} = C_{ijkl}^s p(\xi) + C_{ijkl}^l (1 - p(\xi))$. Thus, the local stress is influenced by the stress localization on the electrodeposit, its relaxation inside the electrodeposit, and the surrounding electrolyte. The elastic strain, $\vec{\varepsilon}^e$, is obtained from the relation, $\vec{\varepsilon}^e = \vec{\varepsilon} - \sum_{i=1} \vec{\varepsilon}^i$, where $\vec{\varepsilon}$ is the total or geometric strain and $\vec{\varepsilon}^i$ denotes all possible inelastic and chemical strains. Lithium is a very ductile metal ($\sigma_y = 0.56$ MPa [128]), and undergoes large plastic deformation [101, 114, 115, 118, 119, 126–128]. The plastic strain rate, $\dot{\varepsilon}_p$, is obtained from a power law creep model [129] given by:

$$\dot{\varepsilon}_p = A \sigma_{\rm s}^n \tag{4.3}$$

where $\sigma_{\rm s}$ is the von Mises stress. Here, $A = A_{\circ}D\mu^{1-n}b/kT$, where A_{\circ} is Dorn's constant, $D = D_{\circ}\exp\left(-Q/RT\right)$ is the diffusion coefficient, and b is the Burgers vector.

4.2.3 Transport and Phase Transformation Kinetics

Away from equilibrium, spatial inhomogeneities of the variational derivatives in Equation 4.2 are the driving forces for microstructure evolution. The kinetic equations are thus:

$$\begin{split} \frac{\partial \xi}{\partial t} &= -M_{\xi} \frac{\delta G}{\delta \xi} + \sum_{i=1}^{N} \Omega_{i} \vec{\Gamma}_{i} \cdot \nabla \xi - \vec{v}_{p} \cdot \nabla \xi \\ &= -M_{\xi} \left[\left(\Delta g(\{c\}, T) + \sum_{i=1}^{N} \sum_{j=1}^{i} \frac{1}{2} (\zeta_{s}^{2} - \zeta_{l}^{2}) \nabla c_{i} \cdot \nabla c_{j} \right) \frac{\partial p}{\partial \xi} - \zeta_{\xi}^{2} \nabla^{2} \xi \right. \\ &+ W_{\xi} \frac{\partial h}{\partial \xi} + \frac{1}{2} \frac{\partial \vec{\sigma}}{\partial \xi} \cdot \vec{\varepsilon}^{e} \right] + \sum_{i=1}^{N} \Omega_{i} \vec{\Gamma}_{i} \cdot \nabla \xi - \vec{v}_{p} \cdot \nabla \xi \\ \frac{\partial c_{i}}{\partial t} &= \nabla \cdot M_{i} \nabla \frac{\delta G}{\delta c_{i}} + \sum_{j=1, j \neq i}^{N} \nabla \cdot M_{ij} \nabla \frac{\delta G}{\delta c_{j}} - \Omega_{i} \vec{\Gamma}_{i} \cdot \nabla \xi - \vec{v}_{p} \cdot \nabla c_{i} \quad (4.4) \\ &= \nabla \cdot M_{i} \nabla \left(\frac{\partial g}{\partial c_{i}} - \sum_{j=1}^{N} \zeta_{ij}^{2} \nabla^{2} c_{j} - \frac{z_{i} \mathcal{F} \lambda}{\Omega_{i}} \right) \\ &+ \sum_{j=1, j \neq i}^{N} \nabla \cdot M_{ij} \nabla \left(\frac{\partial g}{\partial c_{j}} - \zeta_{ij}^{2} \nabla^{2} c_{i} \right) - \Omega_{i} \vec{\Gamma}_{i} \cdot \nabla \xi - \vec{v}_{pi} \cdot \nabla c_{i} \\ &\frac{\partial \rho}{\partial t} = \nabla \cdot M_{\rho} \nabla \frac{\delta G}{\delta \rho} - \sum_{i=1}^{N} z_{i} \mathcal{F} \vec{\Gamma}_{i} \cdot \nabla \xi \\ &= \nabla \cdot M_{\rho} \nabla (\phi + \lambda) - \sum_{i=1}^{N} z_{i} \mathcal{F} \vec{\Gamma}_{i} \cdot \nabla \xi \end{split}$$

The spatially varying Lagrange multiplier, $\lambda(\vec{x})$, is identified from the relation, $\sum_{i=1}^{N} \frac{z_i \mathcal{F}}{\Omega_i} \frac{\partial c_i}{\partial t} = \frac{\partial \rho}{\partial t}$ [146] and by substituting Equation Set 4.4:

$$\lambda = \frac{\sum_{i=1}^{N} \left(\frac{z_i \mathcal{F}}{\Omega_i}\right) M_i \left(\frac{\partial g}{\partial c_i} - \sum_{j=1}^{N} \zeta_{ij}^2 \nabla^2 c_j\right) - M_\rho \phi}{M_\rho + \sum_{i=1}^{N} \left(\frac{z_i \mathcal{F}}{\Omega_i}\right)^2 M_i}$$
(4.5)

 λ is defined as the time-dependent electrochemical potential, where the numerator is a mobility-weighted driving force and the denominator is a normalizing factor. Direct substitution of Equation 4.5 in Equation 4.4, leads to:

$$\begin{split} \frac{\partial \xi}{\partial t} &= -M_{\xi} \left[\left(\Delta g(\{c\}, T) + \sum_{i=1}^{N} \sum_{j=1}^{i} \frac{1}{2} (\zeta_{s}^{2} - \zeta_{l}^{2}) \nabla c_{i} \cdot \nabla c_{j} \right) \frac{\partial p}{\partial \xi} - \zeta_{\xi}^{2} \nabla^{2} \xi \right. \\ &+ W_{\xi} \frac{\partial h}{\partial \xi} + \frac{1}{2} \frac{\partial \sigma}{\partial \xi} \cdot \hat{c}^{\diamond} \right] + \sum_{i=1}^{N} \Omega_{i} \vec{\Gamma}_{i} \cdot \nabla \xi - \vec{v}_{p} \cdot \nabla \xi \\ \frac{\partial c_{i}}{\partial t} &= \nabla \cdot D_{i}^{*} \frac{\partial^{2} g}{\partial c_{i}^{2}} \nabla c_{i} - \nabla \cdot D_{i}^{*} \sum_{j=1}^{N} \nabla \zeta_{ij}^{2} \nabla^{2} c_{j} + \nabla \cdot \left(\left(\frac{z_{i} \mathcal{F}}{\Omega_{i}} \right) D_{i}^{*} \nabla \phi \right) \right. \tag{4.6} \\ &+ \sum_{j=1, j \neq i}^{N} \left(\nabla \cdot D_{ij}^{*} \frac{\partial^{2} g}{\partial c_{j}^{2}} \nabla c_{j} - \nabla \cdot D_{ij}^{*} \nabla \zeta_{ij}^{2} \nabla^{2} c_{i} \right) \\ &- \Omega_{i} \vec{\Gamma}_{i} \cdot \nabla \xi - \vec{v}_{p} \cdot \nabla c_{i} \\ \frac{\partial \rho}{\partial t} &= \nabla \cdot \kappa \nabla \phi + \sum_{i=1}^{N} \nabla \cdot \left(\left(\frac{z_{i} \mathcal{F}}{\Omega_{i}} \right) D_{i}^{*} \frac{\partial^{2} g}{\partial c_{i}^{2}} \nabla c_{i} \right) \\ &- \sum_{i=1}^{N} \sum_{j=1}^{i} \nabla \cdot \left(\left(\frac{z_{i} \mathcal{F}}{\Omega_{i}} \right) D_{i}^{*} \nabla \zeta_{ij}^{2} \nabla^{2} c_{j} \right) - \sum_{i=1}^{N} z_{i} \mathcal{F} \vec{\Gamma}_{i} \cdot \nabla \xi \end{split}$$

Here, $M_{\xi} = \alpha \sum_{i=1}^{N} j_{oi} \Omega_i^2 / 6RT \delta_{\xi}$ is the interfacial mobility of the electrochemical interface. $M_i/2 = \frac{\Omega_i}{RT} c_i (1 - c_i) D_i = D_i^*$, $D_i^* \frac{\partial^2 g}{\partial c_i^2}$ is the diffusivity of the *i*th species, and $M_{\rho}/2 = \kappa$ is the total electrical conductivity [146]. Further, $M_{\rho} = \sum_{i=1}^{N} \left(\frac{z_i \mathcal{F}}{\Omega_i}\right)^2 M_i$ [131]. The term $\Omega_i \vec{\Gamma}_i \cdot \nabla \xi$ accounts for mass deposition or dissolution at the interface. $\vec{v}_p \cdot \nabla \xi$ and $\vec{v}_{p,i} \cdot \nabla c_i$ account for convective plastic flow of the solid with a velocity, $\vec{v}_p = \sum_{i=1}^{N} \vec{v}_{p,i}$. $\vec{v}_{p,i}$ is the vectorial plastic velocity of the *i*th chemical species. In the absence of stresses and concentration gradients in the electrolyte, Equation 4.6 reduces to the classical electrochemically induced electrodeposition, as described by Ely and coworkers [105, 138] and results in well-known tip-controlled growth [144].

4.2.4 Interfacial Electrodeposition Kinetics

The electrodeposition kinetics are described by using the Butler-Volmer equation for a stressed electrodeposit [113], in agreement with previous work [144]:

$$\Gamma_{i} = j_{i\circ} \left(\exp\left[\frac{(1-\alpha)}{RT} \left(z_{i} \mathcal{F} \eta + \frac{\Omega_{i}}{2} \overset{\leftrightarrow}{\sigma} \cdot \overset{\leftrightarrow}{\varepsilon^{e}} + \gamma \Omega_{i} \mathcal{K} \right) \right] - \exp\left[\frac{-\alpha}{RT} \left(z_{i} \mathcal{F} \eta + \frac{\Omega_{i}}{2} \overset{\leftrightarrow}{\sigma} \cdot \overset{\leftrightarrow}{\varepsilon^{e}} + \gamma \Omega_{i} \mathcal{K} \right) \right] \right)$$
(4.7)

where $j_{i\circ} = i_{\circ}/(z_i \mathcal{F}) = k_{\rm r}^{\circ} \exp(-\frac{\Omega_i \overleftrightarrow{\sigma} \cdot \overleftrightarrow{\varepsilon}^{\circ}}{2RT}) c_i^{(1-\alpha)} (1-c_i)^{\alpha}$, is the molar exchange current density, in agreement with Ely [138]. The elastic energy density, $\frac{1}{2} \stackrel{\leftrightarrow}{\sigma} \cdot \stackrel{\leftrightarrow}{\varepsilon^{e}}$, suppresses the interfacial deposition rate, as proposed by Newman [113]. Thus, for stressed dendrites, higher overpotentials are required for electrodeposition [94, 101, 113]. The molar electrodeposition rate is $\sum_{i=1}^{N} \Gamma_i = \Gamma = \vec{\Gamma} \cdot \hat{n}$, where $\hat{n} = -\nabla \xi / |\nabla \xi|$, is the outward normal to the interface with a curvature, $\mathcal{K} = \nabla \cdot \hat{n}$, as previously reported [105, 144]. The first term inside the parenthesis, $z_i \mathcal{F} \eta$, accounts for the classical overpotential induced electrodeposition. The second term, $\frac{1}{2}\Omega_i \overleftrightarrow{\sigma} \cdot \overleftrightarrow{\varepsilon}^e$, accounts for the shift in critical overpotential due to elastic energy density localization, as proposed in earlier work [144]. The third term, $\gamma \Omega \mathcal{K}$, accounts for the Laplace pressure of a curved electrodeposit. Laplace pressure and elastic energy density counter the overpotential-induced electrodeposition [113, 116, 124, 144]. In the absence of stresses and for a planar electrodeposit, Equation 4.7 reduces to the classic Butler-Volmer equation [75]. In the limit, $\frac{1}{RT} \left(z_i \mathcal{F} \eta + \frac{\Omega_i}{2} \overset{\leftrightarrow}{\sigma} \cdot \overset{\leftrightarrow}{\varepsilon^e} + \gamma \Omega_i \mathcal{K} \right) \ll 1$ and for a symmetrical electrodeposition-electrodissolution reaction, *i.e.*, $\alpha = 1/2$, Equation 4.7 reduces to [75] $\Gamma_i = \frac{j_{i\circ}}{RT} \left(z_i \mathcal{F} \eta + \frac{\Omega_i}{2} \overset{\leftrightarrow}{\sigma} \cdot \overset{\leftrightarrow}{\varepsilon^e} + \gamma \Omega_i \mathcal{K} \right).$

4.2.5 Large Deformation Approximation

The plastic flow induced in the dendrites during electrodeposition leads to large mechanical deformation that requires to correlate the laboratory reference frame (Euler reference system) and the material reference frame (Lagrangian reference system). In the large deformation approximation, the *Spatial* or *Eulerian* coordinates are fixed in space and are denoted by \vec{x} , and the material description or Lagrangian coordinates are fixed on the material and are denoted by \vec{X} . A subscript "o" is used to distinguish variables in the Lagrangian frame from those in the Eulerian frame. The Lagrangian strain is given by the Green-Lagrange strain tensor, $\overset{\leftrightarrow}{E} = \frac{1}{2} \left[\nabla_{\circ} \vec{u} + (\nabla_{\circ} \vec{u})^{\mathrm{T}} + (\nabla_{\circ} \vec{u}) \cdot (\nabla_{\circ} \vec{u})^{\mathrm{T}} \right] = \frac{1}{2} (\overset{\leftrightarrow}{F}^{\mathrm{T}} \cdot \overset{\leftrightarrow}{F} - \overset{\leftrightarrow}{I}), \text{ which reduces to } \overset{\leftrightarrow}{\varepsilon} \text{ in }$ the small deformation limit. $\stackrel{\leftrightarrow}{F} = \frac{\partial \vec{x}}{\partial \vec{X}}$, is the deformation gradient. The mechanical stress tensor in the undeformed configuration, also known as the second Piola-Kirchoff (PK2) stress, is defined as the transformed force in the undeformed configuration per unit undeformed area, $\overrightarrow{da_{\circ}}$, and is expressed as $\overset{\leftrightarrow}{S} = JF^{-1} \cdot \overset{\leftrightarrow}{\sigma} \cdot F^{-T}$. The elastic energy density in the Lagrangian frame is thus $\frac{1}{2} \stackrel{\leftrightarrow}{S} \cdot \stackrel{\leftrightarrow}{E_e}$, where $\stackrel{\leftrightarrow}{E_e}$ is the elastic part of the Green-Lagrange strain tensor. The variational formulation of the mechanical stored energy is in perfect agreement with Larché and Cahn [159, 160] and most recently with Anand [161], Veritas [162, 163], and Miehe [164]. The deformation gradient is, $\stackrel{\leftrightarrow}{F} = \stackrel{\leftrightarrow}{F_e} \stackrel{\leftrightarrow}{F_p} \stackrel{\leftrightarrow}{F_c}$, where $\stackrel{\leftrightarrow}{F_e}$ is the elastic, $\stackrel{\leftrightarrow}{F_p}$ is the plastic, and $\stackrel{\leftrightarrow}{F_c} = [1 + \beta(\xi_{\circ} - \xi_{\circ,\text{ini}})] \stackrel{\leftrightarrow}{I}$ is the electrode position part of the deformation gradient. ξ_{\circ} is the electrode position phase in the Lagrangian frame, $\xi_{\circ,\text{ini}}$ is its initial value and β is the electrodeposition differential strain given by $\beta = (\Omega_s - \Omega_l)/3\Omega_l$. Local differential strains imposed by the SEI and adjoining interacting phases, such as neighboring electrodeposits and separators are captured in this description [165–167].

The mechanical equilibrium equation in the Lagrangian frame is:

$$\nabla_{\circ} \cdot \overset{\leftrightarrow}{S} = \vec{0} \tag{4.8}$$

The plastic strain rate is $\stackrel{\leftrightarrow}{L_p} = \frac{\partial \vec{v}_p}{\partial x} = \stackrel{\leftrightarrow}{F_p} \stackrel{\leftrightarrow}{F_p} \stackrel{\rightarrow}{F_p}^{-1}$. $\stackrel{\leftrightarrow}{L_p}$ is decomposed into a symmetric part, $\stackrel{\leftrightarrow}{W_p} = 0$; thus:

The transformation of the individual terms in Equation Set 4.6 from the Eulerian to the Lagrangian frame is listed in Table 4.1. The resultant kinetic equations in the Lagrangian frame are given by:

$$\begin{split} \frac{\partial \xi_{\circ}}{\partial t} &= -M_{\xi} \bigg[\left(\Delta g(\{c_{\circ}\}, T) + \sum_{i=1}^{N} \sum_{j=1}^{i} \frac{1}{2} (\zeta_{s\circ}^{2} - \zeta_{l\circ}^{2}) \nabla_{\circ} c_{i\circ} \cdot \nabla_{\circ} c_{j\circ} \right) \frac{\partial p}{\partial \xi_{\circ}} + W_{\circ,\xi} \frac{\partial h}{\partial \xi_{\circ}} \\ &+ \frac{1}{2} \overset{\leftrightarrow}{E_{e}} \cdot \frac{\partial \overset{\leftrightarrow}{S}}{\partial \xi_{\circ}} - \operatorname{Tr}[F^{\leftarrow T} \nabla_{\circ} \cdot \zeta_{\xi_{\circ}}^{2} \nabla_{\circ} \xi_{\circ} F^{\leftarrow 1}] \bigg] + \sum_{i=1}^{N} \Omega_{\circ i} (C^{\leftarrow 1} \vec{\Gamma}_{\circ j}) \cdot \nabla_{\circ} \xi_{\circ} - \vec{v}_{p} \cdot \nabla_{\circ} \xi_{\circ} \\ \frac{\partial c_{\circ i}}{\partial t} &= \operatorname{Tr} \bigg[F^{\leftarrow T} \bigg(\nabla_{\circ} \cdot D_{i}^{*} \frac{\partial^{2} g}{\partial c_{\circ i}^{2}} \nabla_{\circ} c_{\circ i} \bigg) F^{\leftarrow 1} \bigg] \\ &- \operatorname{Tr}[F^{\leftarrow T} (\nabla_{\circ} \cdot D_{i}^{*} \sum_{j=1}^{N} \nabla_{\circ} (\operatorname{Tr}[F^{\leftarrow T} (\nabla_{\circ} \cdot \zeta_{ij}^{2} \nabla_{\circ} c_{\circ j}) F^{\leftarrow 1}])) F^{\leftarrow 1}] \\ &+ \bigg(\frac{z_{i} \mathcal{F}}{\Omega_{\circ i}} \bigg) \operatorname{Tr}[F^{\leftarrow T} (\nabla_{\circ} \cdot D_{i}^{*} \nabla_{\circ} \phi_{\circ}) F^{\leftarrow 1}] \\ &+ \sum_{j=1, j \neq i}^{N} \bigg[\operatorname{Tr} \bigg[F^{\leftarrow T} \bigg(\nabla_{\circ} \cdot D_{ij}^{*} \frac{\partial^{2} g}{\partial c_{\circ j}^{2}} \nabla_{\circ} c_{\circ j} \bigg) F^{\leftarrow 1}] \bigg] \\ &- \operatorname{Tr}[F^{\leftarrow T} (\nabla_{\circ} \cdot D_{ij}^{*} \nabla_{\circ} (\operatorname{Tr}[F^{\leftarrow T} (\nabla_{\circ} \cdot \zeta_{ij}^{2} \nabla_{\circ} c_{\circ i}) F^{\leftarrow 1}]] \bigg) F^{\leftarrow 1}] \bigg]$$

$$(4.10)$$

$$- \Omega_{\circ i} (\overset{\leftrightarrow}{C^{-1}} \vec{\Gamma}_{\circ i}) \cdot \nabla_{\circ} \xi_{\circ} - \vec{v}_{pi} \cdot \nabla_{\circ} c_{\circ i}$$

$$\frac{\partial \rho_{\circ}}{\partial t} = \operatorname{Tr}[\overrightarrow{F^{-T}}(\nabla_{\circ} \cdot \kappa \nabla_{\circ} \phi_{\circ})\overrightarrow{F^{-1}}] + \sum_{i=1}^{N} \operatorname{Tr}\left[\overrightarrow{F^{-T}}\left(\nabla_{\circ} \cdot \left(\frac{z_{i}\mathcal{F}}{\Omega_{\circ i}}D_{i}^{*}\frac{\partial^{2}g}{\partial c_{\circ i}^{2}}\nabla_{\circ}c_{\circ i}\right)\right)\overrightarrow{F^{-1}}\right] \\
- \sum_{i=1}^{N} \sum_{j=1}^{i} \operatorname{Tr}\left[\overrightarrow{F^{-T}}\left(\nabla_{\circ} \cdot \left(\frac{z_{i}\mathcal{F}}{\Omega_{\circ i}}D_{i}^{*}\nabla_{\circ}\left(\operatorname{Tr}[\overrightarrow{F^{-T}}(\nabla_{\circ} \cdot \zeta_{ij}^{2}\nabla_{\circ}c_{\circ j})\right)\overrightarrow{F^{-1}}]\right)\right)\overrightarrow{F^{-1}}\right] \\
- \sum_{i=1}^{N} z_{i}\mathcal{F}(\overrightarrow{C^{-1}}\overrightarrow{\Gamma}_{\circ i}) \cdot \nabla_{\circ}\xi_{\circ}$$

Quantity or Operator	Eulerian frame	Lagrangian frame	Ref.
Gradient	$ abla \xi$	$\overset{\leftrightarrow}{F^{-1}} abla_{\circ}\xi_{\circ}$	[168]
Laplacian	$ abla \cdot abla \xi$	$\operatorname{Tr}\left[\stackrel{\leftrightarrow}{F^{-\mathrm{T}}} \nabla_{\circ} \cdot \left(\nabla_{\circ} \xi_{\circ} \right) \stackrel{\leftrightarrow}{F^{-1}} \right]$	[169]
Surface energy	γ	$\stackrel{\leftrightarrow}{F}^{\Gamma}\gamma/J$	[168]
Unit normal	\hat{n}	$\frac{\overleftarrow{F}\hat{n}_{\circ}}{\sqrt{(\overleftarrow{F}\hat{n}_{\circ})\cdot(\overleftarrow{F}\hat{n}_{\circ})}}$	[168]
Interfacial thickness	$\delta_{\xi} \hat{n}$	$\overleftarrow{F}\delta_{\xi,\circ}\hat{n}_{\circ}$	[168]
Molar volume	Ω	$J\Omega_{\circ}$	[168]
Butler-Volmer flux	$ec{\Gamma}$	$J\vec{F^{-1}}\vec{\Gamma_{o}}$	
Deposition term	$\Omega \vec{\Gamma} \cdot \nabla \xi$	$\Omega_{\circ}(\overset{\leftrightarrow}{C^{-1}}\vec{\Gamma}_{\circ})\cdot abla_{\circ}\xi_{\circ}$	

Table 4.1.: Transformation of operators and quantities from Eulerian frame to Lagrangian frame.

Equation Set 4.10 allows to naturally and consistently couple the large deformation kinematics to the electrochemical kinetics of the system. $\mu_{\circ i} = \frac{\partial g}{\partial c_{\circ i}} - \sum_{j=1}^{N} \operatorname{Tr}[F^{-T}(\nabla_{\circ} \cdot \zeta_{c_{\circ j}}^{2} \nabla_{\circ} c_{\circ j}) F^{-1}]$ is defined herein as the large deformation chemomechanical potential. The terms $\operatorname{Tr}[F^{-T}(\nabla_{\circ} \cdot D_{i}^{*} \frac{\partial^{2}g}{\partial c_{\circ i}^{2}} \nabla_{\circ} c_{\circ i}) F^{-1}]$ and $\operatorname{Tr}[F^{-T}(\nabla_{\circ} \cdot \kappa \nabla_{\circ} \phi_{\circ}) F^{-1}]$ are the large deformation-induced anisotropic diffusivity and electrical conductivity.

4.3 Application to Lithium Electrodeposition

The chemical species in a lithium electrodeposition system are lithium ions, electrons, salts, and solvents in the electrolyte. Electronic concentration remains uniform in the solid and fully absent in the electrolyte phase and hence is trivially solved. The specific large deformation equations for lithium electrodeposition are shown in the Appendix.

Equations 4.3 to 4.10 were implemented in parallel by applying the finite element method using open source libraries in Python and C++. Electrodeposition calculations were performed by coupling two overlapped meshes. The first mesh corresponds to the solid electrodeposit, and the second mesh corresponds to the liquid electrolyte. The interfacial electrodeposition flux spatially couples both phases and determines lithium depletion in the electrolyte and an equimolar lithium deposition on the solid electrodeposit surface.

At t = 0, a lithium nucleus of radius of 1.33 μ m was placed at the center of the bottom anode surface. The initial radius was chosen such that it was larger than the critical thermodynamic radius (see Table 4.2). Galvanostatic lithium electrodeposition simulations from a 1 M LiPF₆ in 1:1 EC:DMC electrolyte on an inert substrate were performed. Values of material properties used are summarized in Table 4.2.

Symbol	Value	Reference
$\overline{A_{\circ}}$	2.9×10^6	[127]
b	$3.04 \times 10^{-10} \mathrm{m}$	[127]
c_{\circ}	$\Omega_l \times 1 \ { m M}$	[103]
$\widetilde{D_l} \frac{\partial^2 g}{\partial c^2} _{c_o}$	$4 \times 10^{-10} \mathrm{m^2 s^{-1}}$	[170]
$\widetilde{D_s} \frac{\partial^2 g}{\partial c^2} _{c_\circ}$	$10^{-5}{ m m}^2{ m s}^{-1}$	[127]
$\Delta H_l^{ m m}$	$1315{ m J}{ m m}^{-3}$	[171, 172]
$\Delta H_s^{ m m}$	$62238{ m J}{ m m}^{-3}$	[171, 172]
i_{\circ}	$30{ m A}{ m m}^{-2}$	[103]
L_{s0}	$24706{ m J}{ m mol}^{-1}$	[171, 172]
L_{s1}	$24706{ m J}{ m mol}^{-1}$	[171, 172]
L_{s2}	$9882\mathrm{Jmol^{-1}}$	[171, 172]
L_{l0}	$-2467{ m J}{ m mol}^{-1}$	[171, 172]
L_{l1}	0	[171, 172]
L_{l2}	0	[171, 172]
n	6.4	[127]
r_{\circ}	$1.33~\mu{ m m}$	[105, 138]
T_l^{m}	267 K	[21]
T_s^{m}	$453~\mathrm{K}$	[173]
α	0.5	[75]
γ	$1.716{ m J}{ m m}^{-2}$	[103]
δ_{ξ}	$0.07\mu{ m m}$	[174]
κ_l	$1.07{ m S}{ m m}^{-1}$	[21, 170]
κ_s	$1.1 imes10^7\mathrm{Sm^{-1}}$	[173]
σ_y	$0.56\mathrm{MPa}$	[128]
Ω_l	$6.93 imes 10^{-5} { m m}^3 { m mol}^{-1}$	[21]
Ω_s	$1.3 imes 10^{-5} { m m}^3 { m mol}^{-1}$	[103]

Table 4.2.: Values of physical parameters used in calculations.

Simulations were carried out on a 2.6 GHz, 28-core, Ubuntu 16.04 workstation with 128 GB of RAM. The numerical tolerance for the convergence and the tolerance for the Newton solver were both set to 10^{-6} . One hour of electrodeposition simulation took ~ 3 days of wall time. Figure 4.2(a) shows the numerical setup for the galvanostatic lithium electrodeposition simulations discussed in the rest of the chapter.

4.4 Model Validation

Mass conservation is validated through the half-cell setup shown in Figure 4.2(b). Galvanostatic electrodeposition for a set of selected applied current densities is performed on a layer of lithium substrate with initial thickness, h_{ξ}° . The time-dependent thickness of the electroplated flat lithium layer (*i.e.*, $\mathcal{K} = 0$) in the absence of stress is, $h_{\xi}(t) = h_{\xi}^{\circ} + \int_{0}^{t} \Gamma \Omega dt = h_{\xi}^{\circ} + k_{r}^{\circ} c^{(1-\alpha)} (1-c)^{\alpha} z \mathcal{F} \eta \Omega t$, for a linearized Butler-Volmer electrodeposition kinetics.



Figure 4.2.: Summary of simulation setups. Inset (a) shows the setup for the galvanostatic electrodeposition simulations. A fixed current density is applied from the top. The bottom edge is electrically grounded and mechanically constrained. The electrodeposit is hemispherical at t = 0. The area visualized in the analysis herein is highlighted by the dashed box. Inset (b) shows the half-cell setup used for mass and charge conservation validation. h_{ξ}° corresponds to the initial lithium metal anode thickness (in orange). The gray region represents the liquid electrolyte. Inset (c) shows the plasticity validation setup. Solid metallic lithium is pushed horizontally through a funnel-shaped section at a fixed applied velocity from the left edge. The top and the bottom edges are mechanically constrained.

For low applied current densities, *i.e.*, in the absence of diffusion limitations, the lithium concentration, c, in the electrolyte remains unchanged and $h_{\xi}(t)$ increases linearly with time. For higher current densities, $h_{\xi}(t)$ deviates from the linear growth rule due to diffusion limitations. Figure 4.3(a) shows the numerically predicted thickness against the analytical thickness for a set of selected current densities. Charge conservation is validated through the same setup (Figure 4.2(b)). The electrical conductivity of the liquid electrolyte (1 M LiPF₆ in 1:1 EC:DMC) is $1.07 \,\mathrm{S \,m^{-1}}$ and that of solid lithium is $1.1 \times 10^7 \,\mathrm{S \,m^{-1}}$. Numerical prediction from Equation 4.10 is compared against the analytical voltage distribution, $\phi(x) = \frac{i_{\mathrm{app}l}}{\kappa(x)}(1 - x/l)$, where l is the width of the domain and $i_{\mathrm{app}} = 1 \,\mathrm{mA/cm^2}$.



Figure 4.3.: Validation of the developed theory. Mass conservation validation is shown in inset (a). The red line denotes the thickness of lithium layer plated on a planar substrate in 1.4 hours of electrodeposition as obtained through the analytical linearized Butler-Volmer equation, $\Gamma = \frac{j_{\circ}}{RT} z \mathcal{F} \eta$. The blue circles show the predicted lithium thickness as a function of selected current densities. The model agrees very well with the linearized Butler-Volmer kinetics for small current densities, $i_{\rm app} < 0.4 \,\mathrm{mA/cm^2}$ and for higher current densities, deviations from the linearized rate highlight diffusion limitations. Inset (b) demonstrates validation of charge conservation. The red line indicates the analytical voltage profile, $\phi(x) = \frac{i_{\rm app}l}{\kappa(x)} \left(1 - \frac{x}{l}\right)$ through the thickness of the half cell, and the blue dashed line shows the simulated result. Inset (c) shows the validation for Equation 4.3. The red line shows the analytical plastic strain rate from power law creep, $\dot{\varepsilon}_p = A\sigma_s^n$. The blue circles denote the corresponding numerically obtained plastic strain rates in a computer simulation where metallic lithium is pushed through a constrained channel.

Figure 4.3(b) shows perfect agreement between the numerical and analytical voltages. The plasticity model was validated by pushing a block of solid lithium

through a perfectly stiff funnel, shown in Figure 4.2(c), and by taking advantage of the continuity relation, $\vec{a}_1 \cdot \vec{v}_1 = \vec{a}_2 \cdot \vec{v}_2$, for two arbitrary horizontally spaced points, where \vec{a}_i is the local cross-sectional area. The corresponding strain rate and the numerical von Mises stress at selected points in the central horizontal line of the funnel are compared against power law creep, $\dot{\varepsilon}_p = A\sigma_s^n$ (Equation 4.3) and shows excellent agreement (see Figure 4.3(c)).

4.5 Results and Discussion

Figure 4.4 shows the growth of an isolated lithium dendrite at a fixed current density of 1 mA/cm^2 . In the initial stages, the electric field is higher in the liquid electrolyte and nearly zero inside the highly conducting metallic lithium electrodeposit. The electric field localizes at the electrodeposit tip (see Figure 4.4(d),(e),(f)) and induces an overpotential-induced tip-controlled growth, which in turn induces stress accumulation, as a result of the local molar volume changes as the solid lithium locally displaces the SEI and the liquid electrolyte in the vicinity of the dendrite tip. Electrodeposition at the tip increases the local elastic energy density and suppresses subsequent electrodeposition in the very center of the stressed region. The local stress (see Figure 4.4(b)). This process repeats itself as the newly formed dendrite tips are directly exposed to the applied current density, thus forming secondary and tertiary branches (see Figure 4.4(c)).



Figure 4.4.: Electrodeposition of lithium subjected to constant current density of 1 mA/cm^2 at selected times: 0 s (left column), 1200 s (middle column), and 4800 s (right column). The top row shows the microstructure evolution, wherein solid metallic lithium is shown in orange and liquid electrolyte in gray. The middle row shows the corresponding electric field distribution. The vectorial field describes the direction of the electric field, while its color shows the magnitude. The bottom row shows the corresponding local electrodeposition (in red) and electrodissolution (in green). High electric field localizes at the dendrite tip and enhances tip electrodeposition. Electric field is nearly zero inside the highly conductive lithium metal. At longer times, a stress-induced non-zero electric field between two adjacent branches develops and causes local electrodeposition and electrodissolution that alters the dendrite morphology (inset (i)).

As these branches develop, the electrolyte between the central branch is electrically shielded (see Figure 4.4(f)). This results in large lobes of metal electrodeposits on the dendrite top that sit on thinner base sections and thus bend, buckle, or kink the structure and expose new sites to electrodeposition, as observed in recent experiments by Steiger and coworkers [134, 175]. While the tips of the dendrite undergo electrodeposition, the base of each of the dendrite arms are electrically shielded, do not undergo electrodeposition (see Figure 4.4(g) and (i)), and result in further elongating the dendrite branches. For oblique dendrites with bases exposed to the electric field, electrodeposition will occur, in agreement with experiments [134]. The side dendrites develop a lateral overpotential that results in local mass exchange between adjoining branches (see Figure 4.4 (f) and (i)).

Figure 4.5 shows the stress tensor distribution described in terms of Lamé's ellipses [176], where the principal stresses define the major and minor axes, and the orientation is specified by the principal directions. Results demonstrate that during the initial stages of dendrite growth the electrodeposit is subjected to a laterally compressive state of stress that pushes the lithium nucleus to grow vertically, as proposed by Wang and coworkers [177], Li and Bazant [94,101], Crowther and West [48], Tarascon and coworkers [97], Yamaki and Arakawa [133], and most recently in analytical work [144] (see Figure 4.5(a)). In addition, high compressive stresses in the initial stages induce electrodeposition suppression, in agreement with Newman [113] and electrodeposition experiments by Wilkinson and Wainwright [120].

As the electrodeposit grows and branches develop, stresses continuously relax at the base but remain localized at the tip. Growth at this stage is a result of both base-controlled growth at the bottom and tip-controlled growth at the top and results in an overall mixed growth mode, in agreement with previous work [144]. Further, highly localized elastic energy density at the tip suppresses electrodeposition at the tip, but favors electrodeposition and electrodissolution on the side branches (compare Figures 4.4(h) and 4.5(b)). Repeated bifurcations cause the electrodeposit to develop secondary and tertiary branches. A direct comparison between Figure 4.5(c) and 4.4(f) and (i) shows three unreported growth mechanisms: 1) closer to the base, where stresses are relaxed and the surfaces of the electrodeposit are electrochemically shielded there is practically no electrodissolution; 2) along the length of the lower side branches stresses induce electrodissolution and electrodeposition on those interfaces directly facing each other, generating a self-sustained overpotential that moves the branches up; and 3) in those side branches experiencing non-hydrostatic stresses, local, lateral extrusion is observed.



Figure 4.5.: Stress distribution in a lithium electrodeposit subjected to a current density of 1 mA/cm^2 . Three instants are shown: (a) 0 s, (b) 1200 s, and (c) 4800 s, and are visualized in terms of Lamé's ellipses [176]. Lithium microstructure is highlighted in gray. Ellipse orientation denotes the principal stress direction. A pure hydrostatic stress state is denoted by a circle. Compressive regions are in blue and tensile regions are in red. For short times, the electrodeposit is under compressive stress and is pushed towards the counter electrode, thus favoring base-controlled growth (inset (a)), in agreement with [101, 133, 144]. As electrodeposition progresses and stresses relax at the base, compressive stresses develop near the dendrite tip (inset (b)). To compensate for the compressive electrodeposition stresses, the internal structure of the dendrite develops a non-hydrostatic tensile state of stress, which further drives the microstructural evolution of the dendrite. Secondary dendrites become tensile, induce lateral extrusion of lithium whiskers (inset (c)) and local electrodissolution/electrodeposition between and along the length of the secondary branches (see Figure 4.4(i)).

Recent analytical work [144] shows that for the applied boundary conditions, the incubation time is $t_{\circ} \sim 1$ s and the stress relaxation time is $t_{\sigma} \sim 300$ s. Also, for the stress tensor anisotropy, $a = \sigma_2/\sigma_1 \sim -2$, plastic flow is maximal as predicted herein (see Figure 4.6(a)). Further, results demonstrate that base-controlled growth dominates at the initial stages of electrodeposition [94], independent of the applied current density. Thus, while electrodeposition is taking place, growth from both the tip and the base concurrently occurs, enabling the development of additional, simultaneously occurring growth mechanisms.



Figure 4.6.: Plastic displacement rate at a current density of 1 mA/cm^2 at selected times: (a) 0 s, (b) 1200 s, and (c) 4800 s. Electrodeposition-induced lateral compressive stress defines base-controlled growth, inset (a)). As electrodeposition process proceeds, the highest plastic flow rate is localized at the tips and induces mass flow towards the lower stressed regions (inset (b)). This induces a morphological bifurcation event, and thus the electrodeposit transitions into a dendritic structure (inset (c)). Afterwards, lithium flows from the internal to the external faces of the dendrite and results in lobe-shaped morphologies that will further lead to split into other branched structures.

The corresponding shear-induced plastic flow is summarized in Figure 4.6. In the initial stages, mass flows towards the top to relax the stresses, much like toothpaste being squeezed out of its tube (see Figure 4.6(a)) [94, 133, 144]. The streamlines highlight the direction of local plastic flow. After stresses relax through basecontrolled growth, tip electrodeposition further induces stress accumulation at the tip of the electrodeposit. For current densities $\sim 1 \,\mathrm{mA/cm^2}$, the electrodeposition rate is faster than the plastic flow-induced stress relaxation rate (see Figure 4.6(b)). The streamlines show that mass internally flows from high to low stressed regions and induces dendrite bending. Further, such directional flow stretches the dendrite branches and makes them susceptible to localized electrodeposition.

Figure 4.7 shows the lithium-ion concentration distribution for a high current density, $i_{\rm app} = 10 \,\mathrm{mA/cm^2}$. Figure 4.7(a) shows the concentration at $t = 300 \,\mathrm{s}$. For $t > t_{\rm Sand} = 292 \,\mathrm{s}$, the concentration drops to zero in the vicinity of the dendrite tip, in those locations where the local electric field is concentrated (see Figure 4.8), suppressing the local electrodeposition rate. Also, results demonstrate that the width of the depletion layer remains unchanged as the dendrite grows, as shown experimentally by Brissot [95]. Crevices between dendrite branches are not lithium depleted due to electrochemical shielding. Stress-driven electrodeposition/electrodissolution in the side branches that induces lithium depletion in the intervening electrolyte becomes apparent in those branches whose diffusion distance to the counter-electrode is the largest.



Figure 4.7.: Normalized lithium concentration for a high current density, 10 mA/cm^2 , at four selected instants: (a) 300 s (~ t_{Sand}), (b) 600 s, (c) 1200, and (d) 2600 s, in agreement with Bazant *et al.* [94]. The branched structure is a result of the combined effects of the localized stress distribution at the dendrite tip and the concentration depletion at the tip for $t > t_{\text{Sand}} = 292$ s. Localized elastic energy at the tip induces microstructural perturbations and results in the growth of thin and elongated dendrite branches. Repeated bifurcations of the initial hemispherical electrodeposit cause the growth of secondary, tertiary, and higher order dendrite arms. Darker regions high-light locations where overpotential and stress-induced electrodeposition dominate the kinetics.
Simulation results support the conclusion drawn by Brissot [96], and most recently by Bazant and Li [101] that dendritic growth under current densities of ~ 10 mA/cm² is a function of complex, local microstructural heterogeneities rather than due to long-range diffusion limitations. Analytically, the limiting current density is, $i_{\rm lim} = z \mathcal{F} D_l C_{\circ}/l = 321 \,\mathrm{mA/cm^2}$, and the corresponding Sand's time, $t_{\rm Sand} = \pi D_l \left(\frac{zC_{\circ}}{2i_{\rm app}}\right)^2 = 292 \,\mathrm{s}$, for $D_l = 4 \times 10^{-10} \,\mathrm{m^2 \, s^{-1}}$ [170], $C_{\circ} = 1 \,\mathrm{M} = 10^3 \,\mathrm{mol \, m^{-3}}$, $l = 12 \mu \mathrm{m}$ (Figure 4.2(c)), and $i_{\rm app} = 10 \,\mathrm{mA/cm^2}$. This limiting current value is consistent with the experimentally reported measurements by Brissot (164 mA/cm² for $l = 29 \mu \mathrm{m}$ and 241 mA/cm² for $l = 20 \mu \mathrm{m}$) [96] and Cui (152 mA/cm², 198 mA/cm²) [178]. For thicker cells, with $l \sim 300 \mu \mathrm{m}$, experimentally reported limiting current densities are smaller, in the 50 – 150 mA/cm² range, as reported in several experimental and theoretical studies [94,179,180]. Thus, the macroscopic applied current density always lies below the limiting current density but results in dendritic growth, as widely reported in literature [48, 96, 180, 181].

Figure 4.8 shows the heterogeneous electric field distribution ahead of the dendrite tip, for $i_{app} = 10 \text{ mA/cm}^2$. Results demonstrate that the local electric field in front of the dendrite tip is twice that of the macroscopic electric field for an initial hemispherical electrodeposit (see Figure 4.8(a)). As the electrodeposit grows and bifurcates into thinner whiskers, the electric field at the tip reaches ~ three times that of the macroscopic value (see Figure 4.8(c, d)), in agreement with numerical calculations from Srinivasan and coworkers [182]. This suggests that the local current density, $\vec{i} = \kappa_l \vec{E}$ reaches ~ 30 mA/cm² ~ 0.1 i_{lim} in front of the dendrite tips.



Figure 4.8.: Electric field distribution for a current density of 10 mA/cm^2 at four selected times: (a) 300 s, (b) 600 s, (c) 1200 s, and (d) 2600 s. Electric fields are highest at the dendrite branch tips (see inset (a)). As the dendrite grows, the metallic electrodeposit is shielded near the base regions (see insets (a) and (b)). The formation of secondary dendrite arms redistributes the electric field: the branch tips experience even higher electric fields while the electrolyte between the branches induce alternating regions of high and low electrical fields, which in turn results in preferential electrodeposition and electrodissolution regions. The shielded inner regions grow through electrochemically induced plastic flow.

Concurrently occurring local electrodeposition and electrodissolution (shown in Figure 4.9(c) and (d)) result in lateral asymmetry of the dendrite arms and make the dendrite prone to bend or develop kinks and thereby change the growth direction [134]. Similarly, once the dendrite branches fully develop, lithium slowly dissolves from the outer regions of the dendrite base (see Figure 4.9(d)) and increases the local ionic concentration in the electrolyte (see Figure 4.7(d)). Overall, these results demonstrate that for very high current densities ($i_{app} = 10 \text{ mA/cm}^2$), diffusion limitations influence the local electrodeposition rates and change the electrodeposit microstructure heterogeneously as a result of local electrochemical gradients. Further, branching of the electrodeposit is a result of the competition of concentration gradients and stresses. High electrodeposition rates induce compressive stresses at the tip [117], suppress electrodeposition, and enhance electrodeposition on the side branches.



Figure 4.9.: Lithium electrodeposition and electrodissolution rates for a current density of 10 mA/cm² at four selected times: (a) 300 s, (b) 600 s, (c) 1200 s, and (d) 2600 s. Inset (a) shows that the electrodeposition rate at the tip decreases due to diffusion limitations as specified by Sand's time ($t_{\text{Sand}} = 292$ s). Once the hemispherical electrodeposit splits into branches, the electrically shielded region becomes electrically and mechanically insulated (see inset (b)). Faces of the branch that are oriented away from the electric field are shielded. However, if they extend laterally, opposite overpotentials induce electrodissolution, as shown by the green regions in inset (c). Local mass transfer results due to electrodeposition and electrodissolution between adjoining secondary branches. Here, the externally exposed surfaces of the dendrite undergo slow electrodeposition on the sides (see inset (c)) until the dendrite branches fully develop (inset (d)). Similarly, the base of the dendrite is either electrochemically shielded or displays weak electrodissolution as a result of the dendrite contact area being in a compressive state of stress (see inset (d)).

Figure 4.10 shows the effect of applied current density on the electrodeposited microstructure, for fixed total amount of deposited charge. For a low current density (0.1 mA/cm^2) , the electrodeposit growth is driven by tip-controlled electrodeposition, but shaped through plastic flow (see Figure 4.10), and results in planar lithium growth [101,143]. For higher current densities (~ 1 mA/cm^2), electrodeposition rates dominate over the stress relaxation kinetics and favors the growth of dendrite arms, due to elastic energy localization [94, 133, 177]. The morphologies that are produced are a result of the joint spatial distribution of electrodeposition-controlled regions coupled to the plastic flow induced dendrite growth, in agreement with analytical results [144]. For very high current densities (~ 10 mA/cm^2), stress relaxation at the tip is slow due to fast mass accretion and thus remains confined at the the lower branches. A highly branched or dendritic morphology develops as a result of both

stress localization at the tips and concentration gradients ahead of the tips [94, 136]. This heterogeneous electrodeposition forms small surficial perturbations that are preferentially electrodeposited and results into thin and long, highly branched, lithium structures.



Figure 4.10.: Effect of applied current density on lithium growth for a total charge of 2600 C for three selected current densities: 0.1 mA/cm^2 (left column), 1 mA/cm^2 (middle column), and 10 mA/cm^2 (right column). The top row shows the lithium microstructure and the stress tensor distribution. The bottom row shows the plastic flow rate. For all three current densities, base-controlled growth dominates the initial stages of deposition. For very low current densities (0.1 mA/cm^2), stresses relax faster than the rate of electrodeposition and thus a planar electrodeposit is favored [95,143]. For intermediate current densities (1 mA/cm^2), surficial mechanical energy density localizes, suppresses local electrodeposition, and promotes dendrite branches [94, 136]. For high current densities (10 mA/cm^2), the system becomes diffusion limited, inducing large concentration depletion gradients in front of the dendrite tip that result in tip-controlled growth. Stress accumulation results in elongated branches, which in turn promotes further dendrite branching.

Figure 4.11 shows the concurrent growth of lithium electrodeposits on a flat anode substrate. The initial size distribution considered is in agreement with experimental reports from Cui and coworkers [100]. In Figure 4.11, the first column denotes the microstructure, the second column denotes the electric field, and the third column denotes the deposition rate. Results demonstrate that the electric field preferentially localizes at the tip of the larger dendrites, which thereby renders the smaller dendrites electrically shielded. Thus, the larger dendrites have more contributions from tip-controlled mechanism. After longer times, the larger dendrites bifurcate into branches. Faces of the branches that are electrically shielded either undergo no deposition or undergo dissolution and causes thinning of the branches.



Figure 4.11.: Electrochemical interactions of a multiple dendrite system for an applied current density of 10 mA/cm^2 . First column shows the microstructure, second column shows the electrical field, and third column shows the electrodeposition rate. Initial electrodeposit sizes are selected from the experimental lithium electrodeposit size distribution, as reported by Cui and coworkers [100]. Results show that large initial sizes dominate the growth process over the smaller sizes. From the initial instant, large hemispheres, nucleated on a flat substrate, favor localization of electric fields at their tips. Smaller electrodeposits in the vicinity of the large dendrites are electrically shielded. Electrodeposition rates are thus higher on the larger electrodeposits. With time, the size difference between the large and the smaller dendrites increases. At longer times, electrolyte between dendrite branches are also electrochemically shielded.

Figure 4.12 shows the mechanical interactions of the multiple dendrite system. The first column shows the stress distribution, the second column shows the hydrostatic stresses, and the third column shows the von Mises stress. At initial times, all electrodeposits are highly compressive stressed. Initial high von Mises stress cause base-controlled growth. At longer times, the base of the dendrite gets mechanically relaxed and the regions of the dendrite subjected to active electrodeposition gets stressed for continued electrodeposition. Thus lithium plastic flow occurs at the base at initial times and later at tip regions.



Figure 4.12.: Mechanical interactions of a multiple dendrite system for an applied current density of $10 \,\mathrm{mA/cm^2}$. First column shows the stress distribution, second column shows the hydrostatic stress, and third column shows the von Mises stress. Initial electrodeposit sizes are selected from the experimental lithium electrodeposit size distribution, as reported by Cui and coworkers [100]. Stresses are visualized in terms of Lamé's ellipses. Ellipse orientation denotes the principal stress direction. A pure hydrostatic stress is represented by a circle. Compressive regions are in blue and tensile regions are in red. At initial times, all electrodeposits are under large compressive stress. Initially high von Mises stress push the electrodeposits towards the counter electrode until stresses at the base are relaxed. Peripheral regions of the electrodeposits are under compressive stresses, while zero or tensile regions appear in the internal regions where stresses are relaxed. Smaller dendrites, electrically shielded, grow through the base-controlled mechanism until stresses are relaxed.

4.6 Conclusions

Figure 4.13 summarizes the different regimes of lithium electrodeposition as a function of normalized electrodeposit size, $\hat{r} = -\Delta g r/2\gamma \sim -\Delta g V^{1/3}/2\gamma$ and normalized applied current density, $\hat{i} = (z^2 \mathcal{F}^2 D_l C_{\circ}/\Delta g \Omega \kappa_i) \left(\frac{i_{\text{app}}}{i_{\text{lim}}}\right)$.



Figure 4.13.: Roadmap of lithium dendrite growth regimes as a function of electrodeposit size and applied current density. The black line denotes the kinetic limit of electrodeposit growth, and the blue line denotes the thermodynamic line for the stability of a hemispherical lithium nucleus. To the left of the red line and above the black line is the *base-controlled regime* where growth is driven by plastic flow of lithium. To the right of the orange line is the *Sand's regime*, where diffusion limitations at current densities, $\hat{i} = (z^2 \mathcal{F}^2 D_l C_{\circ} / \Delta g \Omega \kappa_i) \left(\frac{i_{\text{app}}}{i_{\text{lim}}}\right) > 2.5 \times 10^5$ result in the formation of branched dendritic structures. To the right of the green line is the *tip-controlled* regime, characterized by interfacial electrodeposition at the tip. Between the red, green and orange lines is the *mixed regime*, with contributions from the both the base and the tip. The dashed gray line denotes the onset of lithium plastic flow. Below the yield stress, elastic energy localized at the electrodeposit tips results in suppression of the electrodeposition rate and branching of the electrodeposit at sub-limiting current densities. Above the yielding limit, plasticity at the tips modifies, bends, or kinks the dendrite branches. In practical lithium battery operations, lithium grows mostly through the mixed-mode of growth, as denoted by the markers corresponding to experimental microstructures shown in Figure 4.1, which are compared with those simulated from the proposed framework.

The blue curve denotes the critical thermodynamic size of the electrodeposit. Lithium dendrites above the blue curve are stable, while those below the blue curve are unfavorable and will dissolve back into the electrolyte. Dendritic growth is completely suppressed by charging the cell with current densities in the *thermodynamic* suppression regime, as proposed earlier [104], and experimentally verified by Cui [100]. The black line embodies the kinetic limit for electrodeposits. Between the blue and the black line is the *incubation regime*, where stable lithium nuclei grow through local coarsening kinetics [100, 104]. To the left of the red line, *i.e.*, for low current densities and above the kinetic limit is the *base-controlled growth regime*, where lithium plasticity at the base dominates microstructural evolution. A critical current density, $\hat{i}^* = (z \mathcal{F} i_{\text{lim}} l) / (\Delta g \Omega \kappa_i) = 2.5 \times 10^5$, defined by the orange line, (for the chosen material properties, see Table 4.2), denotes the onset of the diffusion-controlled or Sand's regime, where highly branched dendritic structures develop due to diffusion limitations in the electrolyte, in agreement with Bazant *et al.* [94] At moderate current densities, in the $10^3 < \hat{i} < 2.5 \times 10^5$ range, tip-controlled growth occurs through interfacial electrodeposition kinetics. Below the plastic flow limit of lithium, shown schematically by the dashed gray line [144], localized elastic energy density suppresses electrodeposition kinetics at the tips and results in dendrite branches. For long deposition times, highly localized stresses result in plastic flow at the tips that distort and modify the shape of the dendrites, as noted in recent experiments by Steiger and coworkers [134]. Tip branching for $\hat{i} < 2.5 \times 10^5$ is driven by elastic energy density localization, while for $\hat{i} > 2.5 \times 10^5$ is driven by concentration gradients, as observed in classical dendritic growth. Typical current densities lie in the $0.1 < \hat{i} < 100$ range, with contributions from electrodeposition and elastic-plastic deformation, referred herein as the *mixed regime* [144]. Base-controlled growth induces initial columnar growth in the mixed regime, while at later stages, tip branching is induced by elastic energy density localization and enhanced by concentration gradients.

A direct comparison with experimental microstructures (see Figure 4.1 and corresponding markers in Figure 4.13) show excellent agreement with the numerical simulations – low current densities result in columnar structures and high current densities result in branched dendritic structures. Further, Figure 4.13 shows that most lithium electrodeposition experiments lie in a narrow strip in the mixed regime. In order to completely suppress dendritic growth, the electrodeposits should be limited to smaller sizes, as depicted by the thermodynamic suppression regime. Thus, dendrite-free lithium anodes are possible by designing time-dependent charging patterns that make incursions of length $t < \min(t_{\sigma}, t_{\text{Sand}})$ into the high current density regimes, without enabling the electrodeposit to grow beyond the kinetic limit (black line) and avoid either base-controlled, tip-controlled, or mixed mode of growth. The amplitude of the current density incursions will be a function of the state of charge, for larger dendrites will require a shorter characteristic time to develop a morphological instability.

In summary, a comprehensive theory has been developed to describe the microstructural evolution of lithium electrodeposits. This theory provides a roadmap to explore and identify the microstructural mechanisms controlling dendrite growth. Specifically, stresses on an electrodeposit arise from the local molar volume changes, as induced by the SEI layer, from adjoining electrodeposits, from the separator layer, or from the cell casing. Results suggest that lithium dendrite growth originates from a set of complex, coupled, electrochemomechanical driving forces that result in six regimes of behavior: (i) thermodynamic suppression regime, (ii) incubation regime, (iii) basecontrolled growth regime, (iv) tip-controlled growth regime, (v) mixed regime, and (vi) Sand's regime, each referring to a distinct growth (or suppression) mechanism.

5. DENDRITE-SEPARATOR INTERACTIONS

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5.1 Introduction

Theories and models that predict the dendrite nucleation and growth process in lithium-based batteries include the seminal work from Chazalviel, who proposed the concept of dendrite incubation time and critical current in the context of dendrites growing in a dilute electrolyte [110]. Monroe and Newman demonstrated dendrite growth as a function of the applied current density and incorporated the contribution of the dendrite tip radius [103]. Ely and García proposed regimes to denote stable, unstable, and growth conditions of an electrodeposit, and suggested that dendrite suppression can be improved by decreasing surface roughness of anode particles, engineering the size of the particles below the critical thermodynamic radius, limiting the plating potential below a critical value, and controlling the wetting properties of the electrodeposits [104]. Akolkar proposed an analytical model of the dendrite tip current density and commented that dendrite growth can be suppressed by lowering the cathodic transfer coefficient [179]. White and coworkers studied the effect of overcharging on lithium deposition and subsequent capacity fade [183]. Ryan et al. demonstrated power-law growth of dendrite morphologies, and delineated the flow of current and the variation of voltage along dendrite arms [184]. Recently, Ding et al. have suggested that dendrite growth can be suppressed by the addition of cations that form a protective shield on the dendrite, and force deposition of lithium ions in other non-dendritic regions [185].

Among the first phase field model descriptions on electrochemical systems [145– 147, 186], Guyer et al. spatially resolved the charge distribution, modeled the electrodeposition from an electrolytic medium, introduced the concept of electrodissolution, and proposed parameters to tune a Butler-Volmer (sharp interface) description. García, Bishop and Carter pioneered the generalities of phase field in electrically active systems, and formulated generalized variational principles to describe the kinetics in ceramic and metallic systems alike [145, 146]. Okajima et al. proposed a phase field model that incorporated Butler-Volmer kinetics in the diffusivity of the depositing species [148]. Chen et al. proposed a non-linear one dimensional phase field model that included a source term to capture the qualitative kinetic behavior of an electrodepositing solid with a scalar fixed overpotential [154]. Most recently, Ely et al. [138] described the phase evolution of dendritic structures that account for the Butler-Volmer kinetics as a contribution to Allen-Cahn type kinetics, and readily predicted the interactions of growing dendritic structures on the underlying substrate, as well as the lateral nuclei-nuclei interactions, in agreement with existing experimental data [48, 103, 187] and a previous analytical formulation [104].

In this context, and in spite of the great progress, a thermodynamic description that includes the effect of the separator on dendritic growth, or that attempts to rationalize the porous structure of emerging or existing separator structures remains unavailable. In this thesis, we systematically examine the effect of pore size in a separator to outline its effect on the resultant dendrite morphology in order to provide a rational basis to design improved battery separators that can suppress or at least delay dendrite growth.

5.2 Theoretical Framework

For a microstructurally inhomogeneous system, the total Gibbs free energy of transformation of lithium dissolved in the liquid electrolyte to solid metallic lithium is defined as:

$$\Delta G_T[\xi,\rho] = \int_V \left[\Delta g_v(\beta)p(\xi) + \rho\phi\right] dV + \int_V \left[W_{\xi}g(\xi) + \frac{\varepsilon_{\xi}^2}{2}|\nabla\xi|^2\right] dV \tag{5.1}$$

where metallic lithium is denoted by the phase field variable ξ [188–194], which varies continuously from zero in the electrolyte to one inside the solid lithium phase. The electrolyte and the polymer phase that comprises the separator is described through a static phase field variable β , which is zero inside the polymer phase of the separator, and one otherwise. The charge density is represented by the phase variable ρ . $\Delta g_v(\beta)$ is the bulk chemical free energy density of transformation, ϕ is the local electrostatic potential, W_{ξ} is the interfacial energy barrier for phase transformation, and ε_{ξ}^2 is the gradient energy coefficient. $p(\xi) = \xi^3(6\xi^2 - 15\xi + 10)$ is an interpolation function, and $g(\xi) = \xi^2(1-\xi)^2$ is a double well function [191, 195]. The definitions of all the used variables are summarized in Table 3.1.

The first integral on the right side of Equation (5.1) embodies the volumetric contributions for electrodeposition, so negative free energies of transformation or negative galvanostatic potentials will locally favor the formation of the solid lithium phase, while positive contributions will favor redissolution of lithium into the electrolyte phase. The second integral corresponds to the free energy contributions to create a solid-electrolyte interface, as it has been classically described [188,189,191,192]. The bulk chemical free energy density of transformation in the electrolyte is distinguished from the spatial contributions of the polymer fibers through the equation:

$$\Delta g_v(\beta) = \Delta g_{v,\xi} p(\beta) + \Delta g_{v,\beta} (1 - p(\beta))$$

 $\Delta g_{v,\xi}$ is the chemical free energy density of transformation to solid lithium from the electrolyte, and $\Delta g_{v,\beta}$ corresponds to the free energy density of transformation of dissolved lithium to solid lithium inside the polymer phase.

The time evolution of the solid lithium phase ξ , a locally non-conserved order parameter, and the local charge density ρ , a locally conserved order parameter is described by [131, 188]:

$$\frac{\partial \xi}{\partial t} = -M_{\xi} \frac{\delta \Delta G_T}{\delta \xi} + \Omega \vec{\Gamma} \cdot \nabla \xi$$

$$= -M_{\xi} \left[\Delta g_v \frac{\partial p}{\partial \xi} + W_{\xi} \frac{\partial g}{\partial \xi} - \varepsilon_{\xi}^2 \nabla^2 \xi \right] + \Omega \vec{\Gamma} \cdot \nabla \xi;$$

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot M_{\rho} \nabla \frac{\delta \Delta G_T}{\delta \rho}$$

$$= -\nabla \cdot M_{\rho} \nabla \phi$$
(5.2)

where $M_{\xi} = (\alpha j_o \Omega^2)/(6RT\delta_{\xi})$, is the mobility of the interface, $W_{\xi} = 3\gamma_{NE}/\delta_{\xi}$, $\varepsilon_{\xi}^2 = 6\gamma_{NE}\delta_{\xi}$, and δ_{ξ} is the width of lithium-electrolyte interface, as described by Ely *et al.* [138]. The charge mobility, *i.e.*, the electrical conductivity is, $M_{\rho} = \sigma_{\xi} p(\xi) + \sigma_{\beta}(1-p(\xi))$, where σ_{ξ} is the electrical conductivity of metallic lithium, and $\sigma_{\beta} = \sigma_L p(\beta) + \sigma_P(1-p(\beta))$ is the conductivity in the separator phase. Here, σ_L is the conductivity in the electrolyte and σ_P is the conductivity in the polymer fibers of the separator. The source term $\Omega \vec{\Gamma} \cdot \nabla \xi$ accounts for lithium plating at the dendrite-electrolyte interface. The lithium electrodeposition rate, $\Gamma = \vec{\Gamma} \cdot \hat{n}$, where \hat{n} is the normal to the interface, is described by the modified Butler-Volmer equation: [104]

$$\Gamma = j_{\circ} \left(\exp\left[\left(1 - \alpha\right) \left(\frac{zF\eta}{RT} + \frac{\gamma_{NE}\kappa\Omega}{RT} \right) \right] - \exp\left[-\alpha \left(\frac{zF\eta}{RT} + \frac{\gamma_{NE}\kappa\Omega}{RT} \right) \right] \right)$$
(5.3)

which for small deviations from equilibrium, *i.e.*, for $(zF\eta + \gamma_{NE}\kappa\Omega)/RT \ll 1$, reduces to:

$$\Gamma \approx \frac{j_{\circ}}{RT} (zF\eta + \gamma_{NE}\kappa\Omega)$$
(5.4)

 j_{\circ} is the exchange current density, α is the charge transfer coefficient, γ_{NE} is the surface tension, and κ is the curvature of the interface. η is the interfacial overpotential, and is described by the equation $\eta = -\vec{\delta_{\xi}} \cdot \nabla(\delta \Delta G_T/\delta \rho) = -\vec{\delta_{\xi}} \cdot \nabla \phi$, in agreement with Tang *et al.* [196] and Cogswell and Bazant [197]. Equations (5.3) and (5.4) suggest that the lithium deposition rate depends on two opposing contributions: the local overpotential-induced plating that assists deposition and grows the electrodeposit, and the Laplace pressure-induced lithium dissolution that inhibits deposition and shrinks negatively curved electrodeposits.

5.3 Microstructure Representation and Numerical Setup

At its core, the separator comprises a porous layer of characteristic pore size a, whose fibers provide mechanical integrity to the layer and tend to deflect the growing dendrite. In order to assess the impact of these fibers, to distinguish between the potential detrimental contributions that a random porous structure will have, and to systematically rationalize the impact of the different geometrical configurations, a two dimensional separator morphology was modeled. Here, parameters such as the horizontal interlayer spacing, x, and vertical interlayer spacing, h, as well as the inclination, θ , between fiber arrangements can be systematically assessed. Figure 5.1 shows the modeled simulation domain.



Figure 5.1.: Simulated separator cross-section. A hemispherical lithium nucleus (in orange) is shown at the bottom surface at t = 0. An array of circles (in dark gray) denotes the polymer fibers of the separator. The light gray background denotes the electrolyte. A constant current density, I, is imposed on the top boundary (cathode side). The substrate (anode side) is electrically grounded. θ is the angle of inclination of the separator channel. x is the horizontal distance between centers of two neighboring fibers, and h is the vertical distance between the two horizontal center lines through the centers of the fibers in two consecutive layers. a is the pore radius, and r is the radius of the inclined channel.

At t = 0, a lithium nucleus of radius 1.33 μ m was placed at the center of the bottom anode surface. The initial radius was chosen such that it was bigger than the critical thermodynamic radius (see Table 5.1). The contact angle of the lithium nucleus with the anode surface was 90°. A constant current density, I, was imposed on the top boundary, and the bottom boundary was electrically grounded. Used material parameters are summarized in Table 5.1.

Parameter	Value	Units	Refs.
F	96 485.33	$ m Cmol^{-1}$	_
K	1/12	_	
T	300	Κ	_
j_{\circ}	-3.1×10^{-4}	$ m mols^{-1}m^{-2}$	[48]
r_{eq}^{*}	1.25×10^{-6}	m	[48]
z	1	_	—
$\Delta g_{v,\xi}$	-2.7456×10^{6}	${ m J}{ m m}^{-3}$	[48]
$\Delta g_{v,\beta}$	$-100 \times \Delta g_{v,\xi}$	$\mathrm{Jm^{-3}}$	—
Ω	1.3×10^{-5}	$\mathrm{m}^3\mathrm{mol}^{-1}$	[132]
γ_{NE}	1.716	$\mathrm{Jm^{-2}}$	[103]
δ_{ξ}	7×10^{-8}	m	[174]
σ_L	4.44×10^{-6}	${ m S}{ m m}^{-1}$	[198]
σ_P	$\sigma_L/10^4$	${ m S}{ m m}^{-1}$	_
σ_{ξ}	$100 \times \sigma_L$	${ m S}{ m m}^{-1}$	_

Table 5.1.: Values of physical parameters used in calculations.

Equations (5.1) through (5.4) were implemented in FiPy, a set of open source finite volume libraries [199]. Simulations were carried out on a 2.4 GHz, sixteen core, Ubuntu 10.04 server with 128 GB of RAM. The tolerances for both the convergence and the Newton solver were set to 1×10^{-6} . Each simulation took approximately 36 h of wall time.

5.4 Results and Discussion

Figure 5.2 shows the growth of a dendrite for a current density $I = 0.11 \text{ mA/cm}^2$, for a separator whose pore radius, $a = 1.05\mu\text{m}$, and layer interspacing, $h = 0.7\mu\text{m}$. Here, the lithium electrodeposit deviates from its initial hemispherical shape (see Figure 5.2(a)) early on the simulation, and grows vertically until it penetrates the central the pore space between the polymer fibers (see Figure 5.2(b)). Growth also proceeds laterally and non-uniformly because every pore is not a favorable location for the electrodeposit to penetrate the separator (see Figure 5.2(c)). After a long period of time, t = 10.32 h, the central branch fully retreats while the side dendrites fully penetrate into the counter electrode (see Figure 5.2(d)).



Figure 5.2.: Dendrite growth through the separator for a current density of $I = 0.11 \text{ mA/cm}^2$, pore radius, $a = 1.05\mu\text{m}$ and layer interspacing, $h = 0.7\mu\text{m}$. (a) shows initial lithium hemispherical shape morphology at t = 0 s. (b) shows lithium dendrite penetrating through central pore at t = 3.44 h. (c) shows growth of side branches through alternate pores at t = 6.88 h, and (d) shows retreat of the central branch, while side branches grow through lateral oblique linear channels at t = 10.32 h.

The resultant electrodeposit morphology at the end of the recharge sequence (Figure 5.2(d)) is a result of the overpotential localization during growth (see Figure 5.3(a)). Here, the interfacial overpotential, $\eta = \vec{\delta_{\xi}} \cdot \vec{E}$, is enhanced at the tip of the dendrite due to its coupling to the local electric field. The electric field has its highest value in the electrolyte at the tip of the dendrite, controls the growth direction, and shields the electric field behind the lithium tip. Such a localized, oriented electric field is a result of the local pore space that follows the fiber arrangement. As a result, the two side branches self-induce an electrochemically shielded region between them that is responsible for suppressing the growth of the central branch (see Figure 5.3(b)). In addition, the low electrical conductivity of the polymer fibers in the separator imposes an additional scattering effect on the electric field that favors dendrite suppression.



Figure 5.3.: Electrodeposition fields distribution for lithium growth subjected to a current density of $I = 0.11 \text{ mA/cm}^2$. (a) shows dendrite morphology at t = 10.32 h, (b) shows the corresponding electric field distribution, and (c) shows local electrode-position and electrodissolution rates. The vectorial electric field is localized at the dendrite tip and scatters away from the separator fibers. The electric field is negligible inside the dendrite, and has a high value inside the polymer phase of the separator. Simulations demonstrate that the electric field concentrates at the tip of the dendrite and enhances the localized electrodeposition rate. Neighboring branches, constrained by the separator fibers, become unstable and attempt to redissolve. Joule heating is favored along the dendrite branches.

Inside the dendrite, the large potential difference that exists across the thickness of the separator induces an electronic current along the length of the dendrite arms (see Figure 5.3(b)), in agreement with experimental investigations carried out by Rosso and coworkers [200]. Performed simulations show that such a current would induce a large localized Joule heating, $P = \sigma_{\xi} E^2 \approx 10^8 \text{ W m}^{-3}$, which in turn would favor the appearance of other irreversible side reactions such as the melting of the separator polymer, exothermic reactions in the electrodes, ignition of the electrolyte, and degradation of the SEI layer [201–203]. In contrast, in the back of the anode, the current density in the bulk of the electrodeposit is negligible because of its high electrical conductivity combined with its large width. Additional snapshots of the electric field distribution can be seen in the Appendix.

As a result of the inhomogeneous electric field distribution, the dendrite tips experience increased deposition rates (see Figure 5.3(c)), which in turn further pro-

mote dendritic growth. In contrast, the dendrite branches along their length comprise alternating regions of localized plating and electrodissolution due to the disruptive effect of the separator fibers. Thus, those regions that experience local negative curvature are prone to redissolve back into the electrolyte, and those regions along the length of the oblique dendrite that directly face the counter electrode will undergo enhanced electrodeposition. The central region directly in contact with the polymer fibers will be in dynamic equilibrium; while the large negative overpotential will favor the dendrite to grow inwards, the positive chemical free energy of transformation inside the fibers will force them out. Similarly, the growth between the fibers will be a result of the competition between the overpotential-induced plating and the Laplace pressure-induced electrodissolution.

For the simulated separator architecture, for current densities $I < 0.10 \text{ mA/cm}^2$, e.g., $I = 0.09 \text{ mA/cm}^2$, the dendrite was completely stopped by the separator (see Figure 5.4(a) and 5.4(i)), and the electrodeposition rate is locally balanced by the dissolution rate. Simulations demonstrate that for the simulated separator morphology, a critical current density $I_c = 0.10 \text{ mA/cm}^2$ exists, below which the dendrite will be stopped by the separator (see Figure 5.4(b) and 5.4(ii)). For higher current densities, e.g., $I = 0.11 \text{ mA/cm}^2$, dendrites will traverse the entire width of the separator (see Figure 5.4(c) and 5.4(ii)).



Figure 5.4.: Effect of current density on dendrite growth. (a) shows that a dendrite is fully arrested for $I = 0.09 \text{ mA/cm}^2 < I_c$. Inset (i) shows that dendrite morphology is a result of the dynamic balance between electrodeposition that occurs in the pore space between the polyethylene fibers and the electrodissolution that is induced by the curvature of the lithium growth and the energy barrier imposed by the fiber. (b) shows that a critical current $I_c = 0.10 \text{ mA/cm}^2$ exists at which the dendrite penetrates the first row of polyethylene fibers, but is arrested by the next layer. (ii) shows that the localized increase of electrodeposition rate is balanced in the central branch by lateral electrodeposition, surface tension driving forces, and symmetry of the separator geometry. The symmetry is broken in the side branches because of selfshielding effects. (c) shows that for a higher current density, $I = 0.11 \text{ mA/cm}^2 > I_c$, the dendrite fully penetrates the separator that might cause a short-circuit. (iii) shows that the tip of the dendrite favors local lithium plating, while the length of the dendrite is subjected to localized electrochemical dissolution events as a result of the local electrochemical interactions with the polyethylene fibers.

Overall, the performed analysis suggests that as the current density increases, the lithium electrodeposit finds a pore orientation at a local angle θ , to grow where the local electric field is maximized. For the analyzed separator configuration, these orientations are locally determined by position-determined differences of electrodeposition and electrodissolution at the dendrite tip, which in turn will lead to find pore orientations with minimal tortuosity. An expression for the critical current density, I_c , can be analytically cast by calculating the potential drop along a side branch inclined at an angle θ . Since the potential drop along the metallic dendrite is negligible, the only significant potential drop occurs at the dendrite-electrolyte interface. Following Ohm's law, $I_c \cos \theta = -\sigma_i \eta / \delta_{\xi}$, and the local overpotential, η , in the electrolyte at the tip of the dendrite is expressed as:

$$\eta = -\frac{(I_c \cos \theta)\delta_{\xi}}{\sigma_i} \tag{5.5}$$

where I_c is the critical current density, and δ_{ξ} is the width of the interface at the dendrite tip. σ_i is the conductivity at the metal-electrolyte interface, and is defined as $\sigma_i = K(\sigma_{\xi} + \sigma_L)/2$, where K = 1/12 is a shielding factor that is fit to account for the non-idealities of the dendrite tip shape. θ is the oblique path angle that the dendrite makes with the in-plane vertical axis (see Figure 5.1).

The critical radius to form a thermodynamically stable nucleus in the separator is $r_{eq}^* = -2\gamma_{NE}\Omega/(zF\eta_{eq} + \Delta g_v\Omega)$ [104], where $\Delta g_v = \Delta g_v(\beta)$ and the separator pore radius $a = r_{eq}^*/\cos\theta$. Thus, the critical thermodynamic current density, $I_{c,eq}$, is:

$$I_{c,eq} = \frac{\sigma_i \Delta g_v \Omega}{zF \delta_{\xi}} \left(\frac{2\gamma_{NE}}{a \Delta g_v \cos^2 \theta} + \frac{1}{\cos \theta} \right)$$
(5.6)

Equation (5.6) is written in dimensionless form as:

$$\hat{I}_{c,eq} = \frac{1}{\hat{a}\cos^2\theta} - \frac{1}{\cos\theta},\tag{5.7}$$

where $\hat{I} = I/I_{char}$, and $\hat{a} = a/a_{char}$. Here, $I_{char} = -(\sigma_i \Delta g_v \Omega)/(zF\delta_{\xi})$ is the characteristic current density, and $a_{char} = -2\gamma_{NE}/\Delta g_v$ is the characteristic pore radius.

Similarly, the growth rate of a single isolated dendrite of curvature $\kappa = 2/r$ can be expressed as $v = dr/dt = \Gamma\Omega = j_{\circ}\Omega(zF\eta + 2\gamma_{NE}\Omega/r)/RT$ from Equation (5.4). Thus, for dr/dt = 0, the critical kinetic radius, $r_k^* = -2\gamma_{NE}\Omega/zF\eta_k$, *i.e.*, $\eta_k = -2\gamma_{NE}\Omega/zFr_k^*$. Hence from Equation (5.5), for a separator pore radius $a = r_k^*/\cos\theta$, the critical kinetic current density at which the local overpotential is balanced by the Laplace pressure-induced dissolution, is:

$$I_{c,k} = \frac{2\gamma_{NE}\Omega\sigma_i}{zFa\delta_{\xi}\cos^2\theta}$$

and is expressed in dimensionless form as:

$$\hat{I}_{c,k} = \frac{1}{\hat{a}\cos^2\theta} \tag{5.8}$$

where $\hat{I}_{c,k} = I_{c,k}/I_{char}$ is the dimensionless critical kinetic current density.

As readily demonstrated by the performed PFM simulations, the orientation of the pore structure affects the stability of the dendrite inside the separator. Until the dendrite reaches the separator, the growth is vertical, *i.e.*, $\theta = 0^{\circ}$. However, as the dendrite attempts to grow through the separator, it inclines at angle θ according to the internal pore structure of the separator (see Figure 5.1). Equations (5.7) and (5.8) suggest that the critical current densities $I_{c,eq}$ and $I_{c,k}$ that the separator can withstand are maximal when θ reaches an extremal value, *i.e.*, $\theta_{max} = 90^{\circ}$. Therefore, a fully horizontal pore structure provides perfect dendrite suppression. However, due to the periodicity of the separator morphology, the optimal orientation is constrained by the horizontal and vertical spacing between each layer. For the specific case in which x = h, $\theta = 45^{\circ}$ and $\theta = 0^{\circ}$ are equivalent orientations. Hence, the maximum inclination angle occurs when a fiber cross-section is placed directly above the mid-point between two neighboring fibers in the layer below it, *i.e.*, $\theta_{max} = \arctan((x/2)/h) = 26.5^{\circ}$.

The analytical description summarized by Equations (5.7) and (5.8) defines the existence of several regimes of dendrite stability and growth (see Figure 5.5). Specifically, four experimentally accessible regimes of behavior are identified.



Figure 5.5.: Predicted regimes of dendrite behavior in a porous separator: the *suppression regime*, below the blue curve, highlights the loci of pore sizes and recharge rates that are thermodynamically unfavorable for dendrites to grow; the *permeable regime*, below the black line, where dendrites cannot penetrate more than the very surface of the separator (the first layer of fibers); the *penetration regime*, between the red and the black line where dendrites rely on electrochemical shielding to find a thermodynamically stable pore to persist inside the separator; and finally, the *short-circuit regime*, to the right of the red line, where a combination of electrochemical enhancement at the dendrite tip and lateral shielding favors a subpopulation of electrode posit branches to traverse the entire width of a separator to reach the counter electrode and cause a short-circuit. A fifth regime, delineated by the gray dotted line highlights the stability of the dendrite inside the inclined channels. Insets show predicted morphologies at representative locations.

The blue solid line represents the critical thermodynamic limit for $\theta = 0^{\circ}$ and outlines the boundary of thermodynamic stability of a dendrite in contact with the

bottom surface of a separator layer. Dendrites below this line, in the suppression regime, will redissolve into the electrolyte until they are not in contact with the separator. The black continuous line embodies the kinetic limit for $\theta = 0^{\circ}$. Thus, the region between the blue and the black line is the *permeable regime*, where dendrites are energetically favored, and hence wet the separator. The red solid line denotes the kinetic limit for pores at an orientation $\theta = 26.5^{\circ}$. The region between the black and the red line is the *penetration regime*, where dendrites will grow into the separator, but the internal structure of the separator will make dendrites kinetically prohibitive to go through the porous structure. Finally, the region to the right of the red line denotes the *short-circuit regime*, where ramified electrodeposits will find a path to traverse the length of the separator and internally short-circuit the battery. Dendrites in separators with pore sizes greater than the thermodynamic critical radius, *i.e.* $\hat{a} = -a\Delta g_v/2\gamma_{NE} > 1$, will be deflected by the polyethylene fiber structure, but will not stop the dendrites from crossing. Such condition is represented by the vertical red line. A potential fifth regime, delineated by the dotted gray line, represents the thermodynamic limit for $\theta_{max} = 26.5^{\circ}$, and denotes the stability of the dendrite inside the inclined channel. However, as seen from Figure 5.5, this regime extends over a very narrow region and hence is not distinguishable from the already defined suppression regime.

In order to fully assert the validity of the described regimes of behavior, PFM simulations were performed as a function of pore size and current density, for separators that satisfy $\theta = \theta_{max} = 26.5^{\circ}$, at representative locations shown in Figure 5.5. Simulations demonstrate perfect agreement with the general trends analytically predicted, and support the fact that dendrite growth across the separator is inhibited below the critical kinetic current $I_{c,k}$. Further, for $\hat{a} = 0.2$ and $\hat{I} = 7.5$, a high plating rate and small pore spacing induce a morphological instability (see Figure 5.6(a)), that leads to lithium deposits detachment in the electrolyte inside the porous cathode. Such an event is a result of localized electrodissolution in the vicinity of localized high electroplating rate.



Figure 5.6.: Dendrite morphology for different current densities and pore sizes. (a) shows that for small pore sizes and high current densities, e.g., $\hat{a} = 0.2$, $\hat{I} = 7.5$, the dendrite detaches inside the separator channel as the width of the dendrite arm falls far below the critical thermodynamic radius. (b) shows that for intermediate values of pore size and current densities, e.g., $\hat{a} = 0.45$, $\hat{I} = 3.5$, the dendrite growth is stable, and further grows lithium branches. (c) shows that for porosities larger than the critical thermodynamic radius, and even low current densities, $\hat{a} = 1.2$, $\hat{I} = 0.95$, the dendrite penetrates the separator entirely. (i - iii) show the spatial distribution of local lithium plating and dissolution rate.

The resultant isolated deposits constitute Joule heating centers that are detrimental to the electrochemical stability of the cell. The truncated branch from which the lithium arm detached will temporarily retreat until the local power density increases to values that will enable to repeat the kinetic event and grow another branch. Dendrites in pore sizes that are comparable in size to the critical nuclei will remain stable and will traverse the separator width (see Figure 5.6(b)). Such structures will result in a local internal short-circuit event. Finally, for pore sizes larger than the critical pore size, $\hat{a} > 1$, e.g., $\hat{a} = 1.2$, $\hat{I} = 0.95$ (see Figure 5.6(c)), the effect of curvature is so small that it imposes no limits for electrodeposits to traverse the separator. For large pore sizes, i.e., $\hat{a} > 1$, even low current densities, $\hat{I} < 1$, will favor the growth of the arborescent morphology when lithium interacts with the polyethylene fibers, and will not stop its further development. For a very high current density, $\hat{I} = 11$ ($I = 0.22 \text{ mA/cm}^2$) and small pore radius, $\hat{a} = 0.2$ ($a = 0.25 \mu$ m), a floating lithium deposit facing the cathode is subjected to a high overpotential that favors its growth, while the sides directly facing the anode experience an overpotential of opposite polarity that favors its dissolution into the electrolyte (see Figure 5.7). The combined effect leads to the apparent motion of the deposit predicted as "dead lithium," in agreement with experimental observations by Arakawa *et al.* [99,133] and others [102,204].



Figure 5.7.: Dendrite detachment and apparent motion process, for $\hat{a} = 0.2$, $\hat{I} = 11$. (a) captures dendrite dissolution rate at the region of detachment at t = 2.30 h. (b) shows that at t = 2.68 h, an electrodeposit detaches from the main dendrite arm. (c) shows that the detached electrodeposit has moved towards the cathode at t = 3.09 h. The surface of the electrodeposit that faces the cathode undergoes deposition due to a positive overpotential, whereas the surface facing the anode, undergoes electrodissolution due to a negative overpotential. Concurrent deposition and dissolution on two opposite faces creates an apparent motion of the detached electrodeposit debris towards the cathode. This electrodeposit shields the electric field in the region below it as seen from the decrease in the deposition rates on the right branch of the main dendrite in (b) and (c), and causes it to retreat.

Calculations suggest that small pore sizes, for which $\hat{a} < 1$, will deliver improved recharging performance, and withstand higher current densities. However, in

a real separator the pore size belongs to a probability distribution, so for an average pore size and associated polydispersity, simulations demonstrate that the largest pore radius must lie in the *suppression regime*, given a current density application. For commercial separators, average pore diameters range between 0.1 μ m and 2.2 μ m [50]. At the lower end of the spectrum, and for the material properties in Table 5.1, for $a = 0.05\mu$ m ($\hat{a} = 0.04$), a pore radius $a = 0.0553\mu$ m would allow dendrites to penetrate the separator at even 90% of the average critical current density. Here, the maximum pore size is 10.62% higher than the average pore size. For the same current density restrictions and for larger average pore radii, *e.g.*, $a = 1\mu$ m ($\hat{a} = 0.8$), the maximum allowable pore radius is $a = 1.02\mu$ m, which is only 2% bigger than the average pore radius. Overall, Figure 5.5 shows that the allowable pore size distribution is wider when the average pore size is smaller, and the allowable pore size distribution becomes narrower for larger average pore sizes.

The model accounts for varying properties of the polymeric separators that include the differences in polymeric material and their corresponding electrical properties, the arrangement and size of the pores, and relates these variables to the electrochemical parameters of the system. The Y axis in Figure in 5.5 refers to a dimensionless current density, and the X axis denotes a dimensionless pore size. The dimensionless number on the Y axis, $-(IzF\delta_x i)/(\sigma_i\Omega\Delta g_v)$ explains that if for an algebraic increase of the free energy of lithium nucleation Δg_v , *i.e.*, when dendrite nucleation is unfavorable, the applied current density I must be increased for an equivalent dendrite growth. Similarly, if the electrical conductivity of the medium (either of the electrolyte or the separator) ahead of the dendrite tip increases, the local overpotential η , which is the driving force for electrodeposition, drops, and higher current densities are required for dendrite formation. Hence, higher electrical conductivity of separators and electrolytes, *i.e.*, lower MacMullin numbers, are desired not only to decrease impedance drops across the separator as discussed earlier, but also to suppress dendritic growth. On the other hand, the dimensionless number $a\Delta g_v/2\gamma_{NE} = a/(2\gamma_{NE}/\Delta g_v) = a/r_{eq}^*$ that defines the horizontal axis compares the pore size of the separator to the thermodynamic radius of lithium nucleation. The number delineates that if the critical thermodynamic radius of nucleation is larger, then larger pore sizes of the separator are required for the dendrite to penetrate the separator. From the above interpretations, both Celgard[®] and Solupor[®] separators have some advantages and disadvantages: while Celgard[®] separators have low pore diameters, 0.02 μ m - 0.03 μ m [57], for Solupor[®] separators, the pore diameters are of the order of 1 μ m; on the other hand, the MacMullin numbers for Solupor[®] separators are lower than those of Celgard[®] [50].

5.5 Summary and Conclusions

Phase field simulations of dendrite growth through a separator in a lithium-ion battery demonstrate the existence of a critical current density below which dendrite penetration can be fully suppressed. Calculations highlight the ability of a separator to stop, deflect, and destabilize a dendrite. In addition, dendrites were shown to be favorable Joule heating concentrators that may cause the separator to melt, the SEI to decompose, and the electrolyte to become unstable. Further, for very small pore sizes, dendrites break into smaller metallic debris, referred to as "dead lithium," which have the potential to migrate towards the cathode. An analytical model based on the performed simulations indicates that the critical current density is a function of the pore size of the separator and the angle of inclination of the pore channels between the polymer fibers. Four regimes of dendrite growth have been identified: (i) the suppression regime, where dendrite growth is thermodynamically unfavorable; (ii) the *permeable regime*, where the dendrite growth is kinetically prohibited beyond the first layer of the separator; (iii) the *penetration regime*, in which the dendrites penetrate the first layer, but are trapped within the oblique channels of the separator; and (iv) the short circuit regime, where dendrites penetrate the entire width of the separator. These four regimes of dendrite growth serve as a starting point, a design map, to explore and select the optimal geometry and characteristic pore size of the separator for a given power density application.

6. CONCLUSIONS AND FUTURE WORK

The thesis describes the identification and quantitative demonstration of the physical mechanisms that lead to capacity loss and safety issues in batteries. A full cell, physics-based reduced order capacity loss model was developed for the first time, was validated with commercial $\text{LiNi}_x \text{Mn}_y \text{Co}_z \text{O}_2$ -graphite cells, and can be easily extended to to cells with LiFePO_4 , LiMn_2O_4 , or LiCoO_2 cathode, and $\text{Li}_4\text{Ti}_5\text{O}_{12}$, graphite, or lithium metal anode. The development of capacity loss models for each of these chemistries is largely dependent on the availability of practical, relevant experimental data, ranging from material properties for accurate model behavior and capacity loss data for model validation. With recent advances in computer architectures and computational frameworks, physics-based models, such as the one proposed in Chapter 2, can be integrated in the Battery Management System of an electric vehicle. The framework proposed herein is ideal for on-the-fly capacity loss calculations on the vehicle and for testing battery packs and cells for automotive and electronics applications.

Most EVs are charged overnight through a standard convenience outlet (Level 1, 120 V, AC in US and 230 V, AC in Europe). Level 2 charging involves public or private charging stations (240 V, AC US or 400 V, AC) and usually takes 1–4 hours. Level 3 commercial charging facilities (480 V AC to DC) charge a vehicle typically in less than an hour. While the present charging levels refer to commercial batteries with graphite anodes, the developed dendrite growth framework identifies current densities for more dendrite-prone lithium metal anodes. Results suggest that, currents below 0.1 mA/cm^2 will completely suppress dendrite growth. Fast charging with short current pulses of 100 mA/cm^2 along the minimum growth line (see dashed gray line in Figure 4.13) to charge lithium metal anodes batteries in less than an

hour, following Level 3 charging protocols, is envisioned. Physically, while the high current pulses move lithium rapidly towards the anode, the low current pulses allow the stresses on the lithium metal anode and dendrites to relax and avoid high stresses that cause plastic flow. The duration of these high current pulses must be shorter than both the dendrite incubation time, t_o , and plasticity time, t_σ . For example, for the one of the most widely used commercial LIB electrolytes, 1 M LiPF₆ salt in 1:1 (by volume) EC:DMC liquid organic solvent, $t_o = 1.514$ s and $t_{\sigma} = 507$ s. t_o and t_{σ} for other electrolytes can be readily obtained from the dimensionless map in Figure 4.13. Thus a current density corresponding to the gray line and below the horizontal section of the blue line, *i.e.* ~ 50 mA/cm², 1 s pulse followed by a 1 s rest pulse, *i.e.* $I_{app} = 0$, will result in a maximum dendrite size of 10 nm ($\hat{r} = 1$), which is thermodynamically unstable when the charging ends and will thus dissolve back into the electrolyte. Such a pulse would dramatically decrease the charging time by a factor of 25 ×, and potentially reduce the overnight charging time (~1 mA/cm²) to 30 minutes.

Recent efforts in capacity loss modeling show a transition from regression-based and equivalent circuit models towards more physics-based models. With recent advances in computer architectures and computational frameworks, physics-based models, as the one proposed in Chapter 2, are computationally efficient for integration in the Battery Management System of an electric vehicle. Two topics are potential directions for future research in reduced order battery modeling:

• Reduced order modeling of different NMC chemistries, NMC111, NMC532, NMC811 [205, 206] are potential future directions. Ni-rich NMC chemistries are of particular interest for high energy density batteries [207, 208]. While the fundamental degradation mechanisms of NMC chemistries have been demonstrated in this dissertation, the differences in the electrochemical performance and degradation of these promising NMC grades needs to be better understood before they are fully commercialized.

Design of fast charging protocols with minimal degradation based on reduced order modeling approaches are highly sought by the battery research and industry community [209–211]. Experiments and models thus need to accurately devised to work for charge-discharge rates at least 5 C (*i.e.*, charge or discharge in 1/5 hour). The charge-discharge protocols need to be developed in conjunction with reduced-order degradation models in order to concurrently minimize charging time and degradation.

The accuracy of the reduced order models is largely dependent on the experimental observations and data and their physical interpretation through continuum models that decouple the contribution of individual mechanisms. While recent advances in phase field modeling have modeled individual physical phenomenon, their consistent coupling to describe a battery are still under development. In this regard, phase field modeling for the following topics are potential future work.

- Phase field models of SEI growth: The formation of the solid electrolyte interphase (SEI) layer is one of the less understood mechanisms of battery degradation. The SEI is believed to be composed of two layers: an inorganic and an organic layer. Analytical models [18, 212, 213] have demonstrated a parabolic law for SEI growth. 1D phase field model [214] of SEI growth have also shown a parabolic growth law and demonstrated that the SEI formation reaction is limited by electron diffusion than by reaction kinetics. Future phase field frameworks could extend the available frameworks through incorporating mechanics, particularly fracture of the SEI layer. In addition, integrated phase field models of SEI growth and dendrite growth are potential future research directions and could demonstrate the morphological evolution of the lithium dendrite on interaction with the SEI layer.
- Phase field models of electrochemomechanical fatigue and fracture: Intercalation and deintercalation of lithium in and out of the active material impose pulsating mechanical stresses, and thereby fatigue and eventually fracture of

the electrode particle. Phase field models of fracture have been pioneered by Miehe and coworkers [215,216]. Fracture due to Vegard stresses in battery particle have been demonstrated by Zhao and coworkers [39,45] and show rapid degradation at higher current densities during fast charging. Future work on integrating phase separation, large deformation, and fracture of active materials and thereby predicting the active material loss would enable to better understand battery degradation for a wide range of cathode and anode chemistries.

Finally, developed models need to be integrated across lengthscales and validated with experiments, in order to serve the overall purpose of a basic science understanding of the underlying complex physical phenomenon and simultaneously provide engineering insights and guidelines. Modern computational methods such as machine learning and artificial intelligence are promising ways to decrease the computational complexity of physics-based numerical frameworks or to build regressionbased computational frameworks for less understood physical phenomena. Overall, recent advances in battery modeling have set the stage for more accurate and computationally efficient models, and when coupled with state-of-the-art experiments, will be able to provide design and operational guidelines for the commercialization of high energy density and safe batteries.

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