Mechanical and Electrochemical Response of a LiCoO₂ Cathode using Reconstructed Microstructures

Hector Mendoza^a, Scott A. Roberts^{a,*}, Victor E. Brunini^a, Anne M. Grillet^a

^a*Engineering Sciences Center, Sandia National Laboratories, Albuquerque, NM 87185-0836*

Abstract

As LiCoO₂ cathodes are charged, delithiation of the LiCoO₂ active material leads to an increase in the lattice spacing, causing swelling of the particles. When these particles are packed into a bicontinuous, percolated network, as is the case in a battery electrode, this swelling leads to the generation of significant mechanical stress. In this study we performed coupled electrochemical-mechanical simulations of the charging of a LiCoO₂ cathode in order to elucidate the mechanisms of stress generation and the effect of charge rate and microstructure on these stresses. Energy dispersive spectroscopy combined with scanning electron microscopy imaging was used to create 3D reconstructions of a LiCoO₂ cathode, and the Conformal Decomposition Finite Element Method is used to automatically generate computational meshes on this reconstructed microstructure. Replacement of the ideal solution Fickian diffusion model, typically used in battery simulations, with a more general non-ideal solution model shows substantially smaller gradients of lithium within particles than is typically observed in the literature. Using this more general model, lithium gradients only appear at states of charge where the open-circuit voltage is relatively constant. While lithium gradients do affect the mechanical stress state in the particles, the maximum stresses are always found in the fully-charged state and are strongly affected by the local details of the microstructure and particle-to-particle contacts. These coupled electrochemical-mechanical simulations begin to yield insight into the partitioning of volume change between reducing pore space and macroscopically swelling the electrode. Finally, preliminary studies that include the presence of the polymeric binder suggest that it can greatly impact stress generation and that it is

*Corresponding author

Email addresses: hmendo@sandia.gov (Hector Mendoza), sarober@sandia.gov (Scott A. Roberts), vebruni@sandia.gov (Victor E. Brunini), amgrill@sandia.gov (Anne M. Grillet)

an important area for future research.

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1. Introduction

As lithium-ion batteries (Li-ion batteries, or LIB) are subjected to many charge-discharge cycles, their available energy density decreases over time, a phenomenon known as capacity fade. During these charge-discharge cycles, delithiation of an LiCoO_2 (LCO) cathode leads to an increase in its specific volume, which in turn leads to the development of mechanical stress in the network as it swells [1–4]. We propose that a mechanism for capacity fade is damage to the electrodes’ microstructure from this stress. In this damage mechanism, active material particles become disconnected from the network and no longer contribute to the capacity of the electrode [5–8]. Similarly, John Cannarella and Craig B. Arnold [9] investigated the effect of stack stresses, which arise from lithiation-induced swelling, on capacity fade of lithium-ion batteries, concluding capacity fade is highly influenced by the mechanical stresses experienced throughout the electrodes, where higher stress caused higher rates of capacity fade. Clearly, the development of a thorough understanding of the many sources of stress generation in electrodes could lead to improvements in battery performance.

In the early 1990s, Reimers and Dahn [1] used X-ray diffraction techniques to study lithium intercalation in LCO cathodes, identifying that the LCO structure swells (anisotropically) and undergoes a phase change upon delithiation, an observation expanded on by Amatucci et al. [10]. Later experimental studies have shown that stresses due to intercalation, phase transitions, and thermal loading can cause particle fractures within electrode microstructures [11–13]. Scanning electron microscope (SEM) and transmission electron microscope (TEM) imaging have shown that fracture in the electrodes entails separation of the active conducting material which could result in isolated particles disconnected from the conducting network, potentially leading to capacity fade [11–14]. Wang et al. [11] specifically looked at LCO cathodes and observed varying degrees of damage as the cathode was cycled, including severely strained particles with occasional fractures and high defect densities. Lim et al. [14] further observed that higher discharge rates could increase the propensity for fracture. This type of degradation has inspired the development of computational models to

understand the electrochemical and mechanical processes occurring within batteries as they are cycled.

While low-order models [15] are useful at capturing first-order electrochemical effects in Li-ion batteries, three-dimensional (3D) models of the electrode microstructure are necessary to fully understand the role of particle size, shape, and network morphology on performance. Early models idealized the electrode particles as spheres or ellipsoids and demonstrated variations in lithium concentrations within the electrode as a function of the discharge rate [16–19]. However, recent experiments using focused ion beam-scanning electron microscopy (FIB-SEM) [20–24] and X-ray tomography [24–28] have provided 3D reconstructions of electrode microstructures, revealing highly non-spherical particle shapes, particularly for LCO electrodes. These data enabled Andreas H. Wiedemann et al. [29] to perform electrochemical simulations on a reconstructed FIB-SEM microstructure. Their simulations showed substantial spatial variations in Li concentration and electrostatic potentials within the cathode’s particle structure, indicating that using realistic particle structures was essential, as these variations could not be predicted with models based on idealized microstructures. Hutzenlaub et al. [30] extended this work by including the binder phase in their electrode reconstruction, which further increased the inhomogeneity in the active material.

Similarly, the quest to understand electrode mechanics began with single, idealized (spherical/ellipsoidal) particles, with early studies investigating how particle shape influences the development of stresses [2, 3, 31, 32]. The generation of stress can also lead to fracture of particles, and Woodford et al. [33] developed a particle scale model to address this failure mechanism. However, the deficiency of using idealized particles in stress calculations is even more apparent than it is for electrochemical studies. Lim et al. [34] developed computational simulations using reconstructed Li_yC_6 and LiCoO_2 particles, observing that the diffusion-induced stresses of reconstructed electrode particles are much higher than those observed in idealized particles. Similarly, Malavé et al. [4] showed that small-scale surface morphology, high lithium concentration gradients, and phase transformations combined to have a major influence on the stresses, where the highest tensile stresses are observed near small protuberances and concave notch-like features (stress concentrators) on the electrode surface. Miehe et al. [35] introduced a coupled model for chemo-mechanical induced frac-

ture in Li-ion battery electrode particles. However, their predictions were for single particle analyses. It was only very recently we demonstrated simulations of stress generation in a percolated, bicontinuous network of reconstructed particles, showing significantly higher stresses than observed in single particles or idealized particle packs [36].

Researchers have also recognized the importance of the polymeric binder on mitigating stress generation [37, 38]. In particular, Rahani and Shenoy [38] employ a model where they uniformly coat idealized spherical particles with a layer of polyvinylidene fluoride (PVDF) and carbon black binder composite, thereby establishing the particle-to-particle contacts in the binder phase. However, the binder is known to form a non-continuous layer surrounding the particles [39–42], so Rahani and Shenoy [38] compare their uniform binder coating model to one where the binder is only existent on binder bridges connecting the particles. They concluded that both models revealed similar development of stress, showing that inclusion of binder is essential to predict mechanical stresses. Regardless of the model, a key finding was that the binder’s mechanical properties, particularly yield stress and modulus of elasticity, were a major factor in determining the average stresses developed in the electrode. Delamination of the binder from the active material (breaking electrical transport paths) is also a potential degradation mechanism, an idea investigated in simple axisymmetric models for silicon electrodes [43, 44].

The previous modeling studies are limited by either their idealizations of the particle network structure, investigation of isolated (single) particles, or not coupling the electrochemistry to mechanical deformation. Therefore, in this manuscript, we build on our previous computational and modeling framework [36] to investigate how delithiation of a LCO cathode microstructures affects the generation of stress within the network. We further attempt to provide a more accurate representation of the electrochemistry by using a general diffusion model for lithium within the particle phase (based on electrochemical potential gradients) rather than simply using an ideal solution diffusion model (based on concentration gradients) as is commonly used in the literature [17, 29, 34]. While our simulations focus only on LCO, we expect that the methods and observations generated here should be applicable to other electrode materials.

A full description of the model, computational framework, and analysis can be found in

subsequent sections. First, we discuss the experimental methods used to obtain a reconstruction of the cathode microstructure. We then describe the numerical model used to capture the coupled electrochemistry and mechanics, followed by the computational methods used to solve that model. Finally, we discuss our simulation results and provide concluding remarks.

2. Experimental Methods

This investigation focuses on using a reconstructed representation of a LCO microstructure that was manufactured and imaged in-house. The LCO electrode sample used in this work was prepared in a dry room with a dewpoint no greater than $-40\text{ }^{\circ}\text{C}$. The electrodes consist of 94 wt% LCO (LICO Technology Corp), 3 wt% polyvinylidene fluoride (PVDF, Solvay), and 3 wt% conductive carbon black (CB, Denka). PVDF was first dissolved in N-methyl-2-pyrrolidone, then LCO and CB were added to the slurry. The final viscosity of the obtained slurry was kept near 200 cP to ensure a uniform and homogeneous coating. The slurry was then cast onto a carbon-coated aluminum current collector using a reverse comma coater. Solvent was dried at $100\text{ }^{\circ}\text{C}$ during the coating process and subsequently dried under vacuum at $110\text{ }^{\circ}\text{C}$ for approximately 12 hours. Electrodes were potted in epoxy and coated to an average active material loading of $14.8\text{ mg}\cdot\text{cm}^{-2}$.

To obtain the set of cross-sectional images used for the 3D reconstruction, the cathode was placed in a scanning electron microscope (SEM) while a gallium focused ion beam (FIB) was used to make cross sections into the cathode. At each position, an image was recorded of the backscattered electron intensity and at every fifth cross section, an elemental composition map was taken using energy dispersive X-ray spectroscopy (EDS). The EDS was performed with an accelerating voltage of 5 keV in order to minimize the depth of signal. The complete EDS spectrum at each pixel of the image stack was used as the basis for a multivariate analysis to identify principal components which are groupings of elements that were spatially collocated [45]. To increase signal to noise ratio, groups of four pixels in the EDS maps were binned. Sixty EDS image slices resulted with a resolution of 112×128 pixels, where each of the pixels was $256\text{ nm} \times 200\text{ nm}$ with a 250 nm thickness. Three principal components of interest for this analysis were found including the active material identified by cobalt and oxygen peaks (lithium is not detectable by EDS). The binder and

epoxy component EDS spectra both contained carbon, oxygen and fluorine, but the binder had a higher relative concentration of fluorine while the epoxy used to fill the void space which would otherwise be filled by electrolyte had a more pronounced carbon peak.

Figure 1 shows a sample image of an electrode cross-section used to develop a reconstruction from the described FIB-SEM EDS analysis. A composite of the EDS analysis is shown in Figure 1a, clearly highlighting the three primary components comprising the LCO cathode: the electrolyte in green, the particle phase in red, and the binder in blue. Figure 1b shows a grayscale image of the particle phase used for the reconstruction, which is discussed in detail in §4, and the result of that binarization is shown in Figure 1c.

3. Mathematical Model

A simplified schematic of the geometry used for our analysis is depicted in Figure 2, showing only three particles for simplicity. While in this 2D schematic the electrolyte regions do not appear to be continuous, in 3D it is a bicontinuous network of particles and electrolyte. Cross-sectional images with similar particle orientation and layout (also similar to those in Figure 1) will be used in §5 to visualize results.

The electrochemical model of §3.1 is solved on the particle and electrolyte phases, where the separator maintains a constant Li^+ concentration, serving as an infinite source/sink of lithium ions. Similarly, the current collector serves as a source/sink for electrons (current). The mechanics model discussed in §3.2 is solved only on the particle phase.

3.1. Electrochemistry

The electrochemical model consists of distinct volumetric equations solved in the particle and electrolyte domains depicted in Figure 2, coupled by an interfacial condition capturing the intercalation reaction at the particle-electrolyte interface. Our modeling approach builds on prior work [29, 30, 36] by incorporating a generalized, non-ideal diffusion model for the solid-state transport of lithium within the active particles.

Electron transport in the particles is governed by current conservation using Ohm’s law,

$$\nabla \cdot (\kappa \nabla \phi_s) = 0, \tag{1}$$

and solving for the solid phase voltage, ϕ_s , where κ is the solid-phase electrical conductivity. Conservation of lithium within the particles is expressed as,

$$\frac{\partial C_{\text{Li}}}{\partial t} + \nabla \cdot J_{\text{Li}} = 0, \quad (2)$$

where C_{Li} is the concentration of lithium and J_{Li} is the lithium flux. This lithium flux is traditionally modeled as a linear function of the lithium concentration gradient,

$$J_{\text{Li}} = -D\nabla(C_{\text{Li}}), \quad (3)$$

where D is the diffusivity. However, this approach invokes ideal solution theory, where the mean strength of molecular interactions is the same between all molecules of the solution and where no volume change occurs to each individual species upon mixing [46]. LCO, however, has preferred insertion sites upon intercalation, making specific molecular interactions important [47]. Furthermore, upon de/lithiation, Reimers and Dahn [1] show that the LCO specific volume is not constant. Therefore, LCO should be considered a non-ideal solution, and we instead use a general transport model motivated by thermodynamics where the flux of Li, J_{Li} , is proportional to the gradient of its chemical potential, μ_{Li} [48],

$$J_{\text{Li}} = -MC_{\text{Li}}\nabla(\mu_{\text{Li}}). \quad (4)$$

Here, M is the mobility of Li, obtained from existing diffusivity data [48] using the Nernst-Einstein relation, $M = D/RT$. This form shown by Eq. (4) can more accurately represent the non-ideal thermodynamics in a manner consistent with experimentally measured open-circuit voltages (OCVs) for LCO. Additionally it allows for the consistent incorporation of stress-diffusion coupling. This generalized flux model will be compared to the standard idealized flux in §5.1.

The chemical potential is split into stress-independent and stress-dependent contributions, $\mu_{\text{Li}}^{\text{chem}}$ and $\mu_{\text{Li}}^{\text{stress}}$ respectively:

$$\mu_{\text{Li}} = \mu_{\text{Li}}^{\text{chem}} + \mu_{\text{Li}}^{\text{stress}}. \quad (5)$$

The stress-dependent chemical potential contribution and its impact on solid-phase transport has been studied for a variety of simplifying assumptions by other researchers [32, 49–53], and correspondingly may be treated with varying levels of complexity. For this work, we assume small strains of the active particles, that the strain induced by delithiation is isotropic, and that the mechanical properties of LCO are independent of the Li concentration. These assumptions lead to the simplest stress-dependent chemical potential contribution of the form

$$\mu_{\text{Li}}^{\text{stress}} = \beta \frac{1}{3} \text{tr}(\boldsymbol{\sigma}), \quad (6)$$

where β is a volumetric expansion coefficient described in detail in §3.2 and $\text{tr}(\boldsymbol{\sigma})/3$ is the hydrostatic pressure. Note that the assumptions made here can be relaxed by incorporating a different form for $\mu_{\text{Li}}^{\text{stress}}$.

We take a novel approach for determining the stress-independent chemical potential contribution by fitting it to experimental measurements of the open-circuit voltage for LCO. If we consider the intercalation reaction for Li^+ into LiCoO_2 ,

at equilibrium, the following condition must hold:

$$\mu_{\text{Li}} = \mu_{\text{Li}^+} + \mu_{e^-}. \quad (8)$$

Expanding the chemical potentials to explicitly show the reference, concentration-dependent, and electric potential-dependent contributions for each species yields

$$(\mu_{\text{Li}}^0 + \mu_{\text{Li}}^{\text{chem}} + \mu_{\text{Li}}^{\text{stress}}) = \left(\mu_{\text{Li}^+}^0 + RT \log \frac{\gamma_{\text{Li}^+} C_{\text{Li}^+}}{C_{\text{Li}^+}^0} + F\phi_l \right) + \left(\mu_{e^-}^0 + RT \log \frac{\gamma_{e^-} C_{e^-}}{C_{e^-}^0} - F\phi_s \right). \quad (9)$$

where μ_{Li}^0 , $\mu_{\text{Li}^+}^0$, and $\mu_{e^-}^0$ are the reference chemical potentials of Li in the solid phase, Li^+ ions in the electrolyte, and electrons in the solid phase respectively. γ_{Li^+} and γ_{e^-} are the activity coefficients of Li^+ ions in the electrolyte and electrons in the solid phase. $C_{\text{Li}^+}^0$ and $C_{e^-}^0$ are the concentrations of Li^+ ions in the electrolyte and electrons in the solid phase at

the reference state. Next, several additional assumptions are made: $\mu_{\text{Li}}^{\text{stress}}$ is small relative to $\mu_{\text{Li}}^{\text{chem}}$, the concentration of electrons C_{e^-} in LCO is effectively constant, and that open-circuit voltage measurements are performed at sufficiently low charge or discharge rates so that the Li^+ ion concentration remains constant and uniform throughout the cell. Combining constant terms with terms that result being constant because of these assumptions yields

$$\mu_{\text{Li}}^{\text{chem}} = \mu^0 - F(\phi_s - \phi_l). \quad (10)$$

Recognizing that the equilibrium potential is equivalent to the difference between the solid phase and liquid phase voltages ($\phi_{\text{eq}} = \phi_s - \phi_l$) for an open-circuit voltage measurement relative to a lithium anode, and that we are ultimately only interested in gradients of $\mu_{\text{Li}}^{\text{chem}}$ so the constant factor is irrelevant and may be assumed to be 0, we arrive at

$$\mu_{\text{Li}}^{\text{chem}} = -F\phi_{\text{eq}}, \quad (11)$$

where F is Faraday's constant and ϕ_{eq} is the equilibrium potential. Thus, we can directly extract the stress-independent chemical potential contribution from experimental open-circuit voltage measurements. For the simulations in this work, the equilibrium potential for LCO is modeled using the OCV fit for LCO from Doyle and Fuentes [54], shown in Figure 3.

As in the active particles, we apply current and species conservation in the electrolyte to solve for the liquid phase voltage, ϕ_l , and lithium-ion concentration, C_{Li^+} ,

$$\nabla \cdot \left[F \left(\mathbf{J}_{\text{Li}^+} - \mathbf{J}_{\text{PF}_6^-} \right) \right] = 0, \quad (12)$$

$$\frac{\partial C_{\text{Li}^+}}{\partial t} + \nabla \cdot \mathbf{J}_{\text{Li}^+} = 0. \quad (13)$$

The current conservation equation Eq. (12) includes contributions from both the Li^+ cation and PF_6^- anion. The fluxes of both ions (Li^+ and PF_6^-) are calculated using a Nernst-Planck model,

$$\mathbf{J}_i = -D_i \left(z_i C_i \frac{F}{RT} \nabla \phi_l + \nabla C_i \right), \quad (14)$$

where z_i is the species valence, R is the gas constant, and T is the absolute temperature.

Finally, we assume electroneutrality to determine the anion concentration, $C_{\text{PF}_6^-} = C_{\text{Li}^+}$.

The volumetric equations in the particle and electrolyte domains are coupled by the interfacial conditions for the intercalation reaction at the particle-electrolyte interface. The electrochemical reaction kinetics are modeled using the Butler-Volmer equation [55],

$$r = j_0 \left[\exp \left(\frac{\alpha_a F (\phi_s - \phi_l - \phi_{\text{eq}})}{RT} \right) - \exp \left(\frac{-\alpha_c F (\phi_s - \phi_l - \phi_{\text{eq}})}{RT} \right) \right]. \quad (15)$$

Here, j_0 is the exchange current density taken to be 2.6 mA/cm² and the α_i are the charge transfer coefficients taken to be 0.5, with both values adopted from Doyle and Fuentes [54]. The computed intercalation reaction rate, r , is used to apply normal flux boundary conditions to each of the volumetric conservation equations, as specified below:

$$-\kappa \nabla \phi_s \cdot \mathbf{n} = -r, \quad (16)$$

$$-MC_{\text{Li}} \nabla (\mu_{\text{Li}}^{\text{chem}} + \mu_{\text{Li}}^{\text{stress}}) \cdot \mathbf{n} = \frac{r}{F}, \quad (17)$$

$$F (\mathbf{J}_{\text{Li}^+} - \mathbf{J}_{\text{PF}_6^-}) \cdot \mathbf{n} = r, \quad (18)$$

$$\mathbf{J}_{\text{Li}^+} \cdot \mathbf{n} = -\frac{r}{F}. \quad (19)$$

Here, $\mathbf{n}$ is the normal vector pointing from the particle surface into the electrolyte. Particle-to-particle contacts are considered to be in “perfect contact,” where no electrolyte resides in the space in between.

Finally, boundary conditions must be specified at the separator and current collector interfaces to fully define the model. At the free end of the separator, the liquid phase voltage is set to zero ($\phi_l = 0$) and the Li^+ concentration is fixed to the initial value, serving as an infinite source of lithium ($C_{\text{Li}^+} = C_{\text{Li}^+}^0$). At the free end of the current collector we apply a constant current density set to a value commensurate with the desired C-rate. Due to the nature of the weak form of the equations in the finite element method, no flux of lithium species or current naturally arises at all other boundaries.

3.2. Mechanics

Mechanical deformation of the solid LCO particles is governed by quasi-static conservation of linear momentum,

$$\nabla \cdot \boldsymbol{\sigma} = \mathbf{0}, \quad (20)$$

where $\boldsymbol{\sigma}$ is the Cauchy stress tensor. This stress is composed of two components, a linear-elastic constitutive response and a contribution from the change in the stress-free state of the material due to charging-induced swelling,

$$\boldsymbol{\sigma} = \lambda \text{tr}(\boldsymbol{\varepsilon}) \mathbf{I} + 2\mu \boldsymbol{\varepsilon} - \beta \Delta C_{\text{Li}}. \quad (21)$$

Here, λ and μ are the Lamé parameters, $\boldsymbol{\varepsilon} = \frac{1}{2} [\nabla \mathbf{d} + (\nabla \mathbf{d})^T]$ is the small strain deformation tensor, $\mathbf{d}$ is the mesh displacement vector, and $\beta \Delta C_{\text{Li}}$ represents the delithiation-induced swelling.

Delithiation-induced swelling is governed by the change in lithium concentration from the stress-free initial conditions, $\Delta C_{\text{Li}} = C_{\text{Li}} - C_{\text{Li}}^0$, and a scalar, β , which is a material parameter defined such that $\beta = \boldsymbol{\varepsilon} / \Delta C_{\text{Li}}$. This approach is analogous to Vegard's law [56], which is often used for thermal strains of metal alloys. While this swelling physically induces a stress-free strain by changing the stress-free state of the underlying crystal structure, the use of a linear elastic constitutive model allows the representation of this strain as the additive stress term in Eq. (21). We describe this in detail in our previous work [36]. Although we recognize evidence of LCO swelling anisotropically with volume discontinuities due to phase transitions [1, 10], a scalar, constant form of β is used in this work for simplicity. We use experimental data from Reimers and Dahn [1] to arrive at a value for β . Chemical strain for values of x in Li_xCoO_2 at $x = 0.5$ and $x = 0.9$ was obtained from their work, and a linear, continuous relationship was assumed between these two states for our isotropic model, closely resembling the multiphase model of Malavé et al. [4]. The chemical strain values were then converted to stress using a bulk modulus of 205 GPa, which resulted in $\beta = -48.8 \text{ kPa/mol-m}^{-3}$, where the negative value indicates expansion during delithiation.

For the majority of the simulations shown in §5, no-penetration boundary conditions were used on all edges of the computational domain, $\mathbf{n} \cdot \mathbf{d} = 0$, representing the domain as

a small excerpt of a much larger material. These conditions also assume that there is no macroscopic swelling, or “breathing” of the electrode [9]. This latter assumption is relaxed and its effect is examined in §5.3.

4. Reconstruction and Numerical Method

With the cross-sectional images of the cathode’s microstructure obtained as described in §2, 3D reconstructions of the grayscale 2D image stacks (shown in Figure 1b) were generated in Avizo 9 (FEI; Hillsboro, OR). The 2D images were imported into Avizo and binarized using a pixel intensity threshold to create a binary description of the particle phase. Any pixels not designated as particles corresponded to the combined electrolyte and binder phases, which we refer to as the “void phase”. The selection of the binarization threshold and filter parameters were guided to maintain the expected volume fraction of the solid phase at 55% $\pm$ 3%, which was obtained from direct analysis of the raw backscatter SEM images and from the manufacturing process described in §2. To improve the quality of the binarization, a number of filters were applied, including occasional fine tuning of the threshold limit to better represent the SEM images and removal of regions of void or particle phases smaller than 2 voxels. An example of a binarized image is found in Figure 1c. The exact same processing was used on all images of a stack to ensure consistency.

Once the entire stack of images was binarized, a surface description (surface mesh) was created between the particle and void phases. Default surface meshes were often too fine or too smooth, so coarsening of the mesh was sometimes necessary to obtain a reasonable file size. Any major blemishes that resulted in the surface mesh (triangles with poor aspect ratio, bad intersections, or acute dihedral angles of the surface mesh) were corrected with Avizo’s surface editor. The resulting surface mesh was then exported as a Standard Tessellation Language (STL) file for analysis, shown in Figure 4a.

In order to accurately model the surface electrochemistry and stress concentrations using FEM, a volume mesh conformal to the reconstructed surface was needed. We therefore employed the Conformal Decomposition Finite Element Method (CDFEM) [57] to create a computable, conformal volume mesh using the STL description of the particle surface generated. To use CDFEM, a regular, tetrahedral “background” mesh (Figure 4b) is constructed

that contains the desired simulation volume. The particle surface mesh (Figure 4a) is subsequently imported and imposed on the background mesh. The CDFEM algorithm then decomposes the background mesh (by adding additional nodes and elements) to conform to the surface description. Use of CDFEM for battery electrode applications was described in detail in our previous work [36], and we encourage the reader to refer there for additional details on this approach.

The mathematical model described in §3 was applied to our reconstructed domain and solved using the Galerkin Finite Element Method (FEM), and it was implemented in Sierra Multi-Mechanics Module Aria [58]. The numerical model is solved on this conformal, tetrahedral element mesh using linear (Q1) basis functions. The electrochemical and mechanical equation systems are solved in a segregated, operator-split method using a Newton-Raphson nonlinear iteration scheme for each equation system. The coupling from the mechanics to the electrochemistry is only through the Lagrangian deformation of the mesh. However, the deformations are quite small for these simulations, with equivalent strains generally smaller than 1.5%, making the coupling weak. While in Eq. (11) we also propose a stress coupling to lithium diffusion, in §5.1 we show this effect to be negligible for our system. These conditions allowed the segregated loose coupling scheme to work for this problem. Finally, the systems are integrated in time using a standard second-order backward differentiation formula (BDF2). Analysis of the results from these simulations is discussed in §5.

5. Results

All simulations presented in this section were performed on the reconstructed geometry shown in Figure 4c, which is a domain of size $6\text{ }\mu\text{m} \times 6\text{ }\mu\text{m} \times 14.3\text{ }\mu\text{m}$ with a background mesh size of $0.3\text{ }\mu\text{m}$. Electrochemical and mechanical property values for a LCO cathode with $\text{LiPF}_6/\text{EC-PC}$ electrolyte were obtained from a number of literature publications [1, 4, 54]. Table 1 summarizes the values and sources of the key parameters in this model. Additionally, the electrical conductivity (κ) of the LCO particle phase was taken to be a function of the local lithium concentration, extracted from experimental data [59, Figure 5].

All simulations began with a completely discharged cathode of Li_1CoO_2 . Throughout this manuscript we will refer to this state as having a “state of charge of 0”, or “SOC=0”, and

Table 1: Key parameters used in the simulations.

Property	Symbol	Value	Units	Reference
Young’s modulus	E	370×10^9	Pa	[4]
Bulk modulus	K	205×10^9	Pa	[4]
Poisson’s ratio	ν	0.2		[4]
Volumetric expansion coefficient	β	-48.8×10^3	Pa/mol-m ⁻³	[1]
Li diffusivity in LCO	D_{Li}	5.387×10^{-15}	m ² /s	[4]
Li ⁺ diffusivity in electrolyte	D_{Li^+}	1.7719×10^{-8}	m ² /s	[54]

also refer to the Li_x as a measure of the local lithium concentration, where the x represents the amount of lithium in Li_xCoO_2 . Each simulation then charges the cathode by removing lithium, with a fully charged cathode corresponding to $x = 0.5$ (in Li_x) and SOC=1. The cathode will be charged at various rates, but the baseline simulation case will be a 1C charge rate, which corresponds to a current density of 4.05 mA/m² applied to the current collector surface.

5.1. Electrochemistry

We begin by discussing the electrochemical response of the cathode under the baseline charge rate of 1C. Since a fixed current is drawn from the current collector throughout the simulation, the average Li concentration in the particle phase decreases linearly during the charge. However, this linear decrease for the average Li concentration does not mean that the local spatial distribution of Li is uniform throughout the microstructure. Figure 5 shows the spatial distribution of Li in fully discharged, partially charged, and fully charged states. Of particular interest is the partially charged state shown in Figure 5b with a compressed concentration color scale in Figure 5c. These images show the formation of strong radial Li concentration gradients in the particle phases, as was observed by Andreas H. Wiedemann et al. [29]. These radial concentration gradients are not observed in the other states of charge shown in Figure 5, in contrast with other observations [29].

These concentration gradients can also be appreciated by plotting the mean Li_x concentration as a function of distance from the particle interface, shown in Figure 6. As the reaction occurs on the particle surface (distance of 0 on the abscissa of Figure 6) the Li concentration there is lowered and Li must diffuse from the inner portions of the particle to replenish the interface. While the literature [29, 30] typically shows strong radial gradients,

the present results do not show the development of strong gradients until $\text{SOC} > 0.25$. These gradients are effectively erased soon thereafter and gradients are not observed for $\text{SOC} > 0.45$.

To quantify the concentration gradients during a charge, we define a scalar concentration difference, $\Delta\text{Li}_x = \text{Li}_x^{\text{interior}} - \text{Li}_x^{\text{interface}}$, which corresponds to the difference in the average Li concentration (taken over the entire microstructure) at all points greater than $1\text{ }\mu\text{m}$ inside the particle phase ($\text{Li}_x^{\text{interior}}$) from the average Li concentration at all points less than $0.1\text{ }\mu\text{m}$ inside the particle phase ($\text{Li}_x^{\text{interface}}$). This scalar quantity is depicted graphically in Figure 7a and is plotted as a function of the SOC in Figure 7b. This figure clearly shows that the concentration gradients in the particles peak at $\text{SOC} \approx 0.35$ and then quickly decay down to negligible values. Negative values for the concentration gradient are shown at high SOC values because there are some small particles isolated from the electrically-conductive particle network, leading them to remain at $\text{SOC}=0$. While in a bigger domain these particles might find another electrical conduction pathway, there is always the possibility of isolated particles. Therefore, these small, isolated particles disproportionately affect the “interface” concentration, resulting in the slightly negative values seen in Figure 7b.

The gradients observed near $\text{SOC} \approx 0.35$ are driven by the generalized (non-ideal solution) diffusion model presented in Eq. (4). Specifically, we recall that the driving force for Li diffusion is directly proportional to gradients in the electrochemical potential. Near $\text{SOC} \approx 0.35$, Figure 3 shows that the equilibrium voltage, and therefore electrochemical potential, is nearly independent of SOC. This holds true for the local electrochemical potential at all charge rates used in this study, with the local potential varying from the open circuit values by less than 2%. As a result, large concentration gradients develop in the range between $0.2 < \text{SOC} < 0.5$ without creating a significant driving force for Li diffusion and creating the concentration gradients seen in Figure 7b. Once the cell voltage begins to rise beyond $\text{SOC} = 0.45$, electrochemical gradients create much larger driving forces for diffusion, causing the concentration gradients to relax quickly.

This behavior is in stark contrast to the ideal solution diffusion model Eq. (3) that is typically used in the literature. Lithium concentrations predicted by the two models are compared quantitatively in Figure 8a and visually in Figure 8b. With the ideal solution model, concentration gradients set up very early during the charge process, increase slightly

near SOC=0.35, but then return to a relatively constant value for the remainder of the charge. For the baseline 1C charge rate, this behavior leads to gradients that are moderately strong throughout the entire charge, but never quite as strong as the peak observed with the chemical potential-based approach (general diffusion model, Eq. (4)). This direct comparison clearly demonstrates the importance of modeling solid-phase lithium transport in LCO in a manner that is thermodynamically consistent using the general diffusion model.

Our previous discussion of the electrochemical potential has been limited to the electrochemically-driven portion of Eq. (5) and Eq. (11), neglecting the stress contribution from Eq. (6). Figure 9 compares simulations with and without the presence of the stress contribution. With both curves nearly overlapping throughout the charge, the figure clearly shows how the contribution from $\mu_{\text{Li}}^{\text{stress}}$ is negligible. This negligible contribution is not surprising for LCO considering the modest strain ($< 1.5\%$) it undergoes during delithiation. Consequently, $\mu_{\text{Li}}^{\text{stress}}$ was neglected and all subsequent simulations assumed that there was no stress coupling.

5.1.1. Effect of Charging Rate

The previous discussion focused solely on a 1C charge rate, so we now explore what effect the charging rate has on the electrochemical performance. These spatial distributions are visualized at SOC=0.3 for three C-rates in Figure 10a. The 0.01C case shows negligible concentration gradients while the gradients are very pronounced in the 10C case, consistent with the literature [29]. This effect can also be seen in Figure 10b as a function of distance from the interface. These gradients are larger at higher rates because lithium is depleted more rapidly at the interface due to faster reactions, but the solid-state diffusion can not keep a supply of lithium at the interface as efficiently. Note that these results are for SOC=0.35, the localized region where gradients were observed in Figure 6.

The gradients are again quantified using the scalar lithium difference quantity in Figure 11. The qualitative behavior remains the same at all C-rates, with a peak in the gradient appearing mid-charge, then quickly disappearing. However, at higher C-rates the magnitude of the gradient peak increases and its location shifts to slightly higher SOC values.

Figure 11 also compares the ideal solution Eq. (3) and general, non-ideal solution Eq. (4)

diffusion models. At higher C-rates, the ideal solution model takes some time to reach its maximum concentration gradient before leveling off at a relatively high value for the second half of the charge cycle. At these high C-rates, lithium concentration gradients throughout the entire charge process would be significantly higher than in the general model, possibly leading to a significant difference in the evolution of stress and strain fields. These data reinforce the value in using the general diffusion model when looking at the effect of C-rate. Because of its better thermodynamic consistency, all subsequent simulations will only use this general diffusion model.

5.2. Mechanics

In §1 we discussed how electrochemically-induced delithiation leads to a change in the specific volume of LCO and the development of mechanical stress. In this section we begin to explore that behavior, starting with the baseline 1C charging rate. To quantify the stress, we choose the Von Mises stress scalar, which is typically used for metals as a scalar indicator of the overall stress state and to provide a yield criterion.

In §5.1 we discussed that the average lithium concentration in the entire electrode decreased linearly with SOC. Similarly, Figure 12 shows how the average stress throughout the cathode linearly increases throughout the charge, a direct result of the linear decrease in lithium. This is not necessarily intuitive, as one might have expected the sharp gradients near $\text{SOC} \approx 0.35$ to manifest themselves in the stress profile. This will be explored further in §5.2.1.

At the end of the charging process, lithium gradients in the particles were erased, as visualized in Figure 13a. While the majority of the electrode delithiates to $\text{Li}_x=0.5$ at the end of the charging cycle, two of the particles remain fully lithiated (shown in red). Further interrogation of the 3D particle network structure revealed that these particles were electrically isolated and did not participate in the electrochemical reactions. This effect persists in the mechanical stress and strain shown in Figure 13c and Figure 13b as these particles remain unstressed and unstrained.

As lithium leaves the LCO phase, the stress-free specific volume of the LCO increases. For an isolated, spherical particle under isotropic conditions, this behavior would lead to a

swelling of the entire particle without inducing a stress [2, 3, 31]. However, when particles are irregularly shaped or confined, this stress-free expansion is not the case. Figure 13b shows the magnitude of the particle strain that occurs during delithiation (by the color scale) as well as displacement (shown with vectors). The strains seen here are not spherical; instead, bulk movement of some particles can occur due to the constraints they experience from their neighboring particles. In this cross-section, the large particles in the middle of the domain are effectively bending or bucking to the left in an attempt to swell into the surrounding electrolyte space. Because of the no-penetration boundary conditions used in this simulation, all volume change of the particles must go into the electrolyte volume rather than expanding freely out of the domain. Considering that a majority of the property values were obtained from Malavé et al. [4], if we compare our results to the swelling observed in their single particle studies, the maximum isotropic expansion observed in Figure 13b is approximately 35% less. This reduced expansion indicates that confinement is preventing full expansion during delithiation, which instead shows up as the induced stress shown in Figure 13c.

Confinement in our model leads to further observations that diverge from what is seen in single particle analyses. In their work, Malavé et al. [4] observed the highest stresses to be on stress concentrators, mainly sharp surface features and small protrusions. Figure 13c, however, shows peak stresses at particle-to-particle contacts as well as stress concentrators. Furthermore, the peak stresses observed in our analysis are significantly higher, reaching up to 9 GPa compared to Malavé’s calculations which were as high as 85 MPa. This observation indicates that the stresses in a percolated network of reconstructed particles can reach up to two orders of magnitude greater than isolated reconstructed particles and must only be due to the presence of the confining, percolated network. This difference highlights the necessity of using an entire network of particles for stress analyses. It is also worth noting that the strong stress gradients shown in Figure 13c are at SOC=1 and in the absence of the concentration gradients discussed previously. We will explore the effect of concentration gradients later in §5.2.1.

With peak stresses > 1 GPa, it’s reasonable to think that these stresses may lead to fracture of the LCO particles. Many previous studies, including Zhao et al. [60], use an energy balance approach to investigate particle fracture, suggesting maximum particle sizes

for a given discharge rate [13, 33, 60]. Renganathan et al. [61] suggest that ceramic materials often fracture once reaching a critical strain of 1%, which translates into a fracture stress of 3.7 GPa for LCO. With our work showing stresses up to 9 GPa, it’s highly likely that this stress could lead to fractures of the LCO particles, which would reduce the overall stress load and change the microstructure.

In Eq. (21), the delithiation-induced stress is directly proportional to the volumetric expansion coefficient, β . To verify the significance of this parameter, we ran simulations varying the value of β , with results shown in Figure 14. As a reference, we recall that the original value for β was derived from the work of Reimers and Dahn [1] as -48.8 kPa/mol-m⁻³. The sensitivity of our model to this parameter is shown in Figure 14 for the mean Von Mises stresses as a function of $|\beta|$. Considering that the constitutive model described by Eq. (21) is linear in β , the results shown in Figure 14 correspondingly show a linear pattern.

5.2.1. *Effects of Charging Rate*

Figure 15 shows the maximum stresses that develop throughout the charge as a function of the charging rate. Unlike the electrochemical observations, Figure 15a shows very little effect of the charging rate on the maximum stress in the network. This observation suggests that the state of stress is more-or-less solely a function of the average degree of lithiation.

However, taking a closer look at the stresses between SOC=0.2 and SOC=0.6, differences between the various C-rates do arise. We chose to highlight these differences by normalizing the stress values by the stresses generated at 0.01C, as shown in Figure 15b. With this normalized analysis, we can see that there are indeed differences, particularly between the range of SOC=0.2 through SOC=0.6. Clearly, the peak in the lithium concentration gradients in Figure 11 are reflected in the mechanics with a corresponding peak in Figure 15b. The stress increases as much as 9% over the slow charge case due to the development of electrochemical gradients. This difference suggests that while charging rate has little effect on the maximum stress at SOC=1, the presence of concentration gradients, even when transient, does invoke an increased stress response. However, this response disappears when the lithium gradients disappear.

Focusing at SOC=1, Figure 15a and Figure 15b both show how there is very little de-

pendence of the maximum stresses on C-rate predicted for a fully discharged cathode. This negligible dependence is not consistent with previous experimental work, where the electrodes charged/discharged at higher C-rates experience higher maximum stresses [11, 13]. This disagreement could be partially attributable to the use of the general diffusion model, as gradients disappear by the end of the charge process. Additionally, we have noted that we did not account for the binder in any of our analyses up to this point. The discrepancy between patterns observed in experiment and patterns observed in our model lead us to consider modifications to account for the binder. A preliminary analysis and discussion of simulations including the binder are presented in §5.4.

5.3. Macroscopic Electrode Swelling

As noted in §3.2, the baseline simulation models a domain where all boundaries of the cathode are confined, mimicking a thin cathode layer that is not allowed to macroscopically swell, or “breathe.” This choice forces all volume changes to invade the electrolyte space, decreasing the network’s porosity. In real battery packs, however, particle swelling can macroscopically deform the entire electrode [9, 62]. To model this deformation in macroscopic (volume averaged) simulations, one must assume a partitioning of volume change electrode swelling (breathing) and porosity decrease. In reality, this partitioning is unknown, but it can be studied through microstructural simulations such as these. Throughout this section, we define the *porosity partition* as the fraction of the particle-phase volume equations that manifests in a reduction in pore volume.

Since we are not modeling the entire thickness of a real cathode and the surrounding layers, an approximation must be formulated to investigate the importance of this effect. This approximation was done by allowing the current collector (see Figure 2 to visualize location) to elastically deform and by fixing the outer surface of the collector. The modulus of the current collector varied over a wide range of values to study the behavior under varied macroscopic constraints. While we understand that the actual deformations in a real battery pack are not exactly in this manner, allowing flexibility at the current collector/microstructure interface can mimic the real behavior. The macroscopic flexibility of the constraints will be quantified by the stiffness of the current collector, $k = EA/L$, where E is the modulus, A

is the cross sectional area of the domain, and L is the thickness of layer, all applied to the properties of the flexible current collector. This stiffness is inversely related to the “case compressibility” discussed by Garrick et al. [63], except that k only governs stiffness in one dimension, assuming that the other two dimensions are still constrained by the coating itself, while the case compressibility is a 3D effect.

Figure 16 shows the effect of system (current collector) stiffness on the mechanical stress and defromation. For reference, we marked the effective stiffness of the cathode (1.1×10^5 N/m) as the vertical dashed line in the figure. The case with the highest stiffness ($k = 1.3 \times 10^9$) best resembles the rigid boundary studies of the baseline case, and the results do indeed show identical results (Figure 16a). In this case, Figure 16b shows that all of the volume change the particles experience goes into reducing the porosity (red curve), as the full cathode is not allowed to expand (green curve). This partition is reflected in a porosity partition of unity (indigo curve in Figure 16b).

As the system stiffness is decreased, the network is less constrained and the network confinement stresses allow the particle phase to swell more than in the confined case (blue curve in Figure 16b). This flexibility results in lower network stresses for moderate stiffness values (Figure 16a). Unlike in the confined case, this additional volume expansion of the particle phase does not go into reducing pore volume, but instead macroscopically swells the network (green curve in Figure 16b). In turn, the change in pore space actually *decreases* with this additional particle swelling (red curve in Figure 16b). The partitioning of volume change into porosity loss is again shown with the indigo curve, decreasing through these moderate stiffness values.

At the far extreme of very low stiffness values, the electrode asymptotically reaches a state where it feels no effect from the system constraint. In this case, the mean von Mises stress is still 180 MPa, with maximum stresses reaching nearly 1 GPa. This observation indicates that even with a flexible current collector boundary allowing the cathode to expand, the presence of stresses from both particle-to-particle contacts and the network confinement in the remaining two directions still results in stresses higher than isolated particles [4]. This study is analogous to the work of John Cannarella and Craig B. Arnold [9] where they study varying levels of stack pressures and observe that batteries manufactured at higher

stack pressures allowed less flexibility in the electrodes and exhibited faster degradation with higher rates of capacity fade. In this case, the majority of the particle expansion is translated into macroscopic expansion of the network with relatively small changes to the pore volume, a behavior reflected by the porosity partition fraction approaching zero. Combined with the observations of Figure 16a, this would indicate that softer electrode casings could potentially mitigate damage to the microstructure due to the expanding boundary.

5.4. *Inclusion of the binder*

As Rahani and Shenoy [38] demonstrated the stress reduction delivered by the presence of a polymeric binder at particle-particle contacts, we chose to approximate the binder similar to one of their models, as a uniform layer surrounding the particles. To model the binder this way, we shrink the particles from the original reconstruction (with no binder) while keeping the electrolyte volume constant. This approach then leaves a layer of binder material surrounding the particles, a configuration illustrated in Figure 17b with a 100nm coating of binder. The thickness of the binder layer can be varied by how much the particle volume shrinks. It should be noted that this process does reduce the relative particle volume of the network, but is necessary based on the current constraints of our reconstruction process.

The binder considered is a polyvinylidene flouride (PVDF) polymer impregnated with carbon black (CB), a standard binder for electrodes [38]. In their study, Rahani and Shenoy [38] note that PVDF’s Young’s modulus can take on a range of values but chose 200 MPa for the core of their work. Furthermore, Thomas Humplik et al. [64] experimentally observed a value of 200 MPa for CB ranging between 10-40 wt% in swollen PVDF/CB composites, while Kenji Takahashi et al. [44] found a value of 350 MPa. The consistency of these three studies led us to use 200 MPa as well, and due to the relatively small modulus of the binder (compared to LCO), we expect significant variations in the stresses developed within the microstructure. While the current computational method does not allow us to perform coupled electrochemical-mechanical simulations on all three phases, we sought a preliminary way to measure these effects.

To quantify the effect of the binder on the mechanics, we measured the effective modulus of the electrode with and without the binder by noting the average stresses developed under

a prescribed strain. Figure 18 shows a cross-section with the first stress invariant indicating how the cathode experiences significant stress differences with and without a 100 nm binder coating. Not only are overall stress levels reduced throughout the microstructure by including a binder, but close examination of the edges where the binder is located (at the particle interface) indicates minimal stress at the particle contacts. This result makes it apparent that the binder has a significant role in relaxing the overall stresses throughout the microstructure as well as at particle contacts.

We performed these simulations for a range of binder thicknesses, recognizing that increasing the binder thickness reduces the volume fraction of the particle phase. Inspection of the effective Young’s modulus across the cathode reveals a pattern of decreasing effective Young’s modulus with increasing binder volume. Figure 19 plots this behavior showing the importance of local binder thickness.

In the work of Rahani and Shenoy [38], they identify the binder’s yield stress as one of the key factors in influencing the overall stresses experienced by the electrode. From their studies and previous literature, they arrive at 30 MPa as being the best approximation for the yield stress of their modeled PVDF/CB binder. Although we expect the binder to mitigate the stresses experienced by the microstructure, this yield stress is still much below the stresses we observed in our study, indicating that the binder could experience plastic deformation. These findings emphasize that the properties and behavior of the binder will play a significant role in determining the overall stresses observed by a model like the one described here. While the electrochemical effects resulting from the binder were not included in the simulations of this section, the significant role the binder plays in determining the stresses highlights that a coupled electrochemical/mechanical model on a LCO cathode reconstruction including the binder should be implemented in future work.

6. Conclusion

In this study we investigated the electrochemical and mechanical behavior of a LCO cathode during charging. Cathodes were imaged and manufactured in-house. The resulting images were reconstructed into a 3D representation and the CDFEM algorithm was used to create a conformal 3D mesh of the particle and electrolyte phases. The finite element

method was used to simulate the charging of the electrode and a mechanical model was used to elucidate the generation of stresses and strains during this charging process.

The electrochemical transport model presented here treats lithium diffusion in LCO as driven by a generalized diffusion model based on non-ideal solution theory. For all charging rates studied here, the non-ideal model generally shows lower intra-particle lithium concentration gradients than what is predicted by the simplified ideal solution models typically used in previous work. Although higher concentration gradients were generated near SOC=0.3 due to the relatively constant open-circuit voltage for $0.2 < \text{SOC} < 0.4$, the concentration gradients always relaxed to near zero by the time the cathode was fully charged. We note that the ideal solution models used for LCO in previous work would be thermodynamically inconsistent, and the disparities observed in this study suggest that the general diffusion model employed here should be used in further modeling work.

Delithiation of LCO leads to an expansion of the LCO crystal lattice, leading to the generation of mechanical stresses in the LCO network. Stresses shown in this multi-particle electrode study are significantly larger than those seen in previous studies of single-particle simulations, primarily due to the confinement effects of the percolated network. However, the effect of charging rate is slight ($< 10\%$) and transient, disappearing by the end of charge. If nonlinear effects were included in the model (via a yielding binder or particle fracture mechanism), the transiently higher stresses could result in varying mechanical behavior, but these effects are not studied here. A simple investigation into the effective Young's modulus for particles coated with thin layers of a polymeric binder shows that the presence of the binder significantly mitigates the maximum stresses. Fully coupled electrochemical-mechanical simulations in the presence of binder is an area of ongoing work.

Allowing the cathode to expand in the thickness direction does reduce these stresses as particles are allowed to expand more during delithiation, but the residual stress is still greater than that predicted in single particle studies. We have shown a smooth transition in the partitioning of volume change between reducing the porosity and expanding the entire network as a function of the system stiffness. The fact that the majority of the volume expansion due to particle swelling can be absorbed by a soft, expandable boundary suggests that potential damage to the microstructure from internal stresses can be relieved only up

to the point where the residual stress is reached.

Although our model shows improvement and advantages over previous models developed by other researchers, further extensions could make our model even more robust. The preliminary simulations performed on the cathode suggested the binder’s impact on the mechanics is too significant to ignore accounting for it. Future work extending this research would be to include the binder in the coupled electrochemical/mechanics model. Additionally, we are working to account for anisotropic deformations, which require a reconstruction of the microstructure with each particle represented separately. This model with separated particles would then also allow for relative shear motion to develop as particles strain against one another, which would make our simulations more inclusive of all the dynamics that occur in an actual cathode during charging and discharging conditions. The fundamental platform has already been established for our model, and ongoing modifications are being made to improve the accuracy of the simulations.

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Figure 1: Example 2D slice from the FIB-SEM EDS imaging described in §2. The full elemental analysis is represented in (a), where red denotes the LCO particle phase, blue the PVDF/CB binder, and green the epoxy material used to fill the void space. The grayscale image in (b) shows only the regions identified as LCO particles. The result of binarization is shown in (c).

Figure 2: Schematic of the cathode configuration considered in this work. The separator is at the bottom of the domain (red) with a current collector located at top (blue). Three solid particles are shown in green, with each shade of green denoting a separate particle, surrounded by electrolyte (gray). Particles are typically on the length scale of 1.5 microns.

Figure 3: Fit of the open-circuit voltage (OCV) as a function of state of charge (SOC) from Doyle and Fuentes [54].

Figure 4: Creation of 3D mesh from surface and background meshes using CDFEM. (a) Reconstructed surface mesh from Avizo for particle phase. (b) Background mesh for CDFEM. (c) Resulting 3D mesh from CDFEM, with particle and electrolyte phases conformally meshed.

Figure 5: 2D slice through the middle of the 3D domain showing Li concentration at various states of charge for a 1C charging rate. Images (b) and (c) both show SOC=0.35, but with the color scale compressed in (c) to highlight the Li concentration gradients.

Figure 6: Mean L_{ix} versus distance from particle at varying SOC for a 1C charging rate.

Figure 7: Lithium concentration gradients for a 1C charging rate. (a) Cathode cross-section highlighting interior and interface locations while visualizing local Li gradients. (b) Lithium gradients between particle interior and interfacial region as a function of state of charge.

Figure 8: Lithium concentration gradients comparing the ideal solution vs the general diffusion models for lithium diffusing through the particle phase at a charging rate of 1C. (a) Lithium gradients between particle interior and interfacial region as a function of state of charge. (b) Cathode cross-section highlighting local Li gradients at SOC= 0.35.

Figure 9: Lithium gradients for a 1C charging simulation with and without stress coupling of the chemical potential.

Figure 10: Li particle phase concentration for SOC=0.3 at various charge rates. (a) 2D representation at three charge rates (0.01C, 1C, and 10C). (b) Mean Li_x as a function of distance from the interface.

Figure 11: Lithium gradients for varying C-rates as a function of charge comparing ideal solution and general diffusion models of transport through the particle phase.

Figure 12: Mean Von Mises stress throughout charge for baseline case.

Figure 13: Cross-sections for baseline case (1C) at a SOC=1. (a) Lithium fraction, Li_x . (b) Equivalent Strain. (c) Von Mises Stress [MPa].

Figure 14: Mean Von Mises stress as a function of β .

(a)

(b)

Figure 15: Maximum Von mises stress observed during charge. (a) absolute value, (b) normalized by the mean stress at the lowest charge rate of 0.01C.

(a)

(b)

Figure 16: Role of system flexibility (stiffness) on (a) mean stress state in the particle network and (b) partitioning of volume change between porosity and macroscopic swelling. In (b), the volume fraction is defined as (change in volume)/(total volume of undeformed cathode), where the blue curve represents volume change of the particle phase (representing the total volume change), the red curve shows the volume change that reduces porosity, and the green curve the volume change from macroscopic swelling. The indigo curve (corresponding to the right ordinate axis) is the partition coefficient of the fraction of the total volume change that goes into porosity reduction. The vertical dashed line indicates the effective stiffness of the particle network.

Figure 17: 2D cross sections of cathode configurations that (a) do not contain binder (yellow represents the LCO phase) and (b) contain a uniform coating of binder (blue) on the particles.

Figure 18: Stress distribution under uniaxial tension for a cathode with and without a 100 nm binder coating.

Figure 19: Variation of effective Young's Modulus across cathode for varying relative binder volume.

CDFEM microstructure reconstruction

Lithium concentration gradients for different diffusion models

Von Mises Stress [MPa]
0 250 500 750 100

Effect of system stiffness on partitioning of volume change