On Artifical SEI Layer in Li-ion Batteries

Thesis submitted to the
Indian Institute of Technology Kharagpur
In partial fulfillment for the award of the degree

of

Dual Degree (B.Tech + M.Tech)

by

Himanshu Sharma
21ME33001

Under the guidance of

Dr. Jeevanjyoti Chakraborty

MECHANICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY KHARAGPUR

Autumn Semester, 2024-2025

ABSTRACT

Lorem ipsum dolor sit amet, consectetuer adipiscing elit. Ut purus elit, vestibulum ut, placerat ac, adipiscing vitae, felis. Curabitur dictum gravida mauris. Nam arcu libero, nonummy eget, consectetuer id, vulputate a, magna. Donec vehicula augue eu neque. Pellentesque habitant morbi tristique senectus et netus et malesuada fames ac turpis egestas. Mauris ut leo. Cras viverra metus rhoncus sem. Nulla et lectus vestibulum urna fringilla ultrices. Phasellus eu tellus sit amet tortor gravida placerat. Integer sapien est, iaculis in, pretium quis, viverra ac, nunc. Praesent eget sem vel leo ultrices bibendum. Aenean faucibus. Morbi dolor nulla, malesuada eu, pulvinar at, mollis ac, nulla. Curabitur auctor semper nulla. Donec varius orci eget risus. Duis nibh mi, congue eu, accumsan eleifend, sagittis quis, diam. Duis eget orci sit amet orci dignissim rutrum.

LIST OF SYMBOLS AND ABBREVIATIONS

Contents

Chapter 1

Introduction

Lorem ipsum dolor sit amet, consectetuer adipiscing elit. Ut purus elit, vestibulum ut, placerat ac, adipiscing vitae, felis. Curabitur dictum gravida mauris. Nam arcu libero, nonummy eget, consectetuer id, vulputate a, magna. Donec vehicula augue eu neque. Pellentesque habitant morbi tristique senectus et netus et malesuada fames ac turpis egestas. Mauris ut leo. Cras viverra metus rhoncus sem. Nulla et lectus vestibulum urna fringilla ultrices. Phasellus eu tellus sit amet tortor gravida placerat. Integer sapien est, iaculis in, pretium quis, viverra ac, nunc. Praesent eget sem vel leo ultrices bibendum. Aenean faucibus. Morbi dolor nulla, malesuada eu, pulvinar at, mollis ac, nulla. Curabitur auctor semper nulla. Donec varius orci eget risus. Duis nibh mi, congue eu, accumsan eleifend, sagittis quis, diam. Duis eget orci sit amet orci dignissim rutrum.

Nam dui ligula, fringilla a, euismod sodales, sollicitudin vel, wisi. Morbi auctor lorem non justo. Nam lacus libero, pretium at, lobortis vitae, ultricies et, tellus. Donec aliquet, tortor sed accumsan bibendum, erat ligula aliquet magna, vitae ornare odio metus a mi. Morbi ac orci et nisl hendrerit mollis. Suspendisse ut massa. Cras nec ante. Pellentesque a nulla. Cum sociis natoque penatibus et magnis dis parturient montes, nascetur ridiculus mus. Aliquam tincidunt urna. Nulla ullamcorper vestibulum turpis. Pellentesque cursus luctus mauris.

Nulla malesuada porttitor diam. Donec felis erat, congue non, volutpat at, tincidunt tristique, libero. Vivamus viverra fermentum felis. Donec nonummy pellentesque ante. Phasellus adipiscing semper elit. Proin fermentum massa ac quam. Sed diam turpis, molestie vitae, placerat a, molestie nec, leo. Maecenas lacinia. Nam ipsum ligula, eleifend at, accumsan nec, suscipit a, ipsum. Morbi blandit ligula feugiat magna. Nunc eleifend consequat lorem. Sed lacinia nulla vitae enim. Pellentesque tincidunt purus vel magna. Integer non enim. Praesent euismod nunc eu purus. Donec bibendum quam in tellus. Nullam cursus pulvinar lectus. Donec et mi. Nam vulputate metus eu enim. Vestibulum pellentesque felis eu massa.

Quisque ullamcorper placerat ipsum. Cras nibh. Morbi vel justo vitae lacus tincidunt ultrices. Lorem ipsum dolor sit amet, consectetuer adipiscing elit. In hac habitasse platea dictumst. Integer tempus convallis augue. Etiam facilisis. Nunc elementum fermentum wisi. Aenean placerat. Ut imperdiet, enim sed gravida sollicitudin, felis odio placerat quam, ac pulvinar elit purus eget enim. Nunc vitae tortor. Proin tempus nibh sit amet nisl. Vivamus quis tortor vitae risus porta vehicula.

Fusce mauris. Vestibulum luctus nibh at lectus. Sed bibendum, nulla a faucibus semper, leo velit ultricies tellus, ac venenatis arcu wisi vel nisl. Vestibulum diam. Aliquam pellentesque, augue quis sagittis posuere, turpis lacus congue quam, in hendrerit risus eros eget felis. Maecenas eget erat in sapien mattis porttitor. Vestibulum porttitor. Nulla facilisi. Sed a turpis eu lacus commodo facilisis. Morbi fringilla, wisi in dignissim interdum, justo lectus sagittis dui, et vehicula libero dui cursus dui. Mauris tempor ligula sed lacus. Duis cursus enim ut augue. Cras ac magna. Cras nulla. Nulla egestas. Curabitur a leo. Quisque egestas wisi eget nunc. Nam feugiat lacus vel est. Curabitur consectetuer.

Suspendisse vel felis. Ut lorem lorem, interdum eu, tincidunt sit amet, laoreet vitae, arcu. Aenean faucibus pede eu ante. Praesent enim elit, rutrum at, molestie non, nonummy vel, nisl. Ut lectus eros, malesuada sit amet, fermentum eu, sodales cursus, magna. Donec eu purus. Quisque vehicula, urna sed ultricies auctor, pede lorem egestas dui, et convallis elit erat sed nulla. Donec luctus. Curabitur et nunc. Aliquam dolor odio, commodo pretium, ultricies non, pharetra in, velit. Integer arcu est, nonummy in, fermentum faucibus, egestas vel, odio.

Sed commodo posuere pede. Mauris ut est. Ut quis purus. Sed ac odio. Sed vehicula hendrerit sem. Duis non odio. Morbi ut dui. Sed accumsan risus eget odio. In hac habitasse platea dictumst. Pellentesque non elit. Fusce sed justo eu urna porta tincidunt. Mauris felis odio, sollicitudin sed, volutpat a, ornare ac, erat. Morbi quis dolor. Donec pellentesque, erat ac sagittis semper, nunc dui lobortis purus, quis congue purus metus ultricies tellus. Proin et quam. Class aptent taciti sociosqu ad litora torquent per conubia nostra, per inceptos hymenaeos. Praesent sapien turpis, fermentum vel, eleifend faucibus, vehicula eu, lacus.

Chapter 2

Problem Description

Consider a thin film of Silicon with height H and length L. All the loadings and geometry are independent of the third direction; hence, the problem is formulated using the plane strain assumption. There is an existing solid electrolyte interphase (SEI) layer on top of the Silicon film with a height of H_{SEI}. The origin is placed at the middle of the bottom face of the Silicon film, as shown in figure 2.1. The Si thin film's bottom face is considered rigidly fixed to a metallic substrate. The left and right faces are considered to have a roller-type boundary condition for both Si and SEI. A uniform flux of Li-ions from the top surface of SEI is present.

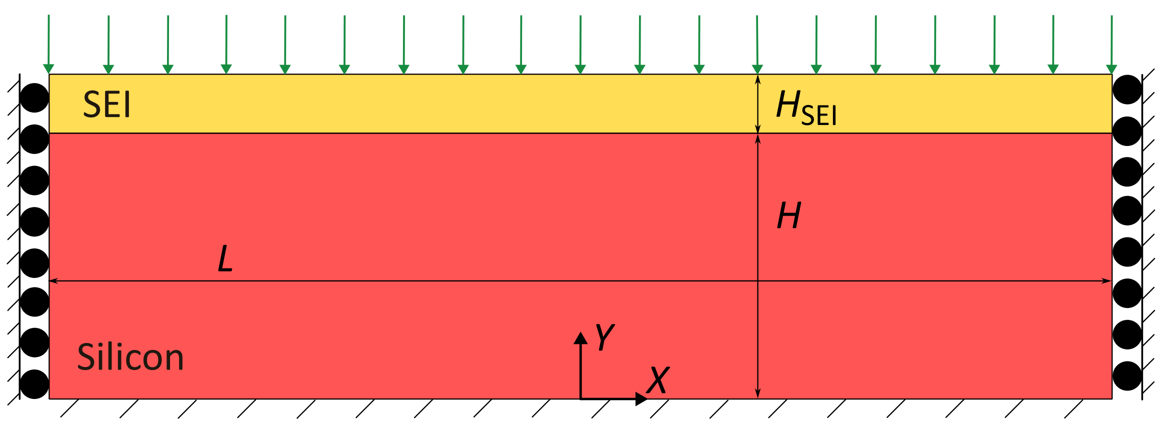

Figure 2.1: Schematic of the problem showing geometric parameters and boundary conditions.

SEI is considered completely permeable to Li-ions. So the flux directly enters the Silicon without any diffusion in the SEI. And the diffusion in Si leads to a stress field. In the literature, this is termed diffusion-induced stress (DIS). The stress field, in

turn, affects the process of diffusion called stress-enhanced diffusion (SED).
Due to the large deformation of the Si during lithiation/delithiation, it is necessary to formulate the problem with finite deformation theory with an elastoplastic constitutive behavior. In the present study, Si is considered to exhibit a viscoplastic nature. The SEI is assumed to undergo only elastic deformation. The constitutive law for the elastic regime is isotropic and concentration-dependent for $Li_{\chi}Si$ and constant for SEI. For Mechanical equilibrium, a quasi-static model is employed. This leads to a two-way coupled system of PDEs which is then solved using the finite element method in COMSOL multiphysics.

Chapter 3

Mathematical Formulation

3.1 Kinematics

Consider a certain particle, initially located at the coordinate $\boldsymbol{X}$. During deformation, this particle follows a path

$$\boldsymbol{x} = \boldsymbol{x}(\boldsymbol{X}, t). \tag{3.1}$$

Let $\boldsymbol{u}(\boldsymbol{X}, t)$ be the displacement of the material particle located at $\boldsymbol{X}$. Then

$$\boldsymbol{u}(\boldsymbol{X}, t) = \boldsymbol{x}(\boldsymbol{X}, t) - \boldsymbol{X}. \tag{3.2}$$

The total deformation gradient is denoted by $\mathbf{F}$. Therefore,

$$\mathbf{F} = \frac{\partial \boldsymbol{x}}{\partial \boldsymbol{X}} = \boldsymbol{\nabla}_{\boldsymbol{X}} \boldsymbol{u} + \mathbf{I}, \tag{3.3}$$

where $\mathbf{I}$ is the second-order isotropic tensor.

Let $\{\hat{\boldsymbol{e}}_1, \hat{\boldsymbol{e}}_2, \hat{\boldsymbol{e}}_3\}$ be the orthonormal basis in the reference configuration. The corresponding components of $\boldsymbol{X}$ are denoted by X, Y and Z and that of $\boldsymbol{u}$ by u, v and w. In the present study, plane strain deformation is assumed. Therefore, the components of $\mathbf{F}$ are given by (Lai et al., 2009)

$$[\mathbf{F}] = \begin{bmatrix} 1 + \frac{\partial u}{\partial X} & \frac{\partial u}{\partial Y} & 0 \\ \frac{\partial v}{\partial X} & 1 + \frac{\partial v}{\partial Y} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} F_{11} & F_{12} & 0 \\ F_{21} & F_{22} & 0 \\ 0 & 0 & F_{33} \end{bmatrix}. \tag{3.4}$$

Both Inelastic, present only in Si, and elastic deformation gradients are considered finite (Bower et al., 2011). Hence, a multiplicative decomposition of $\mathbf{F}$ into elastic and inelastic deformation is necessary. As shown in figure 3.1, the body is first considered to reach an intermediate stress-free state, and then it undergoes an elastic deformation to reach the current configuration. As derived by Lee (1969), the total deformation gradient

$$\mathbf{F} = \mathbf{F}^{\mathrm{el}} \cdot \mathbf{F}^{\mathrm{inel}}, \tag{3.5}$$

where $\mathbf{F}^{\mathrm{el}} = \dfrac{\partial \boldsymbol{x}}{\partial \boldsymbol{x}_{\mathrm{I}}}$ and $\mathbf{F}^{\mathrm{inel}} = \dfrac{\partial \boldsymbol{x}_{\mathrm{I}}}{\partial \boldsymbol{X}}$.

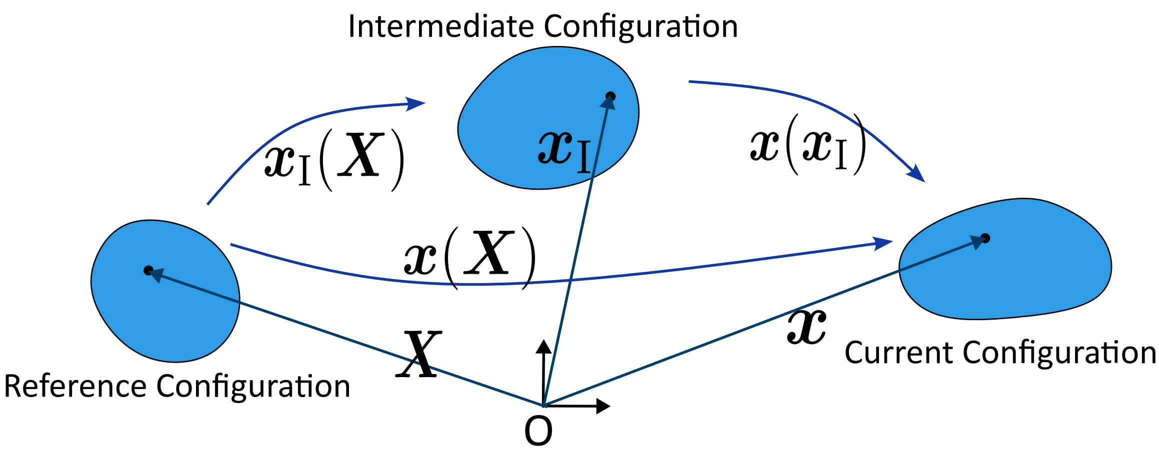

Figure 3.1: Decomposition of the deformation gradient into the elastic and inelastic part.

$\boldsymbol{x}_{\mathrm{I}}(\boldsymbol{X}, t)$ is the position of a material particle in the intermediate configuration with initial position $\boldsymbol{X}$ in the reference configuration. $\mathbf{F}^{\mathrm{el}}$ and $\mathbf{F}^{\mathrm{inel}}$ denote the deformation gradients due to elastic and inelastic deformation, respectively.

The inelastic deformation gradient tensor, $\mathbf{F}^{\mathrm{inel}}$, has contributions from two sources. It is further decomposed as

$$\mathbf{F}^{\mathrm{inel}} = \mathbf{F}^{\mathrm{c}} \cdot \mathbf{F}^{\mathrm{p}}, \tag{3.6}$$

where $\mathbf{F}^{\mathrm{c}}$ and $\mathbf{F}^{\mathrm{p}}$ are deformation gradients due to diffusion and plastic flow, respectively; Both $\mathbf{F}^{\mathrm{c}}$ and $\mathbf{F}^{\mathrm{p}}$ are defined only in the $\mathrm{Li}_{\chi}\mathrm{Si}$.

3.2 Viscoplastic Flow of $\mathrm{Li}_{\chi}\mathrm{Si}$

A viscoplastic constitutive relation of the following form is considered for $\mathrm{Li}_{\chi}\mathrm{Si}$:

$$\mathbf{D}^{\mathrm{P}} = \frac{\partial G(\sigma_{\mathrm{eff}})}{\partial \boldsymbol{\tau}}, \tag{3.7}$$

where $\mathbf{D}^{\mathrm{P}}$ is the rate dependent plastic deformation tensor, $G(\sigma_{\mathrm{eff}})$ is the flow potential, $\boldsymbol{\tau}$ is the deviatoric part of Cauchy stress tensor (see section 3.4). Various studies (Bower et al., 2011; Cui et al., 2012) have adopted a power law of the following form for flow potential

$$G(\sigma_{\mathrm{eff}}) = \frac{\sigma_{\mathrm{f}}\dot{d}_0}{m+1}\left(\frac{\sigma_{\mathrm{eff}}}{\sigma_{\mathrm{f}}}-1\right)^{m+1}\mathrm{H}\left(\frac{\sigma_{\mathrm{eff}}}{\sigma_{\mathrm{f}}}-1\right) \tag{3.8}$$

$$\Rightarrow \mathbf{D}^{\mathrm{P}} = \frac{3\boldsymbol{\tau}\dot{d}_0}{2\sigma_{\mathrm{eff}}}\left(\frac{\sigma_{\mathrm{eff}}}{\sigma_{\mathrm{f}}}-1\right)^{m}\mathrm{H}\left(\frac{\sigma_{\mathrm{eff}}}{\sigma_{\mathrm{f}}}-1\right). \tag{3.9}$$

Where σ_{eff} is the effective von Mises stress (defined in section 3.4) H is the unit step function, σ_{f} is the yield strength of $\mathrm{Li}_{\chi}\mathrm{Si}$ (check if I should write Si or $\mathrm{Li}_{\chi}\mathrm{Si}$ here), m is the stress exponent for plastic flow and $\dot{d}_0$ is the strain rate for plastic flow. Considering an irrotational plastic flow (Gurtin and Anand, 2005*a*,*b*; Bhowmick and Chakraborty, 2023)

$$\mathbf{D}^{\mathrm{P}} = \mathbf{F}^{\mathrm{el}}\cdot\mathbf{F}^{\mathrm{c}}\cdot\dot{\mathbf{F}}^{\mathrm{p}}\cdot(\mathbf{F}^{\mathrm{p}})^{-1}\cdot(\mathbf{F}^{\mathrm{c}})^{-1}\cdot(\mathbf{F}^{\mathrm{el}})^{-1} \tag{3.10}$$

$$\Rightarrow \dot{\mathbf{F}}^{\mathrm{p}} = (J)^{-1}\frac{3}{2}\frac{\mathbf{M}_{\mathbf{0}}^{\mathrm{el}}\cdot\mathbf{F}^{\mathrm{p}}}{\sigma_{\mathrm{eff}}}\dot{d}_0\left(\frac{\sigma_{\mathrm{eff}}}{\sigma_{\mathrm{f}}}-1\right)^{m}\mathrm{H}\left(\frac{\sigma_{\mathrm{eff}}}{\sigma_{\mathrm{f}}}-1\right), \tag{3.11}$$

$$\text{where } \mathbf{M}_{\mathbf{0}}^{\mathrm{el}} = J(\mathbf{F}^{\mathrm{el}})^{\mathsf{T}}\cdot\boldsymbol{\tau}\cdot(\mathbf{F}^{\mathrm{el}})^{-\mathsf{T}}, \tag{3.12}$$

$$\text{and } J = \det(\mathbf{F}). \tag{3.13}$$

$\mathbf{M}_{\mathbf{0}}^{\mathrm{el}}$ is the deviatoric part of Mandel stress (Mandel, 1971). The expression for Mandel stress is $\mathbf{M}^{\mathrm{el}} = J(\mathbf{F}^{\mathrm{el}})^{\mathsf{T}}\boldsymbol{\sigma}(F^{\mathrm{el}})^{-\mathsf{T}}$. Attributing to the assumption of plane strain, $\mathbf{F}^{\mathrm{p}}$ is considered to be of the following form:

$$[\mathbf{F}^{\mathrm{p}}] = \begin{bmatrix}\lambda_{11} & \lambda_{12} & 0\\ \lambda_{21} & \lambda_{22} & 0\\ 0 & 0 & \lambda_{33}\end{bmatrix}. \tag{3.15}$$

Since $\det(\mathbf{F}^{\mathrm{p}}) = 1$, $\lambda_{33} = 1/(\lambda_{11}\lambda_{22}-\lambda_{12}\lambda_{21})$.
In order to simplify the modelling of mechanical equilibrium in both Si and SEI using the same equations (described in 3.4), $\mathbf{F}^{\mathrm{p}} = \mathbf{I}$ in the SEI layer is considered.

3.3 Diffusion Induced Deformation of $\mathrm{Li}_{\chi}\mathrm{Si}$

The SEI layer is taken to be completely permeable to lithiation. So, diffusion only takes place inside the Silicon film. Therefore, for the purpose of modelling $\tilde{c}$ is taken

zero in the SEI, making $\mathbf{F}^{\mathrm{c}} = \mathbf{I}$ in the SEI.
The compound between Lithium and Silicon is $\mathrm{Li}_\chi\mathrm{Si}$. Let the stoichiometric concentration and maximum concentration of Lithium ions per atom of Silicon be denoted by χ_0 and $\chi_{\max}$. Defining a non-dimensional Li-ion concentration measure as $\tilde{c} = (\chi - \chi_0)/\chi_{\max}$. Since χ_0 is the stoichiometric ratio, it signifies the stress-free state; hence, $\tilde{c}$ is a measure of the deviation of the particle from the undeformed state. The deformation due to lithiation is quantified by an isotropic deformation gradient denoted by $\mathbf{F}^{\mathrm{c}}$ and given by

$$\mathbf{F}^{\mathrm{c}} = (J^c)^{1/3}\mathbf{I}, \tag{3.17}$$

where $J^c = 1 + 3\eta\chi_{\max}\tilde{c}$ is the volumetric change experienced by the Silicon film upon insertion of Li-ions. η is a material parameter giving the rate of change in volume w.r.t. $\tilde{c}$. It may be noted that as $\tilde{c}$ approaches 1, $\det(\mathbf{F}^{\mathrm{c}})$ approaches 4. Therefore, the body undergoes a volumetric change of about 300% due to the diffusion of Li-ions, justifying large deformation analysis.

3.4 Mechanical Equilibrium

Attributing to the assumption of an elastic and permeable SEI, using eqs. 3.5 and 3.6

$$\mathbf{F}^{\mathrm{el}} = \begin{cases} \mathbf{F} \cdot (\mathbf{F}^{\mathrm{c}} \cdot \mathbf{F}^{\mathrm{p}})^{-1} & \text{for } \mathrm{Li}_\chi\mathrm{Si} \\ \mathbf{F} & \text{for SEI} \end{cases} \tag{3.19}$$

The elastic Green-Lagrange strain is $\mathbf{E}^{\mathrm{el}} = \frac{1}{2}\left[(\mathbf{F}^{\mathrm{el}})^{\mathsf{T}} \cdot \mathbf{F}^{\mathrm{el}} - \mathbf{I}\right]$.

The constitutive relation for the elastic deformation is expressed in terms of the strain energy per unit volume in the intermediate configuration, $\hat{w}(\mathbf{F}, \tilde{c})$. Denoting the elasticity tensor of the material in the intermediate configuration by $\mathbb{C}$ and its components by C_{ijkl},

$$\hat{w}(\mathbf{F}, \tilde{c}) = \frac{1}{2} C_{ijkl} E^{\mathrm{el}}_{ij} E^{\mathrm{el}}_{kl}. \tag{3.21}$$

$\mathbb{C}$ is concentration-dependent and assumed to be isotropic. Hence, its components can be expressed in terms of Lamé coefficients as

$$C_{ijkl}(\tilde{c}) = \lambda_{\mathrm{mat}}(\tilde{c})\delta_{ij}\delta_{kl} + \mu_{\mathrm{mat}}(\tilde{c})(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}). \tag{3.22}$$

$$\Longrightarrow \hat{w}(\mathbf{F}, \tilde{c}) = \lambda_{\mathrm{mat}}(\tilde{c})(\mathrm{tr}(\mathbf{E}^{\mathrm{el}}))^2 + 2\mu_{\mathrm{mat}}(\tilde{\mathrm{c}})\mathbf{E}^{\mathrm{el}} : \mathbf{E}^{\mathrm{el}}. \tag{3.23}$$

The lamé parameters, $\lambda_{\mathrm{mat}}(\tilde{c})$ and $\mu_{\mathrm{mat}}(\tilde{c})$ are given by

$$\lambda_{\mathrm{mat}}(\tilde{c}) = \frac{E_{\mathrm{mat}}(\tilde{c})\nu_{\mathrm{mat}}}{(1+\nu_{\mathrm{mat}})(1-2\nu_{\mathrm{mat}})}, \qquad \mu_{\mathrm{mat}}(\tilde{c}) = \frac{E_{\mathrm{mat}}(\tilde{c})}{2(1+\nu_{\mathrm{mat}})}.$$

The material properties $E_{\mathrm{mat}}(\tilde{c})$ and ν_{mat} are defined domain-wise as follows:

$$E_{\mathrm{mat}}(\tilde{c}) = \begin{cases} E_{\mathrm{si}}(1+\eta_{\mathrm{E}}\chi_{\max}\tilde{c}) & \text{for Silicon} \\ E_{\mathrm{SEI}} & \text{for SEI} \end{cases} \tag{3.24}$$

$$\nu_{\mathrm{mat}} = \begin{cases} \nu_{\mathrm{si}} & \text{for Silicon} \\ \nu_{\mathrm{SEI}} & \text{for SEI} \end{cases} \tag{3.25}$$

The elastic second Piola-Kirchhoff stress, which can be *visualized* as the second Piola-Kirchhoff stress in the intermediate configuration, is denoted by $\mathbf{S}^{\mathrm{el}}$. Therefore,

$$\begin{aligned} \mathbf{S}^{\mathrm{el}} &= \frac{\partial \hat{w}(\mathbf{F},\tilde{c})}{\partial \mathbf{E}^{\mathrm{el}}} \\ \Longrightarrow \mathbf{S}^{\mathrm{el}} &= \lambda_{\mathrm{mat}}(\tilde{c})\mathrm{tr}(\mathbf{E}^{\mathrm{el}})\mathbf{I} + 2\mu_{\mathrm{mat}}(\tilde{\mathrm{c}})\mathbf{E}^{\mathrm{el}}. \end{aligned} \tag{3.26}$$

(note that in COMSOL, $\mathbf{S}^{\mathrm{el}} = J^{c}\left[\lambda_{\mathrm{mat}}(\tilde{c})\mathrm{tr}(\mathbf{E}^{\mathrm{el}})\mathbf{I} + 2\mu_{\mathrm{mat}}(\tilde{\mathrm{c}})\mathbf{E}^{\mathrm{el}}\right]$. This affects how the equations for μ are written.)

Let $\mathbf{S}$ denote the second Piola-Kirchhoff stress. Now, by pulling back $\mathbf{S}^{\mathrm{el}}$ from the intermediate configuration to the reference configuration (Gurtin et al., 2010) the second Piola-Kirchhoff stress is obtained as

$$\begin{aligned} \mathbf{S} = J^{\mathrm{inel}}\left(\mathbf{F}^{\mathrm{inel}}\right)^{-1}\cdot\mathbf{S}^{\mathrm{el}}\cdot\left(\mathbf{F}^{\mathrm{inel}}\right)^{-\mathsf{T}} &= J^{c}\left(\mathbf{F}^{\mathrm{p}}\cdot\mathbf{F}^{\mathrm{c}}\right)^{-1}\cdot\mathbf{S}^{\mathrm{el}}\cdot\left(\mathbf{F}^{\mathrm{p}}\cdot\mathbf{F}^{\mathrm{c}}\right)^{-\mathsf{T}} \\ &\Longrightarrow \mathbf{S} = (J^{c})^{1/3}(\mathbf{F}^{\mathrm{p}})^{-1}\cdot\mathbf{S}^{\mathrm{el}}\cdot(\mathbf{F}^{\mathrm{p}})^{-\mathsf{T}}. \end{aligned} \tag{3.27}$$

The first Piola-Kirchhoff stress is

$$\mathbf{P} = \mathbf{F}\cdot\mathbf{S}. \tag{3.28}$$

The Cauchy stress tensor, $\boldsymbol{\sigma}$, is obtained by pulling forward $\mathbf{S}$ and is given by $\boldsymbol{\sigma} = (J)^{-1}\mathbf{F}\cdot\mathbf{S}\cdot\mathbf{F}^{\mathsf{T}}$. The deviatoric part of Cauchy stress is $\boldsymbol{\tau} = \boldsymbol{\sigma} - (1/3)\mathrm{tr}(\boldsymbol{\sigma})\mathbf{I}$. The von Mises stress is $\sigma_{\mathrm{eff}} = \sqrt{\frac{3}{2}\tau_{ij}\tau_{ij}}$.

In the absence of any body forces, the conservation of momentum leads to

$$\boldsymbol{\nabla}_{\boldsymbol{X}}\cdot\mathbf{P} = 0. \tag{3.32}$$

3.5 Diffusion in $Li_\chi Si$

Assuming flux to be negligible in the z direction, the conservation of mass is expressed as

$$\frac{\partial c}{\partial t} = -\boldsymbol{\nabla}_{\boldsymbol{X}} \cdot \boldsymbol{j} = -\left(\frac{\partial j_X}{\partial X} + \frac{\partial j_Y}{\partial Y}\right), \tag{3.33}$$

where $\boldsymbol{j}$ is the flux vector in the reference configuration and c is a dimensional measure of Li-ions concentration, defined as $c = \tilde{c}\,\chi_{\max}/V_{\mathrm{m}}^{\mathrm{B}}$. In the current configuration, the flux is denoted by $\hat{\boldsymbol{j}}(\boldsymbol{x}, t)$ and it is given by (Hong et al., 2008)

$$\hat{\boldsymbol{j}}(\boldsymbol{x}, t) = -\frac{1}{R_g T}\frac{D\chi_{\max}\tilde{c}}{V_{\mathrm{m}}^{\mathrm{B}}}\nabla_{\boldsymbol{x}}\mu, \tag{3.35}$$

where R_g is the universal gas constant, T is the operating temperature, D is the diffusivity of $Li_\chi Si$, $V_{\mathrm{m}}^{\mathrm{B}}$ is the partial molar volume of Silicon and μ is the chemical potential. Diffusivity is related to the state of stress by the following equation (Haftbaradaran et al., 2011) :

$$D = D_0 \exp\left(\frac{\alpha S_h}{E_0}\right) = D_0 \exp\left(\alpha \frac{S_{11} + S_{33}}{2E_0}\right), \tag{3.36}$$

where E_0 is defined in section 3.6.

Let the flux in the reference configuration be denoted by $\boldsymbol{j}(\boldsymbol{X}, t)$. One can relate $\boldsymbol{j}(\boldsymbol{X}, t)$ and $\hat{\boldsymbol{j}}(\boldsymbol{x}, t)$ by considering two infinitesimal areas, ΔA_0 and ΔA with respectively normals $\boldsymbol{n}_0$ and $\boldsymbol{n}$, in the reference and current configuration, respectively. From Nanson's formula

$$\begin{aligned} \Delta A_0 J\, {\boldsymbol{n}_0}^{\mathsf{T}} \cdot \mathbf{F}^{-1} &= \Delta A \boldsymbol{n}^{\mathsf{T}} \\ \Delta A_0 J\, {\boldsymbol{n}_0}^{\mathsf{T}} \cdot \mathbf{F}^{-1} \cdot \hat{\boldsymbol{j}} &= \Delta A \boldsymbol{n}^{\mathsf{T}} \cdot \hat{\boldsymbol{j}} \\ \text{or, } \Delta A_0\, {\boldsymbol{n}_0}^{\mathsf{T}} \cdot \underbrace{\left(J\, \mathbf{F}^{-1} \cdot \hat{\boldsymbol{j}}\right)}_{\boldsymbol{j}(\boldsymbol{X}, t)} &= \Delta A \boldsymbol{n}^{\mathsf{T}} \cdot \hat{\boldsymbol{j}}. \end{aligned} \tag{3.37}$$

The RHS of equation 3.37 is the mass crossing the area ΔA in the current configuration. With the same argument, term in the parenthesis is regarded as the flux vector in the reference configuration. Therefore,

$$\boldsymbol{j}(\boldsymbol{X}, t) = J\, \mathbf{F}^{-1} \cdot \hat{\boldsymbol{j}}. \tag{3.38}$$

Now,

$$\begin{aligned}(\nabla_{\boldsymbol{x}}\mu)_i &= \frac{\partial \mu}{\partial x_i} = \frac{\partial \mu}{\partial X_j}\frac{\partial X_j}{\partial x_i} \\ \implies \nabla_{\boldsymbol{x}}\mu &= \mathbf{F}^{-\mathsf{T}} \cdot \nabla_X \mu. \end{aligned} \tag{3.39}$$

From above equations, the flux vector in Lagrangian description is expressed as

$$\boldsymbol{j} = -\frac{1}{R_g T}\frac{D\chi_{\max}\tilde{c}}{V_{\mathrm{m}}^{\mathrm{B}}}\mathbf{F}^{-1} \cdot \mathbf{F}^{-\mathsf{T}} \cdot \boldsymbol{\nabla}_{\boldsymbol{X}}\mu. \tag{3.40}$$

The chemical potential μ is composed of two parts: $\mu = \mu_0 + \mu_{\mathrm{s}}$, where μ_0 and μ_{s} are the stress-independent and stress-dependent part, respectively. μ_0 can be written as $\mu_0 = R_g T \log(\gamma\tilde{\mathrm{c}})$, where γ is the activity coefficient and considered to be concentration dependent, given by the following equation (Haftbaradaran et al., 2011):

$$\gamma = \frac{1}{1-\tilde{c}}\exp\left(\frac{1}{R_g T}[2(A_0 - 2B_0)\tilde{c} - 3(A_0 - B_0)\tilde{c}^2]\right). \tag{3.42}$$

Where A_0 and B_0 are constants which were determined by Shenoy et al. (2010) using first principles. The stress-dependent part of the chemical potential is (Cui et al., 2012)

$$\mu_s = \frac{V_m^b}{\chi_{\max}}\left[-\frac{1}{3}\frac{\partial J^c}{\partial \tilde{c}}F_{im}^{\mathrm{el}}F_{in}^{\mathrm{el}}C_{mnkl}E_{kl}^{\mathrm{el}} + \frac{1}{2}\left(J^c\frac{\partial C_{ijkl}}{\partial \tilde{c}} + \frac{\partial J^c}{\partial \tilde{c}}C_{ijkl}\right)E_{ij}^{\mathrm{el}}E_{kl}^{\mathrm{el}}\right]. \tag{3.43}$$

State of charge (soc) is a measure of the degree of lithiation. It is expressed as an average concentration over the domain as follows:

$$\begin{aligned}\mathrm{soc} &= \frac{1}{LH}\int_{-L/2}^{L/2}\int_0^H \tilde{c}\mathrm{dydx} \\ &= H^2\frac{1}{LH}\int_{-L/2H}^{L/2H}\int_0^1 \tilde{c}(\tilde{x},\tilde{y})\mathrm{d\tilde{y}d\tilde{x}} \\ &= \frac{H}{L}\int_{-L/2H}^{L/2H}\int_0^1 \tilde{c}(\tilde{x},\tilde{y})\mathrm{d\tilde{y}d\tilde{x}}. \end{aligned} \tag{3.44}$$

3.6 Non-dimensionalisation

As a notation, let $\tilde{(\cdot)}$ denote the non-dimensional variable corresponding to the phyical quantity denoted by $(\cdot)$.

$$\tilde{X}, \tilde{Y}, \tilde{u}, \tilde{v} = \frac{1}{H}(X, Y, u, v) \tag{3.45}$$

$$\tilde{t} = D_0 t / H^2 \tag{3.46}$$

$$\tilde{j}_X, \tilde{j}_Y, \tilde{J}_0, \tilde{\boldsymbol{j}} = \frac{H V_{\mathrm{m}}^{\mathrm{B}}}{(\chi_{\max} D_0)}(j_X, j_y, J_0, \boldsymbol{j}) \tag{3.47}$$

$$\tilde{\mu}_0, \tilde{\mu}_s = \frac{1}{R_g T}(\mu_0, \mu_s) \tag{3.48}$$

$$\tilde{D} = \frac{D}{D_0} \tag{3.49}$$

$$\dot{\tilde{d}}_0 = \frac{\dot{d}_0 H^2}{D_0} \tag{3.50}$$

$$\tilde{\mu}_{\mathrm{si}}, \tilde{\lambda}_{\mathrm{si}}, \tilde{E}_{\mathrm{si}} = \frac{1}{E_0}(\mu_{\mathrm{si}}, \lambda_{\mathrm{si}}, E_{\mathrm{si}}), \text{ where } E_0 = \frac{R_g T}{V_{\mathrm{m}}^{\mathrm{B}}} \tag{3.51}$$

$$\tilde{\mathbf{S}}^{\mathrm{el}}, \tilde{\mathbf{S}}, \tilde{\mathbf{P}}, \tilde{\boldsymbol{\sigma}}, \tilde{\boldsymbol{\tau}}, \tilde{\mathbf{M}}_0^{\mathrm{el}}, \tilde{\sigma}_{\mathrm{eff}}, \tilde{\sigma}_{\mathrm{f}} = \frac{1}{E_0}(\mathbf{S}^{\mathrm{el}}, \mathbf{S}, \mathbf{P}, \boldsymbol{\sigma}, \boldsymbol{\tau}, \mathbf{M}_0^{\mathrm{el}}, \sigma_{\mathrm{eff}}, \sigma_{\mathrm{f}}) \tag{3.52}$$

3.7 Interface, Boundary and Initial Conditions

At the Interface, continuity of displacement and traction vector is imposed. This gives

$$\tilde{u}(\tilde{X}, 1^-, \tilde{t}) = \tilde{u}(\tilde{X}, 1^+, \tilde{t}), \tag{3.53}$$

$$\tilde{v}(\tilde{X}, 1^-, \tilde{t}) = \tilde{v}(\tilde{X}, 1^+, \tilde{t}), \tag{3.54}$$

$$\boldsymbol{t}(\tilde{X}, 1^-, \tilde{t}) = \boldsymbol{t}(\tilde{X}, 1^+, \tilde{t}). \tag{3.55}$$

The initial composition is taken to be $\mathrm{Li}_{\chi_0}\mathrm{Si}$, which is a stress-free state with $\tilde{c}$ being zero.

$$\tilde{c}(\tilde{X}, \tilde{Y}, 0) = 0, \tag{3.56}$$

$$\tilde{u}(\tilde{X}, \tilde{Y}, 0) = 0, \tag{3.57}$$

$$\tilde{v}(\tilde{X}, \tilde{Y}, 0) = 0, \tag{3.58}$$

$$\lambda_{11}(\tilde{X}, \tilde{Y}, 0) = \lambda_{22}(\tilde{X}, \tilde{Y}, 0) = 1, \tag{3.59}$$

$$\lambda_{12}(\tilde{X}, \tilde{Y}, 0) = \lambda_{21}(\tilde{X}, \tilde{Y}, 0) = 0. \tag{3.60}$$

The bottom face is considered fixed, and the two sides can only exhibit motion in the Y-direction. Therefore,

$$\tilde{u}(\tilde{X}, 0, \tilde{t}) = \tilde{v}(\tilde{X}, 0, \tilde{t}) = 0, \tag{3.61}$$

$$\tilde{u}(-1/2, \tilde{Y}, \tilde{t}) = \tilde{u}(1/2, \tilde{Y}, \tilde{t}) = 0. \tag{3.62}$$

There is a flux from the top surface, which is considered to be of the following form:

$$\text{During Lithiation, } \tilde{j}_y(\tilde{X}, 1, \tilde{t}) = \tilde{J}_0(1 - \tilde{c}(\tilde{X}, 1, \tilde{t})) \text{ and} \tag{3.63}$$

$$\text{During Delithiation, } \tilde{j}_y(\tilde{X}, 1, \tilde{t}) = -\tilde{J}_0 \tilde{c}(\tilde{X}, 1, \tilde{t}). \tag{3.64}$$

Table 3.1: Values of material properties and operating parameters

Material property or parameter	Value
D_0, diffusivity of pure Silicon	10^{-16} m^{2}s^{-1}
α, coefficient of diffusivity	0.18
A_0, parameter used in activity coefficient	-29549 Jmol^{-1}
B_0, parameter used in activity coefficient	-38618 Jmol^{-1}
$V_{\mathrm{m}}^{\mathrm{B}}$, molar volume of Silcon	1.2052×10^{-5} m^{3}mol^{-1}
$\chi_{\max}$, maximum concentration of Li in Si	4.4
η, coefficient of compositional expansion	0.2356
η_E, rate of change of elastic modulus of Li$_\chi$Si with $\tilde{c}$	-0.1464
$\tilde{J}_0$, (parameter used in flux boundary condition)	0.1
R_g, universal gas constant	8.314 JK^{-1}mol^{-1}
T, temperature	300 K
E_{si}, elastic modulus of pure silicon	90.13 GPa
E_{SEI}, elastic modulus of SEI layer	3-10 GPa
ν_{si}, poisson's ratio of pure Silicon	0.22
ν_{SEI}, poisson's ratio of SEI layer	0.30
σ_f, yield strength of pure Silicon	1.5GPa
$\dot{d}_0$, characteristic strain rate for plastic flow in Si	1×10^{-3} s^{-1}
m, stress exponent for plastic flow in Si	4
H, initial height of Silicon thin film	200 nm
L, initial length of Silicon thin film	2000 nm
H_{SEI}, initial length of SEI layer	20 nm

Appendix A

Equations in Component Form for COMSOL

In the development of following equations only non-zero components of various tensors are mentioned.

Introducing $\tilde{X}$, $\tilde{Y}$, $\tilde{u}$ and $\tilde{v}$ in equation 3.4, the component of $\mathbf{F}$ are

$$[\mathbf{F}] = \begin{bmatrix} 1+\frac{\partial \tilde{u}}{\partial \tilde{X}} & \frac{\partial \tilde{u}}{\partial \tilde{Y}} & 0 \\ \frac{\partial \tilde{v}}{\partial \tilde{X}} & 1+\frac{\partial \tilde{v}}{\partial \tilde{Y}} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} F_{11} & F_{12} & 0 \\ F_{21} & F_{22} & 0 \\ 0 & 0 & F_{33} \end{bmatrix}. \tag{A.1}$$

From 3.19

$$F_{11}^{\mathrm{el}} = \frac{F_{11}\,\lambda_{22} - F_{12}\,\lambda_{21}}{J{c}^{1/3}\,\left(\lambda_{11}\,\lambda_{22} - \lambda_{12}\,\lambda_{21}\right)} \tag{A.2a}$$

$$F_{21}^{\mathrm{el}} = \frac{F_{21}\,\lambda_{22} - F_{22}\,\lambda_{21}}{J{c}^{1/3}\,\left(\lambda_{11}\,\lambda_{22} - \lambda_{12}\,\lambda_{21}\right)} \tag{A.2b}$$

$$F_{12}^{\mathrm{el}} = -\frac{F_{11}\,\lambda_{12} - F_{12}\,\lambda_{11}}{J{c}^{1/3}\,\left(\lambda_{11}\,\lambda_{22} - \lambda_{12}\,\lambda_{21}\right)} \tag{A.2c}$$

$$F_{22}^{\mathrm{el}} = -\frac{F_{21}\,\lambda_{12} - F_{22}\,\lambda_{11}}{J{c}^{1/3}\,\left(\lambda_{11}\,\lambda_{22} - \lambda_{12}\,\lambda_{21}\right)} \tag{A.2d}$$

$$F_{33}^{\mathrm{el}} = \frac{1}{J{c}^{1/3}\,\lambda_{33}} \tag{A.2e}$$

The components of $\mathbf{E}^{\text{el}}$ are

$$E^{el}_{11} = \frac{{F^{\text{el}}_{11}}^2}{2} + \frac{{F^{\text{el}}_{21}}^2}{2} - \frac{1}{2} \tag{A.3a}$$

$$E^{el}_{21} = \frac{F^{\text{el}}_{11}\, F^{\text{el}}_{12}}{2} + \frac{F^{\text{el}}_{21}\, F^{\text{el}}_{22}}{2} \tag{A.3b}$$

$$E^{el}_{12} = \frac{F^{\text{el}}_{11}\, F^{\text{el}}_{12}}{2} + \frac{F^{\text{el}}_{21}\, F^{\text{el}}_{22}}{2} \tag{A.3c}$$

$$E^{el}_{22} = \frac{{F^{\text{el}}_{12}}^2}{2} + \frac{{F^{\text{el}}_{22}}^2}{2} - \frac{1}{2} \tag{A.3d}$$

$$E^{el}_{33} = \frac{{F^{\text{el}}_{33}}^2}{2} - \frac{1}{2} \tag{A.3e}$$

Non-dimensionalizing lamé constants and using 3.26

$$\tilde{S}^{\text{el}}_{11} = J^c\, \left(2\, E^{\text{el}}_{11}\, \tilde{\mu}_{\text{si}} + \tilde{\lambda}_{\text{si}}\, \left(E^{\text{el}}_{11} + E^{\text{el}}_{22} + E^{\text{el}}_{33}\right)\right) \tag{A.4a}$$

$$\tilde{S}^{\text{el}}_{21} = 2\, E^{\text{el}}_{21}\, J^c\, \tilde{\mu}_{\text{si}} \tag{A.4b}$$

$$\tilde{S}^{\text{el}}_{12} = 2\, E^{\text{el}}_{12}\, J^c\, \tilde{\mu}_{\text{si}} \tag{A.4c}$$

$$\tilde{S}^{\text{el}}_{22} = J^c\, \left(2\, E^{\text{el}}_{22}\, \tilde{\mu}_{\text{si}} + \tilde{\lambda}_{\text{si}}\, \left(E^{\text{el}}_{11} + E^{\text{el}}_{22} + E^{\text{el}}_{33}\right)\right) \tag{A.4d}$$

$$\tilde{S}^{\text{el}}_{33} = J^c\, \left(2\, E^{\text{el}}_{33}\, \tilde{\mu}_{\text{si}} + \tilde{\lambda}_{\text{si}}\, \left(E^{\text{el}}_{11} + E^{\text{el}}_{22} + E^{\text{el}}_{33}\right)\right) \tag{A.4e}$$

From 3.27 and 3.28

$$\tilde{S}_{11} = \frac{\tilde{S}^{\text{el}}_{11}\, {\lambda_{22}}^2 + \tilde{S}^{\text{el}}_{22}\, {\lambda_{12}}^2 - \tilde{S}^{\text{el}}_{12}\, \lambda_{12}\, \lambda_{22} - \tilde{S}^{\text{el}}_{21}\, \lambda_{12}\, \lambda_{22}}{J^{c\,2/3}\, \left(\lambda_{11}\, \lambda_{22} - \lambda_{12}\, \lambda_{21}\right)^2} \tag{A.5a}$$

$$\tilde{S}_{21} = \frac{\tilde{S}^{\text{el}}_{12}\, \lambda_{12}\, \lambda_{21} - \tilde{S}^{\text{el}}_{22}\, \lambda_{11}\, \lambda_{12} - \tilde{S}^{\text{el}}_{11}\, \lambda_{21}\, \lambda_{22} + \tilde{S}^{\text{el}}_{21}\, \lambda_{11}\, \lambda_{22}}{J^{c\,2/3}\, \left(\lambda_{11}\, \lambda_{22} - \lambda_{12}\, \lambda_{21}\right)^2} \tag{A.5b}$$

$$\tilde{S}_{12} = \frac{\tilde{S}^{\text{el}}_{12}\, \lambda_{11}\, \lambda_{22} - \tilde{S}^{\text{el}}_{22}\, \lambda_{11}\, \lambda_{12} - \tilde{S}^{\text{el}}_{11}\, \lambda_{21}\, \lambda_{22} + \tilde{S}^{\text{el}}_{21}\, \lambda_{12}\, \lambda_{21}}{J^{c\,2/3}\, \left(\lambda_{11}\, \lambda_{22} - \lambda_{12}\, \lambda_{21}\right)^2} \tag{A.5c}$$

$$\tilde{S}_{22} = \frac{\tilde{S}^{\text{el}}_{11}\, {\lambda_{21}}^2 + \tilde{S}^{\text{el}}_{22}\, {\lambda_{11}}^2 - \tilde{S}^{\text{el}}_{12}\, \lambda_{11}\, \lambda_{21} - \tilde{S}^{\text{el}}_{21}\, \lambda_{11}\, \lambda_{21}}{J^{c\,2/3}\, \left(\lambda_{11}\, \lambda_{22} - \lambda_{12}\, \lambda_{21}\right)^2} \tag{A.5d}$$

$$\tilde{S}_{33} = \frac{\tilde{S}^{\text{el}}_{33}}{J^{c\,2/3}\, {\lambda_{33}}^2} \tag{A.5e}$$

$$\tilde{P}_{11} = F_{11}\,\tilde{S}_{11} + F_{12}\,\tilde{S}_{21} \tag{A.6a}$$

$$\tilde{P}_{21} = F_{21}\,\tilde{S}_{11} + F_{22}\,\tilde{S}_{21} \tag{A.6b}$$

$$\tilde{P}_{12} = F_{11}\,\tilde{S}_{12} + F_{12}\,\tilde{S}_{22} \tag{A.6c}$$

$$\tilde{P}_{22} = F_{21}\,\tilde{S}_{12} + F_{22}\,\tilde{S}_{22} \tag{A.6d}$$

$$\tilde{P}_{33} = \tilde{S}_{33} \tag{A.6e}$$

$$\tilde{\sigma}_{11} = \frac{F_{11}\,\tilde{P}_{11} + F_{12}\,\tilde{P}_{12}}{J} \tag{A.7a}$$

$$\tilde{\sigma}_{21} = \frac{F_{11}\,\tilde{P}_{21} + F_{12}\,\tilde{P}_{22}}{J} \tag{A.7b}$$

$$\tilde{\sigma}_{12} = \frac{F_{21}\,\tilde{P}_{11} + F_{22}\,\tilde{P}_{12}}{J} \tag{A.7c}$$

$$\tilde{\sigma}_{22} = \frac{F_{21}\,\tilde{P}_{21} + F_{22}\,\tilde{P}_{22}}{J} \tag{A.7d}$$

$$\tilde{\sigma}_{33} = \frac{\tilde{P}_{33}}{J} \tag{A.7e}$$

$$\tilde{\tau}_{11} = \frac{2\,\tilde{\sigma}_{11}}{3} - \frac{\tilde{\sigma}_{22}}{3} - \frac{\tilde{\sigma}_{33}}{3} \tag{A.8a}$$

$$\tilde{\tau}_{21} = \tilde{\sigma}_{21} \tag{A.8b}$$

$$\tilde{\tau}_{12} = \tilde{\sigma}_{12} \tag{A.8c}$$

$$\tilde{\tau}_{22} = \frac{2\,\tilde{\sigma}_{22}}{3} - \frac{\tilde{\sigma}_{11}}{3} - \frac{\tilde{\sigma}_{33}}{3} \tag{A.8d}$$

$$\tilde{\tau}_{33} = \frac{2\,\tilde{\sigma}_{33}}{3} - \frac{\tilde{\sigma}_{22}}{3} - \frac{\tilde{\sigma}_{11}}{3} \tag{A.8e}$$

$$\tilde{\sigma}_{\mathrm{eff}} = \sqrt{\frac{3}{2}(\tilde{\tau}_{11}^2 + \tilde{\tau}_{22}^2 + \tilde{\tau}_{33}^2 + 2\tilde{\tau}_{12}^2)} \tag{A.9}$$

Using 3.12

$$\tilde{M}^{\text{el}}_{11} = -\frac{J\,\left(F^{\text{el}}_{11}\,F^{\text{el}}_{12}\,\tilde{\tau}_{12} - F^{\text{el}}_{11}\,F^{\text{el}}_{22}\,\tilde{\tau}_{11} + F^{\text{el}}_{12}\,F^{\text{el}}_{21}\,\tilde{\tau}_{22} - F^{\text{el}}_{21}\,F^{\text{el}}_{22}\,\tilde{\tau}_{21}\right)}{F^{\text{el}}_{11}\,F^{\text{el}}_{22} - F^{\text{el}}_{12}\,F^{\text{el}}_{21}} \tag{A.10a}$$

$$\tilde{M}^{\text{el}}_{21} = -\frac{J\,\left({F^{\text{el}}_{12}}^2\,\tilde{\tau}_{12} - {F^{\text{el}}_{22}}^2\,\tilde{\tau}_{21} - F^{\text{el}}_{12}\,F^{\text{el}}_{22}\,\tilde{\tau}_{11} + F^{\text{el}}_{12}\,F^{\text{el}}_{22}\,\tilde{\tau}_{22}\right)}{F^{\text{el}}_{11}\,F^{\text{el}}_{22} - F^{\text{el}}_{12}\,F^{\text{el}}_{21}} \tag{A.10b}$$

$$\tilde{M}^{\text{el}}_{12} = \frac{J\,\left({F^{\text{el}}_{11}}^2\,\tilde{\tau}_{12} - {F^{\text{el}}_{21}}^2\,\tilde{\tau}_{21} - F^{\text{el}}_{11}\,F^{\text{el}}_{21}\,\tilde{\tau}_{11} + F^{\text{el}}_{11}\,F^{\text{el}}_{21}\,\tilde{\tau}_{22}\right)}{F^{\text{el}}_{11}\,F^{\text{el}}_{22} - F^{\text{el}}_{12}\,F^{\text{el}}_{21}} \tag{A.10c}$$

$$\tilde{M}^{\text{el}}_{22} = \frac{J\,\left(F^{\text{el}}_{11}\,F^{\text{el}}_{12}\,\tilde{\tau}_{12} - F^{\text{el}}_{12}\,F^{\text{el}}_{21}\,\tilde{\tau}_{11} + F^{\text{el}}_{11}\,F^{\text{el}}_{22}\,\tilde{\tau}_{22} - F^{\text{el}}_{21}\,F^{\text{el}}_{22}\,\tilde{\tau}_{21}\right)}{F^{\text{el}}_{11}\,F^{\text{el}}_{22} - F^{\text{el}}_{12}\,F^{\text{el}}_{21}} \tag{A.10d}$$

$$\tilde{M}^{\text{el}}_{33} = J\,\tilde{\tau}_{33} \tag{A.10e}$$

These equations need editing if Fpdot_mat.tex is changed

$$\dot{\tilde{F}}^{\text{p}}_{11} = \dot{\tilde{d}}_0 \left(\frac{\tilde{\sigma}_{\text{eff}}}{\tilde{\sigma}_f} - 1\right)^m \left(\frac{3\,\tilde{M}^{\text{el}}_{11}\,\lambda_{11}}{2\,J\,\tilde{\sigma}_{\text{eff}}} + \frac{3\,\tilde{M}^{\text{el}}_{12}\,\lambda_{21}}{2\,J\,\tilde{\sigma}_{\text{eff}}}\right) \mathrm{H}\left(\frac{\sigma_{\text{eff}}}{\sigma_{\text{f}}} - 1\right) \tag{A.11a}$$

$$\dot{\tilde{F}}^{\text{p}}_{21} = \dot{\tilde{d}}_0 \left(\frac{\tilde{\sigma}_{\text{eff}}}{\tilde{\sigma}_f} - 1\right)^m \left(\frac{3\,\tilde{M}^{\text{el}}_{21}\,\lambda_{11}}{2\,J\,\tilde{\sigma}_{\text{eff}}} + \frac{3\,\tilde{M}^{\text{el}}_{22}\,\lambda_{21}}{2\,J\,\tilde{\sigma}_{\text{eff}}}\right) \mathrm{H}\left(\frac{\sigma_{\text{eff}}}{\sigma_{\text{f}}} - 1\right) \tag{A.11b}$$

$$\dot{\tilde{F}}^{\text{p}}_{12} = \dot{\tilde{d}}_0 \left(\frac{\tilde{\sigma}_{\text{eff}}}{\tilde{\sigma}_f} - 1\right)^m \left(\frac{3\,\tilde{M}^{\text{el}}_{11}\,\lambda_{12}}{2\,J\,\tilde{\sigma}_{\text{eff}}} + \frac{3\,\tilde{M}^{\text{el}}_{12}\,\lambda_{22}}{2\,J\,\tilde{\sigma}_{\text{eff}}}\right) \mathrm{H}\left(\frac{\sigma_{\text{eff}}}{\sigma_{\text{f}}} - 1\right) \tag{A.11c}$$

$$\dot{\tilde{F}}^{\text{p}}_{22} = \dot{\tilde{d}}_0 \left(\frac{\tilde{\sigma}_{\text{eff}}}{\tilde{\sigma}_f} - 1\right)^m \left(\frac{3\,\tilde{M}^{\text{el}}_{21}\,\lambda_{12}}{2\,J\,\tilde{\sigma}_{\text{eff}}} + \frac{3\,\tilde{M}^{\text{el}}_{22}\,\lambda_{22}}{2\,J\,\tilde{\sigma}_{\text{eff}}}\right) \mathrm{H}\left(\frac{\sigma_{\text{eff}}}{\sigma_{\text{f}}} - 1\right) \tag{A.11d}$$

$$\dot{\tilde{F}}^{\text{p}}_{33} = \frac{3\,\tilde{M}^{\text{el}}_{33}\,\dot{\tilde{d}}_0\,\lambda_{33}\left(\frac{\tilde{\sigma}_{\text{eff}}}{\tilde{\sigma}_f} - 1\right)^m}{2\,J\,\tilde{\sigma}_{\text{eff}}} \mathrm{H}\left(\frac{\sigma_{\text{eff}}}{\sigma_{\text{f}}} - 1\right) \tag{A.11e}$$

$$\tilde{\boldsymbol{j}} = \frac{\boldsymbol{j}H}{\frac{\chi_{\max}}{V_{\mathrm{m}}^{\mathrm{B}}}D_0} = -\frac{1}{R_g T}\tilde{D}\tilde{c}(\mathbf{F})^{-1}(\mathbf{F})^{-\mathsf{T}}\boldsymbol{\nabla}_{\boldsymbol{X}}\mu \tag{A.12}$$

$$D = D_0\exp(\frac{\alpha S_h}{E_0}) = D_0\exp(\alpha\tilde{S}_h) = D_0\exp\left(\alpha\frac{\tilde{S}_{11}+\tilde{S}_{33}}{2}\right) \tag{A.13}$$

$$\tilde{\mu_0} = \log(\gamma\tilde{c}) \tag{A.14}$$

$$\tilde{\mu}_s = \frac{1}{R_g T}\mu_s \tag{A.15}$$

$$\begin{aligned}
&= \frac{V_m^b}{R_g T\chi_{\max}}\left[-\frac{1}{3}\frac{\partial J^c}{\partial\tilde{c}}\tilde{F}^{\mathrm{el}}_{im}\tilde{F}^{\mathrm{el}}_{in}C_{mnkl}\tilde{E}^{\mathrm{el}}_{kl} + \frac{1}{2}\left(J^c\frac{\partial C_{ijkl}}{\partial\tilde{c}} + \frac{\partial J^c}{\partial\tilde{c}}C_{ijkl}\right)\tilde{E}^{\mathrm{el}}_{ij}\tilde{E}^{\mathrm{el}}_{kl}\right] \\
&= \frac{1}{\chi_{\max}}\left[-\frac{1}{3}\frac{\partial J^c}{\partial\tilde{c}}\tilde{F}^{\mathrm{el}}_{im}\tilde{F}^{\mathrm{el}}_{in}\tilde{C}_{mnkl}\tilde{E}^{\mathrm{el}}_{kl} + \frac{1}{2}\left(J^c\frac{\partial\tilde{C}_{ijkl}}{\partial\tilde{c}} + \frac{\partial J^c}{\partial\tilde{c}}\tilde{C}_{ijkl}\right)\tilde{E}^{\mathrm{el}}_{ij}\tilde{E}^{\mathrm{el}}_{kl}\right]
\end{aligned} \tag{A.16}$$

$$\tilde{C}_{ijkl}\tilde{E}^{\mathrm{el}}_{kl} = \tilde{P}^{\mathrm{el}}_{ij} = \tilde{S}^{\mathrm{el}}_{ij}/J^c \tag{A.17}$$

(Above equation is correct only for how I am writing equations in COMSOL)

$$\Longrightarrow \tilde{C}_{ijkl} = \tilde{\lambda}_{si}(\tilde{c})\delta_{ij}\delta_{kl} + \tilde{\mu}_{si}(\tilde{c})(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \tag{A.18}$$

$$\begin{aligned}
\tilde{\mu}_s &= \frac{1}{\chi_{\max}}\left[-\frac{1}{3}\frac{\partial J^c}{\partial\tilde{c}}\tilde{F}^{\mathrm{el}}_{im}\tilde{F}^{\mathrm{el}}_{in}\tilde{P}^{\mathrm{el}}_{mn} + \frac{1}{2}J^c\frac{\partial\tilde{C}_{ijkl}}{\partial\tilde{c}}\tilde{E}^{\mathrm{el}}_{ij}\tilde{E}^{\mathrm{el}}_{kl} + \frac{1}{2}\frac{\partial J^c}{\partial\tilde{c}}\tilde{C}_{ijkl}\tilde{E}^{\mathrm{el}}_{ij}\tilde{E}^{\mathrm{el}}_{kl}\right] \\
&= \frac{1}{\chi_{\max}}\left[-\frac{1}{3}\frac{\partial J^c}{\partial\tilde{c}}\tilde{F}^{\mathrm{el}}_{im}\tilde{F}^{\mathrm{el}}_{in}\tilde{P}^{\mathrm{el}}_{mn} + \frac{1}{2}J^c\frac{\partial\tilde{C}_{ijkl}}{\partial\tilde{c}}\tilde{E}^{\mathrm{el}}_{ij}\tilde{E}^{\mathrm{el}}_{kl} + \frac{1}{2}\frac{\partial J^c}{\partial\tilde{c}}\tilde{E}^{\mathrm{el}}_{ij}\tilde{P}^{\mathrm{el}}_{kl}\right] \\
&= \frac{1}{\chi_{\max}}\left[\frac{\partial J^c}{\partial\tilde{c}}\tilde{P}^{\mathrm{el}}_{mn}\left(-\frac{1}{3}\tilde{F}^{\mathrm{el}}_{im}\tilde{F}^{\mathrm{el}}_{in} + \frac{1}{2}\tilde{E}^{\mathrm{el}}_{mn}\right) + \frac{1}{2}J^c\frac{\partial\tilde{C}_{ijkl}}{\partial\tilde{c}}\tilde{E}^{\mathrm{el}}_{ij}\tilde{E}^{\mathrm{el}}_{kl}\right] \\
&= \frac{1}{\chi_{\max}}\left[\frac{\partial J^c}{\partial\tilde{c}}\tilde{P}^{\mathrm{el}}_{mn}\left(-\frac{1}{3}(2\tilde{E}^{\mathrm{el}}_{mn} + \delta_{mn}) + \frac{1}{2}\tilde{E}^{\mathrm{el}}_{mn}\right) + \frac{1}{2}J^c\frac{\partial\tilde{C}_{ijkl}}{\partial\tilde{c}}\tilde{E}^{\mathrm{el}}_{ij}\tilde{E}^{\mathrm{el}}_{kl}\right] \\
&= \frac{1}{\chi_{\max}}\left[-\frac{1}{6}\frac{\partial J^c}{\partial\tilde{c}}\tilde{P}^{\mathrm{el}}_{mn}\tilde{E}^{\mathrm{el}}_{mn} - \frac{1}{3}\frac{\partial J^c}{\partial\tilde{c}}\tilde{P}^{\mathrm{el}}_{mn}\delta_{mn} + \frac{1}{2}J^c\frac{\partial\tilde{C}_{ijkl}}{\partial\tilde{c}}\tilde{E}^{\mathrm{el}}_{ij}\tilde{E}^{\mathrm{el}}_{kl}\right] \\
&= \frac{1}{\chi_{\max}}\left[-\frac{1}{6}\frac{\partial J^c}{\partial\tilde{c}}\tilde{P}^{\mathrm{el}}_{mn}\tilde{E}^{\mathrm{el}}_{mn} - \frac{1}{3}\frac{\partial J^c}{\partial\tilde{c}}\tilde{P}^{\mathrm{el}}_{mm} + \frac{1}{2}J^c\frac{\partial\tilde{C}_{ijkl}}{\partial\tilde{c}}\tilde{E}^{\mathrm{el}}_{ij}\tilde{E}^{\mathrm{el}}_{kl}\right] \\
&= \frac{1}{\chi_{\max}}(\tilde{\mu}_1 + \tilde{\mu}_2 + \tilde{\mu}_3)
\end{aligned} \tag{A.19}$$

$$\tilde{\mu}_1 = -\frac{1}{6}\frac{\partial J^c}{\partial \tilde{c}}[\tilde{P}^{\mathrm{el}}_{11}\tilde{E}^{\mathrm{el}}_{11} + \tilde{P}^{\mathrm{el}}_{22}\tilde{E}^{\mathrm{el}}_{22} + 2\tilde{P}^{\mathrm{el}}_{12}\tilde{E}^{\mathrm{el}}_{12} + \tilde{P}^{\mathrm{el}}_{33}\tilde{E}^{\mathrm{el}}_{33}] \tag{A.20}$$

$$\tilde{\mu}_2 = -\frac{1}{3}\frac{\partial J^c}{\partial \tilde{c}}[\tilde{P}^{\mathrm{el}}_{11} + \tilde{P}^{\mathrm{el}}_{22} + \tilde{P}^{\mathrm{el}}_{33}] \tag{A.21}$$

$$\tilde{\mu}_3 = \frac{1}{2}J^c\frac{\partial \tilde{C}_{ijkl}}{\partial \tilde{c}}\tilde{E}^{\mathrm{el}}_{kl}\tilde{E}^{\mathrm{el}}_{ij} \tag{A.22}$$

$$\frac{\partial \tilde{C}_{ijkl}}{\partial \tilde{c}} = \frac{\partial \tilde{\lambda}_{si}(\tilde{c})}{\partial \tilde{c}}\delta_{ij}\delta_{kl} + \frac{\partial \tilde{\mu}_{si}(\tilde{c})}{\partial \tilde{c}}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \tag{A.23}$$

$$\begin{aligned}
\tilde{\mu}_3 &= \frac{1}{2}J^c\frac{\partial \tilde{\lambda}_{si}(\tilde{c})}{\partial \tilde{c}}\delta_{ij}\delta_{kl}\tilde{E}^{\mathrm{el}}_{kl}\tilde{E}^{\mathrm{el}}_{ij} + \frac{1}{2}J^c\frac{\partial \tilde{\mu}_{si}(\tilde{c})}{\partial \tilde{c}}(\delta_{ik}\delta_{jl}\tilde{E}^{\mathrm{el}}_{kl}\tilde{E}^{\mathrm{el}}_{ij} + \delta_{il}\delta_{jk}\tilde{E}^{\mathrm{el}}_{kl}\tilde{E}^{\mathrm{el}}_{ij}) \\
&= \frac{1}{2}J^c\frac{\partial \tilde{\lambda}_{si}(\tilde{c})}{\partial \tilde{c}}\tilde{E}^{\mathrm{el}}_{kk}\tilde{E}^{\mathrm{el}}_{ii} + \frac{1}{2}J^c\frac{\partial \tilde{\mu}_{si}(\tilde{c})}{\partial \tilde{c}}(\tilde{E}^{\mathrm{el}}_{ij}\tilde{E}^{\mathrm{el}}_{ij} + \tilde{E}^{\mathrm{el}}_{ji}\tilde{E}^{\mathrm{el}}_{ij}) \\
&= \frac{1}{2}J^c\frac{\partial \tilde{\lambda}_{si}(\tilde{c})}{\partial \tilde{c}}(\mathrm{tr}(\mathbf{E}^{\mathrm{el}}))^2 + J^c\frac{\partial \tilde{\mu}_{si}(\tilde{c})}{\partial \tilde{c}}\tilde{E}^{\mathrm{el}}_{ij}\tilde{E}^{\mathrm{el}}_{ij} \\
&= \frac{1}{2}J^c[\tilde{\lambda}'_{\mathrm{si}}(c)(\tilde{E}^{\mathrm{el}}_{11} + \tilde{E}^{\mathrm{el}}_{22} + \tilde{E}^{\mathrm{el}}_{33})^2 + 2\tilde{\mu}'_{\mathrm{si}}(\tilde{c})((\tilde{E}^{\mathrm{el}}_{11})^2 + (\tilde{E}^{\mathrm{el}}_{22})^2 + (\tilde{E}^{\mathrm{el}}_{33})^2 + 2(\tilde{E}^{\mathrm{el}}_{12})^2)]
\end{aligned} \tag{A.24}$$

$$\begin{aligned}
\tilde{\boldsymbol{j}} &= \boldsymbol{j}HV^b_m/(\chi_{\max}D_0) \\
&= -\frac{D}{D_0}H\tilde{c}\tilde{\mathbf{F}}^{-1}(\tilde{\mathbf{F}}^{-1})^{\mathsf{T}}\nabla_{\boldsymbol{X}}\tilde{\mu}
\end{aligned} \tag{A.25}$$

$$\begin{aligned}
\tilde{j}_x &= \frac{-\bar{D}H\tilde{c}}{J^2}\left(\frac{\partial \tilde{\mu}}{\partial X}(\tilde{F}^2_{12} + \tilde{F}^2_{22}) - \frac{\partial \tilde{\mu}}{\partial Y}(\tilde{F}_{11}\tilde{F}_{12} + \tilde{F}_{21}\tilde{F}_{22})\right) \\
&= \frac{-\bar{D}\tilde{c}}{J^2}\left(\frac{\partial \tilde{\mu}}{\partial \tilde{X}}(\tilde{F}^2_{12} + \tilde{F}^2_{22}) - \frac{\partial \tilde{\mu}}{\partial \tilde{Y}}(\tilde{F}_{11}\tilde{F}_{12} + \tilde{F}_{21}\tilde{F}_{22})\right)
\end{aligned} \tag{A.26}$$

$$\begin{aligned}
\tilde{j}_y &= \frac{-\bar{D}H\tilde{c}}{J^2}\left(\frac{\partial \tilde{\mu}}{\partial Y}(\tilde{F}^2_{11} + \tilde{F}^2_{21}) - \frac{\partial \tilde{\mu}}{\partial X}(\tilde{F}_{11}\tilde{F}_{12} + \tilde{F}_{21}\tilde{F}_{22})\right) \\
&= \frac{-\bar{D}\tilde{c}}{J^2}\left(\frac{\partial \tilde{\mu}}{\partial \tilde{Y}}(\tilde{F}^2_{11} + \tilde{F}^2_{21}) - \frac{\partial \tilde{\mu}}{\partial \tilde{X}}(\tilde{F}_{11}\tilde{F}_{12} + \tilde{F}_{21}\tilde{F}_{22})\right)
\end{aligned} \tag{A.27}$$

Momentum Conservation equations in non-dimensional form:

$$\frac{\partial \tilde{P}_{11}}{\partial \tilde{X}} + \frac{\partial \tilde{P}_{12}}{\partial \tilde{Y}} = 0 \tag{A.28a}$$

$$\text{and, } \frac{\partial \tilde{P}_{21}}{\partial \tilde{X}} + \frac{\partial \tilde{P}_{22}}{\partial \tilde{Y}} = 0. \tag{A.28b}$$

Mass conservation Equation in non-dimensional form:

$$\begin{aligned}
\frac{\partial c}{\partial t} &= -\boldsymbol{\nabla}_{\boldsymbol{X}} \cdot \boldsymbol{j} = -(\frac{\partial j_x}{\partial X} + \frac{\partial j_y}{\partial Y}) \\
\frac{\chi_{\mathrm{max}}}{V_{\mathrm{m}}^{\mathrm{B}}} \frac{D_0}{H^2} \frac{\partial \tilde{c}}{\partial \tilde{t}} &= -(\frac{1}{H} \frac{\partial \tilde{j}_x}{\partial \tilde{X}} + \frac{1}{H} \frac{\partial \tilde{j}_y}{\partial \tilde{Y}}) \frac{\chi_{\mathrm{max}}}{V_{\mathrm{m}}^{\mathrm{B}}} \frac{D_0}{H} \\
\Longrightarrow \frac{\partial \tilde{c}}{\partial \tilde{t}} &= -(\frac{\partial \tilde{j}_x}{\partial \tilde{X}} + \frac{\partial \tilde{j}_y}{\partial \tilde{Y}})
\end{aligned} \tag{A.29}$$

Bibliography

Bhowmick, A. and Chakraborty, J. (2023), 'Predicting non-axisymmetric growth and facet evolution during lithiation of crystalline silicon anode particles through orientation-dependent interface reaction', *International Journal of Solids and Structures* **273**, 112266.

Bower, A. F., Guduru, P. R. and Sethuraman, V. A. (2011), 'A finite strain model of stress, diffusion, plastic flow, and electrochemical reactions in a lithium-ion half-cell', *Journal of the Mechanics and Physics of Solids* **59**(4), 804–828.

Cui, Z., Gao, F. and Qu, J. (2012), 'A finite deformation stress-dependent chemical potential and its applications to lithium ion batteries', *Journal of the Mechanics and Physics of Solids* **60**(7), 1280–1295.

Gurtin, M. E. and Anand, L. (2005*a*), 'A theory of strain-gradient plasticity for isotropic, plastically irrotational materials. part i: Small deformations', *Journal of the Mechanics and Physics of Solids* **53**(7), 1624–1649.

Gurtin, M. E. and Anand, L. (2005*b*), 'A theory of strain-gradient plasticity for isotropic, plastically irrotational materials. part ii: Finite deformations', *International Journal of Plasticity* **21**(12), 2297–2318.

Gurtin, M. E., Fried, E. and Anand, L. (2010), *The mechanics and thermodynamics of continua*, Cambridge university press.

Haftbaradaran, H., Song, J., Curtin, W. and Gao, H. (2011), 'Continuum and atomistic models of strongly coupled diffusion, stress, and solute concentration', *Journal of Power Sources* **196**(1), 361–370.

Hong, W., Zhao, X., Zhou, J. and Suo, Z. (2008), 'A theory of coupled diffusion and large deformation in polymeric gels', *Journal of the Mechanics and Physics of Solids* **56**(5), 1779–1793.

Lai, W. M., Rubin, D. and Krempl, E. (2009), *Introduction to continuum mechanics*, Butterworth-Heinemann.

Lee, E. H. (1969), 'Elastic-plastic deformation at finite strains', *Journal of Applied Mechanics* **36**, 1–6.

Mandel, J. (1971), 'Plastidite et viscoplasticite', *CISM Lectures Notes* **97**.

Shenoy, V. B., Johari, P. and Qi, Y. (2010), 'Elastic softening of amorphous and crystalline li–si phases with increasing li concentration: a first-principles study', *Journal of Power Sources* **195**(19), 6825–6830.