BTP-1

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

CERTIFICATE

This is to certify that the thesis entitled **BTP-1**, submitted by **Himanshu Sharma** to the Indian Institute of Technology Kharagpur, is a record of bona fide research work under my supervision and I consider it worthy of consideration for the award of the degree of **Dual Degree (B.Tech + M.Tech)** of the Institute.

Supervisor

Date:

DECLARATION

I certify that

a. The work contained in the thesis is original and has been done by myself under the general supervision of my supervisor.

b. The work has not been submitted to any other Institute for any degree or diploma.

c. I have followed the guidelines provided by the Institute in writing the thesis.

d. I have conformed to the norms and guidelines in the Ethical Code of Conduct of the Institute.

e. Whenever I have used materials (data, theoretical analysis, and text) from other sources, I have given due credit to them by citing them in the text of the thesis and giving their details in the references.

f. Whenever I have quoted written materials from other sources, I have put them under quotation marks and given due credit to the sources by citing them and giving required details in the references.

Signature of the Student

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.

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.

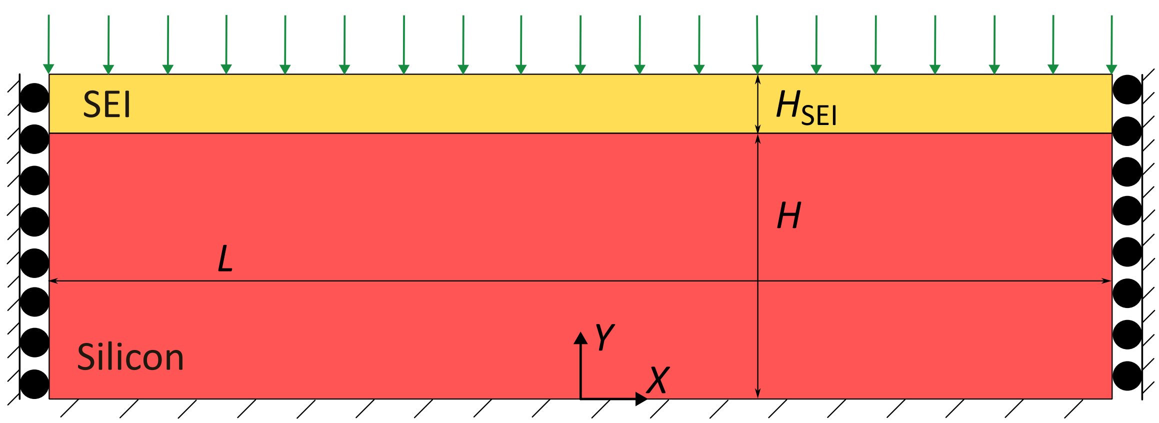

Figure 2.1: Schematic of the problem showing geometric parameters and boundary conditions.

SEI is considered completely permeable to Li-ions and thus does not undergo deformation due to lithiation. In the Silicon thin film, the diffusion 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). This leads to a two-way coupled system of PDEs. Due to the large deformation of the Si during lithiation, it is necessary to formulate the problem with finite deformation theory with an elastoplastic constitutive behavior. In the present study, both Si and SEI are considered to exhibit a viscoplastic nature. The constitutive law for the elastic regime is isotropic and concentration-dependent for Silicon film and constant for SEI. For Mechanical equilibrium, a quasi-static model is employed.

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 and Green-Lagrange strain are denoted by $\mathbf{F}$ and $\mathbf{E}$, respectively. Therefore,

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

$$\mathbf{E} = \frac{1}{2}(\mathbf{F}^{\mathsf{T}} \cdot \mathbf{F} - \mathbf{I}) \tag{3.4}$$

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. 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 F are given by (Lai et al., 2009)

$$[\mathbf{F}] = \begin{bmatrix} 1 + \frac{\partial u}{\partial X} & \frac{\partial u}{\partial Y} & 0 \\ \frac{\partial v}{\partial X} & 1 + \frac{\partial v}{\partial Y} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} F_{11} & F_{12} & 0 \\ F_{21} & F_{22} & 0 \\ 0 & 0 & F_{33} \end{bmatrix}. \tag{3.5}$$

Both Inelastic 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 4.1, 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

$$\mathbf{F} = \mathbf{F}^{\mathrm{el}} \cdot \ \mathbf{F}^{\mathrm{inel}} \tag{3.6}$$

$$\text{where, } \mathbf{F}^{\mathrm{el}} = \frac{\partial \boldsymbol{x}}{\partial \boldsymbol{x}_I} \text{ and } \mathbf{F}^{\mathrm{inel}} = \frac{\partial \boldsymbol{x}_I}{\partial \boldsymbol{X}}$$

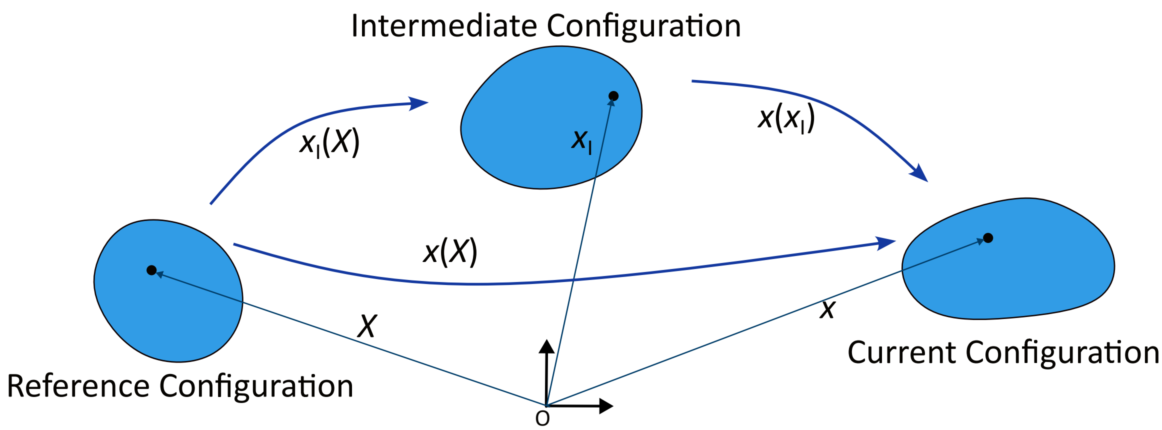

Figure 3.1: Decomposition of the deformation gradient into the elastic and inelastic part.

$\mathbf{F}^{\mathrm{el}}$ 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

$$\mathbf{F}^{\mathrm{inel}} = \mathbf{F}^{\mathrm{c}} \cdot \mathbf{F}^{\mathrm{p}}. \tag{3.7}$$

Where $\mathbf{F}^{\mathrm{c}}$ and $\mathbf{F}^{\mathrm{p}}$ are deformation gradients due to diffusion and plastic flow, respectively.

3.2 Viscoplastic Flow

A viscoplastic constitutive relation of the following form is considered:

$$\mathbf{D}^{\mathrm{P}} = \frac{\partial G(\sigma_{\mathrm{eff}})}{\partial \boldsymbol{\tau}} \tag{3.8}$$

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 and σ_{f} is yield strength defined as

$$\sigma_{\mathrm{f}} = \begin{cases} \sigma_{f,\mathrm{si}} & \text{for Silicon } (-L/2 \leq X \leq L/2 \quad \text{and} \quad 0 \leq Y \leq H) \\ \sigma_{f,\mathrm{SEI}} & \text{for SEI layer } (-L/2 \leq X \leq L/2 \quad \text{and} \quad 0 \leq Y \leq H + H_{\mathrm{SEI}}) \end{cases}$$

Various studies (Bower et al., 2011; Cui et al., 2012) have adopted a power law of the following form for flow potential

$$G(\sigma_{\mathrm{eff}}) = \frac{\sigma_{\mathrm{f}} \dot{d}_0}{\mathrm{m}+1} \left(\frac{\sigma_{\mathrm{eff}}}{\sigma_{\mathrm{f}}} - 1 \right)^{\mathrm{m}+1} \mathrm{H} \left(\frac{\sigma_{\mathrm{eff}}}{\sigma_{\mathrm{f}}} - 1 \right) \tag{3.9}$$

$$\Rightarrow \mathbf{D}^{\mathrm{P}} = \frac{3\boldsymbol{\tau} \dot{d}_0}{2\sigma_{\mathrm{eff}}} \left(\frac{\sigma_{\mathrm{eff}}}{\sigma_{\mathrm{f}}} - 1 \right)^{\mathrm{m}} \mathrm{H} \left(\frac{\sigma_{\mathrm{eff}}}{\sigma_{\mathrm{f}}} - 1 \right). \tag{3.10}$$

where σ_{eff} is the effective von Mises stress, defined in section 4.4, H is the unit step function, σ_{f} is the yield strength of Silicon, 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)

$$\mathbf{D}^{\mathrm{P}} = \mathbf{F}^{\mathrm{el}} \cdot \mathbf{F}^{\mathrm{c}} \cdot \dot{\mathbf{F}}^{\mathrm{p}} \cdot (\mathbf{F}^{\mathrm{p}})^{-1} \cdot (\mathbf{F}^{\mathrm{c}})^{-1} \cdot (\mathbf{F}^{\mathrm{el}})^{-1} \tag{3.11}$$

$$\Rightarrow \dot{\mathbf{F}}^{\mathrm{p}} = (J)^{-1} \frac{3}{2} \frac{\mathbf{M}_{\mathbf{0}}^{\mathrm{el}} \cdot \mathbf{F}^{\mathrm{p}}}{\sigma_{\mathrm{eff}}} \dot{d}_0 \left(\frac{\sigma_{\mathrm{eff}}}{\sigma_{\mathrm{f}}} - 1 \right)^{\mathrm{m}} \mathrm{H} \left(\frac{\sigma_{\mathrm{eff}}}{\sigma_{\mathrm{f}}} - 1 \right) \tag{3.12}$$

$$\text{where } \mathbf{M}_{\mathbf{0}}^{\mathrm{el}} = J(\mathbf{F}^{\mathrm{el}})^{\mathsf{T}} \cdot \boldsymbol{\tau} \cdot (\mathbf{F}^{\mathrm{el}})^{-\mathsf{T}} \tag{3.13}$$

$$\text{and} J = \det(\mathbf{F}). \tag{3.14}$$

$\mathbf{M}_{\mathbf{0}}^{\mathrm{el}}$ 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:

$$[\mathbf{F}^{\mathrm{p}}] = \begin{bmatrix} \lambda_{11} & \lambda_{12} & 0 \\ \lambda_{21} & \lambda_{22} & 0 \\ 0 & 0 & \lambda_{33} \end{bmatrix}. \tag{3.16}$$

Since, $\det(\mathbf{F}^{\mathrm{p}}) = 1$

$$\lambda_{33} = 1/(\lambda_{11}\lambda_{22} - \lambda_{12}\lambda_{21}). \tag{3.17}$$

3.3 Diffusion Induced Deformation

The compound between Lithium and Silicon is $Li_\chi Si$. 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

$$\mathbf{F}^{\mathrm{c}} = (J^c)^{1/3}\mathbf{I} \tag{3.18}$$

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.

Since SEI is permeable to lithiation, $\mathbf{F}^{\mathrm{c}}$ will be considered only for Silicon. Therefore, for the purpose of modelling, $\tilde{c}$ is considered zero in SEI, making $\mathbf{F}^{\mathrm{c}}$ equal to $\mathbf{I}$.

3.4 Mechanical Equilibrium

From equations 4.6 and 4.7,

$$\mathbf{F}^{\mathrm{el}} = \mathbf{F}\cdot(\mathbf{F}^{\mathrm{p}}\cdot\mathbf{F}^{\mathrm{c}})^{-1}. \tag{3.20}$$

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

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 Silicon by $\mathbb{C}$ and its components by C_{ijkl},

$$\hat{w}(\mathbf{F},\tilde{c}) = \frac{1}{2}C_{ijkl}E^{\mathrm{el}}_{ij}E^{\mathrm{el}}_{kl}. \tag{3.22}$$

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

$$C_{ijkl}(\tilde{c}) = \lambda_{\mathrm{mat}}(\tilde{c})\delta_{ij}\delta_{kl} + \mu_{\mathrm{mat}}(\tilde{c})(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}). \tag{3.23}$$

$$\implies \hat{w}(\mathbf{F},\tilde{c}) = \left[\lambda_{\mathrm{mat}}(\tilde{c})(\mathrm{tr}(\mathbf{E}^{\mathrm{el}}))^2 + 2\mu_{\mathrm{mat}}(\tilde{c})\mathbf{E}^{\mathrm{el}}:\mathbf{E}^{\mathrm{el}}\right]. \tag{3.24}$$

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 domainwise as follows:

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

The elastic second Piola-Kirchhoff stress is denoted by $\mathbf{S}^{\mathrm{el}}$. Therefore,

$$\begin{aligned} \mathbf{S}^{\mathrm{el}} &= \frac{\partial \hat{w}(\mathbf{F},\tilde{c})}{\partial \mathbf{E}^{\mathrm{el}}} \\ \implies \mathbf{S}^{\mathrm{el}} &= \lambda_{\mathrm{mat}}(\tilde{c})\mathrm{tr}(\mathbf{E}^{\mathrm{el}})\mathbf{I} + 2\mu_{\mathrm{mat}}(\tilde{c})\mathbf{E}^{\mathrm{el}}. \end{aligned} \tag{3.25}$$

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

$$\begin{aligned} \mathbf{S} = J^{\mathrm{inel}}\,(\mathbf{F}^{\mathrm{inel}})^{-1}\cdot\ \mathbf{S}^{\mathrm{el}}\cdot\ (\mathbf{F}^{\mathrm{inel}})^{-\mathsf{T}} &= J^{c}\,(\mathbf{F}^{\mathrm{p}}\cdot\mathbf{F}^{\mathrm{c}})^{-1}\cdot\mathbf{S}^{\mathrm{el}}\cdot(\mathbf{F}^{\mathrm{p}}\cdot\mathbf{F}^{\mathrm{c}})^{-\mathsf{T}} \\ \implies \mathbf{S} &= (J^{c})^{1/3}(\mathbf{F}^{\mathrm{p}})^{-1}\cdot\mathbf{S}^{\mathrm{el}}\cdot\ (\mathbf{F}^{\mathrm{p}})^{-\mathsf{T}}. \end{aligned} \tag{3.26}$$

The first Piola-Kirchhoff stress is

$$\mathbf{P} = \mathbf{F}\cdot\ \mathbf{S}\ . \tag{3.27}$$

The Cauchy stress tensor, $\boldsymbol{\sigma}$, 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

$$\boldsymbol{\nabla}_{\boldsymbol{X}}\cdot\mathbf{P} = 0. \tag{3.31}$$

3.5 Diffusion

Assuming flux to be negligible in the z direction, the conservation of mass is given by

$$\frac{\partial c}{\partial t} = -\boldsymbol{\nabla}_{\boldsymbol{X}}\cdot\boldsymbol{j} = -\left(\frac{\partial j_X}{\partial X} + \frac{\partial j_Y}{\partial Y}\right). \tag{3.32}$$

Where $\boldsymbol{j}$ is the flux vector 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: (cite a paper which describes the following equation)

$$\hat{\boldsymbol{j}}(\boldsymbol{x},\boldsymbol{t}) = -\frac{1}{R_g T}\frac{D\chi_{\max}\tilde{c}}{V_{\mathrm{m}}^{\mathrm{B}}}\nabla_{\boldsymbol{x}}\mu \tag{3.34}$$

where R_g is the universal gas constant, T is the operating temperature, D is the diffusivity of $\mathrm{Li}_\chi\mathrm{Si}$, $V_{\mathrm{m}}^{\mathrm{B}}$ 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:

$$D = D_0\mathrm{exp}(\frac{\alpha \mathrm{S_h}}{\mathrm{E_0}}) = \mathrm{D_0exp}\left(\alpha\frac{\mathrm{S_{11}}+\mathrm{S_{33}}}{2\mathrm{E_0}}\right) \tag{3.35}$$

where E_0 is defined in section 4.6.
In the reference configuration, the flux is $\boldsymbol{j}(\boldsymbol{X}, t) = J(\mathbf{F})^{-1}\cdot\hat{\boldsymbol{j}}$ (how is the previous expression derived). Now,

$$\begin{aligned}(\nabla_{\boldsymbol{x}}\mu)_i &= \frac{\partial\mu}{\partial x_i} \\ &= \frac{\partial\mu}{\partial X_j}\frac{\partial X_j}{\partial x_i} \\ \Longrightarrow \nabla_{\boldsymbol{x}}\mu &= \mathbf{F}^{-\mathsf{T}}\cdot\nabla_X\mu.\end{aligned} \tag{3.36}$$

From above equations, the flux, $\boldsymbol{j}(\boldsymbol{X}, t)$, in Lagrangian description is expressed as

$$\boldsymbol{j} = -\frac{1}{R_g T}\frac{D\chi_{\max}\tilde{c}}{V_m^b}(\mathbf{F})^{-1}\cdot(\mathbf{F})^{-\mathsf{T}}\cdot\boldsymbol{\nabla}_{\boldsymbol{X}}\mu. \tag{3.37}$$

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 $\mu_0 = R_g T\log(\gamma\tilde{c})$, where γ is the activity coefficient and considered to be concentration dependent, given by the following equation:

$$\gamma = \frac{1}{1-\tilde{c}}\exp(\frac{1}{R_g T}[2(A_0 - 2B_0)\tilde{c} - 3(A_0 - B_0)(\tilde{c}^2)]). \tag{3.39}$$

The stress-dependent part of the chemical potential is (Cui et al., 2012)

$$\mu_s = \frac{V_m^b}{\chi_{\max}}\left[-\frac{1}{3}\frac{\partial J^c}{\partial\tilde{c}}\tilde{F}_{im}^{\mathrm{el}}\tilde{F}_{in}^{\mathrm{el}}C_{mnkl}\tilde{E}_{kl}^{\mathrm{el}} + \frac{1}{2}\left(J^c\frac{\partial C_{ijkl}}{\partial\tilde{c}} + \frac{\partial J^c}{\partial\tilde{c}}C_{ijkl}\right)\tilde{E}_{ij}^{\mathrm{el}}\tilde{E}_{kl}^{\mathrm{el}}\right]. \tag{3.40}$$

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

$$\begin{aligned}
\mathrm{soc} &= \frac{1}{LH}\int_{-L/2}^{L/2}\int_{0}^{H}\tilde{c}\mathrm{dydx} \\
&= H^2\frac{1}{LH}\int_{-L/2H}^{L/2H}\int_{0}^{1}\tilde{c}(\tilde{x},\tilde{y})\mathrm{d\tilde{y}d\tilde{x}} \\
&= \frac{H}{L}\int_{-L/2H}^{L/2H}\int_{0}^{1}\tilde{c}(\tilde{x},\tilde{y})\mathrm{d\tilde{y}d\tilde{x}}
\end{aligned} \tag{3.41}$$

3.6 Non-dimensionalisation

$$\tilde{j}_X, \tilde{j}_Y, \tilde{J}_0, \tilde{\boldsymbol{j}} = \frac{HV_{\mathrm{m}}^{\mathrm{B}}}{(\chi_{\max}D_0)}(j_X, j_y, J_0, \boldsymbol{j}) \tag{3.42}$$

$$\tilde{X}, \tilde{Y}, \tilde{u}, \tilde{v} = \frac{1}{H}(X, Y, u, v) \tag{3.43}$$

$$\tilde{t} = D_0 t/H^2 \tag{3.44}$$

$$\tilde{\mu}_{\mathrm{si}}, \tilde{\lambda}_{\mathrm{si}}, \tilde{E}_{\mathrm{si}} = \frac{1}{E_0}(\mu_{\mathrm{si}}, \lambda_{\mathrm{si}}, E_{\mathrm{si}}) \quad \text{,where} \quad E_0 = \frac{R_g T}{V_{\mathrm{m}}^{\mathrm{B}}} \tag{3.45}$$

$$\tilde{\mu}_0, \tilde{\mu}_1, \tilde{\mu}_2, \tilde{\mu}_3 = \frac{1}{R_g T}(\mu_0, \mu_1, \mu_2, \mu_3) \tag{3.46}$$

$$\tilde{D} = \frac{D}{D_0} \tag{3.47}$$

$$\dot{\tilde{d}}_0 = \frac{\dot{d}_0 H^2}{D_0} \tag{3.48}$$

$$\tilde{\mathbf{S}}^{\mathrm{el}}, \tilde{\mathbf{S}}, \tilde{\mathbf{P}}, \tilde{\boldsymbol{\sigma}}, \tilde{\boldsymbol{\tau}}, \tilde{\mathbf{M}}_0^{\mathrm{el}}, \tilde{\sigma}_{\mathrm{eff}}, \tilde{\sigma}_{\mathrm{f}} = \frac{1}{E_0}(\mathbf{S}^{\mathrm{el}}, \mathbf{S}, \mathbf{P}, \boldsymbol{\sigma}, \boldsymbol{\tau}, \mathbf{M}_0^{\mathrm{el}}, \sigma_{\mathrm{eff}}, \sigma_{\mathrm{f}}) \tag{3.49}$$

3.7 Boundary and Initial Conditions

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

$$\tilde{c}(\tilde{X}, \tilde{Y}, 0) = 0, \tag{3.50}$$

$$\tilde{u}(\tilde{X}, \tilde{Y}, 0) = 0, \tag{3.51}$$

$$\tilde{v}(\tilde{X}, \tilde{Y}, 0) = 0. \tag{3.52}$$

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

$$\tilde{u}(\tilde{X}, 0, \tilde{t}) = \tilde{v}(\tilde{X}, 0, \tilde{t}) = 0, \tag{3.53}$$

$$\tilde{u}(-1/2, \tilde{Y}, \tilde{t}) = \tilde{u}(1/2, \tilde{Y}, \tilde{t}) = 0. \tag{3.54}$$

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

$$\text{During Lithiation, } \tilde{j}_x(\tilde{X}, 1, \tilde{t}) = \tilde{j}_0(1 - \tilde{c}(\tilde{X}, 1, \tilde{t})) \text{ and} \tag{3.55}$$

$$\text{During Delithiation, } \tilde{j}_x(\tilde{X}, 1, \tilde{t}) = \tilde{j}_0\tilde{c}(\tilde{X}, 1, \tilde{t}). \tag{3.56}$$

Table 3.1: Values of material properties and operating parameters

Material property or parameter	Value
D_0, Diffusivity of Silicon	10^{-16} m^{2}s^{-1}
E_{si}, Elastic modulus of pure silicon	90 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
$\sigma_{f,\text{si}}$, Yield strength of pure Silicon	1.5Gpa
$\sigma_{f,\text{SEI}}$, Yield strength of SEI layer	
R_g, Universal gas constant	8.314 JK^{-1}mol^{-1}
T, Temperature	298.15 K
H, Initial height of Silicon thin film	200 μm
L, Initial length of Silicon thin film	20 μm
H_{SEI}, Initial length of SEI layer	10 μm

Chapter 4

Mathematical Formulation

4.1 Kinematics

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

$$\boldsymbol{x} = \boldsymbol{x}(\boldsymbol{X}, t). \tag{4.1}$$

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

$$\boldsymbol{u}(\boldsymbol{X}, t) = \boldsymbol{x}(\boldsymbol{X}, t) - \boldsymbol{X}. \tag{4.2}$$

The total deformation gradient and Green-Lagrange strain are denoted by $\mathbf{F}$ and $\mathbf{E}$, respectively. Therefore,

$$\mathbf{F} = \frac{\partial \boldsymbol{x}}{\partial \boldsymbol{X}} = \boldsymbol{\nabla}_{\boldsymbol{X}} \boldsymbol{u} + \mathbf{I}, \tag{4.3}$$

$$\mathbf{E} = \frac{1}{2}(\mathbf{F}^{\mathsf{T}} \cdot \mathbf{F} - \mathbf{I}) \tag{4.4}$$

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. 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 F are given by (Lai et al., 2009)

$$[\mathbf{F}] = \begin{bmatrix} 1 + \frac{\partial u}{\partial X} & \frac{\partial u}{\partial Y} & 0 \\ \frac{\partial v}{\partial X} & 1 + \frac{\partial v}{\partial Y} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} F_{11} & F_{12} & 0 \\ F_{21} & F_{22} & 0 \\ 0 & 0 & F_{33} \end{bmatrix}. \tag{4.5}$$

Both Inelastic 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 4.1, 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

$$\mathbf{F} = \mathbf{F}^{\mathrm{el}} \cdot \ \mathbf{F}^{\mathrm{inel}} \tag{4.6}$$

$$\text{where, } \mathbf{F}^{\mathrm{el}} = \frac{\partial \boldsymbol{x}}{\partial \boldsymbol{x}_I} \text{ and } \mathbf{F}^{\mathrm{inel}} = \frac{\partial \boldsymbol{x}_I}{\partial \boldsymbol{X}}$$

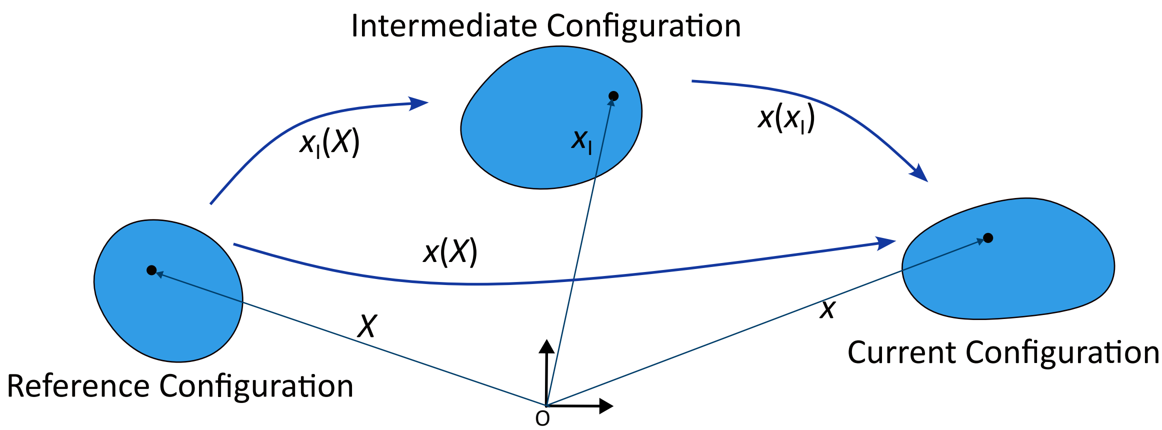

Figure 4.1: Decomposition of the deformation gradient into the elastic and inelastic part.

$\mathbf{F}^{\mathrm{el}}$ 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

$$\mathbf{F}^{\mathrm{inel}} = \mathbf{F}^{\mathrm{c}} \cdot \mathbf{F}^{\mathrm{p}}. \tag{4.7}$$

Where $\mathbf{F}^{\mathrm{c}}$ and $\mathbf{F}^{\mathrm{p}}$ are deformation gradients due to diffusion and plastic flow, respectively.

4.2 Viscoplastic Flow

A viscoplastic constitutive relation of the following form is considered:

$$\mathbf{D}^{\mathrm{P}} = \frac{\partial G(\sigma_{\mathrm{eff}})}{\partial \boldsymbol{\tau}} \tag{4.8}$$

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 and σ_{f} is yield strength defined as

$$\sigma_{\mathrm{f}} = \begin{cases} \sigma_{f,\mathrm{si}} & \text{for Silicon } (-L/2 \leq X \leq L/2 \quad \text{and} \quad 0 \leq Y \leq H) \\ \sigma_{f,\mathrm{SEI}} & \text{for SEI layer } (-L/2 \leq X \leq L/2 \quad \text{and} \quad 0 \leq Y \leq H + H_{\mathrm{SEI}}) \end{cases}$$

Various studies (Bower et al., 2011; Cui et al., 2012) have adopted a power law of the following form for flow potential

$$G(\sigma_{\mathrm{eff}}) = \frac{\sigma_{\mathrm{f}} \dot{d}_0}{\mathrm{m}+1} \left(\frac{\sigma_{\mathrm{eff}}}{\sigma_{\mathrm{f}}} - 1 \right)^{\mathrm{m}+1} \mathrm{H} \left(\frac{\sigma_{\mathrm{eff}}}{\sigma_{\mathrm{f}}} - 1 \right) \tag{4.9}$$

$$\Rightarrow \mathbf{D}^{\mathrm{P}} = \frac{3\boldsymbol{\tau} \dot{d}_0}{2\sigma_{\mathrm{eff}}} \left(\frac{\sigma_{\mathrm{eff}}}{\sigma_{\mathrm{f}}} - 1 \right)^{\mathrm{m}} \mathrm{H} \left(\frac{\sigma_{\mathrm{eff}}}{\sigma_{\mathrm{f}}} - 1 \right). \tag{4.10}$$

where σ_{eff} is the effective von Mises stress, defined in section 4.4, H is the unit step function, σ_{f} is the yield strength of Silicon, 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)

$$\mathbf{D}^{\mathrm{P}} = \mathbf{F}^{\mathrm{el}} \cdot \mathbf{F}^{\mathrm{c}} \cdot \dot{\mathbf{F}}^{\mathrm{p}} \cdot (\mathbf{F}^{\mathrm{p}})^{-1} \cdot (\mathbf{F}^{\mathrm{c}})^{-1} \cdot (\mathbf{F}^{\mathrm{el}})^{-1} \tag{4.11}$$

$$\Rightarrow \dot{\mathbf{F}}^{\mathrm{p}} = (J)^{-1} \frac{3}{2} \frac{\mathbf{M}^{\mathrm{el}}_{\mathbf{0}} \cdot \mathbf{F}^{\mathrm{p}}}{\sigma_{\mathrm{eff}}} \dot{d}_0 \left(\frac{\sigma_{\mathrm{eff}}}{\sigma_{\mathrm{f}}} - 1 \right)^{\mathrm{m}} \mathrm{H} \left(\frac{\sigma_{\mathrm{eff}}}{\sigma_{\mathrm{f}}} - 1 \right) \tag{4.12}$$

$$\text{where } \mathbf{M}^{\mathrm{el}}_{\mathbf{0}} = J(\mathbf{F}^{\mathrm{el}})^{\mathsf{T}} \cdot \boldsymbol{\tau} \cdot (\mathbf{F}^{\mathrm{el}})^{-\mathsf{T}} \tag{4.13}$$

$$\text{and} J = \det(\mathbf{F}). \tag{4.14}$$

$\mathbf{M}^{\mathrm{el}}_{\mathbf{0}}$ 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:

$$[\mathbf{F}^{\mathrm{p}}] = \begin{bmatrix} \lambda_{11} & \lambda_{12} & 0 \\ \lambda_{21} & \lambda_{22} & 0 \\ 0 & 0 & \lambda_{33} \end{bmatrix}. \tag{4.16}$$

Since, $\det(\mathbf{F}^{\mathrm{p}}) = 1$

$$\lambda_{33} = 1/(\lambda_{11}\lambda_{22} - \lambda_{12}\lambda_{21}). \tag{4.17}$$

4.3 Diffusion Induced Deformation

The compound between Lithium and Silicon is $Li_{\chi}Si$. Let the stoichiometric concentration and maximum concentration of Lithium ions per atom of Silicon be denoted by χ_0 and χ_{max}. Defining a non-dimensional Li-ion concentration measure as $\tilde{c} = (\chi - \chi_0)/\chi_{\text{max}}$. Since χ_0 is the stoichiometric ratio,, it signifies the stress-freeparticle's state; henceе, $\tilde{c}$ 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 $\mathbf{F}^{\text{c}}$ and given by

$$\mathbf{F}^{\text{c}} = (J^c)^{1/3}\mathbf{I} \tag{4.18}$$

where $J^c = 1+3\eta\chi_{\text{max}}\tilde{c}$ 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, $\det(\mathbf{F}^{\text{c}})$ approaches 4. Therefore, the body undergoes a volumetric change of about 300% due to the diffusion of Li-ions, justifying large deformation analysis.

Since SEI is permeable to lithiation, $\mathbf{F}^{\text{c}}$ will be considered only for Silicon. Therefore, for the purpose of modelling, $\tilde{c}$ is considered zero in SEI, making $\mathbf{F}^{\text{c}}$ equal to $\mathbf{I}$.

4.4 Mechanical Equilibrium

From equations 4.6 and 4.7,

$$\mathbf{F}^{\text{el}} = \mathbf{F} \cdot (\mathbf{F}^{\text{p}} \cdot \mathbf{F}^{\text{c}})^{-1}. \tag{4.20}$$

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

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 Silicon by $\mathbb{C}$ and its components by C_{ijkl},

$$\hat{w}(\mathbf{F}, \tilde{c}) = \frac{1}{2}C_{ijkl}E^{\text{el}}_{ij}E^{\text{el}}_{kl}. \tag{4.22}$$

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

$$C_{ijkl}(\tilde{c}) = \lambda_{\text{mat}}(\tilde{c})\delta_{ij}\delta_{kl} + \mu_{\text{mat}}(\tilde{c})(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}). \tag{4.23}$$

$$\Longrightarrow \hat{w}(\mathbf{F}, \tilde{c}) = \left[\lambda_{\text{mat}}(\tilde{c})(\text{tr}(\mathbf{E}^{\text{el}}))^2 + 2\mu_{\text{mat}}(\tilde{c})\mathbf{E}^{\text{el}} : \mathbf{E}^{\text{el}}\right]. \tag{4.24}$$

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

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

The material properties $E_{\text{mat}}(\tilde{c})$ and ν_{mat} are defined domainwise as follows:

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

The elastic second Piola-Kirchhoff stress is denoted by $\mathbf{S}^{\text{el}}$. Therefore,

$$\begin{aligned} &\mathbf{S}^{\text{el}} = \frac{\partial \hat{w}(\mathbf{F}, \tilde{c})}{\partial \mathbf{E}^{\text{el}}} \\ \Longrightarrow\ &\mathbf{S}^{\text{el}} = \lambda_{\text{mat}}(\tilde{c})\text{tr}(\mathbf{E}^{\text{el}})\mathbf{I} + 2\mu_{\text{mat}}(\tilde{c})\mathbf{E}^{\text{el}}. \end{aligned} \tag{4.25}$$

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

$$\begin{aligned} \mathbf{S} = J^{\text{inel}}\,(\mathbf{F}^{\text{inel}})^{-1} \cdot\ \mathbf{S}^{\text{el}} \cdot\ (\mathbf{F}^{\text{inel}})^{-\mathsf{T}} = J^{c}\,(\mathbf{F}^{\text{p}} \cdot \mathbf{F}^{\text{c}})^{-1} \cdot \mathbf{S}^{\text{el}} \cdot (\mathbf{F}^{\text{p}} \cdot \mathbf{F}^{\text{c}})^{-\mathsf{T}} \\ \Longrightarrow \mathbf{S} = (J^{c})^{1/3}(\mathbf{F}^{\text{p}})^{-1} \cdot \mathbf{S}^{\text{el}} \cdot\ (\mathbf{F}^{\text{p}})^{-\mathsf{T}}. \end{aligned} \tag{4.26}$$

The first Piola-Kirchhoff stress is

$$\mathbf{P} = \mathbf{F} \cdot\ \mathbf{S}\ . \tag{4.27}$$

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

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

$$\boldsymbol{\nabla}_{\boldsymbol{X}} \cdot \mathbf{P} = 0. \tag{4.31}$$

4.5 Diffusion

Assuming flux to be negligible in the z direction, the conservation of mass is given by

$$\frac{\partial c}{\partial t} = -\boldsymbol{\nabla}_{\boldsymbol{X}} \cdot \boldsymbol{j} = -\left(\frac{\partial j_X}{\partial X} + \frac{\partial j_Y}{\partial Y}\right). \tag{4.32}$$

Where $\boldsymbol{j}$ is the flux vector 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: (cite a paper which describes the following equation)

$$\hat{\boldsymbol{j}}(\boldsymbol{x}, \boldsymbol{t}) = -\frac{1}{R_g T}\frac{D\chi_{\max}\tilde{c}}{V_{\mathrm{m}}^{\mathrm{B}}}\nabla_{\boldsymbol{x}}\mu \tag{4.34}$$

where R_g is the universal gas constant, T is the operating temperature, D is the diffusivity of $\mathrm{Li}_{\chi}\mathrm{Si}$, $V_{\mathrm{m}}^{\mathrm{B}}$ 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:

$$D = D_0 \exp(\frac{\alpha \mathrm{S_h}}{\mathrm{E_0}}) = \mathrm{D_0}\exp\left(\alpha\frac{\mathrm{S_{11}} + \mathrm{S_{33}}}{2\mathrm{E_0}}\right) \tag{4.35}$$

where E_0 is defined in section 4.6.

In the reference configuration, the flux is $\boldsymbol{j}(\boldsymbol{X}, t) = J(\mathbf{F})^{-1} \cdot \hat{\boldsymbol{j}}$ (how is the previous expression derived). Now,

$$\begin{aligned}
(\nabla_{\boldsymbol{x}}\mu)_i &= \frac{\partial \mu}{\partial x_i} \\
&= \frac{\partial \mu}{\partial X_j}\frac{\partial X_j}{\partial x_i} \\
\Longrightarrow \nabla_{\boldsymbol{x}}\mu &= \mathbf{F}^{-\mathsf{T}} \cdot \nabla_X \mu.
\end{aligned} \tag{4.36}$$

From above equations, the flux, $\boldsymbol{j}(\boldsymbol{X}, t)$, in Lagrangian description is expressed as

$$\boldsymbol{j} = -\frac{1}{R_g T}\frac{D\chi_{\max}\tilde{c}}{V_m^b}(\mathbf{F})^{-1} \cdot (\mathbf{F})^{-\mathsf{T}} \cdot \boldsymbol{\nabla}_{\boldsymbol{X}}\mu. \tag{4.37}$$

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 $\mu_0 = R_g T \log(\gamma\tilde{c})$, where γ is the activity coefficient and considered to be concentration dependent, given by the following equation:

$$\gamma = \frac{1}{1-\tilde{c}}\exp(\frac{1}{R_g T}[2(A_0 - 2B_0)\tilde{c} - 3(A_0 - B_0)(\tilde{c}^2)]). \tag{4.39}$$

The stress-dependent part of the chemical potential is (Cui et al., 2012)

$$\mu_s = \frac{V_m^b}{\chi_{\max}}\left[-\frac{1}{3}\frac{\partial J^c}{\partial \tilde{c}}\tilde{F}_{im}^{\mathrm{el}}\tilde{F}_{in}^{\mathrm{el}}C_{mnkl}\tilde{E}_{kl}^{\mathrm{el}} + \frac{1}{2}\left(J^c\frac{\partial C_{ijkl}}{\partial \tilde{c}} + \frac{\partial J^c}{\partial \tilde{c}}C_{ijkl}\right)\tilde{E}_{ij}^{\mathrm{el}}\tilde{E}_{kl}^{\mathrm{el}}\right]. \tag{4.40}$$

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

$$\begin{aligned}
\mathrm{soc} &= \frac{1}{LH}\int_{-L/2}^{L/2}\int_{0}^{H}\tilde{c}\,\mathrm{dydx} \\
&= H^2\frac{1}{LH}\int_{-L/2H}^{L/2H}\int_{0}^{1}\tilde{c}(\tilde{x},\tilde{y})\,\mathrm{d\tilde{y}d\tilde{x}} \\
&= \frac{H}{L}\int_{-L/2H}^{L/2H}\int_{0}^{1}\tilde{c}(\tilde{x},\tilde{y})\,\mathrm{d\tilde{y}d\tilde{x}} \qquad (4.41)
\end{aligned}$$

4.6 Non-dimensionalisation

$$\tilde{j}_X,\tilde{j}_Y,\tilde{J}_0,\tilde{\boldsymbol{j}} = \frac{HV_{\mathrm{m}}^{\mathrm{B}}}{(\chi_{\max}D_0)}(j_X,j_y,J_0,\boldsymbol{j}) \qquad (4.42)$$

$$\tilde{X},\tilde{Y},\tilde{u},\tilde{v} = \frac{1}{H}(X,Y,u,v) \qquad (4.43)$$

$$\tilde{t} = D_0 t/H^2 \qquad (4.44)$$

$$\tilde{\mu}_{\mathrm{si}},\tilde{\lambda}_{\mathrm{si}},\tilde{E}_{\mathrm{si}} = \frac{1}{E_0}(\mu_{\mathrm{si}},\lambda_{\mathrm{si}},E_{\mathrm{si}}) \quad \text{,where} \quad E_0 = \frac{R_gT}{V_{\mathrm{m}}^{\mathrm{B}}} \qquad (4.45)$$

$$\tilde{\mu}_0,\tilde{\mu}_1,\tilde{\mu}_2,\tilde{\mu}_3 = \frac{1}{R_gT}(\mu_0,\mu_1,\mu_2,\mu_3) \qquad (4.46)$$

$$\tilde{D} = \frac{D}{D_0} \qquad (4.47)$$

$$\dot{\tilde{d}}_0 = \frac{\dot{d}_0H^2}{D_0} \qquad (4.48)$$

$$\tilde{\mathbf{S}}^{\mathrm{el}},\tilde{\mathbf{S}},\tilde{\mathbf{P}},\tilde{\boldsymbol{\sigma}},\tilde{\boldsymbol{\tau}},\tilde{\mathbf{M}}_0^{\mathrm{el}},\tilde{\sigma}_{\mathrm{eff}},\tilde{\sigma}_{\mathrm{f}} = \frac{1}{E_0}(\mathbf{S}^{\mathrm{el}},\mathbf{S},\mathbf{P},\boldsymbol{\sigma},\boldsymbol{\tau},\mathbf{M}_0^{\mathrm{el}},\sigma_{\mathrm{eff}},\sigma_{\mathrm{f}}) \qquad (4.49)$$

4.7 Boundary and Initial Conditions

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

$$\tilde{c}(\tilde{X},\tilde{Y},0) = 0, \qquad (4.50)$$

$$\tilde{u}(\tilde{X},\tilde{Y},0) = 0, \qquad (4.51)$$

$$\tilde{v}(\tilde{X},\tilde{Y},0) = 0. \qquad (4.52)$$

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

$$\tilde{u}(\tilde{X}, 0, \tilde{t}) = \tilde{v}(\tilde{X}, 0, \tilde{t}) = 0, \tag{4.53}$$

$$\tilde{u}(-1/2, \tilde{Y}, \tilde{t}) = \tilde{u}(1/2, \tilde{Y}, \tilde{t}) = 0. \tag{4.54}$$

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

$$\text{During Lithiation, } \tilde{j}_x(\tilde{X}, 1, \tilde{t}) = \tilde{j}_0(1 - \tilde{c}(\tilde{X}, 1, \tilde{t})) \text{ and} \tag{4.55}$$

$$\text{During Delithiation, } \tilde{j}_x(\tilde{X}, 1, \tilde{t}) = \tilde{j}_0\tilde{c}(\tilde{X}, 1, \tilde{t}). \tag{4.56}$$

Table 4.1: Values of material properties and operating parameters

Material property or parameter	Value
D_0, Diffusivity of Silicon	10^{-16} m^{2}s^{-1}
E_{si}, Elastic modulus of pure silicon	90 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
$\sigma_{f,\mathrm{si}}$, Yield strength of pure Silicon	1.5Gpa
$\sigma_{f,\mathrm{SEI}}$, Yield strength of SEI layer	
R_g, Universal gas constant	8.314 JK^{-1}mol^{-1}
T, Temperature	298.15 K
H, Initial height of Silicon thin film	200 μm
L, Initial length of Silicon thin film	20 μm
H_{SEI}, Initial length of SEI layer	10 μm

Appendix A

Equations in Component Form

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 4.5, 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 4.20

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

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

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

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

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

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

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

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

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

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

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

Non-dimensionalizing lamé constants and using 4.25

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

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

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

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

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

From 4.26 and 4.27

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Using 4.13

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

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

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

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

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

These equations need editing if Fpdot_mat.tex is changed

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

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

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

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

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

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

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

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

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

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

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

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

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

$$
\begin{aligned}
\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}] && \text{(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}] && \text{(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} && \text{(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}) && \text{(A.23)}\\
\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)] && \text{(A.24)}\\
\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} && \text{(A.25)}\\
\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) && \text{(A.26)}\\
\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) && \text{(A.27)}
\end{aligned}
$$

Momentum Conservation equations in non-dimensional form:

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

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

Mass conservation Equation in non-dimensional form:

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

Appendix B

To do

- Add full stops at the end of equations
- Export equation with "," from MATLAB
- numbering of inline equations
- where
- unwanted vertical space
- one section need explanation
- Add relevant citations
- Table of parameters
- Write about SEI as well
- explanation of BCs and IC
- figure
- Properties of SEI

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.

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**.