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by

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ABSTRACT

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Chapter 1

Introduction

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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.

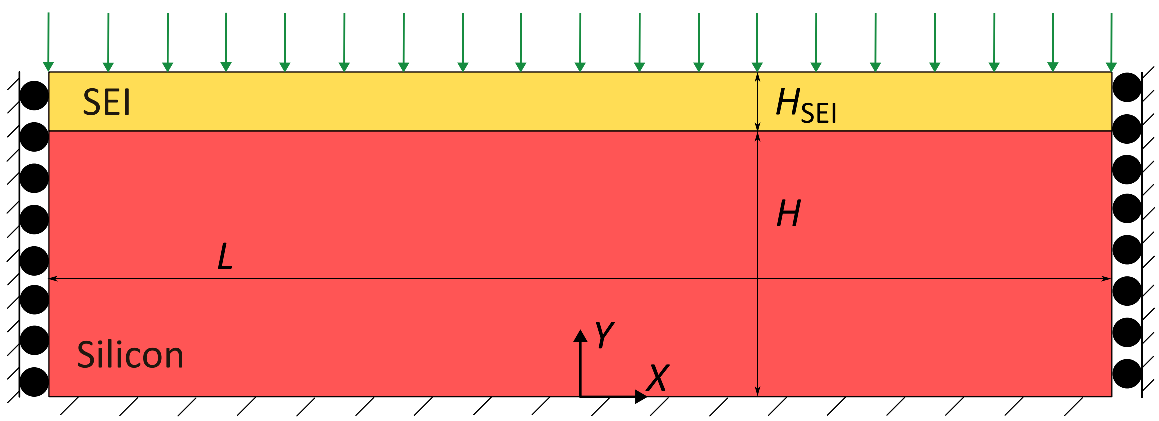

Figure 2.1: Schematic of the problem showing geometric parameters and boundary conditions.

SEI is considered completely permeable to Li-ions and thus does not undergo deformation due to lithiation. The diffusion 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). 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 $Li_\chi Si$ 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 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. 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)

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

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

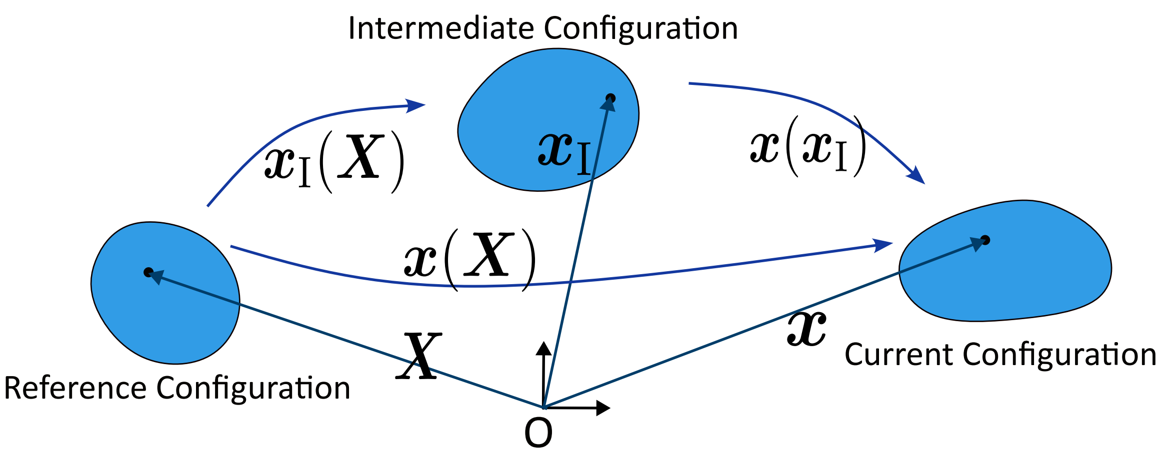

Figure 3.1: Decomposition of the deformation gradient into the elastic and inelastic part.

$\boldsymbol{x}_{\mathrm{I}}(\boldsymbol{X}, t)$ 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.

3.2 Viscoplastic Flow

A viscoplastic constitutive relation of the following form is considered:

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

where $\mathbf{D}^{\mathrm{P}}$ is the rate dependent plastic deformation tensor, $G(\sigma_{\text{eff}})$ 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

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

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

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 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)

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

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

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

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

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

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

Since $\det(\mathbf{F}^{\mathrm{p}}) = 1$, $\lambda_{33} = 1/(\lambda_{11}\lambda_{22} - \lambda_{12}\lambda_{21})$.
σ_{f} is yield strength defined as

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

3.3 Diffusion Induced Deformation

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

From equations 3.5 and 3.6,

$$\mathbf{F}^{\mathrm{el}} = \mathbf{F} \cdot (\mathbf{F}^{\mathrm{c}} \cdot \mathbf{F}^{\mathrm{p}})^{-1}. \tag{3.19}$$

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

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

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

The lamé parameters, $\lambda_{\text{mat}}(\tilde{c})$ 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 domain-wise as follows:

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

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

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

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

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

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

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 $\boldsymbol{\tau} = \boldsymbol{\sigma} - (1/3)\text{tr}(\boldsymbol{\sigma})\mathbf{I}$. 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

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

3.5 Diffusion

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 $\mathrm{Li}_\chi\mathrm{Si}$, $V_{\mathrm{m}}^{\mathrm{B}}$ 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:

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

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

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

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:

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

3.6 Non-dimensionalisation

$$\tilde{j}_X, \tilde{j}_Y, \tilde{J}_0, \tilde{\boldsymbol{j}} = \frac{HV_{\mathrm{m}}^{\mathrm{B}}}{(\chi_{\max} D_0)}(j_X, j_y, J_0, \boldsymbol{j}) \tag{3.45}$$

$$\tilde{X}, \tilde{Y}, \tilde{u}, \tilde{v} = \frac{1}{H}(X, Y, u, v) \tag{3.46}$$

$$\tilde{t} = D_0 t / H^2 \tag{3.47}$$

$$\tilde{\mu}_{\mathrm{si}}, \tilde{\lambda}_{\mathrm{si}}, \tilde{E}_{\mathrm{si}} = \frac{1}{E_0}(\mu_{\mathrm{si}}, \lambda_{\mathrm{si}}, E_{\mathrm{si}}), \text{ where } E_0 = \frac{R_g T}{V_{\mathrm{m}}^{\mathrm{B}}} \tag{3.48}$$

$$\tilde{\mu}_0, \tilde{\mu}_1, \tilde{\mu}_2, \tilde{\mu}_3 = \frac{1}{R_g T}(\mu_0, \mu_1, \mu_2, \mu_3) \tag{3.49}$$

$$\tilde{D} = \frac{D}{D_0} \tag{3.50}$$

$$\dot{\tilde{d}}_0 = \frac{\dot{d}_0 H^2}{D_0} \tag{3.51}$$

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

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:

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

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

Table 3.1: Values of material properties and operating parameters

Material property or parameter	Value
D_0, Diffusivity of 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

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