Intercalation driven porosity effects on the electro-chemo-thermo-mechanical response in continuum models for battery material electrodes

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Abstract

We present a coupled continuum formulation for the electrostatic, chemical, thermal and mechanical processes in battery materials. Our treatment applies on the macroscopic scale, at which electrodes can be modelled as porous materials made up of active particles held together by binders and perfused by the electrolyte. Starting with the description common to the field, in terms of reaction-transport partial differential equations for ions, variants of the classical Poisson equation for electrostatics, and the heat equation, we add mechanics to the problem. Our main contribution is to model the evolution of porosity as a consequence of strains induced by intercalation, thermal expansion and mechanical stresses. Recognizing the potential for large local deformations, we have settled on the finite strain framework. In this first communication we have carried out a detailed computational study on the influence of the dynamically evolving porosity, via the electrostatic and reaction-transport coefficients, upon ion distribution, electrostatic potential fields, and charge-discharge cycles.

1 Introduction

The intercalation of lithium atoms, and mechanical strains drive volume changes in the active material of battery electrodes. The lattice-scale distortions induced by intercalation change the kinetics of lithium transport. At a larger scale, as the particles deform, the porous microstructure of the composite electrode also evolves, which can have a pronounced effect on the effective conductivity, diffusivity and reaction rates of through the cell. On a solely theoretical basis, the physics suggests that there will be changes in the electrochemical response of the cell as a consequence of mechanics.

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The literature on battery materials has seen a number of recent works that explore some of these effects. Cannarella et al. (2014) showed that separators stiffen mechanically under intercalation-induced compressive stresses in the electrodes, externally imposed load. This stiffening is a consequence of the nonlinearly elastic response of polymer separators. Gor et al. (2014) developed a model for the variation of mechanical properties due to such compression. Shi et al. (2011) and Xiao et al. (2010) used a linear relationship between local strain of swelling due to intercalation to model the stress. Mendoza et al. (2016) used a similar linear relationship for the lithiation-induced swelling. The local stress induced in compressible separator is known to cause performance fade of batteries (Cannarella and Arnold, 2014), while variations in the porosity with cycling leads capacity fade (Zhang and White, 2008).

Studies on the changing porosity and microstructure of electrodes and their effect on transport are carried out by reconstructions based on X-ray tomography data (Ebner et al., 2014; Klingele et al., 2015; Zielke et al., 2014, 2015). Numerical investigations also have been carried out for the effect of porosity on transport parameters. These include the work of Kehrwald et al. (2011) for the influence of tortuosity by tomography-based reconstructions of the microstructure of porous electrodes, and of Du et al. (2014) who conducted microscale simulations on microstructures modelled as random packings of ellipsoidal particles to determine the effective diffusivity and conductivity used in macroscopic, homogenized electrode scale models. Also related are the mass transport simulations of Wieser et al. (2015) on solid/void-resolving voxel meshes, derived from image-processing of active particle microstructures, to determine the effective diffusivity. Earlier, Stephenson et al. (2007) had developed an “inter-particle” model to account for different particle sizes and material conductivities in porous electrode. However, these authors ignored the varying microstructural geometry and the resulting transient volume changes in their simulations.

There have been several reported observations of particle expansion and porosity variation driven by lithiation during battery operation (Gonzalez et al., 2014; Channagiri et al., 2013; Ebner et al., 2013). Shearing et al. (2010); Channagiri et al. (2013) and Ebner et al. (2013) also show that, as a result, the porosity can be nonuniform through the thickness of the electrode. However most battery performance simulations assume that the particle size of the active material, and porosity and thickness of the electrode remain constant. A few studies have been extended to varying these as parameters across simulations (Arora et al., 2000; Renganathan et al., 2010), but the coupled physics that drive the variation of these quantities during battery operation have remained beyond the scope of these studies. Rieger et al. (2016) modelled the volume expansion of active material particles due to intercalation by assuming the stress to be linearly dependent on lithium concentration, and extended this model to the macroscopic thickness of the electrode by maintaining a constant volume fraction of the particles. However, if the particles swell with intercalation, their volume fraction increases, as has been reported by Shearing et al. (2010); Gonzalez et al. (2014); Channagiri et al. (2013) and Ebner et al. (2013). Awarke et al. (2011) did study the variation of
porosity in microscale computations on representative volume elements by assuming an expression involving the local state of charge and volumetric strain. Then, in homogenized simulations at the macroscopic, electrode scale, they imposed spatial profiles for the state of charge and studied how the porosity and conductivity varied.

To the best of our knowledge, however, there have not been modelling studies in which (a) pointwise lithium concentrations evolve in space and time under the governing partial differential equations for electro-chemical charge transport, (b) pointwise temperatures evolve under the full governing partial differential equation for heat production and transport, (c) the lithium concentrations and temperatures at a point drive local deformation governed by the partial differential equations of nonlinear elasticity and cause space- and time-varying porosity changes that (d) close the loop by inducing variations in conductivity, diffusivity and reaction rates in the electro-chemical fields. In this communication we aim to fill this gap in the models. We first present such a framework that constitutes an extension of the pseudo-two-dimensional model of Doyle et al. (1993), and accounts for non-constant porosity and particle size in the setting of finite strain elasticity (Section 2). We briefly discuss numerical and computational issues (Section 3), before proceeding to a study of porosity effects on battery performance with and without thermal effects (Section 4). Concluding remarks appear in Section 5.

2 The coupled electro-chemical-thermo-mechanical model

We initially develop the governing electrochemical equations accounting for changes in configuration induced by the finite strain kinematics in three dimensions. This treatment may be viewed as an extension of the pioneering work of Newman and Tiedemann (1975). It is then coupled with the thermal field governed by the equation of heat conduction and production driven by charge transport and reactions. The novel aspect of the framework is the incorporation of mechanics at finite strain driven by lithiation- and temperature-induced swelling, and the porosity evolution model based on the corresponding kinematics. The effect of porosity on transport and electostatic coefficients completes coupled formulation.

2.1 Electrochemical-thermal equations

A battery cell usually consists of positive and negative porous electrodes, a separator and a current collector (see figure 1). The simplified porous electrode model of Doyle et al. (1993) is widely used, based on the theory set forth by Newman and Tiedemann (1975). The equations that follow correspond to those in Newman and Tiedemann (1975) modified with proper assumptions to account for the evolving configuration and porosity, of which the latter was assumed to be constant by Doyle et al. (1993). All equations are finally expressed in the deformed (current) configuration, although some intermediate steps have been pulled back into the reference configuration using the
Figure 1: A schematic of the three-dimensional cell showing porous electrodes and separator.
deformation map. For conciseness, we only define the main quantities; the others can be found in the Appendix.

The material balance for concentration of lithium atoms $C_1$ in a particle in the deformed configuration is

$$\frac{d}{dt} \int_{\Omega_p} C_1 dv + \int_{\Gamma_p} \mathbf{j}_n ds = 0$$  \hspace{0.5cm} (1)$$

where $\mathbf{j}_n$ is the particle surface flux of lithium ions. Suppose that there are $N$ particles, of volume $V_p^i = m(\Omega_p^i)$, $(i = 1, \ldots N)$ in a representative element of volume $V_e = m(\Omega_e)$. Then,

$$\sum_{i=1}^{N} V_p^i = V_e \epsilon_s$$  \hspace{0.5cm} (2)$$

where $\epsilon_s$ is the volume fraction of solid particles. In the representative volume element

$$\frac{d}{dt} \int_{\Omega_e} \epsilon_s C_1 dv + \sum_{i=1}^{N} S_p^i j_n^i = 0,$$  \hspace{0.5cm} (3)$$

where $S_p^i$ is the surface area of particle $i$, and $j_n^i$ is the normal flux, assumed constant over the particle.

$$\frac{d}{dt} \int_{\Omega_e} \epsilon_s C_1 dv + \sum_{i=1}^{N} a_p^i V_p^i j_n^i = 0$$  \hspace{0.5cm} (4)$$

where the specific area is $a_p^i = S_p^i / V_p^i$, and reduces to the inverse radius $3/R_p^i$ for spherical particles. Note that it varies with change in volume of the solid particle during lithium intercalation or deintercalation. Replacing the sum with an integral in the limit of a large number of particles in the volume $\Omega_e$, leads to

$$\frac{d}{dt} \int_{\Omega_e} \epsilon_s C_1 dv + \int_{\Omega_e} \epsilon_s a_p j_n dv = 0$$  \hspace{0.5cm} (6)$$

where quantities in the integrand are regarded as continuous functions of position, $x$. Pulling back the volume integration to the reference configuration by a change of variables,

$$\frac{d}{dt} \int_{\Omega_0} \epsilon_s C_1 J dV + \int_{\Omega_0} \epsilon_s a_p j_n J dV = 0$$  \hspace{0.5cm} (7)$$

where $J = \det F$ and $F$ is the deformation gradient tensor. Recognizing that $C_1(x,t)$ is parameterized in terms of the deformed configuration, and using a standard result for $J = J \text{div} \mathbf{v}$, we have

$$\int_{\Omega_0} \left[ \frac{\partial (\epsilon_s C_1)}{\partial t} + \nabla (\epsilon_s C_1) \cdot \mathbf{v} \right] J + \epsilon_s C_1 \frac{d J}{dt} dV + \int_{\Omega_0} \epsilon_s a_p j_n J dV = 0$$  \hspace{0.5cm} (8)$$
For small velocities \( v \) and volume deformation rates \( \text{div}\nu \), this reduces to

\[
\int_{\Omega_{e_0}} \frac{\partial (\epsilon_s C_1)}{\partial t} JdV + \int_{\Omega_{e_0}} \epsilon_s a_p j_n JdV = 0. \tag{9}
\]

The strong form is obtained by a standard localization argument:

\[
\frac{\partial}{\partial t} (\epsilon_s C_1) + \epsilon_s a_p j_n = 0, \quad \text{in} \Omega_{e_0} \tag{10}
\]

The material balance for lithium cations in the polymer/salt electrolyte \( C_2 \) is,

\[
\frac{\partial C_2}{\partial t} = -\nabla \cdot N_+ - \frac{s_+}{nF} \nabla \cdot \mathbf{i}_2 \tag{11}
\]

where \( N_+ \), the flux of cations homogenized over both matrix and pore, is

\[
N_+ = C_2 v^* - \epsilon_l D_{eff} \nabla C_2 + \frac{Z_0}{z+nF} i_2 \tag{12}
\]

with \( v^* \) being the velocity averaged over matrix and pore. The current density \( i_2 \) in the pore phase is related to pore wall flux \( j_n \) in the electrolyte phase through the relation

\[
a_p F j_n = \nabla \cdot i_2 \tag{13}
\]

Equations (11) to (13) are in the form used by Newman and Tiedemann (1975). Consistent with the assumption of low material velocities, we set \( v^* = 0 \) and \( t_0^+ \) to a constant. Written over the electrode volume the integral form of lithium cation balance is:

\[
\frac{d}{dt} \int_{\Omega_e} \epsilon_l C_2 dv = \int_{\Omega_e} -\nabla \cdot (-\epsilon_l D_{eff} \nabla C_2) dv - \int_{\Omega_e} \left( \frac{t_0^+}{z+nF} + \frac{s_+}{z+n} \right) \epsilon_s a_p j_n dv \tag{14}
\]

Commonly for lithium-ion batteries the choice \( \frac{Z_0}{z+nF} + \frac{s_+}{z+n} = -1 + t_0^0 \) is made (Doyle et al., 1993), leading to:

\[
\frac{d}{dt} \int_{\Omega_e} \epsilon_l C_2 dv = \int_{\Omega_e} \nabla \cdot (\epsilon_l D_{eff} \nabla C_2) dv + (1 - t_0^0) \int_{\Omega_e} \epsilon_s a_p j_n dv \tag{15}
\]

Rewriting the above equation by pulling back to the reference configuration, we have

\[
\frac{d}{dt} \int_{\Omega_{e_0}} \epsilon_l C_2 JdV = \int_{\Omega_{e_0}} \nabla \cdot (\epsilon_l D_{eff} \nabla C_2) JdV + (1 - t_0^0) \int_{\Omega_{e_0}} \epsilon_s a_p j_n JdV \tag{16}
\]

Persisting with the assumption of low velocities \( v \) and volumetric rates of deformation \( \text{div}\nu \), this leads to

\[
\int_{\Omega_{e_0}} \frac{\partial (\epsilon_l C_2)}{\partial t} JdV = \int_{\Omega_{e_0}} \nabla \cdot (\epsilon_l D_{eff} \nabla C_2) JdV + (1 - t_0^0) \int_{\Omega_{e_0}} \epsilon_s a_p j_n JdV \tag{17}
\]
The localization argument leads to the strong form:

$$\frac{\partial}{\partial t}(\epsilon_t C_2) = \nabla \cdot (\epsilon_t D_{ef} \nabla C_2) + (1 - t^0)\epsilon_s a_p j_n$$  

(18)

In widely used porous electrode models [Doyle et al., 1993], the porosity (volume fraction) is assumed to be constant during battery operation, and mechanical deformation is neglected. Here, we also assume low material velocities and volumetric rates of deformation, although we proceed to model the change in porosity due to the deformation; i.e., we only assume rates to be small. Also note that the concentrations $C_1$ and $C_2$ are properly defined with respect to the current configuration; i.e., per unit deformed volume. Here we have begun the derivation of the equations in the current configuration and pulled them back to the reference configuration, mainly because the actual transport coefficients are typically measured over samples that have not undergone large deformation under the effect of lithiation and thermal expansion.

We next consider the equations for the electric fields in the form presented by Doyle et al. (1993). The current density in the solid phase $i_1$ is governed by Ohm’s law:

$$i_1 = -\sigma_{\text{eff}} \nabla \phi_S$$  

(19)

where $\sigma_{\text{eff}}$ is the effective conductivity and $\phi_S$ is the potential in the solid phase. The current density in the electrolyte phase $i_2$ is driven by the gradient of the corresponding potential, $\phi_E$ as well as the cation potential gradient:

$$i_2 = -k_{\text{eff}} \nabla \phi_E + \frac{k_{\text{eff}} RT}{F}(1 + \frac{\partial \ln f}{\partial \ln C_2})(\frac{\epsilon^0}{z_+ n} + \frac{s_+}{z_+ n})\nabla \ln C_2$$  

(20)

Gauss’ Law takes on the form

$$\nabla \cdot i_1 = -aFj_n$$  

(21)

$$\nabla \cdot i_2 = aFj_n$$  

(22)

Note that this guarantees current conservation:

$$\nabla \cdot (i_1 + i_2) = 0$$  

(23)

Then electrochemical equations are completed with specification of the Butler-Volmer equation:

$$j_n = j_0[\exp(\frac{\alpha_a F}{RT}(\phi_S - \phi_E - U) - \exp(-\frac{\alpha_a F}{RT}(\phi_S - \phi_E - U))]$$  

(24)

$$j_0 = k(C_2)^{\alpha_\alpha}(\frac{C_{1\text{surf}}^{\text{max}} - C_{1\text{surf}}}{C_1^{\text{max}}})^{\alpha_a}(\frac{C_{1\text{surf}}}{C_1^{\text{max}}})^{\alpha_c}$$  

(25)

Where $U$ is the open circuit potential and $C_{1\text{surf}}$ is $C_1$ at the particle surface.
Re-arranging equations (13) and (19–23), and using \(1 + \frac{\partial \ln f}{\partial \ln C} \approx 2\) (Pollard and Newman 1980), we obtain

\[
\nabla \cdot [k_{\text{eff}}(-\nabla \phi_E) + k_{\text{eff}} \frac{2RT}{F} (1 - i_+^0) \nabla \ln C_2] = aFj_n \\
\nabla \cdot [\sigma_{\text{eff}}(-\nabla \phi_S)] = -aFj_n
\]

(26)

(27)

Heat generation and transport are governed by the energy balance equation. Here we include heat generation terms that are standard for the field (Bernardi et al., 1985). In the electrodes we have:

\[
\rho C_p \frac{dT}{dt} = \lambda \nabla^2 T + Q_{\text{rxn}} + Q_{\text{rev}} + Q_{\text{ohm}}
\]

(28)

and in the separator:

\[
\rho C_p \frac{dT}{dt} = \lambda \nabla^2 T + Q_{\text{ohm}}
\]

(29)

where the heat generation terms are:

\[
Q_{\text{rxn}} = Faj_n(\phi_S - \phi_E - U)
\]

irreversible entropic heat

(30)

\[
Q_{\text{rev}} = Faj_nT \frac{\partial U}{\partial T}
\]

reversible entropic heat

(31)

\[
Q_{\text{ohm}} = -i_1 \cdot \nabla \phi_S - i_2 \cdot \nabla \phi_E
\]

ohmic heat (Joule heat)

(32)

\[
Q_{\text{conv}} = -\lambda \nabla T = h(T - T_{\text{air}})
\]

heat dissipation at boundary

(33)

Of the full set of electro-chemo-thermal equations (10), (18) and (26–28) hold in the electrode; equations (18), (26) and (29) hold in the in separator.

Temperature- and porosity-dependent coefficients are listed below. All other constant value coefficients are summarized in the Appendix. The Bruggeman relation is often used to calculate the effective values of conductivity and diffusivity: Equations (36–38). Additionally, the effective specific area is Equation (39).

\[
k_{e} = \left(34.5e^{-798/T}(1 \times 10^3C_2)^3 - 485e^{-1080/T}(1 \times 10^3C_2)^2 + 2440e^{-1440/T}(1 \times 10^3C_2))/10\right) \times 1 \times 10^6
\]

(34)

\[
\log D_l = (-4.43 - \frac{54}{T - 5 \times 10^3C_2 - 299} - 2.2 \times 10^2C_2) \times 1 \times 10^8
\]

(35)

\[
k_{\text{eff}} = \epsilon_1^{1.5} k_e
\]

(36)

\[
D_{\text{eff}} = \epsilon_1^{0.5} D_l
\]

(37)

\[
\sigma_{\text{eff}} = \epsilon_s \sigma_S
\]

(38)

\[
a = a_p \epsilon_s
\]

(39)
2.2 Mechanical- porosity model

Lithium atom intercalation/de-intercalation induces particle swelling/contraction which then manifests as electrode deformation at the macro-scale. Additionally, the particle, binder and separator undergo thermal expansion. The kinematics of finite strains lead to the following decomposition:

\[ F = F^e F^c F^T \]

(40)

where \( F \), \( F^e \), \( F^c \) and \( F^T \), are respectively, the total deformation gradient, and its elastic, chemical (induced by lithium intercalation) and thermal components. (Note that \( F^T \) is not the transpose of \( F \).) In the absence of a body force the strong form of the elasticity problem in the current configuration is

\[ \sigma_{ij,j} = 0 \]

(41)

\[ \sigma = \frac{1}{\det F^e} \frac{\partial W}{\partial F^e} F^e T \]

(42)

where \( \sigma \) is Cauchy stress tensor and \( W \) is strain energy density function.

The electrode are composed of solid particles, electrolyte-filled pores and other material such as binders as illustrated in Figure 2. The summation of all volume fractions gives

\[ \epsilon_s + \epsilon_l + \epsilon_b = 1 \]

(43)

\[ \epsilon_s + \epsilon_1 + \epsilon_b = 1 \]

(44)

where \( \epsilon_s \), \( \epsilon_l \) and \( \epsilon_b \) are volume fraction of solid particle, pores (assumed filled with electrolyte) and other material. The subscript \((\bullet)_0\) denotes the corresponding volume fraction in the initial state.
For a volume element, we denote its total volume by $\delta V$ and the volume of solid particles in it by $\delta V_s$. Then the volume fraction of the solid particle can be defined as:

$$
\epsilon_s = \frac{\delta V_s}{\delta V} = \frac{\delta V_s \delta V_0}{\delta V_0 \delta V}
$$

$$
= \frac{\det F_s}{\det F} \epsilon_{s0}
$$

(45)

(46)

where $F_s$ is the deformation gradient tensor over the particle. Similarly we have

$$
\epsilon_l = \frac{\det F_l}{\det F} \epsilon_{l0}
$$

(47)

$$
\epsilon_b = \frac{\det F_b}{\det F} \epsilon_{b0}
$$

(48)

where $F_l$ and $F_b$ are, respectively, the deformation gradient tensors of the pore (assumed filled with electrolyte) and other material. From the theory of mixtures the total stress is (Garikipati et al., 2004):

$$
\sigma = \sigma_l + \sigma_s + \sigma_b
$$

(49)

We assume that the Cauchy stresses in the pores and other binder are constant and isotropic such that $\sigma_l = P_l 1$ and $\sigma_b = P_b 1$. Assuming a strain energy density function $W(Fe)$ with volumetric term

$$
W_{vol}(Fe) = \frac{1}{2} \kappa (\det Fe - 1)^2
$$

(50)

and the same form for the solid particle leads to

$$
\text{tr}\sigma = \kappa (\det Fe - 1) tr 1
$$

(51)

$$
\text{tr}\sigma_s = \kappa_s (\det Fs - 1) tr 1
$$

(52)

Computing the trace of equation (49), using (51) and (52), we have

$$
\kappa (\det Fe - 1) = \kappa_s (\det Fs - 1) + P_l + P_b
$$

(53)

We write the volumetric deformation of the element due to lithium intercalation and thermal expansion using empirical forms

$$
\det Fe = 1 + \beta(C_1)
$$

(54)

$$
\det FT = 1 + \beta^T(T)
$$

(55)
and similarly for its solid component:

$$\det F^c_s = 1 + \beta_s(C_1)$$ (56)

$$\det F^T_s = 1 + \beta_s^T(T).$$ (57)

Then the volumetric deformation of the element and its solid component can be expressed as

$$\det F = \det F^e \det F^c \det F^T$$ (58)

$$= \det F^e(1 + \beta)(1 + \beta^T)$$ (59)

$$\det F_s = \det F^e_s \det F^c_s \det F^T_s$$ (60)

$$= \det F^e_s(1 + \beta_s)(1 + \beta_s^T)$$ (61)

On substituting in Equation (46) we obtain

$$\epsilon_s = \left( \frac{\kappa(\frac{\det F^T}{(1 + \beta)(1 + \beta^T)} - P_1 - P_b)}{\epsilon_s} + 1 \right)(1 + \beta_s)(1 + \beta_s^T) \epsilon_{s0}$$ (62)

$$= \left( \frac{\kappa(\frac{J}{(1 + \beta)(1 + \beta^T)} - P_1 - P_b)}{J} + 1 \right)(1 + \beta_s)(1 + \beta_s^T) \epsilon_{s0}$$ (63)

Assuming the binder to be rigid, such that \(\text{tr}\epsilon_b = 0\), we have

$$\epsilon_b = \frac{1}{\det F} \epsilon_{b0}$$ (64)

$$\epsilon_l = 1 - \epsilon_s - \epsilon_b$$ (65)

The functions \(\beta(C_1)\) and \(\beta_s(C_1)\) may be obtained from studying the evolution of the particle and electrode microstructures during intercalation. In this work we have fit them using experimental data. Furthermore we choose

$$\beta_s^T(T) = \Omega_s(T - T_0)$$ (66)

$$\beta^T(T) = \Omega(T - T_0)$$ (67)

Returning to Equation (40), and assuming the swelling of the electrode to be unidirectional along the \(e_2\)-direction, and thermal expansion to be isotropic, we obtain

$$F^c_{iJ} = \beta_2 \delta_{i2} \delta_{2J} + \delta_{iJ}$$ (68)

$$F^T_{iJ} = (1 + \beta^T)^{1/3} \delta_{iJ}$$ (69)

Equations (40), (68), (69) and (41) allow the volume fractions to be then calculated by Equations (63) and (65).
2.3 Revised specific area

We assume that the spherical particles swell isotropically. The particle radius needs to be updated accordingly to determine the specific area, \( a_p = S_0/V_p = 3/R \), where the particle volume is \( V_p = V_{p_0} \det F_s \). From equations \((53)\), \((59)\) and \((61)\), this give

\[
V_p = V_{p_0} \left( \frac{\kappa J}{(1+\beta)(1+\beta T)} - 1 - P_1 - P_b \right) \frac{\kappa_s}{\kappa_s} + 1)(1 + \beta_s)(1 + \beta_s^T) \tag{70}
\]

and the spherical radius can also be written as

\[
R = \left( \frac{3}{4\pi V_p} \right)^{\frac{1}{3}} \tag{71}
\]

2.4 The analytic diffusion profile for lithium in a particle

We note that equation \((10)\) is derived by using the particle volume-averaged concentration, but ignoring diffusion of lithium atoms in the solid particle. It is the tradition in this field, to assume a spherically symmetric distribution of lithium due to uniform boundary conditions on the particle surface, with a parabolic profile along the particle radius with the form:

\[
C_1 = a_0 + a_1 r + a_2 r^2 \tag{72}
\]

The profile satisfies an influx boundary condition at the particle’s surface

\[
D_s \frac{\partial C_1}{\partial r} \bigg|_{r=R} = -j_n \tag{73}
\]

while symmetry at \( r = 0 \) requires

\[
\frac{\partial C_1}{\partial r} \bigg|_{r=0} = 0 \tag{74}
\]

The local concentration, volume-averaged over the particles is \( \overline{C}_1 \) and is obtained by solving Equation \((10)\), and using

\[
\overline{C}_1 = \frac{1}{V} \int_0^R C_1 4\pi r^2 dr \tag{75}
\]

Solving Equation \((75)\) with Equations \((74)\) and \((73)\) we can determine the three coefficients in the parabolic profile as

\[
a_0 = \overline{C}_1 - \frac{3a_2 R^2}{5}; \quad a_1 = 0; \quad a_2 = \frac{-j_n}{2D_s R} \tag{76}
\]

Then the surface concentration is

\[
C_1 \big|_{r=R} = \overline{C}_1 - \frac{Rj_n}{5D_s} \tag{77}
\]
3 Numerical treatment

Equations (10), (18), (26-29) and (41) are coupled and highly nonlinear. Furthermore, the coefficients depend on the primary variables, introducing further nonlinearity to the system of equations. Here, they are solved by the finite element method using code implemented in the open source finite element library deal.II (Bangerth et al., 2007, 2016). The Galerkin weak form is written for each strong form (10), (18), (26-29) and (41), and expressed as residuals \( \mathcal{R}(\bullet) = 0 \), where

\[
\mathcal{R}_{C_1} = \int_{\Omega_{eq}} w_1 \varepsilon_s \frac{\partial C_1}{\partial t} J dV + \int_{\Omega_{eq}} w_1 C_1 \frac{\partial \varepsilon_s}{\partial t} J dV + \int_{\Omega_{eq}} w_1 J \varepsilon_s a_p j_n J dV
\]

(78)

\[
\mathcal{R}_{C_2} = \int_{\Omega_{eq}} w_2 \varepsilon_l \frac{\partial C_2}{\partial t} J dV + \int_{\Omega_{eq}} w_2 C_2 \frac{\partial \varepsilon_l}{\partial t} J dV - \int_{\Omega_{eq}} w_2 (1 - t_0^0) \varepsilon_s a_p j_n J dV
\]

\[+ \int_{\Omega_{eq}} \nabla w_2 D_{eff} \nabla C_2 J dV - \int_S w_2 D_{eff} \nabla C_2 \cdot \mathbf{n} dS \]

(79)

\[
\mathcal{R}_{\phi_S} = -\int_{\Omega_{eq}} \nabla w_S [\sigma_{eff} (-\nabla \phi_S)] J dV + \int_{\Omega_{eq}} w_3 a F j_n J dV + \int_S w_3 [\sigma_S (-\nabla \phi_S)] \cdot \mathbf{n} dS
\]

(80)

\[
\mathcal{R}_{\phi_E} = -\int_{\Omega_{eq}} \nabla w_E [k_{eff} (-\nabla \phi_E) + k_{eff} \frac{2RT}{F} (1 - t_0^0) \nabla \ln C_2] J dV - \int_{\Omega_{eq}} w_4 a_p F j_n J dV
\]

\[+ \int_S w_4 [k_{eff} (-\nabla \phi_E) + k_{eff} \frac{2RT}{F} (1 - t_0^0) \nabla \ln C_2] \cdot \mathbf{n} dS \]

(81)

\[
\mathcal{R}_T = \int_{\Omega_{eq}} w_T \rho C_p \frac{\partial T}{\partial t} J dV + \int_{\Omega_{eq}} \nabla w_5 \lambda \nabla T dV - \int_{\Omega_{eq}} w_5 Q J dV - \int_S w_5 \lambda \nabla T \cdot \mathbf{n} dS
\]

(82)

\[
\mathcal{R}_u = \int_{\Omega_{eq}} \nabla w_u \mathbf{P} dV - \int_S w_u \mathbf{f} \cdot \mathbf{n} dS
\]

(83)

where \( Q = Q_{\text{rxn}} + Q_{\text{rev}} + Q_{\text{ohm}} \) in the electrodes as in Equation (28) and \( Q = Q_{\text{ohm}} \) in the separator as in Equation (29). The boundary conditions are discussed in the numerical examples.

3.1 Algorithmic differentiation

The analytical linearization of the residual equations (78-82) to obtain the Jacobian matrix is tedious and is fraught with the danger of algebraic mistakes. Symbolic differentiation is an option, but its speed can be a limitation for complicated nonlinear and coupled problems for whose treatment the present communication is intended as a prelude. A standard alternative is the use of numerical
differentiation tools built into many standard solver packages. However, for a highly non-linear set of equations, numerical differentiation is inaccurate and ultimately unstable. An effective and efficient alternative is the use of algorithmic (or automatic) differentiation (AD), which works by application of the chain rule to algebraic operations and functions (polynomial, trigonometric, logarithmic, exponential or reciprocal) in the code. AD thus works to machine precision at a computational cost that is comparable to the cost of evaluation of the original equations. We use AD in this work to linearize equations \( 78-83 \), and compute the Jacobian matrix. Specifically, we use the Sacado package, which is part of the open-source Trilinos project \cite{Heroux2005, Phipps2012}.

4 Numerical examples

4.1 The initial/boundary value problem

We model a 3D cell (figure\[3\]) with geometry \( 120,000 \times 234 \times 85,000(um) \). In this first communication, however, the results we present to verify our framework are effectively one-dimensional for ease of interpretation. Details of all parameters and initial conditions are summarized in the Appendix. The partial differential equations solved are either parabolic \( 79,82 \) or elliptic \( 80,81,83 \), and so boundary conditions must be specified on each surface.

\[
\begin{align*}
\mathcal{R}_C_1 : & \text{ No B.C need} \\
\mathcal{R}_C_2 : & \nabla C_2 \cdot \mathbf{n} = 0 & \text{on all surfaces} \\
\mathcal{R}_{\phi_S} : & [-\nabla \phi_S] \cdot \mathbf{n} = I & \text{on all surfaces} \\
& \phi_S = 0 & \text{on surface 2} \\
& [-\nabla \phi_S] \cdot \mathbf{n} = 0 & \text{on surface 1} \\
& \quad & \text{on other surfaces} \\
\mathcal{R}_E : & [k_{eff}(-\nabla \phi_E) + k_{eff}^2 \frac{2RT}{F}(1 - t^0)\nabla \ln C_2] \cdot \mathbf{n} = 0 & \text{on all surfaces} \\
\mathcal{R}_T : & -\lambda \nabla T \cdot \mathbf{n} = h(T - T_{air}) & \text{on all surfaces} \\
\mathcal{R}_u : & u = u_0 \quad u = 0 & \text{on surface 2 and 1} \\
& \sigma n = 0 & \text{on other surfaces}
\end{align*}
\]

(84)

We modeled a full cycle (discharging and charging) under 10C and 1C current rates\[^{1}\]. For each case we first ran a computation with fixed porosity, i.e. decoupled from lithiation and strain, and temperature not evolving via the heat equation. This was our benchmark, which we followed by including both effects. We noted for cases with decoupled porosity, that the initial porosity for discharging is higher than in the coupled porosity case, since this porosity is closer to the value when fully charged. All initial porosity distributions were taken to be uniform. For studies of the effect of porosity we considered two cases: (a) \( \beta = 0, \beta_s \neq 0 \), and (b) \( \beta \neq 0 \) and \( \beta_s \neq 0 \). We

\[^{1}\]A 1C rate means that a battery rated at 1 Ah should supply 1 Amp for 1 hour.
Figure 3: A schematic of the initial/boundary value problem showing the fields solved for in the electrode and separator sub-domains.
obtained $\beta$ from experimental measurements \cite{Oh2014} (see Equation (85) and Figure 4) and $\beta_s$ from data \cite{Takami1995} fitted by Equation (86).

$$\beta = \frac{0.0189x^5 - 0.039x^4 + 0.053x^3 - 0.034x^2 + 0.009x - 0.0002}{x^2 - 0.885x + 0.258}, \quad \text{where} \ x = \frac{C_1}{C_{1\max}}. \quad (85)$$

Figure 4: Data for the electrode lithiation expansion function $\beta$, is from experimental measurements \cite{Oh2014}. The solid line is a fit given by Equation (85).

$$\beta_s = 1.496x^3 - 1.739x^2 + 1.020x - 0.033\exp(2.972x) - 0.046$$

$$\tanh\left(\frac{x - 0.1}{0.1}\right) - 0.004\tanh\left(\frac{x - 0.3}{0.1}\right) + 0.021\tanh\left(\frac{x - 0.65}{0.1}\right), \quad \text{where} \ x = \frac{C_1}{C_{1\max}}. \quad (86)$$

The function $\partial U/\partial T$ in Equation (31) was fit to data from experimental measurements \cite{Oh2014}. The fit is shown in Equation (87) and Figure 6.
Figure 5: Data for the particle expansion function $\beta_S$, is from Takami et al. (1995). The solid line is a fit given by Equation (86)

$$\frac{\partial U}{\partial T} = \begin{cases} 
0.01442 \times x^2 - 0.00291 \times x - 0.000138 & x \leq 0.2 \\
0.00634 \times x^3 - 0.00625 \times x^2 + 0.002635 \times x - 0.0004554 & 0.2 < x \leq 0.4 \\
0.001059 \times x - 0.0004793 & 0.4 < x \leq 0.5 \\
0.00025 \times x - 7.5e - 5 & 0.5 < x \leq 0.7 \\
-0.001 \times x + 0.0008 & 0.7 < x \leq 0.8 \\
0.0333 \times x^2 - 0.057 \times x + 0.02427 & 0.8 < x \leq 0.85 \\
0.002 \times x^2 - 0.0039 \times x + 0.00177 & 0.85 < x \leq 0.95 \\
-0.0014 \times x + 0.0012 & 0.95 < x \leq 1
\end{cases}$$

(87)

where $x = C_1/C_1^\text{max}$. All other parameter values are listed in the Appendix.
Figure 6: Data for $\partial U/\partial T$ is from our experimental measurements. The solid line is a fit given by Equation (87).
4.2 Simulation results

For expansion/contraction caused by lithium atom intercalation/de-intercalation, with $\beta_s \neq 0, \beta = 0$, the particle expands with Li intercalation; however, the composite electrode does not itself expand but accommodates the expanding particle in the microstructure’s free volume. For $\beta_s \neq 0, \beta \neq 0$, both the particle and composite electrode expand with Li intercalation. Figures (7) and (9) show the porosity distribution through the electrodes and separator at the indicated time for the 10C rate, without and with the temperature evolving governed by the heat equation. During discharge, lithium atoms undergo de-intercalation from the solid particles in the negative electrode and cause its porosity to increase. When the cell is fully discharged, the porosity has increased by about 11%. We note that the negative electrode also contracts due to the de-intercalation. When fully discharged, the negative electrode has contracted by about 9% causing a roughly 3% higher porosity in it relative to the case wherein the porosity is decoupled from the lithiation/delithiation.

From the computations we note that temperature significantly affects the coefficients of the electro-chemical equations; i.e., the transport, conductivity and reaction parameters. At fixed temperature; i.e., without solving the heat equation, the lithium atom concentration is much higher in the neighborhood of the separator, as seen in figure (10) and the porosity is also highly nonuniform. The contracting electrode causes the thickness of separator to increase due to stress equilibrium. Thereby, its porosity increases by about 2% as seen in Figure (11). The porosity is recovered during charging.

The high concentration of lithium atoms forces a numerical divergence of the Butler-Volmer model (Equations (24) and (25)) during the charging process before the cell is fully charged. However, this holds only for the case without coupling with the heat equation. During operation, the battery heats up to $\sim 45^\circ$C at the 10C rate (Figure 12) leading to a more uniform distribution of lithium atom concentration, as shown in Figure (8), and the cell can be fully charged. Porosity also comes back largely. Figure (13 a and b) show the solid phase potential profile. In the computations shown in (a) every case is fully discharged, then charged again. In the computations shown in (b) discharging ends and charging begins in every case at same time. The computations in both Figure 13 (a) and (b) demonstrate that with higher porosity, the potential drops more rapidly when the cell is close to being fully charged. The non-symmetric potential profile reflects the fundamental irreversibilities in battery operation, here arising due to the transport-reaction and heat conduction-generation phenomena.

During operation, the electrodes deform due to lithium intercalation, thermal expansion and external traction. Since the stress induced by cell deformation is uniform through the cell thickness in these effectively one-dimensional phenomena, Figure (14) shows the surface traction force evolving with time. The displacement boundary condition in Equation (84) imposes an initial compressive stress on the cell. This compressive stress relaxes since the electrode contracts during discharging,
Figure 7: Porosity evolving at the 10C rate at fixed temperature; i.e., without solving the heat equation. □: $\beta \neq 0$ and $\beta_s \neq 0$; ◦: $\beta = 0$. Porosity is highly nonuniform in the negative electrode and does not recover its initial distribution even when fully recharged.
Figure 8: Lithium atom concentration under 10C rate at fixed temperature; i.e., without solving
the heat equation. solid line: \( \beta = 0 \) and \( \beta_s = 0 \); □: \( \beta \neq 0 \) and \( \beta_s \neq 0 \); ◦: \( \beta = 0 \).

and increases again as the electrode swells due to intercalation during charging. Figure (14) also
shows that the force induced by lithium atom intercalation is large, but that generated by thermal
expansion is small which and also evolves steadily.

The same initial and boundary value problem was also run at the 1C current rate (Figures
15-19). Under this low current rate, thermal effects are insignificant, the kinetics are slow and
thermodynamic dissipation rates are also low. Consequently the battery’s performance is much
more symmetric in a discharging-charging cycle. Additionally, porosity evolution is uniform, as
shown in Figure (15), and the lithium atom concentration is also uniform as shown in Figure (16).
The porosity evolution in the separator appears in Figure (17), the potential is in Figure (18) and
the force is in Figure (19). These quantities’ evolution is symmetric over the discharging→charging
cycle; however the porosity evolution still affects the potential.

5 Discussion and conclusions

Porosity studies in the literature on battery materials have focused on modeling fixed microstructure
of porous electrodes as outlines in the Introduction. However the connection between microscale
models, which have access to the porous microstructure and its evolution, and the reflection of such
evolution in macroscale simulation of electrodes has remained hard to bridge. Porosity evolution is
usually attributed to the electro-chemical process of lithiation. However, it induces kinematics of
expansion and contraction, which are mechancial phenomena and must satisfy the governing partial
differential equations of elasticity. These phenomena related to lithiation are often described in
terms of the cell-level quantitiy of SOC (e.g. Awarke et al. (2011)). One important contribution
Figure 9: Porosity evolving at the 10C rate with evolving temperature; i.e., while solving the heat equation. □: $\beta \neq 0$ and $\beta_s \neq 0$; ○: $\beta = 0$. 
Figure 10: Lithium atom concentration at 10C rate with evolving temperature; i.e., while solving the heat equation. solid line: $\beta = 0$ and $\beta_s = 0$; □: $\beta \neq 0$ and $\beta_s \neq 0$; ◦: $\beta = 0$.

Figure 11: Porosity in the separator at 10C rate. The initial drop is due to the compressive mechanical traction boundary condition. For “HeatEqnIgnored” and “HeatEqnSol”, there is no swelling due to lithium atom intercalation, and these cases have lower porosity in the separator initially. These two cases have been included to act as references.
of our work is that we have rigorously modeled porosity evolution in electrode particles, at the electrode scale based on mixture theory. Our model was developed in three dimensions with finite strain elasticity, motivated by the large expansions caused by lithiation (Figures 4 and 5) and the potential for inhomogeneous deformation in battery applications. In this first communication, however, rather than immediately demonstrate three-dimensional effects at finite strain, we have chosen to study the changes wrought in the quantities traditionally observed by employing the coupled electro-chemo-thermo-mechanical models. Our main focus in this regard has been on the effects of the evolving porosity.

Porosity changes affect the coefficients of transport-reaction and electrostatics, and thereby affect battery performance. Our numerical simulations show that higher porosity makes potential drops more rapidly. Lithium atom intercalation causes swelling and decreases porosity in the electrodes. Swelling electrode decrease the porosity in the separator by compressing it from both sides. External load affects porosity uniformly and instantaneously, unlike lithiation, which is subject to the rates dictated by kinetics. Porosity decreases more sharply in the separator than that in the electrodes due to the low stiffness of the separator. Thermal expansion has little effect on porosity since it is small compared to the swelling caused by lithium intercalation and external loads. However, it strongly affects almost all transport-reaction parameters. In our computations the thickness change (∼ 9%) of the electrode caused by lithium intercalation does not have a very strong effect on porosity, but this may not be the case when studying material such as tin.

Figure 12: The temperature rises by ∼ 45° C at the 10C rate during a full discharge-charge cycle.
Figure 13: Potential profile at the 10C rate. (a) The computations were run from fully charged to fully discharged, to fully charged again. (b) The computations start at the fully charged state, are discharged for 338s, and then fully charged again. The initial porosities for “HeatEqnIgnored”, “noExp-HeatEqnSolv” and “HeatEqnSolv” are identical to that in the other two cases when fully discharged, i.e., initially they have higher porosities in the negative electrode, and lower porosities in the separator.
oxide which undergoes 250% volume expansion (Ebner et al., 2013). The accompanying extreme mechanical deformation will have very pronounced effects on porosity, which our model can capture by properly parametrizing the $\beta_s$ and $\beta$ functions. We note that $\beta$ is essentially the volume deformation averaged over the micro scale, and can only be fully understood by studying the electrode microstructure. The particle lithiation-expansion function, $\beta_s$ similarly must come from particle-level studies. In this study we have only fitted them as functions of SOC, but our framework offers the potential to use these functions after extracting them from microscale computations at the particle scale, and even more fundamental models such as atomic-scale computations. In this work we have adopted the Bruggeman relation with constant coefficients to describe effects of porosity upon transportation parameters. However, it could be easily replaced by more detailed models to represent the effects of porosity evolution during battery performance.

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Figure 15: Porosity evolving at the 1C rate. □: $\beta \neq 0$ and $\beta_s \neq 0$; ○: $\beta = 0$. Porosity at the low current rate is reasonably uniform.
Figure 16: Lithium atom concentration at the 1C rate. solid line: $\beta = 0$ and $\beta_s = 0$; $\square$: $\beta \neq 0$ and $\beta_s \neq 0$; $\circ$: $\beta = 0$

Figure 17: Porosity in the separator at the 1C rate. The porosity changes in the separator due to its compression/expansion as the adjacent electrodes deform. As a result for $\beta = 0$ there is no discernible porosity change in the separator, given that thermal expansion is also insignificant. At this low current rate the small thermal expansion causes the porosity to decrease slightly.
Figure 18: Potential profile at the 1C rate. (a) The computations were run from fully charged to fully discharged, to fully charged again. (b) Same as (a), but the charging cycles have been shifted on the time axis to start at the same time. (c) The computations start at the fully charged state, are discharged for 3400s, and then fully charged again. The initial porosities for “HeatEqnIgnored”, “noExp-HeatEqnSolv” and “HeatEqnSolv” are identical to that in the other two cases when fully discharged.
Figure 19: Force generated at 1C. The force induced by lithium atom intercalation is large, but a very low force is generated by thermal expansion at this low current rate.
## Appendix

| Symbol | Name                                      | Value  | Unit          |
|--------|-------------------------------------------|--------|---------------|
| F      | Faraday’s constants                       | 96487  | pC/pmol       |
| R      | Universal gas constant                    | 8.3143 | pJ/(pmol * K) |
| $T_0$  | Initial (atmosphere) temperature          | 298    | K             |

### Cell geometry

| $l_{neg}$ | length of negative electrode              | 120    | um            |
| $l_s$     | length of separator                       | 23     | um            |
| $l_{pos}$ | length of positive electrode              | 91     | um            |
| $w_1$     | Side length                               | 120e3  | um            |
| $w_2$     | Side length                               | 85e3   | um            |

### Electric-chemical parameters

| $\alpha_a$ | Transfer coefficients                      | 0.5    |               |
| $\alpha_c$ | Transfer coefficients                      | 0.5    |               |
| $k_{neg}$  | Product of forward and backward           | 8.0e-4 | $\sqrt{pmol/(um^2s)}$ |
| $k_{pos}$  | Product of forward and backward           | 8.0e-4 | $\sqrt{pmol/(um^2s)}$ |
| $R_0^{neg}$| Radius of solid particles of negative electrode | 8.0    | um            |
| $R_0^{pos}$| Radius of solid particles of positive electrode | 6.0    | um            |
| $\sigma_{neg}$ | Conductivity of solid active material of negative electrode | 1.5e8  | p/(Ωum)      |
| $\sigma_{pos}$ | Conductivity of solid active material of positive electrode | 1.5e8  | p/(Ωum)      |
| $D_{neg}^{s}$ | Diffusivity of lithium atom inside particle of negative electrode | 5e-13  | um²/s        |
| $D_{pos}^{s}$ | Diffusivity of lithium atom inside particle positive electrode | 1e-13  | um²/s        |
| $t_0$      | Initial transfer number of positive species | 0.2    |               |
| $\epsilon_{neg0}$ | Initial solid volume fraction of negative electrode | 0.53   |               |
| $\epsilon_{pos0}$ | Initial solid volume fraction of positive electrode | 0.5    |               |
| $\epsilon_{sep0}$ | Initial solid volume fraction of separator | 0.35   |               |
| $\epsilon_{neg0}$ | Initial porosity of negative electrode    | 0.32   |               |
| $\epsilon_{pos0}$ | Initial porosity of positive electrode    | 0.35   |               |
| $\epsilon_{sep0}$ | Initial porosity of separator             | 0.65   |               |
| $\epsilon_{neg0}$ | Initial solid volume fraction of negative electrode for no porosity change case | 0.485  |               |
| $\epsilon_{pos0}$ | Initial solid volume fraction of positive electrode for no porosity change case | 0.5    |               |
| Symbol      | Name                                                      | Value     | Unit            |
|------------|-----------------------------------------------------------|-----------|-----------------|
| $\epsilon_{sep}$ | Initial solid volume fraction of separator for no porosity change | 0.362     |                 |
| $\epsilon_{neg}$ | Initial porosity of negative electrode for no porosity change | 0.362     |                 |
| $\epsilon_{pos}$ | Initial porosity of positive electrode for no porosity change | 0.638     |                 |
| C$_{neg}^{max}$ | Maximum lithium atom concentration of negative electrode | 28.7e-3   | pmol/um$^3$     |
| C$_{pos}^{max}$ | Maximum lithium atom concentration of positive electrode | 28.7e-3   | pmol/um$^3$     |
| C$_{neg,100}$ | Maximum SOC in negative electrode                         | 0.915     |                 |
| C$_{neg,0}$  | Minimum SOC in negative electrode                         | 0.02      |                 |
| C$_{pos,100}$ | Maximum SOC in positive electrode                         | 0.022     |                 |
| C$_{pos,0}$  | Minimum SOC in positive electrode                         | 0.98      |                 |
| C$_{2,ini}$  | Initial concentration of lithium ion                      | 1.0e-3    | pmol/um$^3$     |

**Thermal parameters**

| Symbol      | Name                                                      | Value     | Unit            |
|------------|-----------------------------------------------------------|-----------|-----------------|
| $\rho_{neg}$ | Density of negative electrode                             | 2.5e-15   | kg/um$^3$       |
| $\rho_{pos}$ | Density of positive electrode                             | 2.5e-15   | kg/um$^3$       |
| $\rho_{sep}$ | Density of separator                                     | 1.1e-15   | kg/um$^3$       |
| $C_p$       | Specific heat                                             | 7e14[a]   | pJ/(kgK)        |
| $h$         | heat transfer coefficient                                  | 5         | W/(m$^2$K)      |
| $\lambda_{neg}$ | Thermal conductivity of negative electrode              | 1.04e6[b] | W/(mK)          |
| $\lambda_{sep}$ | Thermal conductivity of separator                       | 0.33e6[b] | W/(mK)          |
| $\lambda_{pos}$ | Thermal conductivity of positive electrode               | 5e6[b]    | W/(mK)          |
| $\Omega_{neg}$ | Thermal expansion coefficient of negative electrode    | 9.615e-6[c] | 1/K          |
| $\Omega_{pos}$ | Thermal expansion coefficient of positive electrode   | 6.025e-6[c] | 1/K          |
| $\Omega_{sep}$ | Thermal expansion coefficient of AM particle            | 82.46e-6[c] | 1/K          |
| $\Omega_s$  | Thermal expansion coefficient of AM particle            | 6e-6      | 1/K            |

**Elasticity parameters**

| Symbol      | Name                                                      | Value     | Unit            |
|------------|-----------------------------------------------------------|-----------|-----------------|
| $\kappa_{neg}$ | Bulk modulus of negative electrode                        | 4.94e-3   | Gpa             |
| $\kappa_{pos}$ | Bulk modulus of positive electrode                        | 7.4e-3    | Gpa             |
| $\kappa_{sep}$ | Bulk modulus of separator                                 | 0.42e-3   | Gpa             |
| $\kappa_{sep}$ | Bulk modulus of carbon solid                              | 25e-3     | Gpa             |
| $E_{neg}$   | Young’s modulus of negative electrode                     | 5.93[c]   | Gpa             |
| $E_{pos}$   | Young’s modulus of positive electrode                     | 8.88[c]   | Gpa             |
| $E_{sep}$   | Young’s modulus of separator                              | 0.5[c]    | Gpa             |
| $\nu$       | Poisson’s ratio                                           | 0.3       |                 |

a: [Northrop et al. 2015] ; b: [Sun et al. 2015] ; c: [Shi et al. 2011]
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