



ICED Theory Guide Version 1.0.0

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Glossary

Term	Description
a or A_s	surface area of the pore walls per unit volume of the total electrode; specific interfacial area (m^2/m^3)
$a j_{in}$	rate of transfer of species i from the solid phase to the pore solution per unit volume of the total electrode ($\text{mol}/\text{m}^3 \cdot \text{s}$)
c	concentration of the electrolyte, c_i/ν_i (mol/m^3)
c_0	concentration of polymer solvent (mol/m^3)
c_i	concentration of species i (mol/m^3)
c_T	maximum concentration in solid (mol/m^3)
c_s	concentration in solid (mol/m^3)
c_{max}	maximum concentration in polymer (mol/m^3)
D or D_i	diffusion coefficient of electrolyte in the polymer or of species i in the solid matrix (m^2/s)
D_0	diffusion coefficient of electrolyte in the polymer in the absence of a pore network (m^2/s)
\mathcal{D}_{ij}	interaction coefficient between species i and j
e	fundamental charge on an electron ($1.6021766 \times 10^{-19} \text{ C}$)
f or f_{\pm}	activity coefficient
\mathcal{F}	Faraday's constant, $\mathcal{F} = e \cdot N_A$ ($9.64853399 \times 10^4 \text{ C/mol}$ or $\text{J}\cdot\text{V}^{-1}\cdot\text{mol}^{-1}$)
\mathbf{i}	current density (A/m^2)
i_0	exchange current density (A/m^2)
I	superficial current density (A/m^2)
j_{in}	pore wall flux of species i averaged over a ($\text{mol}/\text{m}^2 \cdot \text{s}$)
k_a or k_c	anodic or cathodic rate constant (m^3/s)
K_{ij}	frictional coefficient between species i and j ($\text{J}\cdot\text{s}/\text{m}^5$)
n	number of electrons transferred in an electrode reaction
\mathbf{n}	vector normal to the surface
N_A	Avogadro's number ($6.022141 \times 10^{23} \text{ mol}^{-1}$)
\mathbf{N}_i	molar flux of species i ($\text{mol}/\text{m}^2 \cdot \text{s}$)
r	distance normal to the surface of cathode material (m)
\mathcal{R}	universal gas law constant ($8.3143 \text{ J/mol}\cdot\text{K}$)
R_s	radius of cathode material particle (m)
R_i	bulk reaction term of species i
s_i	stoichiometric coefficient of species i in an electrode reaction
t	time (s)
T	temperature (K)
t_i^0 or t_+^0	transference number of species i
u_i	mobility of species i ($\text{m}^2 \cdot \text{mol} \cdot \text{J}^{-1} \cdot \text{s}^{-1}$)
U or U_s	open circuit potential (V)
\mathbf{v}_i or \mathbf{v}_0	velocity of species i or the solvent (m/s)
V	cell potential (V)
z_i	charge number of species i

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Term	Description
$z_i \mathcal{F}$	charge per mole of species i
α_a or α_c	anodic or cathodic transfer coefficient
β	fraction of applied potential that promotes a cathodic reaction; symmetry parameter
η	surface overpotential (V)
ϵ	volume fraction of pores within a matrix; porosity
κ	ionic conductivity of electrolyte (S/m)
κ_0	ionic conductivity of electrolyte in the absence of a pore network (S/m)
μ_i	electrochemical potential of species i (J/mol)
ν_i	number of cations or anions into which 1 mole of electrolyte dissociates, $\nu_+ + \nu_- = \nu$
Φ	electric (or reference) potential (V)
σ	electronic conductivity of solid matrix (S/m)



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1 Introduction: Li ion battery

Lithium-ion batteries are making significant impacts on a range of applications. The objective of the present effort is to develop models at the electrode–particle scale that incorporate fundamental thermodynamics and chemical kinetics. The derivation discussed herein is based on the foundation established by Newman and coworkers [3, 6, 4].

Species- and charge-conservation equations are solved to predict temporal and spatial profiles of lithium concentration and electric potentials. Transport through the composite electrodes is modeled using porous electrode theory. Thus, the electrolyte and active electrode material are treated as a superimposed continua [3]. Concentrated solution theory is used to describe transport within the binary liquid electrolyte. The concepts utilized by each of these theories as well as some of the mathematical derivations are presented below.

Now consider a real system, such as the battery shown in Figure 1.1. At the electrode–particle scale, the three main components are visible: a composite anode on the left, a separator in the center, and a composite cathode on the right.

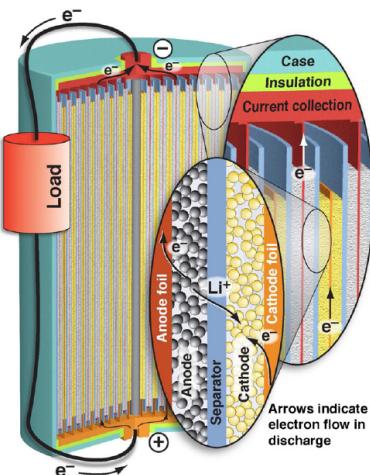


Figure 1.1: Schemata of the structure of a cylindrical Li ion battery, showing three length scales: device scale, cell scale and electron–particle scale. At the electron–particle scale the composite electrodes and the separator are most easily observable. Figure from [2].

The composite electrodes consist of active particles, binder, and conductive connectors, all of which are surrounded by the lithium ion-conducting electrolyte phase. Lithiated graphite (Li_xC_6 , where $0.1 < x < 0.8$) is commonly used as the active material in the anode (negative electrode). The cathode (positive electrode) active material is often a metal oxide (e.g., Li_yCoO_2 where $0.4 < y < 1.0$). A microporous separator film electrically isolates the cathode from the anode. The electrolyte phase is contained within the pores of the separator, which enables ion conduction across the separator.

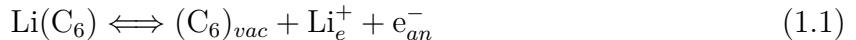
During discharge intercalated* Li leaves anode particles and enters the electrolyte as Li^+ . This charge-transfer process delivers electrons to a current collector and an external load. The Li ions are transported via diffusion and migration through the electrically insulating

*Intercalation or insertion: An ion from the solution enters into the crystal lattice of a solid.



electrolyte solution toward the cathode. Reacting with electrons from the external load, a charge-transfer process delivers Li into the cathode particles. During charging the processes are reversed.

The reversible charge transfer process at the graphite anode may be represented globally as:



where $\text{Li}(\text{C}_6)$ are the intercalated Li in graphite, Li_e^+ are the positively charged Li ions in the electrolyte phase, $(\text{C}_6)_{vac}$ are the intercalation vacancies in within the graphite, and e_{an}^- are the electrons in the anode phase, where the anode phase consists of graphite, conductive filler surrounding the graphite, and the current collector.

The reversible charge transfer process at the cathode (e.g., CoO_2) may be represented globally as:



where $(\text{CoO}_2)_{vac}$ are the intercalation vacancies within the cathode (metal oxide) particles, Li_e^+ are the positively charged Li ions in the electrolyte phase, e_{cd}^- are the electrons in the electronically conducting phases of the cathode, and $\text{Li}(\text{CoO}_2)$ are the intercalated Li in the metal oxide.

2 Fundamentals

Mass transport in an electrolytic solution requires a description of the movement of mobile ionic species, material balances, current flow, and fluid mechanics. The main quantity of interest is the **flux density** of a given species i in solution: \mathbf{N}_i . The flux density depends on the following phenomena [7].

1. Migration in an electric field ($-\nabla\Phi$).
2. Diffusion in a concentration gradient ($-\nabla c_i$).
3. Convection with the fluid velocity ($c_i \mathbf{v}_i$).

These processes contribute to sources of **resistance** for total system. The potential difference across a cell (i.e., the cell potential $V = \Phi_{anode} - \Phi_{cathode}$) will depend on four components:

1. Open circuit potential – The maximum work that can be obtained from the system.
2. Surface overpotential – Resistance to electrochemical reaction (kinetic resistance).
3. Ohmic potential drop – Resistance to ionic or electronic current.
4. Concentration overpotential – Resistance to concentration gradients.



These potential drops are interrelated, making the calculation of the total potential of the cell more complicated than that given by the ohmic drop alone.

Below are three of the four principal equations for mass transport in an electrolytic solution.[†] The exact form of the flux density depends on the type of solution, i.e., infinitely dilute or concentrated (or somewhere in between), and thus the type of theory applied. For now it will be discussed in general terms and presented in more detail in the following section.

Material balance:

Change in the mass of species i with time (also known as Fick's (1st) Law).

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{N}_i \quad (2.3)$$

Electroneutrality:

To a very good approximation, the solution is electrically neutral.

$$\sum_i z_i c_i = 0 \quad (2.4)$$

Current density:

Due to motion of charges particles in an electrolytic solution.

$$\mathbf{i} = \mathcal{F} \sum_i z_i \mathbf{N}_i \quad (2.5)$$

3 Dilute and concentrated solution theories

As discussed above, migration, diffusion, and convection all contribute to the species flux density, and its exact expression can take different forms. For example, let's begin with its form within (infinitely) dilute solution theory; the expression is simpler and requires significantly less manipulation.

$$\mathbf{N}_i = -z_i u_i \mathcal{F} c_i \nabla \Phi - D_i \nabla c_i + c_i \mathbf{v}_i \quad (3.1)$$

Given the three phenomena affecting mass transport, we can see that the first term depends on the gradient of the electrostatic potential ($-\nabla \Phi$) and thus is the **migration** term. The second term depends on the gradient of the concentration ($-\nabla c_i$) and thus is the **diffusion** term. The last term depends on the velocity (\mathbf{v}_i) and thus is the **convection** term. (The constants out front are ignored for the time being and are related to measurable transport properties for the species.) For the mathematical description presented herein, in an unstirred or stagnant solution with no density gradients, the solution velocity \mathbf{v} is zero (i.e., the bulk

[†]The expression for material balance actually has a second term dependent on the bulk reaction, R_i : $\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{N}_i + R_i$. Since, however, reactions are frequently restricted to the surface of electrodes, $R_i = 0$ in electrochemical systems and thus does not appear in our general form.

velocity of the electrolyte is neglected) and, therefore, there is no convection term [1]. The expression for flux then reduces to

$$\mathbf{N}_i = -z_i u_i \mathcal{F} c_i \nabla \Phi - D_i \nabla c_i \quad (3.2)$$

Unlike dilute solution theory in which migration is treated independently from diffusion, concentrated solution theory presents a unifying treatment of the two, and these terms take on a much more complicated form.

In actuality the flux equation is replaced by the **multicomponent diffusion equation**, which is more general than eqn. (3.1) because it relates the driving force to a linear combination of resistances instead of just to one resistance (that of the solvent).

$$c_i \nabla \mu_i = \sum_i K_{ij} (\mathbf{v}_i - \mathbf{v}_j) = \mathcal{R} T \sum_i \frac{c_i c_j}{c_T \mathcal{D}_{ij}} (\mathbf{v}_i - \mathbf{v}_j) \quad (3.3)$$

As evident from eqn. (3.3), the gradient of the electrochemical potential ($\nabla \mu_i$), which is the driving force for *both* migration *and* diffusion, is proportional to the velocity difference between species i and j via a friction (or interaction) coefficient, K_{ij} (or \mathcal{D}_{ij}).

Assuming that the electrolyte is a binary solution (i.e., anion, cation, and solvent) and after much rearrangement (e.g., inversion) and substitution, the flux equation within concentrated solution theory can be obtained.

$$\mathbf{N}_i = c_i \mathbf{v}_i = -\frac{\nu_i \mathcal{D}}{\nu \mathcal{R} T} \frac{c_T}{c_0} c \nabla \mu_e + \frac{t_i^0}{z_i \mathcal{F}} \mathbf{i} + c_i \mathbf{v}_0 \quad (3.4)$$

Making the same assumption about the solution velocity as before (i.e., $\mathbf{v}_0 = 0$) and by representing the chemical potential in terms of the concentration gradient,

$$\frac{\mathcal{D}}{\nu \mathcal{R} T} \frac{c_T}{c_0} c \nabla \mu_e = D \left(1 - \frac{d \ln c_0}{d \ln c} \right) \nabla c \quad (3.5)$$

the expression for the flux density within concentrated solution theory becomes

$$\mathbf{N}_i = -D \left(1 - \frac{d \ln c_0}{d \ln c} \right) \nabla c + \frac{t_i^0}{z_i \nu_i \mathcal{F}} \mathbf{i} \quad (3.6)$$

where

$$\mathbf{i} = -\kappa \nabla \Phi - \frac{\kappa \mathcal{R} T}{\mathcal{F}} \left(1 + \frac{\partial \ln f_\pm}{\partial \ln c} \right) \left(\frac{s_i}{n \nu_i} + \frac{t_i^0}{z_i \nu_i} \right) \nabla \ln c \quad (3.7)$$

[Note that the terms in eqn. (3.6) have been divided through by ν_i , and thus they appear slightly different than is implied by direct substitution of eqn. (3.5) into eqn. (3.4).]

As evident from eqn. (3.7), the current density \mathbf{i} is dependent on *both* the electrostatic potential *and* the concentration gradient, thus illustrating the coupling between the diffusion



and migration terms in concentrated solution theory. (Differentiating between \mathbf{N}_i and \mathbf{i} becomes somewhat circuitous, but it is apparent that \mathbf{i} is really a place holder for several other terms.)

In both dilute and concentrated solution theories, the coefficients out front pertain to solutions of a single salt and are characterized by three measurable transport properties.

ionic conductivity (κ) Measure of a solution's ability to conduct electricity (S/m)

diffusion coefficient (D) Measure of "how quickly" an ion moves through solution(m²/s)

transference number (t_i^0) Fraction of current carried by an ion in a solution of uniform composition

Applying Fick's law in eqn. (2.3) to eqn. (3.6) yields the (mass balance) expression for ion concentration in the electrolyte:

$$\frac{\partial c_i}{\partial t} = \nabla \cdot \left[D \left(1 - \frac{d \ln c_0}{d \ln c} \right) \nabla c \right] - \mathbf{i} \cdot \frac{\nabla t_i^0}{z_i \nu_i \mathcal{F}} \quad (3.8)$$

The explicit concentration dependence of the transport properties, $D(c)$, $\kappa(c)$, and $t_i^0(c)$, has been excluded from eqn. (3.6), (3.7), and (3.8) in an attempt to reduce the already complicated equations, but the user should be aware of this dependence when applying the theory to his/her actual system.

4 Porous electrode theory

Using the configuration shown in Figure 1.1 as a guide, the anode and cathode are *porous* electrodes. Porous electrodes consist of porous matrices of a single reactive electronic conductor (or mixtures of solids) that include essentially nonconductive reactive materials in addition to the electronic conductors. Because of this arrangement, *porous electrode theory* is a special blend of dilute solution theory and electron transfer.

In this macroscopic treatment, we disregard the actual geometric details of the pores. Thus we can define a potential Φ_s in the solid, conducting matrix material and another Φ_e in the pore-filling electrolyte.

In effect, the electrode is treated as a superposition of the two continua, one representing the solution and another representing the matrix. In the model, both are present at any point in space. Within this framework, the material balance expression in eqn. (2.3) and eqn. (3.8) become the following:

$$\epsilon \frac{\partial c_i}{\partial t} = \nabla \cdot (\epsilon D \nabla c) - \mathbf{i} \cdot \frac{\nabla t_i^0}{z_i \nu_i \mathcal{F}} + \frac{aj_{in}(1-t_i^0)}{\nu_i} \quad (4.1)$$



There are a number of similarities to eqn. (3.8) as well as a number of differences, and we shall consider each in turn. Again the explicit concentration dependence of the transport properties, $D(c)$, $\kappa(c)$, and $t_i^0(c)$, has been excluded.

Let's begin with the added term of ϵ . Since the porous electrode consists of a solid, conducting matrix material and the pore-filling electrolyte, we must consider the effect that the void fraction has on transport. Thus the *porosity* (or tortuosity) is the void volume fraction ϵ within the matrix.

As one might have guessed, the presence of voids changes the amount of open space available for mass transport, thus there is a net decrease in the concentration *and* the flow; hence, ϵ appears on the left hand side *and* on the right hand side as part of the diffusion term. Moreover since the concentration of the bulk solution (solvent) in the pores is much larger than that of the ions, *dilute solution theory* prevails, and therefore the diffusion term looks much more like that in eqn. (3.2) than in eqn. (3.6).

Now let's turn our attention the last term dependent on aj_{in} . Remember back to Section 1 and Figure 1.1:

During discharge intercalated Li leaves the anode particles and enters the electrolyte as Li^+ .

Because the electrode has a portion that is a solid, conducting matrix, we need to take into account the rate of transfer of the species from the solid phase into the pore solution (per unit volume of the total electrode), i.e. the **wall flux**, or j_{in} , which depends on the current density. Now recalling the material balance expression in eqn. (2.3), there is actually a term missing, one that depends on aj_{in} :

$$\frac{\partial c_i}{\partial t} = aj_{in} - \nabla \cdot \mathbf{N}_i \quad (4.2)$$

$$aj_{in} = -\frac{s_i}{n\mathcal{F}} \nabla \cdot \mathbf{i} \quad (4.3)$$

Now the last term in eqn. (4.1) looks similar to that in eqn. (3.6), but now weighted by aj_{in} . Note that in the expression for Faraday's Law, eqn. (4.3), \mathbf{i} should have a subscript e because it is the superficial current density in the pore (solution) phase part of the electrode (\mathbf{i}_e) and is the same \mathbf{i} as in eqn. (3.7). It is important to note, however, that because the *material* is different, the transport properties take on a slightly different meaning. They become *effective* properties, i.e., κ and D need to be weighted by ϵ as well because the pores change the transport properties relative to the bulk solution.

$$\kappa = \kappa_0 \epsilon^{3/2} \quad (4.4)$$

$$D = D_0 \epsilon^{1/2} \quad (4.5)$$

where κ_0 and D_0 are the conductivity of the solution and the ionic diffusion in the absence of the pore network.



A significant class of electrodes involves insertion or intercalation in which an ion from the solution enters into the crystal lattice of a solid, as discussed in Figure 1.1. At the same time electrons enter or leave the crystal to maintain electroneutrality. This process oxidizes or reduces the crystal. The open circuit potential of the crystal, relative to the reference electrode, will depend on the concentration c_s of the intercalating ions:

$$\frac{\partial c_s}{\partial t} = \nabla \cdot D \nabla c_s \quad (4.6)$$

$$\frac{\partial c_s}{\partial t} = D_s \left[\frac{\partial^2 c_s}{\partial r^2} + \frac{2}{r} \frac{\partial c_s}{\partial r} \right] \quad (4.7)$$

and then from symmetry

$$\left. \frac{\partial c_s}{\partial r} \right|_{r=0} = 0. \quad (4.8)$$

For the purposes of modeling intercalation, ion transport between particles is neglected. That is intercalated ions diffuse with a particle, but not from particle to particle. Additionally the active electrode material is assumed to be made up of spherical particles of radius R_s with diffusion being the mechanism of ion intercalation transport.

5 Total resistance

Up to this point, we have only discussed mass transfer, i.e., the transport through the electrolyte to bring the reactants to the interface (concentration overpotential). Recalling from Section 2, there are other types of resistance that contribute to the overall system description: reaction kinetics (surface overpotential) and electron transfer (ohmic potential drop).

5.1 Reaction kinetics

The electrode reaction rate, characterized by the current density, depends on the following:

1. The nature and treatment of the electrode surface.
2. The composition of the electrolytic solution adjacent to the electrode.
3. The electrode potential, characterized by the surface overpotential η .

The Butler–Volmer equation is one of the most fundamental relationships in electrochemical kinetics. It describes how the electrical current on an electrode depends on the electrode potential, considering that both a cathodic and anodic reaction occur *on the same electrode*.



The Butler–Volmer relation (or variations derived from it) is used in the treatment of almost every problem requiring an account of heterogeneous kinetics. The net (electrical) current on an electrode is the algebraic sum of the anodic and cathodic currents: $\mathbf{i} = i_a + i_c$.

$$\mathbf{i} = i_0 \left[\exp\left(\frac{\alpha_a \mathcal{F}\eta}{RT}\right) - \exp\left(-\frac{\alpha_c \mathcal{F}\eta}{RT}\right) \right] \quad (5.1)$$

where

$$i_0 = \mathcal{F}(k_a)^{\alpha_c}(k_c)^{\alpha_a}(c_{max} - c)^{\alpha_c}(c)^{\alpha_a} \quad (5.2)$$

In expression eqn. (5.2), k_a and k_c are the reaction rate constants for the anodic and cathodic reactions, respectively, (and implies a first order reaction in the reactant concentrations); and c_{max} is the total number of sites available in the polymer lattice when the ion solubility limit is taken into account, in other words, the maximum concentration of the polymer.

The other two constants in eqn. (5.2), α_a and α_c , are related to the symmetry parameter β : $\alpha_a = 1 - \beta$; $\alpha_c = \beta$; and $\alpha_a + \alpha_c = 1$. The symmetry parameter β is the fraction of the applied potential that promotes the cathodic reaction and is usually assumed to be $\frac{1}{2}$ (i.e, the potential is equally as like to promote the anodic reaction as the cathodic reaction).

Recall from Section 4, that there are two phase: the solid, conducting matrix material and the pore-filling electrolyte. The surface overpotential η is the difference between the potential in the solid and solution (electrolyte) phases *on the same electrode*:

$$\eta = \Phi_s - \Phi_e - U_s \quad (5.3)$$

where U_s is the theoretical open circuit cell potential and is taken to be zero.

5.2 Electron transfer

The last piece of the puzzle is the electron transfer at the interface between the electrode and the electrolyte. The driving force for the flow of the electrons is the same as the migration term for ionic conduction, the electric field, and is governed by Ohm's Law:

$$\mathbf{i} = -\sigma \nabla \Phi \quad (5.4)$$

In eqn. (5.4) current \mathbf{i} and potential Φ could have a subscript s , indicating that they relate to the solid matrix phase of the electrode, but they are left off here for simplicity. Now recall the first term in eqn. (3.7) which relates ion migration to the electrostatic potential via the ionic conductivity κ . These two terms are virtually identical with the exception of the proportionality constant. In eqn. (5.4) we use σ instead of κ to indicate that the mobile charge carriers in metals are electrons, as opposed to ions in electrolytes.



6 Species and charge conservation

There are three forms of conservation, pertaining to either the electrolyte phase or the electrode (matrix) phase. The most important factors are charge conservation / electroneutrality and species (mass) conservation.

1. Charge conservation in the electrolyte phase.
2. Species conservation in the electrolyte phase.
3. Charge conservation in the electrode phase.

A volume element within the porous electrode will be, in essence, electrically neutral because it requires a large electric force to create an appreciable separation of charge of an appreciate distance. Likewise we shall also take each phase separately to be electrically neutral.

Recall from eqn. (2.4),

$$\sum_i z_i c_i = 0 \quad (6.1)$$

$$\therefore c = \frac{c_+}{\nu_+} = \frac{c_-}{\nu_-} \quad (6.2)$$

As for charge conservation in the electrolyte phase, we will force the divergence of the current to be zero.

$$\nabla \cdot \mathbf{i} = 0; \nabla^2 \Phi = 0 \quad (6.3)$$

$$\therefore \nabla \cdot \mathbf{i} = -\nabla [\kappa \nabla \Phi] - \nabla \left[\frac{\kappa R T}{\mathcal{F}} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c} \right) \left(\frac{s_i}{n \nu_i} + \frac{t_i^0}{z_i \nu_i} \right) \nabla \ln c \right] = 0 \quad (6.4)$$

As for species conservation, the material balance expression in eqn. (3.8) is sufficient. The last requirement is charge conservation in the electrode phase, which is a combination of eqn. (5.4) and the divergence theorem:

$$\nabla \cdot (\sigma_{eff} \nabla \Phi_s) - A_s \mathbf{i} = 0 \quad (6.5)$$

Here the current density \mathbf{i} is the same as that in eqn. (5.1), i.e., the result of the charge transfer reactions delivering electrons into the electrode phase. (Recall from eqn. (4.5) and eqn. (5.4), that the conductivity coefficients must be weighted by the void fraction of the matrix.)

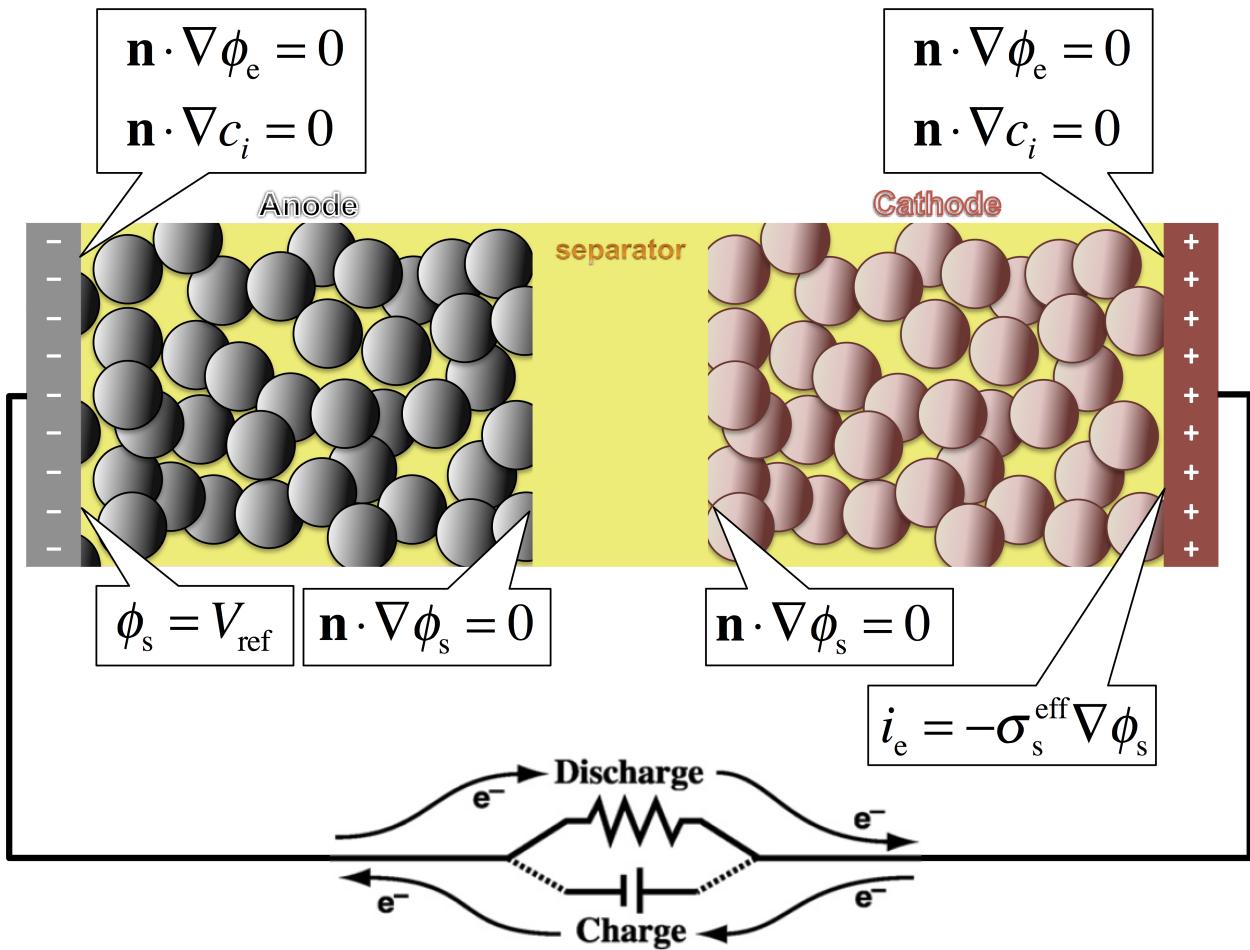


Figure 6.1: Section of a Li ion cell, showing cell-scale conservation equations and boundary conditions where \mathbf{n} is the vector normal to the interface.

6.1 Boundary conditions

The expressions in (3.8), eqn. (6.4), and (6.5) are spatially second order and thus each require boundary conditions. The boundary conditions for the electrochemical cell are relatively straightforward, a cartoon of which is shown in Figure 6.1.

At the current collector-electrode interface, the flux of each species and charge in a direction normal to the surface must be zero. This assumes that the current collector is a pure electron conductor.

$$\mathbf{n} \cdot \nabla c_i = 0 \quad (6.6)$$

$$\mathbf{n} \cdot \nabla \Phi_e = 0 \quad (6.7)$$

In addition, at the anode, we set the solid phase electric potential to be the reference voltage.

$$\Phi_s = V_{\text{ref}} \quad (6.8)$$

while at the cathode we set the gradient of the solid phase electric potential (the current density) to be the specified current density.

$$\mathbf{n} \cdot \nabla \Phi_s = i_{ref} \quad (6.9)$$

At the electrode–separator (electrolyte) interface, a similar equation holds but now the current density is specified to be zero. This assumes that the separator is made up entirely of ion conductor.

$$\mathbf{n} \cdot \nabla \Phi_s = 0 \quad (6.10)$$

As discussed above, the active electrode material is assumed to be made up of spherical particles. Then the next boundary condition is provided by the relationship between the pore wall flux across the interface, j_{in} term in eqn. (4.3), and the rate of diffusion of ions into the surface of the electrode matrix:

$$j_{in} = -D_s \frac{\partial c_s}{\partial r}. \quad (6.11)$$

6.2 Reference potential

Since the absolute potential of a single electrode cannot be measured, all potential measurements in electrochemical systems are performed with a reference electrode. An ideal reference electrode should be reversible and reproducible. In other words, the species that can cross the phase boundary of the reference electrode should exist in equilibrium in both phases of the half-cell.

For the mathematical description presented herein, at the anode current collector, the anode-phase electric potential is set to a reference voltage $\Phi_{a,cc} = V_{ref}$. At the cathode current collector, the cathode-phase electric potential gradient is set to meet the specified current density:

$$\mathbf{i} = -\sigma_{eff} \nabla \Phi_c \quad (6.12)$$

The current density \mathbf{i} is positive when the cell is discharging and negative when the cell is charging. The total current produced by the cell is $I = \mathbf{i}A$, where A is the area of the electrode current-collection surface (e.g., the foil in Figure 1.1).

The cell operating voltage is equal to the difference in potential at the current-collector interfaces $V_{cell} = \Phi_{c,cc} - \Phi_{a,cc}$. Assuming that the separator is a pure ion conductor, the electric current must vanish at the interfaces between the electrode-particle networks and the separator (e.g., $\mathbf{n} \cdot \nabla \Phi_i$).



7 Discretization

With all of the relevant equations in hand, we can now discretize the expressions in preparation for code implementation. We summarize the relevant equations here for reference. The first equation is the diffusion of Lithium ions in the electrolyte eqn. (4.1).

$$\epsilon \frac{\partial c}{\partial t} = \nabla \cdot (\epsilon D \nabla c) - [\kappa \nabla \phi_e + \kappa_D \nabla \ln c] \cdot \frac{\nabla t^0}{z\nu \mathcal{F}} + \frac{aj_n(1-t^0)}{\nu} \quad (7.1)$$

where κ_D is defined as

$$\kappa_D = \frac{\kappa \mathcal{R}T}{\mathcal{F}} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c} \right) \left(\frac{s_i}{n\nu_i} + \frac{t_i^0}{z_i\nu_i} \right) \quad (7.2)$$

Here we have modified slightly eqn. (4.1) by substituting eqn. (3.7) in for \mathbf{i} and expanding the dot product with the transference number. This allows us to eliminate \mathbf{i} as an unknown in our system of equations. The right-hand-side of this equation defines our first three modules. The first term we refer to as the species transport module (Section 7.5). The second is our wall flux module (Section 7.10) and the third is our current density concentration module (Section ??)

need to write the section for current density concentration

Next we solve the two charge migration equations, first in the solid:

$$\nabla \cdot (\sigma \nabla \Phi) - A_s j_n F = 0 \quad (7.3)$$

This equation forms our solid Ohms law module (Section 7.7.1) and its counterpart in the electrolyte

$$\nabla \cdot (\kappa \nabla \Phi) + \nabla \cdot (\kappa_D \nabla \ln c) + A_s j_n F = 0 \quad (7.4)$$

forms our electrolyte Ohms law module (Section 7.8). In both equations we have used the divergence free property of the current field to couple the charge migration in both materials to the interchange between the two via the source term $A_s j_n F$.

The last piece of information that we need is the transfer rate of electrons from the solid to electrolyte (j_n). The rate of ion production (or consumption) is directly related to the concentration gradient of Lithium ions in the solid (Equation 6.11). The production of ions can be defined in terms of a global reaction rate through the Butler-Volmer kinetics relation (Equation 5.1). We combined the two to generate a relationship between the cell potential and the ion production rate.

$$j_{in} = -D_s \frac{\partial c_s}{\partial r} = i_0 \left[\exp \left(\frac{\alpha_a \mathcal{F} \eta}{RT} \right) - \exp \left(-\frac{\alpha_c \mathcal{F} \eta}{RT} \right) \right] \quad (7.5)$$



The RHS of this equation forms our Butler-Volmer module (Section ??). By adding this equation, we have also introduced an additional unknown, the concentration of Lithium ions in the solid matrix. We can solve the time-dependent, second-order diffusion equation for ion migration (Equation 4.7) in the solid to close the problem. This piece defines our intercalation module (Section 7.11)

$$\frac{\partial c_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 D_s \frac{\partial c_s}{\partial r} \right] \quad (7.6)$$

need to write the section for intercalation

We now have a system of five equations with five unknowns. They are

- potential in the electrolyte (ϕ_e)
- potential in the solid (ϕ_s)
- the concentration of Lithium ions in the electrolyte (c_e)
- the concentration of Lithium ions in the solid (c_s)
- the transfer rate of Lithium ions between the solid and electrolyte (j_n)

We outline the solution strategy and discretization for each module in the following sections.

7.1 Time discretization

Our system as outlined thus far forms a coupled set of non-linear PDE's in space and time. We choose to solve the system implicitly with the NOX package from Trilinos. This choice simplifies much of our work in generating in solving the non-linear system and only requires us to correctly populate the data structures required for the solver for both interior and exterior computation nodes (still a non-trivial task). We form a global solution vector and require that each physics module populate their local portion of a residual function F and the Jacobian matrix $J = \frac{\partial F_i}{\partial c_j}$. Note that both the residual function and the Jacobian can have distinct values at each mesh point due to the non-linearity of the problem.

We provide time discretizations with both the explicit forward Euler method

$$\frac{\partial c_{k,n}}{\partial t} = \frac{c_{(k+1),n} - c_{k,n}}{\Delta t} = F_{k,n} \quad (7.7)$$

and implicit backward Euler.

$$\frac{\partial c_{k,n}}{\partial t} = \frac{c_{(k+1),n} - c_{k,n}}{\Delta t} = F_{(k+1),n} \quad (7.8)$$



In the case of the forward Euler method, we can use the function evaluation implemented for the NOX nonlinear solver to find the right hand side of our system of equations at the current timestep, denoted here as $F_{k,n}$. For the backward Euler method, we use the NOX nonlinear solver to find $F_{(k+1),n}$ implicitly as a function of the solution at the next point in time ($c_{(k+1),n}$).

7.2 Spatial discretization

Figure 7.1 shows a graphic representation of our electrochemical device hierarchy. In our implementation, we denote a device level solution. This is a global solution space and is where we solve for our solution as a function of time. We divide the device domain into arbitrary components, with each component being either an electrode or separator. This allows us the flexibility to arrange the components and to add new component types (e.g. a current collector) in the future. In turn, each component is made up of several physics modules. Each physics module implements a piece of the governing equations. No physics module is responsible for more than one equation or variable in our system.

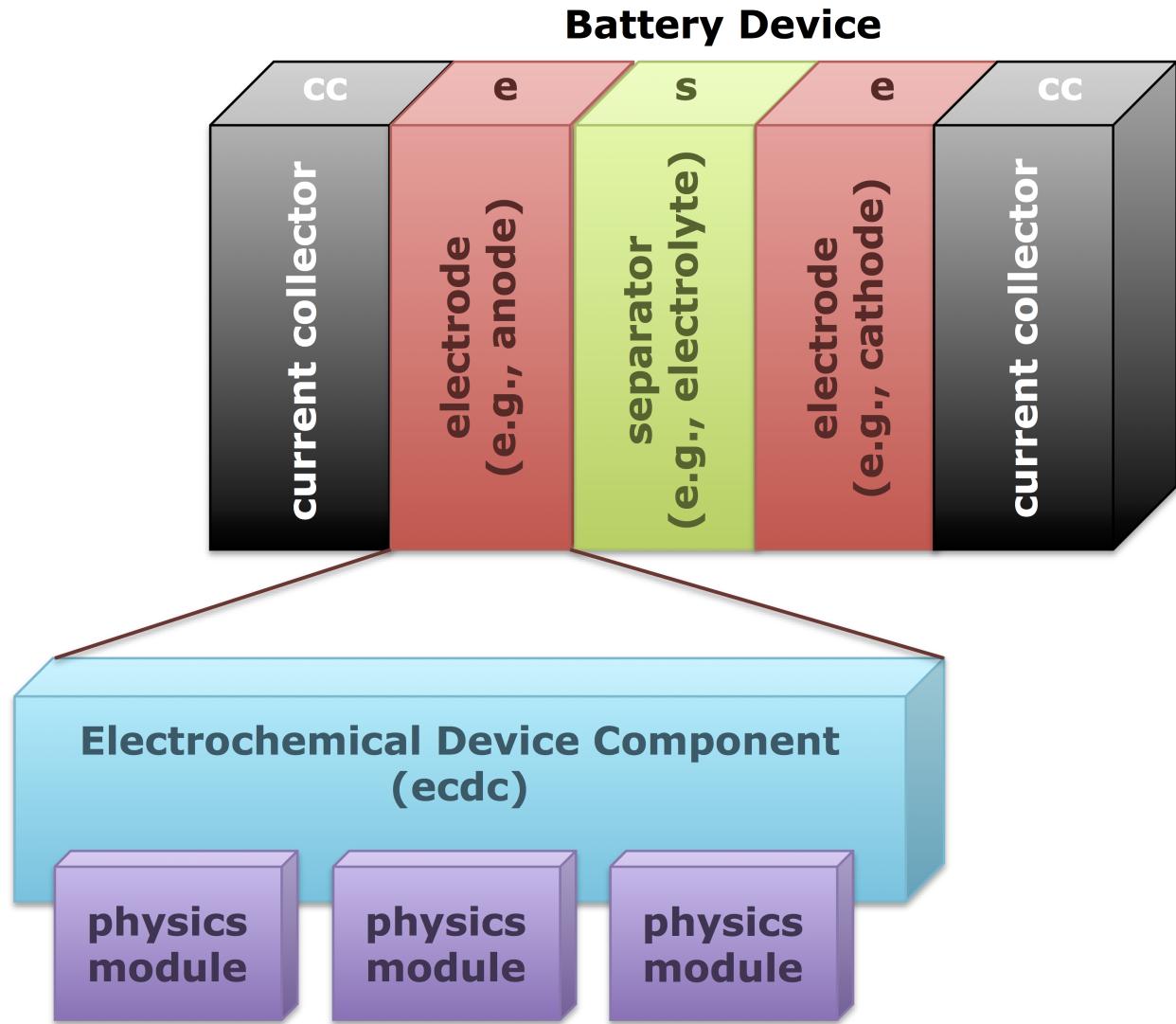


Figure 7.1: Schematic showing the relationship between the device, component, and module levels.

7.2.1 Finite Difference

The problem at hand requires the discretization of first and second derivatives. There are many options of computational stencils, but for now, we will consider a central difference scheme. Consider the Taylor series expansion of the function f_{i+1} about the point i .

$$f_{i+1} = f_i + h_{i+1}f' + \frac{1}{2}h_{i+1}^2f'' + \frac{1}{6}h_{i+1}^3f''' + \dots \quad (7.9)$$

Where h_{i+1} represents the distance from point i to $i + 1$. Similarly, we consider the Taylor series expansion of the function at f_{i-1} about the point i .

$$f_{i-1} = f_i + h_{i-1}f' + \frac{1}{2}h_{i-1}^2f'' + \frac{1}{6}h_{i-1}^3f''' + \dots \quad (7.10)$$



Again, h_{i-1} represents the distance from point i to $i - 1$. Then, by subtracting the two expressions and ignoring higher order terms we get

$$f_{i+1} - f_{i-1} = (h_{i+1} + h_{i-1}) f' + \left(\frac{1}{2} h_{i+1}^2 - \frac{1}{2} h_{i-1}^2 \right) f'' + \left(\frac{1}{6} h_{i+1}^3 + \frac{1}{6} h_{i-1}^3 \right) f''' \quad (7.11)$$

Which can be rearranged to get the central difference for a first-order derivative

$$f' = \frac{f_{i+1} - f_{i-1}}{h_{i+1} + h_{i-1}} - \frac{h_{i+1} - h_{i-1}}{2} f'' + \frac{h_{i+1}^3 + h_{i-1}^3}{6(h_{i+1} + h_{i-1})} f''' \quad (7.12)$$

We see that if the grid spacing is non-uniform the error is on the order of $h_{i+1} - h_{i-1}$, we will ignore the f'' and f''' error terms in our implementation. When the grid spacing is uniform, the error becomes h^2 and the familiar form is returned, again ignoring the f''' term.

$$f' = \frac{f_{i+1} - f_{i-1}}{2h} + \frac{h^2}{6} f''' \quad (7.13)$$

To find an expression for the second-order derivatives, we add f_{i+1} and $\frac{h_{i+1}}{h_{i-1}} f_{i-1}$

$$f_{i+1} + \frac{h_{i+1}}{h_{i-1}} f_{i-1} = \left(1 + \frac{h_{i+1}}{h_{i-1}} \right) f_i + \left(h_{i+1}^2 + h_{i+1} h_{i-1} \right) \frac{f''}{2} + \left(h_{i+1}^3 - h_{i+1} h_{i-1}^2 \right) \frac{f'''}{6} \quad (7.14)$$

Rearranging for the second derivative yields

$$f'' = \frac{2 \left(f_{i+1} + \frac{h_{i+1}}{h_{i-1}} f_{i-1} \right) - 2 \left(1 + \frac{h_{i+1}}{h_{i-1}} \right) f_i - (h_{i+1} - h_{i-1}) f'''}{3(h_{i+1}^2 + h_{i+1} h_{i-1})} \quad (7.15)$$

We again see that our error term is on the order of $h_{i+1} - h_{i-1}$. When the nodes are uniformly spaced, we again retain the familiar form

$$f'' = \frac{f_{i+1} - 2f_i + f_{i-1}}{h^2} \quad (7.16)$$

which is second order.

7.3 Boundary Conditions

Boundary conditions are handled at the module level. This is done to ensure that the boundary conditions are applied in a manner that is consistent with the physics module discretization. Where possible, implementation is provided by the base **PhysicsModule** class (e.g. Dirichlet boundaries). Discretization dependent boundary conditions must be implemented by the derived physics modules, i.e. Neumann boundaries.



Each module applies the appropriate Dirichlet or Neumann boundary condition dependent on whether the user specifies a current collector or separator boundary type. We also specify a number of ghost nodes for each component that lie outside the component boundary for each component. These nodes are filled by their neighboring components and maybe be modified by the component for specific boundary types (e.g. when specifying Neumann boundary conditions). Where no boundary condition is specified (e.g. internal boundaries), the node solutions are determined by each module and volume-averaged at the device level.

Currently supported boundary conditions are Dirichlet and Neumann. The base physics module class provides a default implementation for both kinds at the left and right boundary.

7.3.1 Dirichlet Boundary Condition Implementation

Dirichlet boundary conditions specify a value at a node. The default implementation sets the value of the solution data structure at the boundary nodes to that read in from the user input.

add information about what happens to the jacobian and function vectors, I might need to do something further than this

7.3.2 Neumann Boundary Condition Implementation

Neumann boundary conditions specify the value of a derivative at a node. The physics module base class provides a default implementation for a first order derivative with a 2nd order central difference. If other discretizations are used by a derived physics module, then a new implementation is required (this requirement is not checked). At a left boundary node n with first derivative value A the implementation is:

$$\frac{\partial c_{kn}}{\partial x} = \frac{c_{k(n+1)} - c_{k(n-1)}}{x_{(n+1)} - x_{k(n-1)}} = A \quad (7.17)$$

which becomes

$$c_{k(n-1)} = c_{k(n+1)} - (x_{(n+1)} - x_{k(n-1)}) A \quad (7.18)$$

We specify the distance between node points $(n + 1)$ and $(n - 1)$ as the mesh spacing may not be identical on different components. Similarly, at the right boundary we have

$$c_{k(n+1)} = c_{k(n-1)} + (x_{(n+1)} - x_{k(n-1)}) A \quad (7.19)$$

add information about what happens to the jacobian and function vectors, I believe they are processed normally.



7.4 Calculation of κ_D

Note that Equation 7.2 implies functional dependence of κ_D on the concentration. This dependence is due to the terms involving f_{\pm} and t_i^0 . Care is warranted when calculating derivatives of terms involving κ_D . The following expression for κ_D exposes its dependence on concentration:

$$\kappa_D = \frac{\kappa \mathcal{R}T}{\mathcal{F}} \left(1 + \frac{c_i}{f_{\pm}(c_i)} \frac{\partial f_{\pm}(c_i)}{\partial c_i} \right) \left(\frac{s_i}{n\nu_i} + \frac{t_i^0(c_i)}{z_i\nu_i} \right) \quad (7.20)$$

We indicate the derivatives wrt c_i with *prime* notation, and note that

$$\frac{\partial \kappa_D}{\partial c_i} = \frac{\kappa \mathcal{R}T}{\mathcal{F}\nu_i} \left[\left(\frac{f'_{\pm}}{f_{\pm}} \left(1 - \frac{c_i f'_{\pm}}{f_{\pm}} \right) + \frac{c_i f''_{\pm}}{f_{\pm}} \right) \left(\frac{s_i}{n} + \frac{t_i^0}{z_i} \right) + \frac{(t_i^0)'}{z_i} \left(1 + \frac{c_i}{f_{\pm}} f'_{\pm} \right) \right] \quad (7.21)$$

$$\frac{\partial \kappa_D}{\partial x^j} = \frac{\partial \kappa_D}{\partial c_i} \frac{\partial c_i}{\partial x^j} = \kappa'_D \frac{\partial c_i}{\partial x^j} \quad (7.22)$$

It is useful to indicate the expression for κ''_D for future reference:

$$\begin{aligned} \kappa''_D &= \frac{\kappa \mathcal{R}T}{\mathcal{F}\nu_i} \left\{ \frac{1}{f_{\pm}} \left(\frac{s_i}{n} + \frac{t_i^0}{z_i} \right) \left[\frac{2c(f'_{\pm})^3}{f_{\pm}^2} - \frac{2(f'_{\pm})^2}{f_{\pm}} - \frac{3cf'_{\pm}f''_{\pm}}{f_{\pm}} + f''_{\pm} + cf'''_{\pm} \right. \right. \\ &\quad \left. \left. + (t_i^0)' \left(f'_{\pm} - \frac{c(f'_{\pm})^2}{f_{\pm}} + cf''_{\pm} \right) \right] + \frac{(t_i^0)''}{z_i} \left(1 + \frac{cf'_{\pm}}{f_{\pm}} \right) + \frac{(t_i^0)'}{f_{\pm}z_i} \left(f'_{\pm} - \frac{c(f'_{\pm})^2}{f_{\pm}} + cf''_{\pm} \right) \right\} \end{aligned} \quad (7.23)$$

These formulae imply that when f_{\pm} and t_i^0 are functions of c_i , that we need functions that return their value, as well as f'_{\pm} , f''_{\pm} , f'''_{\pm} , $(t_i^0)'$, and $(t_i^0)''$. We further note that spatial derivatives of c_i -dependent quantities, $g(c_i)$, can be written:

$$\frac{\partial g}{\partial x^j} = g' \frac{\partial c_i}{\partial x^j} \quad (7.24)$$

and it follows that:

$$\nabla g = g' \nabla c_i \quad (7.25)$$

7.5 Nonlinear diffusion part

For the diffusion term (i.e. first term on RHS) of Equation 4.1, we have the following basic function:

$$\phi_d \equiv \nabla \cdot (D(c_i) \nabla c_i) = D'(c_i) (\nabla c_i \cdot \nabla c_i) + D(c_i) \nabla^2 c_i \quad (7.26)$$

where $D' \equiv \frac{d}{dc_i} D(c_i)$. The discrete system will be discussed for the i^{th} species only and so the i subscript will be dropped. Recall that the concentration c is a scalar field on the solution domain, Ω :

$$c(\mathbf{r}, t) : \mathbb{R}^{(N+1)} \Rightarrow \mathbb{R}; \quad \mathbf{r} \in \mathbb{R}^N, 0 \leq t < \infty \quad (7.27)$$

After discretization of the solution domain Ω into n_s spatial points and n_t temporal points (i.e. into Ω_{hk}), we have:

$$c_{kn}(\mathbf{r}_n, t_k) : \mathbb{R}^{(N+1)} \Rightarrow \mathbb{R}; n \in [0, n_s + 1], t_k \in [t_i, t_f] \quad (7.28)$$



That is, the concentration at each N-dimensional point \mathbf{r}_n and time t_k will be denoted by c_{kn} . Using central differences for the spatial derivatives we have:

$$\nabla c_{kn} \approx \frac{c_{k(n+1)} - c_{k(n-1)}}{2h} \frac{\mathbf{r}_n}{|\mathbf{r}_n|} \quad (7.29)$$

in each of the N spatial dimensions where regular spacing $h = |\mathbf{r}_{(n+1)} - \mathbf{r}_n|$ is assumed. Likewise we have:

$$\nabla^2 c_{kn} \approx \frac{c_{k(n+1)} - 2c_{kn} + c_{k(n-1)}}{h^2} \quad (7.30)$$

again with one such term for each of N spatial dimensions. For the discrete version of Equation 7.26 we have:

$$f_{kn} \equiv \frac{1}{h^2} \left(\frac{D'_n}{4} (c_{k(n+1)}^2 - 2c_{k(n+1)}c_{k(n-1)} + c_{k(n-1)}^2) + D_n (c_{k(n+1)} - 2c_{kn} + c_{k(n-1)}) \right) \quad (7.31)$$

with the discrete version of $D(c_i)$, $D_n \equiv D(c_{kn})$ and similar for D'_n . These n_s equations 7.31 and their Jacobian matrix:

$$\mathbf{J}_{dk} = \frac{\partial(f_{k1}, f_{k2}, \dots, f_{kn})}{\partial(c_{k1}, c_{k2}, \dots, c_{kn})} \quad (7.32)$$

must be calculated by the module implementing the nonlinear diffusion component of the ECD. If we define the off-diagonal term:

$$g_n = \frac{D'_n}{2} (c_{k(n+1)} - c_{k(n-1)}) \quad (7.33)$$

The Jacobian non-zero entries are these:

$$j_n^0 \equiv \frac{\partial f_{kn}}{\partial c_{kn}} = \frac{-2D_n}{h^2} \quad (7.34a)$$

$$j_n^- \equiv \frac{\partial f_{kn}}{\partial c_{k(n-1)}} = \frac{1}{h^2} (D_n - g_n) \quad (7.34b)$$

$$j_n^+ \equiv \frac{\partial f_{kn}}{\partial c_{k(n+1)}} = \frac{1}{h^2} (D_n + g_n) \quad (7.34c)$$

Note that boundary conditions and quantities are not treated by the foregoing. The goal of the modules in this case is to update the functions and Jacobians for the interior nodes only assuming boundaries will be handled specifically by other (external) modules/components.

7.5.1 Nonlinear diffusion for non-uniform meshes

Following from the above, we now start with the non-uniform finite difference equations for first the second order derivatives Equations 7.12 and 7.12 to obtain the non-uniform analog

to Equation 7.31.

$$f_{kn} \equiv \frac{D'_n \left(c_{k(n+1)}^2 - 2c_{k(n+1)}c_{k(n-1)} + c_{k(n-1)}^2 \right)}{(h_{n+1} + h_{n-1})^2} + \frac{2D_n \left[\left(1 + \frac{h_{n-1}}{h_{n+1}} \right) \left(c_{k(n+1)} - c_{kn} \right) + \left(1 + \frac{h_{n+1}}{h_{n-1}} \right) \left(c_{k(n-1)} - c_{kn} \right) \right]}{(h_{n+1} + h_{n-1})^2} \quad (7.35)$$

with the discrete version of $D(c_i)$, $D_n \equiv D(c_{kn})$ and similar for D'_n . These n_s equations 7.35 and their Jacobian matrix:

$$\mathbf{J}_{dk} = \frac{\partial(f_{k1}, f_{k2}, \dots, f_{kn})}{\partial(c_{k1}, c_{k2}, \dots, c_{kn})} \quad (7.36)$$

must be calculated by the module implementing the nonlinear diffusion component of the ECD. If we define the off-diagonal term:

$$g_n = 2D'_n \left(c_{k(n+1)} - c_{k(n-1)} \right) \quad (7.37)$$

The Jacobian non-zero entries are these:

$$j_n^0 \equiv \frac{\partial f_{kn}}{\partial c_{kn}} = \frac{-2D_n \left(2 + \frac{h_{n+1}}{h_{n-1}} + \frac{h_{n-1}}{h_{n+1}} \right)}{(h_{n+1} + h_{n-1})^2} \quad (7.38a)$$

$$j_n^- \equiv \frac{\partial f_{kn}}{\partial c_{k(n-1)}} = \frac{\left(2D_n \left(1 + \frac{h_{n+1}}{h_{n-1}} \right) - g_n \right)}{(h_{n+1} + h_{n-1})^2} \quad (7.38b)$$

$$j_n^+ \equiv \frac{\partial f_{kn}}{\partial c_{k(n+1)}} = \frac{\left(2D_n \left(1 + \frac{h_{n-1}}{h_{n+1}} \right) + g_n \right)}{(h_{n+1} + h_{n-1})^2} \quad (7.38c)$$

7.6 Ion migration part

The ion migration portion of the system, ϕ_m , is as follows:

$$\phi_m = \frac{1}{z_i \nu_i \mathcal{F}} \left[\nabla t_i^0 \cdot \left(\kappa \nabla \Phi + \frac{\kappa_D}{c_i} \nabla c_i \right) \right] \quad (7.39)$$

These terms are calculated according to the following:

$$\nabla t_i^0 = (t_i^0)' \nabla c_i \quad (7.40)$$

Using 7.40, the ion migration expression becomes:

$$\phi_m = \frac{(t_i^0)'}{z_i \nu_i \mathcal{F}} \left[\kappa (\nabla c_i \cdot \nabla \Phi) + \frac{\kappa_D}{c_i} (\nabla c_i)^2 \right] \quad (7.41)$$



∇c_i is calculated using central differencing as in Equation 7.29, and likewise $\nabla \Phi$ according to:

$$\nabla \Phi_{kn} \approx \frac{\Phi_{k(n+1)} - \Phi_{k(n-1)}}{2h} \frac{\mathbf{r}_n}{|\mathbf{r}_n|} \quad (7.42)$$

in each of the N spatial dimensions. These expressions give the following for the discrete version:

$$\phi_m = \frac{(t_i^0)'}{z_i \nu_i \mathcal{F}} \frac{1}{4h^2} \left[\kappa (\Phi_{k(n+1)} - \Phi_{k(n-1)}) (c_{k(n+1)} - c_{k(n-1)}) + \frac{\kappa_D}{c_{kn}} (c_{k(n+1)} - c_{k(n-1)})^2 \right] \quad (7.43)$$

Denoting by [...] the bracketed term from Equation 7.43, the Jacobian contributions are as follows:

$$\frac{\partial \phi_m}{\partial c_{kn}} = \frac{1}{4z_i \nu_i \mathcal{F} h^2} \left[(t_i^0)'' [...] + (t_i^0)' \left(\frac{\kappa'_D}{c_{kn}} - \frac{\kappa_D}{c_{kn}^2} \right) (c_{k(n+1)} - c_{k(n-1)})^2 \right] \quad (7.44a)$$

$$\frac{\partial \phi_m}{\partial c_{k(n+1)}} = \frac{(t_i^0)'}{4z_i \nu_i \mathcal{F} h^2} \left(\kappa (\Phi_{k(n+1)} - \Phi_{k(n-1)}) + \frac{2\kappa_D}{c_{kn}} (c_{k(n+1)} - c_{k(n-1)}) \right) \quad (7.44b)$$

$$\frac{\partial \phi_m}{\partial c_{k(n-1)}} = -\frac{\partial \phi_m}{\partial c_{k(n+1)}} \quad (7.44c)$$

$$\frac{\partial \phi_m}{\partial \Phi_{k(n+1)}} = -\frac{\partial \phi_m}{\partial \Phi_{k(n-1)}} = \frac{(t_i^0)'}{z_i \nu_i \mathcal{F}} \frac{\kappa}{4h^2} (c_{k(n+1)} - c_{k(n-1)}) \quad (7.44d)$$

7.6.1 Ion migration for non-uniform meshes

Following from the above, we now start with the non-uniform finite difference equations for first the second order derivatives Equations 7.12 and 7.12 to obtain the non-uniform analog to Equation 7.43.

$$\phi_m = \frac{(t_i^0)'}{z_i \nu_i \mathcal{F}} \frac{\kappa (\Phi_{k(n+1)} - \Phi_{k(n-1)}) (c_{k(n+1)} - c_{k(n-1)}) + \frac{\kappa_D}{c_{kn}} (c_{k(n+1)} - c_{k(n-1)})^2}{(h_{n+1} + h_{n-1})^2} \quad (7.45)$$

Denoting by [...] the bracketed term from Equation 7.43, the Jacobian contributions are as follows:

$$\frac{\partial \phi_m}{\partial c_{kn}} = \frac{1}{z_i \nu_i \mathcal{F}} \left[\frac{(t_i^0)'' [...] + (t_i^0)' \left(\frac{\kappa'_D}{c_{kn}} - \frac{\kappa_D}{c_{kn}^2} \right) (c_{k(n+1)} - c_{k(n-1)})^2}{(h_{n+1} + h_{n-1})^2} \right] \quad (7.46a)$$

$$\frac{\partial \phi_m}{\partial c_{k(n+1)}} = \frac{(t_i^0)' \left(\kappa (\Phi_{k(n+1)} - \Phi_{k(n-1)}) + \frac{2\kappa_D}{c_{kn}} (c_{k(n+1)} - c_{k(n-1)}) \right)}{z_i \nu_i \mathcal{F} (h_{n+1} + h_{n-1})^2} \quad (7.46b)$$

$$\frac{\partial \phi_m}{\partial c_{k(n-1)}} = -\frac{\partial \phi_m}{\partial c_{k(n+1)}} \quad (7.46c)$$

$$\frac{\partial \phi_m}{\partial \Phi_{k(n)}} = 0 \quad (7.46d)$$

$$\frac{\partial \phi_m}{\partial \Phi_{k(n+1)}} = -\frac{\partial \phi_m}{\partial \Phi_{k(n-1)}} = \frac{(t_i^0)' \kappa (c_{k(n+1)} - c_{k(n-1)})}{z_i \nu_i \mathcal{F} (h_{n+1} + h_{n-1})^2} \quad (7.46e)$$

7.7 Ohm's Law discretization for the solid

The equation for Ohm's Law for the solid phase is

$$\frac{\partial}{\partial x} \left(\sigma \frac{\partial}{\partial x} \Phi_s \right) - A_s j_n F = 0 \quad (7.47)$$

where σ , A_s , and F are constants and Φ_s and j_n are two of the unknown variables for which the code solves. The s subscript denotes that this equation is relevant in the solid phase of the battery, and it will now be dropped for simplicity. Rewriting this equation as a basic function we have the following

$$\phi_O = \frac{\partial}{\partial x} \left(\sigma \frac{\partial}{\partial x} \Phi_s \right) - A_s j_n F \quad (7.48)$$

Since we may treat σ as a constant, we may rewrite Equation 7.48 as

$$\phi_O = \sigma \frac{\partial^2 \Phi}{\partial x^2} - A_s j_n F \quad (7.49)$$

Recall that Φ (electric potential) is a scalar function. Following the discretization and nomenclature used in Section 7.5, we discretize $\frac{\partial^2 \Phi}{\partial x^2}$ using central difference method as shown below

$$\frac{\partial^2 \Phi}{\partial x^2} \approx \frac{\Phi_{k(n+1)} - 2\Phi_{kn} + \Phi_{k(n-1)}}{h^2} \quad (7.50)$$



where Φ_{kn} represents the electric potential at temporal discretization point k and spatial discretization point n . Also, $h = |\mathbf{r}_{(n+1)} - \mathbf{r}_n|$ where \mathbf{r}_n is an N-dimensional argument taken by Φ , and regular spacing in the spatial discretization is assumed. Now, the discretization of Equation 7.49 is

$$f_{kn} = \sigma \frac{\Phi_{k(n+1)} - 2\Phi_{kn} + \Phi_{k(n-1)}}{h^2} - A_s j_{n_{kn}} F \quad (7.51)$$

There exists an f_{kn} function for every node in the discretization space. These functions and their Jacobian matrices:

$$\mathbf{J}_{O\Phi_k} = \frac{\partial(f_{k1}, f_{k2}, \dots, f_{kn})}{\partial(\Phi_{k1}, \Phi_{k2}, \dots, \Phi_{kn})} \quad (7.52)$$

$$\mathbf{J}_{Oj_{nk}} = \frac{\partial(f_{k1}, f_{k2}, \dots, f_{kn})}{\partial(j_{n_{k1}}, j_{n_{k2}}, \dots, j_{n_{kn}})} \quad (7.53)$$

must be calculated by the module implementing Ohm's Law for the solid phase. The Jacobian non-zero entries are as follows:

$$j_n^0 \equiv \frac{\partial f_{kn}}{\partial \Phi_{kn}} = \frac{-2\sigma}{h^2} \quad (7.54)$$

$$j_n^- \equiv \frac{\partial f_{kn}}{\partial \Phi_{k(n-1)}} = \frac{\sigma}{h^2} \quad (7.55)$$

$$j_n^+ \equiv \frac{\partial f_{kn}}{\partial \Phi_{k(n+1)}} = \frac{\sigma}{h^2} \quad (7.56)$$

$$j_{jn} \equiv \frac{\partial f_{kn}}{\partial j_{n_{kn}}} = -A_s F \quad (7.57)$$

7.7.1 Ohm's Law for the solid for non-uniform meshes

Following from the above, we now start with the non-uniform finite difference equations for first the second order derivatives Equations 7.12 and 7.12 to obtain the non-uniform analog to Equation 7.51.

$$f_{kn} = 2\sigma \frac{\left(1 + \frac{h_{n-1}}{h_{n+1}}\right) (\Phi_{k(n+1)} - \Phi_{kn}) + \left(1 + \frac{h_{n+1}}{h_{n-1}}\right) (\Phi_{k(n-1)} - \Phi_{kn})}{(h_{n+1} + h_{n-1})^2} - A_s j_{n_{kn}} F \quad (7.58)$$

There exists an f_{kn} function for every node in the discretization space. These functions and their Jacobian matrices:

$$\mathbf{J}_{O\Phi_k} = \frac{\partial(f_{k1}, f_{k2}, \dots, f_{kn})}{\partial(\Phi_{k1}, \Phi_{k2}, \dots, \Phi_{kn})} \quad (7.59)$$

$$\mathbf{J}_{Oj_{kn}} = \frac{\partial(f_{k1}, f_{k2}, \dots, f_{kn})}{\partial(j_{n_{k1}}, j_{n_{k2}}, \dots, j_{n_{kn}})} \quad (7.60)$$

must be calculated by the module implementing Ohm's Law for the solid phase. The Jacobian non-zero entries are as follows:

$$j_n^0 \equiv \frac{\partial f_{kn}}{\partial \Phi_{kn}} = \frac{-2\sigma \left[2 + \frac{h_{n+1}}{h_{n-1}} + \frac{h_{n-1}}{h_{n+1}} \right]}{(h_{n+1} + h_{n-1})^2} \quad (7.61)$$

$$j_n^- \equiv \frac{\partial f_{kn}}{\partial \Phi_{k(n-1)}} = \frac{2\sigma \left(1 + \frac{h_{n+1}}{h_{n-1}} \right)}{(h_{n+1} + h_{n-1})^2} \quad (7.62)$$

$$j_n^+ \equiv \frac{\partial f_{kn}}{\partial \Phi_{k(n+1)}} = \frac{2\sigma \left(1 + \frac{h_{n-1}}{h_{n+1}} \right)}{(h_{n+1} + h_{n-1})^2} \quad (7.63)$$

$$j_{jn} \equiv \frac{\partial f_{kn}}{\partial j_{n_{kn}}} = -A_s F \quad (7.64)$$

7.8 Current density concentration

The current density concentration equation is Ohm's law for the liquid phase and the 1D form is shown below:

$$\frac{\partial}{\partial x} \left(\kappa \frac{\partial}{\partial x} \Phi_e \right) + \frac{\partial}{\partial x} \left(\kappa_D \frac{\partial}{\partial x} \ln c_e \right) + A_s j_n F = 0 \quad (7.65)$$

where κ , A_s , and F are constants. Φ_e , c_e , and j_n are three of the unknown variables for which the code is solving, and κ_D is given in Equation 7.2. The e subscript refers to the fact that this equation is valid in the electrolyte phase and will be dropped. Rewriting this equation as a basic function gives

$$\phi_c = \frac{\partial}{\partial x} \left(\kappa \frac{\partial}{\partial x} \Phi_e \right) + \frac{\partial}{\partial x} \left(\kappa_D \frac{\partial}{\partial x} \ln c_e \right) + A_s j_n F \quad (7.66)$$

This function will be discretized in two parts: by dealing with the first term on the RHS first and then dealing with the second term on the RHS.

Since κ is a constant, we may rewrite the first term on the RHS of Equation 7.66 as follows

$$\frac{\partial}{\partial x} \left(\kappa \frac{\partial}{\partial x} \Phi \right) = \kappa \frac{\partial^2 \Phi}{\partial x^2} \quad (7.67)$$



Recall that Φ (electric potential) is a scalar function. Following the discretization and nomenclature used in Section 7.5, we discretize $\frac{\partial^2 \Phi}{\partial x^2}$ using central difference method as shown below

$$\frac{\partial^2 \Phi}{\partial x^2} \approx \frac{\Phi_{k(n+1)} - 2\Phi_{kn} + \Phi_{k(n-1)}}{h^2} \quad (7.68)$$

where Φ_{kn} represents the electric potential at temporal discretization point k and spatial discretization point n . Also, $h = |\mathbf{r}_{(n+1)} - \mathbf{r}_n|$ where \mathbf{r}_n is an N-dimensional argument taken by Φ , and regular spacing in the spatial discretization is assumed.

Calculus is used to rewrite the second term on the RHS of Equation 7.66 in several steps shown below

$$\begin{aligned} \frac{\partial}{\partial x} \left(\kappa_D \frac{\partial}{\partial x} \ln c \right) &= \frac{\partial}{\partial x} \left(\kappa_D \frac{1}{c} \frac{\partial c}{\partial x} \right) \\ &= \kappa_D \frac{\partial}{\partial x} \left(\frac{1}{c} \frac{\partial c}{\partial x} \right) + \frac{\partial \kappa_D}{\partial x} \left(\frac{1}{c} \frac{\partial c}{\partial x} \right) \\ &= \kappa_D \left(\frac{1}{c} \frac{\partial^2 c}{\partial x^2} - \frac{1}{c^2} \left(\frac{\partial c}{\partial x} \right)^2 \right) + \frac{\partial \kappa_D}{\partial c} \left(\frac{\partial c}{\partial x} \right) \left(\frac{1}{c} \frac{\partial c}{\partial x} \right) \\ &= \kappa_D \left(\frac{1}{c} \frac{\partial^2 c}{\partial x^2} - \frac{1}{c^2} \left(\frac{\partial c}{\partial x} \right)^2 \right) + \frac{\partial \kappa_D}{\partial c} \left(\frac{1}{c} \right) \left(\frac{\partial c}{\partial x} \right)^2 \end{aligned} \quad (7.69)$$

Recall that c (concentration of the electrolyte) is a scalar function. Following the discretization and nomenclature used in Section 7.5, we discretize $\frac{\partial c}{\partial x}$ and $\frac{\partial^2 c}{\partial x^2}$ using central difference method as shown below

$$\frac{\partial c_{kn}}{\partial x} \approx \frac{c_{k(n+1)} - c_{k(n-1)}}{2h} \quad (7.70)$$

$$\frac{\partial^2 c}{\partial x^2} \approx \frac{c_{k(n+1)} - 2c_{kn} + c_{k(n-1)}}{h^2} \quad (7.71)$$

where c_{kn} represents the electric potential at temporal discretization point k and spatial discretization point n . Also, $h = |\mathbf{r}_{(n+1)} - \mathbf{r}_n|$ where \mathbf{r}_n is an N-dimensional argument taken by c , and regular spacing in the spatial discretization is assumed.

Using the rewritten forms of the first two terms on the RHS shown in Equation 7.67 and Equation 7.69, Equation 7.66 can be rewritten as shown below.

$$\phi_c = \kappa \frac{\partial^2 \Phi}{\partial x^2} + \kappa_D \left(\frac{1}{c} \frac{\partial^2 c}{\partial x^2} - \frac{1}{c^2} \left(\frac{\partial c}{\partial x} \right)^2 \right) + \frac{\partial \kappa_D}{\partial c} \left(\frac{1}{c} \right) \left(\frac{\partial c}{\partial x} \right)^2 + A_s j_n F \quad (7.72)$$

The following terms will be defined for all variables in order to ease notation

$$\Delta c \equiv \frac{c_{k(n+1)} - c_{k(n-1)}}{2h} \quad (7.73)$$

$$\Delta_2 c \equiv \frac{c_{k(n+1)} - 2c_{kn} + c_{k(n-1)}}{h^2} \quad (7.74)$$

Using the central difference discretizations shown in Equation 7.68, Equation 7.73, and Equation 7.74, Equation 7.72 can be discretized as shown below.

$$f_{kn} = \kappa \Delta_2 \Phi + \kappa_{D_{kn}} \left(\frac{\Delta_2 c}{c_{kn}} - \left(\frac{\Delta c}{c_{kn}} \right)^2 \right) + \frac{\partial \kappa_{D_{kn}}}{\partial c_{kn}} \left(\frac{1}{c_{kn}} \right) \Delta c^2 + A_s j_{n_{kn}} F \quad (7.75)$$

where $\frac{\partial \kappa_{D_{kn}}}{\partial x}$ is given in Equation 7.22. There exists an f_{kn} function for every node in the discretization space. These functions and their Jacobian matrices must be calculated by the module implementing the current density concentration. The formulas for the Jacobian matrices are shown below

$$\mathbf{J}_{c\Phi_k} = \frac{\partial(f_{k1}, f_{k2}, \dots, f_{kn})}{\partial(\Phi_{k1}, \Phi_{k2}, \dots, \Phi_{kn})} \quad (7.76)$$

$$\mathbf{J}_{cck} = \frac{\partial(f_{k1}, f_{k2}, \dots, f_{kn})}{\partial(c_{k1}, c_{k2}, \dots, c_{kn})} \quad (7.77)$$

$$\mathbf{J}_{cj_{n,k}} = \frac{\partial(f_{k1}, f_{k2}, \dots, f_{kn})}{\partial(j_{n_{k1}}, j_{n_{k2}}, \dots, j_{n_{kn}})} \quad (7.78)$$

The Jacobian non-zero entries are as follows:

$$j_{\Phi n} \equiv \frac{\partial f_{kn}}{\partial \Phi_{kn}} = \frac{-2\kappa}{h^2} \quad (7.79)$$

$$j_{\Phi n}^- \equiv \frac{\partial f_{kn}}{\partial \Phi_{k(n-1)}} = \frac{\kappa}{h^2} \quad (7.80)$$

$$j_{\Phi n}^+ \equiv \frac{\partial f_{kn}}{\partial \Phi_{k(n+1)}} = \frac{\kappa}{h^2} \quad (7.81)$$

$$\begin{aligned} j_{cn} \equiv \frac{\partial f_{kn}}{\partial c_{kn}} &= \kappa_{D_{kn}} \left(\frac{-\Delta_2 c}{c_{kn}^2} - \frac{2}{c_{kn} h^2} + \frac{2(\Delta c)^2}{c_{kn}^3} \right) + \frac{\partial \kappa_{D_{kn}}}{\partial c_{kn}} \left(\frac{\Delta_2 c}{c_{kn}} - \left(\frac{\Delta c}{c_{kn}} \right)^2 \right) \\ &\quad - \frac{\partial \kappa_{D_{kn}}}{\partial c_{kn}} \left(\frac{(\Delta c)^2}{c_{kn}^2} \right) + \frac{\partial^2 \kappa_{D_{kn}}}{\partial c_{kn}^2} \left(\frac{(\Delta c)^2}{c_{kn}} \right) \end{aligned} \quad (7.82)$$

$$j_{cn}^- \equiv \frac{\partial f_{kn}}{\partial c_{kn-1}} = \kappa_{D_{kn}} \left(\frac{1}{h^2 c_{kn}} + \frac{\Delta c}{c_{kn}^2 h} \right) - \frac{\partial \kappa_{D_{kn}}}{\partial c_{kn}} \left(\frac{\Delta c}{c_{kn} h} \right) \quad (7.83)$$

$$j_{cn}^+ \equiv \frac{\partial f_{kn}}{\partial c_{kn+1}} = \kappa_{D_{kn}} \left(\frac{1}{h^2 c_{kn}} - \frac{\Delta c}{c_{kn}^2 h} \right) + \frac{\partial \kappa_{D_{kn}}}{\partial c_{kn}} \left(\frac{\Delta c}{c_{kn} h} \right) \quad (7.84)$$

$$j_{jn} \equiv \frac{\partial f_{kn}}{\partial j_{n_{kn}}} = A_s F \quad (7.85)$$

7.8.1 Current density concentration on non-uniform meshes

Following from the above, we now start with the non-uniform finite difference equations for first the second order derivatives Equations 7.12 and 7.12 to obtain the non-uniform analog to Equation 7.75.

$$f_{kn} = \kappa \Delta_2 \Phi + \kappa_{D_{kn}} \left(\frac{\Delta_2 c}{c_{kn}} - \left(\frac{\Delta c}{c_{kn}} \right)^2 \right) + \frac{\partial \kappa_{D_{kn}}}{\partial c_{kn}} \left(\frac{1}{c_{kn}} \right) \Delta c^2 + A_s j_{n_{kn}} F \quad (7.86)$$

$$\begin{aligned} f_{kn} = & 2\kappa \frac{\left(1 + \frac{h_{n-1}}{h_{n+1}}\right) (\Phi_{k(n+1)} - \Phi_{kn}) + \left(1 + \frac{h_{n+1}}{h_{n-1}}\right) (\Phi_{k(n-1)} - \Phi_{kn})}{(h_{n+1} + h_{n-1})^2} + \\ & \frac{2\kappa_D}{c_i} \frac{\left(1 + \frac{h_{n-1}}{h_{n+1}}\right) (c_{k(n+1)} - c_{kn}) + \left(1 + \frac{h_{n+1}}{h_{n-1}}\right) (c_{k(n-1)} - c_{kn})}{(h_{n+1} + h_{n-1})^2} - \\ & \frac{\kappa_D}{c_i^2} \frac{(c_{kn+1} - c_{kn-1})^2}{(h_{n+1} + h_{n-1})^2} + \frac{\kappa'_D}{c_i} \frac{(c_{kn+1} - c_{kn-1})^2}{(h_{n+1} + h_{n-1})^2} + A_s j_{n_{kn}} F \end{aligned} \quad (7.87)$$

where $\frac{\partial \kappa_{D_{kn}}}{\partial x}$ is given in Equation 7.22. There exists an f_{kn} function for every node in the discretization space. These functions and their Jacobian matrices must be calculated by the module implementing the current density concentration. The formulas for the Jacobian matrices are shown below

$$\mathbf{J}_{c\Phi k} = \frac{\partial(f_{k1}, f_{k2}, \dots, f_{kn})}{\partial(\Phi_{k1}, \Phi_{k2}, \dots, \Phi_{kn})} \quad (7.88)$$

$$\mathbf{J}_{cck} = \frac{\partial(f_{k1}, f_{k2}, \dots, f_{kn})}{\partial(c_{k1}, c_{k2}, \dots, c_{kn})} \quad (7.89)$$

$$\mathbf{J}_{cj_{nk}} = \frac{\partial(f_{k1}, f_{k2}, \dots, f_{kn})}{\partial(j_{n_{k1}}, j_{n_{k2}}, \dots, j_{n_{kn}})} \quad (7.90)$$

The Jacobian non-zero entries are as follows:

$$j_{\Phi n}^0 \equiv \frac{\partial f_{kn}}{\partial \Phi_{kn}} = \frac{-2\kappa \left[2 + \frac{h_{n+1}}{h_{n-1}} + \frac{h_{n-1}}{h_{n+1}} \right]}{(h_{n+1} + h_{n-1})^2} \quad (7.91)$$

$$j_{\Phi n}^- \equiv \frac{\partial f_{kn}}{\partial \Phi_{k(n-1)}} = \frac{2\kappa \left(1 + \frac{h_{n+1}}{h_{n-1}}\right)}{(h_{n+1} + h_{n-1})^2} \quad (7.92)$$

$$j_{\Phi n}^+ \equiv \frac{\partial f_{kn}}{\partial \Phi_{k(n+1)}} = \frac{2\kappa \left(1 + \frac{h_{n-1}}{h_{n+1}}\right)}{(h_{n+1} + h_{n-1})^2} \quad (7.93)$$

$$\begin{aligned} j_{cn}^- \equiv \frac{\partial f_{kn}}{\partial c_{kn}} &= \frac{2\kappa'_D \left(1 + \frac{h_{n-1}}{h_{n+1}}\right) (c_{k(n+1)} - c_{kn}) + \left(1 + \frac{h_{n+1}}{h_{n-1}}\right) (c_{k(n-1)} - c_{kn})}{c_i (h_{n+1} + h_{n-1})^2} - \\ &\quad \frac{\kappa'_D (c_{kn+1} - c_{kn-1})^2}{c_i^2 (h_{n+1} + h_{n-1})^2} + \frac{\kappa''_D (c_{kn+1} - c_{kn-1})^2}{c_i (h_{n+1} + h_{n-1})^2} - \\ &\quad \frac{2\kappa_D \left(1 + \frac{h_{n-1}}{h_{n+1}}\right) (c_{k(n+1)} - c_{kn}) + \left(1 + \frac{h_{n+1}}{h_{n-1}}\right) (c_{k(n-1)} - c_{kn})}{c_i^2 (h_{n+1} + h_{n-1})^2} - \\ &\quad \frac{2\kappa_D \left(2 + \frac{h_{n-1}}{h_{n+1}} + \frac{h_{n+1}}{h_{n-1}}\right)}{c_i (h_{n+1} + h_{n-1})^2} + \frac{2\kappa_D (c_{kn+1} - c_{kn-1})^2}{c_i^3 (h_{n+1} + h_{n-1})^2} - \\ &\quad \frac{\kappa'_D (c_{kn+1} - c_{kn-1})^2}{c_i^2 (h_{n+1} + h_{n-1})^2} \end{aligned} \quad (7.94)$$

$$j_{cn}^- \equiv \frac{\partial f_{kn}}{\partial c_{kn-1}} = \frac{2\kappa_D \left(1 + \frac{h_{n+1}}{h_{n-1}}\right)}{c_i (h_{n+1} + h_{n-1})^2} - \frac{2\kappa_D (c_{kn-1} - c_{kn+1})}{c_i^2 (h_{n+1} + h_{n-1})^2} + \frac{2\kappa'_D (c_{kn-1} - c_{kn+1})}{c_i (h_{n+1} + h_{n-1})^2} \quad (7.95)$$

$$j_{cn}^+ \equiv \frac{\partial f_{kn}}{\partial c_{kn+1}} = \frac{2\kappa_D \left(1 + \frac{h_{n-1}}{h_{n+1}}\right)}{c_i (h_{n+1} + h_{n-1})^2} - \frac{2\kappa_D (c_{kn+1} - c_{kn-1})}{c_i^2 (h_{n+1} + h_{n-1})^2} + \frac{2\kappa'_D (c_{kn+1} - c_{kn-1})}{c_i (h_{n+1} + h_{n-1})^2} \quad (7.96)$$

$$j_{jn} \equiv \frac{\partial f_{kn}}{\partial j_{n_{kn}}} = A_s F \quad (7.97)$$

7.9 Butler-Volmer part

The Butler-Volmer (BV) part of the system computes a scalar current density, i_n (i.e. at current density at every mesh node) as described in Section 5.1. The BV depends on several parameters and input data. In addition to the concentration, c_i which is discretized to c_{kn} as described in Section 7.5, the scalar potential for solid and electrolyte phases, $\Phi_s(\mathbf{r}_n, t_k)$ and $\Phi_e(\mathbf{r}_n, t_k)$ resp., are required. Both potentials are scalar fields on the discrete solution domain Ω_{hk} .

The BV module should be configured with the following constants:

- c_{max} : maximum polymer concentration

- β : symmetry parameter
- k_a : rate constant for anodic reaction
- k_c : rate constant for cathodic reaction

The BV physics function requires the following arguments:

- U_s : open circuit potential (defaults to zero)
- T_k : system temperature at t_k
- c_{nk} : concentration field in the solid on the mesh
- $\Phi_s(\mathbf{r}_n, t_k) = (\Phi_s)_{nk}$: material potential on the mesh
- $\Phi_e(\mathbf{r}_n, t_k) = (\Phi_e)_{nk}$: electrolyte potential on the mesh

The BV function calculates η_{nk} :

$$\eta_{nk} = (\Phi_s)_{nk} - (\Phi_e)_{nk} - U_s \quad (7.98)$$

then $(i_0)_{nk}$:

$$(i_0)_{nk} = \mathcal{F}(k_a)^\beta (k_c)^{(1-\beta)} (c_{max} - c_{nk})^\beta (c_{nk})^{(1-\beta)} \quad (7.99)$$

and finally i_{nk} :

$$i_{nk} = (i_0)_{nk} [\exp(\theta^+ \eta_{nk}) - \exp(-\theta^- \eta_{nk})] \quad (7.100)$$

where

$$\theta^+ = \frac{(1-\beta)\mathcal{F}}{\mathcal{R}T_k} \quad (7.101a)$$

$$\theta^- = \frac{\beta\mathcal{F}}{\mathcal{R}T_k} \quad (7.101b)$$

The following derivatives are useful for calculating the Jacobian:

$$\frac{\partial \eta_{nk}}{\partial (\Phi_s)_{nk}} = -\frac{\partial \eta_{nk}}{\partial (\Phi_e)_{nk}} = 1 \quad (7.102)$$

$$\frac{\partial i_{nk}}{\partial \eta_{nk}} = (i_0)_{nk} [\theta^+ \exp(\theta^+ \eta_{nk}) + \theta^- \exp(-\theta^- \eta_{nk})] \quad (7.103)$$

The Jacobian for the BV has non-zero entries only on the diagonals corresponding to c_{nk} , $(\Phi_s)_{nk}$, and $(\Phi_e)_{nk}$. The Jacobian components are calculated as follows:

U, and thus η , is a function of c_s , so we need to include that in the Jacobian

$$\frac{\partial i_{nk}}{\partial (\Phi_s)_{nk}} = \frac{\partial i_{nk}}{\partial \eta_{nk}} \quad (7.104a)$$

$$\frac{\partial i_{nk}}{\partial (\Phi_e)_{nk}} = -\frac{\partial i_{nk}}{\partial \eta_{nk}} \quad (7.104b)$$

$$\frac{\partial i_{nk}}{\partial c_{nk}} = \gamma \left((1-\beta)(c_{max} - c_{nk})^\beta (c_{nk})^{-\beta} - \beta(c_{max} - c_{nk})^{(\beta-1)} (c_{nk})^{(1-\beta)} \right) \quad (7.104c)$$

with γ given by:

$$\gamma = \mathcal{F}(k_a)^\beta (k_c)^{(1-\beta)} \left[\exp \left(\frac{(1-\beta)\mathcal{F}\eta_{nk}}{\mathcal{R}T_k} \right) - \exp \left(\frac{-\beta\mathcal{F}\eta_{nk}}{\mathcal{R}T_k} \right) \right] \quad (7.105)$$

7.10 Wall flux discretization

The wall flux portion of Equation 7.1 refers to the last term on the RHS of the equation. Using only this term we have the following basic function:

$$\phi_w \equiv \frac{aj_{in}(1-t_i^0)}{\nu_i} \quad (7.106)$$

where a and ν_i are constants, t_i^0 is a function of c , and j_{in} is one of the five unknown variables to be solved for by the code (termed `s_dot` in the code). Discretizing this function at every node simply requires utilizing the values for t_i^0 and j_{in} at every node. Following the discretization and nomenclature used in Section 7.5, we discretize Equation 7.106 as shown below

$$f_{kn} = \frac{aj_{in_{kn}}(1-t_{i_{kn}}^0)}{\nu_i} \quad (7.107)$$

There exists an f_{kn} function for every node in the discretization space. These functions and their Jacobian matrices:

$$\mathbf{J}_{wk_j} = \frac{\partial(f_{k1}, f_{k2}, \dots, f_{kn})}{\partial(j_{in_{k1}}, j_{in_{k2}}, \dots, j_{in_{kn}})} \quad (7.108)$$

$$\mathbf{J}_{wk_c} = \frac{\partial(f_{k1}, f_{k2}, \dots, f_{kn})}{\partial(c_{k1}, c_{k2}, \dots, c_{kn})} \quad (7.109)$$

must be calculated by the module implementing the wall flux component of the ECD. The Jacobian non-zero entries are as follows:

$$j_{n_j} \equiv \frac{\partial f_{kn}}{\partial j_{in_{kn}}} = \frac{a(1-t_{i_{kn}}^0)}{\nu_i} \quad (7.110)$$



$$j_{nc} \equiv \frac{\partial f_{kn}}{\partial c_{kn}} = \frac{-aj_{in_{kn}} t_{i_{kn}}^{0'}}{\nu_i} \quad (7.111)$$

where $t_{i_{kn}}^{0'} = \frac{\partial t_{i_{kn}}^0}{\partial c_{kn}}$, and the value of it is supplied by a function outside of this module.

7.11 Intercalation

If D_s , the solid diffusion coefficient, is (approximately) constant, then Equation 7.6 the concentration in the particle resulting from a time-varying rate of reaction at the surface can be obtained by superposing the concentration changes resulting from simple step changes in concentration at the surface. Here we follow the approach outlined by [3] Each step change is initiated at a different time t_n and the effect of that step at future times is damped as the response decays. In the limit as the time step goes to zero, the flux into the particle can be expressed by Duhamel's superposition integral

$$\frac{\partial c_s}{\partial r}(R, t) = \int_0^t \frac{\partial c_s}{\partial t}(R, \delta) \frac{\partial \bar{c}_s}{\partial r}(R, t - \delta) d\delta \quad (7.112)$$

where $\bar{c}_s(r, t)$ is the dimensionless concentration resulting from a unit step change in concentration at the surface of the particle at time t . Here, we only need the history of the of the surface concentration, and not the concentration in the particle. The s represents that c refers to the ion concentration in the solid. We drop this notation from this point forward as this module only deals with the solid species.

$$\frac{\partial c_n}{\partial t} = \frac{c_{kn} - c_{(k-1)n}}{\Delta t} \quad (7.113)$$

where c_n is the concentration of lithium ions in the solid at spatial point n and temporal time k . Substituting into Equation 7.112 gives

$$\frac{\partial c_n}{\partial r}(R, t_k) = \frac{c_{kn} - c_{(k-1)n}}{\Delta t} A_{1n} + \sum_{j=0}^{k-2} \frac{c_{(j+1)n} - c_{jn}}{\Delta t} A_{(k-j)n} \quad (7.114)$$

$$\frac{D}{R} A_{kn} = a(t_k) - a(t_{k-1}) = \frac{D}{R} \int_0^{t_k} \frac{\partial c_n}{\partial r}(R, \delta) d\delta - \frac{D}{R} \int_0^{t_{k-1}} \frac{\partial c_n}{\partial r}(R, \delta) d\delta \quad (7.115)$$

we write the summation in this split manner to illustrate that it can be stored and updated at each time step. We use a Laplace transform to obtain series expansions for $a(t)$. The first expression is valid at long times

$$a(\tau) = \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} [1 - \exp(-n^2 \pi^2 \tau)] \quad (7.116)$$



and a second that is valid at short times

$$a(\tau) = -\tau + 2 \left(\frac{\tau}{\pi} \right)^{0.5} \left\{ 1 + 2 \sum_{n=1}^{\infty} \left[\exp \left(-\frac{n^2}{\tau} \right) - n \sqrt{\frac{\pi}{\tau}} \operatorname{erfc} \left(\frac{n}{\sqrt{\tau}} \right) \right] \right\} \quad (7.117)$$

Here τ is dimensionless time defined as

$$\tau = \frac{t D_s}{R^2} \quad (7.118)$$

[3] states that evaluating three terms of the short-time solution or five terms in the long-time solution provides sufficient accuracy. We should test this (should be easy with a unit test). The long-time solution is used when $\tau > 0.06$. This solution assumes spherical particles.

The intercalation model couples with the governing equations through the wall flux j_n . Through

$$j_n = -D \frac{\partial c}{\partial r}(R, t) \quad (7.119)$$

Our function evaluation then becomes (we have dropped the n from the wall flux to avoid confusion)

$$f_{kn} = j_{kn} + D_s \left(\frac{\partial c_s}{\partial r} \right)_{kn} \quad (7.120)$$

$$= j_{kn} + D_s \frac{c_{kn} - c_{(k-1)n}}{\Delta t} A_{1n} + D_s \sum_{j=0}^{k-2} \frac{c_{(j+1)n} - c_{jn}}{\Delta t} A_{(k-j)n} \quad (7.121)$$

There exists a f_{kn} function for every node in the discretized space. We have access to c_{kn} as part of the solution data. We additionally need to store the concentration at the previous time step $c_{(k-1)n}$. The third term accumulates the previous functional results and is stored at each grid point. Both the previous concentration and this term are calculated during a finalize step (after solution convergence).

The formulas for the Jacobian matrices are shown below

$$\mathbf{J}_{ck} = \frac{\partial(f_{k1}, f_{k2}, \dots, f_{kn})}{\partial(c_{k1}, c_{k2}, \dots, c_{kn})} \quad (7.122)$$

$$\mathbf{J}_{jk} = \frac{\partial(f_{k1}, f_{k2}, \dots, f_{kn})}{\partial(j_{k1}, j_{k2}, \dots, j_{kn})} \quad (7.123)$$

The Jacobian has non-zero entries on the diagonal as follows:

$$j_{ckn} \equiv \frac{\partial f_{kn}}{\partial c_{kn}} = \frac{DA_{1n}}{\Delta t} \quad (7.124)$$

$$j_{jkn} \equiv \frac{\partial f_{kn}}{\partial j_{kn}} = 1 \quad (7.125)$$

There are no off-diagonal terms.

7.11.1 Implementation

The method for implementing the intercalation module follows the discretization notes and the accessing of data used in all the modules. A few notes are necessary, however, on the method used in implementing the aspects which are unique to the intercalation module. The intercalation module is the only one which deals with solution data at multiple time steps. First, the following variables were added to the `solutionData` class: `time`, `deltaTime`, and `timeStep`. The first two variables are doubles and represent the total simulation time and the delta in time between time steps. The `timeStep` variable is an integer and holds the count of time steps taken.

Currently, the intercalation module assumes the same delta in time is used throughout the simulation. If, however, the simulation needs to take varying time steps the `deltaTime` variable will have to be altered to a vector and the appropriate changes made in the module. Additionally, the intercalation module calculation depends on the solution at the previous time step. Therefore, it cannot actually begin solving its function until after the first time step. It does need to save the values of the concentration of the solid and its own computed `aTK` from the first time step, however. In order to accomplish this task, when the module's `SolvePhysics` function is called and the global `timeStep` variable is still set to 0, the module will not complete all the calculations but only save the initial values needed for solving at the next time step.

The intercalation module has a list named `aTK` and a list of vectors named `prevConcS`. The `aTK` list saves the $a(t_k)$ from Equation 7.115 at every time step. The `prevConcS` list saves the concentration of the solid at every node at every time step.

7.11.2 Testing

As discussed in Section 7.11 the intercalation module solves (equations repeated for reference)

$$j_n = -D_s \frac{\partial c_s}{\partial r}(R, t) \quad (7.126)$$

where

$$\frac{\partial c_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 D_s \frac{\partial c_s}{\partial r} \right] \quad (7.127)$$



In order to test the numerical method implemented to solve this equation, the analytical solution of the quenching problem for a sphere with fixed temperature at its boundary is considered [5]. In this case, a sphere with radius $r = b$ has an initial temperature of $T = f(r)$ and a surface temperature equal to zero for $t > 0$. The governing equation for this problem in 1D spherical coordinates is as follows:

$$\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad (7.128)$$

Note that when D_s is constant (we are treating it as such) Equation 7.127 has the same form as Equation 7.128. The general solution to this problem is as follows [5]

$$T(r, t) = \sum_{n=1}^{\infty} \frac{A_n}{r} \sin(\lambda_n r) \exp(-\alpha \lambda_n^2 t) \quad (7.129)$$

where, when the initial temperature $f(r) = T_i = \text{constant}$,

$$A_n = -2 \frac{T_i b}{n \pi} (-1)^n \quad (7.130)$$

In order to check the implemented numerical solution the concentration of the solid is set to 1 at the first time step and then changed to 0 for all remaining time steps. In the numerical implementation the concentration is only considered at the surface of the sphere at every node so there is no need to set the concentration value at other radii. $\frac{dc_s}{dt}$ is then calculated at 1, 2, 3, ..., and 10 time steps using the analytical solution and the numerical implementation. The values are compared at each time step. The test is considered passing if the computational value is within 7% of the analytical value and the percentage error decreases with each additional time step.

8 Solver

This section contains some information about the nonlinear solver implemented to solve the equations defined above.

The code uses the NOX solver from the Trilinos package. The solver requires an interface, which is specified by the SolverInterface class. There is an concrete implementation for Epetra objects for the abstract interface. It provides for the calculation of the function evaluation (required), the jacobian (optional), and a preconditioner (optional).

The interface only appears to support Epetra_Vectors, while the underlying calculations at the component level is implemented with Epetra_MultiVectors. There is code that translates between the two types of data structures at the device level to enable interface with NOX. Note also that the current implementation in the physics modules uses std::vector and we transfer from this to our MultiVectors. There is a fair amount of copying that is done by the code that can be optimized out to improve efficiency.



The NOX requires a linear algebra package to perform its computations. There is an implementation of an interface to the AztecOO parallel iterative linear solver (also from Trilinos) and we make use of this in our development.

9 Summary

Some summary here.

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