

# Numerical Implementation of the Doyle-Fuller-Newman (DFN) Model

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In this note we document the numerical implementation of the DFN model.

## 1 Doyle-Fuller-Newman Model

We consider the Doyle-Fuller-Newman (DFN) model in Fig. 1 to predict the evolution of lithium concentration in the solid  $c_s^\pm(x, r, t)$ , lithium concentration in the electrolyte  $c_e(x, t)$ , solid electric potential  $\phi_s^\pm(x, t)$ , electrolyte electric potential  $\phi_e(x, t)$ , ionic current  $i_e^\pm(x, t)$ , molar ion fluxes  $j_n^\pm(x, t)$ , and bulk cell temperature  $T(t)$  [1]. The governing equations are given by

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

$$\varepsilon_e^j \frac{\partial c_e^j}{\partial t}(x, t) = \frac{\partial}{\partial x} \left[ D_e^{\text{eff}}(c_e^j) \frac{\partial c_e^j}{\partial x}(x, t) + \frac{1 - t_c^0}{F} i_e^j(x, t) \right], \quad (2)$$

$$0 = \frac{\partial \phi_s^\pm}{\partial x}(x, t) - \frac{i_e^\pm(x, t) - I(t)}{\sigma^{\text{eff}, \pm}}, \quad (3)$$

$$0 = \kappa^{\text{eff}}(c_e) \cdot \frac{\partial \phi_e}{\partial x}(x, t) + i_e^\pm(x, t)$$

$$0 = \frac{\partial i_e^\pm}{\partial x}(x, t) - a_s^\pm F j_n^\pm(x, t), \quad (4)$$

$$-\kappa^{\text{eff}}(c_e) \cdot \frac{2RT}{F} (1 - t_c^0) \times \left( 1 + \frac{d \ln f_{c/a}}{d \ln c_e}(x, t) \right) \frac{\partial \ln c_e}{\partial x}(x, t), \quad (5)$$

$$0 = \frac{1}{F} i_0^\pm(x, t) \left[ e^{\frac{\alpha_a F}{RT} \eta^\pm(x, t)} - e^{-\frac{\alpha_c F}{RT} \eta^\pm(x, t)} \right] - j_n^\pm(x, t), \quad (6)$$

$$\rho^{\text{avg}} c_P \frac{dT}{dt}(t) = h_{\text{cell}} [T_{\text{amb}}(t) - T(t)] + I(t)V(t) - \int_{0^-}^{0^+} a_s F j_n(x, t) \Delta T(x, t) dx, \quad (7)$$

where  $D_e, \kappa, f_{c/a}$  are functions of  $c_e(x, t)$  and  $D_e^{\text{eff}} = D_e(c_e) \cdot (\varepsilon_e^j)^{\text{brug}}$ ,  $\sigma^{\text{eff}} = \sigma \cdot (\varepsilon_s^j + \varepsilon_f^j)^{\text{brug}}$ ,  $\kappa^{\text{eff}} = \kappa(c_e) \cdot (\varepsilon_e^j)^{\text{brug}}$  are the effective electrolyte diffusivity, effective solid conductivity, and

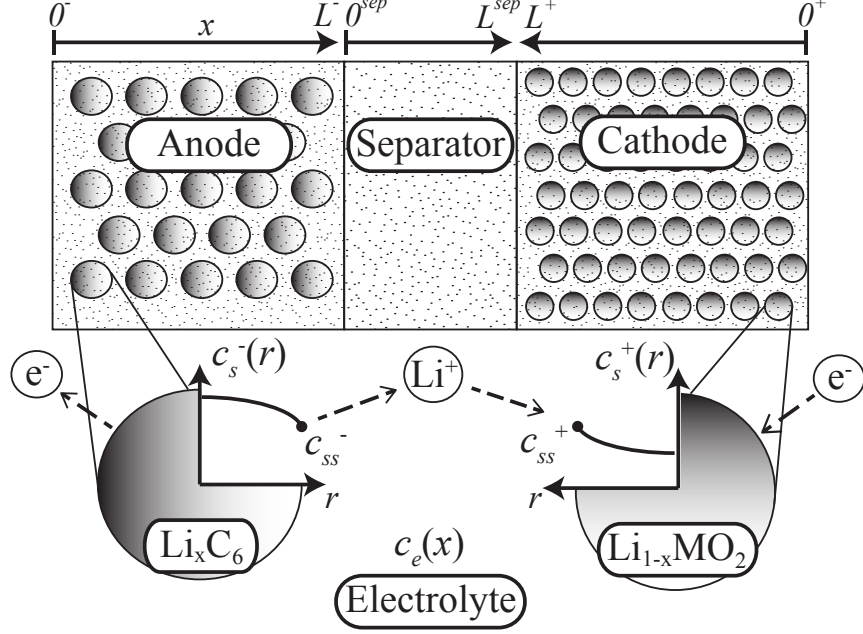


Figure 1: Schematic of the Doyle-Fuller-Newman model [1]. The model considers two phases: the solid and electrolyte. In the solid, states evolve in the  $x$  and  $r$  dimensions. In the electrolyte, states evolve in the  $x$  dimension only. The cell is divided into three regions: anode, separator, and cathode.

effective electrolyte conductivity given by the Bruggeman relationship. We also have

$$i_0^\pm(x, t) = k^\pm [c_{ss}^\pm(x, t)]^{\alpha_c} [c_e(x, t) (c_{s, \max}^\pm - c_{ss}^\pm(x, t))]^{\alpha_a}, \quad (8)$$

$$\eta^\pm(x, t) = \phi_s^\pm(x, t) - \phi_e(x, t) - U^\pm(c_{ss}^\pm(x, t)) - FR_f^\pm j_n^\pm(x, t), \quad (9)$$

$$c_{ss}^\pm(x, t) = c_s^\pm(x, R_s^\pm, t), \quad (10)$$

$$\Delta T(x, t) = U^\pm(\bar{c}_s^\pm(x, t)) - T(t) \frac{\partial U^\pm}{\partial T}(\bar{c}_s^\pm(x, t)), \quad (11)$$

$$\bar{c}_s^\pm(x, t) = \frac{3}{(R_s^\pm)^3} \int_0^{R_s^\pm} r^2 c_s^\pm(x, r, t) dr \quad (12)$$

Along with these equations are corresponding boundary and initial conditions. The boundary conditions for the solid-phase diffusion PDE (1) are

$$\frac{\partial c_s^\pm}{\partial r}(x, 0, t) = 0, \quad (13)$$

$$\frac{\partial c_s^\pm}{\partial r}(x, R_s^\pm, t) = -\frac{1}{D_s^\pm} j_n^\pm. \quad (14)$$

The boundary conditions for the electrolyte-phase diffusion PDE (2) are given by

$$\frac{\partial c_e}{\partial x}(0^-, t) = \frac{\partial c_e}{\partial x}(0^+, t) = 0, \quad (15)$$

$$D_e^{\text{eff},-}(c_e(L^-)) \frac{\partial c_e}{\partial x}(L^-, t) = D_e^{\text{eff,sep}}(c_e(0^{\text{sep}})) \frac{\partial c_e}{\partial x}(0^{\text{sep}}, t), \quad (16)$$

$$D_e^{\text{eff,sep}}(c_e(L^{\text{sep}})) \frac{\partial c_e}{\partial x}(L^{\text{sep}}, t) = D_e^{\text{eff},+}(c_e(L^+)) \frac{\partial c_e}{\partial x}(L^+, t), \quad (17)$$

$$c_e(L^-, t) = c_e(0^{\text{sep}}, t), \quad (18)$$

$$c_e(L^{\text{sep}}, t) = c_e(0^+, t). \quad (19)$$

The boundary conditions for the solid-phase potential ODE (3) are given by

$$\frac{\partial \phi_s^-}{\partial x}(L^-, t) = \frac{\partial \phi_s^+}{\partial x}(L^+, t) = 0. \quad (20)$$

The boundary conditions for the electrolyte-phase potential ODE (5) are given by

$$\phi_e(0^-, t) = 0, \quad (21)$$

$$\phi_e(L^-, t) = \phi_e(0^{\text{sep}}, t), \quad (22)$$

$$\phi_e(L^{\text{sep}}, t) = \phi_e(L^+, t). \quad (23)$$

The boundary conditions for the ionic current ODE (4) are given by

$$i_e^-(0^-, t) = i_e^+(0^+, t) = 0 \quad (24)$$

and also note that  $i_e(x, t) = I(t)$  for  $x \in [0^{\text{sep}}, L^{\text{sep}}]$ .

In addition, the parameters  $D_s^\pm, D_e, \kappa_e, k^\pm$  vary with temperature via the Arrhenius relationship:

$$\psi = \psi_{ref} \exp \left[ \frac{E_\psi}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad (25)$$

where  $\psi$  represents a temperature dependent parameter,  $E_\psi$  is the activation energy [J/mol], and  $\psi_{ref}$  is the reference parameter value at reference temperature  $T_{ref}$ .

The input to the model is the applied current density  $I(t)$  [A/m<sup>2</sup>], and the output is the voltage measured across the current collectors

$$V(t) = \phi_s^+(0^+, t) - \phi_s^-(0^-, t) - R_c I(t) \quad (26)$$

Further details, including notation definitions, can be found in [1, 2].

## 2 Time-stepping

Ultimately, the equations are discretized to produce a **DAE** in the following format:

$$\dot{x} = f(x, z, u), \quad (27)$$

$$0 = g(x, z, u) \quad (28)$$

with initial conditions  $x(0), z(0)$  that are consistent. That is, they verify (28). The function  $f(x, z, u)$  and  $g(x, z, u)$  are computed in Matlab function **dae\_dfn.m**.

The time-stepping is done by solving the nonlinear equation

$$0 = F(x(t + \Delta t), z(t + \Delta t)), \quad (29)$$

$$0 = \begin{bmatrix} x(t) - x(t + \Delta t) + \frac{1}{2}\Delta t [f(x(t), z(t), u(t)) + f(x(t + \Delta t), z(t + \Delta t), u(t + \Delta t))] \\ g(x(t + \Delta t), z(t + \Delta t), u(t + \Delta t)) \end{bmatrix} \quad (30)$$

for  $x(t + \Delta t), z(t + \Delta t)$ . The function `cfn_dfn.m` returns the solution  $(x(t + \Delta t), z(t + \Delta t))$  of (29)-(30), given  $x(t), z(t), u(t), u(t + \Delta t)$ . Note that we solve (29)-(30) using Newton's method, meaning analytic Jacobians of  $F(\cdot, \cdot)$  are required w.r.t.  $x, z$ .

$$J = \begin{bmatrix} F_x^1 & F_z^1 \\ F_x^2 & F_z^2 \end{bmatrix} \quad (31)$$

$$= \begin{bmatrix} -I + \frac{1}{2}\Delta t \cdot \frac{\partial f}{\partial x}(x(t + \Delta t), z(t + \Delta t), u(t + \Delta t)) & \frac{1}{2}\Delta t \cdot \frac{\partial f}{\partial z}(x(t + \Delta t), z(t + \Delta t), u(t + \Delta t)) \\ \frac{\partial g}{\partial x}(x(t + \Delta t), z(t + \Delta t), u(t + \Delta t)) & \frac{\partial g}{\partial z}(x(t + \Delta t), z(t + \Delta t), u(t + \Delta t)) \end{bmatrix} \quad (32)$$

The analytic Jacobian is computed in two functions: (i) Function `jac_dfn_pre.m` computes Jacobian elements that are NOT state/time-dependent. (ii) Function `jac_dfn.m` computes Jacobian elements that are state/time-dependent. The secret to realizing fast and accurate simulations is carefully deriving the Jacobians and coding them in the functions above.

### 3 DAEs

To perform the time-stepping in the previous section, we must compute functions  $f(x, z, u)$  and  $g(x, z, u)$ . These functions, which represent the RHS of (27)-(28), are calculated by the Matlab function `dae_dfn.m`, given the inputs  $x, z, u$ . The role of variables  $x, z, u$  are played by the DFN variables shown in Table 1.

Table 1: DAE notation for DFN states in Matlab Code

DAE Variable	DFN Variable
$x$	$c_s^-, c_s^+, c_e = [c_e^-, c_e^{sep}, c_e^+], T$
$z$	$\phi_s^-, \phi_s^+, i_e^-, i_e^+, \phi_e = [\phi_e^-, \phi_e^{sep}, \phi_e^+], j_n^-, j_p^+$
$u$	$I$

In the subsequent sections, we go through each DFN variable listed in Table 1 and document its numerical implementation.

### 4 Solid Concentration, $c_s^-, c_s^+$

[DONE] The PDEs (1) and BCs (13)-(14) governing Fickian diffusion in the solid phase are implemented using third order Padé approximations of the transfer function from  $j_n^\pm$  to  $c_{ss}^\pm$  [3, 4]:

$$\frac{C_{ss}^\pm(s)}{J_n^\pm(s)} = \frac{-\frac{(R_s^\pm)^3}{165(D_s^\pm)^2}s^2 - \frac{4R_s^\pm}{11D_s^\pm}s - \frac{3}{R_s^\pm}}{\frac{(R_s^\pm)^4}{3465}s^3 + \frac{3(R_s^\pm)^2}{55D_s^\pm}s^2 + s}, \quad (33)$$

which we notate more simply by

$$\frac{C_{ss}^\pm(s)}{J_n^\pm(s)} = \frac{b_2s^2 + b_1s + b_0}{a_3s^3 + a_2s^2 + a_1s + a_0}. \quad (34)$$

Next we multiply top and bottom by  $\frac{1}{a_3}$  to yield a unity coefficient on the highest-order term in the denominator, yielding

$$\frac{C_{ss}^\pm(s)}{J_n^\pm(s)} = \frac{\bar{b}_2s^2 + \bar{b}_1s + \bar{b}_0}{s^3 + \bar{a}_2s^2 + \bar{a}_1s + \bar{a}_0}, \quad (35)$$

where  $\bar{b}_i = b_i/a_3$  and  $\bar{a}_i = a_i/a_3$ .

The transfer function (35) is converted into controllable canonical state-space form, thus producing the subsystem:

$$\frac{d}{dt} \begin{bmatrix} c_{s1}^\pm(t) \\ c_{s2}^\pm(t) \\ c_{s3}^\pm(t) \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ -\bar{a}_0 & -\bar{a}_1 & -\bar{a}_2 \end{bmatrix} \begin{bmatrix} c_{s1}^\pm(t) \\ c_{s2}^\pm(t) \\ c_{s3}^\pm(t) \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} j_n^\pm(t) \quad (36)$$

$$\begin{bmatrix} c_{ss}^\pm(t) \end{bmatrix} = \begin{bmatrix} \bar{b}_0 & \bar{b}_1 & \bar{b}_2 \end{bmatrix} \begin{bmatrix} c_{s1}^\pm(t) \\ c_{s2}^\pm(t) \\ c_{s3}^\pm(t) \end{bmatrix} \quad (37)$$

for each discrete point in  $x$ .

To simplify analytical applications for the DFN model, we seek a different state-space realization in which bulk concentration  $\bar{c}_s^\pm(t)$  is expressed as a state. This can be found by pursuing a Jordan-form state-space realization, which diagonalizes the system matrix. The diagonal elements represent the system eigenvalues. The zero eigenvalue corresponds to bulk concentration. **All the aforementioned calculations are performed in Matlab function `c_s_mats.m`.** The final result produces system matrices:

$$\frac{d}{dt} \begin{bmatrix} c_{s1}^\pm(t) \\ c_{s2}^\pm(t) \\ c_{s3}^\pm(t) \end{bmatrix} = A_{cs}^\pm \begin{bmatrix} c_{s1}^\pm(t) \\ c_{s2}^\pm(t) \\ c_{s3}^\pm(t) \end{bmatrix} + B_{cs}^\pm j_n^\pm(t) \quad (38)$$

$$\begin{bmatrix} c_{ss}^\pm(t) \\ \bar{c}_s^\pm(t) \end{bmatrix} = C_{cs}^\pm \begin{bmatrix} c_{s1}^\pm(t) \\ c_{s2}^\pm(t) \\ c_{s3}^\pm(t) \end{bmatrix} \quad (39)$$

where the second row of  $C_{cs}^\pm$  is  $[C_{cs}^\pm]_2 = [0, 0, 1]$ . Note we have abused notation. The states in (38)-(39) are not the same as those in (36)-(37), due to the different realizations. Also, these matrices must be computed online, due to the temperature dependence of  $D_s^\pm$  described in (25).

## 5 Electrolyte Concentration, $c_e$

[DONE] The electrolyte concentration PDE (2) combined with (4), and BCs (15)-(19) are implemented using the central difference method, which ultimately produces the matrix differential equation:

$$\frac{d}{dt}c_e^j(t) = \frac{dD_e^{\text{eff},j}}{dc_e}(c_e^j) [M_{ce}^{j,1}c_e^j(t) + M_{ce}^{j,2}c_{e,bc}^j(t)]^2 + D_e^{\text{eff},j}(c_e^j) [M_{ce}^{j,3}c_e^j(t) + M_{ce}^{j,4}c_{e,bc}^j(t)] + M_{ce}^{j,5}j_n^j(t) \quad (40)$$

where  $c_e, j_n^j$  are vectors whose elements represent discrete points along the  $x$ -dimension of the DFN model. The variable  $c_{e,bc}^j$  represents the boundary values for region  $j$ , namely  $c_{e,bc}^- = [c_{e,bc,1}, c_{e,bc,2}]^T$ ,  $c_{e,bc}^{\text{sep}} = [c_{e,bc,2}, c_{e,bc,3}]^T$ ,  $c_{e,bc}^+ = [c_{e,bc,3}, c_{e,bc,4}]^T$ . The boundary values are computed by:  $c_{e,bc}(t) = C_{ce} c_e(t)$  where  $c_{e,bc} = [c_{e,bc,1}, c_{e,bc,2}, c_{e,bc,3}, c_{e,bc,4}]^T$ .

Note that the effective diffusivity,  $D_e^{\text{eff},j}(c_e^j)$ , and its derivative,  $\frac{dD_e^{\text{eff},j}}{dc_e}(c_e^j)$ , are state-dependent and must be computed online. The matrices  $M_{ce}^{j,1}, M_{ce}^{j,2}, M_{ce}^{j,3}, M_{ce}^{j,4}, M_{ce}^{j,5}, C_{ce}$  are computed offline by Matlab function `c_e_mats.m`. These matrices are given by

$$M_{ce}^{j,1} = \frac{1}{2L^j\Delta x^j} \begin{bmatrix} 0 & 1 & 0 & \dots & 0 \\ -1 & 0 & 1 & \dots & 0 \\ 0 & -1 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & & \\ 0 & 0 & \dots & \dots & 1 \\ 0 & 0 & \dots & -1 & 0 \end{bmatrix}, \quad M_{ce}^{j,2} = \frac{1}{2L^j\Delta x^j} \begin{bmatrix} -1 & 0 \\ 0 & 0 \\ \vdots & \vdots \\ 0 & 0 \\ 0 & 1 \end{bmatrix}, \quad (41)$$

$$M_{ce}^{j,3} = \frac{1}{(L^j\Delta x^j)^2} \begin{bmatrix} 1 & -2 & 1 & \dots & 0 \\ 0 & 1 & -2 & \dots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ 0 & 0 & \dots & 1 & -2 & 1 \\ 0 & 0 & \dots & 0 & 1 & -2 \end{bmatrix}, \quad M_{ce}^{j,4} = \frac{1}{(L^j\Delta x^j)^2} \begin{bmatrix} 1 & 0 \\ 0 & 0 \\ \vdots & \vdots \\ 0 & 0 \\ 0 & 1 \end{bmatrix}, \quad (42)$$

$$M_{ce}^{j,5} = \frac{(1 - t_c^0)a_s^j}{\varepsilon_e^j}. \quad (43)$$

for  $j \in \{-, \text{sep}, +\}$ . The matrix  $C_{ce}$  is given by

$$C_{ce} = -(N_{ce}^2)^{-1}(N_{ce}^1) \quad (44)$$

where

$$N_{ce}^1 = \left[ \begin{array}{cccc|ccccc} 4 & -1 & \dots & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & \dots & \frac{(\varepsilon_e^-)^{\text{brug}}}{2L^- \Delta x^-} & -4 \frac{(\varepsilon_e^-)^{\text{brug}}}{2L^- \Delta x^-} & -4 \frac{(\varepsilon_e^{\text{sep}})^{\text{brug}}}{2L^{\text{sep}} \Delta x^{\text{sep}}} & \frac{(\varepsilon_e^{\text{sep}})^{\text{brug}}}{2L^{\text{sep}} \Delta x^{\text{sep}}} & \dots \\ 4 & 0 & \dots & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & \dots & 0 & 0 & 0 & 0 & \dots \end{array} \right]$$

$$\begin{array}{ccc|ccc} \dots & 0 & 0 & 0 & 0 & \dots & 0 & 0 \\ \dots & 0 & 0 & 0 & 0 & \dots & 0 & 0 \\ \dots & \frac{(\epsilon_e^{\text{sep}})^{\text{brug}}}{2L^{\text{sep}}\Delta x^{\text{sep}}} & -4\frac{(\epsilon_e^{\text{sep}})^{\text{brug}}}{2L^{\text{sep}}\Delta x^{\text{sep}}} & -4\frac{(\epsilon_e^+)^{\text{brug}}}{2L^+\Delta x^+} & \frac{(\epsilon_e^+)^{\text{brug}}}{2L^+\Delta x^+} & \dots & 0 & 0 \\ \dots & 0 & 0 & 0 & 0 & \dots & 1 & -4 \end{array} \quad (45)$$

$$N_{ce}^2 = \begin{bmatrix} -3 & 0 & 0 & 0 & 0 \\ 0 & 3\frac{(\epsilon_e^-)^{\text{brug}}}{2L^-\Delta x^-} + 3\frac{(\epsilon_e^{\text{sep}})^{\text{brug}}}{2L^{\text{sep}}\Delta x^{\text{sep}}} & 0 & 0 & 0 \\ 0 & 0 & 3\frac{(\epsilon_e^{\text{sep}})^{\text{brug}}}{2L^{\text{sep}}\Delta x^{\text{sep}}} + 3\frac{(\epsilon_e^+)^{\text{brug}}}{2L^+\Delta x^+} & 0 & 0 \\ 0 & 0 & 0 & 0 & 3 \end{bmatrix}. \quad (46)$$

Note, we have used second-order accurate finite difference approximations for the boundary conditions.

## 6 Temperature, $T$

[DONE] Temperature is scalar, so the ODE (7) is directly implemented as:

$$\rho^{\text{avg}} c_P \frac{dT}{dt}(t) = h_{\text{cell}} [T_{\text{amb}}(t) - T(t)] + I(t)V(t) - \int_{0^-}^{0^+} a_s F j_n(x, t) \Delta T(x, t) dx, \quad (47)$$

$$\Delta T(x, t) = U^\pm(\bar{c}_s^\pm(x, t)) - T(t) \frac{\partial U^\pm}{\partial T}(\bar{c}_s^\pm(x, t)), \quad (48)$$

$$\bar{c}_s^\pm(x, t) = \frac{3}{(R_s^\pm)^3} \int_0^{R_s^\pm} r^2 c_s^\pm(x, r, t) dr \quad (49)$$

## 7 Solid Potential, $\phi_s^-, \phi_s^+$

[DONE] The solid potential ODE (3) and BCs (20) are implemented using the central difference method, which ultimately produces the matrix equation:

$$\frac{d}{dt} \phi_s^-(t) = F_{psn}^1 \phi_s^-(t) + F_{psn}^2 i_{e, \text{aug}}^-(t) + G_{psn} I(t) = 0 \quad (50)$$

$$\frac{d}{dt} \phi_s^+(t) = F_{psp}^1 \phi_s^+(t) + F_{psp}^2 i_{e, \text{aug}}^+(t) + G_{psp} I(t) = 0. \quad (51)$$

where  $i_{e, \text{aug}}^\pm$  are

$$i_{e, \text{aug}}^-(t) = \begin{bmatrix} 0 \\ i_e^-(x, t) \\ I(t) \end{bmatrix}, \quad i_{e, \text{aug}}^+(t) = \begin{bmatrix} I(t) \\ i_e^+(x, t) \\ 0 \end{bmatrix} \quad (52)$$

This section also computes the terminal voltage  $V(t)$  from (26) using matrix equations

$$\phi_{s, bc}^-(t) = C_{psn} \phi_s^-(t) + D_{psn} I(t), \quad (53)$$

$$\phi_{s, bc}^+(t) = C_{psp} \phi_s^+(t) + D_{psp} I(t), \quad (54)$$

$$V(t) = \phi_{s,bc,2}^+(t) - \phi_{s,bc,1}^-(t) - R_c I(t) \quad (55)$$

where the following matrices are computed a priori by Matlab function `phi_s_mats.m`

$$(F1n) = (M1n) - (M2n)(N2n)^{-1}(N1n), \quad (56)$$

$$(F2n) = (M3n), \quad (57)$$

$$(Gn) = (M4n) - (M2n)(N2n)^{-1}(N3n), \quad (58)$$

$$(F1p) = (M1p) - (M2p)(N2p)^{-1}(N1p), \quad (59)$$

$$(F2p) = (M3p), \quad (60)$$

$$(Gp) = (M4p) - (M2p)(N2p)^{-1}(N3p), \quad (61)$$

$$(Cn) = -(N2n)^{-1}(N1n), \quad (62)$$

$$(Dn) = -(N2n)^{-1}(N3n), \quad (63)$$

$$(Cp) = -(N2p)^{-1}(N1p), \quad (64)$$

$$(Dp) = -(N2p)^{-1}(N3p), \quad (65)$$

where the  $(Mij)$  and  $N(ij)$  matrices result from central difference approximations of the ODE in space (3) and boundary conditions (20).

$$(M1j) = \begin{bmatrix} 0 & \alpha_j & 0 & \dots & 0 \\ -\alpha_j & 0 & \alpha_j & \dots & 0 \\ 0 & -\alpha_j & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & & \\ 0 & 0 & \dots & \dots & \alpha_j \\ 0 & 0 & \dots & -\alpha_j & 0 \end{bmatrix}, \quad (M2j) = \begin{bmatrix} -\alpha_j & 0 \\ 0 & 0 \\ \vdots & \vdots \\ 0 & 0 \\ 0 & \alpha_j \end{bmatrix}, \quad (66)$$

$$(M3j) = \frac{1}{\sigma_{\text{ref},\pm}} \begin{bmatrix} 0 & -1 & 0 & \dots & 0 \\ 0 & 0 & -1 & \dots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ 0 & 0 & \dots & -1 & 0 & 0 \\ 0 & 0 & \dots & 0 & -1 & 0 \end{bmatrix}, \quad (M4j) = \frac{1}{\sigma_{\text{ref},\pm}} \mathbb{I} \quad (67)$$

$$(N1j) = \begin{bmatrix} 4\alpha_j & -\alpha_j & 0 & \dots & 0 & 0 \\ 0 & 0 & 0 & \dots & 1\alpha_j & -4\alpha_j \end{bmatrix}, \quad (N2j) = \begin{bmatrix} -3\alpha_j & 0 \\ 0 & 3\alpha_j \end{bmatrix}, \quad (68)$$

$$(N3n) = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad (N3p) = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad (69)$$

for  $j \in \{n, p\}$ ,  $\alpha_j = 1/(2L^j \Delta x^j)$ . Note, we have used second-order accurate finite difference approximations for the boundary conditions.

## 8 Electrolyte Current, $i_e^-, i_e^+$



[DONE] The electrolyte current ODE (4) and BCs (24) are implemented using the central difference method, which ultimately produces the matrix equation:

$$\frac{d}{dt}i_e^-(t) = F_{ien}^{1-} i_e^-(t) + F_{ien}^{2-} j_n^-(t) + F_{ien}^{3-} I(t) \quad (70)$$

$$\frac{d}{dt}i_e^+(t) = F_{iep}^{1+} i_e^+(t) + F_{iep}^{2+} j_n^+(t) + F_{iep}^{3+} I(t) \quad (71)$$

where the following matrices are computed a priori by Matlab function `i_e_mats.m`

$$F_{ien}^{1-} = (M1n) - (M2n)(N2n)^{-1}(N1n), \quad (72)$$

$$F_{ien}^{2-} = (M3n) - (M2n)(N2n)^{-1}(N3n), \quad (73)$$

$$F_{ien}^{3-} = (M2n)(N2n)^{-1}(N4n), \quad (74)$$

$$F_{iep}^{1+} = (M1p) - (M2p)(N2p)^{-1}(N1p), \quad (75)$$

$$F_{iep}^{2+} = (M3p) - (M2p)(N2p)^{-1}(N3p), \quad (76)$$

$$F_{iep}^{3+} = (M2p)(N2p)^{-1}(N4p) \quad (77)$$

where the  $(Mij)$  and  $N(ij)$  matrices result from central difference approximations of the ODE in space (4) and boundary conditions (24).

$$(M1j) = \begin{bmatrix} 0 & \alpha_j & 0 & \dots & 0 \\ -\alpha_j & 0 & \alpha_j & \dots & 0 \\ 0 & -\alpha_j & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & & \\ 0 & 0 & \dots & \dots & \alpha_j \\ 0 & 0 & \dots & -\alpha_j & 0 \end{bmatrix}, \quad (M2j) = \begin{bmatrix} -\alpha_j & 0 \\ 0 & 0 \\ \vdots & \vdots \\ 0 & 0 \\ 0 & \alpha_j \end{bmatrix}, \quad (M3j) = -\beta_j \mathbb{I}, \quad (78)$$

$$(N1j) = \begin{bmatrix} 0 & 0 & 0 & \dots & 0 \\ 0 & 0 & 0 & \dots & 0 \end{bmatrix}, \quad (N2j) = \mathbb{I}, \quad (N3j) = (N1j), \quad (79)$$

$$(N4n) = \begin{bmatrix} 0 \\ 1 \end{bmatrix}, \quad (N4p) = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad (80)$$

for  $j \in \{n, p\}$ ,  $\alpha_j = (2L^j \Delta x^j)^{-1}$ ,  $\beta_j = a_s^j F$ .

## 9 Electrolyte Potential, $\phi_e$

[INCOMPLETE] The electrolyte potential is implemented using the central difference method, which ultimately produces the matrix equation:

$$\frac{d}{dt}\phi_e^-(t) = F_{pe}^1(c_{e,x}) \cdot \phi_e(t) + F_{pe}^2(c_{e,x}) \cdot i_{e,x}(t) + F_{pe}^3(c_{e,x}) \cdot \ln(c_{e,x}(t)) \quad (81)$$

where vectors  $i_{e,x}$  and  $c_{e,x}$  represent the entire electrolyte current and concentration, respectively, across the entire battery, including boundary values,

$$i_{e,x}(t) = [0, i_e^-(x, t), I(x, t), i_e^+(x, t), 0]^T, \quad (82)$$

$$c_{e,x}(t) = [c_{e,bc,1}(t), c_e^-(x, t), c_{e,bc,2}(t), c_e^{sep}(x, t), c_{e,bc,3}(t), c_e^+(x, t), c_{e,bc,4}(t)]^T, \quad (83)$$

$$c_{e,bc}(t) = C_{ce} c_e(t) \quad (84)$$

Note that the system matrices  $F_{pe}^1, F_{pe}^2, F_{pe}^3$  are state-varying. These state matrices are computed online as follows:

$$F_{pe}^1 = \kappa^{\text{eff}}(c_e) \cdot M_{pe,1} + M_{pe,2} C_{pe}, \quad (85)$$

$$F_{pe}^2 = M_{pe,3}, \quad (86)$$

$$F_{pe}^3 = \kappa_D^{\text{eff}}(c_e) M_{pe,4} \quad (87)$$

where

$$\kappa^{\text{eff}}(c_e) = \kappa(c_e) \cdot (\varepsilon_e^j)^{\text{brug}}, \quad (88)$$

$$\kappa_D^{\text{eff}}(c_e) = \kappa^{\text{eff}}(c_e) \frac{2RT}{F} (t_c^0 - 1) \left( 1 + \frac{d \ln f_{c/a}}{d \ln c_e}(x, t) \right). \quad (89)$$

The matrices  $M_{pe,1}, M_{pe,2}, M_{pe,3}, M_{pe,4}, C_{pe}$  are computed offline by Matlab function `phi_e_mats.m` as follows. Let

$$\alpha^j = \frac{1}{2L^j \Delta x^j} \quad (90)$$

## 10 Molar ion fluxes, i.e. Butler-Volmer Current, $j_n^-, j_n^+$

[DONE] Since the Butler-Volmer equation (6) is algebraic, and we always assume  $\alpha_a = \alpha_c = 0.5 = \alpha$ , it is trivially implemented as:

$$\frac{d}{dt} j_n^-(t) = \frac{2}{F} i_0^-(t) \sinh \left[ \frac{\alpha F}{RT} \eta^-(t) \right] - j_n^-(t), \quad (91)$$

$$\frac{d}{dt} j_n^+(t) = \frac{2}{F} i_0^+(t) \sinh \left[ \frac{\alpha F}{RT} \eta^+(t) \right] - j_n^+(t) \quad (92)$$

where

$$i_0^\pm(t) = k^\pm [c_{ss}^\pm(t) c_e(t) (c_{s,\max}^\pm - c_{ss}^\pm(t))]^\alpha, \quad (93)$$

$$\eta^\pm(t) = \phi_s^\pm(t) - \phi_e(t) - U^\pm(c_{ss}^\pm(t)) - F R_f^\pm j_n^\pm(t) \quad (94)$$

for each discrete point in  $x$ , in the electrodes only. Note that  $\frac{d}{dt} j_n^\pm(t)$  is a dummy variable used to save the corresponding element of vector  $g(x, z, t)$ .

## 11 Nomenclature

See Table 2.

## References

- [1] K. Thomas, J. Newman, and R. Darling, *Advances in Lithium-Ion Batteries*. New York, NY USA: Kluwer Academic/Plenum Publishers, 2002, ch. 12: Mathematical modeling of lithium batteries, pp. 345–392.
- [2] N. A. Chaturvedi, R. Klein, J. Christensen, J. Ahmed, and A. Kojic, “Algorithms for advanced battery-management systems,” *IEEE Control Systems Magazine*, vol. 30, no. 3, pp. 49 – 68, 2010.
- [3] J. C. Forman, S. Bashash, J. L. Stein, and H. K. Fathy, “Reduction of an electrochemistry-based li-ion battery model via quasi-linearization and pade approximation,” *Journal of the Electrochemical Society*, vol. 158, no. 2, pp. A93 – A101, 2011.
- [4] C. D. Rahn and C.-Y. Wang, *Battery Systems Engineering*. John Wiley & Sons, 2012.

Table 2: Symbol Definitions

Symbols in order of appearance

<b>Electrochemical model states, inputs, outputs</b>	
$c_s^\pm$	Lithium concentration in solid phase [mol/m <sup>3</sup> ]
$c_e$	Lithium concentration in electrolyte phase [mol/m <sup>3</sup> ]
$\phi_s^\pm$	Solid electric potential [V]
$\phi_e$	Electrolyte electric potential [V]
$i_e^\pm$	Ionic current [A/m <sup>2</sup> ]
$j_n^\pm$	Molar ion flux [mol/m <sup>2</sup> -s]
$i_0^\pm$	Exchange current density [A/m <sup>2</sup> ]
$\eta^\pm$	Overpotential [V]
$c_{ss}^\pm$	Lithium concentration at solid particle surface [mol/m <sup>3</sup> ]
$\theta^\pm$	Normalized surface concentration $c_{ss}^\pm/c_{s,\max}^\pm$ [-]
$I$	Applied current [A/m <sup>2</sup> ]
$V$	Terminal voltage [V]
<b>Electrochemical model parameters</b>	
$D_s^\pm, D_e$	Diffusivity of solid, electrolyte phase [m <sup>2</sup> /s]
$t_c^0$	Transference number [-]
$\varepsilon_s^\pm, \varepsilon_e$	Volume fraction of solid, electrolyte phase [-]
$F$	Faraday's constant [C/mol]
$\sigma^\pm$	Conductivity of solid [1/Ω-m]
$\kappa$	Conductivity of electrolyte [1/Ω-m]
$R$	Universal gas constant [J/mol-K]
$T$	Temperature [K]
$f_{c/a}$	Mean molar activity coefficient in electrolyte [-]
$a^\pm$	Specific interfacial surface area [m <sup>2</sup> /m <sup>3</sup> ]
$\alpha_a, \alpha_c$	Anodic, cathodic charge transfer coefficient [-]
$k^\pm$	Kinetic reaction rate [(A/m <sup>2</sup> )(mol <sup>3</sup> /mol) <sup>(1+α)</sup> ]
$c_{s,\max}^\pm$	Maximum concentration of solid material [mol/m <sup>3</sup> ]
$U^\pm$	Open circuit potential of solid material [V]
$R_f^\pm$	Solid-electrolyte interphase film resistance [Ω-m <sup>2</sup> ]
$R_c$	Resistance of connectors, current collectors [Ω-m <sup>2</sup> ]
$R_s^\pm$	Particle radius in solid phase [m]
$L^j$	Length of region $j \in \{-, \text{sep}, +\}$
$E_\psi$	Activation energy of parameter $\psi$ , [J/mol]