Nonlinear State-Variable Method (NSVM) for Li-Ion Batteries: Finite-Element Method and Control Mode

Meng Guo, a Xinfang Jin, b,* and Ralph E. White a,**

a Department of Chemical Engineering, University of South Carolina, Columbia, South Carolina 29208, USA
b Department of Mechanical Engineering, University of South Carolina, Columbia, South Carolina 29208, USA

The finite element method (FEM) was used in our nonlinear state-variable method (NSVM) presented recently (J. Electrochem. Soc., 164, E3001 (2017)). The details of the application of the FEM to solve the lithium ion pseudo-2D (P2D) model equations using the NSVM are presented here for several control modes (constant current, voltage, power, or load). Validation of the method was performed by comparison to rigorous full-order models and experimental data. The FEM based NSVM shows excellent performance, and the estimated cell parameters are determined with a high confidence level.

© The Author(s) 2017. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI:10.1149/2.0221711jes] All rights reserved.
$\kappa_L^\text{eff} \frac{\partial \phi_L}{\partial x}$ by introducing the modified electrolyte potential $\phi_L^\text{ref}$:

$$\phi_L^\text{ref} = \phi_L - \frac{2RT}{F} (1 - r^+) \ln \left[ \frac{c_l}{c_L(x = 0, t)} \right] - \phi_L^\text{ref}$$  \[5\]

where $\phi_L^\text{ref} = \phi_L|_{x=0}$ is the reference electrolyte potential selected for the boundary $x = 0$. Therefore, Equation 4 can be simplified to contain only one field variable $\phi_L^\text{ref}$:

$$\frac{\partial}{\partial x} \left( \kappa_L^\text{eff} \frac{\partial \phi_L^\text{ref}}{\partial x} \right) + a_j = 0$$  \[6\]

and it can be derived from Equation 5 that $\phi_L^\text{ref} = 0$ at boundary $x = 0$:

$$\phi_L^\text{ref}|_{x=0} = 0$$  \[7\]

where Equation 7 serves as the imposed boundary condition to determine the absolute electrolyte potential values. The charge conservation in the solid phase is described by the following equation:

$$\frac{\partial}{\partial x} \left( \sigma_L^\text{eff} \frac{\partial \phi_S}{\partial x} \right) - a_j = 0$$  \[8\]

where $\phi_S$ is the potential of the solid phase and $\sigma_L^\text{eff}$ is the effective electrical conductivity of the solid phase. As the solid phase potentials are distributed through two separate regions (anode and cathode), two imposed boundary conditions are set for both the anode at $x = 0$ and the cathode at $x = l_a + l_s + l_p$:

$$\phi_S|_{x=0} = 0 \quad \phi_S|_{x=l_a+l_s+l_p} = \phi_L^\text{ref}$$  \[9\]

**Table I. Equations for pseudo-2D (P2D) model of Li-ion cell.**

| Physics                              | Equations                                                                 |
|--------------------------------------|---------------------------------------------------------------------------|
| Electrolyte diffusion                | $\phi_L = \phi_L - \frac{2RT}{F} (1 - r^+) \ln \left[ \frac{c_l}{c_L(x = 0, t)} \right] - \phi_L^\text{ref}$  \[5\] |
| Electrolyte charge conservation      | $\frac{\partial}{\partial x} \left( \kappa_L^\text{eff} \frac{\partial \phi_L^\text{ref}}{\partial x} \right) + a_j = 0$  \[6\] |
| Solid phase charge conservation      | $\frac{\partial}{\partial x} \left( \sigma_L^\text{eff} \frac{\partial \phi_S}{\partial x} \right) - a_j = 0$  \[8\] |
| Solid phase diffusion                | $\frac{\partial}{\partial x} \left( \sigma_L^\text{eff} \frac{\partial \phi_S}{\partial x} \right) - a_j = 0$  \[8\] |
| Butler-Volmer equation               | $j_i = j_0 (1 - \eta)^n \sigma_L^\text{eff} \frac{\partial \phi_L^\text{ref}}{\partial x}$ \[6\] |
| External conditions                  | $I_{ex} = -j_0(t) A_c V_{ph} = \phi_L^\text{ref}(t) + I_{ex} R_{load}$  \[10\] |

**Figure 1.** Schematic for pseudo-2D model: modeling domains, mesh pattern, and external electrical conditions.
where $\phi_{\text{ref}}$ is the reference electrical potential of the cathode. Introduce the modified solid phase potential as follows:

$\phi_{\text{S}}^* = \phi_{\text{S}}$ for anode domain $0 \leq x \leq l_{\text{a}}$

$\phi_{\text{S}}^* = \phi_{\text{S}} - \phi_{\text{ref}}$ for cathode domain $l_{\text{a}} + l_{\text{i}} \leq x \leq l_{\text{a}} + l_{\text{i}} + l_{\text{c}}$

The governing equation for $\phi_{\text{S}}^*$ is same as Equation 8,

$$\frac{\partial}{\partial x} \left( \sigma_S \frac{\partial \phi_{\text{S}}^*}{\partial x} \right) - a_j = 0 \quad [10]$$

and the imposed boundary conditions for $\phi_{\text{S}}^*$ are made homogeneous:

$$\phi_{\text{S}}^* \bigg|_{x=0} = 0 \quad \phi_{\text{S}}^* \bigg|_{x=l_{\text{a}}+l_{\text{i}}+l_{\text{c}}} = 0 \quad [12]$$

Accordingly, the overpotential of the electrodes can be expressed in terms of the modified potentials:

$$\eta = \phi_{\text{S}}^* - \phi_{\text{L}}^* - j_{\text{e}} R_{\text{lim}} - \phi_{\text{ref}} \quad 0 \leq x \leq l_{\text{i}}$$

$$\eta = \phi_{\text{S}}^* - \phi_{\text{L}}^* - j_{\text{e}} R_{\text{lim}} + \phi_{\text{ref}} \quad l_{\text{a}} + l_{\text{i}} \leq x \leq l_{\text{a}} + l_{\text{i}} + l_{\text{c}} \quad [13]$$

where $U^*$ denotes the modified open circuit potential expressed by

$$U^* = U(0^+) + \frac{2RT}{F} \left( 1 - t^+ \right) \ln \left[ \frac{c_{\text{Li}}}{c_{\text{Li}}(0, \Omega)} \right] \quad [14]$$

Note that the SEI resistance $R_{\text{lim}}$ is neglected for the cathode and the definition of $\theta^*$ is given in Table I. With the introduction of $\phi_{\text{ref}}$ and $\phi_{\text{S}}^*$, two extra equations are needed to solve for these variables. Integration of Equation 8 through the two electrode domains yields the following equation:

$$\int_0^{l_{\text{a}}} a_j(x,t) \, dx + \int_{l_{\text{a}}}^{l_{\text{a}}+l_{\text{i}}+l_{\text{c}}} a_j(x,t) \, dx = \frac{-\sigma_{\text{S}}^* \frac{\partial \phi_{\text{S}}}{\partial x} \bigg|_{x=0}}{l_{\text{a}}} + \frac{\sigma_{\text{S}}^* \frac{\partial \phi_{\text{S}}}{\partial x} \bigg|_{x=l_{\text{a}}}}{l_{\text{a}}+l_{\text{i}}+l_{\text{c}}} \quad [15]$$

The boundary current density for the solid phase is defined as follows:

$$-\sigma_{\text{S}}^* \frac{\partial \phi_{\text{S}}}{\partial x} \bigg|_{x=0} = i_{\text{b}} \quad \sigma_{\text{S}}^* \frac{\partial \phi_{\text{S}}}{\partial x} \bigg|_{x=l_{\text{a}}} = 0 \quad \sigma_{\text{S}}^* \frac{\partial \phi_{\text{S}}}{\partial x} \bigg|_{x=l_{\text{a}}+l_{\text{i}}+l_{\text{c}}} = 0 \quad [16]$$

where $i_{\text{b}}$ is the current density passing through the interfaces between the electrodes and the current collectors. Substituting boundary conditions 16 into the right-hand-side of Equation 15, the first limiting electrical equation is found to be:

$$\int_0^{l_{\text{a}}} a_j(x,t) \, dx + \int_{l_{\text{a}}}^{l_{\text{a}}+l_{\text{i}}+l_{\text{c}}} a_j(x,t) \, dx = 0 \quad [17]$$

Integration of Equation 8 through the cathode domain and application of the boundary conditions 16 yields the second limiting electrical equation as follows:

$$\int_0^{l_{\text{a}}} a_j(x,t) \, dx = i_{\text{b}} \quad [18]$$

The diffusion of Li ions in the electrolyte phase is described by the following equation:

$$\frac{\partial c_{\text{Li}}}{\partial t} = \frac{\partial}{\partial x} \left( D_{\text{Li}}^n \frac{\partial c_{\text{Li}}}{\partial x} \right) + a \left( 1 - t^+ \right) \frac{j_{\text{e}}}{F} \quad [19]$$

where $c_{\text{Li}}$ is the concentration of electrolyte, $\eta_{\text{S}}$ is the volume fraction of electrolyte in the porous electrode, and $D_{\text{Li}}^n$ is the effective diffusivity of the electrolyte in the porous electrode. As shown above, Equations 6, 11, and 19 are all consistent with the standard form given in Equation 3, and the interpretation for these equation variables are listed in Table II.

| Symbol | Electrolyte diffusion | Electrolyte charge conservation | Solid phase charge conservation |
|--------|-----------------------|---------------------------------|-------------------------------|
| $w(x,t)$ | $c_{\text{Li}}(x,t)$ | $\phi_{\text{L}}^*(x,t)$ | $\phi_{\text{S}}^*(x,t)$ |
| $\rho(x)$ | $D_{\text{Li}}^n$ | $\sigma_{\text{eff}}^n$ | $a$ |
| $\gamma(x)$ | $\mu(x,t)$ | $\kappa_{\text{eff}}^n$ | $\sigma_{\text{S}}^*$ |

Mesh pattern for modeling domains.—The pseudo-2D model includes three computational domains: anode, separator, and cathode, and these domains are discretized into segmental elements ($\Omega_1, \Omega_2, \cdots$). Let $m_1, m_2,$ and $m_3$ denote the number of elements in the anode, separator, and cathode, respectively. The domain contains two adjacent elements $\Omega_1$ and $\Omega_1$, as the interior boundary. Figure 2 illustrates the meshing of nodes and elements, and the nodes of the $i$th element are, respectively, labeled as $x_{2i-1}, x_{2i},$ and $x_{2i+1}$, and node $x_{2i+1}$ is shared by two adjacent elements $\Omega_i$ and $\Omega_{i+1}$ as the interior boundary. There are in total $2 \times (m_1 + m_2 + m_3) + 1$ nodes in the $x$ dimension, where each domain contains $2m_{n=1,2,3} = 3$ nodes. Several integer parameters are specifically defined to facilitate our derivations:

$$m = m_1 + m_2 + m_3$$

$$m' = m_1 + m_3$$

$$n_1 = 2m_1 + 1$$

$$n_2 = 2m_1 + 2m_2 + 1$$

$$n' = 2m_1 + 2m_2 + 2$$

$$n = 2m_1 + 2m_2 + 2m_3 + 1$$

$$m(m' + 1)$$

where $m$ denotes the total number of elements through the entire geometry, $m'$ denotes the number of elements included in the two electrode domains where electrochemical reactions occur, $n_1$ is the node index for anode/separator interface, $n_2$ is the node index for separator/cathode interface, $n'$ is the number of nodes included in the two electrode domains, and $n$ is the total number of nodes through the entire geometry.

| Basis functions.—Two types of basis functions are developed over the discretized geometry as shown in Figure 3. A series of piecewise quadratic polynomials $p_1(x), p_2(x), \cdots, p_n(x)$, whose expressions are given as below, are defined through node points:

$$p_1(x) = \begin{cases} \frac{(x-x_1)(x-x_3)}{(x_1-x_2)(x_3-x_1)} & \text{in element } \Omega_1 \\ 0 & \text{in other elements} \end{cases}$$

$$X_{2i-1} \quad X_{2i} \quad X_{2i+1} \quad X_{2i+2} \quad X_{2i+3}$$

Figure 2. Illustration of mesh elements and nodes.
A series of boxcar functions \( q_i(x) \), \( q_2(x) \), \( \cdots \), \( q_m(x) \) are defined over the elements, whose expressions are given by:

\[
q_i(x) = \begin{cases} 
1 & \text{In element } \Omega_i \\
0 & \text{In other elements}
\end{cases} 
\]

for \( i = 1, 2, \cdots, m \) and Equation 23 is illustrated by Figure 3e.

**Discretized variables.**—Table III lists the variable vectors in the discretized P2D model. According to Equations (R-1) through (R-3), vectors \( \mathbf{c}_i(t) \), \( \mathbf{\Phi}_i(t) \), and \( \mathbf{\Phi}_j(t) \) are made up by the nodal values of the field variables \( c_L(x, t) \), \( \phi_{1x}(x, t) \), and \( \phi_{1z}(x, t) \); the volume-average for these field variables in each element, \( \mathbf{\bar{c}}_i(t) \), \( \mathbf{\bar{\phi}}_{1x}(t) \), and \( \mathbf{\bar{\phi}}_{1z}(t) \), are defined by Equations (R-4) through (R-6), and vectors \( \mathbf{\bar{c}}_i(t) \), \( \mathbf{\bar{\Phi}}_i(t) \), and \( \mathbf{\bar{\Phi}}_j(t) \) are formed by these element average values as shown in Equations (R-7) through (R-9). The electrochemical current density \( j_i(x, t) \) is assumed to be uniformly distributed in each element, and variables \( j_i(x, t) \), which form vector \( \mathbf{j}(t) \) as shown in Equation (R-10), stands for the homogenized element value for \( j_i(x, t) \). The vectors for basis functions are given by Equations (R-11) though (R-14), where vectors \( \mathbf{p}_i(x) \) and \( \mathbf{q}_i(x) \) are respectively formed by the node and element basis functions throughout the entire geometry (anode, separator, and cathode), and vectors \( \mathbf{\bar{p}}_i(x) \) and \( \mathbf{\bar{q}}_i(x) \) are respectively formed by the node and element basis functions in the two electrode domains. The effective electrolyte conductivity \( \kappa_{x}^\text{eff}(x, t) \) is evaluated

\[
p_i(x) = \begin{cases} 
1 & i = j \\
0 & i \neq j
\end{cases} 
\]

for \( i, j = 1, 2, \cdots, n \).

\[
\begin{align*}
p_{2i}(x) &= \begin{cases} 
\frac{(x-x_{2i-1})}{(x_{2i-1}-x_{2i})} & \text{In element } \Omega_i \\
0 & \text{In other elements}
\end{cases} \\
p_{2i+1}(x) &= \begin{cases} 
\frac{(x-x_{2i-1})}{(x_{2i-1}-x_{2i})} & \text{In element } \Omega_i \\
\frac{(x-x_{2i+2})}{(x_{2i+2}^* - x_{2i+2})} & \text{In element } \Omega_{i+1} \\
0 & \text{In other element}
\end{cases} \\
p_n(x) &= \begin{cases} 
\frac{(x-x_{2i-1})}{(x_{2i-1}-x_{2i})} & \text{In element } \Omega_i \\
0 & \text{In other elements}
\end{cases}
\end{align*}
\]
where \( \hat{c}_{L,i}(t) \) in each element according to Equation (15), where the expression for the bulk electrolyte conductivity \( \kappa_{L,bulk}(\hat{c}_L, T) \) is given in Appendix A; and \( \kappa_{eff}^{i} (x, t) \) can be calculated by following expression:

\[
\kappa_{eff}^{i}(x, t) = \sum_{i=1}^{m} q_{i}(x) \kappa_{L,i}^{eff} \quad [24]
\]

where \( \kappa_{L,i}^{eff} \) is the effective electrolyte conductivity for element \( \Omega_{i} \) as defined by (R-15). In each element, the solid phase diffusion can be regarded as a submodel in which \( j_{s,i}(t) \) serves as the single input, and \( \tilde{\sigma}_{i}^{0} \) denotes the surface state-of-charge value corresponding to \( j_{s,i}(t) \); the solution procedure for the solid phase diffusion is shown in Appendix B. Kinetic variables related to the electrochemical reactions are also homogenized in each element, in Equations (16) through (R-18), variables \( U_{i}^{*}, \eta_{i} \), and \( j_{ex,i} \) respectively denote the modified open circuit potential, the overpotential, and the exchange current density values in each element; and in Equations (R-19) and (R-20), variables \( U_{i}^{*} \) and \( \eta_{i} \) form vectors \( \mathbf{U} \) and \( \eta \). With Equations (R-21) and (R-22), the overpotential vector \( \eta \) can be expressed as follows:

\[
\eta = \mathbf{\Phi}_{i}(t) - \mathbf{\dot{\Phi}}_{i}(t) - \mathbf{U} - R_{\text{lim}} \mathbf{j}(t) + B_{s} \begin{bmatrix} \phi_{L}^{eff}(t) \\ \phi_{S}^{eff}(t) \end{bmatrix} \quad [25]
\]

The Butler-Volmer equation in element \( \Omega_{i} \) is given by:

\[
j_{ex,i} = j_{ex,i} \left[ \exp \left( \frac{0.5F}{RT} \eta_{i} \right) - \exp \left( -\frac{0.5F}{RT} \eta_{i} \right) \right] \quad [26]
\]

where \( i = 1, 2, \cdots, \Omega, m_{1} + m_{2} + 1, m_{1} + m_{2} + 2, \cdots, m \). Take 1st order Taylor expansion for the right-hand-side of Equation 26:

\[
j_{ex,i} \approx j_{ex,i} \left[ \left( 1 + \frac{0.5F}{RT} \eta_{i} \right) - \left( 1 - \frac{0.5F}{RT} \eta_{i} \right) \right] \quad [27]
\]

and the following approximation can be derived from Equations 26 and 27:

\[
\eta \approx Z_{k,i} j_{ex,i}(t) \quad [28]
\]

where the expression for the kinetic resistance \( Z_{k,i} \) is given by (R-23). Equation 28 can be expanded in matrix-vector format through a diagonal matrix \( Z_{k} \) defined in Equation (R-24):
Table IV: Definition of operators for different transport phenomena.

| Operator | Electrolyte diffusion | Electrolyte charge conservation | Solid phase charge conservation |
|----------|------------------------|---------------------------------|--------------------------------|
| $\mathbf{w}^i(t)$ | $\mathbf{q}^i(t)$ | $\mathbf{q}^i(t)$ | $\mathbf{q}^i(t)$ |
| $\mathbf{p}^i(x)$ | $\mathbf{p}^i_{ac}(x)$ | $\mathbf{p}^i_{ac}(x)$ | $\mathbf{p}^i_{ac}(x)$ |
| $\mathbf{w}(t)$ | $\mathbf{q}_{ac}(x)$ | $\mathbf{q}_{ac}(x)$ | $\mathbf{q}_{ac}(x)$ |
| $\mathbf{q}^i(x)$ | $\mathbf{q}_{ac}(x)$ | $\mathbf{q}_{ac}(x)$ | $\mathbf{q}_{ac}(x)$ |

Therefore Equation 33 can be written as follows:

$$
\int_{\Omega} \mathbf{p}(x) \rho(x) \frac{\partial \mathbf{w}}{\partial t} dx = \sum_{i \in \Omega} \mathbf{p}(x_i) n_H \mathbf{\mu}(x_i, t) \frac{\partial \mathbf{w}}{\partial x} |_{x_i} \\
- \int_{\Omega} \frac{d\mathbf{p}}{dx} \mathbf{\mu}(x, t) \frac{\partial \mathbf{w}}{\partial x} dx + \mathbf{\int}_{\Omega} \mathbf{p}(x) \gamma(x) j_h(x, t) dx
$$

Substitute $w(x, t)$ and $j_h(x, t)$ with the approximate expressions shown in Equations 30 and 31, and Equation 35 can be written as follows:

$$
\mathbf{M} \frac{d\mathbf{w}}{dt} = -\mathbf{K} \mathbf{w}(t) + \mathbf{F}(t) + \mathbf{L}_B
$$

where $\mathbf{M}$ is the mass matrix defined by

$$
\mathbf{M} = \int_{\Omega} \mathbf{p}(x) \rho(x) \mathbf{p}^i(x) dx
$$

$\mathbf{K}$ is the stiffness matrix defined by

$$
\mathbf{K} = \int_{\Omega} \frac{d\mathbf{p}}{dx} \mathbf{\mu}(x, t) \frac{d\mathbf{p}^i}{dx} dx
$$

$\mathbf{F}$ is the forcing matrix defined by

$$
\mathbf{F} = \int_{\Omega} \mathbf{p}(x) \gamma(x) \mathbf{q}_{ac}(x) dx
$$

and $\mathbf{L}_B$ is the boundary loading vector defined by

$$
\mathbf{L}_B = \sum_{i \in \partial \Omega} \mathbf{p}(x_i) n_H \mathbf{\mu}(x_i, t) \frac{\partial \mathbf{w}}{\partial x} |_{x_i}
$$

Starting from the weak form Equation 36, we have presented in Ref. 15 the solution procedure for the electrolyte diffusion (in which $\mathbf{L}_B = \mathbf{0}$ for the insulated boundaries) over a discrete time domain. In the following sections of this work, we will focus on solving the coupled charge conservation and electrochemical kinetics under different control modes.

Charge conservation equations.—For the charge conservation equations, the mass matrix $\mathbf{M} = \mathbf{0}$ and the boundary loading vector $\mathbf{L}_B$ can be expressed by $\mathbf{L}_B = \mathbf{h}_B(t)$ as shown in Table IV; therefore, the weak form Equation 36 can be written as follows:

$$
\mathbf{K} \mathbf{w}(t) = \mathbf{F}(t) + \mathbf{h}_B(t)
$$

The reference potential Equations 7 and 9 are expressed as:

$$
\mathbf{D} \mathbf{w}(t) = \mathbf{0}
$$

where the definition for the reference boundary operator $\mathbf{B}_r$ is given in Table IV. The limiting electrical Equations 17 and 18 are, respectively, expressed as follows:

$$
\mathbf{C}_i \mathbf{j}(t) = 0
$$

and the operators $\mathbf{C}_1$ and $\mathbf{C}_2$ are given by:

$$
\mathbf{C}_1 = \int_0^{t_h} \mathbf{a}_q^i(x) dx + \int_{t_h}^{t_{I_i} + t_h} \mathbf{a}_q^i(x) dx
$$

$$
\mathbf{C}_2 = \int_0^{t_h} \mathbf{a}_q^i(x) dx
$$
Left multiply Equation 42 by $\mathbf{Br}^t$ and add the result to Equation 39, then substitute $i_B(t)$ with expression 44 to obtain, 

$$\left( K + \mathbf{Br}^t \mathbf{Br} \right) \mathbf{w}(t) = \left( \mathbf{F} + h \mathbf{C}_t \right) \tilde{j}(t)$$  

and the expression for $\mathbf{w}(t)$ can be written as follows:

$$\mathbf{w}(t) = \left( K + \mathbf{Br}^t \mathbf{Br} \right)^{-1} \left( \mathbf{F} + h \mathbf{C}_t \right) \tilde{j}(t)$$  

According to Equations 32 and 48, the element-average potentials can be expressed as follows:

$$\tilde{\mathbf{w}}(t) = \mathbf{Z} \tilde{j}(t)$$  

where the transport resistance operator is given by:

$$\mathbf{Z} = \mathbf{H} \left( K + \mathbf{Br}^t \mathbf{Br} \right)^{-1} \left( \mathbf{F} + h \mathbf{C}_t \right)$$  

Equation 49 can be written, respectively, for the electrolyte and solid phases:

$$\Phi_{\mathbf{L}}(t) = \mathbf{Z} \tilde{j}_{\mathbf{L}}(t) \quad \Phi_{\mathbf{S}}(t) = \mathbf{Z} \tilde{j}_{\mathbf{S}}(t)$$  

Substitute expressions 51 into Equation 25, so that the overpotential can be written as a linear expression for $\tilde{j}(t)$, $\Phi_{\mathbf{L}}^{\text{ref}}(t)$, and $\Phi_{\mathbf{S}}^{\text{ref}}(t)$:

$$\eta = \mathbf{Z}_{\mathbf{L}} \tilde{j}_{\mathbf{L}}(t) - \mathbf{Z}_{\mathbf{S}} \tilde{j}_{\mathbf{S}}(t) - U + B_{\mathbf{LS}} \left[ \Phi_{\mathbf{L}}^{\text{ref}}(t) - \Phi_{\mathbf{S}}^{\text{ref}}(t) \right]$$  

Model linearization and approximate solution.—To solve the nonlinear Butler-Volmer equations with the Newton method, good initial guesses are important to reduce the numerical difficulties. Initial values can be determined from the linearized kinetics. Substitute the approximate expression 29 into Equation 52 to yield:

$$\mathbf{Z}_{\mathbf{L}} \tilde{j}_{\mathbf{L}}(t) = \left( \mathbf{Z}_{\mathbf{S}} - \mathbf{Z}_{\mathbf{L}} - R_{\mathbf{LS}} \right) \tilde{j}_{\mathbf{S}}(t) - U + B_{\mathbf{LS}} \left[ \Phi_{\mathbf{L}}^{\text{ref}}(t) - \Phi_{\mathbf{S}}^{\text{ref}}(t) \right]$$  

where $\tilde{j}_{\mathbf{L}}(t)$, $\Phi_{\mathbf{L}}^{\text{ref}}(t)$, and $\Phi_{\mathbf{S}}^{\text{ref}}(t)$ are approximate solutions for the corresponding variables. Vector $\tilde{j}(t)$ can be determined from Equation 53 as follows:

$$\tilde{j}_{\mathbf{L}}(t) = \mathbf{Z}_{\mathbf{L}}^{-1} \left( \mathbf{Z}_{\mathbf{S}} - \mathbf{Z}_{\mathbf{L}} - R_{\mathbf{LS}} \right) \tilde{j}_{\mathbf{S}}(t) - U + B_{\mathbf{LS}} \left[ \Phi_{\mathbf{L}}^{\text{ref}}(t) - \Phi_{\mathbf{S}}^{\text{ref}}(t) \right]$$  

where the operator $\mathbf{Z}_{\mathbf{L}}$ is given by:

$$\mathbf{Z}_{\mathbf{L}} = \mathbf{Z}_{\mathbf{S}} - \mathbf{Z}_{\mathbf{L}} + \mathbf{Z}_{\mathbf{S}} + R_{\mathbf{S}}$$  

Substitute expression 54 into the limiting electrical Equations 43 and 44 to yield

$$\begin{bmatrix} C_1 \\ C_2 \end{bmatrix} Z_{\mathbf{L}}^{-1} B_{\mathbf{LS}} \begin{bmatrix} \Phi_{\mathbf{L}}^{\text{ref}}(t) \\ \Phi_{\mathbf{S}}^{\text{ref}}(t) \end{bmatrix} - \begin{bmatrix} C_1 \\ C_2 \end{bmatrix} Z_{\mathbf{L}}^{-1} U = \begin{bmatrix} 0 \\ 1 \end{bmatrix} i_{B}(t)$$  

and the reference potentials $\Phi_{\mathbf{L}}^{\text{ref}}(t)$, and $\Phi_{\mathbf{S}}^{\text{ref}}(t)$ can be expressed as linear functions of $i_{B}(t)$:

$$\begin{bmatrix} \Phi_{\mathbf{L}}^{\text{ref}}(t) \\ \Phi_{\mathbf{S}}^{\text{ref}}(t) \end{bmatrix} = \begin{bmatrix} C_1 & C_2 \end{bmatrix} Z_{\mathbf{L}}^{-1} B_{\mathbf{LS}} \begin{bmatrix} 0 \\ 1 \end{bmatrix} i_{B}(t)$$  

$$+ \begin{bmatrix} C_1 \\ C_2 \end{bmatrix} Z_{\mathbf{L}}^{-1} B_{\mathbf{LS}} \begin{bmatrix} 0 \\ 1 \end{bmatrix} C_1 Z_{\mathbf{L}}^{-1} U$$  

Left multiply Equation 57 by $[0, 1]$ to yield the expression for $\Phi_{\mathbf{S}}^{\text{ref}}(t)$:

$$\Phi_{\mathbf{S}}^{\text{ref}}(t) = u_B + z_B i_B(t)$$  

where the coefficients $u_B$ and $z_B$ are given by:

$$u_B = \begin{bmatrix} 0 & 1 \end{bmatrix} \begin{bmatrix} C_1 & C_2 \end{bmatrix} Z_{\mathbf{L}}^{-1} B_{\mathbf{LS}} \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$  

$$z_B = \begin{bmatrix} 0 & 1 \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \end{bmatrix} Z_{\mathbf{L}}^{-1} B_{\mathbf{LS}} \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$  

According to Equations 54 and 57, values for $\Phi_{\mathbf{L}}^{\text{ref}}(t)$, and $\Phi_{\mathbf{S}}^{\text{ref}}(t)$ can all be determined by setting $i_{B}(t)$.  

**Electrical control equations.**—For the current control mode, $i_{B}(t)$ can be evaluated using the following equation:

$$i_{B}(t) = -\frac{I_{app}(t)}{A_C}$$  

where $I_{app}(t)$ is the total current applied to the cell which is defined as positive in charge and negative in discharge, and $A_C$ is the total area of the cathode/current collector interface. For voltage control mode, the control equation is given as follows:

$$V_{ex} = V_{app}(t)$$  

where $V_{app}(t)$ is the applied voltage and the terminal current $I_{ex}$ and terminal voltage $V_{ex}$ are defined as follows:

$$I_{ex} = -i_B(t) A_C$$  

$$V_{ex} = \Phi_{S}^{\text{ref}}(t) + I_{ex} R_{ex}$$  

Substituting $\Phi_{\mathbf{S}}^{\text{ref}}(t)$ with expression 58 and according to Equations 62 and 63, the voltage control equation can be expressed as follow:

$$u_B + z_B i_B(t) - i_B(t) A_C R_{ex} = V_{app}(t)$$  

and $i_B(t)$ can be solved from Equation 64 as follow:

$$i_B(t) = -\frac{V_{app}(t) - u_B}{A_C R_{ex} - z_B}$$  

For the power control mode, the control equation is given as follows:

$$I_{ex} V_{ex} = P_{app}(t)$$  

where $P_{app}(t)$ is the applied power. According to Equations 58, 62, and 63, the control Equation 66 can be expressed as follows:

$$- [u_B + z_B i_B(t) - i_B(t) A_C R_{ex}] i_B(t) A_C = P_{app}(t)$$  

and $i_B$ can be determined from Equation 67 through the quadratic solution:

$$i_B(t) = \frac{A_C u_B + \sqrt{(A_C u_B)^2 + 4 P_{app}(t) A_C (A_C R_{ex} - z_B)}}{2 A_C (A_C R_{ex} - z_B)}$$  

Equation 68 contains a quadratic discriminant $D_m$ which is determined as follows:

$$D_m = (A_C u_B)^2 + 4 P_{app}(t) A_C (A_C R_{ex} - z_B)$$  

and the solution for $i_B$ according to Equation 68 is valid only for $D_m \geq 0$. Under high power conditions, the value for $D_m$ might be negative, which means the linearized Butler-Volmer kinetics cannot guarantee a valid solution; in this case try the following equation:

$$i_B(t) = \frac{u_B}{2 (A_C R_{ex} - z_B)}$$  

For the load control mode, the correlation between terminal voltage $V_{ex}$ and the load resistance $R_{load}(t)$ is as follows:

$$V_{ex} = -I_{ex} R_{load}(t)$$
According to Equations 62, 63, and 71, the expression for \( i_B \) in load control mode is as follows:

\[
    i_B(t) = \frac{u_B}{A_C [R_{ex} + R_{load}(t)] - z_B}
\]

[72]

Note that the \( i_B(t) \) values evaluated above are not accurate, they are only used to estimate the approximate solutions \( \tilde{I}_t(t) \), \( \tilde{\phi}_L(t) \), and \( \tilde{\phi}_C(t) \), which are used as initial values for the nonlinear step.

Nonlinear refinement of solutions.—According to Equation 26, the residue for Butler-Volmer equation in element \( \Omega_i \) is expressed as follows:

\[
    R_{BV,i} = j_{ex,i} \left[ \exp \left( \frac{0.5F}{RT} \eta_i \right) - \exp \left( \frac{-0.5F}{RT} \eta_i \right) \right] - j_{s,i}(t)
\]

[73]

where \( R_{BV,i} \) is the Butler-Volmer equation residue and \( i = 1, 2, \cdots, m_1, m_1 + m_2 + 1, m_1 + m_2 + 2, \cdots, m \). The residue vector for Butler-Volmer equations \( \mathbf{R}_{BV} \) are given by:

\[
    \mathbf{R}_{BV} = \left[ R_{BV,1}, R_{BV,2}, \cdots, R_{BV,m_1}, R_{BV,m_1+m_2+1}, \right]
\]

[74]

According to Equations 43 and 44, the residues for the electrical limiting equations, \( \mathbf{R}_{LE} \), are given by:

\[
    \mathbf{R}_{LE} = \begin{bmatrix} \mathbf{C} \end{bmatrix} \mathbf{J}_t(t) - \begin{bmatrix} 0 \\ 1 \end{bmatrix} i_B(t)
\]

[75]

For the current control mode, the residue for the control equation, \( \mathbf{R}_{CE} \), is given by:

\[
    \mathbf{R}_{CE} = i_B(t) + \frac{I_{app}(t)}{A_C}
\]

[76]

for voltage control mode, \( \mathbf{R}_{CE} \) given by:

\[
    \mathbf{R}_{CE} = \phi_{S}^{ref}(t) - i_B(t) A_C R_{ex} - V_{app}(t)
\]

[77]

and for power control mode, \( \mathbf{R}_{CE} \) is given by:

\[
    \mathbf{R}_{CE} = \phi_{S}^{ref}(t) - i_B(t) A_C R_{ex} + \phi_{L}^{ref}(t) i_B(t) + \frac{P_{app}(t)}{A_C}
\]

[78]

Define the unknown vector \( \mathbf{y} \) and the model residue vector \( \mathbf{Res} \) as follows:

\[
    \mathbf{y} = \begin{bmatrix} \frac{1}{A} (t) \\ \phi_{L}^{ref}(t) \\ \phi_{C}^{ref}(t) \\ i_B(t) \end{bmatrix} \quad \mathbf{Res} = \begin{bmatrix} \mathbf{R}_{BV} \\ \mathbf{R}_{LE} \\ \mathbf{R}_{CE} \end{bmatrix}
\]

[79]

The Jacobian matrix \( \mathbf{Jac} \) is expressed as the derivative of \( \mathbf{Res} \) with respect to \( \mathbf{y} \):

\[
    \mathbf{Jac} = \frac{d\mathbf{Res}}{d\mathbf{y}}
\]

[80]

### Table V. Test protocols for different cells.

| Cell | Test protocol |
|------|---------------|
| LIB4 | Charge at 1.25 C for 20 min — charge at 5/6 C for 18 min — charge at 0.5 C to 4.35 V — constant voltage at 4.35 V until current tapers to 0.05 V — open circuit for 10 min |
| LIB6 | Charge at 0.7 C to 4.35 V — constant voltage at 4.35 V until current tapers to 0.05 V — open circuit for 10 min |
| LIB7 | Charge at 1 C to 4.35 V — constant voltage at 4.35 V until current tapers to 0.05 V — open circuit for 10 min |

---

Figure 4. Newton loop for nonlinear solution.

The solution for the nonlinear equations can be estimated with high accuracy using the Newton loop shown in Figure 4, where \( y^{(k)} \) denotes the value of \( y \) at the \( k \)-th iteration, and \( y \) is updated with Equation 81 until the absolute value |Res| is smaller than the tolerance \( \delta \) (i.e., \( \delta = 10^{-8} \)).

Results and Discussion

In the previous work,15 we have examined the accuracy of our NSVM algorithm for current control mode through model-to-model comparisons. In this work, we focus on model vs experimental validation and simulation of different control modes.

**Model validation.**—The computational algorithm described in Mathematical Model section was applied in modeling the Samsung commercial cells (the nominal cell capacity is 2.6 Ah), where the cell design parameters and basic physical properties are given in Appendix A. Three cells, labeled as LIB4, LIB6, and LIB7, respectively, were tested at room temperature (\( T = 25^\circ C \)) using different protocols. The experimental details for these cells are listed in Table V. MATLAB was used to develop the code for our cell model.

In simulation of the mixed cell control modes, the voltage control algorithm was applied for the constant voltage steps and the current control algorithm was applied for other steps. The cell temperature change was neglected in these simulations, and the SEI film resistance was only applied for the anode. Using the least-squares method,
Figure 5. Optimized model predictions vs test data for cells: (a) voltage profiles for cell LIB4; (b) current profiles for cell LIB4; (c) voltage profiles for cell LIB6; (d) current profiles for cell LIB6; (e) voltage profiles for LIB7; (f) current profiles for cell LIB7; (g) Relative error plots for cell voltage between model and data.
Table VI. Estimated parameter values for different cells.

| Parameter                             | Estimated values |
|---------------------------------------|------------------|
| LIB4                                  | LIB6             | LIB7             |
| SEI film resistance at anode \( R_{\text{film}} \) (\( \Omega \cdot \text{m}^2 \)) | 0.1115           | 0.1413           | 0.1477           |
| Solid phase diffusivity \( D_s \) (\( \text{m}^2/\text{s} \)) | Anode 1.3143 \( \times 10^{-14} \) | Cathode 9.6117 \( \times 10^{-14} \) |
| Exchange current density \( j_0 \) (A/m\(^2\)) | Anode 29.867 | Cathode 1.5986 |

several cell parameters were estimated to fit the model to the test data. Among the estimated cell parameters, the solid phase diffusivities \( D_s \) and exchange current densities \( j_0 \) for the anode and cathode materials were assumed to be the same for all three cells, while the anode SEI film resistances varied between the cells. The optimized model results with comparisons to test data are presented in Figure 5 and the estimated parameter values are listed in Table VI. These results show that our NSVM algorithm works well with current and voltage control modes and the error for the model is below 2% for most parts of the simulated voltage profiles.

**Power and load control simulation.**—Using the optimized parameter sets from the previous section, our NSVM algorithm was implemented to simulate a power control step. The high frequency power input was scaled from the drive cycle current profile given in Ref. 15, where the applied power \( P_{\text{app}} \) is calculated as follow:

\[
P_{\text{app}} = \text{C rate} \times I_{1C} \times 3 \text{ [V]}
\]

where \( I_{1C} = 2.6 \text{A} \) is the 1 C rate current for the cell. The input profiles are shown in Figure 6, the power signal plot includes 8 periodic cycles and the peak power pulse of each cycle is around 17 W. The sampling frequency for the input power is 1 Hz or 1 data per second. The power control simulation was implemented for cell LIB4, and a rigorous model developed by COMSOL 5.2 was used as the baseline, in which the maximum time step is set to be 1 sec in accordance with the input sampling rate. The simulated voltage and current profiles are presented in Figure 7, and our algorithm shows excellent accuracy as compared with the baseline mode. However, it takes only 3.06 sec for our algorithm to finish the simulation as compared to the 762 sec for the baseline model. The simulated current profile in Figure 7a shows...
that the magnitude for peak current in each cycle increases toward the end of discharge; the reason is that the power control mode requires $I_{ex}V_{ex} = P_{app}$, as the cell voltage $V_{ex}$ drops with the depth of discharge, more current is needed to meet the power request. Other important results are presented in Figure 8 for analysis. The profile for the quadratic determinant $D_m$, which is defined in Equation 69, is plotted in Figure 8a and the results show that $D_m$ takes negative values at high power pulses near the end of discharge; this suggests that a fully linearized model fails to provide valid solution at these points. In Figure 8b, the current values estimated by Equation 68 or Equation 70 are compared to those calculated through the nonlinear refinement loop (see Figure 4), the plots show that there are significant deviations between the two simulated current curves near the end of discharge, and these results suggest that the refinement loop is necessary to achieve good accuracy. To simulate the load control mode, a dynamic profile for the resistance load $R_{load}(t)$ was synthesized and presented in Figure 9. The simulated current and voltage profiles for the load control discharge are presented in Figures 10a and 10b. Similar to the power control results, the NSVM algorithm has excellent agreement with the baseline model, and the simulation takes only 3.24 sec for NSVM algorithm as contrast to the 510 sec for the baseline model. The error plots shown in Figure 11 confirm the accuracy of NSVM approach in the power and load control cases.
Figure 10. Results for load control simulation: (a) voltage profile; (b) current profile.

**Numerical discussion.**—As shown in Power and load control simulation section, the NSVM runs much faster than COMSOL and provides excellent accuracy. The time step approach presented by Equation 1 is the main reason for this significant improvement in simulation time efficiency. However, the FEM approach described in this article also contributes to this speedup. In COMSOL, the electrolyte and solid phase potentials ($\phi_L(x, t)$ and $\phi_S(x, t)$) are solved iteratively with the electrochemical current density ($j_s(x, t)$) at each node; in NSVM, only $j_s(x, t)$ is solved in the Newton loop and potential values are derived as linear expressions of $j_s(x, t)$. In addition, COMSOL defines the discretized current density $j_s(x, t)$ values at each node while NSVM defines $j_s(x, t)$ in each element, this means vector $\mathbf{j}(t)$ has smaller size in NSVM than in COMSOL. As $\mathbf{j}(t)$ is coupled with the solid phase diffusion, NSVM also includes fewer solid phase concentration variables than COMSOL. The FEM approach in NSVM greatly simplifies the solution procedure for the constraint Equation 2.

**Conclusions**

In this work, we made in-depth discussion on the application of finite element method to the P2D physic-based Li-ion cell model. Galerkin’s weighted residual approach with quadratic basis functions was employed for our finite element analysis. The discretized field variables are defined into two categories: node variables and element variables, and the conversion between these two types of variables can be performed through a simple linear transform. The Butler-Volmer equations and the solid phase diffusion equations are solved in each element rather than at each node, which significantly lowers the computation load in simulation. We also developed simulation approaches for different battery control modes (current, voltage, load, and power control modes), and identified the limitations for a fully linearized model in the power control mode. For a linearized model, the Butler-Volmer equations are approximated using a 1st order Taylor series expansion, and the interface kinetic resistance is independent from the current density; when high power is applied, the linear polarization causes electrode potentials to drop sharply with increased current, and the cell might not meet the power request. Therefore, nonlinear compensation through an iterative Newton loop is important for the accuracy of model, because for nonlinear Butler-Volmer equations, the kinetic polarization drops exponentially with current density which prevents the cell voltage from being too low under high power. The model was also validated by test data with mixed current-voltage control modes and key parameters for the cell materials were estimated using least squares approach.

**Appendix A**

The basic cell design parameters and physical properties are listed in Table A1. The electrical conductivity of bulk electrolyte is a function of electrolyte concentration and temperature:

$$\kappa_{L, bulk} = 3.45 \exp \left( -\frac{798}{T} \right) \left( \frac{c_L}{1000} \right)^{3} - 48.5 \exp \left( -\frac{1080}{T} \right) \left( \frac{c_L}{1000} \right)^{2} + 244 \exp \left( -\frac{1440}{T} \right) \left( \frac{c_L}{1000} \right)$$

[A1]

The effective diffusivity and electrical conductivity for electrolyte is defined as follows:

$$D_{L}^{eff} = D_{L, bulk} \epsilon_{L}^{1.5}$$

[A2]

$$\kappa_{L}^{eff} = \kappa_{L, bulk} \epsilon_{L}^{1.5}$$

[A3]
Table A1. Design and physical parameters.

| Parameter                                      | Value          |
|------------------------------------------------|----------------|
| Thickness $l_a, l_c, l_p$ [m]                  |                |
| Volume fraction of electrolyte $\epsilon_e$   |                |
| Volume fraction of active material $\epsilon_s$|                |
| Specific surface area of active material $\alpha$ [1/m] |        |
| Maximum Li concentration in active material $c_{\text{max}}$ [mol/m$^3$] |        |
| Radius of active material particles $R_i$ [m]  |                |
| Electrical conductivity of solid phase $\sigma_s$ [S/m] |        |
| Bulk electrolyte diffusivity at 25°C $D_{b, \text{bulk}}(T_{\text{ref}})$ [m$^2$/s] |        |
| Transference number of electrolyte $+^{\text{t}}$ |                |
| Area of the cathode/current collector interface $A_C$ [m$^2$] |        |
| External ohmic resistance $R_\text{ex}$ [Ω]    |                |
| Average electrolyte concentration $c_0$ [mol/m$^3$] |        |
| Universal gas constant $R$ [J/mol/K]           |                |
| Faraday constant $F$ [C/mol]                   |                |
| Reference temperature $T_{\text{ref}}$ [°C]    |                |

The open circuit potentials for anode and cathode materials $(U)$ are functions of the surface state-of-charge of solid phase $(\theta^s)$, and the $U$ vs $\theta^s$ profiles are presented in Figure A1.

The open circuit potentials for anode and cathode materials $(U)$ are functions of the surface state-of-charge of solid phase $(\theta^s)$, and the $U$ vs $\theta^s$ profiles are presented in Figure A1.

\[
\sigma_s^e = \sigma_s \epsilon_s^{1/5} \tag{A4}
\]

The integral of $q_i(x)$ over the cell geometry equals to the length of element $\Omega_i$:

\[
\int_{\Omega} q_i(x) \, dx = x_{b_{i+1}} - x_{b_{i-1}} = \Delta x_i \tag{C3}
\]

To address the integral of $q_i(x)$ over the cell geometry equals to the length of element $\Omega_i$:

\[
\int_{\Omega} q_i(x) \, dx = x_{b_{i+1}} - x_{b_{i-1}} = \Delta x_i \tag{C3}
\]

The integral of $q_i(x)$ over the cell geometry equals to the length of element $\Omega_i$:

\[
\int_{\Omega} q_i(x) \, dx = x_{b_{i+1}} - x_{b_{i-1}} = \Delta x_i \tag{C3}
\]

Table B1. Values for coefficients in Equation B3.

|   | $k=1$   | $k=2$   | $k=3$   | $k=4$   |
|---|---------|---------|---------|---------|
| $a_k$ | 35058.7 | 1382.966| 141.595 | 22.32279|
| $b_k$ | -268.261| -30.9242| -7.59606| -2.59525|
therefore the integrals for matrix \( q_\text{ex}(x) q_\text{ex}(x)^T \) can be expressed as follows:

\[
\int_{\Omega_2} q_\text{ex}(x) q_\text{ex}(x)^T \, dx = \text{diag}(\Delta x_1, \Delta x_2, \ldots, \Delta x_n) \tag{C4}
\]

The integral of \( q_i(x) w(x, t) \) over the cell geometry equals to the integral \( w(x, t) \) of over element \( \Omega_2 \):

\[
\int_{\Omega_2} q_i(x) w(x, t) \, dx = \int_{\Omega_2} w(x, t) \, dx \tag{C5}
\]

therefore the integral of vector \( q_i(x) w(x, t) \) is expressed as follow:

\[
\int_{\Omega_2} q_i(x) w(x, t) \, dx = \int_{\Omega_2} w(x, t) \, dx \tag{C6}
\]

and the element-average vector \( \vec{w}(t) \) can be calculated as follow:

\[
\vec{w}(t) = \left[ \int_{\Omega_2} q_i(x) q_i(x)^T \, dx \right]^{-1} \int_{\Omega_2} q_i(x) w(x, t) \, dx \tag{C7}
\]

Substitute \( w(x, t) \approx \vec{p}_i(x) \vec{w}(t) \) into Equation \( C7 \) to yield

\[
\left[ \int_{\Omega_2} q_i(x) q_i(x)^T \, dx \right]^{-1} \int_{\Omega_2} q_i(x) \vec{p}_i(x) \, dx \vec{w}(t) = \vec{w}(t) \tag{C8}
\]

therefore the linear transform from \( \vec{w}(t) \) to \( \vec{w}(t) \) can be expressed as follow:

\[
\vec{w}(t) = H \vec{w}(t) \tag{C9}
\]

where the operator \( H \) is given by:

\[
H = \left[ \int_{\Omega_2} q_i(x) q_i(x)^T \, dx \right]^{-1} \int_{\Omega_2} q_i(x) \vec{p}_i(x) \, dx \tag{C10}
\]

### List of Symbols

| Symbol | Description | Unit |
|--------|-------------|------|
| \( \theta \) | Zero-filled matrix of \( m \times n \) dimension | |
| \( a \) | Specific surface area of electrodes | \( 1/m \) |
| \( A \) | Area for the electrode/current collector interface | \( m^2 \) |
| \( a_q \) | Parameter in the solid phase diffusion equation | |
| \( B_i \) | Index set for non-insulation boundary nodes | |
| \( \mathbf{B}_{\text{H}} \) | Operator for reference potentials | |
| \( \mathbf{B}_{\text{Br}} \) | Operator for reference boundary condition | |
| \( c_0 \) | Average electrolyte concentration | \( \text{mol}/\text{m}^3 \) |
| \( c_i(x, t) \) | Electrolyte concentration | \( \text{mol}/\text{m}^3 \) |
| \( \bar{c}_i(x, t) \) | Element-average electrolyte concentration | \( \text{mol}/\text{m}^3 \) |
| \( \vec{c}_i(t) \) | Node value vector for electrolyte concentration | \( \text{mol}/\text{m}^3 \) |
| \( \bar{c}_i(t) \) | Element-average vector for electrolyte concentration | \( \text{mol}/\text{m}^3 \) |
| \( c_{\text{max}} \) | Maximum concentration in solid phase | \( \text{mol}/\text{m}^3 \) |
| \( D_e^{\text{eff}} \) | Effective diffusivity of electrolyte | \( \text{m}^2/\text{s} \) |
| \( D_m^{\text{bulk}} \) | Diffusivity of bulk electrolyte | \( \text{m}^2/\text{s} \) |
| \( D_s \) | Diffusivity of solid phase | \( \text{m}^2/\text{s} \) |
| \( F \) | Faraday constant | \( \text{C/mol} \) |
| \( F \) | Forcing matrix | |
| \( \mathbf{F} \) | Operator for boundary current | |
| \( \mathbf{I} \) | Operator for element-average values | |
\[ \theta_{avg}(t) \] Average state-of-charge in solid phase
\[ \kappa_{eff} \] Effective electrical conductivity of electrolyte
\[ k_{L,bulk} \] Electrical conductivity of bulk electrolyte
\[ \mu(x, t) \] Transport coefficient
\[ \rho(x) \] Mass function
\[ \sigma_{eff} \] Effective electrical conductivity of solid phase
\[ \tau \] Superscript meaning transpose
\[ \phi_L(x, t) \] Electrical potentials for electrolyte
\[ \phi_{L,x}^e(x, t) \] Modified electrical potentials for electrolyte
\[ \phi_{L,x}^t(t) \] Element-average value for modified electrolyte potential
\[ \phi_{ref}^L(t) \] Reference electrolyte potential
\[ \Phi_{L}(t) \] Node value vector for modified electrolyte potential
\[ \hat{\Phi}_{L}(t) \] Element-average vector for modified electrolyte potential
\[ \phi_S(x, t) \] Electrical potentials for solid phase
\[ \phi_{S,x}^e(x, t) \] Modified electrical potentials for solid phase
\[ \phi_{S,x}^t(t) \] Element-average value for modified solid phase potential
\[ \phi_{ref}^S(t) \] Reference solid phase potential
\[ \Phi_{S}(t) \] Node value vector for modified solid phase potential
\[ \hat{\Phi}_{S}(t) \] Element-average vector for modified solid phase potential

References
1. T. F. Fuller, M. Doyle, and J. Newman, “Simulation and Optimization of the Dual Lithium Ion Insertion Cell,” *Journal of the Electrochemical Society*, 141(1), 1 (1994).
2. S. Santhanagopalan, Q. Z. Guo, P. Ramadass, and R. E. White, “Review of models for predicting the cycling performance of lithium ion batteries,” *Journal of Power Sources*, 156(2), 620 (2006).
3. G. G. Botte, V. R. Subramanian, and R. E. White, “Mathematical modeling of secondary lithium batteries,” *Electrochimica Acta*, 45(15), 2595 (2000).
4. V. Ramadesigan, P. W. C. Northrop, S. De, S. Santhanagopalan, R. D. Braatz, and V. R. Subramanian, “Modeling and Simulation of Lithium-Ion Batteries from a Systems Engineering Perspective,” *Journal of the Electrochemical Society*, 159(3), R31 (2012).
5. P. W. C. Northrop, B. Suthar, V. Ramadesigan, S. Santhanagopalan, R. D. Braatz, and V. R. Subramanian, “Efficient Simulation and Reformulation of Lithium-Ion Battery Models for Enabling Electric Transportation,” *Journal of the Electrochemical Society*, 161(8), E3149 (2014).
6. L. Cai and R. E. White, “Reduction of Model Order Based on Proper Orthogonal Decomposition for Lithium-Ion Battery Simulations,” *Journal of the Electrochemical Society*, 156(3), A154 (2009).
7. V. Ramadesigan, V. Boovaragavan, J. C. Pirkle, and V. R. Subramanian, “Efficient reformulation of solid-phase diffusion in physics-based lithium-ion battery models,” *Journal of the Electrochemical Society*, 157(7), A854 (2010).
8. T. R. Ashwin, A. McGordon, W. D. Widanage, and P. A. Jennings, “Modified electrochemical parameter estimation of NCR18650BD battery using implicit finite volume method,” *Journal of Power Sources*, 341, 387 (2017).
9. K. A. Smith, C. D. Rahn, and C. Y. Wang, “Control oriented ID electrochemical model of lithium ion battery,” *Energy Conversion and Management*, 49(9), 2565 (2007).
10. K. A. Smith, C. D. Rahn, and C. Y. Wang, “Model-based electrochemical estimation and constraint management for pulse operation of lithium ion batteries,” *IEEE Transactions on Control Systems Technology*, 18(3), 654 (2010).
11. K. A. Smith, C. D. Rahn, and C. Y. Wang, “Model-based electrochemical estimation of lithium-ion batteries,” 2008 IEEE International Conference on Control Applications: p. 714.
12. M. Guo and R. E. White, “A distributed thermal model for a Li-ion electrode plate pair,” *Journal of Power Sources*, 221, 334 (2013).
13. M. Guo, G. H. Kim, and R. E. White, “A three-dimensional multi-physics model for a Li-ion battery,” *Journal of Power Sources*, 240, 80 (2013).
14. M. Guo and R. E. White, “Mathematical model for a spirally-wound lithium-ion cell,” *Journal of Power Sources*, 250, 220 (2014).
15. M. Guo, X. Jin, and R. E. White, “Nonlinear State-Variable Method for Solving Physics-Based Li-Ion Cell Model with High-Frequency Inputs,” *Journal of the Electrochemical Society*, 164(11), E3001 (2017).