A nonlinear state-variable method is presented and used to solve the pseudo-2D (P2D) Li-ion cell model under high-frequency input current and temperature signals. The physics-based governing equations are formulated into a nonlinear state variable method (NSVM), in which the mass transfer variables are evaluated using a 1st order exponential integrator approach at each discrete time point and the electrochemical kinetics (Butler-Volmer) equations are solved by either an iterative or an explicit method. This procedure provides an accurate, computationally efficient method to develop physics-based simulations of the performance of a dual-foil Li-ion cell during practical drive cycles.© 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: 10.1149/2.0021711jes] All rights reserved.

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Nonlinear State-Variable Method for Solving Physics-Based Li-Ion Cell Model with High-Frequency Inputs

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Physically based Li-ion cell models are useful tools for analyzing the battery cell performances, characterizing material properties, supporting cell design, and developing battery management systems (BMS). The development of macroscopic, physics-based models of lithium ion cells and batteries began with a relatively simple solid phase lithium ion diffusion model, extended from Atlung et al.’s work in 1979 and named by Santhanagopalan et al. as the single particle (SP) model in 2006. Another most dominant Li-ion cell full-order model (FOM) was also extended from Atlung et al.’s work and developed in 1994 by Fuller et al. in their work, a dual-foil Li-ion cell was represented by a pseudo-two-dimensional domain; and therefore, this model is usually referred as the “pseudo-2D model (P2D)”. This model contains several coupled transport phenomena described by nonlinear partial differential equations (PDEs). Due to the numerical complexity of these models, various reduced-order models (ROMs) have been proposed as substitutes for either the single particle (SP) or the P2D full-order model (FOM) in practical online simulation applications. Also, ROMs have been published to simulate capacity fading and for use in parameter estimations.

The single particle model dates back to 1979, when Atlung et al. presented a relatively simple cell model for the LiTiS2 couple. Their model includes the diffusion of lithium ions in different shaped particles of TiS2, which they called a solid solution. They used their model to predict several aspects of this cell including the specific energy. Their model was used later by Haran et al. to model the impedance of a spherical metal hydride particle. After that, Subramanian et al. extended Atlung et al.’s model to include a variable diffusion coefficient. Also, Subramanian et al. developed an approximate solution for the concentration distribution in a spherical particle, which reduced the computation time needed to simulate cycling of a cell. Next, Ning and Popov used Atlung et al.’s model to simulate cycling of a graphite, MCMB (Meso Carbon Micro Beads)/LiCoO2 cell with formation of a film on the graphite electrode on charge. This simple model provided the capability to estimate the capacity fade for tens of thousands of low rate cycles in less than an hour of computation time. In 2006, Santhanagopalan et al. presented a review of several lithium ion cell models including the extension of Atlung et al.’s model and named this model the single particle (SP) model. Zhang and White used the SP model to make capacity fade predictions for small cells cycled at very low rate. Safari et al. used the SP model to study capacity fade as did Deshpande et al. who extended the SP model to include crack growth in a graphite particle followed by film formation in the resulting cracks with loss of lithium ions. Rahimian et al. used the SP model to study several possible mechanisms that could cause capacity fade of lithium ion cells. Wang et al., Santhanagopalan et al. and Subramanian et al. solved the single particle diffusion equations by polynomial approximation (2nd order or higher). Prasad and Rahn applied the SP model for identifying the aging parameters in lithium ion batteries. Guo and White presented an approximate solution to the spherical diffusion problem with a fixed flux which provides high accuracy with only a few terms in a series when compared to the analytic solution with at least 100 terms. This approximate solution provides significant savings in computation time.

In order to predict the performance of lithium ion cells operating at higher rates, more complicated models were developed. In 1982, West et al. presented a Nernst-Planck model for porous insertion electrodes for a Li/TiS2 cell. They pointed out the importance of coupling the transport of lithium ions between the insertion electrode and the electrolyte. In 1993, Mao and White presented a Nernst-Planck model of the Li/TiS2 cell which included transport of lithium ions through the separator and demonstrated quantitatively how the utilization of the TiS2 electrode could be improved by decreasing the thickness of the separator. Also in 1993, Doyle et al. published a concentrated solution theory model for a lithium/polymer/TiS2 cell. Shortly after that in 1994 Fuller et al. published a concentrated solution theory model for a dual lithium ion insertion cell (“dual foil”), which is known as “pseudo-2D model (P2D)”. In 1996, Doyle et al. published a comparison of their model predictions to experimental data from a Bellcore plastic lithium ion cell. Unfortunately, the computation burden associated with using the program dual foil is too great to use their program for extensive simulations needed for parameter estimation and cell life predictions. Consequently, many papers have been published to provide methodology to reduce this computation burden.

To simplify the P2D models, assumptions have been made to decouple the nonlinear PDEs to reduce the numerical complexity. Doyle and Newman derived analytic expressions for simplified models for two limiting cases: a constant reaction rate in the porous electrode, and no concentration gradient. Kumar, Dao et al., and Tanin et al. assumed a constant reaction rate in each electrode assumption in their models. These results are of limited utility. Smith et al. and Plett et al. used Taylor series to linearize nonlinear Butler-Volmer equation, which only applies when the overpotential is close to zero volt. Also, Smith et al. (p2568) and Plett (p218) assumed that it is reasonable to decouple the electrolyte potential from the electrolyte concentration by neglecting the concentration term of the electrolyte

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charge conservation equation. Models with these two assumptions lose the nonlinear features between the electrolyte potential and concentration, and introduce errors in the simulation results.

Another approach that has been used to reduce the computation burden for solving the P2D model equations is to use different mathematical techniques. Cai and White used the proper orthogonal decomposition method and the orthogonal collocation method to solve the model equations for lithium ion cells to reduce the computation needed for simulation. Subramanian and his coworkers applied coordinate transformation, orthogonal collocation and model reformulation techniques to facilitate the efficient simulation of the P2D model equations. In later work, Subramanian et al. extended the polynomial approximation approach to the diffusion equation in electrolyte phase. Their coordinate transformation was aimed to rescale each domain to [0,1], which will reduce the problem from three regions to a single region and decrease the required computation. Similarly, the model reformulation technique was a series of mathematical operations of the governing equations, which will reduce the total numbers of governing equations without losing any accuracy. Han et al. used several first order processes to approximate the diffusion equation and a quadratic function to simulate the electrolyte concentration. Dao et al. used the Galerkin method with cosine functions and constant reaction rates to solve the P2D model equations. Howey et al. used a spectral orthogonal collocation method to solve the P2D model equations. These mathematical approaches to approximate the solutions of the partial differential equations will introduce errors since a limited number of trial functions were used, such as orthogonal collocation, polynomial approximation, etc. These methods can save time and memory in simulating the steady input cell operations (i.e. constant current/voltage modes), but lose accuracy if the input signal varies rapidly with time (i.e., high-frequency current pulses). Smith et al. developed a ROM by a control-oriented method: by linearizing the material thermodynamics and electrochemical kinetics, the P2D model is first converted to a single-input transfer function in the Laplace-domain, and then a state variable model (SVM) is derived using approximated poles and gains. Smith’s SVM approach provides excellent convergence at high current rates (up to 50 C) and has been adopted into the multi-scale multi-dimensional framework to model the distributed thermal behavior over large-format cell geometry. Using a similar approach to SVM, Plett and his coworkers derived a ROM from the Laplace transfer function by using a discrete-time realization algorithm (DRA) and the resulting model was used to simulate the Urban Dynamometer Driving Schedule (UDDS). Plett’s approach achieves a significant speedup for the high-frequency simulation as compared with the nonlinear FOM. Following Smith’s SVM method, Chen et al. reported a reduced order model based on the unit-form concentration distribution in both solid and electrolyte phases. However, the SVM methods also have limits: to take the Laplace transfer, P2D model must be linearized around a specific SOC and the temperature must be assumed constant, therefore, their approach will lose accuracy when implemented over wide operation windows.

In this work, we present a discrete-time algorithm to solve the nonlinear P2D model equations. The partial differential equations for mass transfer are numerically translated into an ordinary-differential-equation (ODE) system which is solved using a 1st order exponential integrator approach at discrete time points. The charge conservation equations are included as algebraic constraints, and two procedures are presented to solve these nonlinear equations. It is shown that linearization of the Butler-Volmer equation can provide a good approximation for potentials to reach a fast convergence of the nonlinear Butler-Volmer equation. With our approach, the high-frequency drive cycles for Li-ion cells can be simulated through a 0%-100% SOC window with 20 °C temperature rise, with both high accuracy and computation time efficiency. Our method has also been used to estimate model parameters from synthetic voltage data from the FOM for the US06 drive cycle by using a nonlinear least-square regression technique. A detailed description of our method is presented in the following sections.

Mathematical Model

Description of the P2D model.—The P2D modeling domains for a Li-ion cell are illustrated in Figure 1, where the linear dimension x goes through the thicknesses of electrodes and separator, the radius dimension r is defined between the center and the surface of spherical particles, R_ex is the contact resistance between the cell and the external terminals, and V_ex is the voltage drop across the external terminals. The governing equations and boundary conditions for the P2D model are listed in Table 1, and the symbols for the variables are listed in Table II. The constant parameter values listed in Table III are cited from reference; in our model, certain physical properties are assumed to vary with temperature through the Arrhenius expression:

$$\psi = \psi_{|T=ref} \exp \left( \frac{E^*}{R} \left( \frac{1}{T} - \frac{1}{T^{ref}} \right) \right) \quad [1]$$

where ψ denotes a physical parameter, ψ|T=ref is the value for that parameter at reference temperature, E* is the activation energy, and T^ref = 298 K is the reference temperature. The Arrhenius coefficients for the temperature-dependent parameters are listed in Table IV.

State-variable model.—The P2D model (See Table 1) using our nonlinear state variable method can be transformed into a nonlinear state-variable model (NSVM). The transport phenomena in the solid

![Figure 1](image-url)
Table I. Governing equations and boundary conditions for the pseudo-2D model.

| Model                          | Equations                                                                 |
|-------------------------------|---------------------------------------------------------------------------|
| Solution phase diffusion      | \[ \dot{x} = D_{1,eff} \frac{\partial^2 x}{\partial t^2} + (1-t^+) \frac{\partial x}{\partial t} + D_{l,bulk} \dot{i}_{l} \] |
| Charge conservation in electrolyte | \[ \frac{\partial \phi}{\partial x} \bigg|_{x=0} = 0 \quad \frac{\partial \phi}{\partial x} \bigg|_{x=l_a+l_b} = 0 \] |
| Charge conservation in solid phase | \[ j_s = 0 \quad \text{in the separator region} (l_a < x < l_a + l_b) \] |

The charge conservation and electrochemical kinetic equations can be written as a non-linear algebraic constraint:

\[ \begin{bmatrix} [d] \\ y \end{bmatrix} = F \left( [x], [u] \right) \]

where \( [x] \) is the state variable vector, \( A \) and \( B \) are coefficient matrices, and \( [d] \) is the source vector. These are explained in detail below. The Butler-Volmer equation for electrochemical reactions

\[ \dot{i}_{app} = D_a \frac{\partial^2 \phi}{\partial x^2} \left( \frac{\partial \phi}{\partial x} \bigg|_{x=0} = 0 \right) - D_l \frac{\partial \phi}{\partial x} \bigg|_{x=l_a+l_b} = 0 \quad \text{Not applied in the separator region} (l_a < x < l_a + l_b) \]

Both the applied current density \( (\dot{i}_{app}) \) and the cell temperature \( T \) can be measured in real-time, so these two variables are taken as the input vector \( u \):

\[ u = [\dot{i}_{app}, T]^T \]

Table III. Constant parameter values for P2D model.

| Parameter                           | Value               |
|-------------------------------------|---------------------|
| Maximum Li capacity \( c_{s,max} \) (mol/m^3) | 26390               |
| Radius of particle \( R_e \) (m) | 12.5 × 10^{-6}       |
| Thickness of components \( l_{a/l_p} \) (m) | 100 × 10^{-6}       |
| Porosity of electrode \( \varepsilon_1 \) | 0.357               |
| Volume fraction of active material \( \varepsilon_a \) | 0.471               |
| Specific surface area \( a (1/m) \) | 100 × 10^{-6}       |
| Solid electronic conductivity \( \sigma (S/m) \) | 0.363               |
| Universal gas constant \( R (J/mol/K) \) | 8.314               |
| Faraday constant \( F (C/mol) \) | 96485               |
| Reference temperature \( T^0 (K) \) | 298                 |
| Electrolyte ion transfer number \( t^+ \) | 0.363               |
| 1C rate current density \( i_{1C} (A/m^2) \) | 17.5                |
| External connection resistance \( R_{a} (\Omega m^2) \) | 0.005               |
| Average electrolyte concentration \( \epsilon_1 (mol/m^3) \) | 2000                |
| Activity coefficient of reaction \( f_{k} \) | 1                  |

Table II. List of variables for pseudo-2D model.

| Variable name                        | Symbol |
|--------------------------------------|--------|
| Li^+ concentration in electrolyte (mol/m^3) | \( c_1 \) |
| Electric potential of electrolyte (V) | \( \phi_1 \) |
| Electric potential of solid phase (V) | \( \phi_s \) |
| Surface electrochemical current density (A/m^2) | \( j_s \) |
| Exchange current density (A/m^2) | \( j_0 \) |
| Open circuit potential (V) | \( U \) |
| Electrochemical overpotential (V) | \( \eta \) |
| Li^+ concentration in solid phase (mol/m^3) | \( c_s \) |

\( \partial \phi/\partial x \big|_{x=0} = 0 \quad \partial \phi/\partial x \big|_{x=l_a+l_b} = 0 \)
Table IV. Temperature-dependent properties for certain transport and kinetic parameters.

| Parameter                        | Value at reference temperature $T^{ref}$ | Activation energy $E^*$ [J/mol] | Units         |
|----------------------------------|------------------------------------------|--------------------------------|---------------|
| Solid phase diffusivity $D_i$    | Anode $3.9 \times 10^{-14}$               | $2.0 \times 10^4$               | m$^2$/s       |
|                                  | Cathode $1.0 \times 10^{-13}$             | $2.0 \times 10^4$               | m$^2$/s       |
| Reaction rate constant $k_i$     | Anode $2.334 \times 10^{-11}$             | $3.0 \times 10^4$               | m$^2$/mol s$^{-1}$/s |
|                                  | Cathode $2.334 \times 10^{-11}$           | $3.0 \times 10^4$               | m$^2$/s       |
| Diffusivity in bulk electrolyte $D_{i,bulk}$ | Anode $7.5 \times 10^{-11}$              | $2.0 \times 10^4$               | m$^2$/s       |
| Electric conductivity in bulk electrolyte $\kappa_{i,bulk}$ | See below* | $3.0 \times 10^4$               | S/m           |

* $\kappa_{bulk} = 4.153 \times 10^{-2} + 5.007 \times 10^{-4}c_1 - 4.7212 \times 10^{-7}c_1^2 + 1.5094 \times 10^{-10}c_1^3 - 1.6018 \times 10^{-14}c_1^4$ (where $c_1$ in mol/m$^3$)
$T^{ref} = 298$K

In the following sections, we will introduce the transformation of the P2D model into the NSVM expressed by Equations 2 and 3.

Electrolyte diffusion.—The finite element method was used to yield an ODE system from the electrolyte mass transfer equation (See Table I):

$$\frac{\partial \mathbf{c}}{\partial t} = -\mathbf{Kc} + \mathbf{J}_s$$

[6]

where $\mathbf{M}$, $\mathbf{K}$, and $\mathbf{F}$ are, respectively, the mass, stiffness, and force matrices, $\mathbf{c}$ is the vector containing the discretized electrolyte concentration values distributed through different nodes in the electrodes and separator domains, $\mathbf{J}_s$ is the vector containing the discretized surface electrochemical current density values distributed through different meshed elements in the two electrode domains. The dimensions of matrices and vectors in Equation 6 are determined specifically by the mesh pattern of the finite element method. Each element in $\mathbf{c}$ and $\mathbf{J}_s$ is a lumped variable depending only on time. Left-multiply Equation 6 by $\mathbf{M}^{-1}$ to obtain:

$$\frac{\partial}{\partial t} \mathbf{\tilde{c}} = -\mathbf{M}^{-1}\mathbf{Kc} + \mathbf{M}^{-1}\mathbf{J}_s$$

[7]

Form the eigen-decomposition matrix for $\mathbf{M}^{-1}\mathbf{K}$:

$$\mathbf{M}^{-1}\mathbf{K} = \mathbf{V}\mathbf{\Lambda}\mathbf{V}^{-1}$$

[8]

where $\mathbf{D} = \text{diag} (\lambda_1, \lambda_2, \ldots)$ is a diagonal matrix formed by eigenvalues (\tilde{\lambda}_i), and $\mathbf{V}$ is the matrix whose column vectors are the eigenvectors of $\mathbf{M}^{-1}\mathbf{K}$. Multiply Equation 7 by $\mathbf{V}^{-1}$ to obtain:

$$\mathbf{V}^{-1}\frac{\partial}{\partial t} \tilde{\mathbf{c}} = -\mathbf{V}^{-1}\mathbf{D}\mathbf{\tilde{c}} + \mathbf{V}^{-1}\mathbf{M}^{-1}\mathbf{J}_s$$

[9]

Let $\tilde{x} = \mathbf{V}^{-1}\mathbf{\tilde{c}}$, $\tilde{A} = -\mathbf{D}$, $\tilde{B} = \mathbf{V}^{-1}\mathbf{M}^{-1}\mathbf{F}$, and $\tilde{d} = \mathbf{J}_s$, so that the electrolyte mass transport equation is in the state equation form, $\frac{\partial \tilde{x}}{\partial t} = \tilde{A}\tilde{x} + \tilde{B}\tilde{d}$.

[2]

The concentration vector can be obtained from $x$:

$$\mathbf{c} = \mathbf{V}\tilde{x}$$

[10]

where $\mathbf{x}$ is included in the algebraic constraint(3). It can be shown from the finite element formula that in the matrix $\mathbf{D}$ is diagonal, $\lambda_i' \lambda_2' \ldots'$, each eigenvalue is proportional to the electrolyte diffusivity $D_{i,bulk}$ and is therefore scale by a factor of $\exp[-\frac{E^*}{RT} (\frac{1}{T} - \frac{1}{T^{ref}})]$ (where $E^*$ is the activation energy for $D_{i,bulk}$) during a temperature change; and as a result, extra computation for the eigen decomposition is not required at each time step.

Solid phase diffusion.—To transform the solid particle diffusion PDE into a state equation, we used an approximate transfer function approach presented earlier, as shown in Appendix A, which is also used by Smith et al.,13 Lee et al.,38 and Leek et al.39

The resulting transfer function is:

$$\tilde{\theta}^*(\beta) - \tilde{\theta}_{avg} = \left[ \frac{\beta \tan(\sqrt{\beta}) + 3 \tan(\sqrt{\beta}) - 3 \sqrt{\beta}}{\beta \tan(\sqrt{\beta}) - \sqrt{\beta}} \right] \delta_i(\beta)$$

[11]

Where $\tilde{\theta}^*$, $\tilde{\theta}_{avg}$, and $\delta_i$ are respectively the dimensionless Laplace transform for the concentration at the surface of the particles, the average concentration in the spherical particle, and the surface flux for solid phase diffusion, and $\beta$ is the dimensionless Laplace variable.

We used a finite Heaviside expansion $G'(\beta)$ to approximate $G(\beta)$:

$$G'(\beta) = \sum_{i=1}^{N} \frac{b_i}{\beta + a_i} \approx G(\beta)$$

[12]

where $a_i$ and $b_i$ are adjustable parameters obtained by minimizing the absolute value $|G(\beta) - G'(\beta)|$ through frequency response after substituting $\beta = \tilde{\omega}j$ (where $\tilde{\omega}$ is the dimensionless angular frequency) in Equation 12. Therefore after parameter optimization, Equation A17 can be expanded into the following series:

$$\tilde{\theta}^*(\beta) = \tilde{\theta}_{avg} + \sum_{i=1}^{N} \tilde{\theta}_i \beta$$

[13]

where $\tilde{\theta}_i$ is the eigenfunction defined as:

$$\tilde{\theta}_i(\beta) = \frac{b_i}{\beta + a_i} \delta_i(\beta)$$

[14]

So the inverse Laplace transform $L^{-1}\{\tilde{\theta}_i(\beta)\}$ is equivalent to the solution of following ODE:

$$\frac{d\tilde{Q}_i}{dt} = -a_i\tilde{Q}_i + b_i\tilde{\theta}_i |_{\tilde{\omega}=0} = 0$$

[15]

Scale the dimensionless time $\tau$ to time $t$ through expression A5 and use Equation A8 to substitute the dimensionless flux $\delta_i$ and Equation 15 can be converted into the dimensional time domain:

$$\tilde{Q}_i = \frac{d\tilde{Q}_i}{dt} = \frac{-a_iD_i\tilde{Q}_i}{R_i} + \frac{b_i\tilde{j}_s}{FR_i c_{i,max}} |_{\tilde{\omega}=0} = 0$$

[16]

The inverse Laplace transform for $\tilde{\theta}_{avg}$ can be obtained from Equation A16, and then the derivative of $\tilde{\theta}_{avg}$ to time could be derived as:

$$\frac{d\tilde{\theta}_{avg}}{dt} = \tilde{\theta}_{avg} = -\frac{3\tilde{j}_s}{R_i c_{i,max}}$$

[17]

Let $\tilde{d} = \tilde{j}_s(t, x)$, $\tilde{x} = [\tilde{Q}_1, \tilde{Q}_2, \ldots, \tilde{Q}_N, \tilde{\theta}_{avg}]^T$, $\tilde{A} = -\frac{D_i}{R_i} \text{diag} (a_1, a_2, \ldots, a_N, 0)$, and $\tilde{B} = \frac{1}{R_i c_{i,max}} [b_1, b_2, \ldots, b_N, -3]^T$, and the solid phase diffusion equation is formulated to be in the same form as the state Equation 2:

$$\frac{d\tilde{x}}{dt} = \tilde{A}\tilde{x} + \tilde{B}\tilde{d}$$

[2]

The dimensionless surface concentration $\tilde{\theta}^*$ is expressed as $\tilde{\theta}^* = [1, 1, \ldots, 1]^T \tilde{x}$ and is included in constraint Equation 3. As the surface electrolyte current density $\tilde{j}_s(t, x)$ is expressed as the discretized vector $\tilde{J}_s$ through the electrode domains, the reformulated solid phase diffusion equations are repeatedly implemented for each element of $\tilde{J}_s$. 
Electrical submodels.—Initial solution.—Our formulation of the electrical submodel (the coupled charge conservation and Butler-Volmer kinetics) begins with the linearization of electrochemical kinetics. The nonlinear Butler-Volmer equation is expressed as follow:

\[ j_i = j_0 \left[ \exp \left( \frac{0.5F}{RT} \eta \right) - \exp \left( - \frac{0.5F}{RT} \eta \right) \right] \]  \hspace{1cm} [18]

where, \( j_0 \) is calculated by:

\[ j_0 = F k c_i 0.5 \left( c_{\text{max}} - c_{\ell=r=R_i} \right) 0.5 \left( c_{\ell=r=R_i} \right) 0.5 \]  \hspace{1cm} [19]

with \( c_1 \) and \( c_c \) are the concentrations of Li species in the electrolyte and solid phases respectively, \( k_i \) is the reaction rate constant, and \( c_{\text{max}} \) is the maximum concentration of Li\(^{+}\) in the solid phase.

Taking 1st order Taylor expansion for the Butler-Volmer Equation 18, an approximate expression for the surface electrochemical current density \( j_s \) can be obtained:

\[ j_s \approx j_0 \left[ \left( 1 + \frac{0.5F}{RT} \eta \right) - \left( 1 - \frac{0.5F}{RT} \eta \right) \right] \]  \hspace{1cm} [20]

The superscript ' indicates the variable is obtained by linearized BV function. Substitute Equation 20 into the charge conservation Equation 3, and the electrical submodel can be simplified as follows:

\[ \frac{\partial}{\partial x} \left( -\kappa \frac{\partial \phi'}{\partial x} + \kappa_d \frac{\partial s}{\partial x} \right) = a_j 0 \frac{\partial}{\partial x} F \left( \phi'_{\text{ref}} - \phi' - U \right) \]  \hspace{1cm} [21]

\[ \frac{\partial}{\partial x} \left( -\sigma e \frac{\partial \phi'}{\partial x} \right) = - \frac{\partial}{\partial x} \left( \phi'_{\text{ref}} - \phi' - U \right) \]  \hspace{1cm} [22]

\[ \frac{\partial \phi'}{\partial x} |_{x=0} = 0 \frac{\partial \phi'}{\partial x} |_{x=n_{e}+l_{s}+l_{p}} = 0 \]  \hspace{1cm} [23]

\[ \phi'_{\text{ref}} |_{x=0} = 0 \frac{\partial \phi'}{\partial x} |_{x=n_{e}+l_{s}} = 0 \frac{\partial \phi'}{\partial x} |_{x=n_{e}+l_{s}+l_{p}} = 0 \]  \hspace{1cm} [24]

\( i_{\text{app}} \) is negative for discharge cycle and positive for charge cycle. Equations 21 through 24 can be solved linearly through the meshed geometry but the solutions are inaccurate due to the linear approximation, therefore we use the symbols \( \phi_s' \) and \( \phi_e' \) to distinguish them from full-order solutions. Figure 2 shows the general procedure for solving the electrical submodel: the linear solution from Equations 21 through 24 is used as initial values for a refinement subroutine from which variables \( j_s \) and \( V_{\text{app}} \) can be calculated by:

\[ \phi_i = \phi_i' \quad \phi_s = \phi_s' \]  \hspace{1cm} [25]

The initial value for \( j_s \) is calculated using Equation 20, and the initial reference potential values are defined as follows:

\[ \phi^0_{\text{ref}} = \phi^0_{\text{ref}} |_{x=0} \quad \phi^0_{\text{ref}} = \phi^0_{\text{ref}} |_{x=n_{e}+l_{s}+l_{p}} \]  \hspace{1cm} [26]

where \( \phi^0_{\text{ref}} \) and \( \phi^0_{\text{ref}} \) are respectively the absolute references for electrolyte and solid phase potentials. The residue for Butler-Volmer equation, \( \text{Res}_{\text{BV}} \), is expressed as:

\[ \text{Res}_{\text{BV}} = j_s - j_0 \left[ \exp \left( \frac{0.5F}{RT} \eta \right) - \exp \left( - \frac{0.5F}{RT} \eta \right) \right] \]  \hspace{1cm} [27]

where \( \eta = \phi_s - \phi_e - U \) denotes the overpotentials for electrochemical reactions. If the electrode domains are discretized into \( N_e \) nodes, Equation 27 will be implemented at each node, and therefore \( \text{Res}_{\text{BV}} \) is expressed by a \( N_e \times 1 \) column vector \( \text{Res}_{\text{BV}} \). The two reference potentials, \( \phi^0_{\text{ref}} \) and \( \phi^0_{\text{ref}} \), are extra unknown variables which are determined by the electrical limiting equations defined as follows:

\[ \int_{0}^{l_{n}} a j_{i} \, dx = -i_{\text{app}} \quad \int_{l_{n}+l_{s}}^{l_{n}+l_{s}+l_{p}} a j_{i} \, dx = i_{\text{app}} \]  \hspace{1cm} [28]

and the residues for Equation 28 are expressed as:

\[ \text{Res}_{\text{app}} = \int_{0}^{l_{n}} a j_{i} \, dx + i_{\text{app}} \quad \text{Res}_{p} = \int_{l_{n}+l_{s}}^{l_{n}+l_{s}+l_{p}} a j_{i} \, dx - i_{\text{app}} \]  \hspace{1cm} [29]

where \( \text{Res}_{\text{app}} \) and \( \text{Res}_{p} \) are scalars. Therefore, the full residue vector for the electrical submodel is expressed as follows:

\[ \text{Res} = \begin{bmatrix} \text{Res}_{\text{BV}} \\ \text{Res}_{\text{app}} \\ \text{Res}_{p} \end{bmatrix} \]  \hspace{1cm} [30]

where \( \text{Res} \) is a \( (N_e + 2) \times 1 \) column vector. The equation system includes totally \( N_e + 2 \) unknowns: the discretized \( j_i \) values at \( N_e \) elements (\( j_i \) is expressed by a \( N_e \times 1 \) column vector \( j_i \)) and the two reference potentials, \( \phi^0_{\text{ref}} \) and \( \phi^0_{\text{ref}} \). Next, we use Newton’s method to decide the \( j_i \), \( \phi^0_{\text{ref}} \), and \( \phi^0_{\text{ref}} \) values that make the norm for residue vector \( \text{Res} \rightarrow 0 \). Derive the Jacobian matrix for the residue vector as:

\[ \text{Jac} = \begin{bmatrix} \frac{\partial \text{Res}}{\partial j_i} & \frac{\partial \text{Res}}{\partial \phi^0_{\text{ref}}} & \frac{\partial \text{Res}}{\partial \phi^0_{\text{ref}}} \\ \frac{\partial \text{Res}}{\partial j_i} & \frac{\partial \text{Res}}{\partial \phi^0_{\text{ref}}} & \frac{\partial \text{Res}}{\partial \phi^0_{\text{ref}}} \\ \frac{\partial \text{Res}}{\partial j_i} & \frac{\partial \text{Res}}{\partial \phi^0_{\text{ref}}} & \frac{\partial \text{Res}}{\partial \phi^0_{\text{ref}}} \end{bmatrix} \]  \hspace{1cm} [31]

where the Jacobian matrix \( \text{Jac} \) has \( (N_e + 2) \times (N_e + 2) \) dimension. The step change for the unknown variables, \( \Delta y \), is evaluated as follow:

\[ \Delta y = - \text{Jac}^{-1} \text{Res} \]  \hspace{1cm} [32]
Figure 3. Nonlinear refinement for the solutions of electrical submodels: (a) the implicit method, (b) the explicit method.

The unknown variables are updated for the next iteration through the following equation:

\[
\begin{bmatrix}
\phi_i \\
\phi_s
\end{bmatrix}
= \begin{bmatrix}
\frac{\partial}{\partial x} (k_i \phi_i - k_s \phi_s) + a_i \\
\frac{\partial}{\partial x} (\sigma_i \phi_i) - a_s
\end{bmatrix} = 0
\]

With the updated \( j_s \), \( \phi_i^{ref} \), and \( \phi_s^{ref} \) values, the electric potentials \( \phi_i \) and \( \phi_s \) can be solved from the charge conservation equations with the imposed boundary conditions:

\[
\begin{bmatrix}
\phi_i \\
\phi_s
\end{bmatrix}
= \begin{bmatrix}
\frac{\partial \phi_i}{\partial x} \\
\frac{\partial \phi_s}{\partial x}
\end{bmatrix}^{ref} + dy
\]

\[
\begin{bmatrix}
\phi_i \\
\phi_s
\end{bmatrix}
= \begin{bmatrix}
j_s \\
V_{ex}
\end{bmatrix}^{ref} + i_{app} R_{ex}
\]

\[
\begin{bmatrix}
\phi_i \\
\phi_s
\end{bmatrix}
= \begin{bmatrix}
j_s \\
V_{ex}
\end{bmatrix}^{ref}
\]

\[
\eta = \phi_i - \phi_s - U
\]

\[
\begin{bmatrix}
\eta \phi_i \\
\eta \phi_s
\end{bmatrix} = \begin{bmatrix}
\eta \\
\eta
\end{bmatrix} + dy
\]

\[
\begin{bmatrix}
\frac{\partial}{\partial x} (k_i \phi_i - k_s \phi_s) + a_i \\
\frac{\partial}{\partial x} (\sigma_i \phi_i)
\end{bmatrix} = 0
\]

\[
\begin{bmatrix}
\phi_i \\
\phi_s
\end{bmatrix}
= \begin{bmatrix}
\frac{\partial \phi_i}{\partial x} \\
\frac{\partial \phi_s}{\partial x}
\end{bmatrix}^{ref} + dy
\]

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With the updated solution for \( \phi \) and \( \phi_s \), repeat steps described by Equation 26 through 34 until \([\text{Res}]\) value is small enough (<10^-8), then exit the loop and output the \( \frac{j}{2} \) and \( \phi_s \) values from the last iteration. The terminal voltage \( V_{ex} \) is evaluated through the following equation:

\[
V_{ex} = \phi_s^{ref} + i_{app} R_{ex} \tag{35}
\]

**Explicit method.**—As shown above, the implicit method involves the derivation of analytical Jacobian matrix, which is usually difficult for in-house code scripting. Therefore, as shown in Figure 3b, we developed a simplified approach to solve the electrical submodels explicitly without iterative loops. In the explicit approach, the overpotential is split into two parts:

\[
\eta = \tilde{\eta} + \eta^{ref} \tag{36}
\]

The first term on the right-hand-side of Equation 36 is expressed as:

\[
\tilde{\eta} = (\phi_s' - 0) - (\phi_s' - \phi_s|_{x=0}) - \left( U - \frac{1}{l_p} \int_{0}^{l_p} U dx \right) \left( 0 \leq x \leq l_a \right)
\]

\[
\eta^{ref} = (\phi_s' - \phi_s^{ref}) - (\phi_s'' - \phi_s|_{x=0}) - \left( U - \frac{1}{l_p} \int_{0}^{l_p} U dx \right) \left( l_a + l_i \leq x \leq l_a + l_i + l_p \right)
\]

and as shown in Equation 37, \( \eta^{ref} \) varies with both time and space. The second term on the right-hand-side of Equation 36 is expressed as:

\[
\eta^{ref} = -\phi_s'' - \frac{1}{l_p} \int_{0}^{l_p} U dx \left( 0 \leq x \leq l_a \right)
\]

\[
\eta^{ref} = \phi_s^{ref} - \phi_s'' - \frac{1}{l_p} \int_{l_a+l_i}^{l_a+l_i+l_p} U dx \left( l_a + l_i \leq x \leq l_a + l_i + l_p \right)
\]

and in each electrode region, \( \eta^{ref} \) is a variable only varying with time. Therefore, the Butler-Volmer equation can be written as follow:

\[
j_s = j_0 \left[ \exp \left( \frac{0.5F}{RT} \tilde{\eta} \right) \exp \left( \frac{0.5F}{RT} \eta^{ref} \right) - \exp \left( -\frac{0.5F}{RT} \tilde{\eta} \right) \exp \left( -\frac{0.5F}{RT} \eta^{ref} \right) \right] \tag{39}
\]

Next, substitute Equation 39 into the electrical limiting Equation 28, to obtain the following hyperbolic equations for each electrode region:

\[
i_{app} = AX - B \frac{1}{X} \left( 0 \leq x \leq l_a \right) \tag{40}
\]

\[
i_{app} = AX - B \frac{1}{X} \left( l_a + l_i \leq x \leq l_a + l_i + l_p \right)
\]

where the unknown variable \( X \) is expressed as:

\[
X = \exp \left( \frac{0.5F}{RT} \eta^{ref} \right) \tag{41}
\]

and coefficients \( A \) and \( B \) are, respectively, expressed as:

\[
A = \int_{0}^{l_a} a j_0 \exp \left( \frac{0.5F}{RT} \tilde{\eta} \right) dx
\]

\[
B = \int_{0}^{l_a} a j_0 \exp \left( -\frac{0.5F}{RT} \tilde{\eta} \right) dx \left( 0 \leq x \leq l_a \right)
\]

\[
A = \int_{l_a+l_i}^{l_a+l_i+l_p} a j_0 \exp \left( \frac{0.5F}{RT} \tilde{\eta} \right) dx
\]

\[
B = \int_{l_a+l_i}^{l_a+l_i+l_p} a j_0 \exp \left( -\frac{0.5F}{RT} \tilde{\eta} \right) dx \left( l_a + l_i \leq x \leq l_a + l_i + l_p \right)
\]

From Equation 40, the unknown variable \( X \) can be solved explicitly:

\[
X = \frac{-i_{app} + \sqrt{i_{app}^2 + 4AB}}{2A} \left( 0 \leq x \leq l_a \right) \tag{43}
\]

\[
X = \frac{i_{app} + \sqrt{i_{app}^2 + 4AB}}{2A} \left( l_a + l_i \leq x \leq l_a + l_i + l_p \right)
\]

and \( \eta^{ref} \) can be derived from Equation 41:

\[
\eta^{ref} = \frac{RT}{0.5F} \ln X \tag{44}
\]

According to Equation 38, the reference potentials can be calculated from \( \eta^{ref} \) values in the two electrode regions:

\[
\phi_s^{ref} = \eta^{ref} \left[ x_{a+p} \leq x \leq x_{a+p} + \eta^{ref} \right] + \frac{i_{app}}{l_p} \int_{l_a+l_i}^{l_a+l_i+l_p} U dx + \eta^{ref} \left( \frac{i_{app}}{l_p} \int_{l_a+l_i}^{l_a+l_i+l_p} U dx \right)
\]

The terminal voltage \( V_{ex} \) can be evaluated from Equation 35, and \( j_s \) is calculated by the Butler-Volmer equation. According to the flowchart shown in Figure 3b, \( j_s \) and \( V_{ex} \) can be calculated approximately by only going through several sequential steps and no iteration is needed.

**Formulation of electrical equations.**—As shown in Figure 2, the electrical submodel takes \( i_{app} \) as a direct input, while the state variable \( x \) and input temperature \( T \) are also involved to evaluate certain coefficients (i.e. \( j_0, U, \eta^{ref} \), and \( k_\lambda \)). The outputs of the electrical submodel include \( j_s \) (expressed as vector \( \mathbf{j} \) over the discretized nodes) and \( V_{ex} \); as defined previously, \( \mathbf{d} = [1] \) and \( y = \mathbf{V}_{ex} \), so the electrical submodel is formulated same as the constraint Equation 3:

\[
\begin{bmatrix} \mathbf{d} \\ y \end{bmatrix} = \mathbf{F}(x, \mathbf{u}) \tag{3}
\]

**Simulation on discrete time domain.**—For discrete time simulation, it is usually assumed that all coefficients and the source terms in state Equation 2 are constant during a small time interval \([t_{k-1}, t_k] \). As shown in sections Electrolyte diffusion and Solid phase diffusion, the coefficient matrix \( \mathbf{A} \) in Equation 2 is diagonal:

\[
\mathbf{A} = \begin{bmatrix} \lambda_1 & 0 & 0 & \cdots & 0 \\ 0 & \lambda_2 & 0 & \cdots & 0 \\ 0 & 0 & \lambda_3 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & \lambda_N \end{bmatrix} \tag{46}
\]

where \( \lambda_i (i = 1, 2, 3, \ldots, N) \) are the diagonal elements evaluated at time point \( t_{k-1} \). Before moving to the next time point \( t_k = t_{k-1} + \Delta t \), the following matrix exponential operators are defined:

\[
\mathbf{A} = \begin{bmatrix} e^\lambda_1 \Delta t \\ e^\lambda_2 \Delta t \\ e^\lambda_3 \Delta t \\ \vdots \\ e^\lambda_N \Delta t \end{bmatrix} \tag{47}
\]

\[
\mathbf{A} = \begin{bmatrix} e^{\lambda_1 \Delta t} & 0 & 0 & \cdots & 0 \\ 0 & e^{\lambda_2 \Delta t} & 0 & \cdots & 0 \\ 0 & 0 & e^{\lambda_3 \Delta t} & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & e^{\lambda_N \Delta t} \end{bmatrix} \tag{48}
\]

and the state variables at the next time point, \( \mathbf{x}_k \), can be calculated through the following equation:

\[
\mathbf{x}_k = \mathbf{A} \mathbf{x}_{k-1} + \mathbf{B} \mathbf{d}_{k-1} \tag{49}
\]

where \( \mathbf{x}_{k-1}, \mathbf{d}_{k-1} \), and \( \mathbf{B} \) are respectively the variable and coefficient values at \( t_{k-1} \), and \( \Delta t \) is the time interval between \( t_{k-1} \) and \( t_k \).
that if $\lambda_i = 0$, the corresponding diagonal element in Equation 48 is estimated by taking the limit for $\lambda_i \to 0$:

$$\lim_{\lambda_i \to 0} \frac{e^{\lambda_i \Delta t} - 1}{\lambda_i} = \Delta t$$

[50]

At time point $t_k$, the source term $d_k$ and output $y_k$ can be obtained by solving the algebraic constraint described in Electrical submodels section:

$$d_k, y_k = F(x_k, u_k)$$

[51]

where $u_k$ is the input vector at $t_k$.

This simulation procedure is illustrated by a flowchart in Figure 4 and can be described as follow:

1) At the initial time point ($k = 0$), the state vector $x_k$ equals to the preset initial values (in this work, the initial values are $c_1 = 2000 \text{ mol/m}^3$, $\theta_n = 0.5635$, and $\theta_p = 0.1706$);
2) Evaluate the coefficients and operators in the model with $x_k$ and $u_k$;
3) Solve Equation 51 to obtain $d_k$ and $y_k$;
4) Update the index $k = k + 1$;
5) Calculate $x_k$ from Equation 50 using $d_k - 1$ and $x_{k-1}$;
6) Repeat steps 2) through 5).

**Results and Discussion**

**Particle diffusion parameters.**—As stated in Solid phase diffusion section, several dimensionless parameters ($a_i, b_i$, where $i = 1, 2, \ldots N$) in Equation 12 should be optimized by frequency response so that the transfer function for the particle diffusion can be approximated by a Heaviside series. To determine these parameter values, the dimensionless Laplace variable $\beta$ is expressed into imaginary frequency:

$$\beta = \sigma j$$

[52]

where $\sigma$ is the dimensionless angular frequency and $j$ is the unit imaginary number. Substitute Equation 52 into Equations 11 and 12, scan $\sigma$ from $10^{-6}$ through $10^6$, evaluate the dimensionless transfer functions $G(\beta)$ and $G'(\beta)$ at each frequency; and the profile of $G'(\beta)$ can be fit to $G(\beta)$ using a least square approach. The optimization results in Figure 5 show that a good agreement between $G'(\beta)$ and $G(\beta)$ can be achieved with only 4 terms ($N = 4$), and the optimized $a_i$ and $b_i$ values are presented in Table V. These parameters are implemented in Equation 16 to simulate the solid phase diffusion in both anode and cathode.

**Table V. Optimized parameter values in approximated transfer function $G'(\beta)$ with $N = 4$.**

| $i$   | $a_i$     | $b_i$     |
|-------|-----------|-----------|
| 1     | 35058.7   | −268.261  |
| 2     | 1382.966  | −30.9242  |
| 3     | 141.595   | −7.59606  |
| 4     | 22.32279  | −2.59525  |
We use this approximate transfer function approach only for the solid phase diffusion; in this case, the transfer function \( G(\beta) \) contains only one dimensionless group \( \beta \), so the values for \( a_i \) and \( b_i \) are unaffected by other parameters or temperature. If this approach is extended to the full-cell scale, the resulting transfer function will take the form like \( G'(s, k_{\text{eff}}, U, T) \), so the optimized ROM parameters would implicitly depend on temperature, SOC, and electrolyte concentration. As a result, the ROM developed by a full-cell transfer function must be re-evaluated for different operating windows, however our NSVM method has no such limitations.

The implicit model solves the algebraic constraint 51 using the method shown in Implicit method section, while the explicit model uses method shown in Explicit method. The cell domain is meshed into 12 quadratic finite elements (5 elements for each electrode and 2 elements for separator), and both NSVM versions includes 75 states \( (c_7 \times 25 \text{ nodes from 12 quadratic elements}) + c_8 \times 10 \text{ electrode elements}) \). Using the linear assumptions given by reference12 (i.e. a fully-linearized Butler-Volmer equation and constant electrolyte conductivity), a state-variable model (SVM) was also developed with MATLAB to compare to our NSVM. A rigorous pseudo-2D model was also developed using live link between MATLAB and COMSOL5.2a, in which COMSOL is called by MATLAB as a numerical solver. As a result, the SVM, the NSVM, and the baseline model are compared under the same MATLAB environment.

**Input profiles.**—The input current signal was synthesized using the speed profile of US06 drive cycles,35,56 the maximum discharge current rate was scaled to 2.5C (see Figure 6a). A repetition of eight drive cycles were simulated to cover the full 0–100% SOC window. A temperature profile rising from 25°C to 45°C was also artificially synthesized with random noise (see Figure 6b).

**Simulation results.**—With the synthesized input profiles, the two versions of NSVM and the baseline model were implemented for the drive cycle simulation with full SOC window, the sampling time interval \( \Delta t \) was set at 1 sec, and a 2.75 V cutoff voltage was applied as the stop condition. The simulated drive cycle hit the stop voltage limit at \( t = 4471 \text{ sec} \), so there were totally 4472 solution sets computed during the simulation. The implicit NSVM requires 8.95 sec to simulate this drive cycle (2.0 msec per solution) and the explicit NSVM requires 8.50 sec (1.9 msec per solution). There is very little difference between the two NSVM versions in terms of simulation speed, so the iterative loop for the implicit model does not necessarily add to the computational load. However, the COMSOL model requires 470 sec (107 msec per sample) to process this simulation on the same PC, so the NSVM achieves a 50:1 speedup. Compared with NSVM, the SVM does not show much benefit in terms of computation time efficiency (8 sec for one simulation or 1.7 msec per solution).

The simulated terminal voltage responses \( (V_{\text{ex}}) \) are presented in Figure 7a, and the absolute error for the two NSVM versions and SVM are plotted in Figure 7b. According to these results, accuracy for the two different NSVM versions basically resides at the same level (absolute error \(< 15 \text{ mV} \) or relative error \(< 0.5\% \)); however, the SVM shows higher error \( (> 30 \text{ mV} \) as compared with the NSVM. The error plots

**Drive cycle simulation.**—The NSVM developed in this work was coded with MATLAB into two versions: the implicit model solves the algebraic constraint 51 using the method shown in Implicit method section, while the explicit model uses method shown in Explicit method. The cell domain is meshed into 12 quadratic finite elements (5 elements for each electrode and 2 elements for separator), and both NSVM versions includes 75 states \( (c_7 \times 25 \text{ nodes from 12 quadratic elements}) + c_8 \times 10 \text{ electrode elements}) \). Using the linear assumptions given by reference12 (i.e. a fully-linearized Butler-Volmer equation and constant electrolyte conductivity), a state-variable model (SVM) was also developed with MATLAB to compare to our NSVM. A rigorous pseudo-2D model was also developed using live link between MATLAB and COMSOL5.2a, in which COMSOL is called by MATLAB as a numerical solver. As a result, the SVM, the NSVM, and the baseline model are compared under the same MATLAB environment.

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also show that the NSVM has relatively lower accuracy at the early and final states of discharge, and we attribute this to the steeper $\frac{dU}{d\theta}$ slopes. The time-integral approach provided by Equations 47 through 50 requires all coefficients and the source term be constant over the small time interval $[t_{k-1}, t_k]$, a greater $|\frac{dU}{d\theta}|$ value will increase variation to related parameters and therefore weaken the ground for this assumption. To check the simulation results for solid phase diffusion, the particle surface concentration $\theta$ was averaged through $x$ dimension in each electrode (the anode-average $\theta^*$ is defined as $\frac{1}{l_n} \int_{l_n}^{l_n+0} \theta^* dx$ and the cathode-average $\theta^*$ is defined as $\frac{1}{l_p} \int_{l_p}^{l_p+l_s+l_p} \theta^* dx$). The electrode-average $\theta$ vs time profiles are plotted in Figure 8, and both NSVM versions provided excellent agreement with the baseline results; therefore, the approximation approach presented in Solid phase diffusion section provides high accuracy for dynamic simulation. Simulation results for electrolyte diffusion are shown in Figure 9, the boundary concentration vs time plots (Figure 9a and 9b) and the distributed concentration profiles (Figure 9c) all confirm the good accuracy of NSVM. Results for electrolyte potential $\phi_l$ are available in Figure 10, the reference electrolyte potential $\phi_l^{ref} = \phi_l|_{x=0}$ is plotted against time in Figure 10a, and two distributed $\phi_l$ profiles at $t = 332$ sec and $t = 3896$ sec (the 2.4C high rate pulses occur at these time points) are presented in Figures 10b and 10c. According to Figure 10a, the NSVM basically fit with the baseline model and the maximum deviation is about 8 mV, however, this error may cause observable offsets to the potential distribution under a high current pulse at low SOC (Figure 10c where SOC < 10%). In Figure 11, distributed profiles for the surface electrochemical current density $j_s$ are plotted at $t = 332$ sec and $t = 3896$ sec, and the deviation between NSVM and baseline model is higher near the electrode/separator interface because the gradients of electrolyte potential are largest at these interior boundaries.
Parameter identification.—As shown in Simulation results section, both versions of NSVM show excellent accuracy; also, the NSVM is much faster than the rigorous baseline model. Another advantage for NSVM is that the model formulation is unaffected by parameter values. Therefore, it can be used to estimate key parameter values in the pseudo-2D model. In this work, the solid phase diffusivities and reaction rate constants at reference temperature ($D_s|_{T=T_{ref}}$ and $k_r|_{T=T_{ref}}$) are chosen as adjustable parameters, and values listed in Table IV are taken as the truth values for these parameters. The synthetic data for US06 drive cycle were created by running the baseline model with the truth parameter values. We initially scaled these parameters by a factor of 10, and then implemented NSVM for US06 simulation with the scaled parameter values; a MATLAB subroutine for nonlinear least-square regression was used to fit the NSVM to the synthetic data by iteratively adjusting the parameters. Comparisons between the simulated voltage profiles before and after the optimization are presented in Figure 12, and the optimized curves have much better fit to the synthetic data. Table VI lists the ratios of estimated parameters to truth values, and these numbers should ideally converge to 1; therefore the nonlinear parameter estimation in this case deviates from expectation by 2%~17%. To check the cause of inaccuracy, we implemented NSVM with the true parameter values, and the simulated voltage results have an average error of 2.5 mV from the synthetic data; however, when the values listed in Table VI were implemented in NSVM, the average error dropped to 1.2 mV; therefore, these parameters were over-optimized.
Figure 11. Plots for surface electrochemical current density vs $x$: (a) at $t = 332$ s, (b) at $t = 3896$ s.

Table VI. Optimized key parameter values in NSVM through least-squares fitting.

|                | $k_1|T=T_{ref}$ | $D_1|T=T_{ref}$ |
|----------------|-----------------|-----------------|
| Implicit NSVM  | 0.857838        | 1.020308        |
| Explicit NSVM  | 0.833355        | 1.102079        |

Conclusions

The NSVM can be used to implement the pseudo-2D model for a Li-ion cell on a discrete time domain with multiple inputs. The formulated equations include the nonlinear features for pseudo-2D model, and the simulation speed of NSVM is approximately 50 times faster than that of a COMSOL baseline model. In general, the NSVM has excellent accuracy in predicting the concentrations of solid and electrolyte phases, but shows some error for the electrical potentials. The reason is due to the accumulation terms $\frac{\partial c}{\partial t}$ in mass transfer equations, which make the concentration results less sensitive to instantaneous current changes than the solutions of charge conservation equations. For the voltage response at cell terminals, which is determined by coupled mass transfer and charge conservation physics, the NSVM has $\pm 0.5\%$ agreement with the rigorous baseline model. Two types of NSVM, the implicit and explicit versions, are presented; the implicit NSVM solves Butler-Volmer equations by an iterative Newton method, while the explicit NSVM approximates the nonlinear electrochemical kinetics by a quadratic equation. Both NSVM versions achieve approximately the same levels of accuracy and time efficiency, but the explicit NSVM reduces the complexity of code development.

Appendix A: Solid Phase Diffusion

The governing equation and boundary conditions for the solid phase diffusion are given as follows:

$$\frac{\partial c_s}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_s}{\partial r} \right)$$ \[A1\]

$$\frac{\partial c_s}{\partial r} \bigg|_{r=0} = -\frac{D_s}{r} \frac{\partial c_s}{\partial r} \bigg|_{r=R_s} = \frac{j_s}{F} c_s|_{t=0} = c_s,_{\text{ini}}$$ \[A2\]

Considering the temperature-dependency of diffusivities, $D_s$ can be a variable changing with time since the input temperature varies with time, and Laplace transform does not apply to the above equations; therefore, we need to first make the model dimensionless. The modified variables are defined as follows:

$$\theta = \frac{c_s}{c_s,_{\text{ini}}}$$

$$\bar{r} = \frac{r}{R_s}$$ \[A3\]

where $\theta$ and $\bar{r}$ are, respectively, the dimensionless concentration and radius coordinate. Using the expressions shown in A3, the governing equation can be converted as follow:

$$\frac{\partial \theta}{\partial \tau} = \frac{D_s}{R_s^2 \bar{r}^2} \frac{\partial}{\partial \bar{r}} \left( \bar{r}^2 \frac{\partial \theta}{\partial \bar{r}} \right)$$ \[A4\]

Next, the dimensionless time, $\tau$, is defined by the integral of $\frac{D_s}{R_s^2}$ with time:

$$\tau = \int_0^t D_s \frac{dt}{R_s^2}$$ \[A5\]

and the left-hand-side of equation A4 can be derived as follow:

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial \bar{r}}{\partial \tau} \frac{\partial \theta}{\partial \bar{r}} = \frac{\partial}{\partial \bar{r}} \left( \bar{r}^2 \frac{\partial \theta}{\partial \bar{r}} \right)$$ \[A6\]
Substitute Equation 6 into A4 and the time-dependent variable term $\frac{\partial}{\partial t}$ can be canceled form both sides to yield:

$$\frac{\partial}{\partial t} = \frac{\partial}{\partial x} \left( \frac{\partial}{\partial x} \right) \left( \frac{\partial}{\partial y} \right) \left( \frac{\partial}{\partial z} \right)$$  \[A7\]

The dimensionless mass flux at the surface of particle ($r = R$), $b$, is defined as follow:

$$b = \frac{R_i}{FDs}$$  \[A8\]

and the dimensionless boundary/initial conditions can be derived as:

$$\frac{\partial}{\partial r} = 0 \quad \frac{\partial}{\partial t} = -b, \quad 0 = 0 = 0 = \cos \left( \frac{\partial}{\partial \theta} \right)$$  \[A9\]

The Laplace transform can be defined on the dimensionless time domain:

$$L\{ f(t) \} = \int_0^\infty e^{-s t} f(t) \, dt = \tilde{f}(s)$$  \[A10\]

where $f(t)$ is a given function of $t$ and $s$ is the dimensionless Laplace variable. Take the dimensionless Laplace transform for Equations A7 and A9 to obtain:

$$\hat{b}(\hat{r}, \hat{\beta}) = 0 \quad \hat{b} = -\hat{b}(\hat{\beta})$$  \[A11\]

The solution for the dimensionless average concentration $\hat{b}(\hat{r}, \hat{\beta})$ is:

$$\hat{b}(\hat{r}, \hat{\beta}) = \frac{\partial}{\partial \beta} \left( \frac{\partial}{\partial \beta} \right) \left( \frac{\partial}{\partial \beta} \right)$$  \[A13\]

and the dimensionless concentration at the particle surface $\hat{r} = 1$ can be solved as:

$$\hat{b}(\hat{\beta}) = \hat{b}(1, \hat{\beta}) = \frac{\partial}{\partial \beta} \left( \frac{\partial}{\partial \beta} \right) \left( \frac{\partial}{\partial \beta} \right)$$  \[A14\]

The dimensionless particle-average concentration $\hat{b}_{av}$ is defined as follows:

$$\hat{b}_{av} = \frac{\partial}{\partial \beta} \left( \frac{\partial}{\partial \beta} \right) \left( \frac{\partial}{\partial \beta} \right)$$  \[A15\]

and $\hat{b}_{av}$ can be solved by multiply Equation A13 by $\beta^2$ and integrate from 0 to 1:

$$\hat{b}_{av} = \frac{\partial}{\partial \beta} \left( \frac{\partial}{\partial \beta} \right) \left( \frac{\partial}{\partial \beta} \right)$$  \[A16\]

Subtract equation A16 from A14 to obtain the following equation:

$$\hat{b}(\hat{\beta}) = \hat{b}_{av}$$  \[A17\]

where variable $\hat{b}(\hat{\beta}) - \hat{b}_{av}(\hat{\beta})$ stands for the transient response of solid diffusion.

### List of Symbols

- $a$: Active surface area, (m$^2$/m$^3$)
- $A$: Approximated poles for the solid phase diffusion function 12
- $A'$: Coefficient involved to derive the explicit solution 42
- $B$: Forcing matrix for the general state Equation 2
- $B'$: Coefficient used to derive the explicit solution 42
- $b_i$: Approximated gains for the solid phase diffusion function 12
- $c_i$: Lithium ion concentration in electrolyte, (mol/m$^3$)
- $c_i$: Lithium ion concentration in the solid phase, (mol/m$^3$)
- $c_{Li, max}$: Maximum lithium ion concentration in the solid phase, (mol/m$^3$)
- $D$: Diagonal stiffness matrix in formulated electrolyte diffusion Equation 9, ($x^3$)
- $D_{bulk}$: Diffusivity of Li$^+$ in bulk electrolyte, (m$^2$/s)
- $D_s$: Lithium ion diffusivity in the solid phase, (m$^2$/s)$^*$
- $E^*$: Activation Energy for transport and kinetic parameters, (J/mol)
- $F$: Forcing matrix in the finite element Equation 6 for electrolyte diffusion, (mol/C)
- $F$: Faraday constant, 96485 (C/mol)
- $f_0$: Mean activity coefficient of the electrolyte
- $G(b)$: Full-order dimensionless transfer function
- $G'(b)$: Finite Heaviside expansion of $G(b)$
- $\hat{j}$: Vector form of surface electrochemical current density in the electrode regions, (A/m$^2$)
- $j$: Surface electrochemical current density in the electrode regions, (A/m$^2$)
- $j_0$: Exchange current density, (A/m$^2$)
- $\kappa$: Unit imaginary number
- $k_r$: Reaction rate constant, (m$^2$)/mol$^0.5$/s
- $n$: Applied current density, (A/m$^2$)
- $\mathbf{K}$: Stiffness matrix in the finite element Equation 6 for electrolyte diffusion, (nV)
- $\mathbf{M}$: Mass matrix in the finite element Equation 6 for electrolyte diffusion, (nV)
- $\mathbf{N}$: Total number of meshed elements in the two electrode domains, $N_e = 5 + 5 = 10$
- $N$: Total number of approximated Heaviside expansion terms for solid phase diffusion, $N = 4$
- $N_s$: Total number of states, $N_s = 75$
- $Q_i$: Laplace transform of eigenfunctions for solid phase diffusion
- $Q_s$: Time derivative of inverse Laplace transform of eigenfunctions $\{Q_s\}$
- $Q_s$: Inverse Laplace transform of eigenfunction for solid phase diffusion
- $R$: Constant, 8.314 (J/mol/K)
- $R$: Radius of the solid particles, (m)
- $\mathbf{R}$: Residual for Butler-Volmer equation, (A/m$^3$)
- $\mathbf{ResBV}$: Residue for spatially discretized Butler-Volmer equation, (A/m$^3$)
- $r$: Radial coordinate of the particle in the electrodes, (m)
- $\bar{r}$: Dimensionless radius coordinate
- $T$: Temperature, (K)
- $\tau$: Time, (s)
- $\tau^+$: Transference number of lithium ion species
- $u$: Input signal for NSVM
- $U$: Open circuit potential, (V), listed in Table I
- $V$: External potential drop across the cell, (V)
- $x$: Matrix for eigenvectors
- $x$: State variable vector in Eq. 2
- $y$: Output signal
- $\chi$: Jacobian matrix
- $\chi$: Step change for the unknown variables
- $\psi$: External resistance, (Ωm$^2$)
- $\psi$: Unknown variable, defined by Eq. 41

### Greek

- $a$: Dimensionless concentration of solid phase
- $\alpha$: Initial dimensionless concentration of solid phase
- $\beta$: Laplace transform of dimensionless concentration of solid phase
- $\beta^*$: Dimensionless Laplace transform for the surface concentration
- $\beta_{av}$: Dimensionless particle-average concentration of solid phase
- $\beta_{avg}$: Dimensionless Laplace transform for the average concentration
- $\delta$: Dimensionless Laplace transform for the boundary mass flux for solid phase diffusion
- $\delta_{avg}$: Dimensionless Laplace variable
- $\epsilon$: Dimensionless time
- $\eta$: Electrochemical overpotential, (V)
- $\eta$: Electrochemical overpotential defined in Eq. 37 (V)
- $\phi_{0}$: Electric Potential in the solid phase, (V)
- $\phi_{0}$: Electric Potential in the electrolyte phase, (V)
- $\phi_{0}$: Absolute reference for solid phase potential, (V)
- $\phi_{0}$: Absolute reference for electrolyte potential, (V)
- $\phi_{l}$: Linear solution of Electric Potential in the solid phase, (V)
- $\phi_{l}$: Linear solution of Electric Potential in the electrolyte phase, (V)
- $\phi_{r}$: Electric conductivity of bulk electrolyte, (S/m)
- $\phi_{s}$: Effective conductivity of the electrolyte phase, (S/m)
- $\kappa_{bulk}$: Conductivity resulted from diffusion in the electrolyte phase, (S/m)$^*$
- $\kappa_{bulk}$: Conductivity of the solid phase, (S/m)$^*$
- $\kappa_{eff}$: Matrix exponential operator defined in Eq. 40
- $\kappa_{eff}$: Matrix exponential operator defined in Eq. 40
- $\kappa_{eff}$: Dimensionless angular frequency
- $\epsilon_0$: Porosity of the void phase in the separator
- $\epsilon_1$: Porosity of the solid phase in the electrode
- $\epsilon_{diag}$: ith diagonal element in Eq. 46
- $\epsilon_{diag}$: ith eigenvalues of matrix $D$ for electrolyte diffusion equation in Eq. 8
References

1. V. Ramadasigan, 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).

2. S. Atlung, K. West, and T. Jacobsen, Dynamic Aspects of Solid-Solution Cathodes for Electrochemical Power Sources. Journal of the Electrochemical Society, 126(8), A1097 (1979).

3. S. Santhanagopalan, Q. Z. Guo, P. Ramadas, and R. E. White, Review of models for predicting the cycling performance of lithium ion batteries. Journal of Power Sources, 156(2), 620 (2006).

4. K. W. Jacobsen, T. Atlas, and S. Atlung, Modeling of Porous Insertion Electrodes with Lumped Electrolyte. Journal of the Electrochemical Society, 129(7), 1480 (1982).

5. 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).

6. M. Doyle and J. Newman, Analysis of capacity-rate data for lithium batteries using simplified models of the discharge process. Journal of Applied Electrochemistry, 27(7), 846 (1997).

7. P. W. C. Northrop, V. Ramadasigan, S. De, and V. R. Subramanian, Coordinate Mathematical Model Reformulation for Lithium-Ion Battery Simulations: Galvanostatic Boundary Conditions. Journal of the Electrochemical Society, 156(4), A260 (2009).

8. V. S. Kumar, Reduced order model for a lithium ion cell with uniform reaction rate approximation. Journal of Power Sources, 222, 426 (2013).

9. V. Booveragavan, S. Harinipriya, and V. R. Subramanian, Towards real-time (millisecond) parameter estimation for lithium-ion batteries using reformulated physics-based models. Journal of Power Sources, 183(1), 361 (2008).

10. G. K. Prasad and C. D. Rahm, Model based identification of aging parameters in lithium ion batteries. Journal of Power Sources, 232, 79 (2013).

11. K. A. Smith, C. D. Rahm, and C. Y. Wang, Control oriented IDElectrochemical model of lithium ion battery. Energy Conversion and Management, 48(9), 2565 (2007).

12. T. S. Dao, C. P. Vyasarayani, and J. McPhee, Simplification and order reduction of lithium-ion battery model based on porous-electrode theory. Journal of Power Sources, 198, 329 (2013).

13. G. L. Plott, Battery Management Systems Volume I: Battery Modeling. 2015, Norwood, MA: Artech House publishing.

14. T. R. Tanm, C. D. Rahm, and C. Y. Wang, State of charge estimation of a lithium ion cell based on a temperature dependent and electrolyte enhanced single particle model. Energy, 80, 731 (2015).

15. S. Santhanagopalan and R. E. White, Online estimation of the state of charge of a lithium ion cell. Journal of Power Sources, 161(2), 1346 (2006).

16. E. Prada, D. Di Domenico, Y. Crefz, J. Bernard, V. Sauvain-Moyart, and F. Huet, A Simplified Electrochemical and Thermal Aging Model of LiFePO4 Graphite Li-Ion Batteries: Power and Capacity Fade Simulations. Journal of the Electrochemical Society, 160(6), A616 (2013).

17. O. Zhang and R. E. White, Capacity fade analysis of a lithium ion cell. Journal of Power Sources, 179(2), 793 (2008).

18. A. Jokar, B. Rajabli, M. Desilets, and M. Laicroc, An Inverse Method for Estimating the Electrochemical Parameters of Lithium-Ion Batteries. Journal of the Electrochemical Society, 163(14), A2876 (2016).

19. D. Di Domenico, A. Stefanopoulou, and G. Fiengo, Lithium-Ion Battery State of Charge and Critical Surface Charge Estimation Using an Electrochemical Model-Based Extended Kalman Filter. Journal of Dynamic Systems Measurement and Control, Transactions of the ASME, 132(6) (2010).

20. R. Masoudi, T. Uchida, and J. McPhee, Parameter estimation of an electrochemistry-based lithium-ion battery model. Journal of Power Sources, 291, 215 (2015).

21. L. Q. Zhang, C. Lyu, G. Hinds, L. X. Wang, W. L. Luo, J. Zheng, and K. H. Ma, Parameter Sensitivity Analysis of Cylindrical LiFePO4 Battery Performance Using Multi-Physics Modeling. Journal of the Electrochemical Society, 161(5), A762 (2014).

22. S. Santhanagopalan, Q. Zhang, K. Kumaresh, and R. E. White, Parameter estimation and life modeling of lithium-ion cells. Journal of the Electrochemical Society, 155(4), A345 (2008).
53. B. V. Minchev and W. M. Wright, A review of exponential integrators for first order semi-linear problems. 2005, Norwegian University of Science and Technology Trondheim, NORWAY.

54. J. N. Reddy, *An Introduction to the Finite Element Method*. 3rd ed. 2006: McGraw-Hill.

55. B. Y. Liaw and M. Dubarry, From driving cycle analysis to understanding battery performance in real-life electric hybrid vehicle operation. *Journal of Power Sources*, 174(1), 76 (2007).

56. S. C. Davis, S. W. Diegel, and R. G. Boundy, *Transportation Energy Data Book*. 34 ed. 2015: DIANE Publishing.