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To cite this article: Le Xu et al 2023 J. Electrochem. Soc. 170 120525

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Comparative Analysis of Numerical Methods for Lithium-Ion Battery Electrochemical Modeling

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Electrochemical models provide insights into the battery internal states and have become powerful tools for battery design and management. These models consist of partial differential equations (PDEs) that are solved numerically. In this paper, we compare two spatial discretization methods commonly used to numerically solve the governing PDEs in the context of Lithium ion batteries, namely finite difference method (FDM) and finite volume method (FVM) in terms of model accuracy and mass conservation guarantee. First, we provide the mathematical details to carry out the spatial discretization for both FDM and FVM to solve the battery single particle model (SPM). SPM parameters are identified from experimental data, and sensitivity analysis is conducted to study parameter identifiability under different current input profiles, followed by model accuracy and mass conservation analysis of the two numerical schemes. Leveraging the third order Hermite extrapolation approach, an enhanced FVM scheme is proposed in this paper to improve the model accuracy of standard FVM which relies on linear extrapolation. This paper shows that the FVM scheme with Hermite extrapolation leads to accurate and robust control-oriented battery model while guaranteeing mass conservation and high accuracy.

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Manuscript submitted April 4, 2023; revised manuscript received November 2, 2023. Published December 21, 2023.

Nomenclature

Cell cross-sectional area [m ²]
Solid-phase diffusion [m ² /s]
Faraday's constant [C/mol]
Electrode thickness [m]
Applied current [A]
Universal gas constant [J/(mol·K)]
Particle radius [m]
Lumped resistance $[\Omega]$
Open-circuit potential [V]
Specific interfacial surface area [m ⁻¹]
Concentration in solid phase [mol/m ³]
Maximum solid-phase concentration [mol/m ³]
Surface solid-phase concentration [mol/m ³]
Electrode volume-average concentration [mol/m ³]
Exchange current [A/m ²]
Reaction rate constant $[m^{2.5}/(mol^{0.5}s)]$
Overpotential [V]
Active volume fraction of solid phase
Reference stoichiometry at 100% SOC
Reference stoichiometry at 0% SOC
Bulk normalized lithium concentration
Cathode (j=p) and anode (j=n)

Lithium-ion battery (LIB) is one energy storage technology with high specific energy density and long cycle life.¹ A battery management system (BMS) is a combination of software and firmware that monitors and optimizes battery utilization to guarantee safety and longevity of the battery system. BMSs rely on models, either in the form of empirical models² or physics-based models,³ to predict internal battery states that are not measurable via physical sensors. Empirical models, in the form of equivalent circuit models, simulate the battery electrical behavior⁴ and they are in the form of ordinary differential equations (ODEs). Although, their mathematical simplicity makes them good candidates for BMS implementation, they require a high calibration effort. In recent years, more attention has been given to physics-based models expressed in the form of partial differential equations (PDEs) describing the thermodynamic and electrochemical processes within the solid and electrolyte phase inside the cell. Most notable physics-based models include the Doyle-Fuller-Newman (DFN) model⁵ and its reduced counterparts, such as the single particle model (SPM),³ and the enhanced single particle model (ESPM)⁶. All these models require some numerical scheme to solve the governing PDEs.

The finite difference method (FDM) is one of the most widely used methods to solve LIB PDEs. For example, DUALFOIL⁷ uses the FDM scheme to solve all the governing PDEs in the DFN model. Padé approximation and spectral methods⁸ are also used to solve the LIB PDEs. For example, fastDFN⁹ uses the Padé approximation to solve the solid-phase diffusion equations and FDM to solve the electrolyte concentration and potential equations, and solid potential equation in DFN. One limitation of using Padé approximation to solve physics-based battery models is in that this method does not handle moving boundary conditions like the one for example, used in the core-shell ESPM, where a moving boundary ODE is used to model the phase transition in the positive electrode of LFP batteries.^{10,11}

The finite volume method (FVM) is an efficient numerical scheme for solving PDEs.^{12,13} When simulating electrochemical models, one concern is the mass concentration guarantee of the numerical method used, in terms of the simulated amount of lithium that intercalates and de-intercalates remains the same during cycling. Among the above methods, FVM is the only one that guarantee mass conservation by design. Yet, very few works in the literature use FVM to entirely solve battery electrochemical models. In one study,¹⁴ FDM is used to solve the solid-phase diffusion equation while FVM is used to solve the electrolyte diffusion equation in a ESPM. FVM is used in M-PET¹⁵ to solve the DFN model, and a variant of FVM is used to discretize the solid-phase diffusion equation. LIONSIMBA¹⁶ uses FVM to solve the electrolyte concentration, electrolyte potential, and solid potential equations in DFN, whereas the solid-phase diffusion equation is solved using the spectral scheme or FDM scheme. Python Battery Mathematical Modeling (PyBaMM)¹³ provides the option to use FVM as numerical method to solve the DFN and its reduced versions. In another study,¹⁷ FVM is used to solve the DFN model, and three different FVM-based spatial discretization schemes were adpoted to discretize the solid-phase diffusion equation.

There is a gap in the literature regarding analysis of mass conservation property of different spatial discretization schemes used to solve LIB physics-based models. Current studies mainly focus on comparison of different numerical methods in terms of their

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output accuracy.¹⁸ For instance, in one study,¹⁹ a lithium metal battery model is used to show that lack of mass conservation in the electrolyte cannot be ignored when using FDM, and proper revision for the boundary conditions is needed. In another study,²⁰ an additional correction equation is added to SPM to guarantee conservation of total lithium-ion in the solid phase. Ashlee et al.,²¹ proposed two revised FDM schemes to solve the solid diffusion equation showing that with sufficient spatial grid resolution (i.e., 100 spatial discretization nodes), mass conservation is guaranteed. These studies do not look at electrochemical models using FDM under low spatial discretization nodes for control applications or the dependence of current C-rate.

In this work, through simulation-based analysis, we aim to investigate the mass conservation property of FDM when used to solve battery electrochemical models as a function of spatial discretization nodes and C-rate. This study focuses on SPM model, because we keen on control-oriented applications. This work provides four contributions: (1) the implementation details of FVM applied to spherical coordinates governing equations. To the best of our knowledge, this result has not been shown in any publication before. (2) a new FVM scheme based on Hermite extrapolation leading to higher accuracy when compared to the normally used FVM scheme with linear extrapolation. (3) a comprehensive parameter sensitivity analysis based on sensitivity matrix under different current input profiles. (4) comparison of FDM and two FVM schemes in terms of model accuracy and mass conservation property, with the aim of generality of the controloriented model.

This paper is structured as follows. First, the electrochemical SPM model and the numerical FDM and two FVM spatial discretization methods are introduced. Second, the Hermite extrapolation method is used in the FVM to calculate solid-phase surface concentration of the SPM. Then, model parameter sensitivity is studied, and parameter identification is performed using experimental data from a graphite/silicon anode and Nickel-Manganese-Cobalt (NMC) cathode cylindrical cell. This is followed by a series of simulations to explore the model accuracy and mass conservation behavior. Finally, the last Section provides a summary of the main findings of this paper and concluding remarks. **Notation**.

(1) ∇ is the Nabla operator defined as^{22,23}:

$$\nabla = \frac{\partial}{\partial x}\mathbf{i} + \frac{\partial}{\partial y}\mathbf{j} + \frac{\partial}{\partial z}\mathbf{k} \text{ (Cartesian coordinates)}$$
$$\nabla = \frac{\partial}{\partial r}\mathbf{u} + \frac{1}{r\sin\phi}\frac{\partial}{\partial\theta}\mathbf{v} + \frac{1}{r}\frac{\partial}{\partial\phi}\mathbf{w} \text{ (Spherical coordinates)}$$

where **i**, **j**, and **k** are unit vectors in the x, y, and z direction in the cartesian coordinate system, and **u**, **v**, and **w** are unit vectors in the r, θ , and ϕ direction in the spherical coordinate system.

(2) ∇f is the Nabla operator applied to a scalar variable *f*, which results in the gradient of *f* given by²²:

$$\nabla f = \frac{\partial f}{\partial x} \mathbf{i} + \frac{\partial f}{\partial y} \mathbf{j} + \frac{\partial f}{\partial z} \mathbf{k} \text{ (Cartesian coordinates)}$$
$$\nabla f = \frac{\partial f}{\partial r} \mathbf{u} + \frac{1}{r \sin \phi} \frac{\partial f}{\partial \theta} \mathbf{v} + \frac{1}{r} \frac{\partial f}{\partial \phi} \mathbf{w} \text{ (Spherical coordinates)}$$

(3) $\nabla \cdot (\nabla f)$ is the divergence of the gradient of *f*, and is defined as:²²

$$\nabla \cdot (\nabla f) = \nabla^2 f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} (Cartesian coordinates)$$
$$\cdot (\nabla f) = \nabla^2 f = \frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial f}{\partial r} \right) + \frac{1}{\sin \phi} \frac{\partial}{\partial \phi} \left(\sin \phi \frac{\partial f}{\partial \phi} \right) + \frac{1}{\sin^2 \phi} \frac{\partial^2 f}{\partial \theta^2} \right] (Spherical coordinates)$$

(4) Given the vector $\mathbf{x} = (x_1, x_2, \dots, x_n) \in \mathbb{R}^n, \|\mathbf{x}\|_2$ is the Euclidean norm calculated by:

$$\|\mathbf{x}\|_2 = \sqrt{x_1^2 + \dots x_n^2}.$$

(5) In this paper, the positive electrode, and negative electrode are referred to as cathode and anode, respectively.

Battery Model and Numerical Spatial Discretization Schemes

In this study, we focus on the analysis and comparison of FDM and FVM schemes for the SPM electrochemical model.

SPM model.—SPM approximates each electrode by a single spherical particle, assuming constant electrolyte concentration and potential²⁴ as graphically depicted in Fig. 1. These simplifications greatly reduce the complexity of the model, and they are usually valid under low C-rate of operation. The equations and output of SPM are listed in Table I, where the mass transport PDE governing the solid-phase is described by the PDE in Eq. 1.

In this study, the FDM and FVM numerical schemes are used to spatially discretize Eq. 1 into a set of ODEs that can be solved using numerical solvers, such as ode15s in MATLAB, or SUNDIALS developed by Lawrence Livermore National Laboratory²⁵. Figure 2 shows a schematic representation of the FDM (top) and FVM (bottom) schemes. In FDM, the calculation domain is discretized using nodal points, and the unknown variable ϕ is solved at each node points (i.e., ϕ_i). In FVM scheme, on the other hand, the calculation domain is divided into control volumes (CVs), where each volume has a representative point located at its center, and the volume-averaged value of the unknown variable ϕ calculated in each CV and referred to as $\bar{\phi}_i$ is given as:

$$\bar{\phi}_i = \frac{1}{V_i} \int_{CV_i} \phi_i dV$$
^[7]

where V_i represents the volume of the i^{th} CV.



Table I. Governing equations and output of SPM.		
Variable	Equation	
Mass transport in solid phase	$\frac{\partial c_{s,j}}{\partial t} = \frac{D_{s,j}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_{s,j}}{\partial r} \right), \ j = n, \ p$	[1]
B.C.	$\frac{\partial c_{s,j}}{\partial r}\Big _{r=0} = 0, \ D_{s,j}\frac{\partial c_{s,j}}{\partial r}\Big _{r=R_{s,j}} = \frac{-l_{appg}(l_{app})}{a_{s,j}A_{cell}L_{j}F}$ $a_{s,j} = \frac{3}{R_{s,j}}\varepsilon_{j}, g(l_{app}) = \begin{cases} -1, & j = p\\ 1 & j = n \end{cases}$	[2]
Electrode overpotential	$\eta_j = \frac{2RT}{F} \sinh^{-1} \left(\frac{I_{appg}(I_{app})}{2a_{s,j}AL_{j}i_{0,j}} \right), j = n, p$	[3]
	$i_{0,j} = k_j F \sqrt{c_{e,j}^{avg} c_{s,j}^{surf} (c_{s,j}^{\max} - c_{s,j}^{surf})}$	[4]
Cell voltage	$V_{cell} = U_p \left(\frac{c_{s,p}^{surf}}{c_{s,p}^{max}} \right) - U_n \left(\frac{c_{s,n}^{surf}}{c_{s,n}^{max}} \right) + \eta_p - \eta_n - R_l \cdot I_{app}$	[5]
State-of-Charge	$\begin{aligned} \theta_{p}^{bulk} &= \frac{1}{\frac{4}{3}\pi R_{s,p}^{3} c_{s,p}^{\max}} \int_{r=0}^{r=R_{s,p}} 4\pi r^{2} c_{s,p}(r,t) dr \\ \theta_{n}^{bulk} &= \frac{1}{\frac{4}{3}\pi R_{s,n}^{3} c_{s,n}^{\max}} \int_{r=0}^{r=R_{s,n}} 4\pi r^{2} c_{s,n}(r,t) dr \\ SOC_{p} &= \frac{\theta_{p}^{0} - \theta_{p}^{bulk}}{\theta_{p}^{0} - \theta_{p}^{100}}, SOC_{n} &= \frac{\theta_{n}^{bulk} - \theta_{n}^{0}}{\theta_{n}^{100} - \theta_{n}^{0}} \end{aligned}$	[6]



Figure 2. One-dimensional spatial discretization scheme. (a) FDM. (b) FVM.

In the remainder of this paper, we use the index *i* to refer to either the *i*th nodal point in the FDM scheme, or the *i*th control volume in the FVM scheme. ϕ_i used in the context of FDM indicates the variable value at the nodal point, whereas $\bar{\phi}_i$ used in the context of FVM indicates the volume-average value of the variable for each control volume. Also, we use N_r to refer to either the total number of spatial discretization nodes in FDM, or the total number of control volumes in FVM.

Previous studies have provided details on FDM scheme implementation for SPM.^{14,26} However, mathematical details behind the FVM scheme implementation for SPM nor DFN are not well documented. In this paper, we provide two approaches for FVM implementation. The first approach relies on variable substitution to transform Eq. 1 to cartesian coordinates and then solve it, and the second method is based on the solution of Eq. 1 in spherical coordinates. Such approaches developed for SPM in this paper can be extended and applied to ESPM and DFN models.²⁷

Finite difference method scheme.—The two governing PDEs of SPM, describing the lithium concentration within the positive and negative spherical electrode particles, respectively, are commonly solved using the FDM scheme due mainly to its simplicity. Using the central difference FDM scheme, the first and second partial derivates can be approximated as:

$$\frac{\partial c_{s,j}}{\partial r} = \frac{c_{s(i+1),j} - c_{s(i-1),j}}{2\Delta r} + O(\Delta r^2)$$

$$\frac{\partial^2 c_{s,j}}{\partial r^2} = \frac{c_{s(i+1),j} - 2c_{s(i,j} + c_{s(i-1),j}}{\Delta r^2} + O(\Delta r^2), \ j = n, p$$
[8]

where $c_{s,j}$ is the solid-phase concentration, *r* represents the radial direction, and $i = 1 \cdots N_r$ is the index of each nodal point, and $O(\Delta r^2)$ is the truncation error.

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Applying the above second order FDM scheme to the solid diffusion equation Eq. 1, the spatial discretization for each electrode is obtained as:

$$\frac{\partial c_{si,j}}{\partial t} = \frac{D_{s,j}}{\Delta r^2} \left[\left(1 + \frac{1}{i} \right) c_{s(i+1),j} - 2c_{si,j} + \left(1 - \frac{1}{i} \right) c_{s(i-1),j} \right], \ j = n, p$$
[9]

where $i \in [1, N_r]$ is the *ith* nodal point in the radial direction. More details can be found in these studies.^{14,28} The solid-phase diffusion equation Eq. 9 is then transformed into a system of N_r ODEs whose state space representation is as follows¹⁴:

$$\mathbf{\dot{c}}_{s,j} = \frac{D_{s,j}}{(R_{s,j}/N_r)^2} \mathbf{A}_{s,j} \mathbf{c}_{s,j} + \frac{-g(I_{app})}{A_{cell} L_j F_{a_{s,j}}(R_{s,j}/N_r)} \mathbf{B}_{s,j} I_{app}, \quad \mathbf{c}_{s,j} \in \mathbb{R}^{N_r \times 1}, \ j = n, p$$

$$\mathbf{A}_{s,j} = \begin{bmatrix} -2 & 2 & 0 & 0 & \cdots & 0 \\ \frac{1}{2} & -2 & \frac{3}{2} & 0 & \cdots & 0 \\ 0 & \frac{2}{3} & -2 & \frac{4}{3} & \cdots & 0 \\ 0 & 0 & \frac{3}{4} & -2 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & -2 \end{bmatrix}_{N_r \times N_r} , \ \mathbf{B}_{s,j} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ \vdots \\ \left(2 + \frac{2}{N_r}\right) \right]_{N_r \times 1} , \ j = n, p$$
[10]

Finite volume method scheme.—The FVM scheme solves the governing equation in the integral form, thus guaranteeing mass conservation. FVM has been used to solve the transient transport problem in cartesian coordinates in many research fields, such as heat transfer equations²⁹ and multiphase flow equations.²³ Neglecting the convection term and source term, the transient transport equation in cartesian coordinates can be written as³⁰:

$$\frac{\partial \phi}{\partial t} = \frac{\partial}{\partial x} \left(D_s \frac{\partial \phi}{\partial x} \right)$$
[11]

where ϕ is the unknown variable, and D_s is the diffusion coefficient.

FVM scheme in cartesian coordinates.—Special attention must be paid when applying the FVM scheme to SPM where the solid-phase equation Eq. 1 is defined in the spherical coordinate system. In order to solve Eq. 1, the following change of variable is used:

$$u_{s,j} = c_{s,j}r \tag{12}$$

After above variable substitution, the diffusion equation Eq. 1 is transformed into cartesian coordinates:

$$\frac{\partial u_{s,j}}{r\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_{s,j} \frac{\frac{\partial u_{s,j}}{\partial r} r - u_{s,j}}{r^2} \right), \ j = n, p$$
[13]

which can be further written as:

$$\frac{\partial u_{s,j}}{\partial t} = \frac{\partial}{\partial r} \left(D_{s,j} \frac{\partial u_{s,j}}{\partial r} \right), \ j = n, p$$
[14]

with boundary conditions before and after variable substitution listed in Table II.

As can be seen from Eq. 14, the solid diffusion equation written in terms of the new variable $u_{s,j}$ resembles the transport equation defined in the cartesian coordinates (Eq. 11), which makes it easier to solve using the FVM scheme.

The calculation domain is divided into different CVs in spherical coordinates, as shown in Fig. 3(a) and the *ith* CV over which the governing equation is solved in spherical coordinates is shown in Fig. 3(b), and denoted as $CV_i^{\text{spherical}}$. After the variable substitution Eq. 12, Eq. 1 and its boundary conditions, now defined in cartesian coordinates (i.e., Eq. 14), are solved on the $CV_i^{\text{cartesian}}$ control volume, where $CV_i^{\text{cartesian}}$ is obtained by "unrolling" the $CV_i^{\text{spherical}}$, as shown in Fig. 3(c). Here, we approximated the area of the left and the right surface of $CV_i^{\text{cartesian}}$ with the average surface. Specifically, the surface areas of the left (i - 1/2) and right (i + 1/2) boundaries of $CV_i^{\text{spherical}}$ are given by:

$$A_{i-\frac{1}{2}}^{\text{spherical}} = 4\pi r_{i-\frac{1}{2}}^{2}$$

$$A_{i+\frac{1}{2}}^{\text{spherical}} = 4\pi r_{i+\frac{1}{2}}^{2}$$
[15]

and the surface areas of the left (i - 1/2) and right (i + 1/2) boundaries of $CV_i^{\text{cartesian}}$ are given by:

$$A_{i-\frac{1}{2}}^{\text{cartesian}} \approx 4\pi r_i^2$$

$$A_{i+\frac{1}{2}}^{\text{cartesian}} \approx 4\pi r_i^2 \qquad [16]$$

Finally, the volume of $CV_i^{\text{spherical}}$ and $CV_i^{\text{cartesian}}$ are calculated as:

$$V_i^{\text{spherical}} = \frac{4}{3}\pi (r_{i+\frac{1}{2}}^3 - r_{i-\frac{1}{2}}^3)$$

$$V_i^{\text{cartesian}} \approx \frac{4}{3}\pi (r_{i+\frac{1}{2}}^3 - r_{i-\frac{1}{2}}^3)$$
[17]

Integrating Eq. 14 over the control volume $CV_i^{\text{cartesian}}$ gives:

$$\int_{CV_i^{\text{cartesian}}} \frac{\partial u_{s,j}}{\partial t} dV = \int_{CV_i^{\text{cartesian}}} \frac{\partial}{\partial r} \left(D_{s,j} \frac{\partial u_{s,j}}{\partial r} \right) dV, \ j = n, p \quad [18]$$

Applying the Gauss theorem (also known as divergence theorem) to the right-hand side of Eq. 18, the volume integration is replaced by surface integration³⁰:

$$\int_{CV_i^{\text{cartesian}}} \frac{\partial}{\partial r} \left(D_{s,j} \frac{\partial u_{s,j}}{\partial r} \right) dV = \oint_{A_i^{\text{cartesian}}} \left(D_{s,j} \frac{\partial u_{s,j}}{\partial r} \cdot n \right) dA, \ j = n, p$$
[19]

where *n* is the outward pointing unit normal to the surface $A_i^{\text{cartesian}}$.

Table II. Boundary conditions of Eq. 1 before and after the variable substitution Eq. 12.





Figure 3. 2D illustration of control volumes in different coordinates. (a) spherical particle, (b) control volume in spherical coordinates, and (c) control volume in cartesian coordinates.

Substituting Eq. 19 into Eq. 18, we obtain²³:

$$\int_{CV_i^{\text{cartesian}}} \frac{\partial u_{s,j}}{\partial t} dV = \oint_{A_i^{\text{cartesian}}} \left(D_{s,j} \frac{\partial u_{s,j}}{\partial r} \cdot n \right) dA$$
$$= \int_{A_i^{\text{cartesian}}} \left(D_{s,j} \frac{\partial u_{s,j}}{\partial r} \right) dA - \int_{A_i^{\text{cartesian}}} \left(D_{s,j} \frac{\partial u_{s,j}}{\partial r} \right) dA, \quad j = n, p$$
[20]

For each $CV_i^{\text{cartesian}}$, Eq. 20 is further written as:

$$\frac{\partial \bar{u}_{si,j}}{\partial t} V_i^{\text{cartesian}} = D_{s,j} \frac{\partial u_{s,j}}{\partial r} \bigg|_{i+\frac{1}{2}} A_{i+\frac{1}{2}}^{\text{cartesian}} - D_{s,j} \frac{\partial u_{s,j}}{\partial r} \bigg|_{i-\frac{1}{2}} A_{i-\frac{1}{2}}^{\text{cartesian}}, j = n, p$$
[21]

where $\bar{u}_{si,j}$ is the volume-average value of $u_{s,j}$ in cartesian coordinates. Index $i + \frac{1}{2}$ represents the interface between the *ith* and (i + 1)th CV, and index $i - \frac{1}{2}$ represents the interface between the *ith* and (i - 1)th CV.

Then, the diffusion terms $D_{s,j}\left(\frac{\partial u_{s,j}}{\partial r}\right)$ at the two interfaces are numerically approximated with the finite difference scheme:

$$\frac{\frac{\partial u_{s,j}}{\partial r}}{\frac{1}{l_{i+\frac{1}{2}}}} \approx \frac{\bar{u}_{s(i+1),j} - \bar{u}_{si,j}}{\Delta r}$$

$$\frac{\frac{\partial u_{s,j}}{\partial r}}{\frac{1}{l_{i-\frac{1}{2}}}} \approx \frac{\bar{u}_{si,j} - \bar{u}_{s(i-1),j}}{\Delta r}, j = n, p \qquad [22]$$

Finally, when N_r control volumes are used for spatial discretization, Eq. 21 is written as follows:

• i = 1, i.e., the first control volume near the particle center:

$$\frac{\partial \bar{u}_{s_{1,j}}}{\partial t}V_{1}^{\text{cartesian}} = D_{s,j} \frac{\bar{u}_{s_{2,j}} - \bar{u}_{s_{1,j}}}{\Delta r} A_{1+\frac{1}{2}}^{\text{cartesian}}$$
$$- D_{s,j} \frac{\bar{u}_{s_{1,j}} - \bar{u}_{s_{0,j}}}{\Delta r} A_{1-\frac{1}{2}}^{\text{cartesian}}, \ j = n, p$$
[23]

• $1 < i < N_r$, i.e., the control volumes within the particle:

$$\frac{\partial \bar{u}_{si,j}}{\partial t} V_i^{\text{cartesian}} = D_{s,j} \frac{\bar{u}_{s(i+1),j} - \bar{u}_{si,j}}{\Delta r} A_{i+\frac{1}{2}}^{\text{cartesian}} - D_{s,j} \frac{\bar{u}_{si,j} - \bar{u}_{s(i-1),j}}{\Delta r} A_{i-\frac{1}{2}}^{\text{cartesian}}, \ j = n, p$$
[24]

• $i = N_r$, i.e., the last control volume near the particle surface:

$$\frac{\partial \tilde{u}_{sN_{r,j}}}{\partial t} V_{N_{r}}^{\text{cartesian}} = D_{s,j} \frac{\tilde{u}_{s(N_{r}+1),j} - \tilde{u}_{sN_{r},j}}{\Delta r} A_{N_{r}+\frac{1}{2}}^{\text{cartesian}} - D_{s,j} \frac{\tilde{u}_{sN_{r},j} - \tilde{u}_{s(N_{r}-1),j}}{\Delta r} A_{N_{r}-\frac{1}{2}}^{\text{cartesian}}, \ j = n, p \qquad [25]$$

It should be noted that both $\bar{u}_{s0,j}$ and $\bar{u}_{s(N_r+1),j}$ are outside the calculation domain. In FVM, $\bar{u}_{s0,j}$ and $\bar{u}_{s(N_r+1),j}$ are referred to as "ghost cells", and Appendix A describes how to solve their values by using boundary conditions.³¹

Finally, given the discretized solid-phase concentration states vector:

$$\bar{\mathbf{u}}_{s,j} = [\bar{u}_{s1,j}, \bar{u}_{s2,j} \cdots \bar{u}_{sN_r,j}]^T \in \mathbb{R}^{N_r \times 1}, \ j = n, p$$
[26]

Eq. 23-Eq. 25 can be written in the following state-space form:

$$\dot{\mathbf{u}}_{s,j} = \mathbf{A}_{s,j}^{\text{cartesian}} \mathbf{\bar{u}}_{s,j} + \mathbf{B}_{s,j}^{\text{cartesian}} I_{app}, \ j = n, p$$
[27]

where matrices $\mathbf{A}_{s,j}^{\text{cartesian}}$ and $\mathbf{B}_{s,j}^{\text{cartesian}}$ take the following expressions:

$$\int_{CV_i^{\text{spherical}}} \nabla \cdot (D_{s,j} \nabla c_{s,j}) dV = \oint_{A_i^{\text{spherical}}} (D_{s,j} \nabla c_{s,j} \cdot n) dA, \ j = n, p \quad [33]$$

Substituting Eq. 33 into Eq. 32 gives²³:

$$\mathbf{A}_{s,j}^{\text{cartesian}} = \frac{3D_{s,j}}{\Delta r^2} \begin{bmatrix} \frac{-3}{4} & \frac{1}{4} & 0 & 0 & \cdots & 0\\ \frac{9}{28} & \frac{-9}{14} & \frac{9}{28} & 0 & \cdots & 0\\ 0 & \frac{25}{76} & -\frac{25}{38} & \frac{25}{76} & \cdots & 0\\ 0 & 0 & \frac{49}{148} & -\frac{49}{74} & \cdots & 0\\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots\\ 0 & 0 & 0 & \cdots & \frac{\left(\frac{1}{2} + (N_r - 1)\right)^2}{3N_r^2 - 3N_r + 1} & \beta_1 \frac{\left(\frac{1}{2} + (N_r - 1)\right)^2}{3N_r^2 - 3N_r + 1} \end{bmatrix}_{(N_r \times N_r)}$$
[28]

$$\mathbf{B}_{s,j}^{\text{cartesian}} = \begin{bmatrix} 0\\0\\0\\...\\\beta_2 \end{bmatrix}_{(N_r \times 1)} j = n, p$$
[29]

$$\begin{aligned} \beta_1 &= \frac{-2}{\frac{\Delta r}{2R_{s,j}} - 1} - 3, \, \beta_2 \\ &= -\frac{3R_{s,j}^2(2N_r - 1)^2 g(I_{app})}{2\Delta r(2R_{s,j} - \Delta r)(3N_r^2 - 3N_r + 1)(Fa_{s,j}L_jA_{cell})}, \, j = n, \, p \end{aligned} \tag{30}$$

After solving Eq. 27, the lithium concentration in the solid phase before variable substitution (i.e., $\bar{c}_{s,j}$) can be obtained according to $\bar{u}_{s,j} = \bar{c}_{s,j}r$.

In this study, a second method to implement the FVM scheme is also discussed based on solving the solid-phase diffusion equation Eq. 1 directly in spherical coordinates without passing through variable substitution. This is presented in the next section.

FVM scheme in spherical coordinates.—Using the Nabla operator ∇ defined in spherical coordinates, the solid-phase diffusion equation can be expressed as:

$$\frac{\partial c_{s,j}}{\partial t} = \nabla \cdot (D_{s,j} \nabla c_{s,j}), \ j = n, p$$
[31]

where $\nabla c_{s,j}$ is the gradient of the solid-phase concentration, and $\nabla \cdot (\nabla c_{s,j})$ is the divergence of the gradient of $c_{s,j}$, assuming $D_{s,j}$ is constant.

Integrating Eq. 31 over a control volume in spherical coordinates (i.e., $CV_i^{\text{spherical}}$) gives

$$\int_{CV_i^{\text{spherical}}} \frac{\partial c_{s,j}}{\partial t} dV = \int_{CV_i^{\text{spherical}}} \nabla \cdot (D_{s,j} \nabla c_{s,j}) dV, \ j = n, p \quad [32]$$

By applying the Gauss theorem in spherical coordinates, the righthand side of Eq. 32 becomes³⁰:

$$\int_{CV_i^{\text{spherical}}} \frac{\partial c_{s,j}}{\partial t} dV = \oint_{\substack{A_i^{\text{spherical}}\\i+\frac{1}{2}}} (D_{s,j} \nabla c_{s,j} \cdot n) dA$$
$$= \int_{A_i^{\text{spherical}}} \left(D_{s,j} \frac{\partial c_{s,j}}{\partial r} \right) dA - \int_{A_i^{\text{spherical}}} \left(D_{s,j} \frac{\partial c_{s,j}}{\partial r} \right) dA, \quad j = n, p$$
[34]

For each $CV_i^{\text{spherical}}$, the above equation can be further written as:

$$\frac{\partial \overline{c}_{s,i,j}}{\partial t} V_i^{\text{spherical}} = D_{s,j} \frac{\partial c_{s,j}}{\partial r} \bigg|_{i+\frac{1}{2}} A_{i+\frac{1}{2}}^{\text{spherical}} - D_{s,j} \frac{\partial c_{s,j}}{\partial r} \bigg|_{i-\frac{1}{2}} A_{i-\frac{1}{2}}^{\text{spherical}}, \ j = n, p$$
[35]

where $\bar{c}_{si,j}$ is the volume-average value of $c_{s,j}$ in spherical coordinates. Index $i + \frac{1}{2}$ and $i - \frac{1}{2}$ are the interfaces between CV_i/CV_{i+1} and CV_{i-1}/CV_i , respectively.

The second order difference scheme is then used to approximate the diffusion terms (i.e., $D_{s,j}\left(\frac{\partial c_{s,j}}{\partial r}\right)$), and Eq. 35 for each CV_i can be further written as:

$$\frac{\partial \bar{c}_{si,j}}{\partial t} V_i^{\text{spherical}} = D_{s,j} \frac{\bar{c}_{s(i+1),j} - \bar{c}_{si,j}}{\Delta r} A_{i+\frac{1}{2}}^{\text{spherical}} - D_{s,j} \frac{\bar{c}_{si,j} - \bar{c}_{s(i-1),j}}{\Delta r} A_{i-\frac{1}{2}}^{\text{spherical}}, \ j = n, p$$
[36]

Given the discretized solid-phase concentration state vector:

$$\bar{\mathbf{c}}_{s,j} = [\bar{c}_{s1,j}, \, \bar{c}_{s2,j} \cdots \, \bar{c}_{sN_r,j}]^T \in \mathbb{R}^{N_r \times 1}, \ j = n, p$$

$$[37]$$

Eq. 36 can be written in the following state-space form:

$$\dot{\bar{\mathbf{c}}}_{s,j} = \mathbf{A}_{s,j}^{\text{spherical}} \bar{\mathbf{c}}_{s,j} + \mathbf{B}_{s,j}^{\text{spherical}} I_{app}, \ j = n, p$$
[38]

where matrices $\mathbf{A}_{s,j}^{\text{spherical}}$ and $\mathbf{B}_{s,j}^{\text{spherical}}$ take the following expressions:

where $R_{s,j}$ is the electrode radius, r_{N_r} and r_{N_r-1} are the locations of the last two CVs, and $\bar{c}_{sN_r,j}$ and $\bar{c}_{s(N_r-1),j}$ are the volume-average

$$\mathbf{A}_{s,j}^{\text{spherical}} = \frac{4D_{s,j}}{\Delta r^2} \begin{bmatrix} \frac{-3}{4} & \frac{3}{4} & 0 & 0 & \cdots & 0\\ \frac{3}{28} & \frac{-15}{28} & \frac{12}{28} & 0 & \cdots & 0\\ 0 & \frac{12}{76} & -\frac{39}{76} & \frac{27}{76} & \cdots & 0\\ 0 & 0 & \frac{27}{148} & -\frac{75}{148} & \cdots & 0\\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots\\ 0 & 0 & 0 & \cdots & \frac{3(N_r - 1)^2}{12N_r^2 - 12N_r + 4} & \frac{-3(N_r - 1)^2}{12N_r^2 - 12N_r + 4} \end{bmatrix}_{(N_r \times N_r)}$$
[39]

$$\beta_3 = -\frac{3N_r^2 g(I_{app})}{\Delta r (3N_r^2 - 3N_r + 1)(Fa_{s,j}L_jA_{cell})}, \ j = n, p$$
[41]

Simulation results obtained when solving the solid-phase diffusion equation in cartesian coordinates and in spherical coordinates are compared in Appendix B.

When FVM is used to solve the SPM model, one disadvantage is that the surface concentration cannot be directly calculated, as opposed to the FDM case where the surface concentration is obtained from the last nodal point. As it can be seen from Eq. 5, the surface concentration is needed to calculate the equilibrium potential at the electrodes. In order to obtain the electrode surface concentration, the linear extrapolation is usually adopted in the literature:³²

$$u_{s,j}^{surf} = \frac{3\bar{u}_{sNr,j} - \bar{u}_{s(Nr-1),j}}{2}, \quad j = n, p \text{ (Cartesian coordinates)}$$
$$c_{s,j}^{surf} = \frac{3\bar{c}_{sNr,j} - \bar{c}_{s(Nr-1),j}}{2}, \quad j = n, p \text{ (Spherical coordinates)}$$
[42]

The basic assumption of Eq. 42 is that the concentration distribution within the electrodes is linear. However, this is not always the case as there would be steep concentration gradients near the particle surface at the beginning of charge/discharge, which would become more pronounced with the increase of the C-rate. Simulation results obtained by using FVM with N_r =100 are used for illustration, and used in Fig. 4. In order to calculate the surface concentration more accurately in the FVM scheme, the third order Hermite extrapolation is used in this study, where the average concentration from the last three CVs are used. For example, using $\bar{c}_{si,j}$ in Eq. 35, the surface concentration is calculated as (details can be found in Appendix C):

$$\begin{split} c_{s,j}^{surf} &= \left(\left(1 + 2\frac{R_{s,j} - r_{N_r-1}}{r_{N_r} - r_{N_r-1}} \right) \bar{c}_{s(N_r-1),j} + (R_{s,j} - r_{N_r-1}) \frac{\partial c_{s,j}}{\partial r} \Big|_{r=r_{N_r-1}} \right) \left(\frac{R_{s,j} - r_{N_r}}{r_{N_r-1} - r_{N_r}} \right)^2 \\ &+ \left(\left(1 + 2\frac{r_{N_r} - R_{s,j}}{r_{N_r} - r_{N_r-1}} \right) \bar{c}_{sN_r,j} + (R_{s,j} - r_{N_r}) \frac{\partial c_{s,j}}{\partial r} \Big|_{r=r_{N_r}} \right) \left(\frac{R_{s,j} - r_{N_r-1}}{r_{N_r} - r_{N_r-1}} \right)^2, \ j = n, \ p \end{split}$$

$$[43]$$

concentrations for the CV_i in position N_r and $N_r - 1$, respectively. In this study, the FVM scheme using the linear extrapolation Eq. 42 to calculate surface concentration is denoted as FVM-S1, whereas the FVM scheme using the third order Hermite extrapolation Eq. 43 to calculate surface concentration is denoted as FVM-S2.

SPM Model Parameterization

The SPM governing equations reported in Table I are characterized by the following set of parameters:

$$\lambda = \frac{[R_{s,n} \quad R_{s,p} \quad L_n \quad L_p \quad \varepsilon_n \quad \varepsilon_p \quad k_n \quad k_p \quad D_{s,n}}{D_{s,p} \quad A_{cell} \quad R_l \quad c_{s,n}^{\max} \quad c_{s,p}^{\max} \quad \theta_n^0 \quad \theta_n^{100} \quad \theta_p^0 \quad \theta_p^{100}]}$$
(44]

The definition of the above 18 parameters can be found in the Nomenclature Table at the end of the paper. One way to obtain the parameter values is using cell teardown analysis and measure these electrochemical parameters directly, which would require special equipment and skilled technicians.^{33,34} Alternatively, optimization methods can be used to identify the model parameters by fitting the model simulated voltage to experimental measured voltage. However, as it has been shown from a previous work³⁵, not all the parameters in the SPM are identifiable from current-voltage measurement due the complexity and nonlinearity of the model. Also, identifying all the 18 parameters simultaneously may cause overfitting.

In this study, we use data from LG INR21700-M50T cylindrical battery cell with graphite/silicon anode and NMC cathode. An old version of this cell, the LG INR21700-M50 was used in a previous study³³ where a cell teardown analysis was performed and both the electrode-based, transport, and kinetic parameters were measured directly. In this paper, we borrow the following parameters from literature:³³

$$\boldsymbol{\lambda}_{borrowed} = [L_n \ L_p \ A_{cell} \ c_{s,n}^{\max} \ c_{s,p}^{\max} \ \theta_n^0 \ \theta_n^{100} \ \theta_p^0 \ \theta_p^{100}]$$
[45]

The remaining 8 electrode-based, transport, and kinetic parameters are identified using experimental data from a LG INR21700-M50T cell at 23 $^{\circ}C^{36}$

$$\lambda_{iden} = \begin{bmatrix} \lambda_1 & \lambda_2 & \lambda_3 & \lambda_4 & \lambda_5 & \lambda_6 & \lambda_7 & \lambda_8 \end{bmatrix}$$
$$= \begin{bmatrix} R_{s,n} & R_{s,p} & \varepsilon_n & \varepsilon_p & k_n & k_p & D_{s,n} & D_{s,p} \end{bmatrix}$$
[46]

In the next section, a sensitivity analysis is performed on the above 8 parameters.

Local sensitivity analysis.—Local sensitivity analysis investigates how the model output y_V (i.e., battery voltage) is affected when



Figure 4. Solid-phase concentration distribution in the cathode and anode spherical particles. (a) C/4 charge. (b) 2C charge. $\Delta \bar{c}_{s,p}$ represents the cathode concentration difference between location $r = 0.5R_{s,p}$ and $r = 0.6R_{s,p}$ or between $r = 0.9R_{s,p}$ and $r = R_{s,p}$, respectively. $\Delta \bar{c}_{s,n}$ represents the anode concentration difference between location $r = 0.5R_{s,n}$ and $r = 0.6R_{s,n}$ or between $r = 0.9R_{s,n}$ and $r = R_{s,n}$, respectively. Parameters used for simulation were taken from literature ³³.

each of the model parameter in the vector $\lambda_{iden} = [\lambda_1 \cdots \lambda_8]$ is perturbed around its nominal value while the remaining of the parameters are kept equal to their nominal values. In this study, the sensitivity matrix is used to calculate the sensitivity of SPM model parameters. Given the general state-space form of the SPM:

$$\dot{x} = f(\mathbf{x}, \lambda_{iden}, u) y_V = h(\mathbf{x}, \lambda_{iden}, u)$$
[47]

where $x \in \mathbb{R}^n$ is the vector of concentration states, $\lambda_{iden} \in \mathbb{R}^m$ is the vector of parameters, $u \in \mathbb{R}$ is the input current, $y_V \in \mathbb{R}$ is model voltage output, and *f* and *h* are the state-space and output functions, respectively.

Given *M* the number of simulation steps, the SPM voltage output vector is expressed as $[y_V(t_1), y_V(t_2) \cdots y_V(t_M)]$ for a given input current profile, and the sensitivity matrix S^V is denoted as follows:

$$\boldsymbol{S}^{V} = \begin{bmatrix} \frac{\partial y_{V}(t_{1})}{\partial \lambda_{1}} \frac{\lambda_{1,nom}}{y_{V}^{nom}(t_{1})} & \frac{\partial y_{V}(t_{1})}{\partial \lambda_{2}} \frac{\lambda_{2,nom}}{y_{V}^{nom}(t_{1})} & \cdots & \frac{\partial y_{V}(t_{1})}{\partial \lambda_{8}} \frac{\lambda_{8,nom}}{y_{V}^{nom}(t_{1})} \\ \frac{\partial y_{V}(t_{2})}{\partial \lambda_{1}} \frac{\lambda_{1,nom}}{y_{V}^{nom}(t_{2})} & \frac{\partial y_{V}(t_{2})}{\partial \lambda_{2}} \frac{\lambda_{2,nom}}{y_{V}^{nom}(t_{2})} & \cdots & \frac{\partial y_{V}(t_{2})}{\partial \lambda_{8}} \frac{\lambda_{8,nom}}{y_{V}^{nom}(t_{2})} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial y_{V}(t_{M})}{\partial \lambda_{1}} \frac{\lambda_{1,nom}}{y_{V}^{nom}(t_{M})} & \frac{\partial y_{V}(t_{M})}{\partial \lambda_{2}} \frac{\lambda_{2,nom}}{y_{V}^{nom}(t_{M})} & \cdots & \frac{\partial y_{V}(t_{M})}{\partial \lambda_{8}} \frac{\lambda_{8,nom}}{y_{V}^{nom}(t_{M})} \end{bmatrix}_{M \times 8}$$

$$[48]$$

where $\lambda_{m,nom}$, $m = 1 \cdots 8$, denotes the nominal value of the m^{th} model parameter. $y_V^{nom}(t_k)$, $k = 1 \cdots M$ is the nominal value of voltage obtained using the nominal parameter values.

The nominal values of SPM parameters required to calculate Eq. 48, are taken from literature³³. Following the approach presented in a previous study²⁶, we investigate the parameter sensitivity of SPM adding SOC information to the sensitivity matrix, and using cathode SOC, y_{SOC_p} , and anode SOC, y_{SOC_q} , as additional outputs of

SPM, defined as follows:

$$y_{SOC_p}(t_k) = \frac{\theta_p^0 - \theta_p^{bulk}(t_k)}{\theta_p^0 - \theta_p^{100}}, \ y_{SOC_n}(t_k) = \frac{\theta_n^{bulk}(t_k) - \theta_n^0}{\theta_n^{100} - \theta_n^0}$$
[49]

where θ_p^{bulk} and θ_n^{bulk} are defined in Table I

Augmenting the sensitivity matrix Eq. 48 with the two SOC outputs, yields the new sensitivity matrix S^{V+SOC} :

Fig. 5(b), respectively. In these plots, dark color denotes high sensitive parameters and light color denotes low sensitive parameters where low sensitive parameters are hard to identify. From Fig. 5(a), it can be seen that $R_{s,n}$, ε_n , and $D_{s,n}$ have low sensitivity at high SOC region during the first timesteps of discharge, and have higher sensitivity as the SOC decreases. The second way to visualize sensitivity matrix results is to calculate the Euclidean norm of each column (i.e., $\|S^V_{..,m}\|_2$ for Eq. 48 and $\|S^{V+SOC}_{..,m}\|_2$ for Eq. 50). In this way, the average parameter sensitivity throughout the given current input is obtained. Figure 6 (a)-



where $y_{SOC_p}(t_k)$ and $y_{SOC_n}(t_k)$ are the simulated SOC from the cathode and anode at timestep t_k , respectively. $y_{SOC_p}^{nom}(t)$ and $y_{SOC_n}^{nom}(t)$ are the nominal SOC trajectories of cathode and anode, respectively, obtained using the nominal SPM parameters values.

The sensitivity matrix in Eq. 50 consists of three parts: 1) voltagebased sensitivity (i.e., S^{V} from Eq. 48), 2) cathode SOC-based sensitivity (i.e., S^{SOC_p}), and 3) anode SOC-based sensitivity (i.e., S^{SOC_n}). The results of the sensitivity matrix can be visualized in two ways. The first way is to plot the elements of the columns of Eq. 48 or Eq. 50 showing the parameter sensitivity as a function of time, as displayed in Fig. 5 (a)-(b). Figure 5 (a) shows the sensitivity matrix purely based on output voltage (Eq. 48) and Fig. 5 (b) shows the sensitivity based on both output voltage and SOC (Eq. 50). For example, the second row of Fig. 5 is related to the parameter $R_{s,p}$, and the value of the first timestep is calculated as $\left[\frac{\partial y_V(t_1)}{\partial R_{s,p}}\frac{R_{s,p,nom}}{y_V^{nom}(t_1)}\right]$ for Fig. 5(a) and $\left[\frac{\partial y_V(t_1)}{\partial R_{s,p}}\frac{R_{s,p,nom}}{y_V^{nom}(t_1)} + \frac{\partial y_{SOC_p}(t_1)}{\partial R_{s,p}}\frac{R_{s,p,nom}}{y_{SOC_n}^{not}(t_1)}\right]$ for (b) present the sensitivity of the 8 SPM parameters under constant current and dynamic current conditions using both S^{V} and S^{V+SOC} , respectively. As widely reported in the literature^{37–39} and also shown in Fig. 6, the sensitivity of SPM model parameters is a function of the current input, and that using S^{V+SOC} improves the model parameter sensitivity.²⁶ We first identify electrode based parameters $[R_{s,n} \ R_{s,p} \ \varepsilon_n \ \varepsilon_p]$ using C/20 constant current data, given that their sensitivity values are close under both constant discharge and hybrid pulse powercharacterization (HPPC) current profiles. Then, transport and kinetic parameters $[D_{s,n} \ D_{s,p} \ k_n \ k_p]$ are identified using HPPC dynamic data, given that their sensitivity values are higher under the HPPC input.

Parameters identification.—In this section, the identification of the 8 parameters of SPM is performed using the particle swarm optimization (PSO) algorithm, where the cost function of the optimization problem is formulated as follows:



Figure 5. Contour plot results based on FVM-S2 with N_r =100 scheme. (a) C/20 discharge (S^V). (b) C/20 discharge (S^{V+SOC}).



Figure 6. Parameter sensitivity analysis results based on FVM-S2 with N_r =100 scheme. (a) SPM parameters sensitivity under C/20, (b) SPM parameters sensitivity under HPPC, using both S^V and S^{V+SOC}

Table III. Identified electrochemical parameters for the LG INR21700-M50T battery cell.

Parameter	Symbol	Unit	Lower bound λ_{iden}^{\min}	Upper bound λ_{iden}^{\max}	Anode $(i = n)$	Cathode $(i = p)$
Particle radius	$R_{s,j}$	[m]	1.0e-6	1.0e-5	3.60e-6	6.25e-6
Solid-phase volume fraction	ε_j	[-]	0.7	0.8	0.7606	0.7633
Solid-phase lithium diffusivity	$D_{s,j}$	[m ² /s]	1.0e-16	1.0e-14	3.97e-15	6.30e-15
Reaction rate constant	k_j	$[m^{2.5}/(mol^{0.5}s)]$	6.0e-7	6.0e-6	3.17e-6	9.55e-7

$$\underset{\substack{\lambda_{iden}^{\min} \leq \lambda_{iden} \leq \lambda_{iden}}{\operatorname{smax}} = \sqrt{\frac{1}{M} \sum_{k=1}^{M} \left(\frac{V_{\exp}(t_k) - V_{sim}(\lambda_{iden}, t_k, u)}{V_{\exp}(t_k)} \right)} + \sqrt{\frac{1}{M} \sum_{k=1}^{M} \left(\frac{SOC_{\exp}(t_k) - SOC_p^{sim}(\lambda_{iden}, t_k, u)}{SOC_{\exp}(t_k)} \right)} + \sqrt{\frac{1}{M} \sum_{k=1}^{M} \left(\frac{SOC_{\exp}(t_k) - SOC_n^{sim}(\lambda_{iden}, t_k, u)}{SOC_{\exp}(t_k)} \right)}$$
[51]

where λ_{iden}^{\min} and λ_{iden}^{\max} are the vectors containing the lower and upper bounds (defined in Table III) for the parameter vector $\lambda_{iden} = [\lambda_1, \dots, \lambda_8]$, respectively, t_k is the time index, and M is the number of total time steps. $V_{exp}(t_k)$ is the measured voltage at time t_k , $V_{sim}(\lambda_{iden}, t_k, u)$ is the SPM simulated voltage at time t_k for a given parameter vector $\lambda_{iden} = [\lambda_1, \dots, \lambda_8]$. SOC_{exp} is the SOC calculated by Coulomb Counting, SOC_p^{sim} and SOC_n^{sim} are the model simulated cathode and anode SOC (Eq. 6), respectively.

In this study, the Matlab PSO toolbox is used, where the initial guess values for SPM parameters were borrowed from literature³³. In the PSO, the population size was set to 20, and the self-adjustment weight (i.e., c_1) and social adjustment weight (i.e., c_2) were set as 2 and 2, respectively.

Parameter identification is conducted in two steps. First, the electrode based parameters $\begin{bmatrix} R_{s,n} & R_{s,p} & \varepsilon_n & \varepsilon_p \end{bmatrix}$ are identified using C/20 discharge data. Then, the transport and kinetic parameters $\begin{bmatrix} D_{s,n} & D_{s,p} & k_n & k_p \end{bmatrix}$ are identified using HPPC data. The identified SPM model parameters are listed in Table III, and identification results for C/20 discharge and HPPC are shown in Fig. 7. The corresponding values of the cost function (i.e., J_V , J_{SOCp} and J_{SOCn}) are summarized in

Table IV. Model validation is conducted using C/4, C/2 and 1C constant charge current and UDDS discharge current, and results are shown in Fig. 8. The RMSE of voltage under 1C, C/2, C/4 charge, and UDDS are 15.6 mV, 7.8 mV, 9.3 mV, and 9.7 mV, respectively. The RMSE of simulated cathode SOC under 1C, C/2, C/4 charge, and UDDS are 0.13%, 0.05%, 0.05%, and 0.10%, respectively. The RMSE of simulated anode SOC under 1C, C/2, C/4 charge, and UDDS are 0.17%, 0.15%, 0.14%, and 0.14%, respectively.

Numerical Results and Discussion

Upon obtaining SPM model parameters, the performance of FDM, FVM-S1 (using linear extrapolation) and FVM-S2 (using Hermite extrapolation) are compared in terms of model accuracy and mass conservation. In both FDM and FVM methods, the model accuracy can be improved by increasing the number of N_r . In this study, the model benchmark solution^a is obtained using FVM-S2 with N_r =100. Besides the model accuracy, the mass conservation property of the two numerical methods is also analyzed. FVM conserves mass by design, but very few studies investigated the mass conservation of FDM scheme for SPM. In a previous study,²¹ a revised FDM schemes was proposed to conserve mass when solving Eq. 1 with non-constant diffusion coefficient $D_{s,j}$. However, the mass conservation property of this method over multiple cycles simulation was not shown. In this study, the total lithium-ion in the solid phase is used to check mass conservation when running the SPM model with multiple cycles. In the following sections, simulations are conducted using the SPM model parameters taken from Table III.

Model accuracy.—The accuracy of FDM and FVM methods highly depends on the number of spatial discretization nodes/CVs. To evaluate the model accuracy of FDM, FVM-S1, and FVM-S2 against the benchmark solution from FVM-S2 with N_r =100, the root-mean-square-error (RMSE) of voltage and electrode volume-average concentration are utilized in this study.

^aA benchmark solution can also be generated using FDM with N_r =100. The results are very similar to those of the FVM-S2 benchmark.



Figure 7. Identification results. (a) Voltage and SOC under C/20 discharge, and (b) Voltage and SOC under HPPC profile.

Table IV. Values of the cost function Eq. 51 under different current data (identification).

RMSE	Current da	ta
	C/20 discharge	HPPC
J_V	0.0062	0.0067
J_{SOC_p}	0.0010	0.0018
J_{SOC_n}	0.0024	0.0024
J	0.0096	0.0109

$$RMSE_{\text{Voltage}} = \sqrt{\frac{1}{M} \sum_{k=1}^{M} (V_{ref}(\lambda_{iden}, t_k, u) - V_{sim}(\lambda_{iden}, t_k, u))^2}$$
$$RMSE_{c_{s,j}^{avg}} = \sqrt{\frac{1}{M} \sum_{k=1}^{M} (c_{s,j}^{avg,ref}(\lambda_{iden}, t_k, u) - c_{s,j}^{avg,sim}(\lambda_{iden}, t_k, u))^2}, \ j = n, p$$
[52]

where V_{ref} and $c_{s,j}^{avg,ref}$ are the benchmark results for voltage and electrode volume-average concentration, respectively, and V_{sim} and $c_{s,j}^{avg,sim}$ are the simulated voltage and electrode volume-average concentration of SPM, respectively. Simulation results are obtained using FDM, FVM-S1 and FVM-S2,and the electrode volume-average concentration is calculated as follows:

$$c_{s,j}^{avg} = \frac{1}{\frac{4}{3}\pi R_{s,j}^3} \int_{r=0}^{r=R_{s,j}} 4\pi r^2 c_{s,j} dr, \ j=n, p$$
[53]

The RMSE for FDM, FVM-S1 and FVM-S2 under C/4, 1C, and 4C constant-current charge with different N_r are shown in Fig. 9. The RMSE errors decrease with the increase of N_r for all the methods, and it can be seen that the model accuracy for FDM and

FVM-S2 are very similar. However, under small N_r , the RMSE of volume-average concentration for both cathode and anode for FDM is quite large, due to mass conservation issues. It should also be noted that the voltage RMSE for FVM-S1 is the largest. An explanation can be found in Fig. 4 where the lithium concentration distributions within cathode and anode are given. It can be seen from Fig. 4 that the concentration difference near the particle surface (i.e., $\Delta \bar{c}_{s,p}$) is quite large for both cathode and anode. Therefore, using linear extrapolation (i.e., FVM-S1) to calculate electrode surface concentration leads to large errors. According to Eq. 5, the electrode surface concentration is used to calculate cell voltage, which explains the large calculation error of FVM-S1 when compared with FDM and FVM-S2. Pybamm¹³ is an open-source battery simulation package that enables fast battery simulations under a variety of battery chemistries and operating scenarios. In Pybamm, the user can run the battery model with default parameter values, or the user can change parameter values, such as mesh (i.e., number of N_r), to investigate how the battery behavior will change. We compare FVM-S1 and FVM-S2 used in this study with Pybamm under the same model parameter values and number of N_r . The simulated results from Pybamm are shown in green dots in Fig. 9. It can be seen that Pybamm results are very close to FVM-S1. This is because FVM in Pybamm uses the linear extrapolation (Eq. 42) to calculate the surface concentration as its default method. The standard FVM scheme with linear extrapolation, FVM-S1, guarantees mass conservation, but has lower model accuracy than the FDM scheme with the same number of N_r . The proposed FVM-S2 scheme, on the other hand, improves the model accuracy.

Mass conservation.—In addition to the analysis and comparison of model accuracy of FDM, FVM-S1, and FVM-S2 schemes studied in this paper, we investigate the mass conservation over multiple cycles simulations for FDM and FVM-S2 schemes. In this section, the SPM model is cycled multiple times and the electrode volume-



Figure 8. Experimental validation results for the SPM using data from the LG INR21700-M50T battery. (a) constant charge inputs at C/4, C/2 and 1C, and (b) UDDS discharge profile.



Figure 9. RMSE on voltage and electrode volume-average concentration under constant-current charge at several C-rates with respect to the spatial discretization nodes/CVs, N_r . (a) C/4, (b) 1C, and (c) 4C. Simulation results from Pybamm are shown in green dots.

average solid-phase concentration for each electrode (i.e., $c_{s,j}^{avg}$ in Eq. 53) is monitored. N_r is set to 5 for both FDM and FVM-S2 schemes.

During multiple cylces simulation, the battery is subject to constant current discharge and charge with same current rate to ensure that the ampere-hour throughput for charge and discharge are the same. Under this condition, lithium ions that intercalate into and de-intercalate out of the cathode and anode during the charge and discharge cycles are the same.^b Therefore, the peak values of electrode volume-average concentration (i.e., $c_{s,j}^{avg}$ in Eq. 53) should

^bAlso, no side-reaction (i.e., SEI growth or Li plating) is added to the SPM.



Figure 10. Comparative results under 2C-2C constant cycling simulations. (a) Input current. (b) Output voltage. (c) Cathode and anode volume-average concentration from FDM with N_r =5. (d) Cathode and anode volume-average concentration from FVM-S2 with N_r =5.

remain the same under the assumption that total mass of lithium ions is conserved.

In the simulations conducted next, we indicate IC-IC as the IC constant charge of amplitude I followed by IC constant discharge of amplitude I. Figure 10 shows the simulation results under 2C-2C cycling with the initial SOC equals to 0.5. First, a 300 s 2C current was used to discharge the cell, followed by 300 s charge at 2C. In Fig. 10 (c)-(d), the volume-average cathode and anode concentration are given. The dash gray line represents the concentration value when the cell first reaches the lowest voltage (i.e., P₁ point in Fig. 10 (b)). If mass in the solid-phase is conserved, the peak concentration value should always be the same. In Fig. 10 (c)-(d), the difference of the volume-average concentration between two peaks are plotted. The notation $\Delta c_{s,j}^{ayg,P_1-P_2}$, j = n, p is used to represent the difference

of volume-average concentration between the P₁ peak (i.e., P₁ point in Fig. 10 (b)) and P₂ peak (i.e., P₂ point in Fig. 10 (b)) when cell voltage reaches the lowest values. For example, the volume-average concentration difference between the first and second peaks is denoted as $\Delta c_{s,p}^{avg,1-2}$ for cathode and $\Delta c_{s,n}^{avg,1-2}$ for anode, respectively. It can be seen that the volume-average concentration in FVM-S2 remains the same over multiple cycles while these values are drifting in FDM (decreasing in cathode and increasing in anode). Figure 10 shows that mass is conserved in FVM-S2 but is not conserved in FDM. In Table V, we calculate the volume-average concentration difference between peak 1 and peak 2, and between peak 1 and peak 3 (i.e., P₃ point in Fig. 10 (b)) under 1C-1C, 2C-2C and 4C-4C cycling simulations. It can be seen that when FDM scheme is used, the volume-average concentration is drifting with



Figure 11. Multi-current cycling simulation results for FDM and FVM-S2 schemes.

cycling. Also, the concentration difference between two peaks increases with the increase of C-rate. The same simulation results for FVM-S2 are also presented in Table V. We can see that mass is always conserved for FVM-S2 scheme under different C-rates. It should also be noted that under constant diffusion coefficient $D_{s,j}$ and constant current cycling condition, the concentration difference for FDM is relatively small compared to the mean concentration. For example, the mean cathode volume-average concentration during 4C-4C is 31933 mol/m^3 , whereas the cathode concentration

difference between the first and third peak is 122 mol/m^3 , which is 0.38% of the mean cathode concentration.

Besides constant current cycling, the mass conservation of FDM and FVM-S2 schemes under multi-rate current cycling is also investigated, as shown in Fig. 11. The simulated current input profile consists of three parts, namely 2C-2C, 1C-1C, and 0.5C-0.5C. Figure 11 shows that the volume-average concentration for both cathode and anode are drifting with cycling and the variation in concentration is more pronounced than in the constant current



Figure 12. Simulation results for FDM with N_r =100 under (a) 1C-1C cycling, and (b) 4C-4C cycling.

Table V. Volume-average concentration difference of cathode and anode.						
C-		Catho	bde [mol/m ³]	Anode $[mol/m^3]$		
rate	Cycle	$FDM_{N_r=5}$	$FVM - S2_{N_r=5}$	FDM _{Nr=5}	$FVM - S2_{N_r=5}$	
1C- 1C	$\Delta c_{s,j}^{avg,1-2}$, j=n,p	25	0	4	0	
	$\Delta c_{s,j}^{avg,1-3}, j=n,p$	26	0	4	0	
2C- 2C	$\Delta c_{s,j}^{avg,1-2},_{j=n,p}$	58	0	21	0	
	$\Delta c_{s,j}^{avg,1-3}, j=n,p$	67	0	22	0	
4C- 4C	$\Delta c_{s,j}^{avg,1-2},_{j=n,p}$	95	0	54	0	
	$\Delta c_{s,j}^{avg,1-3},_{j=n,p}$	122	0	63	0	

cycling conditions (see Fig. 10). Therefore, large calculation error can accumulate during long-term cycling simulation. On the contrary, FVM-S2 scheme preserves mass.

In Fig. 12, we simulated FDM with number of spatial discretization nodes N_r equal to 100 under 1C-1C and 4C-4C cycling protocols. It can be seen that, the volume-average concentration in FDM almost remains the same. From the results shown in Fig. 10 and Fig. 12, FDM works well even with small N_r , but mass conservation in FDM is guaranteed when N_r is large enough.

For BMS application, it is preferred to use small N_r to reduce the total computational burden. However, as can be seen from Fig. 9, the accuracy of SPM decreases with small N_r for both FDM, FVM-S1, and FVM-S2 schemes. To address this, parameters of the SPM were re-identified and both the model accuracy and mass conservation are analyzed. SPM solved with FVM-S2 with $N_r=100$ is used to generate the reference solution of voltage and SOC. Then, SPM solved by FDM with $N_r=5$ and FVM-S2 with $N_r=5$ are being identified. The simulation results before and after parameter re-



Figure 13. Parameter re-identification results (a) 1C-1C cycling. (b) 2C-2C cycling.

identification are given in Fig. 13. Here, the notation Ref_V indicates the reference voltage. $X_{N_r=Y,Z,S}$ is used to represent different results, where $X = [V, c_{s,p}^{avg}]$ is the SPM model output, Y is the number of N_r , Z = [FDM, FVM - S2] is the chosen numerical method, and $S = [raw, re_{iden}]$ indicates whether SPM parameters are re-identified, S = raw means the original parameters in Table III are used for simulation, and $S = re_{iden}$ represents solutions obtained using reidentified parameters. For example, $V_{N_r=5,FVM-S2,raw}$ represents the simulated voltage obtained from SPM solved by FVM-S2 with $N_r=5$ and original parameters. It can be seen from Fig. 13 that model accuracy increased after parameter re-identification for both FDM and FVM-S2 scheme. Under 1C-1C, the RMSE of voltage before and after re-identify parameters are 11 mV and 4 mV for FDM, respectively, and are 12 mV and 6 mV for FVM-S2, respectively. Under 4C-4C, the RMSE of voltage before and after re-identify parameters are 25 mV and 6 mV for FDM, respectively, and are 28 mV and 6 mV for FVM-S2, respectively. Besides, Fig. 13 shows that

a small volume-average concentration difference (i.e., $\Delta c_{s,p}^{avg,1-3}$) still exists in FDM scheme after parameter re-identification. On the other hand, the volume-average concentration for FVM-S2 before and after parameter re-identification is always conserved.

Conclusion

This paper presented the FDM and FVM applied to the battery SPM model. First, we provided the details of how to transform the governing PDEs into ODEs using both schemes. Second, we proposed a revised FVM scheme, called FVM-S2, which adopts the Hermite extrapolation to calculate the solid-phase surface concentration more accurately as opposed to the adopted linear extrapolation (FVM-S1). Simulation results presented in this study show that the proposed FVM-S2 scheme improves model accuracy significantly compared with standard FVM scheme, FVM-S1. Finally, the model accuracy of FDM, FVM-S1, and FVM-S2 schemes were compared and mass conservation behavior for FDM and FVM-S2 schemes were analyzed. Results show that mass in the FVM-S2 scheme is always conserved, but a small concentration drifting exist when the FDM scheme is used under constant diffusion coefficient and constant current cycling, which becomes more pronounced under multi-current cycling. Besides, we showed model accuracy when using a small number of spatial discretization nodes/ control volumes can be improved by re-identifying parameters. The relatively low number of discrete equations enables the implementation of the model to be run on the BMS.

This study provides findings of mass conservation analysis for FDM and FVM schemes, which we hope can facilitate BMS model selection. Also, the proposed FVM-S2 scheme with higher order Hermite extrapolation can be extended to solve other battery models, such as ESPM model and DFN model.

Appendix A. Ghost cells in the finite volume method

The ghost cells are introduced in the finite volume method to calculate the control volumes near the left and right boundaries³¹. Supposing the calculation domain is divided into N_r control volumes, we introduce the ghost cells at j = 0 (i.e., $\bar{u}_{s0,j}$) and at $j = N_r + 1$ (i.e., $\bar{u}_{s(N_r+1),j}$) which are located just outside the calculation domain, as shown in Fig. 14.

The boundary conditions are used to calculate the values of the ghost cells based on the values in the interior cells.

The boundary conditions of Eq. 1 after variable substitution are shown in the last column in Table II. The boundary condition for particle center is the Dirichlet boundary conditions²³:

$$u_{s,j}|_{r=0} = 0, \quad j = n, p$$
 [54]

Above boundary condition can be approximated using the average value of $\bar{u}_{s0,i}$ and $\bar{u}_{s1,i}$:

$$\frac{\bar{u}_{s0,j} + \bar{u}_{s1,j}}{2} \approx 0$$
[55]

Therefore, the value of ghost cell $\bar{u}_{s0,j}$ is $-\bar{u}_{s1,j}$.

The boundary condition for particle surface after variable substitution is the Robin boundary condition²³:



Figure 14. Boundary conditions with ghost cells

$$u_{s,j}|_{r=R_{s,j}} \approx \frac{\bar{u}_{s(N_r+1),j} + \bar{u}_{sN_r,j}}{2}$$
[58]

Replacing Eq. 57 and Eq. 58 into Eq. 56, yields:

$$\frac{\bar{u}_{s(N_r+1),j} - \bar{u}_{sN_r,j}}{\Delta r} - \frac{\bar{u}_{s(N_r+1),j} + \bar{u}_{sN_r,j}}{2R_{s,j}} = \frac{-I_{app}g(I_{app})R_{s,j}}{a_{s,j}A_{cell}L_jFD_{s,j}}, \quad j = n, p$$
[59]

Finally, the value of ghost cell $\bar{u}_{s(N_r+1),i}$ is given as:

$$\bar{u}_{s(N_r+1),j} = \frac{\bar{u}_{sN_r,j} \left(1 + \frac{\Delta r}{2R_{s,j}} \right) - \frac{I_{app}g(I_{app})R_{s,j}\Delta r}{a_{s,j}A_{cell}L_jFD_{s,j}}}{1 - \frac{\Delta r}{2R_{s,j}}}, \quad j = n, p \quad [60]$$

Appendix B. Comparision of FVM schemes in cartesian coordinates and spherical coordinates

In this paper, we proposed two different ways to solve the solidphase diffusion equation using FVM. The first way is to use variable substitution $u_{s,j} = c_{s,j}r$, and transforms the governing equation from spherical coordinates to cartesian coordinates (i.e., FVM-cartesian). The second way is to solve the equation directly in spherical coordinates (i.e., FVM-spherical). These two methods are compared under different N_r and different current conditions, and the simulation results are summarized in Table VI.

Two metrics are used to measure the difference between these two methods, namely the voltage RMSE and mean absolute relative error (MARE) of the surface concentration, as follows:

$$RMSE_{\text{Voltage}} = \sqrt{\frac{1}{M} \sum_{k=1}^{M} (V_{\text{FVM-cartesian}}(\lambda_{iden}, t_k, u) - V_{\text{FVM-spherical}}(\lambda_{iden}, t_k, u))^2}$$
$$MARE_{c_{s,j}^{\text{suff}}} = \frac{1}{M} \sum_{k=1}^{M} \left(\frac{|c_{s,j}^{\text{suff},\text{FVM-cartesian}}(\lambda_{iden}, t_k, u) - c_{s,j}^{\text{suff},\text{FVM-spherical}}(\lambda_{iden}, t_k, u)|}{c_{s,j}^{\text{suff},\text{FVM-spherical}}(\lambda_{iden}, t_k, u)} \right),$$
$$j = n, p \qquad [61]$$

$$\frac{\partial u_{s,j}}{\partial r}\Big|_{r=R_{s,j}} - \frac{u_{s,j}|_{r=R_{s,j}}}{R_{s,j}} = \frac{-I_{app}g(I_{app})R_{s,j}}{a_{s,j}A_{cell}L_jFD_{s,j}}, \quad j=n,p$$
[56]

Using the finite difference scheme to approximate the $\frac{\partial u_{s,j}}{\partial r}\Big|_{r=R_{s,j}}$ term, one obtains:

$$\left. \frac{\partial u_{s,j}}{\partial r} \right|_{r=R_{s,j}} = \frac{\bar{u}_{s(N_r+1),j} - \bar{u}_{sN_r,j}}{\Delta r} + O(\Delta r^2)$$
[57]

Averaging $\bar{u}_{s(N_r+1),j}$ and $\bar{u}_{sN_r,j}$ to approximate the $u_{s,j}|_{r=R_{s,j}}$ term, yields:

where $V_{\text{FVM-cartesian}}$ and $V_{\text{FVM-spherical}}$ are the SPM simulated voltage at time t_k for the identified parameter vector λ_{iden} using FVM-cartesian and FVM-spherical, respectively. u is the input current. $c_{s,j}^{\text{surf,FVM-cartesian}}(\lambda_{iden}, t_k, u)$ and $c_{s,j}^{\text{surf,FVM-spherical}}(\lambda_{iden}, t_k, u)$ are the SPM simulated electrode surface concentration of time t_k using FVM-cartesian and FVM-spherical, respectively.

Form Table VI, it can be found that the simulated voltage and surface concentration between these two FVM methods are similar.

Appendix C. Hermite extrapolation

In numerical analysis, one often encounters the situation that instead of a function f, only some discrete function values $f(x_i)$ and their derivatives $f'(x_i)$ are known. To interpolate the discrete function values, the Hermite extrapolation method can be used.⁴⁰

Table VI. Comparison between FVM-cartesian and FVM-spherical.

Current condition	Number of N_r		MARE	
		RMSE Voltage [mV]	$c_{s,p}^{surf}$ [%]	$c_{s,n}^{surf}$ [%]
C/2 constant charge	5	0.9691	0.0754	0.1962
	10	0.2456	0.0187	0.0494
	40	0.0153	0.0012	0.0031
1C constant charge	5	1.4201	0.1341	0.2911
C	10	0.3604	0.0336	0.0741
	40	0.0225	0.0021	0.0046
4C constant charge	5	2.5741	0.3302	0.4083
	10	0.6809	0.0884	0.1090
	40	0.0427	0.0055	0.0069



Figure 15. Illustration of the Hermite extrapolation method

Let's assume that two distinct nodes x_0 and x_1 , discrete function values of these two nodes $f(x_0)$, $f(x_1)$ and their corresponding derivatives $f'(x_0)$ and $f'(x_1)$ are given, the third order Hermite extrapolation polynomial (i.e., H_3) is given as⁴⁰:

$$H_3(x) = \sum_{l=0}^{1} f(x_l) H_{1,l}(x) + \sum_{l=0}^{1} f'(x_l) \hat{H}_{1,l}(x)$$
[62]

where $H_{1,l}(x)$ and $\hat{H}_{1,l}(x)$ are given as:

$$H_{1,l}(x) = [1 - 2(x - x_l)L'_{1,l}(x_l)]L^2_{1,l}(x)$$
[63]

$$\hat{H}_{1,l}(x) = (x - x_l) L_{1,l}^2(x)$$
[64]

where $L_{1,l}(x)$ denoting the l^{th} Lagrange coefficient polynomial of degree 1 and is given by:

$$L_{1,0}(x) = \frac{x - x_1}{x_0 - x_1} \text{ and } L_{1,1}(x) = \frac{x - x_0}{x_1 - x_0}$$
[65]

Therefore, the first derivative of $L_{1,0}$ and $L_{1,1}$ are calculated as:

$$L'_{1,0}(x) = \frac{1}{x_0 - x_1}$$
 and $L'_{1,1}(x) = \frac{1}{x_1 - x_0}$ [66]

Using Eq. 65 and Eq. 66 in Eq. 63, we obtain:

$$H_{1,0}(x) = \left[1 - 2\frac{x - x_0}{x_0 - x_1}\right] \left(\frac{x - x_1}{x_0 - x_1}\right)^2$$
$$H_{1,1}(x) = \left[1 - 2\frac{x - x_1}{x_1 - x_0}\right] \left(\frac{x - x_0}{x_1 - x_0}\right)^2$$
[67]

Using Eq. 65 in Eq. 64, we obtain:

$$\hat{H}_{1,0}(x) = (x - x_0) \left(\frac{x - x_1}{x_0 - x_1}\right)^2$$
$$\hat{H}_{1,1}(x) = (x - x_1) \left(\frac{x - x_0}{x_1 - x_0}\right)^2$$
[68]

Substituting Eq. 67 and Eq. 68 into Eq. 62, we have:

$$H_{3}(x) = f(x_{0}) \left[1 - 2\frac{x - x_{0}}{x_{0} - x_{1}} \right] \left(\frac{x - x_{1}}{x_{0} - x_{1}} \right)^{2} + f(x_{1}) \left[1 - 2\frac{x - x_{1}}{x_{1} - x_{0}} \right] \left(\frac{x - x_{0}}{x_{1} - x_{0}} \right)^{2}$$

+ $f'(x_{0})(x - x_{0}) \left(\frac{x - x_{1}}{x_{0} - x_{1}} \right)^{2} + f'(x_{1})(x - x_{1}) \left(\frac{x - x_{0}}{x_{1} - x_{0}} \right)^{2}$
= $\left(f(x_{0}) \left(1 - 2\frac{x - x_{0}}{x_{0} - x_{1}} \right) + f'(x_{0})(x - x_{0}) \right) \left(\frac{x - x_{1}}{x_{0} - x_{1}} \right)^{2}$
+ $\left(f(x_{1}) \left(1 - 2\frac{x - x_{1}}{x_{1} - x_{0}} \right) + f'(x_{1})(x - x_{1}) \right) \left(\frac{x - x_{0}}{x_{1} - x_{0}} \right)^{2}$
[69]

As shown in Fig. 15, Eq. 69 is used to calculate the surface concentration in this study, and we can obtain Eq. 70:

$$c_{s,j}^{surf} = \left(\left(1 + 2\frac{R_{s,j} - r_{N_r-1}}{r_{N_r} - r_{N_r-1}} \right) \bar{c}_{s(N_r-1),j} + (R_{s,j} - r_{N_r-1}) \frac{\partial c_{s,j}}{\partial r} \Big|_{r=r_{N_r-1}} \right) \left(\frac{R_{s,j} - r_{N_r}}{r_{N_r-1} - r_{N_r}} \right)^2 \\ + \left(\left(1 + 2\frac{r_{N_r} - R_{s,j}}{r_{N_r} - r_{N_r-1}} \right) \bar{c}_{sN_r,j} + (R_{s,j} - r_{N_r}) \frac{\partial c_{s,j}}{\partial r} \Big|_{r=r_{N_r}} \right) \left(\frac{R_{s,j} - r_{N_r-1}}{r_{N_r} - r_{N_r-1}} \right)^2, j = n, p$$

$$[70]$$

where, $x = R_{s,j}$, $x_0 = r_{N_r-1}$, and $x_1 = r_{N_r}$ are the locations of the last two control volumes in position $N_r - 1$ and N_r , respectively. $f(x_0) = \bar{c}_{s(N_r-1),j}$ and $f(x_1) = \bar{c}_{sN_r,j}$ are the volume-average concentration for the last two control volumes $\bar{c}_{s(N_r-1),j}$ and $\bar{c}_{sN_r,j}$, respec-

tively. $f'(x_0) = \frac{\partial c_{s,j}}{\partial r} \Big|_{r=r_{N_r-1}}$ and $f'(x_1) = \frac{\partial c_{s,j}}{\partial r} \Big|_{r=r_{N_r}}$ are the deriva-

tives of the last two control volumes $\bar{c}_{s(N_r-1),j}$ and $\bar{c}_{sN_r,j}$, respectively.

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