Efficient Conservative Reformulation Schemes for Lithium Intercalation

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Porous electrode theory coupled with transport and reaction mechanisms is a widely used technique to model Li-ion batteries employing an appropriate discretization or approximation for solid phase diffusion with electrode particles. One of the major difficulties in simulating Li-ion battery models is the need to account for solid phase diffusion in a second—radial—dimension r, which increases the computation time/cost to a great extent. Various methods that reduce the computational cost have been introduced to treat this phenomenon, but most of them do not guarantee mass conservation. The aim of this paper is to introduce an inherently mass conserving yet computationally efficient method for solid phase diffusion based on Lobatto III A quadrature. This paper also presents coupling of the new solid phase reformulation scheme with a macro-homogeneous porous electrode theory based pseudo 2D model for Li-ion battery.
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Lithium-ion chemistry has been identified as a good candidate for high-power/high-energy secondary batteries which are expected to play a vital role in the future of automobile, power storage, military, mobile, and space applications. Significant efforts have been made and reported in literature regarding the modeling and understanding of Lithium-ion batteries using physics based first-principles models. The most widely used first principles model for the lithium-ion battery is the porous electrode pseudo two dimensional (P2D) model,[1] which is based on the fundamentals of electrochemistry and transport phenomena. These models are represented by coupled nonlinear PDEs in 1–2 dimensions, are typically solved numerically and require few minutes to hours to simulate.

For the P2D model, the diffusion of Lithium ion into the solid electrode particles is solved in a pseudo dimension r, which is coupled to the macro-homogenous model at the surface of the intercalation particles. This pseudo 2 dimensional approximation avoids the need for a solution of a full 2 dimensional model and hence the name. Accurate predictions of the concentration at the surface of the particle are therefore important, as it contributes to the exchange current density for the reaction at the particle-electrolyte interface. Typically, solid phase diffusion in the micro-scale is modeled using Fick's law of diffusion. More detailed schemes involving pressure induced diffusion along with solid phase diffusion have also been reported in literature.[2] These models are important especially for high capacity materials where the stress developed affects the concentration profile inside the intercalation particle. For phase changing materials, the shrinking core model[3] has been used and approximate solutions have been proposed.[4] Cahn-Hilliard models[5] have also been employed to track the phase boundary within active material particles during Lithium intercalation.[6,7] One of the major difficulties in the electrochemical engineering models is that even the inclusion of a simple Fickian model for solid phase diffusion in a second dimension r increases the complexity as well as the computation time/cost to a great extent. Use of more detailed physics in the solid phase will contribute toward the decrease of computational efficiency. This decrease occurs because at every point in x for the macro-scale, solid phase equations have to be solved in r, and the number of equations depends on the discretization scheme chosen for the r dimension.

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Several methods have been reported in literature for solving the solid phase diffusion problem. These include Duhamel's superposition integral,[1,8] diffusion length method,[9,10] polynomial approximation,[11–13] finite volume, and finite difference. A brief review of these methods is presented in a Coupling Solid-Phase Diffusion with Rigorous Pseudo-2D Battery Models section of this paper. For this particular discussion, we will focus on inherently mass conserving techniques for solving solid phase diffusion problem. The finite volume method is known for its perfect mass conserving nature. Other methods like finite difference lack this special feature and may require additional constraints to achieve the desired results, especially for variable diffusion coefficient. Although finite volume schemes do conserve mass, they are not computationally efficient. Therefore, to address these issues[14] (Zhang et al.) introduced a control volume scheme, both for uniform and non-uniform meshing. In addition, a recent effort from our group also includes a Chebyshev polynomial[15] based approximation for solid phase diffusion. The method presented in this paper is more robust compared to the Chebyshev approach, but the Chebyshev approach is easier to implement and is better than previous polynomial based approaches.

This paper presents a mass conserving, computationally efficient method for the solution of 1-D Fickian spherical diffusion in solid phase. This method is based on Lobatto IIIA quadrature, the details of which are presented in later sections. The discretized solid phase diffusion model generated by this approach has been derived and explained in detail. Finally, solid phase surface concentration results for this approach have been compared with converged finite volume and finite difference solutions to demonstrate the accuracy and improved efficiency of the proposed method. The derived reformulated model is then coupled with the macro-homogenous P2D model to simulate voltage-time curves for low and high rates of discharge.

1-D Spherical Diffusion Equation

Concentration variations in the solid-phase is governed by Fick's law of diffusion given in spherical coordinates as

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

$$\text{at } t = 0 \text{ for } 0 \le r \le R_s \quad c_s = c_{s0} \quad [2]$$

with the boundary conditions

$$\left.\frac{\partial c_s}{\partial r}\right|_{r=0} = 0 \quad [3]$$

$$j(t) = -D_s \left.\frac{\partial c_s}{\partial r}\right|_{r=R_s} \quad [4]$$

Where $D_s = D_0 f(c)$. The sign of the flux term $j(t)$ determines the charging and discharging conditions. Equation 1 can be converted into dimensionless form using the following dimensionless variables and parameters:

$$\tau = \frac{D_0 t}{R_s^2} \quad x = \frac{r}{R_s} \quad C = \frac{c_s}{c_{s0}} \quad \delta(\tau) = \frac{j(t)R_s}{D_0 c_0} \quad [5]$$

$$\frac{\partial C}{\partial \tau} = \frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2 f(C)\frac{\partial C}{\partial x}\right) \quad [6]$$

with the boundary conditions

$$\text{at } \tau = 0 \text{ for } 0 \le x \le 1 \quad C = 0 \quad [7]$$

$$\text{for } \tau > 0, x = 0 \quad \frac{\partial C}{\partial x} = 0 \quad [8]$$

$$\text{for } \tau > 0, x = 1 \quad f(C)\frac{\partial C}{\partial x} = \delta(\tau) \quad [9]$$

Inherent Mass Conserving Collocation Method—the Lobatto IIIA Approach

Simulations solving the solid phase diffusion problem were completed with an inherently mass conserving efficient approach i.e. the Lobatto IIIA method.[16] For our simulations, we use the fourth order Lobatto IIIA approach, but for simplicity we will first introduce the method for second order or h^2 accuracy where h is the size of the node spacing.

Lobatto IIIA of second order accuracy.— The Lobatto IIIA of second order or h^2 accuracy is a collocation method which reduces to the Crank-Nicholson type technique and is an implicit Runge-Kutta type approach, which is inherently mass conserving and numerically A-stable. The following section shows the generalized discretization scheme used for the above mentioned numerical method. Consider a first order ordinary differential equation

$$\frac{dy}{dx} = f(x, y) \quad [10]$$

This method approximates the solution over an interval $[x_0, x_0 + h]$ by a polynomial p of 2^{nd} degree which satisfies the initial condition $f(x_0) = y_0$ and the differential equation at all the collocation points. Let us consider an interval between 0 and 1 and discretize it with 1 node point.

In the following discussion, f_i and y_i represent the function $f(x, y)$ and the solution to the ordinary differential equation at the node point i respectively. The Lobatto IIIA numerical discretization scheme gives the generalized formula for an approximate solution at any node point $i \neq 0$ which is as follows:

$$y_i = y_{i-1} + \frac{h}{2}(f_i + f_{i-1}) \quad [11]$$

where h is the space between two consecutive internal node points. For the case considered here with $N = 1$ internal node point, a total of 2 equations are generated:

$$y_1 = y_0 + \frac{h}{2}(f_1 + f_0) \quad [12]$$

$$y_2 = y_1 + \frac{h}{2}(f_2 + f_1) \quad [13]$$

As is evident, there are 3 unknowns y_0, y_1, and y_2, where one of them can be solved from the boundary condition.

For the application of the Lobatto IIIA method of second order accuracy to the solid phase diffusion problem, the second order spherical Fickian diffusion equation (Equation 6), has to be reduced to two first order equations. Let us introduce two new variables Y_1 and Y_2 where

$$Y_1 = C \quad [14]$$

and

$$Y_2 = x^2 f(C)\frac{\partial C}{\partial x} \quad [15]$$

Y_1 is used to track the concentration of species in solid phase, and Y_2 represents the flux variable. Using the new variables, the dimensionless Fickian diffusion equation is reduced to

$$\frac{dY_1}{dx} = \frac{Y_2}{x^2 f(Y_1)} \quad [16]$$

$$\frac{dY_2}{dx} = x^2\frac{dY_1}{d\tau} \quad [17]$$

These can be written in a column vector form as

$$\frac{d}{dx}\begin{pmatrix} Y_1 \\ Y_2 \end{pmatrix} = \begin{pmatrix} \dfrac{Y_2}{x^2 f(Y_1)} \\ x^2\dfrac{dY_1}{d\tau} \end{pmatrix} \quad [18]$$

The transformed boundary conditions are

$$Y_2|_{x=0} = 0 \quad [19]$$

$$Y_2|_{x=1} = \delta(\tau) \quad [20]$$

with initial conditions $Y_1|_{\tau=0} = 0$ and $Y_2|_{\tau=0} = 0$ for $0 \le x \le 1$.

Now the Lobatto IIIA 2^{nd} order method can be applied to the mass diffusion problem. At each node in the discretized domain, we have the following equation:

$$\begin{bmatrix} Y_1 \\ Y_2 \end{bmatrix}_i = \frac{1}{2}\left(\begin{bmatrix} \dfrac{Y_2}{f(Y_1)} \\ x^2\dfrac{dY_1}{d\tau} \end{bmatrix}_{i-1} + \begin{bmatrix} \dfrac{Y_2}{f(Y_1)} \\ x^2\dfrac{dY_1}{d\tau} \end{bmatrix}_i\right) h + \begin{bmatrix} Y_1 \\ Y_2 \end{bmatrix}_{i-1} \quad [21]$$

which is solved with the corresponding boundary conditions.

Fig. 1 shows the comparison between Lobatto IIIA 2^{nd} order method with finite volume and finite difference. For this case, the

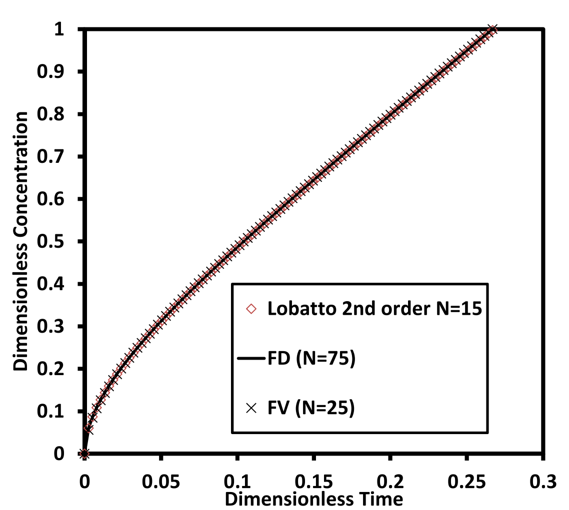

Figure 1. Comparison of Lobatto IIIA 2^{nd} order method with converged Finite Difference and Finite Volume.

diffusivity and the current density are constant. The figure shows good agreement between the three methods during the entire charging process. Though the Lobatto IIIA 2nd order method has a clear advantage in terms of number of state variables needed for convergence compared to both finite volume and finite difference, the number of nodes is still high, especially in situations where the diffusivity or the current density is time or concentration dependent. Next, we introduce a 4th order version of the Lobatto IIIA method that is also mass conservative and most importantly requires a relatively low number of nodes to convergence.

Lobatto IIIA of fourth order accuracy.— As mentioned earlier, Lobatto IIIA method with fourth order accuracy was used to increase accuracy of simulations for the solid phase diffusion.[16] For this particular formulation method, solutions at the points midway between nodes are considered. For example, $y_{i-1/2}$ represents the solution at a point halfway between internal node points $i-1$ and i. Therefore, in general, the formulae for approximate solutions at any node point $i \neq 0$ and any point midway between 2 nodes is given by

$$y_i = \left(\frac{1}{6}f_{i-1} + \frac{2}{3}f_{i-\frac{1}{2}} + \frac{1}{6}f_i\right)h + y_{i-1} \qquad [22]$$

and

$$y_{i-\frac{1}{2}} = \frac{1}{2}y_{i-1} + \frac{1}{8}f_{i-1}h + \frac{1}{2}y_i - \frac{1}{8}f_i h \qquad [23]$$

where h is the space between two consecutive internal node points. For example, using these notations for node spacing between the domain boundary ($x = 0$) and the internal node point 1, we derive the following formulas for the solutions at the internal node point and an intermediate point.

$$y_1 = \left(\frac{1}{6}f_0 + \frac{2}{3}f_{\text{int}} + \frac{1}{6}f_1\right)h + y_0 \qquad [24]$$

$$y_{\frac{1}{2}} = \frac{1}{2}y_0 + \frac{1}{8}f_0 h + \frac{1}{2}y_1 - \frac{1}{8}f_1 h \qquad [25]$$

An appropriate boundary condition will take care of one of the unknown variables in the system.

Using the 4th order Lobatto formulation for the solid phase diffusion problem, the general formulae at internal nodes and intermediate points are presented below in vector form.

$$\begin{bmatrix} Y_1 \\ Y_2 \end{bmatrix}_i = \left(\frac{1}{6}\begin{bmatrix} \dfrac{Y_2}{f(Y_1)} \\ x^2\dfrac{dY_1}{d\tau} \end{bmatrix}_{i-1} + \frac{2}{3}\begin{bmatrix} \dfrac{Y_2}{f(Y_1)} \\ x^2\dfrac{dY_1}{d\tau} \end{bmatrix}_{i-\frac{1}{2}} + \frac{1}{6}\begin{bmatrix} \dfrac{Y_2}{f(Y_1)} \\ x^2\dfrac{dY_1}{d\tau} \end{bmatrix}_i\right)h + \begin{bmatrix} Y_1 \\ Y_2 \end{bmatrix}_{i-1} \qquad [26]$$

$$\begin{bmatrix} Y_1 \\ Y_2 \end{bmatrix}_{i-\frac{1}{2}} = \frac{1}{2}\begin{bmatrix} Y_1 \\ Y_2 \end{bmatrix}_{i-1} + \frac{1}{8}\begin{bmatrix} \dfrac{Y_2}{f(Y_1)} \\ x^2\dfrac{dY_1}{d\tau} \end{bmatrix}_{i-1} h + \frac{1}{2}\begin{bmatrix} Y_1 \\ Y_2 \end{bmatrix}_i - \frac{1}{8}\begin{bmatrix} \dfrac{Y_2}{f(Y_1)} \\ x^2\dfrac{dY_1}{d\tau} \end{bmatrix}_i h \qquad [27]$$

For further illustration, a case of discretization with the proposed method for $N = 1$ internal node point is considered. This generates 8 differential algebraic equations, but some can be eliminated analytically as discussed in the appendix. The DAE system generated is stiff in nature, and therefore the DAE solvers require an additional level of robustness to tackle this system.

Results were simulated for different parameters and operating conditions: constant diffusion coefficient with galvanostatic charging; constant diffusion coefficient with non-uniform current I; concentration dependent diffusion coefficient with galvanostatic charging; and

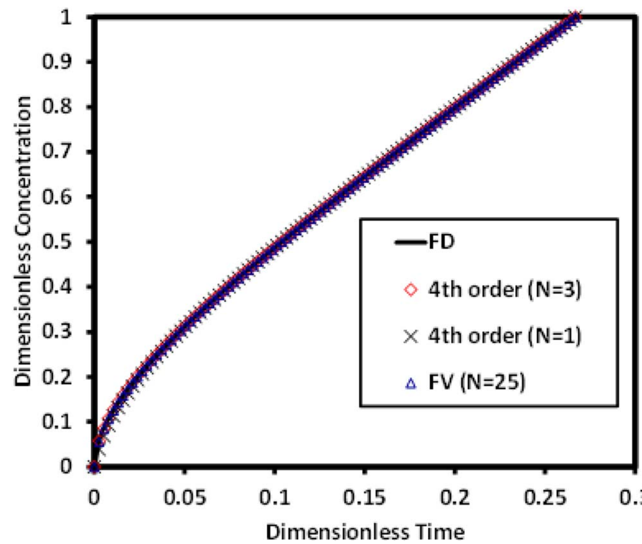

Figure 2. Comparison of Lobatto IIIA 4th order method with Finite Volume and with Finite Difference using constant diffusion coefficient and galvanostatic charging.

concentration dependent diffusion coefficient with non-uniform current I. Simulation results for all cases with the proposed method were compared with standard finite difference (FD) and finite volume (FV) methods. The dimensionless surface concentration $C_{surf}(x, \tau)$ is the quantity of interest because it is required by the macro-homogeneous battery model to keep track of the local current density as a function of time. Therefore, this quantity is the basis of comparison between the numerical techniques for all mentioned cases. All simulations were stopped when the dimensionless surface concentration reached a cutoff magnitude of 1.

Results were simulated for a constant dimensionless diffusion coefficient ($D_s = D_o = 1$) and galvanostatic charging where the dimensionless surface flux is specified as $\delta(\tau) = 1$. Fig. 2 compares results obtained from the proposed Lobatto IIIA 4th order method with finite volume and finite difference techniques. Comparing the Lobatto approach with another mass conserving method, finite volume method, 25 internal cells are required for the finite volume method, while the Lobatto method used only *one* internal node point to yield reasonable accuracy in predicting the surface concentration except for very short time because of the steep concentration gradient at the start of lithium intercalation inside the particle. To capture the short time dynamics of the system, $N = 3$ internal node points were used which generated a converged solution and accurately predicted the dimensionless surface concentration $C_{surf}(x, \tau)$ over the entire time interval. Since both the Lobatto and finite volume methods are mass conserving by nature, we must determine which is more computationally efficient. One basis of comparison is the number of state variables required to solve for a particular numerical method to obtain accurate results for the spherical diffusion problem. For the finite volume method, using 25 internal cells for discretization will generate 27 state variables in total for the system. The additional couple of state variables are present in the system to track the center and surface concentrations. For the Lobatto method, it should be noted that the second order spherical diffusion equation is converted to two first order equations. Therefore, two variables Y_1 and Y_2 at each node point and at each point halfway between two consecutive node points are solved for in this formulation. To avoid confusion, we use $Y_{1,\text{int}}$ and $Y_{2,\text{int}}$ to denote the variables Y_1 and Y_2 at the points midway between nodes. The entire set of $Y_{2,\text{int}}$ variables and the majority of $Y_{1,\text{int}}$ variables can be eliminated analytically in terms of other variables (see Appendix). For $N = 3$ internal node points, this elimination reduces the total number of state variables from 16 to 9, significantly fewer than the finite volume method. The computational efficiency of the method will be most significant when

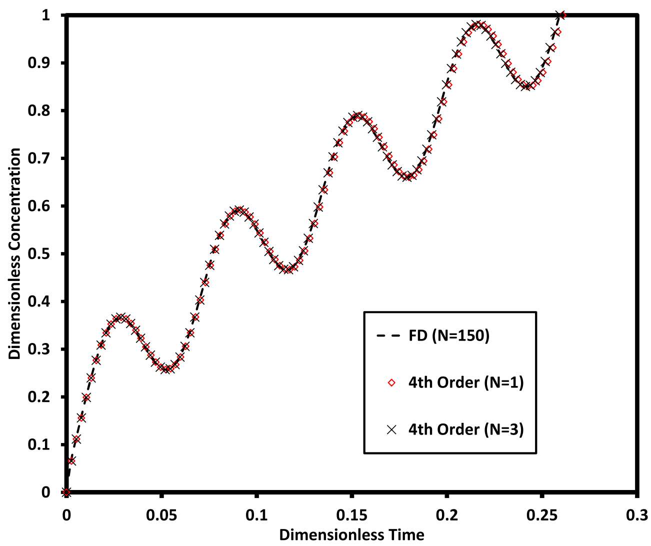

Figure 3. Comparison of Lobatto IIIA 4^{th} order method with Finite Difference with constant diffusion coefficient and time dependent charging current.

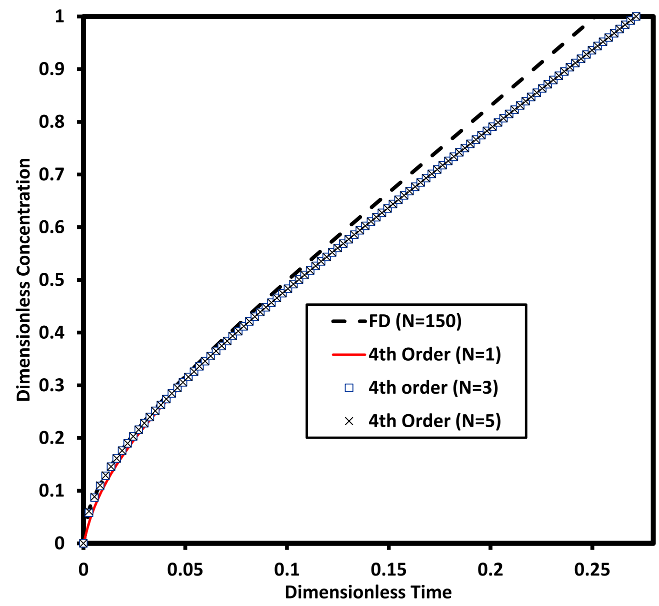

Figure 4. Comparison of Lobatto IIIA 4^{th} order method with Finite Difference with concentration dependent diffusion coefficient and galvanostatic charging current.

the spherical diffusion model is coupled with the macro-homogenous P2D model, where spherical diffusion is solved in the radial direction at every point across the electrode. On the other hand, the finite difference method with second order accuracy requires an excess of 100 node points in x to predict accurate results. Therefore, the proposed Lobatto method provides computational efficiency by reducing the number of state variables while still conserving mass.

Simulations were also performed for a constant dimensionless diffusion coefficient ($D_s = D_o = 1$) and for a non-uniform charging current I, where the dimensionless surface flux varies with time, i.e. $\delta(\tau) = 1 + \sin(100\tau)$. This case is a close representation of the macro-homogeneous P2D battery model as the pore wall flux is a function of time. When the flux at the surface varies with time, conservation of mass and accurate surface concentration predictions present a challenge. Fig. 3 compares the surface concentration profiles for the Lobatto method for two choices of internal node points with the finite difference technique. Using one internal node point, we achieve reasonable accuracy in prediction of the surface concentration, but $N = 3$ internal node points are required to generate a converged solution. Simulations for the Lobatto method for this case were performed with higher number of internal node points as a check for convergence, but a total of three node points was found to be sufficient. For the finite difference (FD) numerical method, more than 100 node points were used for spatial discretization of the system to generate accurate and converged results. The FD method is not inherently mass conserving, therefore it usually requires more discretization points compared to the Lobatto and finite volume formulations, especially for cases where the surface flux varies with time.

Proton diffusion into nickel hydroxide electrodes used in the Ni-MH batteries is a strong function of the solid-phase concentration and decreases approximately by three orders of magnitude when the electrode is discharged from the completely charged state. This varying transport property was captured by using the complex faradaic impedance of the nickel hydroxide active material and reported as Eq. 5 elsewhere.[17] This work has been used for accounting for variable diffusion coefficient by Botte et al.[18] to determine a diffusion coefficient that is a function of the dimensionless flux rate of the material diffusing into the particle. Verbrugge et al.[19] expressed the intercalation diffusion coefficient as an indirect function of solid-phase concentration consisting of a fractional occupancy of intercalating host material and the activity coefficient. The significance of taking an account of this variation in intercalating electrodes was demonstrated by Botte and White.[20] Here, mathematical models are developed to simulate the potentiostatic charge/discharge of a partially graphitic carbon fiber and the galvanostatic discharge of a lithium foil cell under solid diffusion limitations. Evidence that shows the importance of accounting for nonlinear diffusion was shown by Karthikeyan et al.[21] for the recently popular $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ positive active material in lithium-ion batteries, where the thermodynamic expressions along with the activity correction are incorporated into a single particle diffusion model for a Li-ion cell. Hence, the use of nonlinear diffusion, where the diffusion coefficient is a function of concentration, is becoming more and more popular in the battery modeling domain. To test our proposed Lobatto methods, we compared the results with rigorous finite difference solution for constant dimensionless current $\delta(\tau) = 1$, and diffusion coefficient D_s varying as a simple function of $C(x, \tau)$ i.e. $f(C) = 1 + 0.1C$. Fig. 4 presents a comparison of the simulation results for the above mentioned case of study. At least $N = 3$ internal node points are required to achieve a converged profile for the dimensionless surface concentration. Simulation with one internal node point failed to capture the short time dynamics of the system as expected and therefore failed to capture the surface concentration profile accurately at the start of lithiation. Simulations were also performed with the FD method. 150 internal node points were used for discretizing the system. Use of such large number of discretization points was not enough to achieve mass conservation for the FD method. The simulation predicted incorrect higher surface concentration at longer times, which lead it to reach the cutoff limit faster. Therefore, for the case of concentration dependent diffusion coefficient, the Lobatto method is definitely a better choice compared to standard FD method. Moreover, this method reduces the number of state variables considerably when compared to the FD method. Fig. 5 shows the convergence of Lobatto method for diffusivity that is highly dependent on the concentration $f(c) = 0.1 + 9.9C$. It is clear that having $N = 3$ internal node points is enough for a converged solution, which proves the robustness of the method when there are drastic changes in diffusivity.

Simulations were performed for the concentration dependent, dimensionless diffusion coefficient ($D_s = D_o f(c)$) with a non-uniform charging current I, where the dimensionless surface flux varies with time, as $\delta(\tau) = 1 + \sin(100\tau)$. The results are presented in Fig. 6. As seen previously, the Lobatto method with one internal node point failed to capture the highly transient surface concentration $C_{surf}(x, \tau)$ profile. But accurate results were achieved by use of $N = 3$ internal node points. Simulations were run with higher number of node

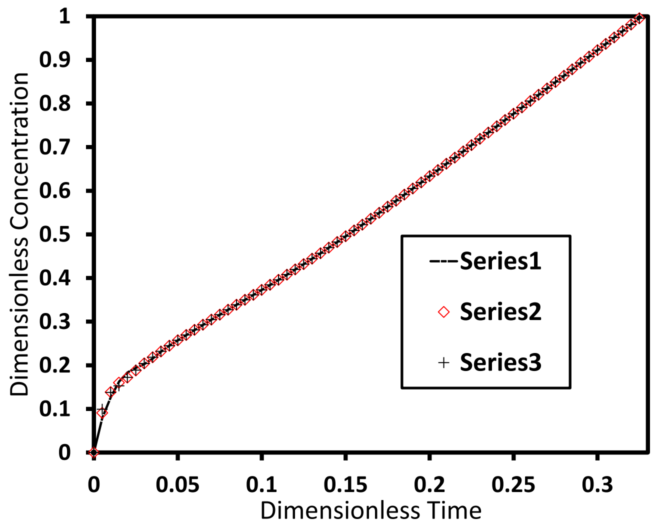

Figure 5. Convergence of the 4th order Lobatto method with concentration dependent diffusion coefficient given by $f(c) = 0.1 + 9.9 * C$ and galvanostatic charging current.

points to check for convergence and accuracy of results for the Lobatto method. Using second order accurate FD with 150 internal node points predicted erroneous surface concentrations. On the other hand, the Lobatto method showed high accuracy and conserved mass using a minimal number of internal node points, therefore reducing computational load.

Coupling Solid-Phase Diffusion with Rigorous Pseudo-2D Battery Models

As mentioned earlier, the coupling of solid phase diffusion physics with the macro-homogenous P2D model,[1] is a crucial step in simulation of battery models. To eliminate the time consuming calculations in the radial dimension r, porous electrode models use approximations for solid phase diffusion. The Duhamel's superposition method[1] is a robust method available for representing the solid phase diffusion for

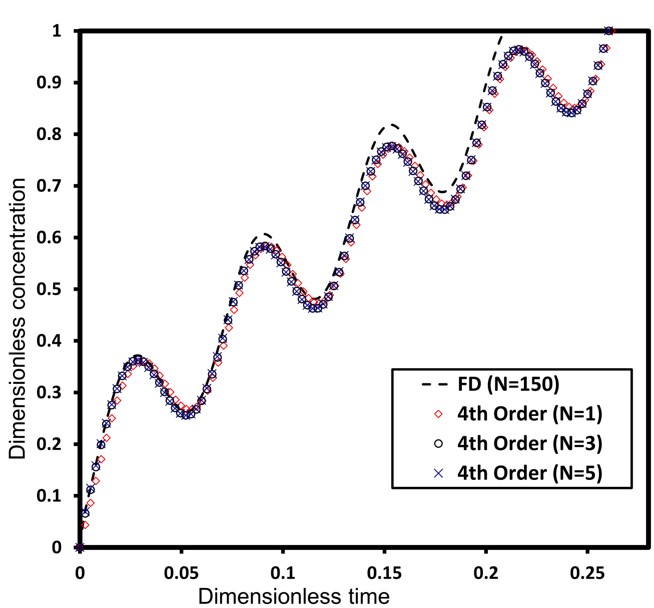

Figure 6. Comparison of Lobatto IIIA 4th order method with Finite Difference with concentration dependent diffusion coefficient and time dependent charging current.

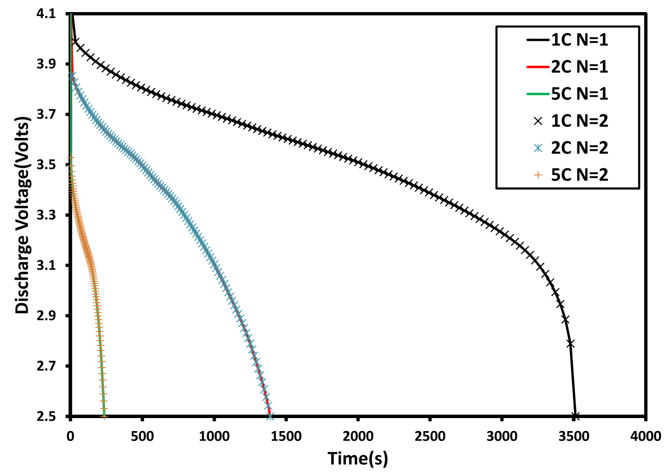

Figure 7. P2D model coupling with Lobatto IIIA 4th with N = 1 and N = 2 internal nodes showing convergence.

constant diffusivities, which is a valid assumption for a wide range of operating conditions. Details about the method and equations are presented in literature.[1,22] This method can sometimes generate stiff sets of equations and therefore may be very difficult for simulations. Liaw et al.[9] introduced the diffusion length method which is based on a parabolic profile approximation for the solid phase and is accurate at long times, low rates, and less dynamic operations. Polynomial approximation methods were introduced by Subramanian et al.[11] where the solid phase concentration was approximated by parabolic or higher order polynomials coupled with volume averaging. These methods have problems similar to the diffusion length method and therefore would not be suitable for implementing in models for HEVs and other high rate applications. Liu et al.[23] reported a very robust method which covers a wide spectrum of high/low rates, pulses, etc. but it may greatly increase the number of equations, adding numerical difficulties for simulation. Other methods in practice are the penetration depth method,[24] which is not very accurate for time varying charging rates, and finite element methods,[24] where the node spacings are derived based on a fixed set of operating conditions and therefore may not be optimal for different conditions or at long times. Ramadesigan et al.[25] introduced Eigen function based Galerkin reformulation of solid phase diffusion with constant diffusivity which is a very robust method applicable for a wide range of operating conditions. The finite difference approach with unequal node spacing or mixed order finite difference method was also reported in literature; this method is applicable for both constant and concentration dependent diffusion coefficients and valid for a wide range of operating conditions.[13,25] An efficient method based on an analytic solution was presented by Guo et al.[26] Recently, Zeng et al.[14] introduced the finite volume and control volume approaches for solid phase diffusion. Both of these schemes are inherently mass conserving, but the finite volume does not give the surface concentration (variable which couples the macro-homogenous model with the solid phase) directly and has to be approximated, which can introduce errors. The control volume method gives the surface concentration directly

This paper presents the Lobatto fourth order method for solid phase diffusion coupled with the rigorous macro-homogeneous P2D battery model.[1] The simulations were run for low to high rates of charging. For all cases, D_s is a constant. Fig. 7. shows the results (voltage-time curves) from the simulations for the Lobatto fourth order approach for solid phase diffusion coupled with the macro-homogenous pseudo 2D model for discharge rates from 1 C to 5 C with a constant diffusion coefficient D_s. The computations were terminated when the potential dropped to 2.5 V. The simulations were done with IDA[27] and a compiled version of Maple's dsolve. Table I. shows the simulation times for both of the solvers for 1C rate and

Table I. Simulation times for the P2D model coupled with Lobatto IIIA 4th order.

Rate	Time with Maple's dsolve (s)	Time with IDA (s)
1C	174.71	0.166
2C	92.165	0.501

2C rate. The results suggest that we have increased computational efficiency.

It should be noted that for this approach, good DAE solvers are needed. Not all solvers can handle stiff nonlinear DAEs. Analytical transformation to reduce the states requires effort but proved important.

Conclusions

An efficient, inherently mass conserving method based on Lobatto IIIA technique was introduced and applied on the 1-D solid phase spherical diffusion problem. Case studies were performed for both constant and concentration dependent solid phase diffusion coefficients. The new method was also tested for constant and time varying currents. As mentioned earlier, our variable of interest is the concentration at the surface of the solid particle, which tracks the local current density when coupled to macro-homogeneous models. The accuracy of the proposed method was proven by comparing the results for surface concentration with converged finite volume and finite difference simulations for all the above mentioned cases. The computational efficiency of this method was also discussed by comparing the number of state variables required for simulation against the other schemes. Finally, the new reformulated model was coupled with the P2D model, and the results for low to high rates of galvanostatic discharge were presented. These results proved that the new reformulated model for solid phase diffusion improves efficiency of simulations of the P2D battery model.

Future work will involve optimizing node spacing for the new efficient mass conserving reformulation method in order to reduce the number of node points and enable faster simulation. The method can also be extended to study phase change materials where the interface has to be tracked by a moving boundary.

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Appendix: Reducing the Number of State Variables Resulting from the Application of Lobatto Fourth Order Method to the Solid State Diffusion Equation

This appendix discusses the reduction of the number of states that results when the Lobatto fourth order method is applied to spherical solid diffusion problem. Here we show the procedure for $N = 1$ internal node points. $Y_{1,\mathrm{int}}$ and $Y_{2,\mathrm{int}}$ are used to denote the variables Y_1 and Y_2 at the intermediate points.

Using one internal node point will generate two discretization cells, and within each cell two internal variables $Y_{1,\mathrm{int}}$ and $Y_{2,\mathrm{int}}$ have to be solved for. That is in addition to two variables at each node. The total number of states is 8, which is also the number of equations to solve. The number of states and equations can be analytically reduced to 5 equation by eliminating most of $Y_{1,\mathrm{int}}$ and $Y_{2,\mathrm{int}}$ variables. Specifically, one can solve for 3 intermediate variables from 3 of the 4 equations resulting from the applications of equation 27 and plugging these variables into the 4 equations that come from equation 26. The one variable that should not be solved for and gotten rid of is the last $Y_{1,\mathrm{int}}$—the concentration in the middle of the cell adjacent to $x = 1$—because doing so would result in a time derivative of the pore wall flux, which is undesirable. In the end, there are only 5 equations left that can be solved to get the surface concentration directly.

In general, discretizing the x domain with N internal node points results in $2(2N + 2)$ first order differential algebraic equations. Elimination of most of the intermediate states can be used to cut that number down to $2N + 3$ equations.

List of Symbols

C	dimensionless concentration of Lithium ions in the intercalation particle of electrode
C_{s0}	reference concentration, mol/m^3
c_s	concentration of Lithium ions in the intercalation particle of electrode, mol/m^3
D_s	Lithium-ion diffusion coefficient in the intercalation particle of electrode, m^2/s
D_0	diffusion coefficient at reference concentration c_0, m^2/s
$j(t)$	pore wall flux of Lithium-ion the intercalation particle of electrode, mol/m^{2}s
R_s	radius of the intercalation particle of electrode, m
t	time, s
τ	dimensionless time
r	dimensional radial distance with the electrode particle, m
x	dimensionless radial distance within the particle

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