Efficient Reformulation of Solid-Phase Diffusion in Physics-Based Lithium-Ion Battery Models

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One of the major difficulties in simulating Li-ion battery models is the inclusion of solid phase diffusion in a second dimension *r*. It increases the complexity of the model as well as the computation time/cost to a great extent. Rigorous approach towards solid phase diffusion leads to more difficulties, with the use of emerging cathode materials, which involve phase changes and thus moving boundaries. This paper compares approaches available today for solid phase reformulation and provides two most efficient forms for constant and varying diffusivities in the solid phase.

Introduction

Physics based Li-ion battery models use porous electrode theory. One of the major difficulties in these models is the inclusion of solid phase diffusion in a second dimension *r* which increases the complexity of the model as well as the computation time/cost to a great extent. Rigorous approach towards solid phase diffusion leads to more difficulties, with the use of emerging cathode materials, which involve phase changes and thus moving boundaries. This paper compares various methods (1-5) for approximating/representing solid-phase concentration variations within the active materials of porous electrodes for a rigorous pseudo-2D model for lithium-ion batteries. Concentration variations in the solid-phase is governed by Fick's law of diffusion and the same in spherical coordinates is given as

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

$$at \ \ t = 0 \ for \ \ 0 \le r \le R_s \ \ \ c = c_0 \qquad [2]$$

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

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

where $D_s = D_0 f(c)$. Equation[1] can be converted to dimensionless form with the following transformations:

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

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

with the boundary conditions

$$\text{at } \tau = 0 \text{ for } 0 \leq x \leq 1 \quad C = 1 \tag{7}$$

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

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

Existing approximations and their drawbacks

Porous electrode models of Li-ion batteries often use approximations to eliminate the time consuming calculation in the second dimension *r* for the solid phase diffusion. These methods include the Duhamel's superposition method (2), diffusion length method (3), the polynomial approximation method (4), the pseudo steady state (PSS) approach by Liu (5) and the penetration depth analysis and finite element approach introduced by K. Smith et al. (6).

Each of the above listed methods has its own advantages and disadvantages when used in Li-ion battery models. For instance, the Duhamel's superposition method is the robust of all methods and is valid for any kind of operating condition. However, it cannot be used in DASSL like solvers which don't accept equations discretized in time. Similarly, the diffusion length method's prediction is inadequate at short times and very efficient at long times and low rates. The polynomial approximation method by Subramanian et al. is very efficient at long times, and for low/ medium rates, and is ideal for adaptive solvers for pseudo-2D models. However, it is inaccurate at short times and for high rates/pulses.

The PSS approach by Liu (5) is very robust and by having enough number of equations, this approach can cover the entire spectrum of high/low rates, pulses, *etc*. The penetration depth analysis approach empirically fits penetration depth near the surface of the particle. The advantage of this method is that it is very accurate at short times/pulses and more accurate and efficient penetration depth solutions can be directly obtained from the partial differential equation. The drawback with this approach being the need to be reinitialized every time, and does not give a good match for varying δ. Though this method is very accurate and efficient at short times, it is not ideal for adaptive solvers in a pseudo-2D model (increases stiffness).

Galerkin reformulation of solid phase diffusion

The reformulation proposed is based on Eigen function based Galerkin collocation for constant diffusivity. In case of constant diffusivity *f(C)* in equations [6] and [9] will be 1. The equations for approximation are given below. A detailed procedure for deriving the equations and their mathematical significance will be published at a later instance by the authors. Using rigorous mathematical analysis it can be shown that $\sum_{n=1}^{m}\frac{1}{\lambda_n^{2}} = \frac{1}{10}$ in Equation[11].

$$\frac{d\bar{c}}{d\tau} = -3\delta(\tau) \qquad [10]$$

$$c_s = \bar{c} - \frac{\delta(\tau)}{5} + 2\delta(\tau)\sum_{n=1}^{m}\frac{1}{\lambda_n^2} - \sum_{n=1}^{m}q_n\lambda_n^2\sin(\lambda_n) \qquad [11]$$

$$\frac{dq_n}{d\tau} + \lambda_n^2 q_n = 2\frac{\delta(\tau)}{\lambda_n^2\sin(\lambda_n)} \qquad [12]$$

$$\lambda_n = \tan(\lambda_n) \qquad [13]$$

An important advantage of this approach is, this reformulation is very robust and by having enough number of q's, in other words, enough number of equations [12], this approach can cover the entire spectrum of high/low rates, pulses, *etc.* like the PSS method by Liu. However, in Liu's PSS approach the q's vary as $q_1<q_2<q_3<q_4$ and the order of q_4 is as high as 10^{40} causing stiffness and numerical instability in the pseudo-2D models using this approach. The present reformulation overcomes this problem. In this method the q's vary as $q_1>q_2>q_3>q_4$, in other words we have a converging series in q_n which makes this approach equivalent to PSS model in accuracy, but highly efficient in pseudo-2D environment for computation avoiding stiffness and computational difficulties.

Finite difference approach with unequal node spacing

For the solid phase diffusivity (D_s) varying as a function of concentration, the Galerkin approach cannot be used. Alternatively, another approach was tried to approximate the solid phase diffusion equations by Smith et al. (6). This involved 5 finite elements of different sizes in the radial coordinate r. We used finite difference (FD) with unequal node spacing in the r direction and discretized the diffusion Equation[6]. The mixed finite difference form of this equation with constant D_s is given as

$$\frac{d}{d\tau}C_i = 2\frac{h_iC_{i+1} - h_iC_i + h_{i+1}C_{i-1} - h_{i+1}C_i}{h_ih_{i+1}(h_{i+1}+h_i)} - 2\frac{h_{i+1}^2C_{i-1} - h_{i+1}^2C_i - h_i^2C_{i+1} + h_i^2C_i}{\sum_{j=1}^{i}h_jh_ih_{i+1}(h_{i+1}+h_i)}, \, i = 1..N$$

$$[14]$$

where N is the number of interior node points. A similar expression for varying D_s can be derived. Further we ran an optimization algorithm to find the best h_1, h_2, h_3, *etc.* and minimize N and the CPU time. This method is very accurate for short times/high rates/pulses; and is recommended for varying diffusion coefficients. Varying diffusivities are important and is likely to get more attention because of its requirement for addressing stress effects in the Li-ion batteries (7).

Results and Discussion

Figure 1 shows the comparison of the Galerkin method, with rigorous numerical solution for varying $\delta(\tau)$, and a constant D_s along with the PSS method by Liu.
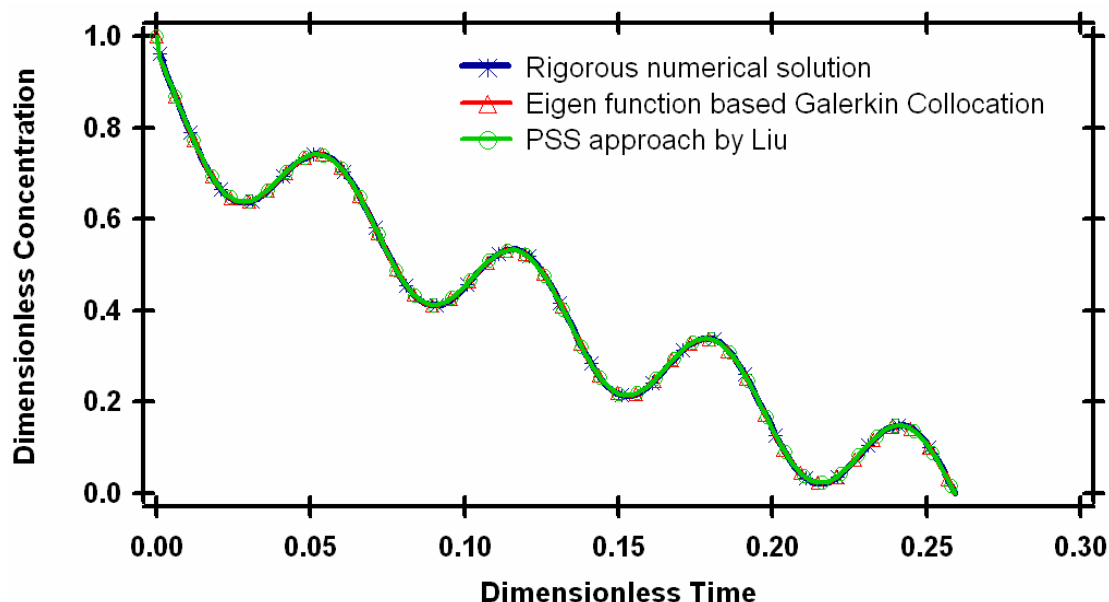
Figure 1. Comparison of Eigen function based Galerkin reformulation with rigorous numerical solution and PSS by Liu for $\delta\,(\tau) = 1 + sin\,(100\,\tau)$ and $m = 5$.

Figure 2 shows the comparison of Mixed FD method with 5 internal nodes for constant $\delta\,(\tau)$, and constant D_s with the rigorous numerical solution. It can be observed that the approximation agrees accurately with the rigorous numerical solution.
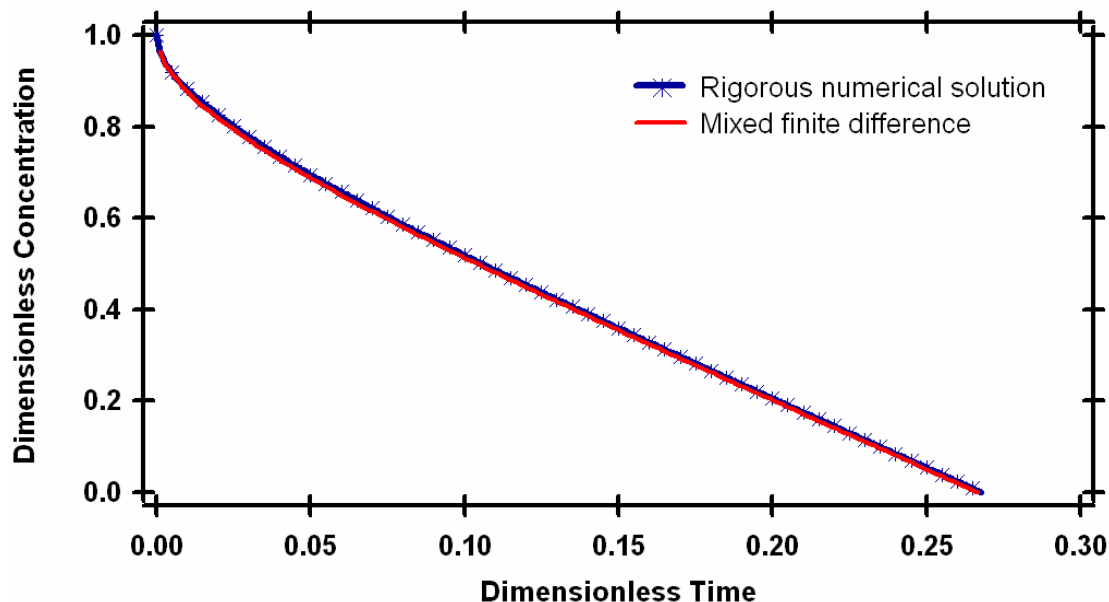

Figure 2. Comparison of mixed FD method with 5 interior nodes with rigorous numerical solution for constant D_s and $\delta\,(\tau) = 1$

The Eigen function based Galerkin collocation approach was included in a rigorous Li-ion battery model and the discharge curves obtained at 5 C and 10 C rates have been shown in Figure 3. The solid phase reformulations are necessary for faster

simulation of Li-ion battery models which help in faster estimation of parameters from these models from the experimental data.
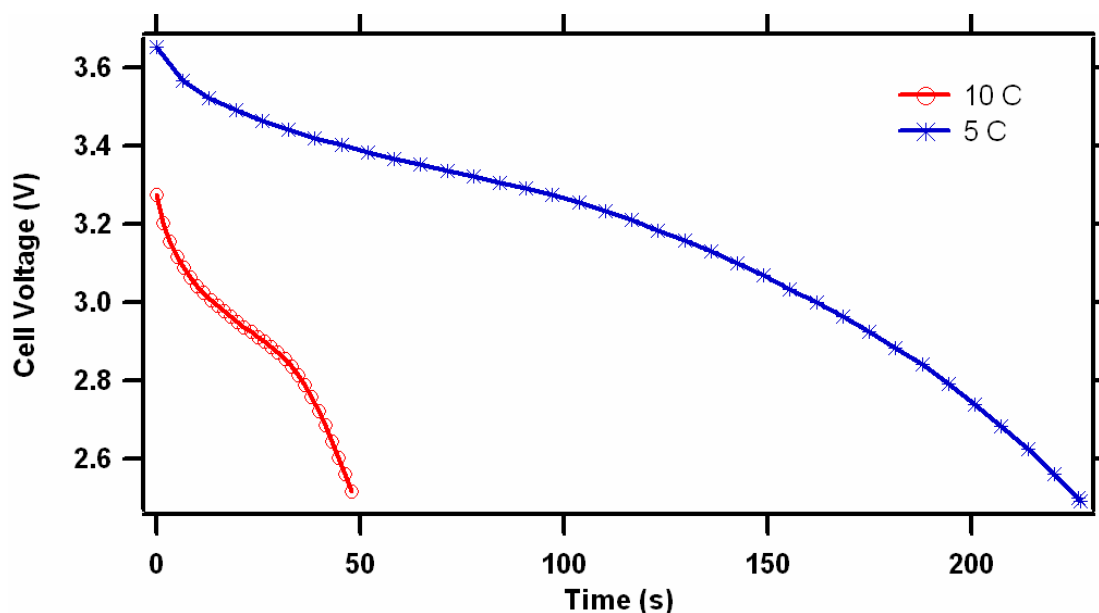

Figure 3. Discharge curves at 5 C and 10 C rates from a Pseudo-2D model for Li-ion battery using the Eigen function based Galerkin reformulation for the solid phase.

Figure 4 shows the comparison of mixed FD method with 5 internal nodes for constant δ (τ), and D_s varying as a simple function of C with the rigorous numerical solution. For varying D_s, $f(C) = 1 + 0.1$ C, mixed FD approach was found to be efficient and accurate at short times.
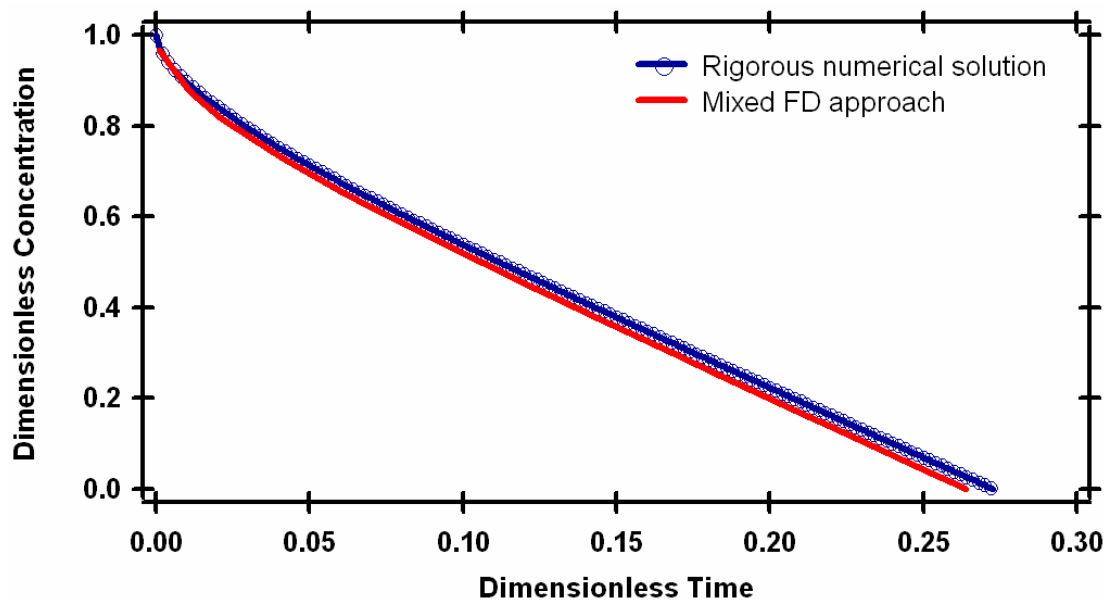

Figure 4.   Comparison of mixed FD method with 5 interior nodes with rigorous numerical solution for $f(C) = 1 + 0.1C$ and δ (τ) $= 1$

Conclusion

The different approximation schemes available for solid phase approximation for Li-ion batteries were reviewed and compared. An Eigen function based Galerkin-weighted residual approximation provides efficient reformulation for the solid-phase equation for constant diffusivities. Mixed finite difference/finite volume equations (unequal node spacing) can be derived for varying diffusion coefficient as a function of concentration, and are very efficient for short times and so far seem to be the only option for reformulating nonlinear diffusivities.

Acknowledgments

List of Symbols

C	concentration of lithium ions in the intercalation particle of electrode, mol/m^3
c_0	reference concentration, mol/m^3
c_s	surface concentration of lithium ions in the intercalation particle of electrode, mol/m^3
$\bar{c}$	average concentration of lithium ions in the intercalation particle of electrode, mol/m^3
C_i	dimensionless concentration at i^{th} node point
D_s	Li-ion diffusion coefficient in the intercalation particle of electrode, m^2/s
D_0	diffusion coefficient at reference concentration c_0, m^2/s
h_i	node spacing at i^{th} node point
$j(t)$	pore wall flux of Li ion the intercalation particle of electrode, mol/m^2s
q	volume averaged concentration flux, $mol\ cm^{-4}$
R_s	radius of the intercalation particle of electrode, m
λ_m	positive eigen values

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