



Semianalytical method of solution for solid phase diffusion in lithium ion battery electrodes: Variable diffusion coefficient

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ABSTRACT

A semianalytical methodology based on the integral transform technique is proposed to solve the diffusion equation with concentration dependent diffusion coefficient in a spherical intercalation electrode particle. The method makes use of an integral transform pair to transform the nonlinear partial differential equation into a set of ordinary differential equations, which is solved with less computational efforts. A general solution procedure is presented and two illustrative examples are used to demonstrate the usefulness of this method for modeling of diffusion process in lithium ion battery electrode. The solutions obtained using the method presented in this study are compared to the numerical solutions.

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1. Introduction

Lithium ion batteries typically consist of intercalation type materials as electrodes. Studies have shown that diffusion coefficient of lithium in the host materials (like carbon for example) is a function of concentration or state of charge (SOC) [1–3]. When the effects of thermodynamic variations [4–7] or the mechanical stress [7–9] on the diffusion process inside the solid phase are taken into consideration, the diffusion equation becomes nonlinear. In most of the literature pertaining to mathematical modeling of lithium ion batteries, diffusion inside the solid phase is treated as a linear problem with constant diffusion coefficient [10–12]. Botte and White using a carbon based electrode as the modeling system, demonstrated the importance of considering the nonlinear effects in the solid phase [5]. In spite of several studies indicating the importance of including the nonlinear effects for the solid phase of the battery electrode, very few models have included these effects because of the added complexity [4–9]. The use of these models for the estimation of parameters and cycle life studies is limited as it involves additional computational cost. There are certain successful efforts taken in the past to simplify the rigorous physics based models with reasonable accuracy [13–15]. Most of these studies have been developed for linear diffusion equation with constant coefficient in the electrode particle.

The objective of this paper is to extend these efforts and develop a methodology to solve the nonlinear diffusion equation in a spherical intercalation electrode. The approach used in the present study is based on the finite integral transform technique that has been previously used to solve nonlinear boundary value problems in heat transfer [16,17] and solute transport in porous media [18]. The attractive feature of this method is the flexibility to handle most of the nonlinear equations and ease of extension to incorporate nonlinear boundary conditions and different geometries (including cylindrical geometry).

The general methodology is presented in the following section. Two simple illustrative examples are discussed to demonstrate the potential of this technique as a competitive mathematical tool for addressing nonlinear diffusion processes in the battery electrode. The Eigen function expansion method presented by Tsang and Hammarstrom [19] is used to further simplify the problem for the two cases considered in this study.

2. Model description

For the purpose of this study the electrode particle is considered to be a sphere and the discharge process in the electrode is described using the single particle model [20]. Diffusion of lithium inside the particle is described by the following equation:

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[D_{eff} r^2 \frac{\partial C}{\partial r} \right] \quad (1)$$

where D_{eff} is the concentration (or SOC) dependent diffusion coefficient arising due to incorporation of the thermodynamic variation or including the effect of mechanical stress on the diffusion process

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Nomenclature

C	concentration of lithium in the solid phase (mol cm ⁻³)
\bar{C}	dimensionless concentration of lithium in particle
D	diffusion coefficient of lithium in the particle including the nonlinear effects (cm ² s ⁻¹)
\bar{D}	dimensionless diffusion coefficient of lithium in the particle
E	Young's modulus (N cm ⁻²)
F	Faraday's constant, 96,487 (C mol ⁻¹)
i_n	applied current density (A cm ⁻²)
j	rate of the electrochemical reaction at the particle surface (mol cm ⁻² s)
K	number of terms considered in the expansion
M	molecular mass (g mol ⁻¹)
n	number of electrons involved in electrochemical reaction.
R	gas constant, 8,314 (J mol ⁻¹ K)
R_p	radius of the particle (Cm)
r	radial coordinate (Cm)
t	time (S)
T	temperature (K)
u	displacement vector (Cm)
\bar{V}_{Li}	partial molar volume of lithium in intercalation material (cm ³ mol ⁻¹)
V	cell potential (V)

Greek Symbols

Γ	nonlinear contribution function in diffusion coefficient
γ	activity coefficient in the solid phase
θ	dimensionless flux at the surface of the particle
λ	eigenvalues
ν	Poisson's ratio
ξ	dimensionless coordinate
ρ	density of the particle (g cm ⁻³)
σ_n	hydrostatic stress (N cm ⁻²)
σ_r	radial component of stress (N cm ⁻²)
σ_t	tangential component of stress (N cm ⁻²)
ϕ	kernel of the transform or eigenfunction
τ	dimensionless time
$\bar{\omega}$	nonlinear contribution to the diffusion process

Subscripts

eff	effective
k	number of terms
l	number of terms
max	maximum
n	number of terms
r	radial
s	separator
t	tangential

of lithium into the host material. At the surface of the electrode particle electrochemical reaction takes place and this dictates the flux of lithium into the particle. The flux at the surface is given by:

$$-D_{eff} \frac{\partial C}{\partial r} \Big|_{r=R_p} = j = \frac{i_n}{nF} \quad (2)$$

where j is the rate of the electrochemical reaction at the electrode surface which is a proportional to local current density at

the particle surface (i_n). n is the number of electron involved in the electrochemical reaction and F is the Faraday's constant.

The flux of lithium at the center of the particle is given by:

$$-D_{eff} \frac{\partial C}{\partial r} \Big|_{r=0} = 0 \quad (3)$$

The initial condition is described by:

$$C(r, 0) = C_0 \quad (4)$$

3. Solution procedure**3.1. Dimensionless governing equations**

The system of Eqs. (1)–(4) is cast into a more convenient form by defining the following dimensionless variables:

$$\xi = \frac{r}{R_p}; \quad \tau = \frac{D_0 t}{R_p^2}; \quad \bar{C} = \frac{C - C_0}{C_{max}} \quad (5)$$

where R_p is the radius of the particle, C_0 is the initial concentration of lithium in the particle, C_{max} is the maximum stoichiometric concentration of lithium in the host. D_0 is the diffusion coefficient of lithium in the particle with the initial concentration of lithium C_0 .

The governing equation (Eq. (1)) is expressed using the above dimensionless variables as given below:

$$\frac{\partial \bar{C}}{\partial \tau} = \frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left[\bar{D}(\bar{C}) \xi^2 \frac{\partial \bar{C}}{\partial \xi} \right], \quad 0 < \xi < 1 \quad (6)$$

where $\bar{D}(\bar{C}) = D_{eff}/D_0$.

And the boundary conditions and initial condition described in Eqs. (2)–(4) are modified as follows:

$$-\bar{D} \frac{\partial \bar{C}}{\partial \xi} \Big|_{\xi=0} = 0 \quad (7)$$

$$-\bar{D} \frac{\partial \bar{C}}{\partial \xi} \Big|_{\xi=1} = \theta \quad (8)$$

$$\bar{C}(\tau = 0) = 0 \quad (9)$$

where θ is the dimensionless flux of lithium at the surface of the particle and is given by the following expression:

$$\theta = \frac{i_n R_p}{n F C_{max} D_0} \quad (10)$$

The flux can be a function of concentration or a constant based on the problem.

3.2. Solution methodology

The governing equation (Eq. (6)) and the boundary conditions described in Eqs. (7)–(9) can be reduced to a set of ordinary differential equations by making use of the integral transform and the inverse transform pair described in the following section.

The integral transform for the spherical coordinate is given below [17]:

$$T(\lambda_n, \tau) = T_n(\tau) = \int_{\xi=0}^1 \xi^2 \phi(\lambda_n, \xi) \bar{C}(\xi, \tau) d\xi; \quad n = 1 \dots K \quad (11)$$

where $\phi(\lambda_n, \xi)$ is the kernel of the transform and λ_n 's are the eigenvalues which are obtained by solving an auxiliary homogenous eigenvalue problem corresponding to the governing equation and boundary conditions. For simplicity $\phi(\lambda_n, \xi)$ is represented as $\phi_n(\xi)$ from this point onwards in the text.

The inverse of the transform is given by the following expression [17]:

$$\bar{C} = \sum_{n=1}^K \frac{\phi_n(\xi)}{N_n} T_n(\tau) \tag{12}$$

where K is a finite number of terms considered in the expansion and the norm of the integral transformation, N is given by the following expression [17]:

$$N_n = \int_0^1 \xi^2 \phi_n^2(\xi) d\xi; \quad n = 1 \dots K \tag{13}$$

The homogeneous eigenvalue problem corresponding to diffusion in a spherical particle is given by:

$$\frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left[\xi^2 \frac{\partial \phi_n(\xi)}{\partial \xi} \right] - \lambda_n^2 \phi_n(\xi) = 0 \tag{14}$$

The homogeneous boundary conditions are expressed as:

$$-\frac{\partial \phi_n}{\partial \xi} \Big|_{\xi=0} = 0; \quad -\frac{\partial \phi_n}{\partial \xi} \Big|_{\xi=1} = 0 \tag{15}$$

Solution of Eq. (14) subjected to the boundary conditions described in Eq. (15) yields the kernel or the eigenfunctions of the system, which are given by:

$$\phi_n(\xi) = \frac{\sin(\lambda_n \xi)}{\xi} \tag{16}$$

And the eigenvalues are the roots of the following equation:

$$\lambda_n \cot(\lambda_n) = 1 \tag{17}$$

Using the transformation given in Eq. (12) on the governing equation (Eq. (6)) the following equation is obtained:

$$\int_0^1 \xi^2 \phi_n(\xi) \frac{\partial \bar{C}}{\partial \tau} d\xi = \int_0^1 \phi_n \frac{\partial}{\partial \xi} \left[\bar{D} \xi^2 \frac{\partial \bar{C}}{\partial \xi} \right] d\xi \tag{18}$$

The expression on the left-hand side of the Eq. (18) can be rewritten using the transform described in Eq. (12) as shown below:

$$\int_0^1 \xi^2 \phi_n(\xi) \frac{\partial \bar{C}}{\partial \tau} d\xi = \frac{\partial}{\partial \tau} \left[\int_0^1 \xi^2 \phi_n(\xi) \bar{C} d\xi \right] = \frac{dT_n(\tau)}{d\tau} \tag{19}$$

Substitution of Eq. (19) into Eq. (18) yields the following modified governing equation:

$$\frac{dT_n(\tau)}{d\tau} = \int_0^1 \phi_n \frac{d}{d\xi} \left[\bar{D} \xi^2 \frac{d\bar{C}}{d\xi} \right] d\xi; \quad n = 1 \dots K \tag{20}$$

The concentration dependent diffusion coefficient in Eq. (20) can be expressed as a polynomial expression in terms of dependent variable (\bar{C}) using simple arithmetic manipulations for most of the problems encountered in battery modeling. In this study the following general functional form of the expression is considered:

$$\bar{D} = 1 + \Gamma \bar{C} \tag{21}$$

where Γ can either be a constant or a function of \bar{C} . The functional form of the diffusion coefficient Eq. (21) is substituted in the right-hand side expression of Eq. (20). The integral on the right side of Eq. (20) is evaluated using Green's integral theorem [21] as shown below:

$$\begin{aligned} \int_0^1 \phi_n \frac{d}{d\xi} \left[(1 + \Gamma \bar{C}) \xi^2 \frac{d\bar{C}}{d\xi} \right] d\xi &= \left\{ \int_0^1 \xi^2 \bar{C} \frac{1}{\xi^2} \frac{d}{d\xi} \left[\xi^2 \frac{d\phi_n}{d\xi} \right] d\xi \right\} \\ &+ \left\{ \sum_{s=0,1} \left[\phi_n \frac{d\bar{C}}{d\xi} - \bar{C} \frac{d\phi_n}{d\xi} \right]_s \right\} \\ &+ \left\{ \int_0^1 \phi_n \frac{d}{d\xi} \left[(\Gamma \bar{C}) \xi^2 \frac{d\bar{C}}{d\xi} \right] d\xi \right\} \end{aligned} \tag{22}$$

Making use of Eqs. (14)–(16) and the integral transform defined in Eqs. (11) and (22) is rewritten as given below:

$$\begin{aligned} \int_0^1 \phi_n \frac{d}{d\xi} \left[(1 + \Gamma \bar{C}) \xi^2 \frac{d\bar{C}}{d\xi} \right] d\xi &= -\lambda_n^2 T_n(\tau) - \phi_n(1)\theta \\ &+ \int_0^1 \phi_n \frac{d}{d\xi} \left[(\Gamma \bar{C}) \xi^2 \frac{d\bar{C}}{d\xi} \right] d\xi \end{aligned} \tag{23}$$

Substitution of Eq. (23) into Eq. (20) yields the following set of differential equations:

$$\begin{aligned} \frac{dT_n(\tau)}{d\tau} + \lambda_n^2 T_n(\tau) &= \int_0^1 \phi_n \frac{d}{d\xi} \left[(\Gamma \bar{C}) \xi^2 \frac{d\bar{C}}{d\xi} \right] d\xi - \phi_n(1)\theta; \\ n &= 1 \dots K \end{aligned} \tag{24}$$

The inverse transform described in Eq. (12) for the dependent variable \bar{C} is substituted in Eq. (24) and the resulting equation can be rewritten in the matrix form as given below:

$$\frac{dT(\tau)}{d\tau} + A(T, \tau) T(\tau) = G(T, \tau) \tag{25}$$

where the matrices A and G depend on the functions Γ and θ respectively.

The set of coupled nonlinear ordinary differential equations (ODEs) described in Eq. (25) is solved numerically to obtain the transform function $T_n(\tau)$ and the concentration profile is obtained using the inverse function given by Eq. (12). The solution to the diffusion problem is therefore analytical with respect to the spatial coordinate, but numerical with respect to time. For certain simple cases complete analytical or approximate solution is possible as demonstrated in Ref. [19].

Two examples are discussed in the following section along with a procedure similar to that presented in Ref. [19], to further simplify the complexity of the differential equations described in Eq. (25).

4. Discussion

4.1. Examples: case A

Let us consider the effect of mechanical stress on the diffusion of lithium into the intercalation material during the galvanostatic discharge process. The intercalation material is treated as a binary solution and the diffusion of lithium into the host material is described by [7–9]:

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[Dr^2 \left\{ \frac{\partial C}{\partial r} + \frac{C}{RT} \left(\bar{V} - \frac{M}{\rho} \right) \frac{\partial \sigma_h}{\partial r} \right\} \right] \tag{26}$$

where \bar{V} is the partial molar volume of lithium in the host, M is the molecular mass of the binary solution, ρ is the density of the solution and σ_h is the hydrostatic stress or pressure.

For an isotropic material Eq. (26) is rewritten as follows [see Appendix for derivation]:

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[D_{eff} r^2 \frac{\partial C}{\partial r} \right] \quad (27)$$

The effective diffusion coefficient is given by the expression:

$$D_{eff} = D_0 \left[1 + \bar{\omega} \left(\frac{C - C_0}{C_{max}} \right) \right] \quad (28)$$

where $\bar{\omega}$ is given by the following expression:

$$\bar{\omega} = - \frac{2\bar{V}EC_{max}}{9RT(1-\nu)} \left(\bar{V} - \frac{M}{\rho} \right) \quad (29)$$

In Eq. (29), E is the Young's modulus and ν is the Poisson's ratio of the material. For the galvanostatic discharge process the flux at the surface is given by:

$$-D_{eff} \frac{\partial C}{\partial r} \Big|_{r=R_p} = \frac{i}{nF} \quad (30)$$

where i is the applied current density, n is the number of electron involved in the electrochemical reaction and F is the Faraday's Constant.

Use of dimensionless variables defined earlier by Eq. (5) reduces the governing Eq. (27) and boundary conditions to the same form as described by Eqs. (6)–(9). The diffusion coefficient for this example depends linearly on the concentration of lithium and Γ described in Eq. (21) is a constant parameter ($\bar{\omega}$).

$$\bar{D} = 1 + \Gamma \bar{C} = 1 + \bar{\omega} \bar{C} \quad (31)$$

$\bar{\omega}$ is the measure of the contribution of stress or mechanical energy towards the diffusion process.

The integral transform approach described in the previous section is used to reduce the nonlinear diffusion equation to a set of ODEs which is given below:

$$\frac{dT_n(\tau)}{d\tau} = \sum_{k=1}^K \sum_{l=1}^K T_k(\tau) \int_0^1 \phi_n \frac{\partial}{\partial \xi} \left[\xi^2 (\bar{D}_l) \frac{\partial \phi_k(\xi)}{\partial \xi} \right] d\xi; \quad n = 1 \dots K \quad (32)$$

As a further simplification the concentration dependent diffusion coefficient is expanded using the first eigenfunction. This has been demonstrated earlier for a planar geometry in Ref. [19]:

$$\bar{D} = 1 + \bar{\omega} \bar{C} = 1 + \bar{\omega} \phi_l(\xi) T_l(\tau); \quad l = 1 \quad (33)$$

After substitution of Eq. (33) into Eq. (32) and considering the first element ($n = 1$), the principal diagonal elements ($n = k$) of the matrix, the nonlinear ODEs given by Eq. (32) are simplified as follows:

$$\frac{dT_n(\tau)}{d\tau} + (\lambda_n^2 + B_{1n})T_n(\tau) = \frac{\phi_n(1)\theta}{1 + \Gamma\phi_n(1)T_1(\tau)}; \quad n = 1 \dots K \quad (34)$$

where

$$B_{1n} = \bar{\omega} T_1(\tau) \int_0^1 \phi_n \frac{\partial}{\partial \xi} \left[\xi^2 \phi_1(\xi) \frac{\partial \phi_n(\xi)}{\partial \xi} \right] d\xi \quad (35)$$

The set of equations described in Eq. (34) is nonlinear with respect to T when $n = 1$ and linear when $n = 2 \dots K$. The Eq. (34) is solved for the case when $n = 1$ and the vector B given in Eq. (35) is updated for each time step (τ). This solution is then used in the subsequent calculations of T for $n = 2 \dots K$. Hence the set of nonlinear ODEs ($n = 1 \dots K$) are decoupled to a single nonlinear ODE ($n = 1$) and a set of linear ODEs ($n = 2 \dots K$). In this example K is 9 and the set of ODEs is solved using gear's numerical method in the Mathematical package, Maple [22]. The results obtained are compared to the

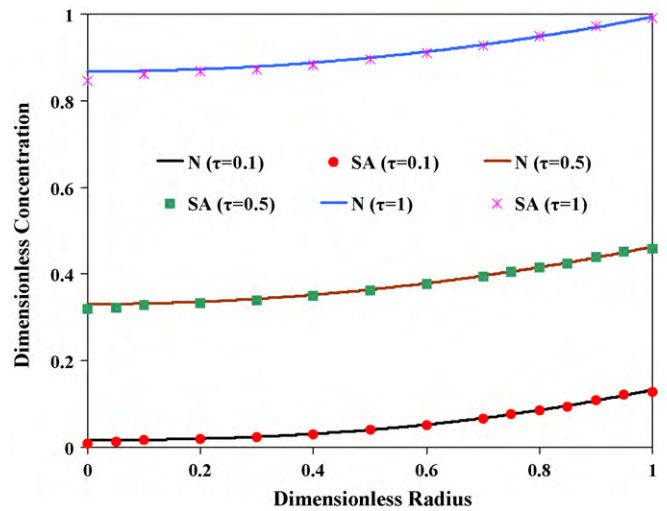


Fig. 1. Comparison of concentration profiles within the particle obtained using the semianalytical method (SA) and numerical solution (N) for $\theta = 0.1$.

corresponding full numerical solutions obtained using the finite element package, COMSOL Multiphysics [23].

It can be observed from Eqs. (27)–(31) that the concentration profile depends on two important parameters: (i) the reaction rate or dimensionless flux at the surface of the particle (θ) and (ii) the nonlinear contribution to diffusion process ($\bar{\omega}$). For a given intercalation material, $\bar{\omega}$ is constant (assuming all mechanical properties are constant). Therefore the flux at the surface of the particle determines the concentration profile within the particle. The first set of simulations was carried out for a low value of $\bar{\omega}$ of 0.1 and two different values of θ (0.3, 2). For a particle of size $8.5 \mu\text{m}$ and a constant diffusion coefficient value of $1 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ [9,10] at the initial concentration, the value of $\theta = 0.3$ corresponds to 1 C rate of discharge. The solutions are compared at different time during the discharge process and the results for the two flux values, θ are shown in Figs. 1 and 2 respectively. It can be observed that the results agree well with each other of low value of θ (0.3) for all time. At high value of θ (2), the surface concentration varies noticeably during the beginning of discharge but the deviation is reduced towards the end of discharge. Therefore for a low value of $\bar{\omega}$, the results predicted by the method presented in the study are valid even at high rates of discharge and the percentage of error in prediction is less than 1%.

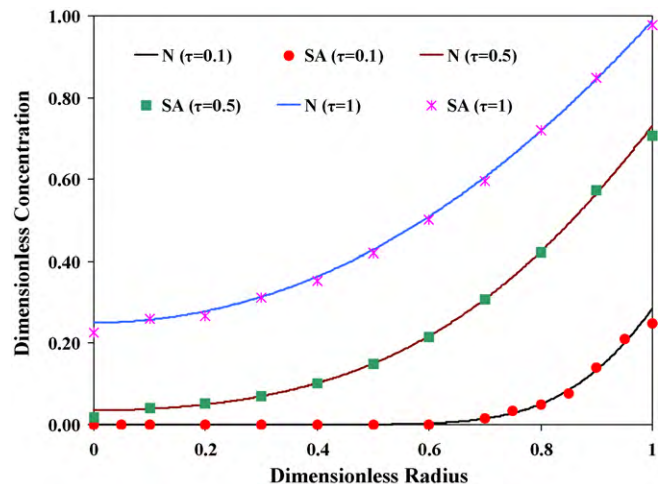


Fig. 2. Comparison of concentration profiles within the particle obtained using the semianalytical method (SA) and numerical solution (N) $\theta = 2$.

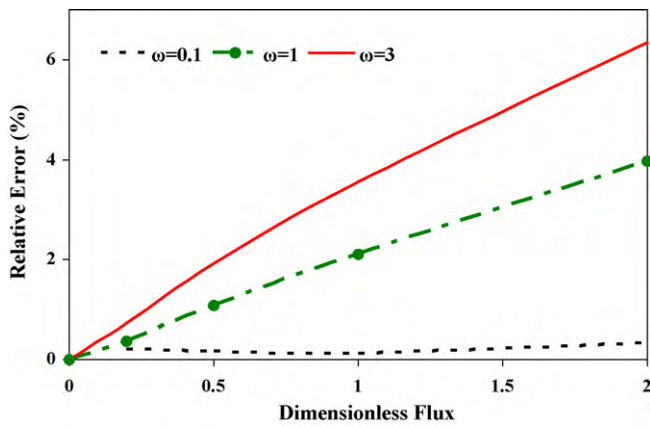


Fig. 3. Error in prediction of surface concentration relative to the numerical solution for three different nonlinear parameter ($\bar{\omega} = 0.1, 1$ and 3).

Fig. 3 compares the percentage of the relative error in the surface concentration for three different values of nonlinear contribution $\bar{\omega}$. Since the electrochemical reaction at the interface depends on the concentration at the surface of the particle, prediction of it with reasonable accuracy determines validity of the approximation used in this study. The values of $\bar{\omega}$ considered in this study are: 0.1, 1 and 3. It can be observed from Fig. 3 that up to a value of $\theta = 1.8$, the error in surface concentration predictions are less than 5% for all the cases presented in this study. This value of θ corresponds to 6 C for the particles considered in this study. The deviation of the solution obtained from the method presented in this study from the numerical solution increased with an increase in the value of $\bar{\omega}$. This is expected as the nonlinear terms are approximated based on the first eigenfunction. Value of $\bar{\omega}$ depends on the extent of change in molar volume of the material during intercalation (\bar{V}). Larger the change in volume, the larger is the value of $\bar{\omega}$. Therefore more terms can be included to improve the accuracy of the solution for materials with larger values of $\bar{\omega}$. The model presented here provides a reasonably accurate prediction over a wide range of parameter values and can be used with reasonable accuracy for materials with low to medium degree of volume expansion ($\bar{\omega} = 3$ being highest in the present study).

4.2. Case B

In the second example considered in this study, lithium and the intercalation host material (carbon in this present case) are considered as a binary nonideal solid solution. The interesting and unique nature of the intercalation process in carbon makes it an ideal candidate for this study. Intercalation of lithium in carbon involves staging. Diffusion coefficient of lithium in each of the stages varies significantly resulting in a concentration dependent diffusion coefficient. Modeling of staging phenomenon with all the details is beyond the scope of this study, hence only the approach to include the concentration dependent diffusion coefficient is presented below. The thermodynamic variation due to the nonideal nature of the intercalation electrode is related to the diffusion coefficient by the following expression [4–6]:

$$\frac{D}{D_0} = 1 + \frac{d \ln \gamma}{d \ln \bar{C}} \quad (36)$$

where $1 + (d \ln \gamma / d \ln \bar{C})$ represents the lithium ion-ion interaction. The activity coefficient (γ) is replaced by an interaction potential term [4] and concentration dependent diffusion coefficient

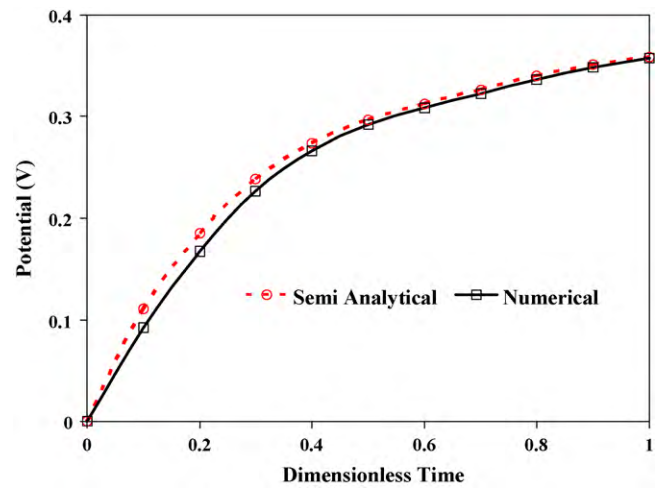


Fig. 4. Comparison of potential as a function of discharge time obtained using the semi-analytical method (SA) and the numerical solution (N) for $\theta = 1$.

cient Eq. (36) is modified as shown below:

$$\bar{D} = 1 + \frac{d \ln \gamma}{d \ln \bar{C}} = 1 + \Gamma \bar{C} = 1 + \bar{C}(1 + \bar{C}) \frac{F}{RT} \frac{dV}{d\bar{C}} \quad (37)$$

Comparison of Eqs. (37) and (21) shows that Γ for this case is a function of the concentration \bar{C} . The interaction potential (V) as a function of concentration \bar{C} used in Eq. (37) is obtained from Ref. [4] and Γ in Eq. (37) is given by the following expression:

$$\Gamma = (1 + \bar{C}) \frac{F}{RT} [a_1 + a_2 \bar{C} + a_3 \bar{C}^2 + a_4 \bar{C}^3 + a_5 \bar{C}^4 + a_6 \bar{C}^5] \quad (38)$$

The values of the parameters [4] a_1 – a_6 respectively are 1.9852, 5.3886, -67.56 , 171.9, -173.52 and 61.656.

Similar to the example case A, the concentration dependent diffusion coefficient is expanded using the first Eigen function. The first element ($n = 1$) and the diagonal elements are considered. The set of differential equations is given by:

$$\frac{dT_n(\tau)}{d\tau} + (\lambda_n^2 + B_{1n}) T_n(\tau) = \frac{\phi_n(1)\theta}{\sum_{m=1}^6 a_m T_1^m \phi_1(1)^m \{1 + \phi_1(1)T_1(\tau)\}}; \quad n = 1 \dots K \quad (39)$$

The nonlinear term B is given below:

$$B_{1n} = \sum_{m=1}^6 a_m T_1^m \int_0^1 \phi_n \frac{\partial}{\partial \xi} \left[\xi^2 \phi_1^m (1 + \phi_1 T_1(\tau)) \frac{\partial \phi_n(\xi)}{\partial \xi} \right] d\xi \quad (40)$$

The set of ODEs in Eq. (39) are solved using gear's numerical method in the Mathematical package, Maple using $K = 9$. The concentration at the surface of the particle is used along with a linear kinetic expression [4] to calculate the potential at the interface.

The solution obtained using this approach is compared with numerical solution for a dimensionless flux $\theta = 0.2$ (equivalent to 1 C for this simulation) as a function of dimensionless discharge time (τ). The results are depicted in Fig. 4. The difference in deviation of results from that predicted using numerical solution decreases with increase in time and beyond a dimensionless discharge time $\tau > 0.35$ the results are in close agreement. The relative error in surface concentration predicted using the present approach and that of the numerical solution are shown in Fig. 5 for different rates of discharge (or θ). The relative error is less than 1.2% for all the parameter values considered in this study (up to 4 C or a θ value of 1).

With the help of two illustrative cases the usefulness of this method to model diffusion process in the intercalation elec-

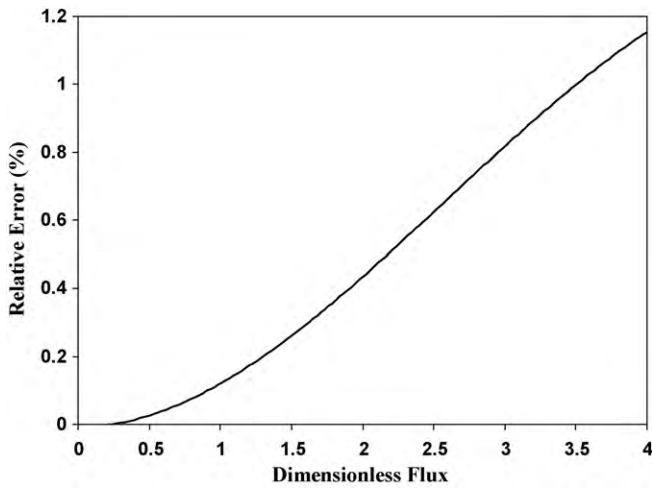


Fig. 5. Error in prediction of surface concentration relative to the numerical solution for various dimensionless flux values at the surface of the particle.

trodes has been demonstrated. Though these simple examples only consider a single spherical and isotropic particle as the model geometry, this methodology can be extended to materials with anisotropic properties and undergoing phase transformation [18,24]. This methodology can be effectively used as a model reduction/reformulation technique for model involving multiple electrodes or battery stacks.

5. Conclusions

A simple and straightforward methodology to solve nonlinear diffusion equation in spherical intercalation electrode is presented. Two different case studies incorporating nonlinear effects on diffusion equation are presented. The first case considered includes the effect of mechanical stress on the diffusion process and in this case the diffusion coefficient had a linear variation with composition. The second case study considered the nonlinear effect due to lithium ion-ion interaction within the solid phase and in this case the diffusion coefficient was a polynomial function of concentration. In both the cases, results obtained from the semi-analytical approach presented in this study were found to be in good agreement with the numerical solution. The average error in the prediction was found to be 1–5%. The significant decrease in the computational efforts combined with a reasonable degree of accuracy in results obtained makes the approach presented in this paper a good alternative for complete numerical solution. This technique can also be used as a tool for parameter estimation.

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Appendix A.

Diffusion of lithium into the host material is described by [7–9]:

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[Dr^2 \left\{ \frac{\partial C}{\partial r} + \frac{C}{RT} \left(\bar{V} - \frac{M}{\rho} \right) \frac{\partial \sigma_h}{\partial r} \right\} \right] \quad (\text{A-1})$$

The hydrostatic stress (σ_h) is the average of the three principle components of the stress tensor and for a spherical particle it can be

expressed as shown below [25]:

$$\sigma_h = \frac{\sigma_r + 2\sigma_t}{3} \quad (\text{A-2})$$

The gradient of hydrostatic stress inside the particle is expressed as:

$$\frac{\partial \sigma_h}{\partial r} = \frac{\partial}{\partial r} \left(\frac{\sigma_r + 2\sigma_t}{3} \right) \quad (\text{A-3})$$

where the radial component of the stress is given by the following expression [25]:

$$\sigma_r = \frac{E}{(1+\nu)(1-2\nu)} \left[(1-\nu) \frac{\partial u}{\partial r} + 2\nu \frac{u}{r} - (1+\nu) \frac{\bar{V}}{3} (C - C_0) \right] \quad (\text{A-4})$$

The tangential component of the stress is given by [25]:

$$\sigma_t = \frac{E}{(1+\nu)(1-2\nu)} \left[\nu \frac{\partial u}{\partial r} + \frac{u}{r} - (1+\nu) \frac{\bar{V}}{3} (C - C_0) \right] \quad (\text{A-5})$$

where C_0 is the stress free concentration in the electrode.

The gradient of the hydrostatic stress inside the particle is modified using Eqs. (A-4) and (A-5) as follows:

$$\frac{\partial \sigma_h}{\partial r} = \frac{E}{3(1-2\nu)} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial u}{\partial r} \right) - \bar{V} \frac{\partial C}{\partial r} \right] \quad (\text{A-6})$$

The equation of momentum inside the spherical particle which is in mechanical equilibrium is as follows [22]:

$$\frac{\partial \sigma_r}{\partial r} + \frac{2}{r} (\sigma_r - \sigma_t) = 0 \quad (\text{A-7})$$

In terms of the radial displacement u , Eq. (A-7) can be re-written using the Eqs. (A-4) and (A-5) as follows:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial u}{\partial r} \right) = \frac{1+\nu}{1-\nu} \frac{\bar{V}}{3} \frac{\partial C}{\partial r} \quad (\text{A-8})$$

The gradient of the hydrostatic stress inside the particle can be expressed using Eqs. (A-6) and (A-8) as follows:

$$\frac{\partial \sigma_h}{\partial r} = -\frac{2\bar{V}E}{9(1-\nu)} \frac{\partial C}{\partial r} \quad (\text{A-9})$$

Therefore the diffusion equation is modified as given below:

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[D_{\text{eff}} r^2 \frac{\partial C}{\partial r} \right] \quad (\text{A-10})$$

The effective diffusion coefficient is given by the following expression:

$$D_{\text{eff}} = D_0 \left[1 - \frac{2\bar{V}EC_{\text{max}}}{9RT(1-\nu)} \left(\bar{V} - \frac{M}{\rho} \right) \left(\frac{C - C_0}{C_{\text{max}}} \right) \right] \quad (\text{A-11})$$

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