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Approximate Solutions for Galvanostatic Discharge of Spherical Particles

I. Constant Diffusion Coefficient

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Approximate models are developed, based on second, fourth, and sixth order polynomials, that describe the concentration profile of an electrochemically active species in a spherical electrode particle. Analytical expressions are obtained that describe the way the concentration profiles, surface concentrations, and electrode utilization change during the galvanostatic discharge of an electrode particle. Based on a comparison with an exact analytical model over a wide range of dimensionless current densities, all three approximate models performed extremely well in predicting these quantities. Quantitative criterion for the validity of these models is also developed and shows that the sixth order, four parameter approximate model is the best. These approximate models, or similarly developed models, should find extensive use in simplifying the modeling of complex electrochemical systems without sacrificing much accuracy as shown in Part II of this series for the concentration-dependent diffusion coefficient case.
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The mathematical modeling of electrochemical systems, *e.g.*, batteries or electrochemical capacitors, involves the simultaneous solution of coupled partial differential and algebraic equations that describe, among other things, current, voltage, and electrochemically active species distributions as functions of both time and position throughout the system.¹ Solution methodologies are therefore both complicated and time consuming. For this reason, approximations are continually sought that simplify the governing set of equations without imparting a significant error in the resulting solution. Moreover, many of these electrochemical systems require the modeling of electrodes comprised of roughly spherical particles, into or out of which an electrochemically active species must diffuse during charge and discharge.

This diffusion process is governed by a partial differential equation that describes the way that the concentration of the electrochemically active species in the particle changes in both time and position during charge and discharge. It is fortuitous that similar diffusion phenomena, and hence equations, arise in many areas of science and engineering, and in particular, describe the uptake of a species in adsorbent or catalyst particles. In these two very related areas, a considerable amount of work has been done on trying to simplify the governing equations by applying various approximations that *a priori* describe how the concentration profiles change in the spherical particles.

The most widely utilized approximations have been based on parabolic and higher order polynomial functions that describe the concentration profile in the particle,²⁻¹⁸ which all began with the work of Liaw *et al.*² The coefficients of these polynomials are generally time dependent. Nevertheless, they have been resolved in terms of known and constant system parameters by applying the governing initial and boundary conditions to them. In this way, the partial differential equation describing the concentration in both time and position inside the particle has been reduced to an ordinary differential equation describing how the volume-averaged concentration in the particle changes with time. This ordinary differential equation essentially describes the flux into or out of the particle; and in many cases, it has the form of a linear driving force, where the flux is proportional to a concentration difference.

In some cases, this equation has been integrated either numerically or analytically to describe the diffusion into or out of a particle, for example, in batch adsorption or reaction systems. But, in most cases, it is coupled with other differential and algebraic equations,

resulting in a simpler approximate solution to a more complex process. This later approach was also used in the modeling of an electrochemical system (batteries), wherein a parabolic species distribution was assumed to describe the distribution in a thin film coating surrounding a particle;¹⁹ however, quantitative justification for such an approximation was not given. Moreover, in a related work,²⁰ a linear driving force flux relationship was assumed, again with little justification and no mention of whether a parabolic profile approximation leads to a linear driving force flux relation as it does in adsorption and catalytic systems. It is also interesting that when Doyle and Newman²¹ simplified the analysis of the discharge process of a lithium-ion battery under solid phase diffusion limitations by assuming a pseudo-steady-state approximation for longer times or slower rates, the concentration profile inside the particle became dependent on the square of the radial coordinate, *i.e.*, it became inherently parabolic. But again this pseudo-steady-state approximation was not quantitatively justified. In contrast, the accuracy of polynomial profile approximations in adsorption and catalytic systems has been shown to depend on many factors, and in many situations, very accurate results have been obtained. Thus, these simple but effective polynomial profile approximations have been widely used in simplifying the modeling of adsorption and catalytic processes that involve diffusion into a spherical particle.

In this work, the utility of different polynomial approximations in describing the diffusion of an electrochemically active species out of a spherical electrode particle during galvanostatic discharge is demonstrated. Part I of this series deals with the constant diffusion coefficient case, whereas Part II extends this work and deals with the concentration (state-of-charge, SOC)-dependent diffusion coefficient case. Second, fourth, and sixth order polynomials are examined. These result in two, three, and four parameter models, respectively, that describe the concentration profiles inside the particle. Strengths and weaknesses of these different polynomial profile approximations are exposed, based on comparing the approximate predictions with those obtained from an exact analytical solution in terms of concentration profiles, surface concentrations, and electrode utilization. Quantitative criteria for the validity of these various approximate models are established and their use in other more complex electrochemical systems and other boundary conditions (*e.g.*, cyclic voltammetry) are suggested, and discussed in Part III of this work.

Diffusion Model

Parabolic profile model.—Consider a spherical electrode particle completely charged with a corresponding initial concentration, c_0 . The transient diffusion in the particle can be expressed as

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

where c is the concentration of the diffusing species (e.g., hydrogen), and D_s is the corresponding diffusion coefficient. In this case, the diffusion coefficient is constant and does not vary with concentration (i.e., SOC). With the electrochemical reaction taking place only at the surface of the particle, the initial and boundary conditions are given by

$$c = c_0 \quad \text{at } t = 0 \quad \text{and for } 0 \leq r \leq R_p \quad (\text{fully charged state}) \quad [2]$$

$$\frac{\partial c}{\partial r} = 0 \quad \text{at } r = 0 \quad \text{and for } t \geq 0 \quad [3]$$

and

$$D_s \frac{\partial c}{\partial r} = -\frac{i_a}{nF} \quad \text{at } r = R_p \quad \text{and for } t \geq 0 \quad [4]$$

where i_a is the applied current density at the surface of the particle, R_p is the radius of the particle, n is the number of electrons taking place in the electrochemical reaction, and F is Faraday's constant. Introducing the following dimensionless variables

$$C = \frac{c}{c_0}; \quad x = \frac{r}{R_p} \quad \text{and} \quad \tau = \frac{D_s t}{R_p^2} \quad [5]$$

simplifies the model to

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

with the corresponding initial and boundary conditions

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

$$\frac{\partial C}{\partial x} = 0 \quad \text{at } x = 0 \quad \text{and or } \tau \geq 0 \quad [8]$$

and

$$\frac{\partial C}{\partial x} = -\delta \quad \text{at } x = 1 \quad \text{and for } \tau \geq 0 \quad [9]$$

where δ is the applied dimensionless current density defined as

$$\delta = \frac{i_a R_p}{n F D_s c_0} \quad [10]$$

An exact analytical solution to this model can be obtained by the separation of variables^{22,23} and given by²⁴

$$C(x, \tau) = 1 - \delta \left[3\tau + \frac{1}{10}(5x^2 - 3) - 2 \frac{1}{x} \sum_{n=1}^{\infty} \frac{\sin(\lambda_n x)}{\lambda_n^2 \sin(\lambda_n)} \right] \times \exp(-\lambda_n^2 \tau) \quad [11]$$

with eigenvalues $\lambda_n = \tan(\lambda_n)$. The number of terms required for convergence of this series can be significant and depends strongly upon the dimensionless current density, δ .

A simpler solution to the same problem can be obtained by assuming that the concentration of the diffusing species inside the particle is described by a parabolic profile

$$C = a(\tau) + b(\tau)x^2 \quad [12]$$

where $a(\tau)$ and $b(\tau)$ are functions of τ . The boundary condition at the center (Eq. 8) is automatically satisfied. Applying Eq. 12 to the boundary condition at the surface (Eq. 9) gives

$$\left. \frac{\partial C}{\partial x} \right|_{x=1} = 2b(\tau) = -\delta \quad [13]$$

According to Eq. 12, the volume-averaged concentration is given by

$$\bar{C} = \int_{x=0}^1 C_0 3x^2 dx = a(\tau) + \frac{3}{5}b(\tau) \quad [14]$$

Both sides of Eq. 6 are now multiplied by the dimensionless differential volume element²⁻¹⁸ $3x^2$, and integrated from 0 to 1 using Eq. 12 for C in Eq. 6. This results in

$$\int_{x=0}^1 \frac{\partial C}{\partial \tau} 3x^2 dx = \int_{x=0}^1 \frac{1}{x^2} \frac{\partial}{\partial x} \left(x^2 \frac{\partial C}{\partial x} \right) 3x^2 dx$$

$$\rightarrow \frac{d\bar{C}}{d\tau} = 6b(\tau) = -3\delta \quad [15]$$

an ordinary time-dependent differential equation in terms of the volume-averaged concentration. However, it is interesting that this analysis does not result in a linear driving force-type expression, as it typically does in adsorption and catalytic systems. The solution to Eq. 15 with the initial condition given in Eq. 7 is

$$\bar{C} = 1 - 3\delta\tau \quad [16]$$

A comparison of Eq. 14 and 16 leads to

$$a(\tau) = 1 - 3\delta\tau + \frac{3}{10}\delta \quad [17]$$

Hence, the concentration profile in the particle, based on the parabolic profile (PP) approximation, is given by

$$C_{PP} = 1 - 3\delta\tau + \frac{3}{10}\delta - \frac{\delta}{2}x^2$$

$$= 1 - \delta \left[3\tau + \frac{1}{10}(5x^2 - 3) \right] \quad [18]$$

A comparison with the exact solution (Eq. 13) shows that the PP model does not yield the exponential terms, and hence, results in a much simpler solution. Note that, for this case, $a(\tau)$ is a function of τ , whereas $b(\tau)$ is a constant. In general, this is not always the case and the results may vary according to the boundary conditions and the initial governing equation.

In an electrode particle, the electrochemical behavior is determined completely by the concentration at the surface. The surface concentration from the exact solution is given by

$$C_{S, \text{exact}} = C_{x=1} = C(x, \tau)$$

$$= 1 - \delta \left[3\tau + \frac{2}{10} - 2 \sum_{n=1}^{\infty} \frac{1}{\lambda_n^2} \exp(-\lambda_n^2 \tau) \right] \quad [19]$$

and that from the PP solution is given by

$$C_{S, PP} = C_{PP, x=1} = 1 - \delta \left[3\tau + \frac{2}{10} \right] \quad [20]$$

Utilization is also a very important property for any electrode particle. It is defined as the amount of active material reacted, according to

$$U = \frac{\text{Initial concentration} - \text{concentration left in the particle after discharge}}{\text{Initial concentration}} \times (100)$$

$$= \frac{1 - \int_{x=0}^1 C(x, \tau_{\text{disch}}) 3x^2 dx}{1} \quad (100) \quad [21]$$

where $3x^2 dx$ is the differential volume element of the spherical particle, and τ_{disch} is the dimensionless time taken for discharge, which is determined by setting the surface concentration to zero. Substitution of Eq. 11 (for the exact concentration) into Eq. 21 and integrating yields

$$U_{\text{exact}}(\%) = 3\delta\tau_{\text{disch,ex}}(100) \quad [22]$$

where $\tau_{\text{disch,ex}}$ is the exact dimensionless time taken for complete discharge. This value is obtained by setting the left-hand side of Eq. 19 to zero and solving for τ . Note that the integral of the infinite series is zero as explained in Ref. 21. Similarly, using the PP solution (Eq. 18) leads to

$$U_{\text{pp}}(\%) = 3\delta\tau_{\text{disch,pp}}(100) \quad [23]$$

where $\tau_{\text{disch,pp}}$ is the dimensionless time taken for complete discharge which is obtained from Eq. 20 with the surface concentration set to zero. Accordingly

$$U_{\text{pp}}(\%) = \left(1 - \frac{\delta}{5}\right)(100) \quad [24]$$

Higher order polynomial profile models.—Three- and four-parameter polynomial profile approximations can also be utilized to obtain simpler but potentially more accurate solutions to the governing equations (Eq. 1-4) for the concentration profile inside the electrode particle. For example, a fourth order, three parameter polynomial such as

$$C = a(\tau) + b(\tau)x^2 + d(\tau)x^4 \quad [25]$$

where $a(\tau)$, $b(\tau)$, and $d(\tau)$ are functions of τ , can be applied in the same way as Eq. 12. As before, the boundary condition at the center (Eq. 8) is automatically satisfied. Applying Eq. 25 to the boundary condition at the surface (Eq. 9) gives

$$\left.\frac{\partial C}{\partial x}\right|_{x=1} = 2b(\tau) + 4d(\tau) = -\delta \quad [26]$$

According to Eq. 25, the volume-averaged concentration is given by

$$\bar{C} = \int_{x=0}^1 C 3x^2 dx = a(\tau) + \frac{3}{5}b(\tau) + \frac{3}{7}d(\tau) \quad [27]$$

Both sides of Eq. 6 are now multiplied by $3x^2$ and integrated from 0 to 1 using Eq. 25 for C in Eq. 6. This results in

$$\frac{d\bar{C}}{d\tau} = 6b(\tau) + 12d(\tau) = -3\delta \quad [28]$$

The solution to Eq. 28 with the initial condition given in Eq. 7 is

$$\bar{C} = a(\tau) + \frac{3}{5}b(\tau) + \frac{3}{7}d(\tau) = 1 - 3\delta\tau \quad [29]$$

Since, in this case, there are three constants [$a(\tau)$, $b(\tau)$, and $d(\tau)$] to evaluate, three equations are needed. So, in addition to Eq. 26 and 29, the governing equation (Eq. 6) is evaluated at $x = 1$, *i.e.*,

$$\left.\frac{\partial C}{\partial \tau}\right|_{x=1} = \frac{1}{x^2} \left.\frac{\partial}{\partial x} \left(x^2 \frac{\partial C}{\partial x}\right)\right|_{x=1} \quad [30]$$

Substituting Eq. 25 into Eq. 30 leads to

$$\frac{da(\tau)}{d\tau} + \frac{db(\tau)}{d\tau} + \frac{dd(\tau)}{d\tau} = 6b(\tau) + 20d(\tau) \quad [31]$$

Solving Eq. 26, 29, and 31 gives the three constants as

$$a(\tau) = 1 - 3\delta\tau + \frac{3}{10}\delta - \frac{27}{140}\delta \exp(-35\tau)$$

$$b(\tau) = -\frac{1}{2}\delta + \frac{1}{2}\delta \exp(-35\tau) \quad [32]$$

and

$$d(\tau) = -\frac{1}{4}\delta \exp(-35\tau)$$

These three parameters give the surface concentration as

$$C_{\text{S,3P}} = 1 - \delta \left[3\tau + \frac{2}{10}\right] + \frac{2}{5}\delta \exp(-35\tau) \quad [33]$$

Similarly, one more parameter can be added to Eq. 25 in the form of the following sixth order polynomial

$$C = a(\tau) + b(\tau)x^2 + d(\tau)x^4 + e(\tau)x^6 \quad [34]$$

To solve for this fourth parameter $e(\tau)$ another equation is needed and obtained by applying the limit, $x = 0$, to both sides of the governing equation, *i.e.*, Eq. 6. For this four parameter model, the following differential equations result and are solved simultaneously using the exponential matrix method²⁵ (which the authors refer to as the semianalytical method)²⁶⁻³⁰

$$\frac{d\bar{C}}{d\tau} = 6b(\tau) + 12d(\tau) + 18e(\tau) = -3\delta \quad [35]$$

$$\begin{aligned} \frac{da(\tau)}{d\tau} + \frac{db(\tau)}{d\tau} + \frac{dd(\tau)}{d\tau} + \frac{de(\tau)}{d\tau} \\ = 6b(\tau) + 20d(\tau) + 42e(\tau) \end{aligned} \quad [36]$$

$$\frac{da(\tau)}{d\tau} = 6b(\tau) \quad [37]$$

This all leads to the following expression for the surface concentration

$$\begin{aligned} C_{\text{S,4P}} = 1 - \delta \left[3\tau + \frac{2}{10}\right] + 0.1135\delta \exp(-100.123\tau) \\ + 0.0864\delta \exp(-18.877\tau) \end{aligned} \quad [38]$$

Results and Discussion

It is clear from the above analysis that the concentration profiles, surface concentrations, and electrode utilization predicted from the

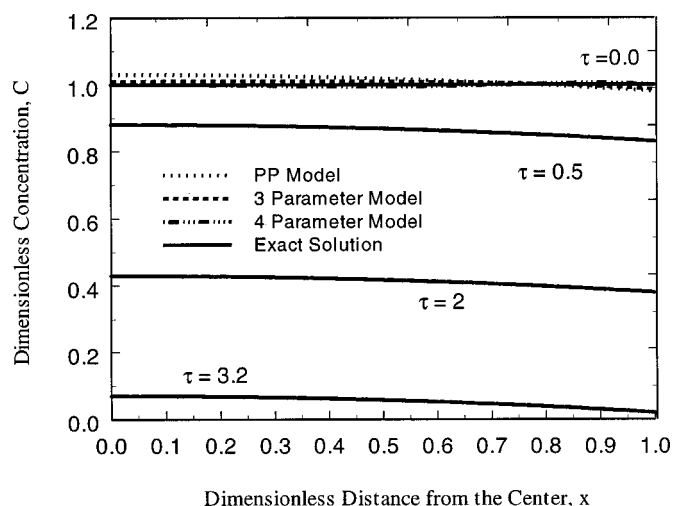


Figure 1. Approximate and exact dimensionless concentration profiles inside a spherical electrode particle for $\delta = 0.1$. For values of $\tau > 0.5$, all four curves overlap.

approximate and exact models depend mainly on the magnitude of the dimensionless current density, δ . Figures 1 and 2 compare the concentration profiles in the particle obtained from the approximate and exact models at different dimensionless times during discharge for two different values of δ . For both values of δ , the exact and approximate models agree well with each other, except at short dimensionless times approaching $\tau = 0$. The deviations increase as δ increases, indicating that the polynomial profile approximations begin to break down as the reaction rates increase, but only during the initial states of discharge. After an initial period of time, the agreement between the approximate and exact models is nearly perfect for all three polynomial functions. This is not the case for the surface concentrations, however.

Figures 3-5 compare the dimensionless surface concentrations predicted from the exact and the three approximate models as a function of the state of discharge, for values of δ equal to 0.1, 2, and 5, respectively. Only the four parameter model is capable of predicting the surface concentration over a broad range of δ with reasonable accuracy. In contrast, the two and three parameter models only do well at low values of δ ; at higher values, they behave similarly

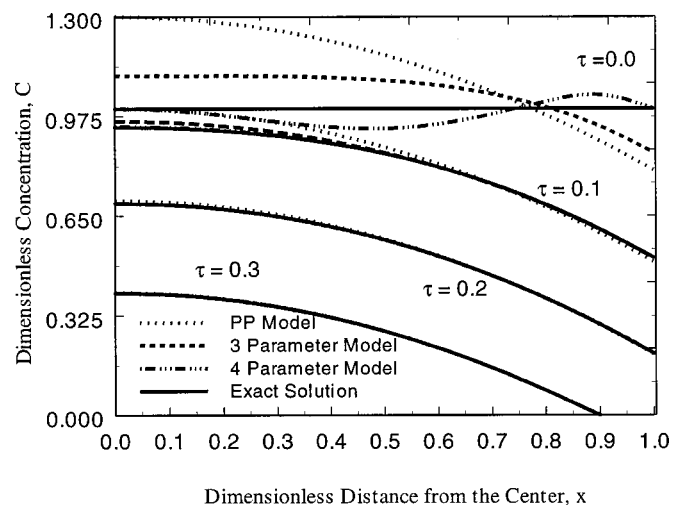


Figure 2. Approximate and exact dimensionless concentration profiles inside a spherical electrode particle for $\delta = 0.5$. For values of $\tau > 0.2$, all four curves overlap.

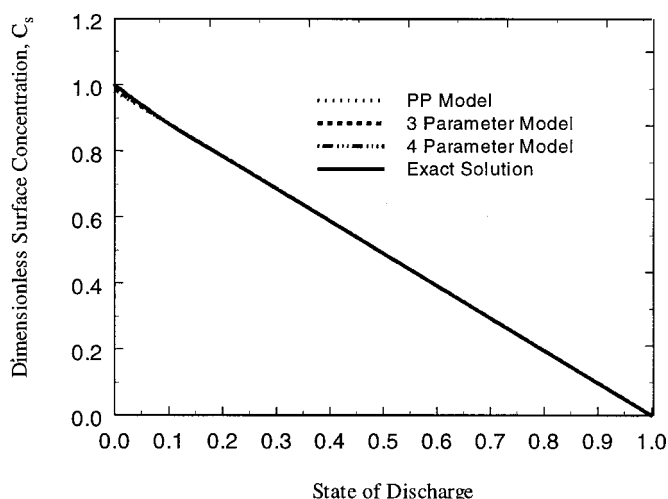


Figure 3. Approximate and exact dimensionless surface concentrations at the surface of a spherical electrode particle as a function of the state of discharge for $\delta = 0.1$ (low value of δ). All four curves overlap for this low value of δ .

and completely misrepresent the surface concentration at zero state of discharge where it should be unity. So, again at high reaction rates, the second and fourth order polynomial approximations break down, but not the sixth order polynomial approximation; and at low values of δ , again all three approximate models agree reasonably well with the exact model. Similar results are realized in predicting the electrode utilization.

Figure 6 compares the utilization predicted from the exact and the three approximate models as a function of δ . The four parameter model agrees extremely well with the exact solution over a broad range of δ up to a δ of about 10. In contrast, the two and three parameter models begin to deviate from the exact model at a δ of around 2 and 4, respectively.

As stated earlier, the surface concentration is one of the more important variables that govern the performance of electrochemical systems; and hence, it is worth quantifying the error in the prediction of the surface concentration from the three approximate models. For this purpose, a time-averaged percent error in the surface concentration is defined as

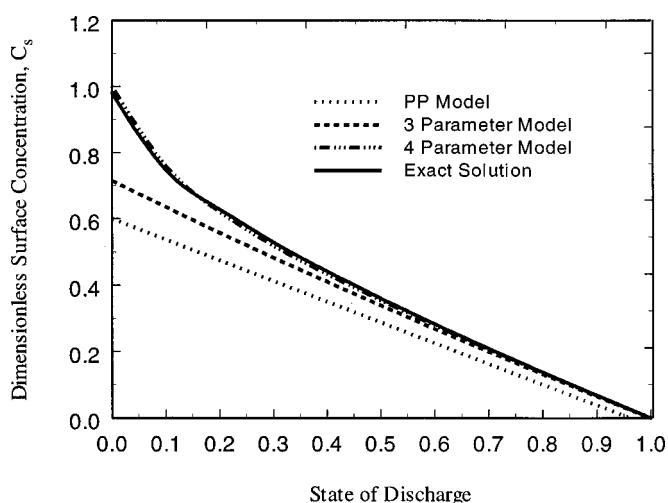


Figure 4. Approximate and exact dimensionless surface concentrations at the surface of a spherical electrode particle as a function of the state of discharge for $\delta = 2$ (high value of δ).

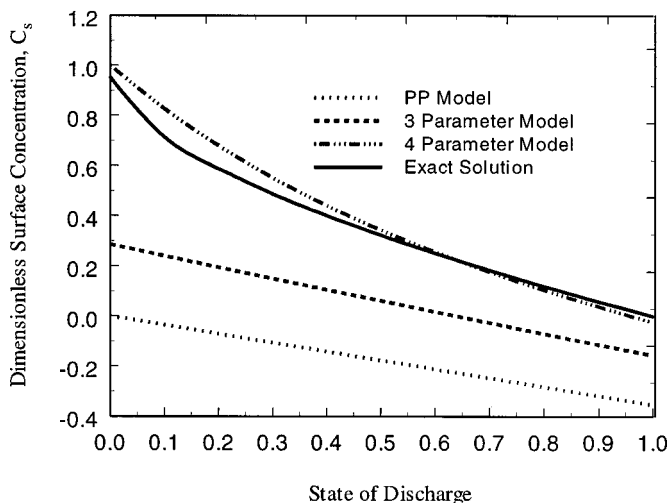


Figure 5. Approximate and exact dimensionless surface concentrations at the surface of a spherical electrode particle as a function of the state of discharge for $\delta = 5$ (extremely high value of δ).

$$\varepsilon = \frac{\int_{\tau=0}^{\tau=\tau_{\text{disch,ex}}} C_{S,\text{exact}} d\tau - \int_{\tau=0}^{\tau=\tau_{\text{disch,app}}} C_{S,\text{approximate}} d\tau}{\int_{\tau=0}^{\tau=\tau_{\text{disch,ex}}} C_{S,\text{exact}} d\tau} \quad (100)$$

[39]

These percent errors are plotted in Fig. 7 as a function of δ , for all three approximate models. The error in predicting the surface concentration from the two and three parameter models is very similar, with errors of less than 5% resulting for values of δ less than 0.5 and 1.0, respectively. In contrast, the error in predicting the surface concentration from the four parameter model is much smaller, with values of δ up to around 4 still only resulting in an error of less than 5%. Overall, the three approximate models provide a relatively accurate prediction of the surface concentration within a specific range of δ . This range varies accordingly for the three approximate models.

Clearly, the solutions to the unsteady-state diffusion equation developed here (*i.e.*, Eq. 20, 33, and 38) are not only much simpler to

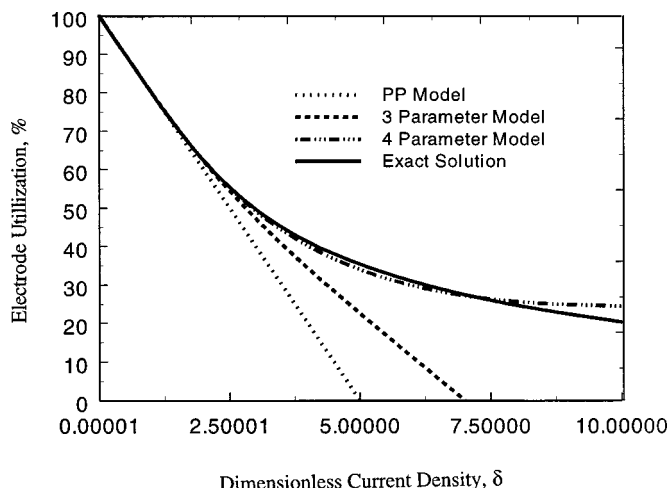


Figure 6. Approximate and exact predictions of the electrode utilization in a spherical electrode particle as a function of the dimensionless current density δ .

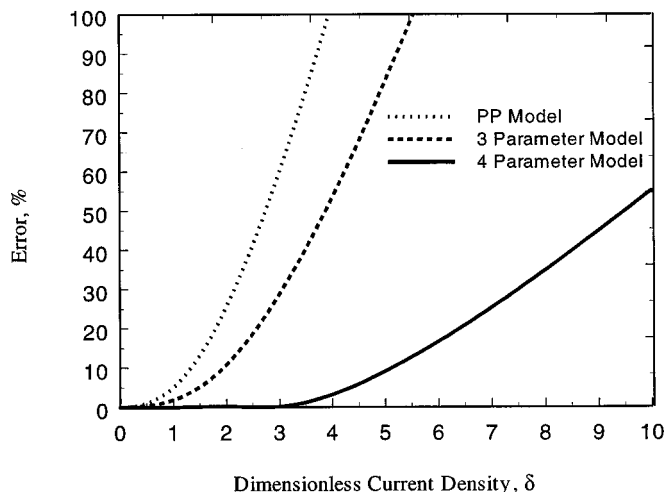


Figure 7. Error in predicting the dimensionless surface concentration at the surface of a spherical electrode particle from the approximate models as a function of the dimensionless current density δ .

use compared to the exact solution (Eq. 18), they also shed some light on the validity of other simplified analyses carried out on electrochemical systems in the literature.¹⁹⁻²¹ For example, they provide a quantitative description of the error that may be incurred by applying a parabolic profile approximation to describe the concentration profile of an electrochemically active species in a thin film surrounding a spherical particle, as done by Wang *et al.*¹⁹ In a similar manner, they provide a quantitative description of the parameter range over which the pseudo-steady-state approximation may be applied, as done by Doyle and Newman.²¹ In other words, the simple solutions developed here can be used to give a quantitative estimate of what longer times or slower rates really means in an electrochemical system, based on the magnitude of the dimensionless current density, for example. The solution methodologies developed here may also be of great use in simplifying the analyses of pseudo two dimensional problems.³¹ For example, instead of integrating the exact solution (Eq. 19), one of the approximate solutions (Eq. 20, 33, or 38) can be easily integrated by applying Duhamel's superposition theorem.

The practical range of δ depends upon the system, particle radius, diffusion coefficient, and initial concentration. Consider, for example, lithium intercalation in carbon.³² For a 1C discharge rate (0.5 mA/cm²), and $R_p = 12.5 \mu\text{m}$, $D_s = 3.9 \times 10^{-10} \text{cm}^2/\text{s}$, $c_0 = 26.39 \text{mol}/\text{dm}^3$ in Eq. 10, a $\delta = 0.63$ is obtained. So for rates up to 0.8C ($\delta = 0.5$), 1.6C ($\delta = 1$), and 6.4C ($\delta = 4$), the two, three, and four parameter models can be used with only about 5% error (based on Fig. 7). Moreover, for a given battery system, one can calculate the value of δ from Eq. 10 and decide beforehand which approximate model to use.

Conclusions

A common assumption used in simplifying the modeling of complex adsorption and catalytic systems is introduced here for simplifying the modeling of complex electrochemical systems. In particular, second, fourth, and sixth order polynomial profile approximations, that describe the concentration profile of an electrochemically active species in a spherical electrode particle, are used to simplify the unsteady-state diffusion equation with a constant diffusion coefficient and describe the galvanostatic discharge of electrode particles. The resulting analytical expressions compare extremely well with the exact analytical solution in predicting the concentration profiles, surface concentrations, and electrode utilization over a broad range of practical dimensionless current densities. Based on a quantitative criterion that is also developed, the sixth order, four parameter polynomial approximation gives the best re-

sults, with errors of less than 5% over a broad range of practical conditions. These relationships should thus be very useful in the design and analysis of electrochemical systems, and also in parameter estimation.

In this paper, only the simple constant diffusion coefficient case was solved and compared with a known analytical solution (Eq. 11) to quantify the accuracy of the approximate models based on parabolic profile approximations. However, the methodology developed in this work is general and should also be very useful in simplifying the analysis of other more complicated electrochemical systems, for example, in solving pseudo-two-dimensional problems. Moreover, this methodology is readily extended to the case where the diffusion coefficient is a function of concentration (*i.e.*, SOC), as shown in Part II of this study. It is also amiable to voltammetry, as shown in Part III of this work. Therefore, it is anticipated that these polynomial profile approximations will find considerable use in simplifying the modeling of complex electrochemical systems without sacrificing much accuracy.

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List of Symbols

$a(\tau)$	time-dependent constant, dimensionless
$b(\tau)$	time-dependent constant, dimensionless
C	concentration, dimensionless
c	concentration, mol/cm ³
c_0	initial concentration, mol/cm ³
C_s	surface concentration, dimensionless
c_s	surface concentration, mol/cm ³
D	diffusion coefficient, cm ² /s
$d(\tau)$	time-dependent constant, dimensionless
i	applied current density, A/cm ²
I	applied current, A/g
R_p	radius of the electrode particle, cm
U	utilization, dimensionless

Greek

δ	dimensionless current density at the surface
τ	dimensionless time

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