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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\[
\frac{\partial c}{\partial t} = D \frac{1}{r} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) \tag{1}
\]

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

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

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

and

\[
D \frac{\partial c}{\partial r} = -\frac{ia}{nF} \quad \text{at} \quad r = R_p \quad \text{and for} \quad t > 0 \tag{4}
\]

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

\[
C = \frac{c}{c_0}, \quad x = \frac{r}{R_p}, \quad \text{and} \quad \tau = \frac{Dt}{R_p^2} \tag{5}
\]

simplifies the model to

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

with the corresponding initial and boundary conditions

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

\[
\frac{\partial C}{\partial x} = 0 \quad \text{at} \quad x = 0 \quad \text{and for} \quad \tau > 0 \tag{8}
\]

and

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

where \(\delta\) is the applied dimensionless current density defined as

\[
\delta = \frac{i_a R_p}{nFDc_0} \tag{10}
\]

An exact analytical solution to this model can be obtained by the separation of variables and given by

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

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, \(\delta\).

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

\[
C = a(\tau) + b(\tau)x^2 \tag{12}
\]

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

\[
\frac{\partial C}{\partial x} \bigg|_{x=1} = 2b(\tau) = -\delta \tag{13}
\]

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

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

Both sides of Eq. 6 are now multiplied by the dimensionless differential volume element, \(x^2 \, dx\), and integrated from 0 to 1 using Eq. 12 for \(C\) in Eq. 6. This results in

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

\[
\Rightarrow \frac{d\bar{C}}{d\tau} = 6b(\tau) = -3\delta \tag{15}
\]

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

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

A comparison of Eq. 14 and 16 leads to

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

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

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

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

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 \(\tau\), 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

\[
C_{S,exact} = C_{x=1} = C(x, \tau)
\]

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

and that from the PP solution is given by

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

Utilization is also a very important property for any electrode particle. It is defined as the amount of active material reacted, according to
$U = \frac{\text{Initial concentration} - \text{concentration left in the particle after discharge}}{\text{Initial concentration}} \times (100)$

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

where $3x^2 dx$ is the differential volume element of the spherical particle, and $\tau_{\text{disch}}$ 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

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

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 $\tau$. Note that the integral of the infinite series is zero as explained in Ref. 21. Similarly, using the PP solution (Eq. 18) leads to

$U_{\text{PP}}(\%) = 3\delta \tau_{\text{disch,PP}}(100)$

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

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

**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

$$C = a(\tau) + b(\tau)x^2 + d(\tau)x^4$$

where $a(\tau), b(\tau),$ and $d(\tau)$ are functions of $\tau,$ 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

$$\frac{\partial C}{\partial x} \bigg|_{x=1} = 2b(\tau) + 4d(\tau) = -\delta$$

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

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

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

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

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

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

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.,

$$\frac{\partial C}{\partial \tau} \bigg|_{x=1} = \frac{1}{x^5} \frac{\partial}{\partial x} \left( x^2 \frac{\partial C}{\partial x} \right) \bigg|_{x=1}$$

Substituting Eq. 25 into Eq. 30 leads to

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

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

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

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

and

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

These three parameters give the surface concentration as

$$C_{S,3P} = 1 - \delta \left[3\tau + \frac{21}{10} + \frac{2}{5} \delta \exp(-35\tau)\right]$$

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

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

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 method" (which the authors refer to as the semianalytical method)"5-30

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

$$\frac{da(\tau)}{d\tau} + \frac{db(\tau)}{d\tau} + \frac{dd(\tau)}{d\tau} + \frac{de(\tau)}{d\tau} = 6b(\tau) + 20d(\tau) + 42e(\tau)$$

This all leads to the following expression for the surface concentration

$$C_{S,4P} = 1 - \delta \left[3\tau + \frac{21}{10} + 0.1135\delta \exp(-100.123\tau)\right]$$

$$+ 0.0864\delta \exp(-18.877\tau)$$

**Results and Discussion**

It is clear from the above analysis that the concentration profiles, surface concentrations, and electrode utilization predicted from the
approximate and exact models depend mainly on the magnitude of the dimensionless current density, \( d \). 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 \( d \). For both values of \( d \), the exact and approximate models agree well with each other, except at short dimensionless times approaching \( \tau = 0 \). The deviations increase as \( d \) 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 \( d \) 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 \( d \) with reasonable accuracy. In contrast, the two and three parameter models only do well at low values of \( d \); at higher values, they behave similarly 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 \( d \), 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 \( d \). The four parameter model agrees extremely well with the exact solution over a broad range of \( d \) up to a \( d \) of about 10. In contrast, the two and three parameter models begin to deviate from the exact model at a \( d \) 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 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.)

![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 \( \delta \)). All four curves overlap for this low value of \( \delta \).)

![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 \( \delta \)).)
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 $\delta$).

$$
\epsilon = \frac{\int_0^{t_{\text{disch}}} C_{S,\text{exact}} \, d\tau - \int_0^{t_{\text{disch}}} C_{S,\text{approximate}} \, d\tau}{\int_0^{t_{\text{disch}}} C_{S,\text{exact}} \, d\tau} \quad (100)
$$

These percent errors are plotted in Fig. 7 as a function of $\delta$, 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 $\delta$ 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 $\delta$ 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 $\delta$. 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 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. 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. 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. 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. 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 $\delta$ depends upon the system, particle radius, diffusion coefficient, and initial concentration. Consider, for example, lithium intercalation in carbon. For a 1C discharge rate (0.5 mA/cm$^2$), and $R_p = 12.5 \ \mu$m, $D_s = 3.9 \times 10^{-10}$ cm$^2$/s, $c_0 = 26.39$ mol/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 $\delta$ 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 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 result.
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

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>$a(\tau)$</td>
<td>time-dependent constant, dimensionless</td>
</tr>
<tr>
<td>$b(\tau)$</td>
<td>time-dependent constant, dimensionless</td>
</tr>
<tr>
<td>$c$</td>
<td>concentration, mol/cm$^3$</td>
</tr>
<tr>
<td>$c_0$</td>
<td>initial concentration, mol/cm$^3$</td>
</tr>
<tr>
<td>$c_s$</td>
<td>surface concentration, dimensionless</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion coefficient, cm$^2$/s</td>
</tr>
<tr>
<td>$d(\tau)$</td>
<td>time-dependent constant, dimensionless</td>
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<tr>
<td>$I$</td>
<td>applied current, $A/g$</td>
</tr>
<tr>
<td>$R_e$</td>
<td>radius of the electrode particle, cm</td>
</tr>
<tr>
<td>$U$</td>
<td>utilization, dimensionless</td>
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Greek

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\delta$</td>
<td>dimensionless current density at the surface</td>
</tr>
<tr>
<td>$\tau$</td>
<td>dimensionless time</td>
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References