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New separation of variables method for composite electrodes with galvanostatic boundary conditions

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Abstract

The separation of variables method is extended to obtain concentration profiles in a particle electrode under galvanostatic boundary conditions. The method is also used to find exact analytical solutions for composite slab and spherical electrodes. Finally, the method is used to obtain a solution for a lithium/polymer cell model that was presented previously by Doyle and Newman.

Keywords: Composite electrode; Galvanostatic boundary conditions; Laplace transform

1. Introduction

The purpose of this paper is to present an extension of the separation of variables method for solving the model equations that govern concentration distributions in solid electrodes operating under galvanostatic conditions (at both the ends). The method presented here is new and is useful because it reduces significantly the work required to obtain an analytical solution to the general class of model equations presented here. We illustrate our method for a thin film electrode, a spherical electrode particle and composite electrodes.

2. Thin film electrode

Consider the unsteady state diffusion in a thin film electrode with zero initial concentration. The governing equation for the concentration in dimensionless form is

$$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2} \tag{1}$$

with the initial condition $c(x,0) = 0$ and boundary conditions

$$\frac{\partial c}{\partial x}(0,t) = 0 \tag{2}$$

and

$$\frac{\partial c}{\partial x}(1,t) = \delta \tag{3}$$

where δ is the dimensionless current density.

The analytical solution for this boundary value problem (BVP) is given by [1]

$$c = \delta\left[t + \frac{1}{6}(3x^2 - 1) - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp(-n^2\pi^2 t)\cos(n\pi x)\right] \tag{4}$$

This solution can be obtained by applying the Laplace transformation technique. Unfortunately, inverting back to time is very difficult and time consuming as shown in Appendix A.

Fortunately, this BVP can be solved easily by our extension of the method of separation of variables by using the following variable transformation:

$$c(x,t) = u(x,t) + w(x) + v(t) \tag{5}$$

The addition of the term $v(t)$ in Eq. (5) is important and is not presented elsewhere to our knowledge. Here $w(x)$ satisfies the inhomogeneous boundary conditions

$$\frac{\mathrm{d}w}{\mathrm{d}x}(0) = 0 \tag{6}$$

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Nomenclature

A	separation constant (Eq. (15))
A_n	coefficient in the infinite series
B	constant
c	dimensionless concentration (Sections 2 and 3 and Appendix A) concentration (mol/cm^3, Sections 4 and 5)
c_1, c_2	concentration (mol/cm^3)
c_0	initial concentration (mol/cm^3)
C_1, C_2	dimensionless concentration
D_1, D_2	diffusion coefficient (cm^2/s)
F	Faraday's constant (96,487 C/g equivalent)
i	applied current density (A/cm^2)
J	dimensionless current density
L	length (cm)
r	radial distance (cm)
R	radius of the particle (cm)
s	Laplace transform variable
t	dimensionless time (s, Sections 2 and 3 and Appendix A) (Sections 4–6)
x	distance (cm)
X	dimensionless distance
y	dimensionless distance

Greek letters

δ	dimensionless current density
ϕ	dimensionless potential
λ	independent variable (only in Section 4)
λ_n	eigenvalue
θ_1, θ_2	dimensionless concentration
τ	dimensionless time

and

$$\frac{\mathrm{d}w}{\mathrm{d}x}(1) = \delta \tag{7}$$

The variable $u(x, t)$ satisfies the homogeneous boundary conditions

$$\frac{\partial u}{\partial x}(0, t) = 0 \tag{8}$$

and

$$\frac{\partial u}{\partial x}(1, t) = 0 \tag{9}$$

The variable $v(t)$ satisfies the initial condition

$$v(0) = 0 \tag{10}$$

and all three variables together also satisfy the initial condition

$$u(x, 0) + w(x) + v(0) = 0 \tag{11}$$

The transformation given by Eq. (5) changes Eq. (1) to

$$\frac{\partial u}{\partial t} + \frac{\mathrm{d}v}{\mathrm{d}t} = \frac{\partial^2 u}{\partial x^2} + \frac{\mathrm{d}^2 w}{\mathrm{d}x^2} \tag{12}$$

Separating the variables, we get

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} \tag{13}$$

and

$$\frac{\mathrm{d}v}{\mathrm{d}t} = \frac{\mathrm{d}^2 w}{\mathrm{d}x^2} \tag{14}$$

Since $v(t)$ is a function of t only and $w(x)$ is a function of x only, we require that

$$\frac{\mathrm{d}v}{\mathrm{d}t} = \frac{\mathrm{d}^2 w}{\mathrm{d}x^2} = A \tag{15}$$

where A is a constant. Typically, when A is 0, Eq. (5) can be replaced by the usual variable transformation [2],

$$c(x, t) = u(x, t) + w(x) \tag{16}$$

For this case, A is nonzero and is determined by the boundary conditions. The second half of Eq. (15) can be solved with the boundary conditions to give

$$A = \delta \tag{17}$$

and

$$w(x) = \tfrac{1}{2}\delta x^2 + B \tag{18}$$

where B is an arbitrary constant. The left-hand side of Eq. (15) can be solved with the initial condition for $v(t)$ (Eq. (10)) to give

$$v(t) = \delta t \tag{19}$$

Hence, the solution is given by

$$c(x, t) = u(x, t) + w(x) + v(t) = u(x, t) + \tfrac{1}{2}\delta x^2 + \delta t + B \tag{20}$$

Now $u(x, t)$ is obtained by solving Eq. (13) with the homogeneous boundary conditions (Eqs. (8) and (9)) to give

$$u(x, t) = \sum_{n=1}^{\infty} A_n \exp(-n^2\pi^2 t)\cos(n\pi x) \tag{21}$$

where A_n $(n = 1, 2, \ldots)$ are constants. Hence, the final solution is given by

$$c(x, t) = \frac{\delta}{2}x^2 + \delta t + B + \sum_{n=1}^{\infty} A_n \exp(-n^2\pi^2 t)\cos(n\pi x) \tag{22}$$

The constants A_n and B are obtained by imposing the initial condition

$$c(x, 0) = 0 = \frac{\delta}{2}x^2 + B + \sum_{n=1}^{\infty} A_n \cos(n\pi x) \tag{23}$$

Eq. (23) is of Sturm–Liouville type. A_n can be obtained by multiplying both sides of Eq. (23) by $\cos(n\pi x)$ and integrating from 0 to 1 to get

$$A_n = -\delta \frac{2(-1)^n}{n^2\pi^2} \tag{24}$$

The constant B can be obtained from Eq. (23) by specifying a value for x (and picking 10 or more terms in the expansion) and solving for B. Alternatively, B can be obtained by integrating both sides of Eq. (23) from 0 to 1

$$B = -\tfrac{1}{6}\delta \tag{25}$$

Substituting Eqs. (24) and (25) into Eq. (22) yields Eq. (4).

Mathews and Walker [2] solved the same problem by using the transformation given by Eq. (16). One cannot solve explicitly for $w(x)$ by using Eq. (16) subject to the boundary conditions given by Eqs. (6) and (7). They assumed arbitrarily a parabolic profile for $w(x)$ satisfying these two boundary conditions (Eqs. (6) and (7)), thereby make the governing equation for $u(x, t)$ inhomogenous. Consequently, their method leads to a more difficult problem to solve and is not general.

Clearly our variable transformation Eq. (5) is a more direct method than that presented by Mathews and Walker (we do not have to assume that $w(x)$ is parabolic) and our method is easier to apply than the classical Laplace transform technique given in Appendix A.

A similar problem is solved by Bird et al. [3] (pages 295–296 and 362) for laminar tube flow with constant heat flux at wall. However, they assumed the form of the solution (see Eq. (9.8.23) of [3]). Also, they introduced another boundary condition (Eq. (9.8.25) of [3]) by heat balance. Our method does not require assuming the form of the solution as in references [2,3]. Also, our method does not need the additional boundary condition introduced by [3].

3. Spherical electrode particle

The utility of our method is even greater for the case of a spherical electrode particle with unsteady state diffusion and zero initial concentration. The governing equation for the concentration in dimensionless form is given by

$$\frac{\partial c}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right) \tag{26}$$

with the initial condition $c(r, 0) = 0$ and boundary conditions

$$\frac{\partial c}{\partial r}(0, t) = 0 \tag{27}$$

and

$$\frac{\partial c}{\partial r}(1, t) = \delta \tag{28}$$

where again δ is the dimensionless current density.

The analytical solution for this BVP is given by [4]

$$c = \delta\left[3t + \frac{1}{10}(5r^2 - 3) - 2\frac{1}{r}\sum_{n=1}^{\infty}\frac{\sin(\lambda_n r)}{\lambda_n^2\sin(\lambda_n)}\exp(-\lambda_n^2 t)\right] \tag{29}$$

where λ_n ($n = 1, 2, \ldots$) are the positive roots of

$$\tan(\lambda_n) = \lambda_n \tag{30}$$

This solution can be obtained by applying the Laplace transformation in the time variable, as shown in Appendix A. Unfortunately, using the Laplace transform technique for this problem is even more difficult and time consuming. Fortunately, our method works well and is easy to apply. As before, the following variable transformation is used:

$$c(r, t) = u(r, t) + w(r) + v(t) \tag{31}$$

where $w(r)$ satisfies the inhomogeneous boundary conditions

$$\frac{\mathrm{d}w}{\mathrm{d}r}(0) = 0 \tag{32}$$

and

$$\frac{\mathrm{d}w}{\mathrm{d}r}(1) = \delta \tag{33}$$

The variable $u(r, t)$ satisfies the homogeneous boundary conditions

$$\frac{\partial u}{\partial r}(0, t) = 0 \tag{34}$$

and

$$\frac{\partial u}{\partial r}(1, t) = 0 \tag{35}$$

The variable $v(t)$ satisfies the initial condition

$$v(0) = 0 \tag{36}$$

and three variables together also satisfy the initial condition

$$u(r, 0) + w(r) + v(0) = 0 \tag{37}$$

Applying the same procedure as before the variables are solved as

$$w(r) = \tfrac{1}{2}\delta r^2 + B \tag{38}$$

$$v(t) = 3\delta t \tag{39}$$

and

$$u(r, t) = \frac{1}{r}\sum_{n=1}^{\infty}A_n\sin(\lambda_n r)\exp(-\lambda_n^2 t) \tag{40}$$

where A_n ($n = 1, 2, \ldots$) are constants. Hence, the final solution is given by

$$c(r, t) = \frac{\delta}{2}r^2 + \delta t + B + \frac{1}{r}\sum_{n=1}^{\infty}A_n\sin(\lambda_n r)\exp(-\lambda_n^2 t) \tag{41}$$

The constants A_n and B are obtained by imposing the initial condition

$$c(r,0) = 0 = \frac{\delta}{2}r^2 + B + \frac{1}{r}\sum_{n=1}^{\infty} A_n \sin(\lambda_n r) \tag{42}$$

Eq. (42) is of Sturm–Liouville type. A_n can be obtained by multiplying both sides of Eq. (42) by $r\sin(\lambda_n r)$ and integrating from 0 to 1 to get

$$A_n = -\delta \frac{2}{\lambda_n^2 \sin(\lambda_n)} \tag{43}$$

The constant B is obtained by multiplying both sides of Eq. (42) by r^2 and integrating from 0 to 1

$$B = -\tfrac{3}{10}\delta \tag{44}$$

4. Composite electrodes

We consider two types of composite electrodes in this section. One is a thin film composite electrode with three layers. The inner layer is made of material different from the outer two layers. An electrochemical reaction is assumed to be occurring on the surfaces of the outer layers so that the centerline of the inner layer can be considered to be a plane of symmetry. The second composite electrode (Section 5) is a spherical electrode with an inner core and an outer layer where an electrochemical reaction is assumed to occur at the surface. These composite electrodes can be used to model intercalation electrodes found in the nickel/metal hydride and lithium ion batteries where charge is stored in a solid phase in the form of charged species (e.g. Li^+). Unfortunately, no analytical solution exists in the literature (that we could find) for a composite electrode with flux conditions.

Fortunately, our method can be used to derive an analytical solution for such cases. Consider a rectangular slab with region 1 ($0 < x < l_1$) of one medium with diffusion coefficient D_1 and region 2 ($l_1 < x < L$) of another medium with diffusion coefficient D_2, respectively. The governing equations for the concentration of diffusing species in regions 1 and 2 (c_1 and c_2) are

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2}, \quad 0 < x < l_1 \tag{45}$$

$$\frac{\partial c_2}{\partial t} = D_2 \frac{\partial^2 c_2}{\partial x^2}, \quad l_1 < x < L \tag{46}$$

Let the initial concentration be c_0, i.e.

$$c_1(x,0) = c_2(x,0) = c_0, \quad \text{for all } x \tag{47}$$

Symmetry at the center ($x = 0$) gives the boundary condition

$$\frac{\partial c_1}{\partial x}(0,t) = 0, \quad \text{for } t > 0 \tag{48}$$

Under galvanostatic discharge conditions, applied current gives the boundary condition at the surface

$$\frac{\partial c_2}{\partial x}(L,t) = \frac{-i}{nFD_2}, \quad \text{for } t > 0 \tag{49}$$

where i is the applied current density (a positive quantity) at the surface of the electrode, F the Faraday's constant and n the number of electrons transferred in the electrochemical reaction. The negative sign in Eq. (49) is used because charge is being removed from the battery. Assuming no charge transfer resistance at the interface ($x = l_1$), the boundary conditions at the interface are

$$c_1(l_1,t) = c_2(l_1,t), \quad t > 0 \tag{50}$$

$$D_1 \frac{\partial c_1}{\partial x}(l_1,t) = D_2 \frac{\partial c_2}{\partial x}(l_1,t), \quad t > 0 \tag{51}$$

Next, we introduce the following dimensionless variables:

$$C_1 = \frac{c_1}{c_0} - 1, \qquad C_2 = \frac{c_2}{c_0} - 1, \qquad X = \frac{x}{L}, \qquad \tau = \frac{D_2 t}{L^2} \tag{52}$$

The governing equations in dimensionless form are

$$\frac{\partial C_1}{\partial \tau} = \frac{1}{\beta^2}\frac{\partial^2 C_1}{\partial X^2}, \quad 0 < X < \alpha \tag{53}$$

$$\frac{\partial C_2}{\partial \tau} = \frac{\partial^2 C_2}{\partial X^2}, \quad \alpha < X < 1 \tag{54}$$

where

$$\alpha = \frac{l_1}{L} \tag{55}$$

and

$$\beta^2 = \frac{D_2}{D_1} \tag{56}$$

The initial and boundary conditions are transformed to

$$C_1(X,0) = C_2(X,0) = 0, \quad \text{for all } X \tag{57}$$

$$\frac{\partial C_1}{\partial X}(0,\tau) = 0, \quad \tau > 0 \tag{58}$$

$$\frac{\partial C_2}{\partial X}(1,\tau) = -\delta, \quad \tau > 0 \tag{59}$$

$$C_1(\alpha,\tau) = C_2(\alpha,\tau) = 0, \quad \tau > 0 \tag{60}$$

$$\frac{\partial C_1}{\partial X}(\alpha,\tau) = \beta^2 \frac{\partial C_2}{\partial X}(\alpha,\tau), \quad \tau > 0 \tag{61}$$

where

$$\delta = \frac{iL}{nFD_2 c_0} \tag{62}$$

is the applied dimensionless current density at the surface of the electrode (a positive number).

Now applying our variable transformation defined by Eq. (5) for both C_1 and C_2 separately and solving with

the initial (Eq. (57)) and boundary conditions (Eqs. (58) and (59)), we get

$$C_1 = \frac{1}{2}k\beta^2X^2 + k\tau + a_1 + \sum_{n=1}^{\infty}B_n\cos(\lambda_n\beta X)\exp(-\lambda_n^2\tau) \tag{63}$$

and

$$C_2 = \frac{1}{2}kX^2 - (\delta + k)X + k\tau + a_2 + \sum_{n=1}^{\infty}E_n\cos(\lambda_n[1-X]) \times \exp(-\lambda_n^2\tau) \tag{64}$$

where k, a_1 and a_2 are constants to be determined by the boundary conditions at the interface ($X = \alpha$), λ_n ($n = 1, 2, 3, \ldots$) are the eigenvalues, and B_n and E_n are the constants associated with the eigenvalues. Boundary conditions λ_n at the interface (Eqs. (60) and (61)) yield

$$k = -\delta \tag{65}$$

$$a_2 - a_1 = \tfrac{1}{2}\delta\alpha^2(1-\beta^2) \tag{66}$$

$$\frac{B_n}{\cos(\lambda_n[1-\alpha])} = \frac{E_n}{\cos(\lambda_n\beta\alpha)} = A_n \tag{67}$$

where A_n is a new constant associated with the eigenvalue λ_n. Now the solutions for C_1 and C_2 are given by the simplified expressions

$$C_1 = -\frac{1}{2}\delta\beta^2X^2 - \delta\tau + a_1 + \sum_{n=1}^{\infty}A_n\cos(\lambda_n[1-\alpha]) \times \cos(\lambda_n\beta X)\exp(-\lambda_n^2\tau) \tag{68}$$

$$C_2 = -\frac{1}{2}\delta X^2 - \delta\tau + a_2 + \sum_{n=1}^{\infty}A_n\cos(\lambda_n[1-X]) \times \cos(\lambda_n\beta\alpha)\exp(-\lambda_n^2\tau) \tag{69}$$

where λ_n are the positive roots of the transcendental equation

$$\tan(\lambda_n[1-\alpha]) + \frac{\tan(\lambda_n\beta\alpha)}{\beta} = 0 \tag{70}$$

which was obtained by equating the flux at the interface (Eq. (61)). Now C_1 and C_2 separately satisfy the initial condition (Eq. (57))

$$C_1(X,0) = 0 = -\frac{1}{2}\delta\beta^2X^2 + a_1 + \sum_{n=1}^{\infty}A_n\cos(\lambda_n[1-\alpha]) \times \cos(\lambda_n\beta X) \tag{71}$$

and

$$C_2(X,0) = 0 = -\frac{1}{2}\delta X^2 + a_2 + \sum_{n=1}^{\infty}A_n\cos(\lambda_n[1-X]) \times \cos(\lambda_n\beta\alpha) \tag{72}$$

Eqs. (71) and (72) are of the Sturm–Liouville type. Applying a procedure similar to the one presented above for the thin film electrode, the constants are obtained as follows:

$$a_1 = \delta(\tfrac{1}{6} + \tfrac{1}{3}\alpha^3[1-\beta^2] - \tfrac{1}{2}\alpha^2[1-\beta^2]) \tag{73}$$

$$a_2 = \delta(\tfrac{1}{6} + \tfrac{1}{3}\alpha^3[1-\beta^2]) \tag{74}$$

and

$$A_n = \frac{2\delta\cos(\beta\lambda_n\alpha)}{\alpha\cos^2(\lambda_n[1-\alpha]) + (1-\alpha)\cos^2(\beta\lambda_n\alpha)} \tag{75}$$

Hence, the concentrations of the diffusing species are given by

$$c_1 = c_0\left[1 - \frac{1}{2}\delta\beta^2X^2 - \delta\tau + a_1 + \sum_{n=1}^{\infty}A_n\cos(\lambda_n[1-\alpha]) \times \cos(\lambda_n\beta X)\exp(-\lambda_n^2\tau)\right]$$

$$c_2 = c_0\left[1 - \frac{1}{2}\delta X^2 - \delta\tau + a_2 + \sum_{n=1}^{\infty}A_n\cos(\lambda_n[1-X]) \times \cos(\lambda_n\beta\alpha)\exp(-\lambda_n^2\tau)\right] \tag{77}$$

where a_1, a_2 and A_n are defined by Eqs. (73)–(75) and the eigenvalues λ_n are given by Eq. (70). When $\beta = 1$, both c_1 and c_2 given by Eqs. (76) and (77) reduce to

$$c = c_0\left[1 - \delta\tau - \frac{\delta}{6}(3X^2-1) + \frac{2\delta}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp(-n^2\pi^2\tau) \times \cos(n\pi X)\right] \tag{78}$$

which is the solution for diffusion in a thin film electrode of diffusion coefficient D_2 ($D_2 = D_1 = D$), as expected. Dimensionless concentration ($c_1/c_0[0 < X < \alpha]$ or $c_2/c_0[\alpha < X < 1]$) profiles for $\delta = 1$, $\alpha = 0.5$ and $\beta = 2$ are given in Fig. 1 for several values of τ.

5. Composite spherical electrodes

A general model for a composite spherical electrode is presented here by using our approach. The governing equations for the concentrations of the diffusing species are

$$\frac{\partial c_1}{\partial t} = \frac{D_1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_1}{\partial r}\right), \quad 0 < r < r_1 \tag{79}$$

$$\frac{\partial c_2}{\partial t} = \frac{D_2}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_2}{\partial r}\right), \quad r_1 < r < R \tag{80}$$

with the initial and boundary conditions

$$c_1(r,0) = c_2(r,0) = c_0, \quad \text{for all } r \tag{81}$$

$$\frac{\partial c_1}{\partial r}(0,t) = 0, \quad t > 0 \tag{82}$$

$$\frac{\partial c_2}{\partial r}(R,t) = \frac{-i}{nFD_2}, \quad t > 0 \tag{83}$$

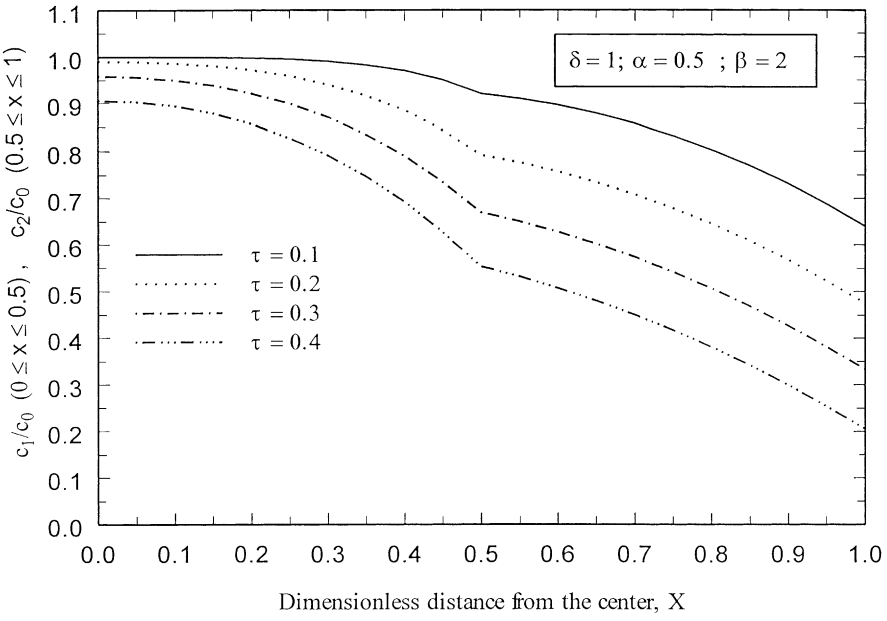

Fig. 1. Concentration profiles during discharge of a composite slab electrode.

$$c_1(r_1,t) = c_2(r_1,t), \quad t > 0 \tag{84}$$

$$D_1 \frac{\partial c_1}{\partial r}(r_1,t) = D_2 \frac{\partial c_2}{\partial r}(r_1,t), \quad t > 0 \tag{85}$$

Using the same procedure followed for a composite rectangular slab presented above, we arrive at the solution for the concentration profiles

$$c_1 = c_0\Bigg[1 - \frac{1}{2}\delta\beta^2 X^2 - 3\delta\tau + a_1 + \frac{1}{X}\sum_{n=1}^{\infty} A_n \times [\lambda_n \cos(\lambda_n[1-\alpha]) - \sin(\lambda_n[1-\alpha])]\sin(\lambda_n\beta X) \times \exp(-\lambda_n^2\tau)\Bigg] \tag{86}$$

$$c_2 = c_0\Bigg[1 - \frac{1}{2}\delta X^2 - 3\delta\tau + a_2 + \frac{1}{X}\sum_{n=1}^{\infty} A_n \times [\lambda_n \cos(\lambda_n[1-X]) - \sin(\lambda_n[1-X])]\sin(\lambda_n\beta\alpha) \times \exp(-\lambda_n^2\tau)] \tag{87}$$

where

$$\delta = \frac{iR}{nFD_2c_0} \tag{88}$$

$$X = \frac{r}{R}, \qquad \tau = \frac{D_2 t}{R^2} \tag{89}$$

$$\alpha = \frac{r_1}{R} \tag{90}$$

$$\beta^2 = \frac{D_2}{D_1} \tag{91}$$

$$a_1 = \delta(\tfrac{3}{10} + \tfrac{1}{5}\alpha^5[1-\beta^2] - \tfrac{1}{2}\alpha^2[1-\beta^2]) \tag{92}$$

and

$$a_2 = \delta(\tfrac{3}{10} + \tfrac{1}{5}\alpha^5[1-\beta^2]) \tag{93}$$

The eigenvalues are given by

$$1 - \frac{1}{\beta^2} + \frac{\lambda_n\alpha}{\beta\tan(\lambda_n\beta\alpha)} + \frac{\lambda_n\alpha}{\tan(\lambda_n[1-\alpha-\phi])} = 0 \tag{94}$$

where

$$\phi = \frac{\tan^{-1}(\lambda_n)}{\lambda_n} \tag{95}$$

The Fourier series constants are given by

$$A_n = \frac{2\delta\sin(\beta\lambda_n\alpha)}{\lambda_n f_n(\alpha)} \tag{96}$$

where

$$f_n(\alpha) = \frac{\alpha u1_{pn}^2}{\lambda_n^2\beta^2} - \frac{u1_{pn}u_n}{\lambda_n^2\beta^2} + u2_n^2 - \frac{\alpha u2_{pn}^2}{\lambda_n^2} + \frac{u2_{pn}u_n}{\lambda_n^2} \tag{97}$$

with

$$u2_n = \lambda_n \sin(\lambda_n\beta\alpha) \tag{98}$$

$$u_n = \sin(\lambda_n\beta\alpha)[\lambda_n\cos(\lambda_n[1-\alpha]) - \sin(\lambda_n[1-\alpha])] \tag{99}$$

$$u1_{pn} = \lambda_n\beta\cos(\lambda_n\beta\alpha)[\lambda_n\cos(\lambda_n[1-\alpha]) - \sin(\lambda_n[1-\alpha])] \tag{100}$$

and

$$u2_{pn} = \lambda_n\sin(\lambda_n\beta\alpha)[\cos(\lambda_n[1-\alpha]) + \lambda_n\sin(\lambda_n[1-\alpha])] \tag{101}$$

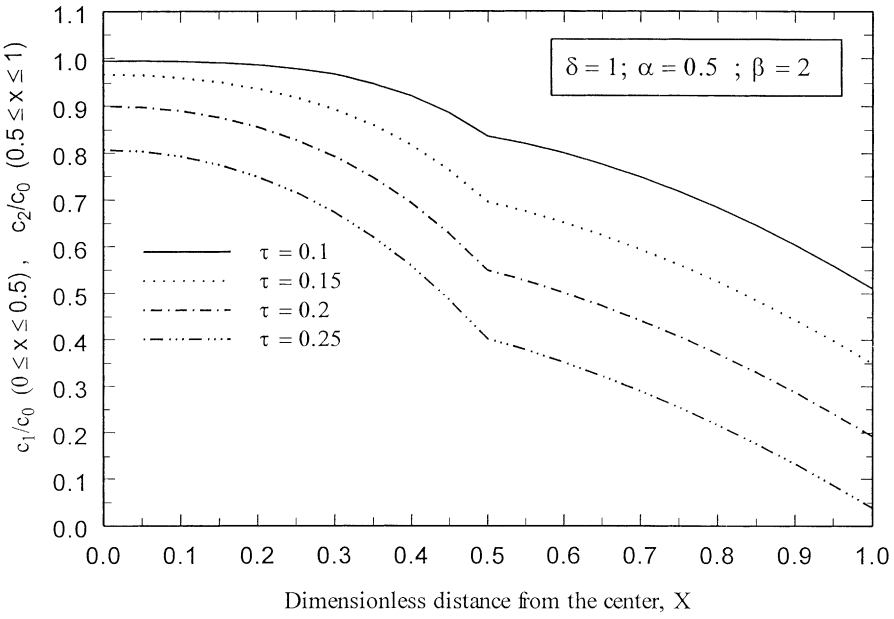

Fig. 2. Concentration profiles during discharge of a composite spherical electrode.

When $\beta = 1$, both c_1 and c_2 given by Eqs. (89) and (90) reduce to

$$c = c_0\left[1 - 3\delta\tau - \frac{\delta}{10}(5X^2 - 3) + \frac{2\delta}{X}\sum_{n=1}^{\infty}\frac{\sin(\lambda_n X)}{\lambda_n^2 \sin(\lambda_n)} \times \exp(-\lambda_n^2\tau)\right]$$

where λ_n $(n = 1, 2, \ldots)$ are the positive roots of

$$\tan(\lambda_n) = \lambda_n \tag{103}$$

which is the solution for diffusion in a single spherical particle of diffusion coefficient D_2 $(=D_1)$ as expected. The dimensionless concentration $(c_1/c_0[0 < X < \alpha]$ or $c_2/c_0[\alpha < X < 1])$ profiles for $\delta = 1$, $\alpha = 0.5$ and $\beta = 2$ are given in Fig. 2.

6. Solution phase limitations in a lithium ion cell

Doyle and Newman [5] presented simplified models for composite lithium/polymer cell sandwich under uniform current distribution. The dimensionless concentration profiles in their cell sandwich (see their Fig. 1) is given by

$$\frac{\partial\theta_1}{\partial\tau} = \frac{\partial^2\theta_1}{\partial y^2} \quad (0 \le y \le 1, \text{ separator}) \tag{104}$$

$$\frac{\partial\theta_2}{\partial\tau} = \varepsilon^{1/2}\frac{\partial^2\theta_2}{\partial y^2} + J \quad (1 \le y \le 1 + r, \text{ cathode}) \tag{105}$$

with the boundary conditions

$$\frac{\partial\theta_1}{\partial y} = J\varepsilon r \text{ at } y = 0 \tag{106}$$

$$\frac{\partial\theta_2}{\partial y} = 0 \text{ at } y = 1 + r \tag{107}$$

$$\theta_1 = \theta_2 \text{ at } y = 1 \tag{108}$$

$$\frac{\partial\theta_1}{\partial y} = \varepsilon^{3/2}\frac{\partial\theta_2}{\partial y} \text{ at } y = 1 \tag{109}$$

with the initial condition

$$\theta_1 = \theta_2 = 1 \text{ at } \tau = 0 \tag{110}$$

Doyle and Newman solved Eq. (104) for steady-state conditions by assuming that the left-hand side of Eq. (104) is zero and integrating the resulting second-order ordinary differential equation (i.e. $d^2\theta_1/dy^2 = 0$) to obtain a linear profile for θ_1

$$\theta_1 = B + J\varepsilon r y \tag{111}$$

where B is an arbitrary constant. Next, they present a steady-state solution for Eq. (105). It appears that they may have assumed a quadratic profile (as did Mathews and Walker [2]). Complete solutions for θ_1 and θ_2 can be obtained by applying our method.

$$C_1 = \frac{\theta_1 - 1}{J}, \qquad C_2 = \frac{\theta_2 - 1}{J} \tag{112}$$

This transformation is substituted into Eqs. (104) and (105) to get

$$\frac{\partial C_1}{\partial\tau} = \frac{\partial^2 C_1}{\partial y^2} \quad (0 \le y \le 1, \text{ separator}) \tag{113}$$

$$\frac{\partial C_2}{\partial\tau} = \varepsilon^{1/2}\frac{\partial^2 C_2}{\partial y^2} + 1 \quad (1 \le y \le 1 + r, \text{ cathode}) \tag{114}$$

and the boundary conditions (Eqs. (106)–(109)) become

$$\frac{\partial C_1}{\partial y} = \varepsilon r \text{ at } y = 0 \tag{115}$$

$$\frac{\partial C_2}{\partial y} = 0 \text{ at } y = 1 + r \tag{116}$$

$$C_1 = C_2 \text{ at } y = 1 \tag{117}$$

$$\frac{\partial C_1}{\partial y} = \varepsilon^{3/2} \frac{\partial C_2}{\partial y} \text{ at } y = 1 \tag{118}$$

with the initial conditions

$$C_1 = C_2 = 0 \text{ at } \tau = 0 \tag{119}$$

This problem is very similar to the composite electrode problem solved in Section 4. We apply the variable transformation (Eq. (5)) for both C_1 and C_2

$$C_1 = u_1(y,\tau) + w_1(y) + v_1(\tau) \tag{120}$$

and

$$C_2 = u_2(y,\tau) + w_2(y) + v_2(\tau) \tag{121}$$

By applying the same procedure as before we get

$$v_1(\tau) = v_2(\tau) = 0, \qquad w_1(y) = B + \varepsilon r y,$$
$$w_2(y) = B + \varepsilon r y - \frac{1}{\sqrt{\varepsilon}}\left(\frac{1}{2} + r\right) - \frac{1}{\sqrt{\varepsilon}}\left(\frac{y^2}{2} - y(1+r)\right) \tag{122}$$

Note that w_1 and w_2 satisfy all the four boundary conditions given by Eqs. (115)–(118). The transient solutions are obtained as before

$$u_1 = \sum_{n=1}^{\infty} A_n \cos\left(\frac{\lambda_n r}{\varepsilon^{1/4}}\right)\cos(\lambda_n y)\exp(-\lambda_n^2 \tau),$$
$$u_2 = \sum_{n=1}^{\infty} A_n \cos\left(\frac{\lambda_n (1 + r - y)}{\varepsilon^{1/4}}\right)\cos(\lambda_n)\exp(-\lambda_n^2 \tau) \tag{123}$$

where λ_n ($n = 1, \ldots, \infty$) and the eigenvalues are given by the transcendental equation

$$\tan(\lambda_n) = -\varepsilon^{5/4}\tan(\varepsilon^{-1/4}\lambda_n r) \tag{124}$$

By applying the initial condition and by using the Sturm–Louiveille theorem (see Section 4) we get

$$B = \frac{1}{1+\varepsilon r}\left(1 + \frac{\varepsilon r}{2} - \varepsilon^2 r^2\right) - \frac{1}{3}\frac{\sqrt{\varepsilon} r^3}{1 + \varepsilon r},$$
$$A_n = \frac{2\lambda_n \cos(\lambda_n r/\varepsilon^{1/4})\varepsilon r - \varepsilon^{5/4}\sin(\lambda_n r/\varepsilon^{1/4})\cos(\lambda_n)}{\lambda_n^3(\cos^2(\lambda_n r/\varepsilon^{1/4}) + \varepsilon r \cos^2(\lambda_n))} \tag{125}$$

Thus, the dimensionless concentration profiles are

$$\theta_1 = 1 + J\left[B + \varepsilon r + \sum_{n=1}^{\infty} A_n \cos\left(\frac{\lambda_n r}{\varepsilon^{1/4}}\right)\cos(\lambda_n y)\exp(-\lambda_n^2 \tau)\right],$$
$$\theta_2 = 1 + J\left[B + \varepsilon r - \frac{1}{\sqrt{\varepsilon}}\left(\frac{1}{2} + r\right) - \frac{1}{\sqrt{\varepsilon}}\left(\frac{y^2}{2} - y(1+r)\right) + \sum_{n=1}^{\infty} A_n \cos\left(\frac{\lambda_n (1 + r - y)}{\varepsilon^{1/4}}\right)\cos(\lambda_n)\exp(-\lambda_n^2 \tau)\right] \tag{126}$$

where the constants B and A_n are given by Eq. (125). Note that Eq. (126) is simpler than the solution reported by Doyle and Newman [5]. The solution given by Doyle and Newman involves two different constants (F_n and G_n) for both θ_1 and θ_2 separately. Even though our solution looks different from that of Doyle and Newman, both are equivalent. The concentration is minimum at the end of the cathode ($y = 1 + r$). The time for this concentration to reach zero is the dimensionless depletion time. This concentration can be obtained by substituting $y = 1 + r$ into Eq. (114). Doyle and Newman used only one term in the expansion for longer times. They found a short time solution by applying the Laplace transform technique. It should be noted that as mentioned by Doyle and Newman one term in the series in Eq. (14) and the short time solution is sufficient for estimating the depletion time. However, if one wants to follow the transient behavior of the cell sandwich, one term is not sufficient. We have used $N = 20$ terms and predicted the concentration profiles inside the cell sandwich for various values of time and plotted them in Fig. 3 for the given value of applied current, $J = -0.1$. As shown in Fig. 3, the one term approximation used by Doyle and Newman is not valid for predicting the transient behavior inside the cell sandwich.

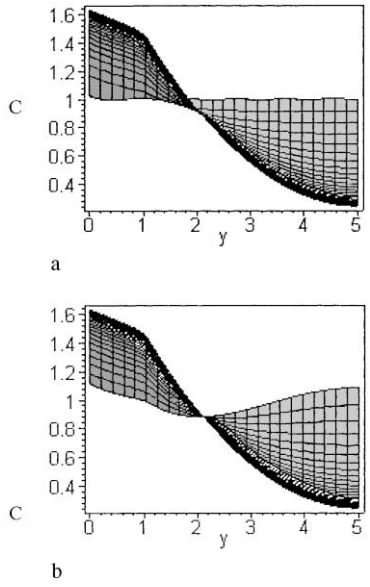

Fig. 3. Dimensionless transient concentration profiles in a time in a lithium ion cell sandwich.

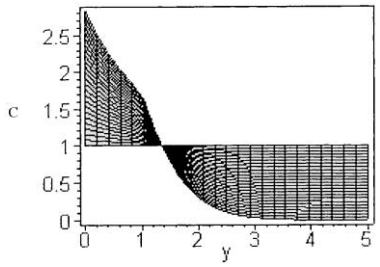

Fig. 4. Concentration profiles in a lithium ion cell sandwich as a function of applied current, J at a particular time ($\tau = 1$).

We would like to stress again that we obtained a simpler but equivalent solution to that obtained by Doyle and Newman. The effect of applied current, J can be seen using the same set of coefficients with our method unlike Doyle and Newman. This is true because their coefficients are functions of the applied current, J (Eqs. (33) and (34), [5]) which means that one has to calculate the coefficients for every value of J. At a particular value of dimensionless time ($\tau = 1$), the concentration profiles inside the cell sandwich are plotted in Fig. 4 for different value of applied current density, J.

7. Conclusion

An extension of the method of separation of variables presented here and given by Eq. (5) is useful for solving BVPs that include flux boundary conditions. This method yields an unambiguous, straightforward way to obtain analytical solutions for problems of this type. The utility of the method is demonstrated for two classical problems (diffusion in a slab and a sphere). Also the method is used to obtain analytical solutions for diffusion in slab and spherical composite electrodes. The transformation proposed helps in obtaining a compact, and easy to use solution for the lithium ion cell sandwich under solution phase diffusion limitations. The method applied can be easily extended to cylindrical coordinates. The method appears to be general and should be useful for solving other similar problems with flux boundary conditions.

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Appendix A. Thin film electrode

The Laplace transform (for the time variable) can be applied to Eqs. (1)–(3) to obtain

$$\frac{d^2c(s)}{dx^2} - sc(s) = 0 \tag{A.1}$$

$$\frac{dc(s)}{dx} = 0 \text{ at } x = 0 \tag{A.2}$$

and

$$\frac{dc(s)}{dx} = \frac{\delta}{s} \text{ at } x = 1 \tag{A.3}$$

Eq. (A.1) can be solved subject to the boundary-conditions given by Eqs. (A.2) and (A.3)

$$c(s) = \frac{\delta \cosh(\sqrt{s}x)}{s\sqrt{s}\sinh(\sqrt{s})} \tag{A.4}$$

Eq. (A.4) can be written in series form

$$c(s) = \frac{P(s)}{Q(s)} = \frac{\delta \sum_{n=1}^{\infty} s^n x^{2n}/2n!}{s^2 \sum_{n=1}^{\infty} s^n/(2n+1)!} \tag{A.5}$$

In Eq. (A.5), the polynomial $Q(s)$ is of higher power in s than $P(s)$. The poles are $s = 0$ (multiplicity 2) and the roots of $\sin(\lambda_n) = 0$ (i.e. $\lambda_n = n\pi$, $n = 1, 2, 3, \ldots$) (where $s = -\lambda_n^2$). The inverse Laplace transform of Eq. (A.5) can be obtained by using the Heaviside expansion theorem [6]. For a function (with multiple poles)

$$f(s) = \frac{\phi(s)}{(s-a)^m} \tag{A.6}$$

where a is the pole of multiplicity m, the inverse transform is given by

$$f(t) = \exp(at) \sum_{n=1}^{m} \frac{\phi^{m-n}(a)}{(m-n)!} \frac{t^{n-1}}{(n-1)!} \tag{A.7}$$

For this case, $a = 0$, $m = 2$ and

$$\phi(s) = (s-a)^m f(s) = \frac{\delta\sqrt{s}\cosh(\sqrt{s}x)}{\sinh(\sqrt{s})} \tag{A.8}$$

In this case, Eq. (A.7) reduces to

$$f(t) = [\phi'(0) + \phi(0)t] \tag{A.9}$$

Now from Eq. (A.8) we have (for $s = 0$)

$$\phi(0) = \frac{(\delta)(0)1}{0} = \frac{0}{0} \tag{A.10}$$

Applying L' Hospital's rule once to Eq. (A.8) we get

$$\phi(s) = \delta \frac{\cosh(\sqrt{s}x) + x\sqrt{s}\sinh(\sqrt{s}x)}{\cosh\sqrt{s}} \tag{A.11}$$

Substituting $s = 0$ and simplifying we get

$$\phi(0) = \delta \tag{A.12}$$

Similarly from Eq. (A.8)

$$\phi'(s) = \frac{\delta}{2}\frac{\cosh(\sqrt{s}x)\sinh(\sqrt{s}) + x\sqrt{s}\sinh(\sqrt{s}x)\sinh(\sqrt{s}) - \sqrt{s}\cosh(\sqrt{s}x)\cosh(\sqrt{s})}{\sqrt{s}[\sinh^2(\sqrt{s})]} \tag{A.13}$$

which for $s = 0$ yields

$$\phi'(0) = \frac{0}{0} \tag{A.14}$$

After applying L' Hospital's rule three times we get

$$\phi'(0) = -\frac{\delta}{6} + \frac{\delta}{2}x^2 \tag{A.15}$$

(The expressions obtained after applying L' Hospital's rule are too big to be included here.) The complete solution can be obtained by using Heaviside expansion theorem for no repeated roots (Eq. (8.3.22) of [6]) and adding the result to Eq. (A.9); the solution is given by

$$c(x,t) = \delta t - \frac{\delta}{6} + \frac{\delta}{2}x^2 + \sum_{n=1}^{\infty}\exp(-\lambda_n^2 t)\,\varphi(\lambda_n) \tag{A.16}$$

where $\lambda_n = n\pi$ and

$$\varphi(\lambda_n) = (s-\lambda_n)f(s) = \frac{P(s=-\lambda_n^2)}{Q'(s=-\lambda_n^2)} = \frac{-2\delta\cos(n\pi x)}{(-1)^n n^2\pi^2} \tag{A.17}$$

Hence, the complete solution is

$$c = \delta\left[t + \frac{1}{6}(3x^2-1) - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2} \times \exp(-n^2\pi^2 t)\cos(n\pi x)\right] \tag{A.18}$$

Eq. (A.19) can be written in series form

$$c(s) = \frac{P(s)}{Q(s)} = \frac{1}{r}\frac{\delta\sum_{n=0}^{\infty}s^{(n+1)/2}r^{2n+1}/(2n+1)!}{s^2\sum_{n=1}^{\infty}s^{(n-1)/2}/(2n+1)(2n-1)!} \tag{A.20}$$

In Eq. (A.20), the polynomial $Q(s)$ has a greater power in s than $P(s)$. The poles are $s = 0$ (multiplicity 2) and the roots of $\tan(\lambda_n) = \lambda_n$ ($n = 1, 2, 3, \ldots$), where $s = -\lambda_n^2$. Using the Heaviside expansion theorem for repeated roots [6]

$$\phi(s) = (s-a)^m f(s) = \frac{1}{r}\frac{\delta s\sinh(\sqrt{s}r)}{\sqrt{s}\cosh\sqrt{s} - \sinh(\sqrt{s})} \tag{A.21}$$

From Eq. (A.21) we have (for $s = 0$)

$$\phi(0) = \frac{(\delta)(0)0}{r(0-0)} = \frac{0}{0} \tag{A.22}$$

After applying L' Hospital's rule to Eq. (A.21) two times and simplifying

$$\phi(s) = \delta\frac{3\cosh(\sqrt{s}x) + x\sqrt{s}\sinh(\sqrt{s}x)}{\cosh\sqrt{s}} \tag{A.23}$$

Substituting $s = 0$ and simplifying we get

$$\phi(0) = 3\delta \tag{A.24}$$

Similarly from Eq. (A.21) we get

$$\phi'(s) = \frac{\delta}{2}\frac{2\sqrt{s}\sinh(\sqrt{s}x)\cosh(\sqrt{s}) - (s+2)\sinh(\sqrt{s}x)\sinh(\sqrt{s}) + xs\cosh(\sqrt{s}x)\cosh(\sqrt{s}) - x\sqrt{s}\cosh(\sqrt{s}x)\sinh(\sqrt{s})}{s\cosh^2(\sqrt{s}) - 2\sqrt{s}\cosh(\sqrt{s})\sinh(\sqrt{s}) + \sinh^2(\sqrt{s})} \tag{A.25}$$

As seen for this case, inversion to the time domain is cumbersome even for simple eigenvalues of $\lambda_n = n\pi$. Evaluation of the residues at $s = 0$ involved using L' Hospital's rule thrice even for this simple case.

A.1. Spherical electrode particle

As before, applying the Laplace transform (in the time variable) to Eq. (26) and solving with the boundary conditions (27) and (28) we get

$$c(s) = \frac{1}{r}\frac{\delta\sinh(\sqrt{s}r)}{s(\sqrt{s}\cosh\sqrt{s} - \sinh(\sqrt{s}))} = \frac{P(s)}{Q(s)} \tag{A.19}$$

which for $s = 0$ yields

$$\phi'(0) = \frac{0}{0} \tag{A.26}$$

After applying L' Hospital's rule six times we get

$$\phi'(0) = -\tfrac{3}{10}\delta + \tfrac{1}{2}\delta r^2 \tag{A.27}$$

When we go from rectangular to spherical coordinates even for finding the residue at the origin, we need to L' Hospital's rule twice the number of times. Next, by using the Heaviside expansion theorem for no repeated roots (Eq. (8.3.22) of [6]), the solution in the time domain is given by

$$c(x,t) = 3\delta t - \frac{3\delta}{10} + \frac{\delta}{2}r^2 + \sum_{n=1}^{\infty}\exp(-\lambda_n^2 t)\varphi(\lambda_n) \tag{A.28}$$

where λ_n is given by $\tan(\lambda_n) = \lambda_n$ and

$$\varphi(\lambda_n) = (s - \lambda_n)f(s) = \frac{P(s = -\lambda_n^2)}{Q'(s = -\lambda_n^2)} = \frac{1}{r}\frac{2\delta \sin(\lambda_n r)}{\lambda_n^2 \sin(\lambda_n)} \tag{A.29}$$

Hence, the complete solution is

$$c = \delta\left[3t + \frac{1}{10}(5r^2 - 3) - 2\frac{1}{r}\sum_{n=1}^{\infty}\frac{\sin(\lambda_n r)}{\lambda_n^2 \sin(\lambda_n)}\exp(-\lambda_n^2 t)\right] \tag{A.30}$$

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