

Formulation for the Prediction of Ionic Concentration Profile in an Electrochemical System

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ARTICLE INFO	ABSTRACT
Published Online: 15 October 2025	An analytical expression to predict the transient concentration profile of a charge-transporting cation in the electrolyte in the vicinity of the cathode electrode of an electrochemical cell is presented in this relatively short paper. To illustrate the application of the developed formulation, the computed data are presented in the form of the Z versus Y plots for four effective diffusivity values of the cation and noting the involvement of the $Z(y)$ -function in the prediction of the cation transient concentration profile.
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KEYWORDS: diffusion, ionic, electrochemical, transient, concentration	

I. INTRODUCTION

We, at the University of Dayton, have been involved in the development of electrochemical systems, i.e. fuel cells and batteries since 1996 [1-12] to deliver electric power more efficiently and safely for space and terrestrial applications. In this pursuit, very recently, it was decided to develop the formulation to predict the transient ionic concentration profiles in the electrolyte between the electrodes of an electrochemical cell.

Electrochemical systems use an electrolyte in the liquid or solid phase. When an electrochemical cell operation is initiated to deliver electric power to an external electric load at a fixed current level, the cell usually undergoes through transient behavior. That is, the ionic species local (spatial) concentrations change.

Figure 1 shows the simple sketch of an electrochemical system used in the development of the formulation presented in Section 2.

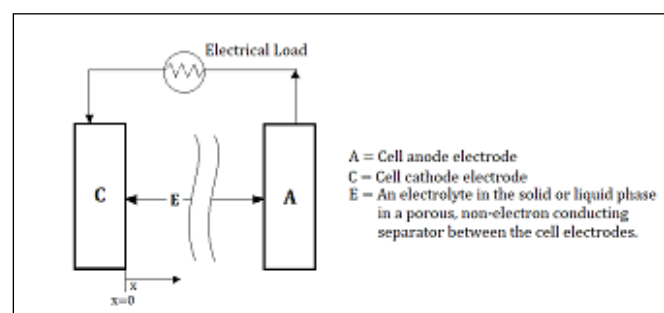


Figure 1: Simple sketch of an electrochemical system.

II. FORMULATION

It is, here, assumed that metallic ions, (e.g., or ions) are generated at the plane surface of the cell anode in contact with the electrolyte during its discharge to provide electric power to an external load. The partial differential equation [13] describing the transport of an ionic species via diffusion is:

$$\frac{\partial c}{\partial t} = D_{diff} \frac{\partial^2 c}{\partial x^2} \quad (1)$$

where $c [=]$ ($mol\ cm^3$) is the molar concentration of an ionic species, M^{n+} , in the cell electrolyte separator between the electrodes, $D_{diff} [=]$ ($cm^2\ s^{-1}$) is the ion effective diffusivity which is conventionally taken to be equal to the product of the ion diffusivity in the electrolyte and the separator volume void fraction divided by the tortuosity factor to account for the zig-zag path along which an ion migrates, and $x [=]$ (cm) is the spatial coordinate as shown in the sketch, and $t [=]$ (s) is time.

To solve the partial differential equation (1), the following initial and boundary conditions have been used:

$$I.C. \quad t \leq 0 \quad c = c_{ini} = c_{\infty} \quad \text{for } 0 < x \leq \infty \quad (2)$$

$$B.C. 1 \quad \text{at } y = 0 \quad \frac{\partial c}{\partial x} = \frac{i}{nFD_{diff}} \quad \text{for all } t > 0 \quad (3)$$

$$B.C. 2 \quad \text{at } x \rightarrow \infty \quad c = c_{\infty} \quad \text{for all } t > 0 \quad (4)$$

where $i [=]$ ($A \cdot cm_{geom}^{-2}$) is the cell geometric current density, F is the Faraday's constant = 96487 Coulombs of charge per g-equivalent, n is the oxidation state number of a cation (e.g., $n = 1$ for Na^+ ions, $n = 2$ for Cu^{2+} ions).

The analytical solution of the P.D.E., Equation (1), is obtained using the Laplace transform method as follows:

taking the Laplace transform of the P.D.E., Equation (1) and the conditions, Equation (2) through (4):

$$L\left(\frac{\partial c}{\partial t}\right) = D_{diff} L\left(\frac{\partial^2 c}{\partial x^2}\right) = D_{diff} \frac{\partial^2}{\partial x^2} (L(c)) \quad (5)$$

$$sL(c(t, x)) - c(at t = 0, x) = D_{diff} \frac{d^2 \bar{c}}{dx^2} \quad (6)$$

with D_{diff} assumed to be constant.

$$s\bar{c} - c_{ini} = D_{diff} \frac{d^2 \bar{c}}{dx^2} \quad (7)$$

where $\bar{c} = \bar{c}(s, x)$, $s =$ the Laplace parameter [=] (sec^{-1}).

Rewriting Equation (7) as:

$$\frac{d^2 \bar{c}}{dx^2} + \left(\frac{-s}{D_{diff}}\right) \bar{c} = \left(\frac{-c_{ini}}{D_{diff}}\right) \quad (8)$$

The Laplace transform of the boundary conditions, Equations (3) and (4) become, respectively:

$$t > 0, \text{ at } x = 0; \frac{d\bar{c}}{dx} = \left(\frac{i}{nFD_{diff}}\right) \left(\frac{1}{s}\right) \quad (9)$$

$$t > 0, \text{ at } x \rightarrow \infty; \bar{c} = \left(\frac{c_{\infty}}{s}\right) \quad (10)$$

The linear differential Equation (8) has been solved using the methods provided in Chapter 3 of reference [14]. The resultant solution is:

$$\bar{c}(s, x) = \frac{c_{ini}}{s} - \left(\frac{i}{nF\sqrt{D_{diff}}}\right) \left[\frac{e^{-\left(\sqrt{\frac{s}{D_{diff}}}\right)x}}{\frac{3}{s^2}} \right] \quad (11)$$

Using the information on the inverse Laplace transforms of the functions [15, 16]

$$L^{-1}\left(\bar{c}(s, x)\right) = L^{-1}\left(\frac{c_{ini}}{s}\right) - L^{-1}\left\{\left(\frac{i}{nF\sqrt{D_{diff}}}\right) \left[\frac{e^{-\left(\sqrt{\frac{s}{D_{diff}}}\right)x}}{\frac{3}{s^2}} \right]\right\} \quad (12)$$

$$c(t, x) = c_{ini} L^{-1}\left(\frac{1}{s}\right) - \left(\frac{i}{nF\sqrt{D_{diff}}}\right) L^{-1}\left[\frac{-\left(\sqrt{\frac{s}{D_{diff}}}\right)x}{\frac{3}{s^2}}\right] \quad (13)$$

$$c(t, x) = c_{ini} - \left(\frac{i}{nF\sqrt{D_{diff}}}\right) \times \left[2\sqrt{\frac{t}{\pi}} \exp\left(\frac{-x^2}{4tD_{diff}}\right) - \frac{x}{\sqrt{D_{diff}}} \operatorname{erfc}\left(\frac{x}{2\sqrt{tD_{diff}}}\right) \right] \quad (14)$$

Or:

$$\left(\frac{c(t, x)}{c_{ini}}\right) = 1 - \left(\frac{i}{nFc_{ini}\sqrt{D_{diff}}}\right) \times \left[2\sqrt{\frac{t}{\pi}} \exp\left(\frac{-x^2}{4tD_{diff}}\right) - \frac{x}{\sqrt{D_{diff}}} \operatorname{erfc}\left(\frac{x}{2\sqrt{tD_{diff}}}\right) \right] \quad (15)$$

Equation (15) can also be expressed as:

$$\left(\frac{c(t, x)}{c_{ini}}\right) = 1 - \left(\frac{i}{nFc_{ini}}\right) \times \left[\frac{2}{\sqrt{\pi}} \sqrt{\frac{t}{D_{diff}}} \exp\left(\frac{-x^2}{4tD_{diff}}\right) - \frac{x}{D_{diff}} \operatorname{erfc}(y) \right] \quad (16)$$

where y is a dimensionless quantity defined as:

$$y = \left(\frac{x}{2\sqrt{tD_{diff}}}\right) \quad (17)$$

Furthermore,

$$\left(\frac{c(t, x)}{c_{ini}}\right) = 1 - \left(\frac{i}{nFc_{ini}}\right) Z \quad (18)$$

where, $Z [=] (s \text{ cm}^{-1})$ is a function of y and is defined below:

$$Z(y) = \underbrace{1.1284 \sqrt{\frac{t}{D_{diff}}} \exp\left(\frac{-x^2}{4tD_{diff}}\right)}_I - \underbrace{\frac{x}{D_{diff}} \operatorname{erfc}(y)}_{II} \quad (19)$$

Further rearrangement of the terms in Equation (18) leads to:

$$\left[(nF) \left(\frac{c_{ini} - c(t, x)}{i} \right) \right] = \left[nF \left(\frac{c_{\infty} - c(t, x)}{i} \right) \right] = Z \quad (20)$$

At any cell operational time $t(s)$, Z can be calculated as a function of x or y . This way a Z vs. x or y profile becomes available at a time. Such profiles have been determined for some selected cell operational times for the same ion diffusivity values. By the utilization of Equation (19), (Z vs. y) data have been computed for some typical ion diffusivity values for an ion, Na^+ , migration through an electrolyte-containing separator between the cell electrodes. Once the

function, $Z(x,t)$ or $Z(y)$ for a given effective diffusivity is known, it is quite apparent from Equation (20) that $(c_{\infty} - c(t,x))$ can be determined for an ion with its charge number (e.g. Na^+ , $n=1$) for an electrode (or cell) current density of i , $A \cdot cm^{-2}$. With known c_{∞} value, then $c(t,x)$ can be computed; thus, $c(t,x)$ vs. x or y profile can be determined for a known or fixed value of the effective diffusivity of a cation in a solid or liquid electrolyte. Also, by the application of Equation (18), the dimensionless concentration $\left(\frac{c(t,x)}{c_{ini}}\right) = \left(\frac{c(y)}{c_{ini}}\right)$ can be calculated at a desired $y\left(= \frac{x}{2\sqrt{tD_{diff}}}\right)$ value.

III. DISCUSSION OF THE CALCULATED DATA

Figures 2 through 5 show the plots of the function, $Z(y)$ vs. y , for four values of the effective diffusivity, $D_{diff} = 10^{-6}, 10^{-8}, 10^{-10}, 10^{-12} (cm^2 \cdot s^{-1})$. For each diffusivity, the plots of Z vs. y are presented for three times of 4, 100 and 900 seconds as an illustration for the effect of a time period on the profile of Z vs. y . The nature of the function Z vs. y plot for each diffusivity values is the same for the same time period except an increase in the value of Z by a factor of ten as the diffusivity changes from $10^{-6}, 10^{-8}, 10^{-10}, 10^{-12} (cm^2 \cdot s^{-1})$. The function Z decreases

as $y\left(= \frac{x}{2\sqrt{tD_{diff}}}\right)$ increases with an increase in the distance x (cm) for a fixed diffusivity value. It is so due to the terms I & II in Equation (19) approaching towards each other in their respective magnitudes with an increase in the distance x measured from the cell cathode-electrode, C, in the cell electrolyte in accordance with the initial and boundary conditions, Equations (2), (3), and (4). For the prediction of the dimensionless concentration profile of a cationic species near the cathode of an electrochemical cell, it is necessary to recognize that the values of the parameters, geometric current density, i ; the charge number, n , on a cationic species being transported in the electrolyte separator; and the initial concentration, c_{ini} , of the cationic species be such that the value of the lumped parameter (i / nFc_{ini}) when multiplied with Z value at an x or y value is less than or equal to one.

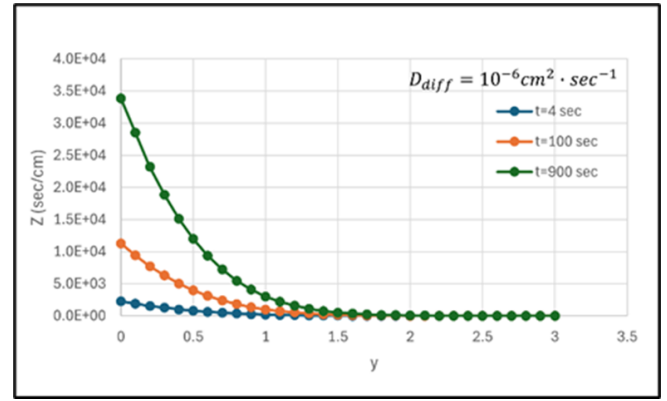


Figure 2: Plot of Z vs. y for $D_{diff} = 10^{-6} cm^2 sec^{-1}$

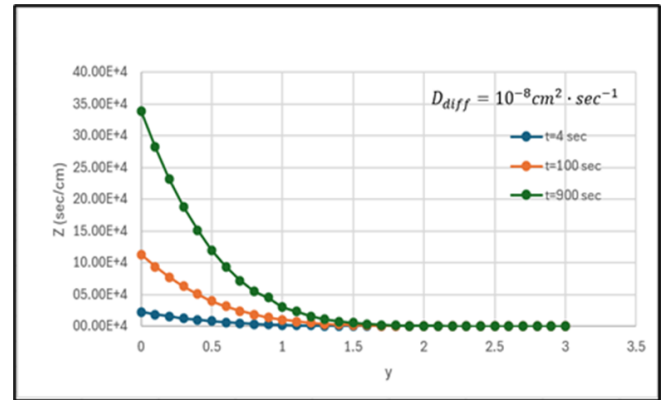


Figure 3: Plot of Z vs. y for $D_{diff} = 10^{-8} cm^2 sec^{-1}$

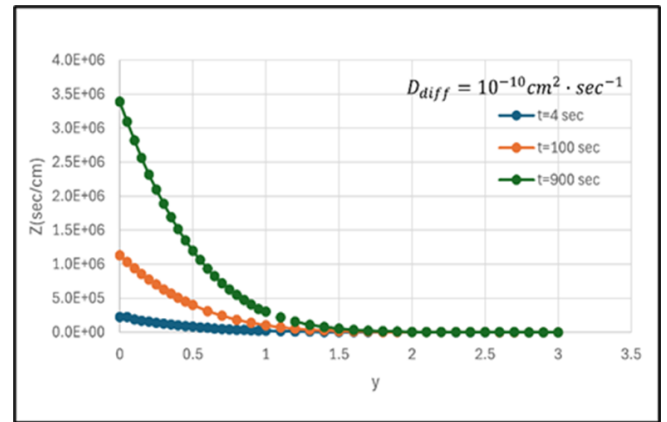


Figure 4: Plot of Z vs. y for $D_{diff} = 10^{-10} cm^2 sec^{-1}$

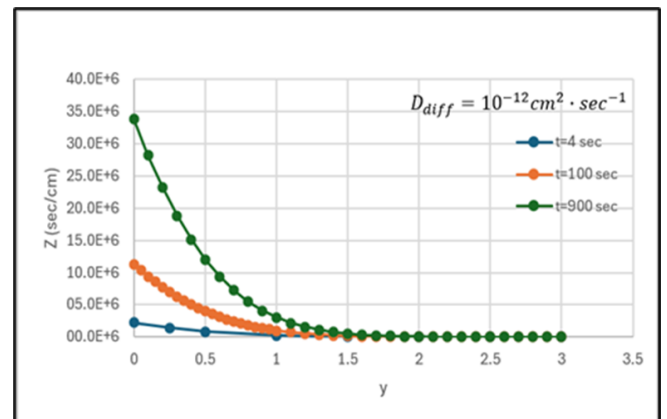


Figure 5: Plot of Z vs. y for $D_{diff} = 10^{-12} cm^2 sec^{-1}$

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Figures 6 and 7 are the plots of the dimensionless Na^+ ion concentration versus the dimensionless distance y ($= \frac{x}{2\sqrt{tD_{diff}}}$), representing the application of the developed formulation, as an illustration, to predict the concentration profile of a charge transporting ionic species in the electrolyte in the neighborhood of the cathode electrode of an electrochemical cell. The nature of these profiles are dependent on the product of the value of the group $\left(\frac{i}{nFc_{ini}}\right)$ and the value of the function, $Z(y)$, at each value of y . These plots (Figures 6 & 7) are for the same diffusivity and the cell operational time of 4 second for two geometric current densities of 10 and 300 mA/cm^2 , respectively. Notice the two $\left(\frac{c(t,x)}{c_{ini}}\right)$ vs. y profiles approaching towards one with an increase in distance away from $y = 0.0$ plane.

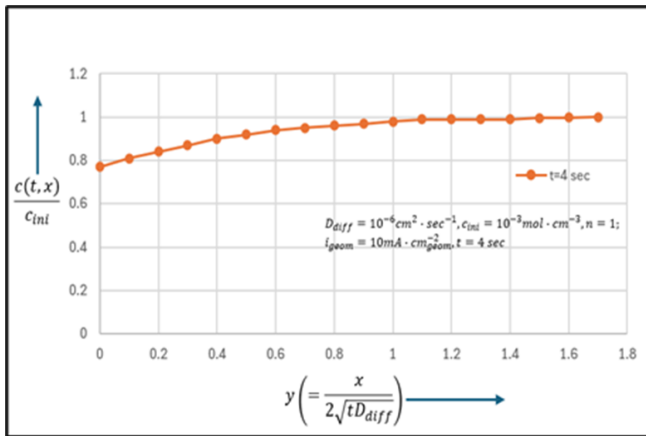


Figure 6: Plot of $\left[\frac{c(t,x)}{c_{ini}} = \frac{c(y)}{c_{ini}}\right]$ vs. y for $i = 10 \text{ mA} \cdot \text{cm}^{-2}$

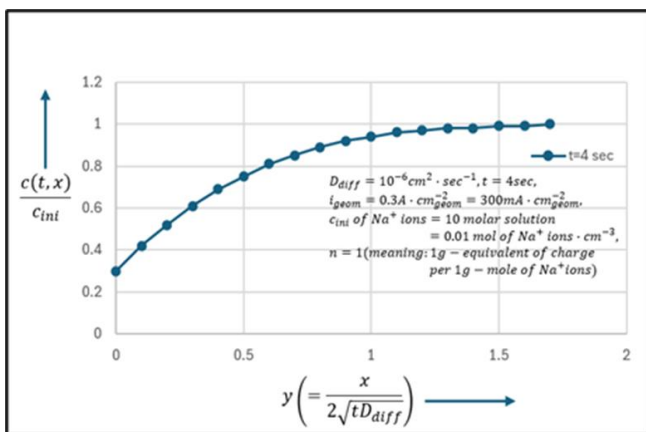


Figure 7: Plot of $\left(\frac{c(t,x)}{c_{ini}}\right)$ vs. $y \left(= \frac{x}{2\sqrt{tD_{diff}}}\right)$ for $i = 300 \text{ mA} \cdot \text{cm}^{-2}$

The computed data presented here in the form of plots for some typical diffusivity values are for the illustration of the application of the developed formulation. An individual

interested in the prediction of $\left[Z(y) \text{ or } \left(\frac{c(t,x)}{c_{ini}}\right) \text{ vs. } y\right]$ plot

to gain insight of the concentration profile of a charge transporting cation near the cell cathode at any other diffusivity can use equations (18) and (19).

IV. CONCLUDING REMARKS

To predict the transient concentration profile of a cation in the electrolyte near the cathode of an electrochemical cell (a fuel cell or battery) used for delivery of electric power to an external load, the partial differential equation (1) was solved using the Laplace transform method with the initial and boundary conditions, equations (2), (3), and (4). The solution for the cation concentration profile in the dimensionless form is given by Equation (18).

For a known value of the diffusivity of the charge-transporting cation in the cell electrolyte at any cell operational time, the function, $Z\left(y = \frac{x}{2\sqrt{tD_{diff}}}\right)$ can be

calculated and hence, the dimensionless concentration profile can be calculated from Equation (18) for a value of the lumped

parameter group, $\left(\frac{i}{nFc_{ini}}\right)$. One should be prudent to

recognize that the product of this group value and the function $Z(y)$ value must be less than one for the prediction of the cation dimensionless concentration profile. This implies that for known value of $(n \text{ and } c_{ini})$, the cell operational geometric current density, i , should be such that the above-mentioned condition is always satisfied.

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