



A semianalytical method for simulating mass transport at channel electrodes



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ABSTRACT

A method for simulating electrode reactions in channel flow is developed and efficiently implemented in the symbolic algebra program Maple™. The steady-state convective diffusion equation for fully developed 2-D laminar (Poiseuille) flow past one or more electrodes in a channel is considered for a charge-transfer electrode reaction between two soluble species. The case where axial diffusion (along the channel, x direction) is neglected and the diffusivities are equal has an exact solution as an infinite series, in which each term is the product of an exponential in x and a confluent hypergeometric function in y (across the channel). The practical implementation consists of evaluating a finite number of terms and numerically evaluating the two parameters in each term. Sturm–Liouville (eigenfunction) theory is used to reliably find the parameters for arbitrary values of the rate constants. Comparison is made with results from a commercial software package that uses a finite-element method.

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0. Introduction

Electrochemical detection is well suited to microfluidic devices [1,2], and the ready availability of new microfluidic fabrication methods has led to renewed interest in channel electrodes [3], with a consequent need for efficient computational methods. We report here an eigenfunction series method for channel electrodes that may be efficiently implemented by a symbolic algebra program. The application of eigenfunction methods for the solution of convective diffusion equations relevant to electrochemistry has a long history. The solution to the Graetz problem, which solves heat transfer to the walls of a tube with laminar flow, was given as an eigenfunction expansion as early as 1883 [4], and an extensive treatment of the electrochemical version was given by Newman [5]. In the context of mass transport in the rectangular channels that we consider here, Moldoveanu and Anderson solved the limiting current case in terms of a series of parabolic cylinder functions [6]. In these cases, the general case of arbitrary rate constants was not attempted, perhaps because a reliable way of locating the eigenvalues was not available. Recently, Schmachtel and Kontturi used eigenfunction methods to numerically solve chronoamperometry currents at the rotating disk electrode [7]. They considered the case of arbitrary rate constants and also

showed that the case of quasireversible electrode reactions could be solved as easily as the case of irreversible reactions.

Here we apply the eigenfunction expansion method to 2-D steady-state flow past electrodes in a channel, for the case where axial diffusion (along the channel) is neglected. We derive the exact solution to this case as an infinite series. The practical implementation of this as a numerical method in the symbolic algebra language Maple™ is presented and compared with the more conventional finite-element (FE) method, as implemented in Comsol Multiphysics®. It is a mesh-free method and so should give good accuracy at the beginning of the electrode, where there is a step change in boundary conditions and the current density is high. Furthermore, the concentration profile, once determined, can be easily manipulated term by term to find local current densities, average current densities, or collection efficiencies, without significant degradation in accuracy. The accuracy is determined by the number of terms processed, and calculation of additional terms allows the global error to be estimated. An important advantage of the present method is that the whole region above an electrode is solved at one time, so the complexity of the calculation is largely independent of the channel height or width of the electrode.

1. Theory

We consider a solution of the steady-state diffusion–convection problem in a 2-D channel with fully developed laminar (Poiseuille) flow. Key notation is given in Fig. 1 and a full set of symbols are

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given in Supplementary Material, see Appendix B. The electrode reaction between two solution species, Eq. (1), has the current density at a particular location at the electrode given by the usual rate law, Eq. (2). The potential at the electrode is fixed, so the rate constants (m s^{-1}) do not vary over the electrode surface. However, we allow the possibility of many electrodes along the wall of the channel, and the potential and rate constants may be different at each. The convective diffusion equation to be solved for each species is Eq. (3). We make the common assumption that the diffusivities of the two species are equal.



$$j(x) = Fv(x) = Fk_f c_R(x, 0) - Fk_b c_P(x, 0) \quad (2)$$

$$0 = D \frac{\partial^2 c_k(x, y)}{\partial y^2} - \frac{4u_{\max}}{h^2} y(h-y) \frac{\partial c_k(x, y)}{\partial x}, \quad k = \text{R, P} \quad (3)$$

Matching of the fluxes at the electrode surface to the reaction rate leads to the boundary conditions, Eq. (4), at the electrode surface. (The convective flux at the walls is zero, so only the diffusive part needs to be considered.) The flux at insulating sections between electrodes and at the top of the channel is zero, Eqs. (5) and (6). The “initial” condition is that the concentrations take the bulk values at a location x_0 upstream of the first electrode, Eq. (7). In the absence of axial diffusion, the solution only propagates downstream, and there is no loss in taking $x_0 = 0$. The measured current density is given by averaging over the electrode surface, Eq. (8).

$$D(\partial c_R(x, y)/\partial y)_{y=0} = -D(\partial c_P(x, y)/\partial y)_{y=0} = v(x) \quad (4)$$

$$(\partial c_R(x, y)/\partial y)_{y=0} = (\partial c_P(x, y)/\partial y)_{y=0} = 0 \quad (5)$$

$$(\partial c_R(x, y)/\partial y)_{y=h} = (\partial c_P(x, y)/\partial y)_{y=h} = 0 \quad (6)$$

$$c_k(x_0, y) = c_k^b, \quad k = \text{R, P} \quad (7)$$

$$j_{\text{ave}} = (FD/w) \int_0^w (\partial c_R(x, y)/\partial y)_{y=0} dx \quad (8)$$

As discussed below, the quasireversible solution including the back reaction can be simply derived from the irreversible solution with apparent rate constant $k = k_f + k_b$, so we need only develop a numerical method for the irreversible case. We change to dimensionless variables (see Fig. 1): $Y = y/h$, $X = x/h$, $W = w/h$, $C(X, Y) = c_R(x, y)/c_R^b$, $K = hk_f/D$, $J = (h/c_R^b DF)j$ and $A = 4u_{\max}h/D = 6Pe$ where $Pe = u_{\text{ave}}h/D = 2u_{\max}h/3D$ is a Péclet number for mass transfer. The convective diffusion equation and boundary conditions are now:

$$0 = \frac{\partial^2 C(X, Y)}{\partial Y^2} - AY(1-Y) \frac{\partial C(X, Y)}{\partial X} \quad (9)$$

$$(\partial C(X, Y)/\partial Y)_{Y=0} = KC(X, 0) \text{ (at electrode)} \quad (10)$$

$$(\partial C(X, Y)/\partial Y)_{Y=0} = 0 \text{ (between electrodes)} \quad (11)$$

$$(\partial C(X, Y)/\partial Y)_{Y=1} = 0 \text{ (top of channel)} \quad (12)$$

$$C(0, Y) = 1 \text{ (upstream)} \quad (13)$$

Writing $C(X, Y) = F(X)G(Y)$ and rearranging gives Eq. (14), which shows that the partial differential equation is separable. The general solution, Eq. (15), is a superposition of products of

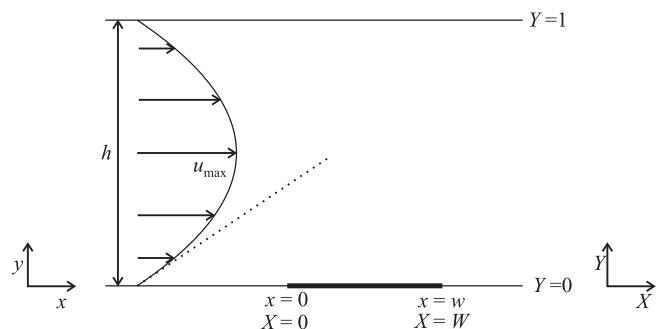


Fig. 1. Notation. Flow is from left to right, with one or more embedded electrodes (bold) in the bottom of the channel. Lower case variables are dimensioned, upper case variables are dimensionless. The dotted line is the velocity profile (extending to infinite height) for the Léveque approximation. The average velocity u_{ave} is $2/3$ of the maximum velocity u_{\max} .

exponential functions of X and functions of Y that satisfy the differential Eq. (16), where the primes indicates differentiation with respect to Y .

$$\frac{1}{Y(1-Y)G(Y)} \frac{d^2 G(Y)}{dY^2} = \frac{A}{F(X)} \frac{dF(X)}{dX} = -b^2 \quad (14)$$

$$C(X, Y) = \sum_{i=1}^{\infty} a_i \exp(-b_i^2 X/A) G_i(Y) \quad (15)$$

$$-G''(Y) = b^2 Y(1-Y)G(Y) \quad (16)$$

Eq. (16) has an operator $-d^2/dY^2$ operating on $G(Y)$ to give a constant b^2 times a weighting function $Y(1-Y)$ times $G(Y)$. According to Sturm–Liouville theory [8], such equations have an infinite set of eigenfunction solutions, $G_i(Y)$, which depend on the boundary conditions at the electrode and top channel surfaces. The eigenvalues are the particular values b_i^2 that give valid solutions. As detailed in Appendix A, we first narrow the solutions to those that satisfy the zero-flux boundary condition at the top of the channel, Eq. (17). This ensures that the concentration, Eq. (15), satisfies the zero-flux condition, Eq. (12). These solutions $G(Y)$, normalized so that $G(1) = 1$, are given in terms of confluent hypergeometric functions in Appendix A.

$$G'(1) = 0 \quad (17)$$

The remaining undetermined constant is b , which is determined by the type of boundary condition at the $Y = 0$ surface, i.e., the electrode surface or an insulating surface between electrodes. Three subcases are considered. The first is the limiting current boundary condition, where the concentration is zero at the electrode surface, Eq. (18). Solving Eq. (18) for b leads to the series of values in Eq. (19).

$$G(0) = 0 \quad (18)$$

$$b_1^{(\infty)} = 3.82, \quad b_2^{(\infty)} = 11.90, \quad b_3^{(\infty)} = 19.92, \dots \quad (19)$$

$$b_i^{(\infty)} \sim \frac{\pi(i - \frac{1}{2})}{\int_0^1 \sqrt{Y(1-Y)} dY} = 8(i - 1/2) \quad (20)$$

$$8(i - 1) < b_i^{(\infty)} < 8(i - 1/2), \quad i = 1, 2, \dots \quad (21)$$

where the superscript ∞ denotes an infinite rate constant ($K = \infty$). Eq. (20) for the eigenvalues¹ is from Sturm–Liouville theory [8], and

¹ We refer to the b_i values as eigenvalues, though strictly these are the square roots of the eigenvalues.

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