Short communication

Analytical solution of the convection-diffusion equation for uniformly accessible rotating disk electrodes via the homotopy perturbation method

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ABSTRACT

The mathematical problem corresponding to a one-electron reversible electron transfer at a rotating disk electrode is solved under transient and steady state conditions by using the homotopy perturbation method. Analytical solutions for the time-dependent and stationary concentration profiles, current response and diffusion layer are deduced for finite values of the Schmidt number. The solutions enable us to obtain the response in chronoamperometry, normal pulse voltammetry and steady state voltammetry. The analytical results are assessed by comparison with previous analytical solutions for limiting cases as well as with numerical simulations, finding a satisfactory agreement.

1. Introduction

Controlled enhancement of the mass transport rate in electrochemical experiments can be achieved by using hydrodynamic methods or microelectrodes. In the former case, mass transport conditions can be varied conveniently to resolve (electro)chemical phenomena of different kinetics: electron transfers, adsorption/desorption processes, coupled chemical reactions, etc. Different hydrodynamic methods have been developed over years (rotating disc/ring, channel, wall-jet and dropping mercury electrodes) and applied to the study of the most frequent reaction mechanisms: EC, EC′, ECE/DISP, etc. [1–9]. The rotating disc electrode (RDE) is still the most popular method [10] to which much theoretical work has been devoted as evidenced in Table S1. This includes both the derivation of analytical solutions and the use of numerical methods (see SI), the present work developing within the former context.

Since Levich's seminal work [11], different analytical solutions for the current response at RDEs have been deduced. For steady state conditions, Levich [11] obtained his well-known expression for the RDE limiting current under the assumption of infinite Schmidt numbers (Sc); this limitation was overcome later by several authors that reported solutions valid for finite Sc-values (Newman [12], Gregory et al. [13], Montella et al. [8], Rajendran et al. [14]). The (semi)analytical theoretical treatment of several reactions mechanisms at an RDE under steady state conditions are also found in the literature: ECE [15], EC_2 [16], DISP [17], … Theoretical works under non-steady state conditions are more scarce, although transient measurements are helpful for

mechanistic deductions and quantitative kinetic studies. Thus, for infinite Sc-values, several expressions for the transient limiting current are available (Bruckenstein [18], Siver [19], Newman [20], Kontturi [5], …).

In this communication analytical expressions for the concentration profiles, diffusion layer and current-potential response of simple electron transfers at RDEs are derived using the homotopy perturbation method (HPM) [21]. The theoretical solutions cover both transient and steady state conditions as well as finite Sc-numbers ($Sc > 100$).

2. Mathematical formulation of the boundary value problem

In general, the convection-diffusion equation can be used to describe the transfer of many physical quantities, such as particles and energy, as long as the transfer occurs only due to two processes: convection and diffusion. The general form of the convection-diffusion equation is

$$\frac{\partial c}{\partial t} = D\nabla^2 c - v . \nabla c \tag{1}$$

where c denotes the concentration of the diffusing species, D is the diffusion coefficient, v is the velocity of the electrolyte and ∇^2 is the Laplacian operator.

For a heterogeneous electron transfer at an RDE,

$$O + e \leftrightarrow R \tag{2}$$

Eq. (1) in one dimensional form can be simplified to [1]

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$$\frac{\partial c_i}{\partial t} + v_z \frac{\partial c_i}{\partial z} = D_i \frac{\partial^2 c_i}{\partial z^2} \qquad (i \equiv O, \ R) \tag{3}$$

where c_i is the concentration profiles of the oxidized and reduced forms and D_i is the corresponding diffusion coefficient and v_z the component of the fluid velocity normal to the RDE surface that can be described by the Cochran series solution of von Kármán equations [1,22,23]

$$v_z = -0.51023 \ v^{-1/2}\Omega^{3/2}z^2 + \frac{1}{3}v^{-1}\Omega^2 z^3 + \dots \tag{4}$$

with v being the kinematic viscosity of the electrolyte, and Ω the angular velocity of the electrode. By considering the first two terms in Eq. (4), an accurate description is achieved for most solvents (Schmidt number ≥ 100 [8,9]) (see below). Thus, taking the first two terms in the Cochran expansion into Eq. (3) yields,

$$\frac{\partial c_i}{\partial t} + \left(-0.51023 v^{-1/2}\Omega^{3/2}z^2 + \frac{1}{3}v^{-1}\Omega^2 z^3\right)\frac{\partial c_i}{\partial z} = D_i \frac{\partial^2 c_i}{\partial z^2} \qquad (i \equiv O, R) \tag{5}$$

subject to the following boundary conditions where it is assumed that only the oxidized species is initially present, the electron transfer is reversible and the diffusion coefficient of the two electroactive species is equal [1]:

$$
\begin{aligned}
&c_O(z,0) = c_b, \qquad c_R(z,0) = 0 \\
&c_O(\infty,t) = c_b, \qquad c_R(\infty,t) = 0 \\
&c_O(0,t) = e^{\eta}c_R(0,t) \\
&D_O\left(\frac{\partial c_O}{\partial z}\right)_{z=0} = -D_R\left(\frac{\partial c_R}{\partial z}\right)_{z=0}
\end{aligned}
\tag{6}
$$

with:

$$\eta = \frac{F}{RT}(E - E^{0'}) \tag{7}$$

where E is the applied potential, $E^{0'}$ the formal potential and F, R and T have their usual meanings [1–3]. Once the above problem is solved and the concentrations profiles are known, the current response ($i(t)$) is calculated from

$$\frac{i(t)}{FA} = -D_O\left(\frac{\partial c_O}{\partial z}\right)_{z=0} \tag{8}$$

Provided that the diffusion coefficients of the two electroactive species are equal ($D_O = D_R = D$), it can be demonstrated that the total concentration of electroactive species remains constant at any time of the experiment and in any region of the solution, that is: $c_O(z,t) + c_R(z,t) = c_b$. Combining this result with the Nernstian condition in Eq. (6), the surface concentrations of the electroactive species are immediately obtained:

$$c_O(0) = \frac{c_b e^{\eta}}{1 + e^{\eta}}, \qquad c_R(0) = \frac{c_b}{1 + e^{\eta}} \tag{9}$$

Note that this also enables us to de-couple the mathematical problems corresponding to species O and R (see below).

To proceed with the resolution of the problem, the following dimensionless parameters are introduced:

$$\tau = (Da^2)^{1/2}t, \qquad \zeta = z\left(\frac{a}{D}\right)^{1/3}, \qquad \theta_i = \frac{c_i}{c_b} \qquad (i \equiv O, R) \tag{10}$$

where $a = 0.51023 v^{-1/2}\Omega^{3/2}$, τ is the dimensionless time, ζ the dimensionless distance and θ_i the dimensionless concentration of the electroactive species i. Taking into account the definitions in Eq. (10), now Eq. (5) becomes into:

$$\frac{\partial \theta_i(\zeta,\tau)}{\partial \tau} = (\zeta^2 - k\zeta^3)\left(\frac{\partial \theta_i(\zeta,\tau)}{\partial \zeta}\right) + \frac{\partial^2 \theta_i(\zeta,\tau)}{\partial \zeta^2} \qquad (i \equiv O, R) \tag{11}$$

and the initial and boundary condition into:

$$
\begin{aligned}
&\theta_O(z,0) = 1, \qquad \theta_R(z,0) = 0 \\
&\theta_O(\infty,t) = 1, \qquad \theta_R(\infty,t) = 0 \\
&\theta_O(0) = \frac{e^{\eta}}{1 + e^{\eta}}, \qquad \theta_R(0) = \frac{1}{1 + e^{\eta}}
\end{aligned}
\tag{12}
$$

where k is a function of the Schmidt number (Sc) defined as:

$$k = 0.8175 \times Sc^{-1/3} = 0.8175 \times \left(\frac{v}{D}\right)^{-1/3} \tag{13}$$

Given that typical Sc values are larger than 100, then typical k-values are below 0.18.

The dimensionless current is given by:

$$\psi(\tau) = \frac{i(\tau)}{nFAc_b D^{2/3}a^{1/3}} = -\left(\frac{\partial \theta_O}{\partial \zeta}\right)_{\zeta=0} \tag{14}$$

and the dimensionless thickness of the linear 'diffusion' layer by:

$$\delta\left(,\frac{a}{D}\right)^{1/3} = \frac{\theta_O(\zeta \to \infty, \tau) - \theta_O(\zeta \to 0, \tau)}{(\partial \theta_O/\partial \zeta)_{\zeta=0}} \tag{15}$$

2.1. Analytical expressions for the transient concentration profile and the current response using the homotopy perturbation method (HPM)

The homotopy perturbation method (HPM) has been proven very powerful in a variety of problems in physics and engineering [24–26]. This method is a combination of homotopy in topology and perturbation techniques in functional analysis and in a new approach of the HPM [27] only a few iterations are needed to find an asymptotic solution.

The problem given by Eqs. (11)–(12) is solved using the HPM (details given in the Appendix) for the application of a potential pulse under limiting current conditions (i.e., $E < \ < E^{0'}$ so that $\theta_O(0) = 0$). The following analytical expression for the dimensionless concentration profile of the oxidized species is obtained:

$$
\begin{aligned}
\theta_O(\zeta,\tau) = {} & erf\left(\frac{\zeta}{2\sqrt{\tau}}\right) + erfc\left(\frac{\zeta}{2\sqrt{\tau}}\right)\left(\frac{\zeta^3}{24} + \frac{\tau\zeta}{4}\right) \\
& + \frac{e^{(-\zeta^2/4\tau)}\sqrt{\tau}}{\sqrt{\pi}}\left(\frac{\zeta^2}{4} - \frac{k\zeta^3}{4} - \frac{k\tau\zeta}{2}\right) + \theta_2(\zeta,\tau)
\end{aligned}
\tag{16}
$$

where $\theta_2(\zeta,\tau)$ is the term obtained in the third iteration (given in SI3). Note that the concentration profile of the reduced species can be immediately calculated from Eq. (16) taking into account that: $\theta_O(\zeta,\tau) + \theta_R(\zeta,\tau) = 1$.

From Eqs. (14) and (16), the following expression for the transient current response under limiting current conditions ($\psi_{\lim}$) is deduced:

$$
\begin{aligned}
\psi_{\lim}(\tau) = {} & \frac{1}{\sqrt{\pi\tau}} + \frac{1}{4}\tau - \frac{k\tau^{3/2}}{2\sqrt{\pi}} + \frac{0.016666}{\sqrt{\pi}}\tau^{5/2} - \frac{0.09375}{6}k\tau^3 \\
& + \frac{1}{\sqrt{\pi}}0.0107142 \ k^2 \ \tau^{7/2}
\end{aligned}
\tag{17}
$$

that reduces to the Cottrell equation in the limit $\tau \to 0$ (i.e., $t \to 0$ and/or $\Omega \to 0$): $\psi_{\lim}(\tau) = \frac{1}{\sqrt{\pi\tau}}$. Also, the thickness of the linear 'diffusion' layer can be calculated from Eq. (17) as follows:

$$\delta\left(,\frac{a}{D}\right)^{1/3} = \frac{\theta_O(\zeta \to \infty, \tau) - \theta_O(\zeta \to 0, \tau)}{(\partial \theta_O/\partial \zeta)_{\zeta=0}} = [\psi_{\lim}(t)]^{-1} \tag{18}$$

When the diffusion coefficients of the electroactive species are equal and there are no chemical or electrochemical kinetic limitations, the current response of any electron transfer mechanism upon the application of a potential pulse only differs from the limiting current value by a potential-dependent factor, the form of which depends on the reaction scheme. In the case of one-electron transfers, this factor is $\frac{1}{1 + e^{\eta}}$