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The wall-jet electrode

Potential step chronoamperometry

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Abstract

A theory is presented which describes the transient current response to a potential step at a wall-jet electrode, thus defining the "response time" of the electrode. Results are given in the form of a normalized transient as a function of a dimensionless time parameter which permits the analysis of experimental data for electrodes of any geometry and for any solution flow rate.

INTRODUCTION

The wall-jet electrode (WJE) is a well-characterized hydrodynamic electrode in which the flow is due to a (submerged) fluid jet which strikes a planar electrode at right-angles and spreads out radially over that surface; the fluid outside the jet is at rest [1]. The mass transport experienced by the electrode depends on its size relative to the impinging jet. The term "wall-jet electrode" is understood by the electrochemical community to imply the case where the electrode is substantially larger than the jet [1–6], whereas the other extreme, in which the relatively tiny electrode is within a stagnant flow region, constitutes a "wall-tube electrode" [7]. The term "impinging jet" has appeared occasionally in engineering parlance usually, but not always [8], as a substitute expression for "wall-tube" [9,10]. This paper is concerned with the wall-jet electrode as electrochemically defined, and the mass transport characteristics of this system are outlined below [1–6]. The extent to which practical electrodes may approximate these characteristics is, of course, a matter for experimental investigation and this point will be discussed at the end of this paper.

WJEs are finding increasing use in analysis (e.g. ref. 11), primarily because of the advantages of on-line detection and fast sample throughput. Moreover, in the context of the mechanistic investigation of electrode processes the wall-jet geometry has been shown to possess considerable advantages most notably because of its highly non-uniform primary current distribution [12]. Further merits arise first from the flow-through nature of the device which means that fresh concentrations of reagents are supplied, and products swept to waste, so that build-up of intermediates and products of the electrode reaction which might alter the course of the electrode process is prevented, and second from the high sensitivity of the WJE (compared with, say, the rotating-disc electrode) to variations in the rate of mass transport.

In this paper we consider the current transient resulting from a potential step at the WJE at hydrodynamic equilibrium under laminar flow conditions. The problem is of interest since it defines the "response time" of the electrode and, additionally, such measurements can be used to determine diffusion coefficients (independently, if necessary, of knowledge of the concentration of the electroactive species or of the number of electrons transferred in the heterogeneous redox process). Moreover, current transient measurements can be used advantageously in mechanistic work, for example where adsorption or film formation interferes with the interpretation of steady-state limiting currents. We are unaware of any previously reported theory, other than empirical, for time-dependent processes at WJEs.

THEORY

We consider the following electrode reaction:

$$\mathrm{A} \pm \mathrm{e}^- \rightarrow \mathrm{B}$$

and assume only A to be present in bulk solution. The convective diffusion equation describing the concentration of A in time t and space is

$$\frac{\partial[A]}{\partial t} = D\frac{\partial^2[A]}{\partial z^2} - \nu_r\frac{\partial[A]}{\partial r} - \nu_z\frac{\partial[A]}{\partial z} \tag{1}$$

where D is the diffusion coefficient of A, ν_r is the radial solution velocity (r direction) and ν_z is the velocity in the direction normal to the electrode surface (z direction). Expressions for ν_r and ν_z under laminar flow are given in ref. 12. It should be noted that in writing eqn. (1) radial diffusion has been neglected; the basis of this approximation has been developed elsewhere [13]. We also assume the presence of sufficient supporting electrolyte to ensure that migration effects are negligible.

If the electrode potential is stepped from a value at which no current flows to one corresponding to the transport-limited conversion of A to B then the relevant boundary conditions to the defined problem can be formulated as

$$t < 0 \qquad \text{all space} \qquad [\mathrm{A}] = [\mathrm{A}]_{\text{bulk}} \tag{2}$$

$$t \geq 0 \qquad z = 0,\ r \leq R, \qquad [\mathrm{A}] = 0 \tag{3}$$

$$t \geq 0 \qquad z \to \infty, \qquad [\mathrm{A}] \to [\mathrm{A}]_{\text{bulk}} \tag{4}$$

where $[\mathrm{A}]_{\text{bulk}}$ is the bulk concentration of A and R is the radius of the electrode.

In order to solve eqn. (1) we approximate the derivatives by their finite-difference equivalents. The r–z plane is thus divided up into a two-dimensional grid such that increments in the r direction are Δr and in the z direction Δz. We use the subscripts k and j to denote distances in the radial and normal directions:

$$(\text{radial distance})_k = k\Delta r \tag{5}$$

$$k = 0, 1, 2, \ldots, K \text{ where } \Delta r = R/K \tag{6}$$

$$(\text{normal distance})_j = j\Delta z \tag{7}$$

$$j = 0, 1, 2, \ldots, J \text{ where } \Delta z = Z/J \tag{8}$$

and Z is the length of the grid in the z direction [12]. Then the notation ${}^{t}a_{j,k}$ indicates the concentration of A at the point (j, k) at the instant $t\Delta t$ where Δt is a selected increment of real time (say, for example, 0.1 ms).

The finite-difference form of eqn. (1) is

$$\begin{aligned} &{}^{t+1}a_{j,k} - {}^{t}a_{j,k} \\ &\quad = \lambda^{y}\left\{{}^{t+1}a_{j+1,k} - 2\,{}^{t+1}a_{j,k} + {}^{t+1}a_{j-1,k}\right\} - \lambda_j^{\nu_r}\left\{{}^{t+1}a_{j,k} - {}^{t+1}a_{j,k'-1}\right\} \\ &\qquad - \lambda_j^{\nu_z}\left\{{}^{t+1}a_{j+1,k} - {}^{t+1}a_{j,k}\right\} \end{aligned} \tag{9}$$

where

$$\lambda^{y} = \frac{D\Delta t}{(\Delta z)^2} \tag{10}$$

$$\lambda_j^{\nu_r} = \frac{\nu_r(j+1,\ k)\Delta t}{\Delta r} \tag{11}$$

$$\lambda_j^{\nu_z} = \frac{\nu_z(j+1,\ k)\Delta t}{\Delta z} \tag{12}$$

and $\nu_r(j,\ k)$ and $\nu_z(j,\ k)$ are the solution velocity components at $(j,\ k)$. Rearrangement of eqn. (9) leads to the following general equation used as the basis for the ensuing (implicit) calculations:

$$\begin{aligned} &\left\{{}^{t}a_{j,k}\right\} + \lambda_j^{\nu_r}\left\{{}^{t+1}a_{j,k-1}\right\} \\ &\quad = -\lambda^{y}\left\{{}^{t+1}a_{j-1,k}\right\} + \left(\lambda_j^{\nu_r} - \lambda_j^{\nu_z} + 2\lambda^{y} + 1\right)\left\{{}^{t+1}a_{j,k}\right\} - \left(\lambda^{y} - \lambda_j^{\nu_z}\right)\left\{{}^{t+1}a_{j+1,k}\right\} \end{aligned} \tag{13}$$

Application of boundary condition (3) leads to

$$\left\{{}^{t}a_{1,k}\right\} + \lambda_1^{\nu_r}\left\{{}^{t+1}a_{1,k-1}\right\}$$
$$= \left(\lambda_1^{\nu_r} - \lambda_1^{\nu_z} + 2\lambda^y + 1\right)\left\{{}^{t+1}a_{1,k}\right\} - \left(\lambda^y - \lambda_1^{\nu_z}\right)\left\{{}^{t+1}a_{2,k}\right\} \qquad (14)$$

and condition (4) leads to

$$\left\{{}^{t}a_{J-1,k}\right\} + \lambda_{J-1}^{\nu_r}\left\{{}^{t+1}a_{J-1,k-1}\right\}$$
$$= -\lambda^y\left\{{}^{t+1}a_{J-2,k}\right\} + \left(\lambda_{J-1}^{\nu_r} - \lambda_{J-1}^{\nu_z} + 2\lambda^y + 1\right)\left\{{}^{t+1}a_{J-1,k}\right\} - \left(\lambda^y - \lambda_{J-1}^{\nu_z}\right) \qquad (15)$$

These $(J-1)\times(J-1)$ simultaneous equations can be expressed as a $(J-1)\times(J-1)$ matrix equation

$$\{d\} = [T]\{u\} \qquad (16)$$

where

$$\begin{bmatrix} d_1 \\ d_2 \\ \cdot \\ \cdot \\ d_j \\ \cdot \\ \cdot \\ d_{J-2} \\ d_{J-1} \end{bmatrix} = \begin{bmatrix} b_1 & c_1 & 0 & & & & & & \\ a_2 & b_2 & c_2 & 0 & & & & & \\ & \cdot & \cdot & \cdot & & & & & \\ & & \cdot & \cdot & \cdot & & & & \\ & & 0 & a_j & b_j & c_j & 0 & & \\ & & & & \cdot & \cdot & \cdot & & \\ & & & & & \cdot & \cdot & \cdot & \\ & & & & & & a_{J-2} & b_{J-2} & c_{J-2} \\ & & & & & & 0 & a_{J-1} & b_{J-1} \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ \cdot \\ \cdot \\ u_j \\ \cdot \\ \cdot \\ u_{J-2} \\ u_{J-1} \end{bmatrix}$$

The matrix elements are given by

$$d_j = \left\{{}^{t}a_{j,k}\right\} + \lambda_j^{\nu_r}\left\{{}^{t+1}a_{j,k-1}\right\} \qquad (17)$$

$$d_{J-1} = \left\{{}^{t}a_{J-1,k}\right\} + \lambda_{J-1}^{\nu_r}\left\{{}^{t+1}a_{J-1,k-1}\right\} + \left(\lambda^y - \lambda_{J-1}^{\nu_z}\right) \qquad (18)$$

$$a = -\lambda^y \qquad (19)$$

$$b_j = 2\lambda^y + \lambda_j^{\nu_r} - \lambda_j^{\nu_z} + 1 \qquad (20)$$

$$c_j = -\left(\lambda^y - \lambda_j^{\nu_z}\right) \qquad (21)$$

Equation (16) is analogous to that arising in the procedure we have previously described [12] for the solution of steady-state problems at the WJE, and we have adopted the same notation here as in that paper. The method of solution below follows the general strategy developed in ref. 12. A brief summary is given in the next paragraph.

It should be noted that the matrix equation (eqn. 16) shows how the concentrations throughout the cell at time $(t+1)\Delta t$ can be calculated if we know those at time $t\Delta t$. To do this we have to find the set of vectors $\{u\}$: each k value has its own vector $\{u\}_k$. Since the matrix $[T]$ is of tridiagonal form, we can use the Thomas algorithm [12,14] to give $\{u\}_k$ from $\{d\}_k$. Boundary condition (2) supplies the vector

$\{d\}_0$ from which $\{u\}_0$ is calculated. Then $\{d\}_{k+1} = \{u\}_k$, so $\{u\}_1$ is calculated from $\{d\}_1$, and so on until $\{u\}_K$ is obtained. The calculation is then repeated. It should be noted that an expanding grid — which increases in size in proportion to the diffusion layer thickness — is used because the electrode is very non-uniformly accessible so as to give accurate results. The protocol for the implementation of this is exactly as in the solution of steady-state WJE problems [12].

In this way the concentration profile of A within the WJE can be calculated as a function of time. The current at the electrode can thus be evaluated at any instant from

$$ {}^{t}I = 2\pi DF \sum_{k=1}^{K} [\mathrm{A}]_0 \, {}^{t}a_{1,k} \frac{k(\Delta r)^2}{\Delta z} \tag{22} $$

RESULTS AND DISCUSSION

Using the theory outlined above, single-step chronoamperometric transients were computed (on a Sun Sparkstation), and the convergence was examined by varying J, K and Δt values. For a typical electrode of geometry of radius $R = 0.4$ cm, cell constant $k_c = 0.9$ and jet diameter $a = 0.0345$ cm with volume solution flow rates in the range $0.1 > V_f/\mathrm{cm}^3\ \mathrm{s}^{-1} > 0.01$, values of $J = 500$, $K = 2000$ and $\Delta t = 0.01$ were found to give satisfactory convergence (to four significant figures) for typical aqueous solution parameters (kinematic viscosity $v = 0.0089\ \mathrm{cm}^2\ \mathrm{s}^{-1}$; $5 \times 10^{-6} < D/\mathrm{cm}^2\ \mathrm{s}^{-1} < 5 \times 10^{-5}$).

We return to eqn. (1) and note that, with the explicit equations for ν_r and ν_z given in ref. 12, the definition of the dimensionless variables

$$ \xi = (r/R)^{9/8} \tag{23} $$

$$ \chi = Az/r^{7/8} \tag{24} $$

$$ \tau = t(A^2 D/R^{14/8}) \tag{25} $$

where $A = R^{-3/8}(9C/8D)^{1/3}$, $C = [(5M)^3/216v^5]^{1/4}$ and $M = k_c^4 V_f^3/2\pi^3 a^2$, leads to the following normalized equation:

$$ \xi^{14/9} \frac{\partial[A]}{\partial\tau} = \frac{\partial^2[A]}{\partial\chi^2} - \chi\frac{\partial[A]}{\partial\xi} \tag{26} $$

On considering eqn. (26) together with the boundary conditions (2), (3) and (4) it is easily shown that the current transient, when normalized to the steady-state limiting current I_{LIM}, should be a unique function of the parameter τ. Accordingly, current transients were computed for different values of D and R. The results are shown in Figs. 1 and 2. It can be seen that in both cases, except at very short times (where effects due to the finite size of Δt are apparent), the computed transients all lie on the same curve when τ is used as the time variable. These observations vindicate the computations carried out and the general strategy

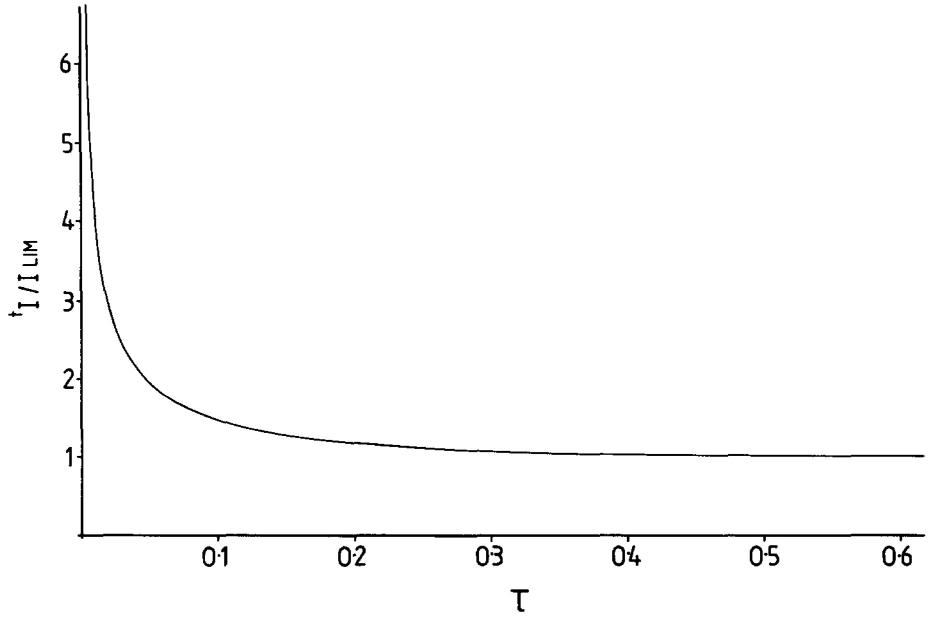

Fig. 1. A plot of the transient current response (normalized to the steady-state limiting current) calculated for electrodes of radii 0.1, 0.2, 0.3, 0.4 and 0.5 cm. The other (fixed) parameters used were $V_f = 0.01$ cm^3 s^{-1}, $a = 0.0345$ cm, $k_c = 0.9$ and $D = 1 \times 10^{-5}$ cm^2 s^{-1}. The results for the five different radii all lie on the curve shown.

proposed. The curves presented in Figs. 1 and 2 define "working curves" which can be used as the basis for the analysis of experimental data. In particular, as indicated in the Introduction, the measurement of normalized transients allows the measurement of diffusion coefficients independent of the knowledge of the concentration of the diffusing species since the latter does not appear in the definition of τ.

Finally we return to the question as to the extent to which the above theory may apply to real electrodes. In practice the realization of true "wall-jet" hydrodynamics requires careful cell design, particularly in relation to the nozzle–electrode separation and other parameters [2–6,8,15]. Nevertheless, numerous viable cells have been constructed (e.g. refs. 2–6) and shown to agree very satisfactorily with theory (usually for the steady-state mass-transport-limited current) based on the hydrodynamics (equations for ν_r and ν_z) assumed above. However, it is important to realize that, since the results of our calculations are presented through Figs. 1 and 2 in terms of normalized time, those working curves will apply to *any* wall-jet cell with the correct hydrodynamics and not simply to the electrode geometries used in our calculations. Indeed, given this approach, it is not even necessary for wall-jet behaviour to be experimentally realizable for the geometries used to generate working curves which are applicable to authentic wall-jet cells!

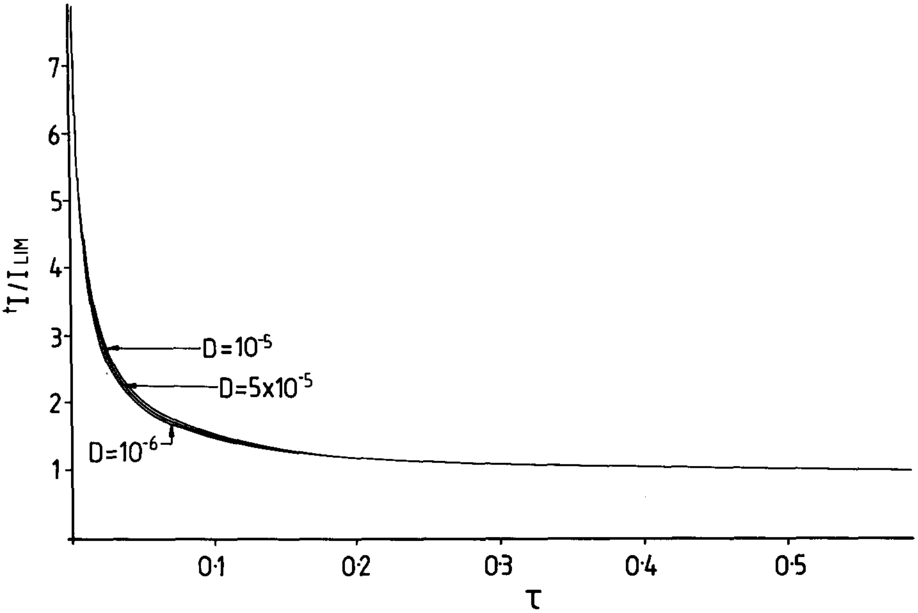

Fig. 2. A plot of the transient current response (normalized to the steady-state limiting current) calculated for varying diffusion coefficients: 10^{-6}, 5×10^{-6} and 10^{-5} cm^2 s^{-1}. The other (fixed) parameters used were $V_f = 0.01$ cm^3 s^{-1}, $a = 0.0345$ cm, $k_c = 0.9$ and $R = 0.4$ cm.

CONCLUSIONS

The form of the chronoamperometric response to a potential step at a wall-jet electrode has been derived and the influence of electrode geometry and solution flow rate identified.

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