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Transient measurements at the wall-jet ring disc electrode

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Theory is presented for the wall-jet ring disc electrode (WJRDE) which predicts the current transient at the ring resulting from a potential step at a WJRDE disc for the case where the ring is potentiostatted so as to reverse the reaction which occurs at the disc. The shape of such transients, in which double-layer charging effects are minimal, is revealed to be very sensitive to differences in the diffusion coefficient of the electroactive species which reacts at the disc and that of the corresponding product. Accordingly such measurements are recommended for the study of complex electrode processes in order to separate mass transport parameters (diffusion coefficients) from homogeneous kinetic phenomena.

1. Introduction

The quantitative investigation of the mechanism of electrode processes through their electrochemical behaviour typically includes the experimental examination of the influence of mass transport on current-voltage characteristics and subsequent comparison with theoretical predictions derived from candidate mechanistic schemes. For all but the simplest of mechanisms several independently variable parameters – rate constants and diffusion coefficients – have to be specified and this necessarily leads one to question the uniqueness of agreement of any preferred complex mechanism. Traditionally this problem has been substantially reduced by making the approximation, for intermediates which are not too structurally dissimilar from the starting reagent, that identical diffusion coefficients may be assumed for all the mechanistically significant species and assigned a value equal to that of the initial reagent. However, we have recently shown that this approximation may be significantly in error and that, for example, the molecule tetrachloro-*p*-benzoquinone and the corresponding anion and di-anions have markedly different diffusion coefficients in acetonitrile [1]. Accordingly it is necessary to identify experimental methodologies which allow the sensitive observation of unequal diffusion coefficients in addition to displaying high resolving power towards different electrode reaction mechanisms.

It has been established that the wall-jet electrode (WJE), where a fluid jet strikes a planar electrode at right angles and spreads out radially over that surface [2], has high mechanistic resolution under steady-state conditions due to its highly nonuniform primary current distribution as compared to other hydrodynamic electrodes [3]. Moreover, the extra information available from transient experiments is recognized [4] and we have developed a theoretical basis for time-domain experiments at the WJE [5]. However such experiments, conducted with large perturbations as in potential step chronamperometry, are inevitably blighted by double-layer charging effects which may mask the processes of interest or at least complicate the analysis of recorded transients. In this paper we explore the use of the wall-jet ring disc electrode (WJRDE) – in which the wall-jet electrode (disc) is surrounded by a concentric annular ring electrode – for chronoamperometric experiments in which the disc, at hydrodynamic equilibrium, is subjected to a double-potential step, typically from a potential at which no current flows to one corresponding to the transport-limited current for the electrode process of interest and then back to the initial potential, whilst the ring is potentiostatted throughout so as to induce the reverse of the process taking place on the disc. It will be shown that the current transient on the ring electrode is highly sensitive to inequality of diffusion coefficients between reagents and intermediates and, since the right has a fixed potential, suffers from minimal double-layer charging effects. In particular we examine the case where the disc reaction A → B is simply reversed at the ring without any intervening homogeneous chemistry. However the extension to mechanistically complex processes is straightforward and the necessary theory readily deduced from that given here and elsewhere [5, 6].

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2. Theory

We consider the following electrode reaction:

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

and assume only A to be present in bulk solution. The convective diffusion equation describing the concentrations of A and B in time (t) and space are

$$\frac{\partial[\mathrm{A}]}{\partial t} = D_\mathrm{A}\frac{\partial^2[\mathrm{A}]}{\partial z^2} - v_r\frac{\partial[\mathrm{A}]}{\partial r} - v_z\frac{\partial[\mathrm{A}]}{\partial z} \tag{1}$$

$$\frac{\partial[\mathrm{B}]}{\partial t} = D_\mathrm{B}\frac{\partial^2[\mathrm{B}]}{\partial z^2} - v_r\frac{\partial[\mathrm{B}]}{\partial r} - v_z\frac{\partial[\mathrm{B}]}{\partial z} \tag{2}$$

where D_A and D_B are the diffusion coefficients of A and B, respectively, v_r is the radial solution velocity (r-direction) and v_z is the velocity in the direction normal to the electrode surface (z-direction). Expressions for v_r and v_z under laminar flow are given in [6]. Note that in writing Equation 1 radial diffusion has been neglected: the basis of this approximation has been developed elsewhere [7]. We also assume the presence of sufficient supporting electrolyte so that migration effects are negligible.

We consider a double potential step on the disc electrode with the ring potentiostatted throughout at a value corresponding to the transport controlled reconversion of B to A. If the disc electrode potential is stepped, at time $t = 0$, from a value at which no current flows to one which induces the transport limited conversion of A to B, and then at time $t = t_\mathrm{step}$ the disc potential is returned to a value at which B is converted back into A, then the relevant boundary conditions to the defined double potential step chronoamperometric problem may be formulated as:

$t < 0$ all space

$$[\mathrm{A}] = [\mathrm{A}]_\mathrm{bulk} \qquad [\mathrm{B}] = 0 \tag{3}$$

all $t \geqslant 0$ $z \to \infty$,

$$[\mathrm{A}] \longrightarrow [\mathrm{A}]_\mathrm{bulk} \tag{4}$$

$t_\mathrm{step} \geqslant t \geqslant 0$

$$z = 0 \qquad r \leqslant R_1,$$

$$[\mathrm{A}] = 0;\ D_\mathrm{A}\frac{\partial[\mathrm{A}]}{\partial z} = -D_\mathrm{B}\frac{[\mathrm{B}]}{\partial z} \tag{5}$$

$$z = 0, \qquad R_1 < r \leqslant R_2,$$

$$\partial\frac{[\mathrm{A}]}{\partial z} = 0 = \partial\frac{[\mathrm{B}]}{\partial z} \tag{6}$$

$$z = 0, \qquad R_2 < r \leqslant R_3$$

$$[\mathrm{B}] = 0;\ D_\mathrm{A}\frac{\partial[\mathrm{A}]}{\partial z} = -D_\mathrm{B}\frac{[\mathrm{B}]}{\partial z} \tag{7}$$

$t > t_\mathrm{step}$

$$z = 0, \qquad r \leqslant R_1,$$

$$[\mathrm{B}] = 0;\ D_\mathrm{A}\frac{\partial[\mathrm{A}]}{\partial z} = -D_\mathrm{B}\frac{[\mathrm{B}]}{\partial z} \tag{8}$$

$$z = 0, \qquad R_1 < r \leqslant R_2,$$

$$\frac{\partial[\mathrm{A}]}{\partial z} = 0 = \frac{\partial[\mathrm{B}]}{\partial z} \tag{9}$$

$$z = 0, \qquad R_2 \leqslant r \leqslant R_3,$$

$$[\mathrm{B}] = 0\colon D_\mathrm{A}\frac{\partial[\mathrm{A}]}{\partial z} = -D_\mathrm{B}\frac{[\mathrm{B}]}{\partial z} \tag{10}$$

where $[\mathrm{A}]_\mathrm{bulk}$ is the bulk concentration of A, R_1 is the radius of the disc and R_2 and R_3, respectively, the inner and outer radii of the ring.

In order to solve Equations 1 and 2 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:

$$(\text{radial distance})_k = k\Delta r \tag{11}$$

$$k = 0, 1, \ldots, K_1, K_1 + 1, \ldots, K_2, K_2 + 1, \ldots, K_3 \tag{12}$$

where $\Delta r = R_1/K_1$, $K_2 = R_2/\Delta r$ and $K_3 = R_3/\Delta r$

$$(\text{normal distance})_j = j\Delta z \tag{13}$$

$$j = 0, 1, 2, \ldots, J \tag{14}$$

where $\Delta z = Z/J$ and Z is the length of the grid in the z-direction [6]. Then the notation ${}^t q_{j,k}$($q = a$ or b) indicates the concentration of Q = A or B, normalized to $[\mathrm{A}]_\mathrm{bulk}$ ($q = [\mathrm{Q}]/[\mathrm{A}]_\mathrm{bulk}$), 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 Equation 1 is:

$$\begin{aligned} {}^{t+1}a_{j,k} - {}^t a_{j,k} = {} & \lambda_\mathrm{A}^y\{{}^{t+1}a_{j+1,k} - 2\,{}^{t+1}a_{j,k} + {}^{t+1}a_{j-1,k}\} \\ & - \lambda_j^{v_r}\{{}^{t+1}a_{j,k} - {}^{t+1}a_{j,k'-1}\} \\ & - \lambda_j^{v_r}\{{}^{t+1}a_{j+1,k} - {}^{t+1}a_{j,k}\} \end{aligned} \tag{15}$$

where

$$\lambda_\mathrm{Q}^y = \frac{D_\mathrm{Q}\Delta t}{(\Delta z)^2} \tag{16}$$

$$\lambda_j^{v_r} = \frac{v_r(j + 1, k)\Delta t}{\Delta r} \tag{17}$$

$$\lambda_j^{v_z} = \frac{v_z(j + 1, k)\Delta t}{\Delta z} \tag{18}$$

and $v_r(j, k)$ and $v_z(j, k)$ are the solution velocity components at (j, k). Rearrangement of Equation 15 leads to the following general equation used as the basis for the ensuing (implicit) calculations:

$$\begin{aligned} \{{}^t a_{j,k}\} + \lambda_j^{v_r}\{{}^{t+1}a_{j,k-1}\} = {} & -\lambda_\mathrm{A}^y\{{}^{t+1}a_{j-1,k}\} \\ & + (\lambda_j^{v_r} - \lambda_j^{v_z} + 2\lambda_\mathrm{A}^v + 1)\{{}^{t+1}a_{j,k}\} \\ & - (\lambda_\mathrm{A}^y - \lambda_j^{v_z})\{{}^{t+1}a_{j+1,k}\} \end{aligned} \tag{19}$$

An analogous equation exists for B. The set of $(J - 1)$ simultaneous equations implied by Equation 19 can be expressed as a matrix equation

$$\{d\}^q = [T]^q\{u\}^q \tag{20}$$

where $[T]^q$ is a $(J-1)\times(J-1)$ matrix;

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

and the matrix elements are as follows

for $t_{\text{step}} \geqslant t \geqslant 0$

$Q = A$

$0 < k < K_1$

$$d_j^{A} = \{{}^{t}a_{j.k}\} + \lambda_j^{v_r}\{{}^{t+1}a_{j,k'-1}\}$$

$$j = 1, 2, \ldots, J-2$$

$$b_j^{A} = 2\lambda_{A}^{y} + \lambda_j^{v_r} - \lambda_j^{v_z} + 1$$

$$j = 1, 2, \ldots, J-2$$

$K_1 < k < K_2$

$$d_j^{A} = \{{}^{t}a_{j,k}\} + \lambda_j^{v_r}\{{}^{t+1}a_{j,k'-1}\}$$

$$j = 2, 3, \ldots, J-2$$

$$b_j^{A} = 2\lambda_{A}^{y} + \lambda_j^{v_r} - \lambda_j^{v_z} + 1$$

$$j = 2, 3, \ldots, J-2$$

$$b_1^{A} = \lambda_{A}^{y} + \lambda_1^{v_r} - \lambda_1^{v_z} + 1$$

$K_2 < k < K_3$

$$d_j^{A} = \{{}^{t}a_{j,k}\} + \lambda_j^{v_r}\{{}^{t+1}a_{j,k'-1}\}$$

$$j = 2, 3, \ldots, J-2$$

$$d_j^{A} = \{{}^{t}a_{j,k}\} + \lambda_j^{v_r}\{{}^{t+1}a_{j,k'-1}\} + \frac{D_{B}}{D_{A}}\lambda_{A}^{y}\{{}^{t}b_{1,k}\}$$

$$b_j^{A} = 2\lambda_{A}^{y} + \lambda_j^{v_r} - \lambda_j^{v_z} + 1$$

$$j = 2, 3, \ldots, J-2$$

$$b_1^{A} = \lambda_{A}^{y} + \lambda_1^{v_r} - \lambda_1^{v_z} + 1$$

$Q = B$

$0 < k < K_1$

$$d_j^{B} = \{{}^{t}b_{j.k}\} + \lambda_j^{v_r}\{{}^{t+1}b_{j,k'-1}\}$$

$$j = 2, 3, \ldots, J-2$$

$$d_1^{B} = \{{}^{t}b_{1,k}\} + \lambda_1^{v_r}\{{}^{t+1}b_{1,k'-1}\} + \frac{D_{A}}{D_{B}}\lambda_{B}^{y}\{{}^{t}a_{1,k}\}$$

$$b_j^{B} = 2\lambda_{B}^{y} + \lambda_j^{v_r} - \lambda_j^{v_z} + 1$$

$$j = 2, 3, \ldots, J-2$$

$$b_1^{B} = \lambda_{B}^{y} + \lambda_1^{v_r} - \lambda_1^{v_z} + 1$$

$K_1 < k < K_2$

$$d_j^{B} = \{{}^{t}b_{j.k}\} + \lambda_j^{v_r}\{{}^{t+1}b_{j.k'-1}\}$$

$$j = 1, 2, \ldots, J-2$$

$$b_j^{B} = 2\lambda_{B}^{y} + \lambda_j^{v_r} - \lambda_j^{v_z} + 1$$

$$j = 2, 3, \ldots, J-2$$

$$b_1^{B} = 2\lambda_{B}^{y} + \lambda_1^{v_r} - \lambda_1^{v_z} + 1$$

$K_2 < k < K_3$

$$d_j^{B} = \{{}^{t}b_{j.k}\} + \lambda_j^{v_r}\{{}^{t+1}b_{j,k'-1}\}$$

$$j = 1, 2, \ldots, J-2$$

$$b_j^{B} = 2\lambda_{B}^{y} + \lambda_j^{v_r} - \lambda_j^{v_z} + 1$$

$$j = 2, 3, \ldots J-2$$

$$b_1^{B} = \lambda_{B}^{y} + \lambda_1^{v_r} - \lambda_1^{v_z} + 1$$

for $t > t_{\text{step}}$

$Q = A$

$0 < k < K_1$

$$d_j^{A} = \{{}^{t}a_{j,k}\} + \lambda_j^{v_r}\{{}^{t+1}a_{j,k'-1}\}$$

$$j = 2, 3, \ldots, J-2$$

$$d_1^{A} = \{{}^{t}a_{1,k}\} + \lambda_1^{v_r}\{{}^{t+1}a_{1,k'-1}\} + \frac{D_{B}}{D_{A}}\lambda_{A}^{y}\{{}^{t}b_{1,k}\}$$

$$b_j^{A} = 2\lambda_{A}^{y} + \lambda_j^{v_r} - \lambda_j^{v_z} + 1$$

$$j = 2, 3, \ldots, J-2$$

$$b_1^{A} = \lambda_{A}^{y} + \lambda_1^{v_r} - \lambda_1^{v_z} + 1$$

$K_1 < k < K_2$

as for $t_{\text{step}} \geqslant t \geqslant 0$

$K_2 < k < K_3$

as for $t_{\text{step}} \geqslant t \geqslant 0$

$Q = B$

$0 < k < K_1$

$$d_j^{B} = \{{}^{t}b_{j,k}\} + \lambda_j^{v_r}\{{}^{t+1}b_{j,k'-1}\}$$

$$j = 1, 2, \ldots, J-2$$

$$b_j^{B} = 2\lambda_{B}^{y} + \lambda_j^{v_r} - \lambda_j^{v_z} + 1$$

$$j = 2, 3, \ldots, J-2$$

$$b_1^{\mathrm{B}} = 2\lambda_{\mathrm{B}}^{y} + \lambda_1^{v_r} - \lambda_1^{v_z} + 1$$

$$K_1 < k < K_2$$

$$\text{as for } t_{\text{step}} \geqslant t \geqslant 0$$

$$K_2 < k < K_3$$

$$\text{as for } t_{\text{step}} \geqslant t \geqslant 0$$

$$\text{all } k$$

$$d_{j-1}^{\mathrm{A}} = \{{}^{t}a_{J-1,k}\} + \lambda_{j-1}^{v_r}\{{}^{t+1}a_{j-1,k'-1}\} + \lambda_{\mathrm{A}}^{y} - \lambda_{J-1}^{v_z}$$

$$c_j^{\mathrm{A}} = -\{\lambda_{\mathrm{A}}^{y} - \lambda_j^{v_z}\}$$

$$j = 1, 2, \ldots, J-2$$

$$c_j^{\mathrm{B}} = -\{\lambda_{\mathrm{B}}^{y} - \lambda_j^{v_z}\}$$

$$j = 1, 2, \ldots, J-2$$

The special matrix elements for $j = 1$ and $j = J - 1$ result from consideration of the finite difference form of the boundary conditions given in Equations 3 to 10. The subscript k' in place of k relates to an interpolated concentration [5, 6].

We have shown previously how to apply the backwards implicit finite difference problem to solve Equation 20 and refer the reader to [5 and 6] for algebraic and computational detail. Notice that the matrix elements for A depend on ${}^{t}\mathrm{b}_{j,k}$, and vice versa, so that an iterative procedure is required [5, 6]. Solution for Q = A and B provides the concentration profiles of A and B within the diffusion layer of the WJRDE as a function of time. The current at the disc may be evaluated from the following:

for $t_{\text{step}} \geqslant t \geqslant 0$

$$ {}^{t}I_{\text{disc}} = 2\pi D_{\mathrm{A}} F \sum_{k=1}^{K_1} [\mathrm{A}]_{\text{bulk}}\, {}^{t}a_{1,k} \frac{k(\Delta r)^2}{\Delta z} \qquad (21)$$

for $t > t_{\text{step}}$

$$ {}^{t}I_{\text{disc}} = -z\pi D_{\mathrm{B}} F \sum_{k=1}^{K_1} [\mathrm{A}]_{\text{bulk}}\, {}^{t}b_{1,k} \frac{k(\Delta r)^2}{\Delta z} \qquad (22)$$

where F is the Faraday constant. The ring current may be analogously computed thus:
for $t \geqslant 0$

$$ {}^{t}I_{\text{ring}} = -2\pi D_{\mathrm{B}} F \sum_{k=K_2}^{K_3} [\mathrm{A}]_{\text{bulk}}\, {}^{t}b_{1,k} \frac{k(\Delta r)^2}{\Delta z} \qquad (23)$$

3. Results

Using the theory outlined above double potential step chronoamperometric transients were computed on a (Sun Sparcstation) and convergence examined by varying J, K_1 and Δt values. For a typical WJRDE of geometry $R_1 = 0.1637\,\mathrm{cm}$, $R_2 = 0.1745\,\mathrm{cm}$, $R_3 = 0.1888\,\mathrm{cm}$, cell constant $k_{\mathrm{c}} = 0.9$ [7] and jet diameter $a = 0.0345\,\mathrm{cm}$, for volume flow rates in the range $0.1 > V_{\mathrm{f}}/\mathrm{cm}^3\,\mathrm{s}^{-1} > 0.01$ values of $J = 500$, $K_3 = 2000$ and $\Delta t = 0.01\,\mathrm{s}$ were found to give satisfactory convergence (to three significant figures) for aqueous solution parameters (kinematic viscosity, $v = 0.0089\,\mathrm{cm}^2\,\mathrm{s}^{-1}$, $10^{-6} < D/\mathrm{cm}^2\,\mathrm{s}^{-1} < 10^{-5}$).

We consider first the transients resulting from stepping the disc potential at time $t = 0$ between a value at which no current flows and one corresponding to the transport limited conversion of A to B. We have shown elsewhere [5] that, if the current is normalized with respect to its steady-state transport limited value, I_{lim}, the disc transient is a unique function of the following dimensionless time parameter:

$$\tau_{\mathrm{A}} = t(A^2 D_{\mathrm{A}}/R^{14/8}) \qquad (24)$$

where $A = R_1^{-3/8}(9C/8D_{\mathrm{A}})^{1/3}$; $C = \{[5M]^3/216v^5\}^{1/4}$ and $M = k_{\mathrm{c}}^4 V_{\mathrm{f}}^3/2\pi^3 a^2$, as shown in Fig. 1. Transients computed for different radii $0.1 < R_1/\mathrm{cm} < 0.5$ and a range of flow rates and diffusion coefficients (see above) were all found to lie on the curve shown.

Turning next to the ring transients Fig. 2 shows the computed behaviour for the step at $t = 0$ for two different electrode geometries, (a) $R_2 = 0.1745\,\mathrm{cm}$ and $R_3 = 0.1888\,\mathrm{cm}$, and (b) $R_2 = 0.2\,\mathrm{cm}$ and $R_3 = 0.23\,\mathrm{cm}$. In both cases R_1 was fixed as 0.1637 cm and $D_{\mathrm{A}} = D_{\mathrm{B}} = 10^{-5}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$. The absolute magnitude of the steady-state ring currents were in quantitative agreement with that prediced by the analytical 'collection efficiency' theory of Albery [7]. In Fig. 2 the ring current has been normalized with respect to its steady-state limiting value. It can be seen that, as expected, with a larger 'gap' (i.e. $R_2 - R_1$) the lag-time before the ring current begins to rise is bigger; also the wider the ring electrode ($R_3 - R_2$) the longer the timescale of the ring transient.

Figure 3 shows the ring transient resulting from a double potential step on the disc of the typical WJRDE defined in the first paragraph of this section with $\tau_{\mathrm{A,step}} = 2.5$ (corresponding to t_{step}) and $D_{\mathrm{A}} = D_{\mathrm{B}} = 10^{-5}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$. Under these conditions the ring current has reached its steady-state value before the disc potential is reversed at t_{step}. The timescales of the current rise and fall are comparable. An analogous disc transient is shown in Fig. 4.Figure 5 shows plots corresponding to Figs 3 and 4 except that now $D_{\mathrm{A}} =$

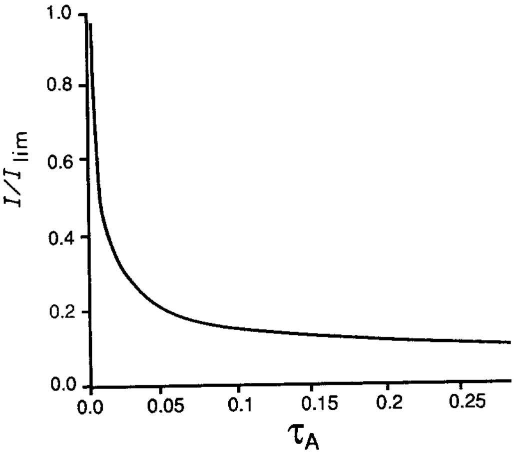

Fig. 1. The disc transient response to the potential step at $t = 0$. Note that the abscissa is normalized time (τ_{A}) and the current is normalized to the steady-state transport limited value so that this curve is entirely general.

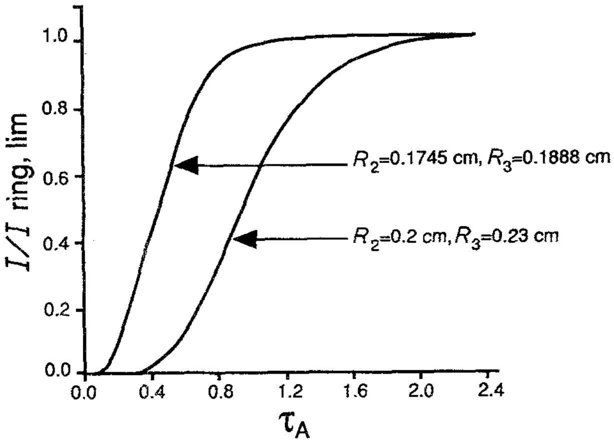

Fig. 2. The ring transient response to a potential step on the disc at $t = 0$ for two WJRDEs of different geometry as specified in the text.

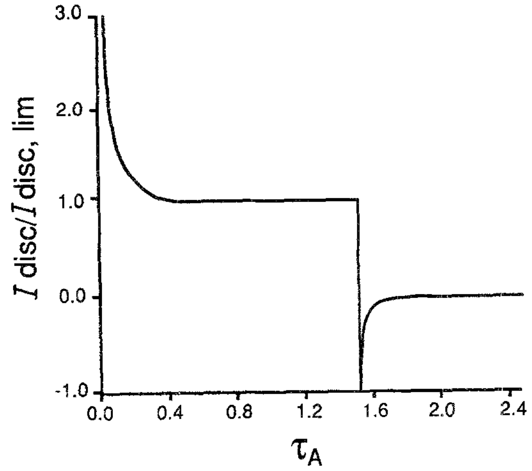

Fig. 4. The disc current response to a double potential step characterized by steps at $\tau_A = 0$ and 1.5. The electrode geometry and other parameters are specified in the text.

6.32×10^{-6} and $D_B = 7.63 \times 10^{-6}\mathrm{cm^2 s^{-1}}$ and the ring current is normalized with respect to its peak value. The diffusion coefficient parameters relate to the oxidation of ferrocyanide to ferricyanide ions (in aqueous solution) at the disc electrode [8]. It can be seen that whilst both disc and ring responses are sensitive to the difference in diffusion coefficients the ring reveals the inequality of diffusion coefficients much more dramatically and a noticeably asymmetric transient results. Moreover, unlike the disc current, double layer charging effects are minimal at the ring, since this electrode is maintained at a constant potential throughout the experiment. The shape of the ring transient can be understood when it is recognised that the amount of material reaching that electrode is controlled both by the diffusion coefficient of B, the species transported between the disc and the ring, and the current passed at the disc which controls the quantity of B 'sent' to the ring. Immediately following the step at $t = 0$ the ring responses is initially influenced by the first of these factors and reflects the magnitude of D_B since then there is only negligible depletion of A near the disc. Subsequently, but before t_{step}, the disc current has falled, A has been depleted in the vicinity of the disc, and the disc current limited by the amount of A reaching the disc and so the ring current also depends on D_A. On this basis it is predicted that if the diffusion coefficients of A and B are interchanged so that $D_B = 6.32 \times 10^{-6}$ and $D_A = 7.63 \times 10^{-6}\mathrm{cm^2 s^{-1}}$ the asymmetry of the transient should be reversed; this is shown in Fig. 6.

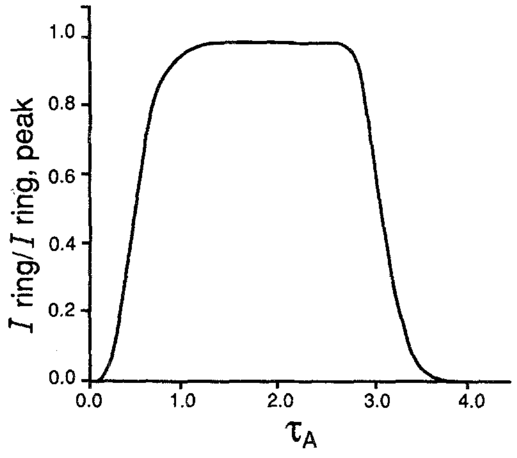

Fig. 3. The ring transient response to a double potential step on the disc defined by steps at $\tau_A = 0$ and $\tau_{A,\mathrm{step}} = 2.5$. The electrode geometry and other parameters are specified in the text.

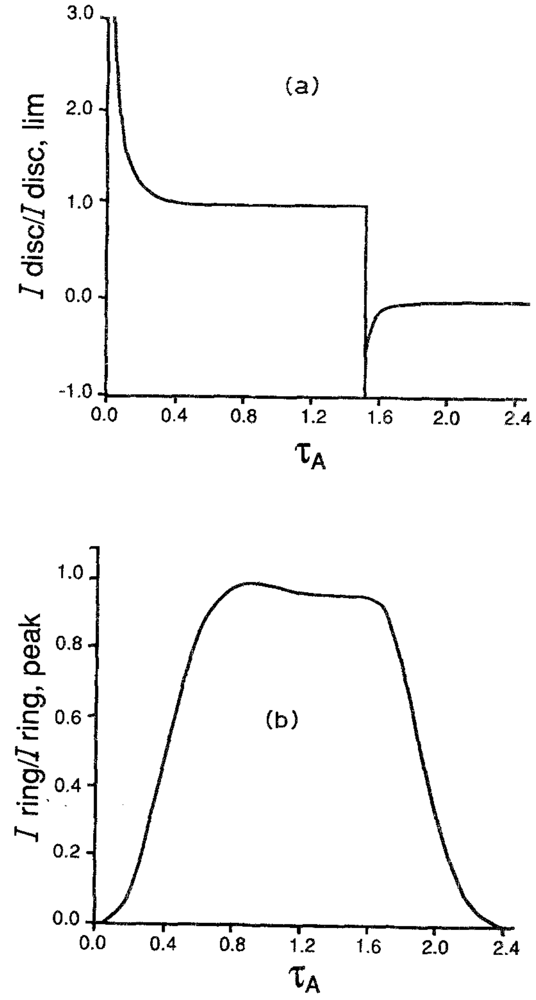

Fig. 5. The disc (A) and ring (B) current responses to a double potential step characterized by $\tau_{A,\mathrm{step}} = 1.5$ for the case where $D_A = 6.32 \times 10^{-6}$ and $D_B = 7.63 \times 10^{-6}\mathrm{cm^2 s^{-1}}$.

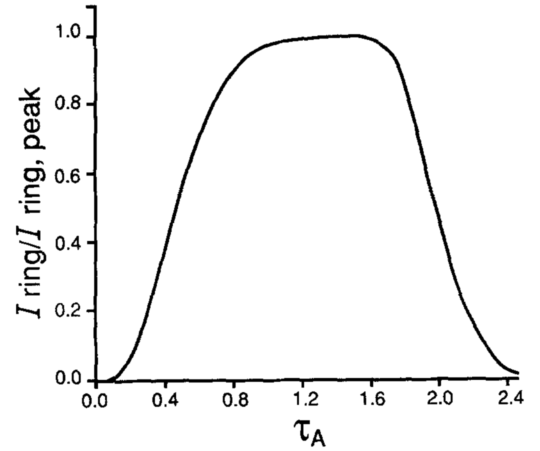

Fig. 6. The ring current response to a double potential step for the case where $D_B = 6.32 \times 10^{-6}$ and $D_A = 7.63 \times 10^{-6}$ cm^{2}s^{-1}.

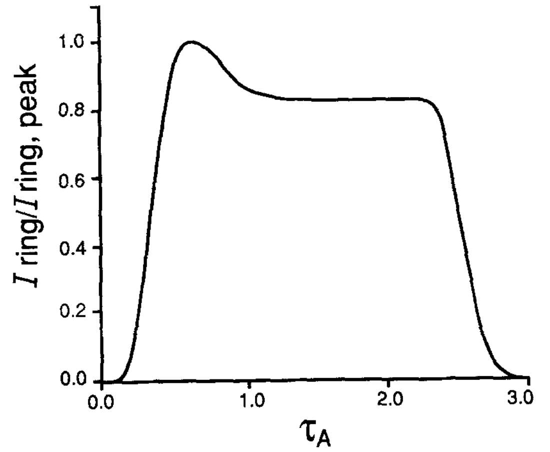

Fig. 7. The ring current response to a double potential step for the case where $D_B = 3.0 \times 10^{-6}$ and $D_A = 9.0 \times 10^{-6}$ cm^{2}s^{-1}.

It can be seen that differences in diffusion coeffcient between A and B are strikingly revealed by ring transients in double potential step chronamperometric experiments. Figure 7 shows an extreme case where $D_A = 3.0 \times 10^{-6}$ and $D_B = 9.0 \times 10^{-6}$ cm^{2}s^{-1} to emphasise the sensitivity of the approach; nevertheless it should be apparent from Figs 5 and 6 that even differences between D_A and D_B can be resolved. Accordingly, and in resolution of the problems posed in the introduction, we recommend the use of double electrode transient measurements for the study of those electrode processes in which different participating species display dissimilar diffusion coefficients.

References

[1] R. G. Compton, B. A. Coles and R. A. Spackman, *J. Phys. Chem.* **95** (1991) 4741.
[2] M. B. Glauert, *J. Fluid Mech.* **1** (1956) 625.
[3] R. G. Compton, A. C. Fisher and G. P. Tyley, *J. Appl. Electrochem.* **21** (1991) 295.
[4] M. Sluyters-Rehbach and J. H. Sluyters, *Comprehensive Chem. Kinet.* **26** (1986) 203.
[5] A. C. Fisher, R. G. Compton, C. M. A. Brett and A. M. C. F. Oliveira Brett, *J. Electroanal. Chem.* **318** (1991) 53.
[6] R. G. Compton, C. R. Greaves and A. M. Waller, *J. Appl. Electrochem.* **258** (1990) 575.
[7] W. J. Albery and C. M. A. Brett, *J. Electroanal. Chem.* **148** (1983) 201.
[8] R. N. Adams, 'Electrochemistry at Solid Electrodes', Marcel Dekker, New York (1969) p. 220.