Steady State Currents at Inlaid and Recessed Microdisc Electrodes for First-order EC’ Reactions.

J. Galceran†, S. L. Taylor* and P. N. Bartlett*

†Departament de Química, Universitat de Lleida. Rovira Roure, 177. E-25198 Lleida, SPAIN.
*Department of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK.

Abstract

The analytical solutions, approximate expressions and a Finite Element simulation of the steady-state currents arising from the diffusion of a regenerating electroactive species towards a disc electrode, either inlaid in an insulator or recessed, are discussed. The results are valid for any reversible charge transfer, regardless of the applied potential (i.e. including limiting currents) and for equal or unequal diffusion coefficient of the species. For the inlaid disc, derivation of the exact analytical solution, via a reformulation of the diffusion-reaction problem as a dual integral equation that can then be solved using a series of Bessel functions, allows us to assess and review the accuracy of existing approximate expressions. We present 3 new formulae for the steady state current under these conditions, among which we highlight one with an accuracy better than 0.27% over the entire range of rate constants and we show that the accuracy of a recently presented two point Padé approximation (L. Rajendran and M.V. Sangaranarayanan, J. Phys. Chem. B 103 (1999) 1518) is better than 0.01%. The analytical solution also allows us to show that the accuracy of the simulation of the same problem using the Finite Element Method is better than 0.4%.

For the recessed disc the exact analytical solution is derived, as an extension of the solution of the inlaid disc, by matching the series representing the concentration of the electroactive species and its derivative. Two approximate expressions are suggested, one of which yields at least 2% accuracy. Concentration profiles for the electroactive species provide physical insight into the processes involved.

Keywords: reaction/diffusion, EC’ mechanism, steady-state, microdisc electrode, homogeneous reaction, finite element method, dual integral equation
Introduction

Microelectrodes are a powerful tool for understanding the mechanism and kinetics of fast reactions. As far back as 1984, Fleischmann et al. [1, 2] used microdisc electrodes to determine the rate constants of coupled homogeneous reactions (CE, EC’, ECE and DISP1 mechanisms). Although the inlaid disc electrode can be considered as one of the most popular microelectrode configurations, there is also a need to consider recessed disc electrodes [3, 4], due to the increasing application of microdisc arrays fabricated using photolithographic techniques which normally produce microdiscs recessed within a layer of insulating photoresist. Mechanistic studies, such as the determination of kinetic constants can be conducted at such recessed microelectrodes but theoretical expressions for the steady state currents at such electrodes are not available.

In a previous paper [5] we have investigated the chronoamperometric response of inlaid and recessed microdisc electrodes in the presence of a coupled first order homogeneous EC’ reaction. In part our interest in this problem arises from the modelling of the homogeneous enzyme/mediator system where pseudo first order EC’ kinetics can be achieved given a sufficiently high substrate concentration and low mediator concentration. Since one of the advantages of the microelectrode configuration is that it attains steady state behaviour within a reasonable time, it seems appropriate to focus on the modelling of the expected values for these steady-state currents.

The two-dimensional geometry of the inlaid (or recessed) electrode poses difficulties for the straightforward mathematical solution of such a system. It is known that the concentration profiles for the diffusing species far away from the disc approximate to those expected for spherical symmetry and, since the problem of spherical diffusion is mathematically easier to deal with, a number of authors have developed approximate treatments drawing on the analogy between the behaviour of microhemisphere and that of microdisc electrodes [1, 6-8]. This analogy has been exploited in the literature in order to use the results obtained for the steady state current for various reaction mechanisms at the microhemisphere to develop corresponding approximate expressions for the microdisc.
Finite difference is the simulation technique most usually resorted to for modelling most electrochemical problems at disc electrodes [9-12]. The inclusion of homogeneous kinetics in these kinds of simulation has also been described [13-16] and the limited validity of one-dimensional approaches for the inlaid electrode pointed out.

The Finite Element Method (FEM) is an alternative simulation technique which has been used for both inlaid and recessed electrode geometries[3, 4, 17, 18], it has the potential advantage that it can be applied to irregular geometries. Both methods (Finite Difference and Finite Element) require expanding meshes to handle the singularity in one region while extending out to infinity in other regions.

Some theoretical work has also been published on the first order EC’ scheme at inlaid disc electrodes. Phillips [19] derived the asymptotic behaviour of the current for low and high values of the kinetic constant. Tutty [20] described the singularity at the edge. Bender and Stone [21] tackled the problem of finding an exact solution for steady-state diffusion towards an arbitrary shaped inlaid electrode coupled with a (pseudo) first-order reaction, by means of integral equations. For the particular case of the limiting current, a Fredholm integral equation of the first kind must be solved. Recently, Phillips and Stone [22] employed the dual integral approach together with Tranter’s method [23] as a first step in the computation of currents in a twin disc arrangement. Most recently, Rajendran and Sangaranarayanan [24] pointed out and adapted a rigorous formal solution available in the field of water infiltration and derived a two-point Padé approximation.

To our knowledge no analytical solution has been reported for the EC’ mechanism at a recessed disc electrode. The related problem of diffusion without reaction at a recessed electrode was solved analytically by Brunn et al. [25] using a Green’s function approach together with a series expansion for the concentration within the recess. In the present work we derive exact solutions for both inlaid and recessed electrodes by using a dual integral equation, rather than by reducing the problem to a Fredholm integral equation. This has the advantage that the series solution makes it easier to obtain approximate analytical expressions, as in our previous work [26, 27]. While the dual integral approach is very convenient for axisymmetrical problems (such as the inlaid and recessed electrodes) with the differential equation to solve being linear, its extension to non-linear problems or irregular
geometries might prove impossible, and then simulation methods (such as the Finite Difference or Finite Element Methods) would be required. In this work we cross-validate the dual integral and the Finite Element Method approach, while developing and comparing approximate expressions.

In section 1 of this paper we lay out the basic mathematical formulation for the axisymmetrical problem of the inlaid and recessed disc in terms of dimensionless parameters. The formulation allows us to treat the case of a reversible redox couple with unequal diffusion coefficients at any applied potential and the limiting current regime for an irreversible redox couple. We devote section 2 to the treatment of the inlaid disc electrode: the derivation of the analytical solution leads to an accurate computation of the steady state current, a validation of our FEM simulation, the proposal of new approximate expressions and the assessment of the accuracy of new and existing expressions. In section 3 we turn our attention to the recessed disc, following the same development as in section 2: analytical treatment, FEM simulation and approximate expressions. Appendix A details the derivation of the exact solutions and Appendix B provides a list of the main symbols used in this work.

1. Mathematical formulation

The EC’ mechanism can be described as follows:

\[ A \pm n_e e^- \rightarrow B \]

\[ B + Z \xrightarrow{k_i} A + Y \quad (1) \]

where \( Z \) and \( Y \) are electroinactive species and \( n_e \) is the number of electrons exchanged. Pseudo-first order kinetics are achieved when the concentration of \( Z \) is sufficiently large. Assuming that the only relevant transport phenomenon is diffusion, the steady-state continuity equations for species \( B \) and \( A \) read:

\[ D_B \nabla^2 c_B = k_f c_B \quad (2) \]

\[ D_A \nabla^2 c_A = -k_f c_B \quad (3) \]

where \( D_B \) and \( D_A \) stand for the diffusion coefficients of \( B \) and \( A \), respectively, \( k_f \) (equal to \( k_2[Z] \)) is the pseudo first-order rate constant for the homogeneous reaction, and \( \nabla^2 \) stands for the (dimensional) laplacian operator.
In both cases (inlaid and recessed disc electrodes), the origin of the coordinate system is taken at the centre of the disc electrode, with the $z$-axis perpendicular to the electrode surface and the radial axis co-planar to it. The spatial coordinates $r$ and $z$ are normalised with respect to the electrode radius $a$.

We consider semi-infinite diffusion with zero concentration for $B$ and $c_A^*$ for $A$ in the bulk ($r$ or $z$ tends to infinity). The boundary conditions corresponding to the reversible reaction at the electrode surface are

$$D_A \left( \frac{\partial c_A}{\partial z} \right)_{z=0} = -D_B \left( \frac{\partial c_B}{\partial z} \right)_{z=0} \quad r \leq 1 \quad z = 0$$

and

$$\frac{c_A^s}{c_A^*} = \exp \left[ \pm \frac{nF}{RT} (E - E^0) \right] \equiv \delta$$

where the superscript $s$ stands for electrode surface concentrations (at $r \leq 1$, $z = 0$). In the particular case when $\delta \to \infty$, we have diffusion limited conditions. Our results can also be used for an irreversible redox couple under limiting current conditions by an obvious and trivial extension. In all cases the concentration gradient of both species at the surfaces of the insulator surrounding the electrode are zero as detailed below.

Addition of eqn. (2) to eqn. (3) yields $\nabla^2 (D_A c_A + D_B c_B) = 0$, which taking into account that the boundary conditions can be stated as the gradient of $(D_A c_A + D_B c_B)$ being zero at any limiting surface while at points remote from the electrode the concentrations have their bulk values, allows one to conclude [19], [24, 28, 29] that, at any point,

$$D_A c_A + D_B c_B = D_A c_A^*$$

Moreover, using the reversibility condition (5), the surface concentration is found to be:

$$c_B^* = \frac{\delta D_A c_A^*}{D_A + \delta D_B}$$

which is uniform on the electrode surface, as expected [30]. Moreover, its value is
independent of the actual geometry of the electrode and insulator [28] [29]. It is therefore convenient to introduce a dimensionless concentration \( \theta \)

\[
\theta \equiv \frac{c_\text{a}}{c_\text{a}^*} = \frac{(D_\text{A} + \delta D_\text{B}) c_\text{a}}{\delta D_\text{A} c_\text{A}^*}
\]  

(8)

Equation (2) can be re-cast in non-dimensional form as:

\[
\frac{\partial^2 \theta}{\partial r^2} + \frac{1}{r} \frac{\partial \theta}{\partial r} + \frac{\partial^2 \theta}{\partial z^2} = K \theta
\]

(9)

where

\[
K \equiv \frac{k_r a^2}{D_\text{B}}
\]

(10)

is a dimensionless kinetic constant.

The boundary condition particular to the inlaid electrode is:

\[
\frac{\partial \theta(r, z)}{\partial z} = 0 \quad r > 1 \quad z = 0
\]

(11)

and the boundary conditions particular to the recessed electrode are:

\[
\frac{\partial \theta(r, z)}{\partial z} = 0 \quad r > 1 \quad z = L
\]

(12)

\[
\frac{\partial \theta(r, z)}{\partial r} = 0 \quad r = 1 \quad 0 \leq z \leq L
\]

(13)

where \( L \) denotes the depth of the recess normalised with respect to the electrode radius.

The boundary conditions common to both disc electrodes are:

\[
\theta(r, z) = 1 \quad r \leq 1 \quad z = 0
\]

(14)

\[
\frac{\partial \theta(r, z)}{\partial r} = 0 \quad r = 0 \quad z \geq 0
\]

(15)
The steady-state current for the inlaid microdisc electrode when there is no homogeneous reaction can be found by re-scaling a well-known expression\[31, 32\]:

$$I_{\text{inlaid}}(k_t = 0) = 4n_e F a D_A \left(c_A^* - c_A^e\right) = 4n_e F a D_A \left(\frac{\delta D_B c_A^e}{D_A + \delta D_B}\right)$$  \hspace{1cm} (17)

We now use this latter expression as the normalisation factor to obtain the normalised current, or flux, $\phi$

$$\phi \equiv \frac{I(k_t \neq 0)}{I_{\text{inlaid}}(k_t = 0)} = \frac{n_e F a D_A}{4n_e F a D_A} \int_{z=0}^{2\pi r} \frac{2\pi r \, dr}{D_A + \delta D_B} = -\frac{\pi}{2} \int_{0}^{1} \left(\frac{\partial}{\partial z}\right)_{z=0} r \, dr$$  \hspace{1cm} (18)

We notice that an advantage of the normalisation is that once the dimensionless problem (in terms of just $K$ and $L$) is solved, the current for any applied potential or pair of diffusion coefficients, bulk concentration, electrode radius and $n_e$ can be computed. In particular, the dependence of the current with the dimensionless potential $\delta$ follows the well-known sigmoidal shape [33], regardless of the shape of the insulator around the disc electrode [29].

2. Inlaid disc electrode

We now consider the problem of the inlaid disc electrode beginning with the exact analytical solution for the EC’ reaction at this electrode.

2.1 Exact solution

Recently, Rajendran and Sangaranarayanan [24] have presented an exact expression for the current which was originally developed for the scattering of waves [34] (where the Helmholtz equation was solved in oblate spheroidal coordinates) and subsequently adapted to water infiltration [35]. However, as recognised by all those workers [24, 35], the computation of the solution becomes cumbersome and impractical, and, thus to the best of our knowledge, has not been used to assess the accuracy of any approximate expressions.
We show in Appendix A that the first-order problem can be reformulated in terms of a dual integral equation (A-6) which, following Tranter’s method [22, 23, 36, 37], is reduced to a system of linear equations in the unknown coefficients $a_m$:

$$\sum_{m=0}^{\infty} \Omega_{m,0} a_m = \frac{2}{\pi}$$

$$\sum_{m=0}^{\infty} \Omega_{m,n} a_m = 0 \quad (n > 0)$$

where

$$\Omega_{m,n} \equiv \int_0^{\infty} \frac{J_{2m+1/2}(\lambda)J_{2n+1/2}(\lambda)}{\sqrt{\lambda^2 + K}} \, d\lambda$$

and $J_\nu$ is a Bessel function of the first kind of order $\nu$.

The flux, or dimensionless current, can be readily computed (see (A-14)) as

$$\phi = \sqrt{\frac{\pi}{2}} a_0$$

This expression, relating the current to just the first of the coefficients in the expansion, is analogous to that obtained in other fields where an expansion has been employed to solve a dual integral equation [27, 38, 39].

The results referred to below as “dual” have been obtained by truncating the linear system (19) after a number of unknown coefficients $a_m$ (typically 4 or 5) such that inclusion of further terms results in an insignificant change in the current (at most sufficiently less than 0.01% so that this could be taken as our estimated accuracy). The convergence process can be seen in Table 1. Using Mathematica 2.0 (Wolfram Research) on a PC Pentium II, the computation of the flux with the 5 x 5 matrix (i.e. the maximum $m$ and $n$ in (19) is 4) and with 101 terms ($i=100$) in (A-15), takes ca. 30 s. All codes mentioned in this article are available from the authors upon request.

2.2 Simulation results

Transient simulations using the Finite Element Method, as described elsewhere [5], were run to steady state by letting the dimensionless time, $\tau \equiv \frac{D_u t}{a^2}$, reach a value of $10^6$. The
simulated results show excellent agreement with the dual solution even over the critical intermediate range of $K$, as seen in Fig. 1 (The discrepancy is between -0.4% and -0.3%). This level of accuracy is very satisfactory for a simulation of the steady state (reached through a complete transient simulation) in a semi-infinite medium with a singularity[20].

Over a larger range of $K$, as seen in Table 2, there is also an excellent agreement with previously published simulation data obtained by Lavagnini et al. [14] using the Hopscotch method and a conformal map. Even for higher values of $K$ than those presented in the table, our simulated fluxes agreed (for finer meshes) with the asymptotic values predicted by equation (25). In any case, the discrepancies found did not exceed -0.42% and, so, this can be considered as the limit of our finite element simulation error.

2.3 Approximate expressions

2.3.1 Previous approaches

The microhemisphere analogy of Oldham [6], as implicitly adapted by Lavagnini et al. [14], can be written as

$$\phi = 1 + \frac{2}{\pi} \sqrt{K}$$  \hspace{1cm} (22)

It can be seen from Table 2 that this expression is accurate to 3% for values of $K$ up to 1.

Fleischmann et al. [1], also exploiting the similarity between the hemispherical and inlaid disc electrode, suggested

$$\phi = 1 + \frac{\pi}{4} \sqrt{K}$$  \hspace{1cm} (23)

This expression tends asymptotically towards the exact solution in both limits (that is as $K \rightarrow 0$ and $K \rightarrow \infty$), as seen in Table 2. For low values of $K$, eqn. (23) is accurate to 3% up to $K \approx 0.07$ and for high $K$ accuracy of 3% is recovered from $K \approx 50$ onwards.

Phillips [19] derived two approximations based on the application of the fact that the steady state current for a system with reaction can be seen as the Laplace transform of the
same problem but with no reaction [5, 40]. Applying this property to previous results for the transient current at an inlaid disc where there was no homogeneous reaction, he found the following asymptotic behaviour for low \(K\)-values

\[
\phi = 1 + \frac{2}{\pi} \sqrt{K} + \left( \frac{4}{\pi^2} - \frac{1}{3} \right) K
\]

and for high \(K\)-values

\[
\phi = \frac{\pi}{4} \left( \sqrt{K} + 1 + \frac{1}{4\sqrt{K}} \right)
\]

Phillips’ expressions are very accurate within their respective regions, as can be seen from Table 2: for low \(K\) expression (24) is accurate to 1.17\% at \(K = 1\), while expression (25) for high \(K\) yields 4.64\% error at \(K = 1\) [21]. For \(K > 10\), expression (25) is more accurate than 0.27\%. In order to compare in detail and subsequent more accurate expressions, the percentage errors (taking the dual integral solution as reference) are plotted in Fig. 1 for the critical intermediate region around \(K = 1\). It can be seen from the figure that Phillips’ low-\(K\) expression is accurate to 1\% for \(K < 0.85\), while the high-\(K\) expression achieves the same accuracy from \(K = 3.65\) onwards. As both asymptotic expressions overestimate the currents, the use of their lower value limits the error to 2.33\% (at \(K = 1.83\)).

Rajendran and Sangaranarayanan [24], adapting the work of Philip [35], also suggested an asymptotic expression for low \(K\)-values

\[
\phi = 1 + \frac{2}{\pi} \sqrt{K} + \left( \frac{4}{\pi^2} - \frac{1}{3} \right) K + \frac{2}{\pi} \left( \frac{4}{\pi^2} - \frac{4}{9} \right) K^{3/2} + \left( \frac{16}{\pi^4} - \frac{20}{9\pi^2} + \frac{1}{15} \right) K^2 + \frac{2}{\pi} \left( \frac{16}{\pi^4} - \frac{8}{3\pi^2} + \frac{71}{675} \right) K^{5/2} + \left( \frac{64}{\pi^6} - \frac{112}{9\pi^4} + \frac{448}{675\pi^2} - \frac{2}{315} \right) K^3
\]

and another for high \(K\)-values

\[
\phi = \frac{\pi}{4} \left( \sqrt{K} + 1 + \frac{1}{4\sqrt{K}} - \frac{1}{8K} + \frac{1}{16K^{3/2}} \right)
\]

These approximations clearly improve on Phillip's asymptotic expressions. No difference can be seen in Table 2 between the low \(K\) asymptotic (26) and the dual solution. The differences for the high \(K\) asymptotic expression (27) are very small, except for \(K=1\). This (relatively) worst behaviour of the high \(K\) asymptotic can be traced back to the fewer number of terms
included in the expression. It is seen in Fig. 1 that the low \( K \) asymptotic expression (26) underestimates the current (see + symbols) and is only -0.5% out for a relatively high value such as \( K=4 \). In the same figure, we see that the high \( K \) value expression (27) overestimates the current (see markers \( o \)) and produces an error of 1.7% for \( K=1 \).

Furthermore, Rajendran and Sangaranarayanan [24], using the previous asymptotic expressions (26) and (27), constructed the following Padé approximant:

\[
\phi = \frac{1 + 2.0016 \sqrt{K} + 1.8235K + 0.96367K^{3/2} + 0.307949K^2 + 0.049925K^{5/2}}{1 + 1.3650 \sqrt{K} + 0.8826K + 0.32853K^{3/2} + 0.063566K^2}
\]  

(28)

Now, we can show that the accuracy of this expression is extraordinary. All digits of the dual solution (i.e. computed with the dual approach) in Table 2 are correctly reproduced by the approximate expression (28). In Fig. 1 no difference can be seen. Numerical differences found in all cases examined were below 0.004%; a value which is comparable to, or less than, the estimated accuracy of our calculations of 0.01%.

### 2.3.2 Zeroth-order approximate expression

The simplest approximate analytical expression for the dimensionless current can be obtained from the zeroth-order approximation [26, 27], which reduces the infinite linear system (19) to just one term.

\[
\Omega_{00}a_0 \approx \frac{2}{\sqrt{\pi}} \Rightarrow \phi \approx \frac{1}{\Omega_{00}}
\]  

(29)

Results in Table 2 (where 100 terms have been used to compute \( \Omega_{00} \)) and Fig. 1 show that this approach is valid for low-\( K \) and yields a maximum error of -1 % for \( K < 3.1 \).

A further approximation consists in taking just a few terms in the evaluation of \( \Omega_{00} \). For instance, we have found it convenient to take 6 terms in (A-15):

\[
\phi = \frac{1}{\Omega_{00}} \approx \frac{1}{1 + \frac{K}{3} + \frac{K^2}{20} - \frac{2\sqrt{K}}{\pi \left( \frac{2K}{9} + \frac{16K^2}{675} \right)}}
\]  

(30)

This alternative simple approximate expression also applies at low \( K \) and underestimates the current (see Fig. 1). For \( K = 1 \) it is accurate to -0.33%. Nevertheless up to \( K = 2 \) it is still
more accurate (-2.08%) than expression (25) (which is only 2.12% accurate at that particular $K$-value).

2.3.3 Semi-analytical approximation

A heuristic approach has been adopted by testing the $n^{th}$ root of a polynomial in $\sqrt{K}$ of degree $n$, such that the asymptotic behaviour of the resulting expression for the flux matches as many terms as possible in equations (24) and (25). The determination of some unknown coefficients from the imposed asymptotic behaviour at two extremes was also used by Shoup and Szabo to suggest their well known "de facto" solution [41] for time dependent diffusion towards an inlaid disc electrode. Thus, we have found taking $n = 3$ and matching the first two terms in each of the asymptotic expressions (24) and (25) to be particularly convenient because it gives a simple expression with constants and is an excellent approximation to the exact solution over the entire range of $K$:

$$\phi \approx 3 \left[ 1 + \frac{6}{\pi} \sqrt{K} + \frac{3\pi^3}{2^6} K + \left( \frac{\pi}{4} \sqrt{K} \right)^3 \right]$$

(31)

In fact this expression yields a maximum error of 0.26 % at $K \approx 3$ (see Fig. 1) and obviously converges to the exact values at both high and low $K$.

2.3.4 Shifted “de facto” solution

By applying the relationship mentioned in section 2.3.1 (and discussed in detail in reference [5] ) relating the steady-state EC’ current with the transient current for the same system but with no reaction [19, 40] to the “de facto” solution [41] for the transient current at the inlaid disc electrode, one obtains:

$$\phi = 0.7854 + 0.4431 \sqrt{K\pi} + 0.4292 K \int_0^\infty u e^{-\frac{0.3915}{u} - Ku} \, du$$

(32)

This expression becomes difficult to evaluate for very low $K$ (e.g. $K < 0.05$), where it is expected to progressively merge with the low $K$ asymptotic expression (24) according to the derivation of the "de facto" expression. The maximum error of expression (32) occurs at $K = 0.64$ (0.37%). Equation (24) behaves in a manner similar to (31), as can be seen in Fig 1.
3. Recessed electrode

We now turn to the recessed microdisc and follow the same development in the discussion as section 2.

3.1 Exact solution

Let $<\theta>$ be the average normalised concentration over a disc of unit radius coaxial with the $z$-axis at a given $z$ (so that each disc is parallel to the electrode surface and above it) then

$$<\theta> = \frac{\int_0^1 \theta 2\pi r dr}{\int_0^1 2\pi r dr} = 2 \int_0^1 \theta r dr$$  \hspace{1cm} (33)

By multiplying the differential eqn. (9) by $2r$ and integrating between $r = 0$ and $r = 1$, within the recess (that is using boundary condition (13)) one obtains

$$\frac{d^2 <\theta>}{dz^2} = K <\theta> \hspace{1cm} z < L$$  \hspace{1cm} (34)

whose solution, taking into account the boundary condition in equation (14), is

$$<\theta> = \cosh(\sqrt{K}z) + A_0 \sinh(\sqrt{K}z) \hspace{1cm} z < L$$  \hspace{1cm} (35)

where $A_0$ is a constant that could be found from a boundary condition at $z = L$. If the known boundary condition is the value $<\theta>|_{z=L}$ of the average concentration at the recess mouth, by differentiation of (35) at the electrode surface one finds

$$\left. \frac{d <\theta>}{dz} \right|_{z=0} = \sqrt{K} <\theta>_{z=L} - \frac{\cosh(\sqrt{KL})}{\sinh(\sqrt{KL})}$$  \hspace{1cm} (36)

which yields the flux

$$\phi = -\frac{\pi}{4} \left. \frac{d <\theta>}{dz} \right|_{z=0} = \frac{\pi}{4} \sqrt{K} \frac{\cosh(\sqrt{KL}) <\theta>_{z=L}}{\sinh(\sqrt{KL})}$$  \hspace{1cm} (37)

Moreover, through separation of variables [25] the concentration within the recess can be written
\[ \theta(r, z < L) = \cosh(\sqrt{K} z) + A_0 \sqrt{K} \sinh(\sqrt{K} z) + \sum_{s=1}^{\infty} A_s \sinh(\sqrt{K + x_s^2} z) J_0(x_s r) \]  

(38)

where \( A_s \) are coefficients to be determined and \( x_s \) is the \( s \)th positive root of \( J_1(x) = 0 \).

For \( z > L \), the semi-infinite half space outside the recess [25, 42], a series solution can be written in terms of Bessel functions (see appendix A). By matching the value of the concentration and its \( z \)-derivative (using the series solutions for the region within the recess and outside the recess) at any point across the mouth of the recess (where \( z = L \)), one obtains the following system of linear equations in the unknown coefficients \( a_m \):

\[
\sum_{m=0}^{\infty} (\Omega_{m,0} + 2S_{m,0}) a_m = \frac{2}{\sqrt{\pi}} \frac{1}{\cosh(\sqrt{K} L)} \cdot \frac{4 \tanh(\sqrt{K} L)}{\pi \sqrt{K}} a_0 \]

(39)

\[
\sum_{m=0}^{\infty} (\Omega_{m,n} + 2S_{m,n}) a_m = 0 \quad (n > 0)
\]

where

\[
S_{m,n} = \sum_{i=1}^{\infty} \frac{\tanh(\sqrt{K + x_s^2} L) J_{2m+1/2}(x_s) J_{2m+1/2}(x_s)}{x_s \sqrt{K + x_s^2} J_0(x_s)}
\]

(40)

By taking \( L = 0 \) in (39), one recovers (19) for the inlaid disc.

The current can be found from (A-14) as

\[
\phi = \frac{\pi}{2} \frac{a_0}{\cosh(\sqrt{K} L)} + \pi \sqrt{K} \tanh(\sqrt{K} L)
\]

(41)

which reduces to the expression for the inlaid disc, equation (21), for \( L \to 0 \). As \( L \to \infty \), equation (41) collapses to the well-known [43] “linear” (corresponding to one-dimensional semi-infinite diffusion):

\[
\phi = \frac{\pi}{4} \sqrt{K}
\]

(42)

Although equation (39) is exact, the accuracy to which it can be evaluated will depend on the number of terms actually taken in the truncation of the infinite sums. Special care is necessary if one seeks more than 1% accuracy or one is dealing with shallow recesses \( L < \)
0.1) because of the slow convergence of the series $S_{m,n}$. For this reason in Appendix A.4 we give a procedure for computing $S_{m,n}$ more accurately than the direct sum. In Table 3 the convergence process is shown, allowing us to estimate an accuracy of 0.1%. In a PC Pentium II it takes around 80 s to compute the flux with a 9 x 9 matrix ($m=n=8$ in (19)) with $s$ (in (A-16), with previously computed $R_{m,n}$ values) up to 50 and $i$ (in (A-15)) up to 100.

### 3.2 Simulation results

Simulation data for the recessed microdisc under pseudo first-order kinetics have been obtained using the program described elsewhere [3] and extended to incorporate the EC′ kinetics [5]. For the inlaid electrode (whose results are presented in section 2.2) and for the recessed electrode (presented here), Finite Element Method programs were written in Fortran 77 and run on an IBM RS6000 RISC workstation with 128Mb memory yielding a typical execution time of ca. 10 min. The simulation has been validated by checking that the computed currents differ by less 0.1% with the currents obtained using the dual solution (39). As can be seen in Table 4, both methods yield practically identical values.

The steady-state concentration profiles for $L = 0.5$ (see Fig. 2) show how the diffusion becomes more planar as the depth within the recess increases and as $K$ increases. For $K = 100$ all of the concentration contours for A (i.e. $c_A/c_A^* < 0.95$) are contained within the recess, where a steady-state is set up by the reaction kinetics, rather than the diffusion-maintained steady-state characteristic of a non-reacting species diffusing towards an inlaid microdisc electrode or a hemispherical microelectrode.

For low $K$ values (see lefthand side in Fig. 3 or the lower continuous line in Fig. 4), the steady state flux decreases with increasing $L$ as expected from the hindered diffusion which arises when the electrode is more deeply recessed. For sufficiently small values of $K$, the flux becomes practically independent of $K$ and tends to the value obtained for recessed electrodes without coupled reaction [3], [25].

For large values of $K$, regardless of recess depth $L$, the normalised current tends to a fixed value for each $K$ (see righthand side of Fig. 3) given by the expression in equation (42) for "linear" diffusion which corresponds to the limiting straight line in the plot. This is because the pseudo first order reaction now occurs predominantly very close to the electrode.
surface and so the actual recess depth becomes unimportant. B is mainly contained within the recess and so the concentration profile is practically planar.

For intermediate values of $K$, the flux depends on both $L$ and $K$ and switches between being independent of $K$ at low values of $K$ and increasing linearly with $\sqrt{K}$ for large $K$ (see Fig. 3).

### 3.3 Approximate expressions

In this section we develop a number of approximate expressions based on different approximate treatments of the recessed disc.

#### 3.3.1 Uniform concentration at the recess mouth

An approximation to the current can be obtained by using the same procedure followed by Bond et al. [32] for recessed electrodes without homogeneous reaction. This consists of matching the fluxes at the mouth of the recess (that is the flux of material arriving from the semi-infinite half space with the flux of material diffusing into the recess) by assuming a uniform concentration, say $\theta_m$, along $z = L$. Obviously, then, the average concentration is also $\theta_m$ and the flux into the recess can be obtained starting with the differentiation of equation (35):

$$
\frac{d < \theta >}{dz} \bigg|_{z=L} = \sqrt{K} \frac{\theta_m \cosh(\sqrt{KL}) - 1}{\sinh(\sqrt{KL})}
$$

Once a uniform concentration across the mouth of the recess is assumed, the flux can be calculated by simply re-scaling the inlaid disc solution given by eqn. (21) with $a_0$ obtained from the system of linear equations (19). However, this is cumbersome and a much simpler final result can be developed if we use a convenient approximate expression for $\theta_m$. We can estimate the incoming flux at $z = L$ by re-scaling the semi-analytical approximation (31): we multiply it by $\theta_m$ to take into account that the previous boundary condition $\theta = 1$ (see eqn. (14) ) is now $\theta = \theta_m$. Setting this equal to the departing flux calculated with eqn. (43), we find

$$
\theta_m \left[ 1 + \frac{6}{\pi} \sqrt{K} + \frac{3\pi}{2^6} K \left( \frac{\pi}{4} \sqrt{K} \right)^3 \right] = -\frac{\pi}{4} \sqrt{K} \left( \theta_m \cosh(\sqrt{KL}) - 1 \right)
$$

Isolating $\theta_m$ and substituting $<\theta>_{z=L}$ for it in (37), the dimensionless current can then be approximated as:
Steady State currents...

\[ \phi = \frac{\pi}{4} \sqrt{K} \left( \coth\left(\sqrt{KL}\right) - \frac{2\pi\sqrt{K}}{\pi\sqrt{K} \sinh\left(2\sqrt{KL}\right) + 4\left(1 + \frac{6}{\pi} \sqrt{K} + \frac{3\pi^3}{2} K + \left(\frac{\pi}{4}\right)^3 \cosh\left(2\sqrt{KL}\right) - 1\right)} \right) \]

(45)

As \( L \) increases, equation (45) (depicted with symbol o in Fig. 4) approaches the linear asymptotic behaviour predicted by eqn. (42) (depicted by a dashed line in Fig. 4). As \( L \) tends to zero, eqn. (45) tends to eqn. (31) which is accurate to better than 0.26%. Thus, eqn. (45) tends to reasonably correct values at extreme values of \( L \) regardless of the value of \( K \); and, for each \( K \), exhibits a maximum error from the value obtained with the dual approach at intermediate \( L \). The maximum errors have been found to be: \( K = 0.5, L = 0.025, \) error = 3.55%; \( K = 1, L = 0.1, \) error = 3.52%; \( K = 10, L = 0.05, \) error = 2.28%. The behaviour of eqn. (45) for \( K = 1 \) and \( K = 10 \) is shown in Fig. 4 (symbol o) and in Table 4.

3.3.2 A finite cylindrical region equivalent to the recess and semi-infinite half space region

Equations (34) and (35) indicate that, within the recess, the average concentration behaves exactly as the solution for planar diffusion and reaction with Dirichlet boundary conditions at two points separated by a finite distance: that is \( \langle \theta \rangle = 1 \) at \( z = 0 \) and \( \langle \theta \rangle = \theta^a \) at \( z = L \). Extrapolating this behaviour beyond the recess (see dashed line in Fig. 5) one finds that at some finite distance \( \zeta \) from the mouth of the recess the extrapolated average concentration reaches zero. Then, if \( \zeta \) is known, we only need the solution of equation (34) (i.e. use eqn. (35)) with boundary conditions given by \( \langle \theta \rangle = 1 \) at \( z = 0 \) and \( \langle \theta \rangle = 0 \) at \( z = L + \zeta \). Analogously to the derivation of eqn. (37), the normalised current can be calculated as:

\[ \phi = \frac{\pi}{4} \sqrt{K} \coth\left(\sqrt{K(L+\zeta)}\right) \]

(46)

Thus we can think of two systems producing the same flux: i) the original system with a recess (\( z<L \)) and a half-space (\( z>L \)) and ii) an equivalent system whose domain is a cylinder (with unity radius and height \( L+\zeta \)) and where the prescribed boundary condition is \( \langle \theta \rangle = 0 \) at \( z = L + \zeta \). Both systems produce the same flux because \( \zeta \) is chosen so that the average \( \langle \theta \rangle \) is the same for \( z<L \) and \( \phi \) can be computed from the derivative of \( \langle \theta \rangle \) at \( z=0 \) (see eqn. (37)
If \( K = 0 \) and \( L = 0 \), then we know that \( \zeta = \pi/4 \), by simply matching the limit of equation (46) when \( K \) tends to 0 and the expected value \( \phi=1 \). However in general, we need to find an approximate expression for \( \zeta \). We know that \( \zeta > 0 \), because at the mouth of the recess there is a (mathematically) non-zero concentration due to semi-infinite diffusion from the half space. As \( K \) increases (for a fixed value of \( L \)), the average concentration decreases more rapidly within the recess and so \( \zeta \) decreases. As \( L \) increases (for a fixed value of \( K \)), the average concentration decreases more slowly as \( z \) increases and so \( \zeta \) increases. This last relationship can be easily understood for the particular case of \( K = 0 \) [25], since the average concentration decreases linearly within the recess and the intersection with the abscissa (which determines \( \zeta \)) is moved further away as \( L \) increases.

We can obtain an estimate of \( \zeta \) by separating out its dependence on \( L \) and \( K \). Since the parameter \( \alpha \) introduced by Brunn et al. is simply \( 4\zeta/\pi \), we can use the approximate expression given in equation 2.32 of Brunn et al.[25] to estimate the variation of \( \zeta \) with \( L \). On the other hand, we have fitted the values arising when \( L = 0 \) to a simple expression in \( \sqrt{K} \), rounding the two adjustable parameters to 0.8 and 3/4. Thus, we propose the following approximation

\[
\zeta = \frac{\pi}{4} \left( 1 + \frac{1}{21.4479 + 0.2564 \coth(0.3439 L)} \right) \frac{1}{1 + 0.8 \sqrt{K}} \tag{47}
\]

Using equation (46) with equation (47) gives a good estimate of \( \phi \) for values of \( L \) and \( K \) which we have examined. The largest errors were found for: \( L = 0.025, K = 10 \), error = 1.04%; \( L = 0.075, K = 0.01 \), error = 1.28%; \( L = 0.075, K = 5 \), error = 1.20%; \( L = 0.2 K = 1 \), error = 0.95%; \( L = 1, K = 0.5 \), error = 0.22%. As seen in Fig. 4, the accuracy improves for large \( L \), this is because \( \coth(\sqrt{K}L) \) is practically 1 and the actual value of \( \zeta \) is relatively unimportant in equation (46). Similar reasoning shows that the approximation in equation (47) is also very accurate for large \( K \). We can interprete both cases (large \( K \) or large \( L \)) physically as the reaction being mainly confined within the recess so that the flux approaches
the planar expression (42). It can be seen in Fig.4 (+ symbols) that, for \( K = 1 \) and \( K = 10 \), equation (46) with equation (47) is clearly a better approximation than the assumption of a uniform concentration across the recess mouth, equation (45).

**Conclusions**

An accurate steady state current for the inlaid disc electrode can be easily obtained (for \( K < 100 \)) by means of the solution of the linear system of equations (19) and by applying the simple expression (21) for the dimensionless current. This allows us to estimate the magnitudes of the errors involved in our simulation and in any approximate expressions. By choosing the lowest value from Phillips’ expressions, equations (24) and (25), one obtains at least 2.33% accuracy in the computed current. By using Rajendran and Sangaranarayanan’s asymptotic expressions, switching from (26) to (27) at \( K = 3 \), one ensures 0.23% of absolute value in accuracy. Their Padé approximation (28) can be consider as the "de facto" solution for this problem, as its error is less than 0.01%. For \( K < 2 \), the zero order approach, equations (29) and (30), yields better approximations than the asymptotic low-\( K \) expression, equation (24). The polynomial approximation, equation (31), and the shifted de facto expression, equation (32), are valid over the whole range of \( K \), with 0.37% and 0.26% accuracy respectively. The advantage of the former expression is that it is easier to compute. In conclusion, the exact solution for the inlaid disc electrode is available as well as several approximations for the current, together with the assessment of their accuracy.

The exact analytical solution for the recessed microdisc has been developed as an extension of the solution for the inlaid electrode, based on Tranter’s method. The key point is the matching of the values of the concentrations and the local fluxes at each point across the recess mouth. The elements of the matrix in the linear system of equations (39) are composed of the integrals, \( \Omega_{mn} \), and the series, \( S_{m,n} \), both of which can be accurately computed as described in Appendix A. The dual solution (i.e. the numerical values obtained from the calculation of (39)) and the Finite Element Method simulation agree satisfactorily. For large values of the dimensionless kinetic constant \( K \), the reaction is confined within the recess. The approximate expression, equation (45), obtained by assuming a uniform concentration across the recess mouth, is accurate to 3.6% for the values examined. Another approximate
expression for the flux can be obtained by estimating an equivalent distance, ζ, of a finite cylindrical region with Dirichlet boundary conditions which should be added to the depth of the recess in order to produce the same profile for the average concentration within the recess. The error from this approximation, i.e. using equation (47) together with (46), is estimated to be less than 2%.

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Appendix A: Analytical Solution of the Steady State for the Pseudo-First-Order EC' mechanism at Recessed and Inlaid Microdisc Electrodes

A.1 The dual integral formulation:

The following derivation for the recessed electrode includes the inlaid electrode as the particular case \( L = 0 \).

If tilde denotes the zero-order Hankel transform\[36\]

\[ \tilde{\theta} \equiv \int_0^\infty r \theta J_0(\lambda r) \, dr \] (A-1)

then, the transform of the steady state diffusion equation (9) is

\[ \frac{d^2 \tilde{\theta}}{dz^2} = \left( \lambda^2 + K \right) \tilde{\theta} \] (A-2)

whose solution in the semi-infinite half space, taking into account the boundary condition of semi-infinite diffusion (16), is

\[ \tilde{\theta} = f_2(\lambda) \, e^{-z\sqrt{\lambda^2 + K}} \] (A-3)

Through the inversion theorem \[36\], we find

\[ \theta = \int_0^\infty \lambda f_2(\lambda) \, e^{-z\sqrt{\lambda^2 + K}} J_0(\lambda r) \, d\lambda \] (A-4)

where \( f_2(\lambda) \) must be found from the boundary conditions at \( z = L \).

Redefining the unknown function as

\[ f(\lambda) \equiv \lambda \sqrt{\lambda^2 + K} \, f_2(\lambda) e^{-z\sqrt{\lambda^2 + K}} \] (A-5)

one converts the differential equation in the semi-infinite half space into the dual integral equation:

\[ z = L \quad r \leq 1 \quad \int_0^\infty \frac{f(\lambda) J_0(\lambda r)}{\sqrt{\lambda^2 + K}} \, d\lambda = \theta(r, L) \] (A-6)

\[ z = L \quad r > 1 \quad \int_0^\infty f(\lambda) J_0(\lambda r) \, d\lambda = 0 \]
Following Tranter’s method [22, 23, 26, 27, 36, 37], we expand

\[
f(\lambda) = \lambda^{1-k} \left\{ a_0 J_k(\lambda) + a_1 J_{2+k}(\lambda) + \ldots \right\} = \lambda^{1-k} \sum_{m=0}^{\infty} a_m J_{2m+k}(\lambda)
\]

where \( k > 0 \) is an arbitrary parameter. The results presented in the body of this paper have been obtained with \( k = 1/2 \). \( f(\lambda) \) chosen in this way satisfies the second equation in (A-6) because of the orthogonality of the Bessel functions.

Now, in the case of the inlaid electrode, we can state \( \theta(r,0) = 1 \) and then determine the unknown coefficients \( a_m \) in a straightforward manner from the infinite system of linear equations (19). When \( L > 0 \), \( \theta(r,L) \) can be expressed in terms of the new unknown coefficients \( A_s \), according to eqn. (38). In order to obtain a relationship between \( a_m \) and \( A_s \), we impose the continuity of the derivative of \( \theta \) at the mouth of the recess [44-46], using the second relationship in (A-6) and (38):

\[
-\int_0^r f(\lambda) J_0(\lambda r) \, d\lambda = \sqrt{K} \sinh(\sqrt{K}L) + A_0 \sqrt{K} \cosh(\sqrt{K}L) + \sum_{s=1}^{\infty} A_s \sqrt{K+x_s^2} \sinh(\sqrt{K+x_s^2}L) J_0(x_s r)
\]

(A-8)

Using the expansion (A-7) for \( f(\lambda) \), multiplying by \( r J_0(x_s r) \) and integrating between \( r = 0 \) and \( r = 1 \), one can finally isolate a particular \( A_s \):

\[
A_s = \frac{-2}{x_s^k \sqrt{K+x_s^2} \cosh(\sqrt{K+x_s^2}L) J_0^2(x_s)} \sum_{m=0}^{\infty} a_m J_{2m+k}(\lambda)
\]

(A-9)

To find \( A_0 \) we multiply (A-8) by \( r \) and integrate between \( r = 0 \) and \( r = 1 \):

\[
A_0 = \frac{-1}{\sqrt{K} \cosh(\sqrt{K}L) 2^{k-1} \Gamma(k+1) \tanh(\sqrt{K}L) a_0}
\]

(A-10)

where \( \Gamma \) stands for the Gamma function.

Returning now to the condition of continuity of \( \theta \) at \( z = L \), Tranter’s method implies multiplying by \( r (1-r^2)^{k-1} F_1(-n,k+n,1,r^2) \) (where \( F_1 \) is the Gauss hypergeometric function and \( n = 0, 1, 2.. \)) and integrating between \( r = 0 \) and \( r = 1 \). This transforms the first
expression in (A-6) into

$$\sum_{m=0}^{\infty} a_m \int_0^{\infty} J_{2m+k}(\lambda) J_{2n+k}(\lambda) d\lambda = \frac{\cosh(\sqrt{KL}) + A_0 \sqrt{K} \sinh(\sqrt{KL})}{k^{2k-1} \lambda^{2k-1} + K} \delta_{m0}$$

\[ (A-11) \]

where \( \delta_{m0} \) is Kronecker’s delta.

Using (A-9) for \( A_s \), (A-10) for \( A_0 \), eqn. (A-11) can be rearranged into

$$\sum_{m=0}^{\infty} a_m \left[ \int_0^{\infty} \frac{J_{2m+k}(\lambda) J_{2n+k}(\lambda)}{\lambda^{2k-1} + K} d\lambda + 2 \sum_{s=1}^{\infty} \frac{\tanh(\sqrt{K + x_s^2} L) J_{2n+k}(x_s) J_{2m+k}(x_s)}{x_s^{2k-1} + K + x_s^2} \right] d\lambda = \frac{\delta_{m0} \tanh(\sqrt{KL}) a_m}{k^{2k-1} \Gamma(k) \cosh(\sqrt{KL})} - \frac{\delta_{m0} \tanh(\sqrt{KL}) a_m}{\sqrt{Kk^{2k-1}} \Gamma(k) \Gamma(k + 1)}$$

\[ (A-12) \]

Taking \( k = 1/2 \), this expression reduces to equation (39) for the recessed electrode and equation (19) for the inlaid electrode.

Apart from the flux, once \( f(\lambda) \) is known (through the coefficients \( a_m \)), the values of the normalised concentration or the flux lines can be derived [26, 27].

### A.2 Flux Computation

Using definitions (18) and (33), and the solution (35) within the recess:

$$\phi = -\frac{\pi}{2} \int_0^{\partial \theta}(\frac{\partial \theta}{\partial z}) r \, dr = -\frac{\pi}{4} \left( \frac{d<\theta>}{dz} \right)_{z=0} = -\frac{\pi}{4} \sqrt{K} A_0$$

\[ (A-13) \]

Replacing \( A_0 \) according to (A-10), one obtains

$$\phi = \frac{\pi}{2^{k+1} \Gamma(k + 1) \cosh(\sqrt{KL})} a_0 + \frac{\pi}{4} \sqrt{K} \tanh(\sqrt{KL})$$

\[ (A-14) \]

Taking \( k = 1/2 \), this yields equation (41), which for \( L = 0 \) reduces to equation (21).
A.3 Computation of $\Omega_{m,n}$

For moderate values of $K$ ($K<100$), a very efficient way of computing $\Omega_{m,n}$ takes advantage of a result by Bouwkamp [47]:

$$\int_0^\infty J_{2m+1/2}(\lambda) J_{2n+1/2}(\lambda) \frac{d\lambda}{\sqrt{\lambda^2 + K}} = \sum_{i=0}^\infty \frac{1}{2} (-1)^{n-m+i} \Gamma^2\left(\frac{i+1}{2}\right) K^{i/2}$$

\begin{align*}
\Omega_{m,n} &= \frac{1}{\sqrt{\lambda^2 + K}} \int_0^\infty J_{2m+1/2}(\lambda) J_{2n+1/2}(\lambda) \frac{d\lambda}{\sqrt{\lambda^2 + K}} \\
&= \sum_{i=0}^\infty \frac{1}{2} (-1)^{n-m+i} \Gamma^2\left(\frac{i+1}{2}\right) K^{i/2} \\
&= \frac{1}{2} \sum_{i=0}^\infty (-1)^{n-m+i} \Gamma^2\left(\frac{i+1}{2}\right) K^{i/2} \\
&= \frac{1}{2} \sum_{i=0}^\infty (-1)^{n-m+i} \Gamma^2\left(\frac{i+1}{2}\right) K^{i/2}
\end{align*}

(A-15)

Usually 100 terms have been used to computed $\Omega_{mn}$ in (A-15). Convergence is achieved with more difficulty the larger the value of $K$ and requires 1000 terms around $K=100$. For higher $K$, the computation of the integrals becomes cumbersome and resort to the asymptotic expressions (25) or (42) should be more convenient.

A.4 Computation of the series $S_{m,n}$

To improve the convergence of $S_{m,n}$, given by (40), we write:

$$S_{m,n} = \sum_{s=1}^\infty \left\{ x_s \tan\left(\sqrt{K+x_s^2 L}\right) - 1 \right\} J_{2m+1/2}(x_s) J_{2n+1/2}(x_s) \frac{x_s^2}{x^2_s J_0^2(x_s)} + R_{m,n}$$

(A-16)

where

$$R_{m,n} = \sum_{s=1}^\infty \frac{J_{2m+1/2}(x_s) J_{2n+1/2}(x_s)}{x_s^2 J_0^2(x_s)} = \sum_{s=1}^\infty \frac{J_{2m+1/2}(x_s) J_{2n+1/2}(x_s)}{x_s^2 J_0^2(x_s)}$$

(A-17)

because $J_0(x_s) = -J_2(x_s)$ arising from $J_1(x_s) = 0$. There is only need to consider the case $m \geq n$, because of the symmetry of $R_{m,n}$. We have noticed that it is possible to apply a result by Tranter [37, 48]:

$$T_{m,n,k} = \sum_{s=1}^\infty \frac{J_{2\nu+1/2}(x_s) J_{2\nu+1/2}(x_s)}{x_s^2 J_0^2(x_s)} = \frac{\delta_{mn}}{8} + (-1)^{m+n} \sin\left(\frac{k\pi}{2}\right) \int \frac{K_s(t)}{t^2} I_1(t) I_{2\nu+1/2}(t) I_{2\nu+1/2}(t) dt$$

(A-18)

when $m$ and $n$ are positive integers and $k > -1$. Then

$$R_{m,n} = T_{m-1,n-1,1/2}$$

$\neq 0$ and $m \neq 0$

(A-19)

$$R_{0,n} = \frac{3}{4n+1} \left( T_{0,n-1,1/2} - T_{0,n,1/2} - T_{0,n-1,1/2} \right)$$

$\neq 0$

(A-20)
Steady State currents...

\[ R_{0,0} = 9 \sum_{j=1}^{\infty} \frac{J_{3/2}(x_j)}{x_j^3} I_{3/2}'(x_j) - \frac{6}{5} \left( T_{0,0,-1/2} + T_{0,1,-1/2} \right) + R_{0,1} \]  \hspace{1cm} (A-21)

Some of the actual numerical values of \( R_{m,n} \) used in the computations were: \( R_{0,0} = 0.0549607 \); \( R_{1,0} = -0.0826958 \); \( R_{2,0} = 0.0174472 \); \( R_{3,0} = -0.00787858 \); \( R_{1,1} = 0.128295 \); \( R_{2,1} = -0.0126471 \); \( R_{3,1} = 0.00678257 \); \( R_{2,2} = 0.0636223 \); \( R_{3,2} = -0.00518736 \).

For \( n \) or \( m \) greater than 5, the integral in (A-18) can converge very slowly and it is convenient to take into account the asymptotic behaviour of the Bessel functions of the second kind and approximate:

\[ \int_0^{t_0} \frac{K_{\nu}(t)}{t_1(t)} I_{2s+2\nu k}(t) I_{2s+2\nu k}(t) dt = \int_0^{t_0} \frac{K_{\nu}(t)}{t_1(t)} I_{2s+2\nu k}(t) I_{2s+2\nu k}(t) dt + \frac{1}{2t_0} \]  \hspace{1cm} (A-22)

where \( t_0 \) is a sufficiently high limit for the asymptotic behaviour to apply to the required accuracy. Obviously, for extremely shallow recesses (such as \( L \) below 0.001, not considered here) other strategies should be required for the practical computation of \( S_{m,n} \).
### Appendix B: Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Eqn. involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>(regenerated) electroactive species</td>
<td>(1)</td>
</tr>
<tr>
<td>$A_0$, $A_s$</td>
<td>Coefficients in series solution within the recess</td>
<td>(35), (38)</td>
</tr>
<tr>
<td>$a$</td>
<td>(dimensional) electrode radius</td>
<td>(10)</td>
</tr>
<tr>
<td>$a_m$</td>
<td>$m^{th}$ coefficient of the unknown function expansion</td>
<td>(19), (A-7)</td>
</tr>
<tr>
<td>B</td>
<td>Reacting species</td>
<td>(1)</td>
</tr>
<tr>
<td>$c_X$</td>
<td>Concentrations of species X (A or B)</td>
<td>(2)</td>
</tr>
<tr>
<td>$D_X$</td>
<td>Diffusion coefficient of species X (A or B)</td>
<td>(2), (6)</td>
</tr>
<tr>
<td>$E$</td>
<td>Electrode potential</td>
<td>(5)</td>
</tr>
<tr>
<td>$f$</td>
<td>Unknown function</td>
<td>(A-5), (A-7)</td>
</tr>
<tr>
<td>$f_2$</td>
<td>Auxiliary unknown function</td>
<td>(A-3)</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant</td>
<td>(18)</td>
</tr>
<tr>
<td>$I$</td>
<td>Dimensional current</td>
<td>(18)</td>
</tr>
<tr>
<td>$I_1$</td>
<td>Modified Bessel function of first kind and first order</td>
<td>(A-18)</td>
</tr>
<tr>
<td>$J_\nu$</td>
<td>Bessel function of order $\nu$</td>
<td>(20), (A-6)</td>
</tr>
<tr>
<td>$k$</td>
<td>Tranter’s arbitrary parameter</td>
<td>(A-7)</td>
</tr>
<tr>
<td>$k_f$</td>
<td>First-order rate constant</td>
<td>(1),(2),(10)</td>
</tr>
<tr>
<td>$K$</td>
<td>Dimensionless kinetic constant</td>
<td>(10)</td>
</tr>
<tr>
<td>$K_1$</td>
<td>Modified Bessel function of second kind and first order</td>
<td>(A-18)</td>
</tr>
<tr>
<td>$L$</td>
<td>Normalised recess electrode depth</td>
<td>(13)</td>
</tr>
<tr>
<td>$m$</td>
<td>Integer generic index</td>
<td>(19), (A-7)</td>
</tr>
<tr>
<td>$n$</td>
<td>Integer generic index</td>
<td>(19)</td>
</tr>
<tr>
<td>$n_e$</td>
<td>Number of electrons exchanged</td>
<td>(1)</td>
</tr>
<tr>
<td>$r$</td>
<td>Dimensionless radial co-ordinate</td>
<td>(9)</td>
</tr>
<tr>
<td>$R_{m,n}$</td>
<td>Auxiliary series</td>
<td>(A-17)</td>
</tr>
<tr>
<td>$s$</td>
<td>Superscript to indicate surface concentration</td>
<td>(5)</td>
</tr>
<tr>
<td>$S_{m,n}$</td>
<td>Series component in the coefficients of the linear</td>
<td>(40)</td>
</tr>
</tbody>
</table>
### Table of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{m,n}$</td>
<td>Auxiliary series</td>
<td>(A-18)</td>
</tr>
<tr>
<td>$x_s$</td>
<td>$s^{th}$ positive root of $J_1(x) = 0$</td>
<td>(38)</td>
</tr>
<tr>
<td>$z$</td>
<td>Dimensionless axial co-ordinate</td>
<td>(9)</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Gamma function</td>
<td>(A-15)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Dimensionless potential</td>
<td>(5)</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Dimensionless concentration</td>
<td>(8)</td>
</tr>
<tr>
<td>$\langle \theta \rangle$</td>
<td>Average dimensionless concentration on a disc of unit radius concentric with, and parallel to, the electrode surface</td>
<td>(33)</td>
</tr>
<tr>
<td>$\theta^m$</td>
<td>Assumed uniform concentration at the recess mouth</td>
<td>(43)</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Equivalent distance in the semi-infinite half space</td>
<td>(46)</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Parameter in Hankel transform</td>
<td>(A-1)</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Dimensionless flux</td>
<td>(18)</td>
</tr>
<tr>
<td>$\Omega_{m,n}$</td>
<td>Integral contribution to the coefficient of $a_m$ in the $n^{th}$ equation of the linear system</td>
<td>(20), (39)</td>
</tr>
</tbody>
</table>

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**Figure Legends**

**Figure 1:** Plot of the percentage of error, with respect to the dual integral solution, equations (19)-(21), in the calculated steady state flux of an inlaid electrode as a function of the dimensionless rate constant, \( K \), for low and intermediate values of \( K \). The solid line represents the finite element simulation results. The broken line represents the semi-analytical polynomial approximation, equation (31). The other results are: × eqn.(24) (low-\( K \) asymptotic behaviour); ◊ eqn. (25) (high-\( K \) asymptotic behaviour); + eqn.(26) (low-\( K \)); − eqn.(27) (high-\( K \)); o eqn. (28) (Padé approximant); • eqn. (29) (zero order approach); Δ eqn. (30) (truncation of zero order); • • • • eqn. (32) (shifted “de facto”).

**Figure 2:** Steady state dimensionless concentration contour plots for species A at an \( L = 0.5 \) recessed microdisc, simulated using the Finite Element Method for various values of the dimensionless constant \( K \) and with \( D_A = D_B \). The concentration of A at the electrode surface is zero and the contours are drawn at 10 even increments (0.085 each time) from 0.100 to 0.950.

**Figure 3:** Double logarithmic plot of the dimensionless current, \( \phi \), as a function of the dimensionless kinetic constant, \( K \), for various recess depths (\( L \)) (computed with either the Finite Element Method or eqn.(39))

**Figure 4:** Plot of the dimensionless steady state current, \( \phi \), as a function of the recess depth, \( L \), calculated for \( K = 1 \) and \( K = 10 \). The solid line represents very accurate values (computed with either the finite element method or eqn.(39)), the points o were calculated assuming a uniform concentration across the recess mouth (eqn. (45)); the points + were calculated using the approximation of a finite cylindrical region equivalent to the recess and semi-infinite half space (eqn. (46)) with a total height \( Z = L + \zeta \) estimated using eqn (47). The broken represents the results of the linear approximation, eqn. (42).

**Figure 5:** Plot of the average concentration, \( <\theta> \) from eqn. (33), on a disc of unit radius (coaxial with, and parallel to, the electrode surface) at different heights, \( z \), above the recessed electrode, calculated for \( L = 1 \) and \( K = 1 \). The dashed line shows the extrapolation of the behaviour inside the recess for \( z > L \). Any estimation of \( \zeta \) leads to an estimation of the...
current through eqn. (46).

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<th>$m=n=2$</th>
<th>$m=n=3$</th>
<th>$m=n=4$</th>
<th>$m=n=5$</th>
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<td>2.5122</td>
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<td>$i=50$</td>
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<td>3.3223</td>
<td>3.3223</td>
<td>3.3223</td>
<td>3.3223</td>
<td>3.3223</td>
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<tr>
<td>$i=100$</td>
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<td>3.3222</td>
<td>3.3223</td>
<td>3.3223</td>
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</table>

Table 1: Convergence of the “dual” steady-state flux for the inlaid electrode with $K=10$.

Each column corresponds to a different truncation of the linear system (19) to the indicated maximum value of $m$ and $n$. In each row $Q_{m,n}$ has been computed using (A-15) with the index up to the indicated $i$ value.

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<tr>
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<tbody>
<tr>
<td>$10^{-4}$</td>
<td>1.006</td>
<td>1.006</td>
<td>1.006</td>
<td>/</td>
<td>1.006</td>
<td>/</td>
<td>1.006</td>
<td>1.006</td>
<td>1.006</td>
<td>1.006</td>
<td>1.010</td>
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<td>$10^{-3}$</td>
<td>1.020</td>
<td>1.025</td>
<td>1.020</td>
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<td>/</td>
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<td>$10^{-2}$</td>
<td>1.064</td>
<td>1.079</td>
<td>1.064</td>
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<td>1.066</td>
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<td>$10^{-1}$</td>
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<td>1.248</td>
<td>1.209</td>
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<td>/</td>
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<td>1.208</td>
<td>1.208</td>
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<td>1.209</td>
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<tr>
<td>1</td>
<td>1.637</td>
<td>1.785</td>
<td>1.709</td>
<td>1.767</td>
<td>1.689</td>
<td>1.718</td>
<td>1.689</td>
<td>1.685</td>
<td>1.692</td>
<td>1.695</td>
<td>1.689</td>
<td>1.682</td>
<td>1.689</td>
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<tr>
<td>$10^4$</td>
<td>64.662</td>
<td>79.540</td>
<td>/</td>
<td>79.327</td>
<td>/</td>
<td>79.327</td>
<td>79.328</td>
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<td>79.328</td>
<td>79.323</td>
<td>79.088</td>
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Table 2: Theoretical and simulated for steady state fluxes in an inlaid disc electrode for various pseudo first-order rate constants $K$. 

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### Table 3: Convergence of the “dual” steady-state flux for the recessed electrode with $L=1$ and $K=1$ using (39) and (A-16). In all cases $\Omega_{m,n}$ has been computed using (A-15) with the index $i$ up to 100. The maximum $s$ index used in (A-16) is given in the column heading. Each row corresponds to a different truncation of the linear system (39) to the indicated maximum value of $m$ and $n.$

<table>
<thead>
<tr>
<th>$m=n$</th>
<th>$s=3$</th>
<th>$s=5$</th>
<th>$s=10$</th>
<th>$s=50$</th>
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<tr>
<td>2</td>
<td>0.86107</td>
<td>0.86107</td>
<td>0.86107</td>
<td>0.86107</td>
</tr>
<tr>
<td>4</td>
<td>0.86119</td>
<td>0.86119</td>
<td>0.86119</td>
<td>0.86119</td>
</tr>
<tr>
<td>6</td>
<td>0.86121</td>
<td>0.86121</td>
<td>0.86121</td>
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<td>8</td>
<td>0.86121</td>
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<td>0.86121</td>
<td>0.86121</td>
<td>0.86121</td>
<td>0.86121</td>
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</tbody>
</table>

### Table 4: Steady state fluxes for recessed electrodes as computed from different approaches for selected values of $K$ and $L.$ The column labelled “dual” has been computed using coefficients up to $a_8$ in (39) and roots up to $x_{50}$ in (A-16).

<table>
<thead>
<tr>
<th>$K$</th>
<th>$L$</th>
<th>Dual</th>
<th>Finite Element Method</th>
<th>Eq. (45)</th>
<th>Eq. (46)&amp;(47)</th>
<th>Linear (42)</th>
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<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>1.408</td>
<td>1.408</td>
<td>1.458</td>
<td>1.420</td>
<td>0.785</td>
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<tr>
<td>1</td>
<td>1</td>
<td>0.861</td>
<td>0.861</td>
<td>0.863</td>
<td>0.863</td>
<td>0.785</td>
</tr>
<tr>
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<td>2.841</td>
<td>2.841</td>
<td>2.900</td>
<td>2.870</td>
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<tr>
<td>10</td>
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</table>
References


Fig 1
Fig 4