



# Double potential step chronoamperometry at a microband electrode: Theory and experiment



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## ABSTRACT

Numerical simulation is used to characterise double potential step chronoamperometry at a microband electrode for a simple redox process,  $A + e^- \rightleftharpoons B$ , under conditions of full support such that diffusion is the only active form of mass transport. The method is shown to be highly sensitive for the measurement of the diffusion coefficients of both A and B, and is applied to the one electron oxidation of decamethylferrocene (DMFc),  $DMFc - e^- \rightleftharpoons DMFc^+$ , in the room temperature ionic liquid 1-propyl-3-methylimidazolium bistrifluoromethylsulfonimide. Theory and experiment are seen to be in excellent agreement and the following values of the diffusion coefficients were measured at 298 K:  $D_{DMFc} = 2.50 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  and  $D_{DMFc^+} = 9.50 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ .

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## 1. Introduction

The field of electrochemistry has been transformed by the introduction of microelectrodes [1], which have the properties of enhanced mass transport allowing steady states to be achieved [2], operate with reduced Ohmic drop [3] and often allow a two electrode setup to be employed with a combined reference/counter electrode [4]. The most widely used microelectrode is the microdisc, which is easily fabricated and has well characterised properties [5,6].

The application of microdisc electrodes are many and varied, including using single potential step chronoamperometry to determine the diffusion coefficient of a species of interest,  $D_A$ , and simultaneously either its concentration,  $c_A$ , or the number of electrons transferred,  $n$ , provided one of these two parameters is known [7]. In a single step chronoamperometry experiment, the potential applied to the working electrode is stepped from a value where no reaction occurs, to one where reduction (or oxidation) occurs at a mass transport controlled rate. The well established Shoup–Szabo equation then describes the current measured within 0.6% error [8]:

$$i = 4nFc_A D_A r_e f(\tau) \quad (1)$$

where

$$f(\tau) = 0.7854 + 0.4432\tau^{-0.5} + 0.2146 \exp(-0.3912\tau^{-0.5}) \quad (2)$$

and

$$\tau = \frac{D_A t}{r_e^2} \quad (3)$$

where  $i$  is the measured current (A),  $F$  is the Faraday constant and  $r_e$  is the radius of the microelectrode (m). The change in the current's dependency on  $D_A$  (from  $\sqrt{D_A}$  at short times to linearly dependent at long times), and the direct proportionality of the current to  $nc_A$  at all times, allows both  $D_A$  and the product  $nc_A$  to be determined by fitting of the Shoup–Szabo equation to experimental data. A knowledge of either  $n$  or  $c_A$  then allows calculation of the final unknown.

Using double potential step chronoamperometry, in conjunction with numerical simulation, this method can be extended to find not only  $D_A$ , but also  $D_B$ , the diffusion coefficient of the other member of the redox couple [9]. In these experiments, the potential is first stepped in the same manner as for single potential step experiments, and held at this reducing potential for a set time,  $t_s$ , before being stepped a second time to a value where the reverse reaction occurs at a mass transport controlled rate, and species B is converted back to species A. Numerical simulations of double potential step experiments can then be used, with  $D_A$ ,  $c_A$  and  $D_B$  as input parameters, and these parameters optimised to obtain a best fit.

In addition to these simple yet powerful techniques, microelectrodes of various geometries have found uses in a wide variety of applications, including weakly supported voltammetry [10] (where their very low Ohmic drop is of great advantage in the study of the effects of migration), generator/collector systems [11],

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electrochemical sensors [12–14], and studies of ionic liquid properties [15,16].

Despite these extensive uses of microelectrodes, investigations of double potential step chronoamperometry have largely confined themselves to microdiscs, except for one case each at spherical [17] and hemispherical [18] electrodes; we can find no report at microband electrodes. This study therefore extends the theory of double potential step chronoamperometry to microband electrodes. Note these electrodes are being manufactured by Nanoflux PTE LTD® [19] and MicruX® [20], have been noted for their ease of construction, cheapness and durability [21], and are finding increasing use in electrochemical sensors.

In addition to these advantages, microband electrodes have emerged as being experimentally useful, and have found steadily increasing use in hydrodynamic voltammetry in a flow cell [22–29], in dual electrode generator–collector mode [30–35], and in impedance spectroscopy [36,37]. One of the key differences in electrochemistry carried out at microbands, as opposed to microdiscs, is the absence of a true steady state in chronoamperometry at microbands [38]. This has the effect that, at all times, the measured current is dependent on both  $D$  and  $\sqrt{D}$ . This lack of a true steady state will make behaviour observed in double potential step chronoamperometry at microbands different to that at microdiscs, and perhaps more useful.

The study of ionic liquids has received a huge amount of attention in recent years (see [39,40] for reviews). Being composed entirely of mobile ions, their intrinsic conductivity removes the need to add any supporting electrolyte to carry out electrochemical experiments. They also have a near zero volatility, and often have a very wide electrochemical window. This has led to their application in electrochemical gas sensors [41], as well as sensors for temperature [41] and humidity [42]. A further property of ionic liquids is that they can show drastic differences between the diffusion coefficients of members of a redox pair, e.g. the factor of 30 difference between the diffusion coefficients of  $O_2$  and  $O_2^-$  in the ionic liquid hexyltriethylammonium bis-((trifluoromethyl)sulfonyl)imide ([N6222][N(Tf)2]) [43]. This is due to the extremely strong ionic interactions hindering the movement of charged species. This large difference between diffusion coefficients in ionic liquids necessitates accurately measuring both of them if their electrochemistry is to be fully understood, and so performing double potential step chronoamperometry in the solvents is a necessity.

In this paper, a model for the numerical simulation of double potential step chronoamperometry at a microband electrode is developed, and used to assess the extent to which this technique can be used to determine both  $D_A$  and  $D_B$  at a microband electrode. We validate this model by simulating the double potential step chronoamperometry of decamethylferrocene in the ionic liquid 1-propyl-3-methylimidazolium bistrifluoromethylsulfonylimide (PmimNTf<sub>2</sub>) and fitting experimental data.

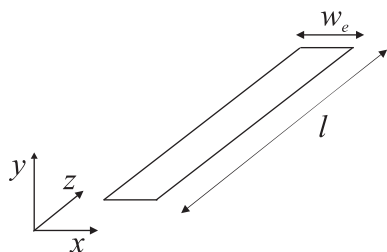


Fig. 1. Schematic diagram of a microband electrode.

## 2. Theory

In this paper, we develop a model to solve the problem of double potential step chronoamperometry, as discussed in the introduction, at a planar microband electrode. A schematic of the electrode being used is shown in Fig. 1, indicating the parameters  $w_e$  (the electrode width),  $l$  (the electrode length) and the orientation of the Cartesian coordinates. A simple one electron redox couple is considered:



If the microband is considered to be infinitely long in the  $z$  direction (relative to its width in the  $x$  direction, see Fig. 1), the edge effects at the ends of the electrode can be neglected, along with diffusion along the length of the electrode, reducing the mass transport equation to be solved to two dimensions:

$$\frac{\partial c_i}{\partial t} = D_i \left( \frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} \right) \quad (5)$$

All symbols are defined in Table 1.

Subject to appropriate boundary conditions described below, this equation is used to simulate the time evolution of the concentration of species in solution.

### 2.1. Boundary conditions

The simulation space used is shown schematically in Fig. 2. Due to symmetry around  $x = 0$ , we only need simulate half of the electrode and surrounding solution, with a zero flux condition imposed by symmetry at  $x = 0$ :

$$\left( \frac{\partial c_i}{\partial x} \right)_{x=0} = 0 \quad (6)$$

A zero flux condition is imposed on the insulating surface around the electrode:

$$\left( \frac{\partial c_i}{\partial y} \right)_{y=\frac{w_e}{2}} = 0 \quad (7)$$

Before the experiment begins at  $t = 0$ , the potential is set such that no reaction occurs and no current is drawn:

$$t < 0; \text{ all } x; \text{ all } y \begin{cases} c_A = c_A^* \\ c_B = 0 \end{cases} \quad (8)$$

Table 1

List of symbols.

Parameter	Description	Units
$\alpha$	Transfer coefficient	Unitless
$c_i$	Concentration of species $i$	$\text{mol m}^{-3}$
$c_i^*$	Bulk solution concentration of species $i$	$\text{mol m}^{-3}$
$D_i$	Diffusion coefficient of species $i$	$\text{m}^2 \text{s}^{-1}$
$E$	Applied potential	V
$E_f$	Formal potential of A/B couple	V
$F$	Faraday constant = 96485	$\text{C mol}^{-1}$
$I$	Current	A
$J$	Flux	$\text{mol m}^{-2} \text{s}^{-1}$
$k^0$	Electrochemical rate constant	$\text{m s}^{-1}$
$l$	Electrode length	m
$R$	Gas constant = 8.314	$\text{J K}^{-1} \text{mol}^{-1}$
$r_e$	Radius of microdisc electrode	m
$T$	Temperature	K
$t$	Time	s
$w_e$	Width of microband electrode	m
$x$	$x$ Coordinate	m
$y$	$y$ Coordinate	m
$z$	$z$ Coordinate	m

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