Dual band electrodes in generator–collector mode: Simultaneous measurement of two species

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ABSTRACT

A computational model for the simulation of a double band collector–generator experiment is applied to the situation where two electrochemical reactions occur concurrently. It is shown that chronoamperometric measurements can be used to take advantage of differences in diffusion coefficients to measure the concentrations of both electroactive species simultaneously, by measuring the time at which the collection efficiency reaches a specific value. The separation of the electrodes is shown to not affect the sensitivity of the method (in terms of percentage changes in the measured time to reach the specified collection efficiency), but wider gaps can provide a greater range of (larger) absolute values of this characteristic time. It is also shown that measuring the time taken to reach smaller collection efficiencies can allow for the detection of smaller amounts of whichever species diffuses faster. The case of a system containing both ascorbic acid and dopamine in water is used to exemplify the method, and it is shown that mole fractions of ascorbic acid between 0.055 and 0.96 can, in principle, be accurately measured.

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1. Introduction

Generator–collector double electrode systems have found great utility in electrochemistry [1] since their conception in the late 1950s [2]. In general, a generator–collector experiment consists of a reduction (or oxidation) at the generator electrode:

$$A \pm e^- \rightleftharpoons B \tag{1}$$

with a subsequent reaction, often the reverse of the first one, occurring at the collector electrode:

$$B \mp e^- \rightleftharpoons A \tag{2}$$

The collection efficiency, N, is defined as the ratio of the current measured at the collector electrode to that measured at the generator electrode:

$$N = -\frac{I_{col}}{I_{gen}} \tag{3}$$

Measuring the collection efficiency can give information on the species involved in the reactions. If, for example, species B in the above scheme is unstable, and decomposes before it can reach the collector electrode, the collection efficiency will decrease, giving a measure of the rate at which the intermediate reaction occurs [3,4].

A great variety of geometries of generator–collector systems have been studied, including Nekresov's original rotating ring disc [2] (also extensively studied by Albery and coworkers [3–26]), wall jet ring discs [27–29], dual band electrodes (used both in static solution [30–33] and hydrodynamic electrochemistry in a flow cell [34–37]), dual discs [38–40] and hemispheres [41–44], and ring- or plane-recessed disc electrodes [45–47].

The uses of generator–collector systems have proved at least as varied as their geometries! In addition to the probing of follow up kinetics mentioned above, mechanistic details can be elucidated, for example the extent to which hydrogen peroxide plays a role as an intermediate in the reduction of oxygen to water [48–50]. Other areas in which generator–collector systems have been successfully employed include detection of micromolar concentrations [44], studies of triple phase boundaries [42], and measurement of one species in the presence of other, interfering, species.

Dual microband electrodes have previously been used by Williams et al. [30–32] in electrochemical titration experiments, where a species which has been electrogenerated at the generator electrode undergoes a reaction with a target analyte in solution. Any surviving electrogenerated species is then detected at the collector electrode:

$$A + e^- \rightarrow B \quad \text{Generator electrode} \tag{4}$$
$$B + W \rightarrow Z \quad \text{Solution} \tag{5}$$
$$B - e^- \rightarrow A \quad \text{Collector electrode} \tag{6}$$
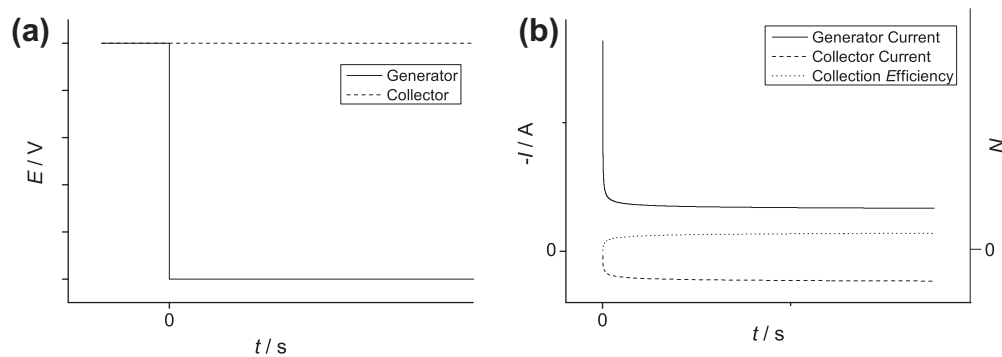
Fig. 1. Schematic diagram of (a) The potentials applied to the generator and collector electrodes during a chronoamperometric experiment. (b) The current responses and the collection efficiency.

Measuring the collection efficiency as a function of time yields information on the rate of the intermediate reaction, and hence the concentration of target analyte, W. Further studies by Amatore et al. [33] have theoretically investigated applying potential pulses to the generator electrode, and using the response at the collector electrode to obtain a time of flight for the electrogenerated species, and hence a measure of its diffusion coefficient.

In this paper, we consider a chronoamperometric experiment using *dual* microband electrodes, with two electroactive species initially present in solution, A and X. Before the experiment starts, the potentials applied to both electrodes are such that no reduction occurs. At the beginning of the experiment, the potential applied to the generator electrode is stepped to a value such that reduction of the electroactive species A and X occurs at a mass transport controlled rate, forming B and Y. The potential at the collector electrode, however, remains at a value to re-oxidise the electrogenerated species at a mass transport controlled rate. Schematic representations of the applied potentials, the currents produced, and the collection efficiency as the experiment progresses are shown in Fig. 1. The collection efficiency is seen to increase with time, and continues to do so until it approaches 1 as time $t \rightarrow \infty$. The rate at which it increases will be dependent on how quickly the intermediate species, B and Y, diffuse across the inter-electrode gap. If all species diffuse at the same rate, then the relative initial concentrations of A and X will have no effect on how the collection efficiency varies with time.

If, however, the diffusion coefficients of the species produced at the generator are different, they will traverse the gap between the two electrodes at different rates, and thus the collection efficiencies attributable to each reaction will increase at different rates. The overall measured collection efficiency will therefore depend upon the relative concentrations of the two species. This study investigates the extent to which this is the case, and explores the application of this to the simultaneous determination of the concentration of both electroactive species in solution.

2. Theory

In this paper we consider potential step chronoamperometry at dual microband electrodes. Two concurrent one electron reductions are considered to occur:

$$A + e^- \rightleftharpoons B \tag{7}$$
$$X + e^- \rightleftharpoons Y \tag{8}$$

The dual microband electrodes are considered to be parallel and effectively of infinite length. One electrode (the generator electrode) has an applied potential such that the reductions both occur at a mass transport controlled rate, and the other electrode (the
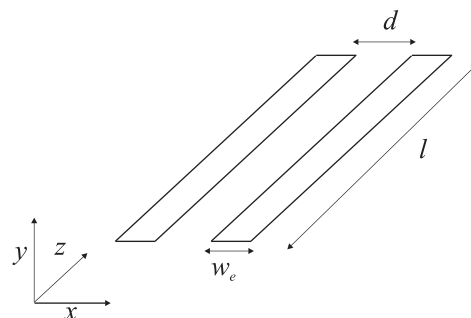

Fig. 2. Schematic diagram of a dual microband electrode system.

Table 1
Parameter definitions.

Parameter	Description	Units
c_i	Concentration of species i	mol m^{-3}
c_i^*	Bulk solution concentration of species i	mol m^{-3}
d	Inter-electrode distance	m
D_i	Diffusion coefficient of species i	mol m^{-2}
I	Current	A
l	Electrode length	m
N	Collection efficiency	Unitless
t	Time	s
t_N	Time taken for collection efficiency to reach N	s
w_e	Electrode width	m
x	x Coordinate	m
y	y Coordinate	m
z	z Coordinate	m

collector electrode) has an applied potential such that the reverse, oxidation, reactions occur at a mass transport controlled rate. A schematic diagram of the dual microband electrodes is shown in Fig. 2, which also defines the Cartesian coordinates.

By considering the case where the length of the electrodes, l, is much greater than their width, w_e, or the distance between them, d, the mass transport equation becomes two dimensional. Assuming an excess amount of inert supporting electrolyte is present, such that mass transport is diffusion only, the mass transport equation is:

$$\frac{\partial c_i}{\partial t} = D_i \left(\frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} \right) \tag{9}$$

where c_i is the concentration of species i (mol m^{-3}), D_i is the diffusion coefficient of species i (m^2 s^{-1}), and x and y are the coordinates defined in Fig. 2. All symbols are defined in Table 1.