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Diffusion-limited chronoamperometry at conical-tip microelectrodes

Dieter Britz[a,*,1], Shaneel Chandra[b], Jörg Strutwolf[c], Danny K.Y. Wong[b]

[a] Department of Chemistry, Aarhus University, 8000 Århus C, Denmark
[b] Department of Chemistry and Biomolecular Sciences, Macquarie University, Sydney, NSW 2109, Australia
[c] Tyndall National Institute, Lee Maltings, Cork, Ireland

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ABSTRACT

In this paper, we present simulated diffusion-limited time-variant currents at conical-tip microelectrodes fabricated by depositing a carbon film in and on pulled quartz capillaries. These mechanically strong microelectrodes are suitable probes for detecting neurotransmitters *in vivo*. The simulated results show that the currents obtained at conical-tip microelectrodes are larger than those at finite conical microelectrodes (e.g. etched carbon fibres protruding from an insulating plane) of comparable dimensions. The currents at conical-tip microelectrodes and finite conical microelectrodes both converge to that of a microdisk electrode at small cone heights and large cone angles, and to that of a cylindrical electrode portion of equal length and half the radius at large cone heights and small cone angles. At short times (scaled by the electrode dimensions), Cottrellian current is achieved at conical-tip microelectrodes and the current densities collapse to the expected chronoamperometric response at a microdisk electrode, subject to some simulation errors. Comparison between a simulated chronoamperogram and an experimental chronoamperogram then allows an estimate of parameters (such as electrode surface area and dimensions) that define the electrode geometry. Steady-state currents based on empirical functions have also been computed for conical-tip microelectrodes and finite conical microelectrodes.

1. Introduction

Coupled with anatomical, physiological and pharmacological evidence, tremendous advances have been made in applying electrochemical techniques to the rapid, real-time *in vivo* analysis of neurotransmitters in specific brain regions [1–5]. This partly arises from the ease of oxidation of several neurotransmitters (dopamine, noradrenaline, serotonin, etc.) at an electrode surface. Another contributing factor stems from significant developments of physically small electrodes that are suitable for implantation into living tissues with minimal physical damage. For example, by recording cyclic voltammograms of dopamine at carbon fibre microelectrodes implanted in the brain of freely moving rats, Hermans et al. demonstrated that cocaine causes significant fluctuations in dopamine concentration in the brain [1]. Following the electrophoretic separations of cytoplasmic samples, Woods et al. relied on the amperometric detection of dopamine at a 2.5 μm diameter carbon fibre electrode to estimate an average cytoplasmic dopamine concentration of 240 μM in rat pheochromocytoma cells [2].

Our laboratory [6] has previously reported the fabrication of physically small carbon electrodes by pyrolysing acetylene gas on quartz capillaries that had been pulled down to a typical 2–5 μm tip diameter. Compared to carbon fibre electrodes of a similar dimension, physically small carbon electrodes were found to show an improved signal-to-noise ratio in detecting dopamine *in vivo* [7]. More recently, after hydrogenating these carbon electrodes, they showed similar effectiveness against electrode fouling to diamond electrodes in detecting dopamine [8].

In this paper, we will focus on a study of the response of physically small carbon electrodes to a potential pulse and the resulting steady-state current. As presented below, fitting simulated chronoamperometric signals to those obtained at physically small carbon electrodes has enabled better estimates of such parameters as the radius and the axial length to define them as electrodes with a conical tip. Therefore, we will hereafter refer to them as conical-tip microelectrodes (CTME). As shown in Fig. 1A, a CTME is characterised by the radius a of the carbon deposit at the electrode base, and the base-to-tip length h measured along the axis of the cone. This yields an angle α, which denotes the inclination of the wall to the axis of the cone. This inclination angle is given by

$$\alpha = \tan^{-1}\left(\frac{a}{h}\right). \quad (1)$$

* Corresponding author. Tel.: +45 89423874; fax: +45 86196199.
E-mail addresses: britz@chem.au.dk (D. Britz), schandra@cbms.mq.edu.au (S. Chandra), jorg.strutwolf@tyndall.ie (J. Strutwolf), danny.wong@mq.edu.au (D.K.Y. Wong).
[1] ISE member.

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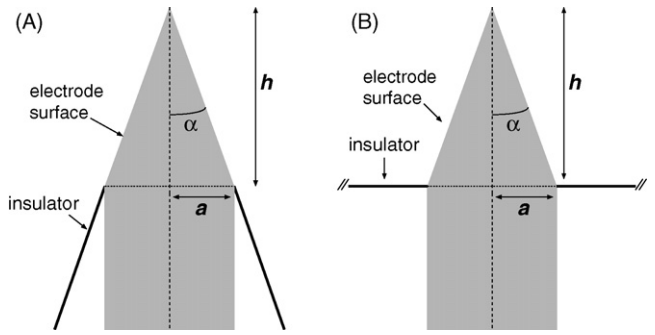

Fig. 1. Schematic of the present conical-tip electrode (CTME) (A) and the similar electrode of Zoski and Mirkin's finite conical electrode (B).

These electrodes are modelled based on an idealised geometry consisting of sharp cones with negligible disk area at the tip. This is an acceptable assumption as the disks are small in comparison to the length of the carbon film along the cone walls.

Previously, Zoski and Mirkin reported a simulation study of finite conical microelectrodes fabricated by sealing an etched carbon fibre in an insulator such that a defined length of the fibre protrudes from the insulating plane [9], as depicted in Fig. 1B. We have defined α in Fig. 1B in a manner that is consistent with that shown in Fig. 1A, whereas in [9], the angle was defined as that of the wall to the base. Dickinson et al. have presented some additional simulation results of these finite conical electrodes, extending the study to include simulation of linear and cyclic voltammetry [10]. Notably, the insulating plane at a finite conical microelectrode limits mass transport to the base edge of the electrode, whereas the base edge on a CTME is more accessible. Both types of conical electrodes become identical to an ultramicrodisk electrode (UMDE) when $h \to 0$, and this is a useful verification of the simulations shown later in this paper. At the other extreme, CTME with a large h/a ratio (i.e. a very sharp cone) will have a response similar to that of a cylindrical electrode of radius $0.5a$ and length h, ignoring edge effects. Overall, the circular disk and cylinder represent extreme cases of a very low ($h/a \to 0$) and a very tall cone ($h/a \to \infty$), respectively. As will be seen below, the CTME deviates significantly in its chronoamperometric response from the finite conical electrode.

The present work aims to present simulation results, both time-dependent and steady state, for the current at a CTME under diffusion limiting conditions. We will then compare these results to those of finite conical microelectrodes. In addition, simulated results will also be compared to experimental results for the reduction of $Ru(NH_3)_6^{3+}$ at CTMEs.

2. Theory

The diffusion equation for our system is

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial z^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2}\right) \tag{2}$$

in which c is concentration, t the time, D the diffusion coefficient, z the vertical axis in the direction of the central axis of the cone and r is the radial coordinate. We define a maximum distance L from points on the electrode, over which there are significant changes in concentration during a given time, given by [11],

$$L = 6\sqrt{T} \tag{3}$$

(T is defined in (4d)), so that L depends on the largest value of T to which the simulation is driven. The quantity L will be used in constructing a suitable spatial grid for the simulation, as further explained below.

It is convenient to normalise (2) using the following dimensionless symbols:

$$C = \frac{c}{c^*} \tag{4a}$$

$$Z = \frac{z}{a} \tag{4b}$$

$$R = \frac{r}{a} \tag{4c}$$

$$T = \frac{Dt}{a^2} \tag{4d}$$

$$H = \frac{h}{a}, \tag{4e}$$

where c^* is the initial bulk concentration of the electroactive species. With these normalisations, the electrode has unity radius R at its base and a height H. Then, (2) becomes

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial Z^2} + \frac{1}{R}\frac{\partial C}{\partial R} + \frac{\partial^2 C}{\partial R^2}. \tag{5}$$

2.1. Cylinder approximation

In what follows, the term "cylinder" refers to a portion of a given length of an infinitely long cylinder, for which there is some theory. As mentioned above, there are approximate solutions for the extreme cases. For very small α, where the cone approximates a cylinder of length h and radius $0.5a$, Szabo et al. [12] provide a solution for the current holding within 1.3% for all times,

$$i_{cyl} = 2\pi nFDc^* hf(\theta) \tag{6}$$

with

$$f(\theta) = \frac{\exp(-0.1\sqrt{\pi\theta})}{\sqrt{\pi\theta}} + \frac{1}{\ln(\sqrt{4\exp(-\gamma\theta)} + \exp(5/3))} \tag{7}$$

in which γ is Euler's constant (0.5772156...), n is the number of electrons transferred, F is the Faraday constant, D the diffusion coefficient and c^* the bulk concentration of the electroactive substance, and θ is the normalised time defined by $\theta = Dt/a^2$, where a is the radius of the cylinder. This is equivalent to definition (4d), but a different symbol is used to highlight the fact that the cone and cylinder have different radii when being compared (see below). The factor 2 in (6) is based on the assumption of a whole cylinder, rather than a hemicylinder, as was the case in Szabo et al. As shown below, for a CTME with large H, this equation fits the simulated currents rather well. At short times, Szabo et al. have

$$f(\theta) = 0.5 + \frac{1}{\sqrt{\pi\theta}}. \tag{8}$$

The actual current in amperes for this case is

$$i = 2\pi nFDc_b h\left(\frac{1}{2} + \frac{a}{\sqrt{\pi Dt}}\right). \tag{9}$$

Hence, based on a linear plot of current against $t^{-1/2}$, the y-intercept will provide an estimate of h, and the slope will yield the radius a of a CTME in the solution of an electroactive species of known concentration.

Note that if a cone current is to be compared to that at a cylinder, then the above equations must be evaluated setting the radius to half that of the cone base. This results in the relation $\theta = 4T$.

2.2. Disk approximation

For a disk electrode, we have the approximation formulae by Mahon and Oldham [13] which, using our present normalisations