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The effect of insulator nano-sheath thickness on the steady state current at a micro-disc electrode

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ABSTRACT

The relative size of the insulating sheath to electrode area at a micro-disc electrode can lead to significant perturbations in the steady state current observed. A minimum, constant steady state current value is realised once the sheath thickness is greater than twice the radius $\Delta l > 2r_d$. However, as the sheath thickness decreases below this value, the observed current increases. In this paper a theoretical model is presented, allowing for the accurate determination of the outer sheath thickness. The effects of an ultra-thin sheath on steady state currents are demonstrated experimentally and these results are shown to accurately fit with the simulated model developed. Therefore, the model presented here can be used to determine the size of a sheath of unknown thickness. Furthermore, it allows these size effects on the steady state current to be explored.

1. Introduction

Micro-electrodes find a wide and diverse application in electroanalytical chemistry particularly where fast response times and high mass transport rates are sought [1–3]. Micro-electrodes are also key to electrochemical imaging methods such as SECM [4]. In conventional designs the electrode is commonly disc shaped and embedded in an insulating sheath presumed of infinite extent (Fig. 1a). For such an electrode the steady state diffusion limited current is given by [5]:

$$I = 4nFDcr \quad (1)$$

where F is the Faraday constant, r the electrode radius, n is the number of electrons transferred, c the concentration of electroactive species and D is the diffusion coefficient. The current to such an electrode is non-uniformly distributed with radial diffusion leading the expected current density at the periphery of the electrode. If the sheath thickness is reduced there is, for sheaths of a thickness of the order of electrode size, the possibility of enhanced mass transport as material from beyond the extent of the electrode can contribute to the diffusional flux.

The simulations yield significant analytical insight and are based on established Fickian transport, unnecessary of validation since the late 19th century. Moreover, the finite difference calculations utilised are more recently established yet equally firmly based. The simulations stand alone but are consistently describing a novel procedure for an ultra-thin sheath insulated electrode in which the transport is increased via spherical, as opposed to hemispherical, diffusion. Not only does the electrode design shown in Fig. 1b have higher mass transport but it may represent an easier electrode to construct. The purpose of the present paper is to explore the mass transport characteristic of a micro-disc insulated with sheaths of different sizes. To this end finite difference simulations are undertaken and the results validated against experiments.

2. Experimental

2.1. Electrode fabrication

First, carbon micro-electrodes were fabricated by attaching individual 7 μm diameter carbon fibres (Goodfellow Cambridge Ltd.) of approximately 1 cm in length to a conducting metal wire by use of silver epoxy conductive adhesive (RS Components Ltd.). The adhesive was heat set for 15 min at approximately 60 °C.

Second, the carbon fibre was cleaned in an oxygen plasma (PF 7100 RF Plasma etcher, Bio-Rad) for 2 min. This provided a uniformly clean surface for the insulation process to occur across.

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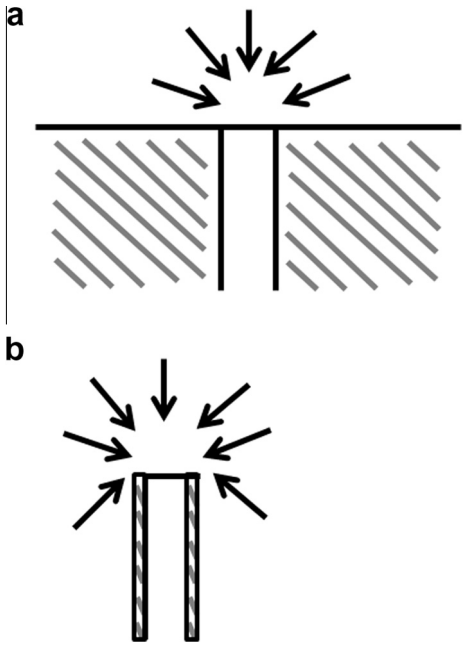

Fig. 1. Micro-disc electrode with (a) an infinite sheath and (b) an infinitesimal sheath.

Third, the carbon fibre electrodes were coated using cathodic electrophoretic paint (Clearclad HSR, LVH Coating, UK), a method that has previously been shown to produce well insulated electrodes [6–9]. Here, the paint was placed in a conducting metal cell with a diameter of 1 cm. The carbon fibre was immersed in the centre of the cell, withdrawn and re-submerged a total of 3 times. This allowed for complete wetting of the carbon fibre surface. A DC voltage of 3 V was then held between the cell and the carbon fibre electrode for 2 min, causing the paint to adhere to the electrode surface. The electrode was then withdrawn and excess solution was removed from the fibre by spray rinsing with water. The paint was set to form a thin insulating film by heat curing for 30 min at 200 °C. During the curing stage the film shrinks and can lead to the formation of pinholes [10], as such the coating process was repeated a further two times to ensure complete coverage and prevent any electrical leakage. To ensure complete insulation of the electrodes a final coat of wax (Apiezon, M7I Materials Ltd.) was applied. Here, the carbon fibre was dipped into the molten wax, removed and allowed to dry at room temperature.

Finally, the electrode tip was cleaved using a razor blade to expose an electrically active carbon fibre disc surrounded by a thin insulating sheath. The relative size of the carbon fibre to the outer sheath was determined electrochemically and by SEM imaging.

2.2. Reagents and equipment

Hexamine ruthenium (III) chloride and potassium chloride were both purchased from Sigma Aldrich (Analytical Grade). Solutions were made using ultrapure water (Millipore, resistivity not less than 18.2 MΩ cm at 25 °C) and were thoroughly degassed by purging with nitrogen gas for 15 min. The electrochemical set up was thermostated to a constant 25.0 ± 0.2 °C.

Electrochemical characterisation was performed using a μAutolab II potentiostat (Metrohm-Autolab BV, Utrecht, Netherlands). A standard three electrode set up was used, consisting of a platinum mesh counter electrode, a saturated calomel reference electrode (SCE, potential E = 0.244 V versus standard hydrogen electrode), and the fabricated micro-disc working electrodes.

SEM imaging was performed using a JEOL JSM-6480LV electron microscope. For this the electrodes were first coated with an ultrathin (approximately 5 nm) layer of platinum to reduce surface charging and thus allow higher resolution images to be taken.

3. Numerical model

We model a cyclic voltammetry measurement in an electrochemical reduction/oxidation system containing a micro (finite) disc electrode coated with varied thickness. Fig. 2a shows the three dimensional geometry of the cylindrical micro electrode used in the simulation model. We define the disc electrode radius, r_d in the r direction, Δl as the thickness of the insulating coat, and r_s to be the whole cylinder ($r_d + \Delta l$). Using the axial symmetry around ($z = 0$) of the disc electrode we can solve the two dimensional mass transport towards the electrode (Fig. 2b).

We describe the transport of the electrochemical species in the solution under fully supporting electrolyte condition, allowing a diffusion controlled system. By assuming the transport to behave in a

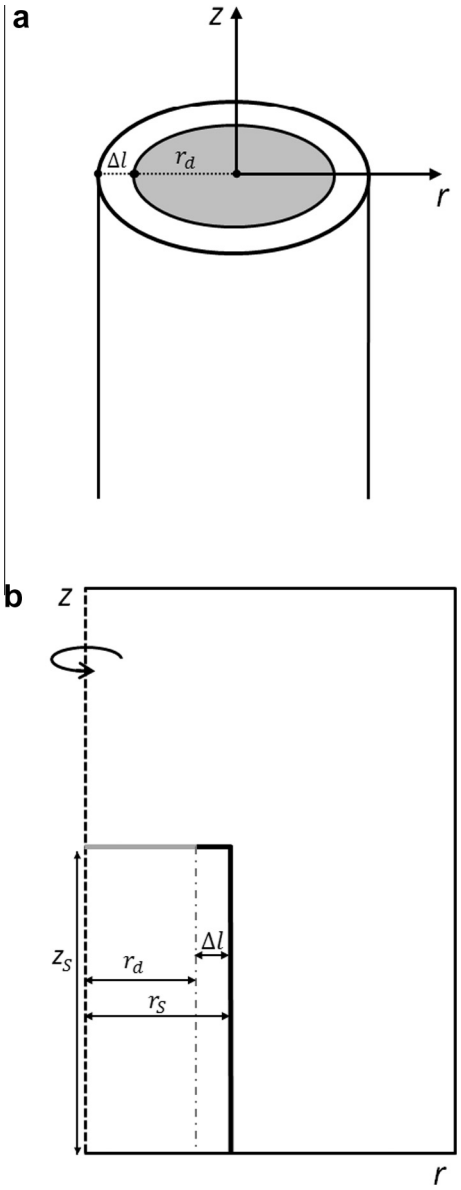

Fig. 2. Illustration of the geometry used for calculation. (a) 3D presentation of the micro cylinder electrode. (b) 2D projection for the geometry used in the calculation.