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Thin-layer vs. semi-infinite diffusion in cylindrical pores: A basis for delineating Fickian transport to identify nano-confinement effects in voltammetry

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ABSTRACT

Using simulation, voltammetry within a partially electroactive cylindrical pore is investigated. The system studied consists of an insulating cylindrical tube with a ring electrode within its inner circumference, which is filled with electroactive solution, such that electron transfer occurs on the tube's interior surface. The voltammetry is examined in terms of the dimensions of the electrode ring (radius, r_e, and width, z_e) as well as the voltammetric scan rate and the diffusion coefficient of the electroactive species. Four limiting cases are observed. In the limit $r_e \to \infty$, the voltammetry varies between that expected for a macro-electrode of equivalent area (as $z_e \to \infty$) and that expected for a microband electrode of equivalent area (as $z_e \to 0$). In the limit $r_e \to 0$, the voltammetry demonstrates thin-layer behaviour as $z_e \to \infty$. Finally, in the case where $r_e, z_e \to 0$, the confinement of the solution leads to the unusual case of planar diffusion towards a micro/nanoscale electrode with a current response that is equivalent to hypothetical 'macro-electrode' of area twice that of the cross sectional area of the cylinder ($2\pi r_e^2$). The conditions under which these limits operate are defined.

1. Introduction

The transition from semi-infinite diffusion to thin-layer behaviour is at the heart of understanding charge transport behaviour in porous media. Moreover, such issues are presently topical because of the extensive use of porous nano-materials in a diversity of areas such as hydrogen storage, fuel cells, and batteries. Of particular interest in the latter case are claimed effects arising from nano-confinement, that is to say that the diffusional properties of solutes become changed at the nanoscale due to the altered structure of solvents when they are confined to nano-sized pores [1–9]. Such effects can impart beneficial properties to the nano-material.

From an electrochemical perspective, it is important to be able to distinguish enhanced transport effects arising from nano-confinement from simple Fickian diffusion giving rise to thin-layer behaviour. To this end, in this paper, we consider voltammetry at an annular electrode located flush with the walls of a cylindrical pore containing electrolyte, and examine the effect of pore size on the Fickian voltammetry. We identify four limiting cases resulting from different length scales and give equations which define the conditions under which they operate. We hope this will provide a partial basis for delineating authentic nano-confinement effects.

2. Theory

2.1. Model system

The electrode system we consider takes the form of a band of conducting electrode material flush with the circumference of an infinitely long cylindrical insulating pore as illustrated in Fig. 1. The electrode is defined by two lengths: the radius of the cylinder, r_e, and the height of the band, z_e, as shown in the figure. Electrodes of this type, so called 'annular microbands', have previously been studied theoretically [10] for the case where the annular band is on the external surface of the cylinder. However our treatment here is different: we instead consider a cylindrical tube (pore) *filled* with electroactive solution so essentially creating a no-flow tubular electrode [11–14].

The electrode system may be modelled in a 3-dimensional cylindrical polar coordinate system (r, z, ϕ) as shown in Fig. 1. Accurate simulation of a 3 dimensional space can be extremely time consuming, however certain properties of the system enable

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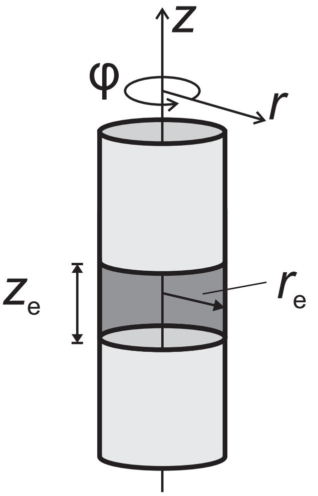

Fig. 1. Band of conducting electrode of height z_e, embedded in a hollow insulating cylinder of radius r_e and the (r, z, ϕ) cylindrical polar coordinate system. The front section of the conducting band is drawn as transparent.

simplifications to be made. First, it is obvious that the system is cylindrically symmetric, consequently there can be no concentration gradient about angle ϕ, i.e. $\partial c/\partial\phi \equiv 0$. The system may therefore be modelled as a 2-dimensional (r, z) plane that is parallel to the central axis of the cylinder; integration across all angles ϕ achieves the full 3-dimensional result.

2.2. Voltammetry

Throughout this study we consider a one-electron oxidation of the form,

$$A \rightleftharpoons B + e^- \tag{2.1}$$

in which only species '*A*' is initially present in solution at a uniform concentration, c^*. In the (r, z) coordinate system described above, the mass transport of a chemical species due to diffusion is described by Fick's second law:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{\partial^2 c}{\partial z^2} + \frac{1}{r}\frac{\partial c}{\partial r}\right) \tag{2.2}$$

where c and D are the concentration and diffusion coefficient of the starting species, '*A*' respectively, and t is the time. Note that we assume that an excess of supporting electrolyte is added to the system and that it is not stirred or heated such that the migratory and convectional contributions to mass transport are negligible [15]. We further assume the diffusion coefficients of both species '*A*' and '*B*' are equal such that at any point in space $c_A + c_B = c^*$.

In a linear sweep voltammetry experiment, the potential at the electrode, E, is swept from some starting potential, E_i, where the starting species '*A*' is electrochemically stable, to some final potential, E_v, at a constant rate, v. This causes '*A*' to be oxidised at the electrode surface, transforming it into species '*B*'. The potential at time, t, is given by:

$$E = E_i + vt \tag{2.3}$$

The flux of species '*A*' normal to the electrode surface at a given potential is described by the Butler–Volmer equation:

$$D\left.\frac{\partial c}{\partial r}\right|_{r=r_e} = k^0\left[c_0 \exp\left(\frac{(1-\alpha)F(E-E_f^0)}{RT}\right) - (1-c_0)\exp\left(\frac{-\alpha F(E-E_f^0)}{RT}\right)\right] \tag{2.4}$$

where c_0 is the concentration of species '*A*' at the electrode surface, k^0 is the rate constant, α is the electron transfer coefficient, E_f^0 is the formal potential of the reaction, F is the Faraday constant, R is the gas constant, and T is the temperature, typically 298 K.

2.3. Simulation procedure

In order to simulate a voltammetry experiment, the complete space–time evolution of the concentration must be obtained by solving Fick's second law (Eq. (2.2)) over all r, z, and t, subject to the boundary conditions imposed by the nature of the electrode system. Fig. 2 shows the 2-dimensional (r, z) plane to be modelled – a cross section parallel to the axis of the cylinder with the origin in the centre of the electrode band. This cross section has mirror symmetry in both the r and z axes so it is only necessary to simulate one quadrant which is marked with hatching in the figure. The space to be simulated is therefore a rectangular region that extends from $r = 0$ (the central axis) to $r = r_e$ (the cylinder radius) in the radial coordinate, r, and from $z = 0$ (the midpoint of the band) to $z = +\infty$ in the axial coordinate, z.

Across the lines of symmetry ($r = 0$ and $z = 0$) there is necessarily no diffusive flux, so at these boundaries we have the conditions:

$$z = 0: \quad \frac{\partial c}{\partial z} = 0 \tag{2.5}$$

$$r = 0: \quad \frac{\partial c}{\partial r} = 0 \tag{2.6}$$

Likewise, the insulating outer wall of the cylinder is a solid boundary which also admits no flux:

$$r = r_e, \quad z > \frac{z_e}{2}: \quad \frac{\partial c}{\partial r} = 0 \tag{2.7}$$

At the conducting section of the cylinder wall ($r = r_e$, $0 < z < z_e/2$), the Butler–Volmer equation (Eq. (2.4)) is used as a boundary condition. Finally, at the $z = +\infty$ boundary, the concentration may be set to its bulk (initial) value, c^*, as the concentration at the boundary cannot possibly be perturbed by the electron transfer processes occurring at the electrode. In practice, the $z = +\infty$ boundary does not need to be infinitely far away from the electrode but just far

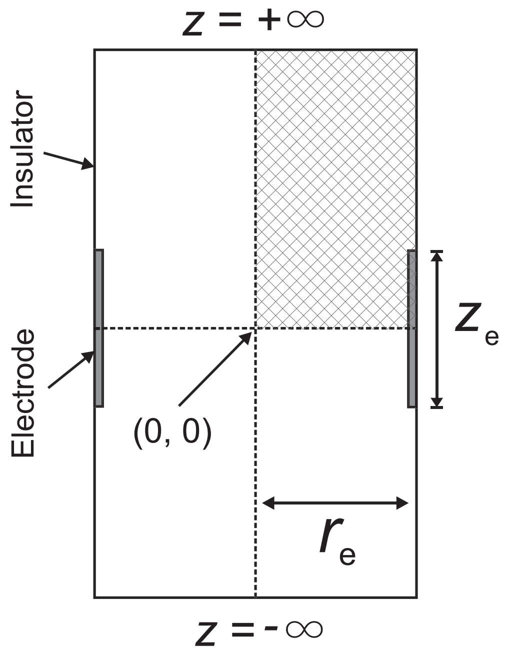

Fig. 2. Cross section of the cylindrical electrode system – an (r, z) plane. Marked quadrant is the simulation space.