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Voltammetry of porous layers: Staircase vs analog voltammetry

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ABSTRACT

The use of staircase ramps for cyclic voltammetry rather than true linear analog ramps can lead to significant misinterpretation of the signals recorded for the measurement of diffusional redox species with either reversible or irreversible electrode kinetics measured at electrodes modified with porous layers. Most notably a large perturbation of the expected peak current is apparent which can preclude the extraction of meaningful data, for example in respect of surface coverages or in the identification of electro-catalysis.

1. Introduction

The voltammetric study of electrodes with porous surfaces is now commonplace since the use of nanoparticles and microparticles to attempt the electrocatalysis of diverse processes lies at the heart of energy transformation technology and much electroanalytical science. Electrochemical processes sought to be catalysed are as varied as the oxygen reduction reaction or the oxidation of glucose. Typical methodology involves the immobilisation of "designer" materials on the surface of an otherwise inert electrode, the measurement of cyclic voltammograms and the analysis of which seeks to identify useful changes in the electrochemical responses due to the presence of the modifying layer. This analysis is not trivial since any voltammetric response represents a subtle interplay between electron transfer kinetics, mass transport and the active surface area. While this analysis is well established for flat, non-porous layers [1,2] and developed to a high level of sophistication [3], such analysis represents at least a gross simplification for most porous surfaces and often is completely misleading. Thus we have shown that the transition from semi-infinite diffusion to thin layer diffusion has led to widespread misinterpretation of the voltammetry of carbon nanotube modified electrodes [4,5] and explained the enhanced selectivity sometimes observed at such electrodes [6] in terms of changed mass transport regimes rather than electrocatalysis. The implications have been extended beyond cyclic and linear sweep voltammetry to differential pulse and square wave voltammetry [7]. Subsequent work showed a change of electrode geometry from flat and planar to non-flat and non-uniform (as for example in nanoparticle modified surfaces) could in itself lead to the false impression of a change of electron transfer kinetics if data were to be analysed erroneously assuming the electrode to be of the former rather than the latter geometry [8,9]. Similar conclusions were drawn in respect of rotating disc electrode voltammetry [10].

Most experimental voltammetry is today carried out using a staircase waveform (shown in Fig. 1) to approximate the linear ramp typically underpinning the theory of cyclic and linear sweep voltammetry. The linear ramp is defined by the voltage scan rate whereas in the case of staircase voltammetry the step height, time step, and the point of current measurement ϵ $(0 \leq \epsilon \leq 1)$ defines the applied potential form and resulting voltammetry (Fig. 1). For flat, planar and uniform surfaces, it has been clearly established that discrepancies between staircase and true linear sweep voltammetry can easily arise [11–17]. Recommendations for the optimal selection of ε have been made [17–19] and correction factors have been reported [5]. Similar differences have been noted for microdisc voltammetry as well as for macroelectrodes [18].

In this paper we explore the implications of approximating true linear sweep voltammetry by staircase voltammetry for the study of diffusional processes at porous electrodes. Significant deviations are found with major implications for the possibility of important misinterpretation if the possibilities for differences are not recognised by experimentalists.

2. Theoretical model

In this work, cyclic voltammetry at a porous electrode is simulated for the cases of true linear potential sweeps and staircase potential

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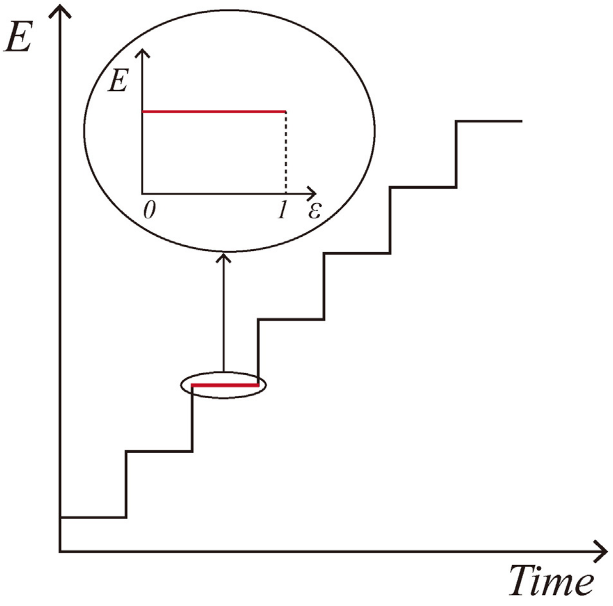


Fig. 1. Plot of potential against time for staircase ramp voltammetry, E is potential and ϵ ($0 \le \epsilon \le 1$) is the point at which current is recorded on each step.

sweeps. The single-electron-transfer reaction,

$$A + e^- \rightleftharpoons B,$$

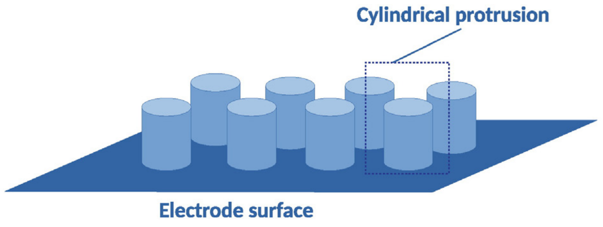
between two species with identical diffusion coefficients ($D_A = D_B = D$ ($m^2\,s^{-1}$)) is considered at the porous electrode surface.

The porous electrode is modelled as a series of uniformly distributed cylindrical protrusions of height z_e that expand from the electrode surface as shown in Fig. 2a. All cylinders are considered to be identical so that the whole system can be represented in terms of a single cylinder within the diffusion domain approximation [20–24]. Thus the electrode surface is first divided into square unit cells each of equal area. Then, within the diffusion domain approximation we replace the square cells by circular cells with a surface area that is identical to the area of the square unit cell. Consequently, the cylinder coverage within the diffusion domain approximation is defined as: $r_e^2 \cdot r_{\max}{}^{-2}$, where r_e and $r_{\max}$ are the radius of the cylinder and the diffusion domain circle, respectively. For a single cylinder, we hence simplify the model to a two-dimensional space as shown in Fig. 2b, which is symmetrical with respect to the vertical z axis.

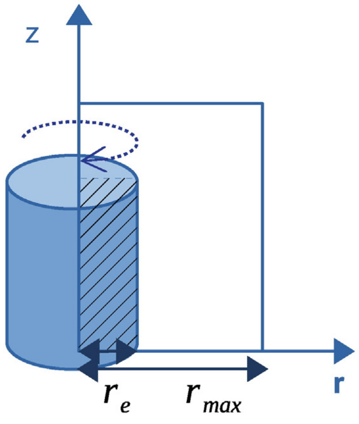
In our model, we assume that there is sufficient supporting electrolyte in the solution, which screens the electric field generated by the electrode [25]. As a result, mass transport exclusively occurs via diffusion without migration, which in the case of the given geometry follows Fick's Second Law [26]:

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

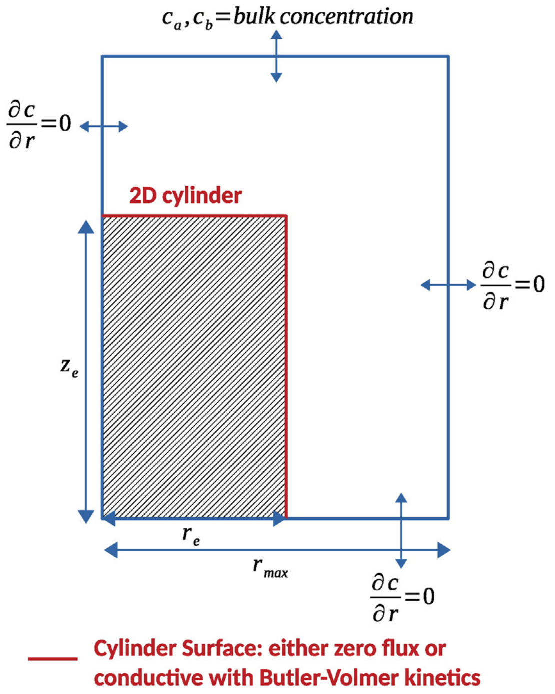
in cylindrical coordinates for an axially symmetrical system, where c ($mol\,m^{-3}$) is the concentration of either species A or B, D (m^2/s^{-1}) is the diffusion coefficient of either A or B, t (s) is the time, z (m) is the normal coordinate, and r (m) is the radial coordinate.



(a) Porous electrode model



(b) A single cylinder in the diffusion domain approximation



(c) 2D cross section of single cylinder

Fig. 2. Porous electrode and simulation model.