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A New Theory of Potential Step Chronoamperometry at Hemispheroidal Electrodes: Complete Explicit Semi-Analytical Formulae for the Faradaic Current Density and the Faradaic Current

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ABSTRACT

The recently described theory of potential step chronoamperometry at inlaid microdisk electrodes [L. K. Bieniasz, Electrochim. Acta 199(2016)1] is extended to hemispheroidal electrodes, assuming diffusional transport under limiting current conditions. Both oblate and prolate hemispheroids are discussed. The theory provides previously unknown, rigorous, complete, and explicit expressions for the concentration, the Faradaic current density, and the Faradaic current. The expressions are in the form of inverse Laplace transforms of infinite series involving spheroidal wave functions. Numerical Laplace transform inversion, applied to the series, yields highly accurate solution values. Hence, the present solutions are advantageous over formerly used low-accurate and/or heuristic approximations, for the purposes of experimental data analysis, and for testing of modelling/simulation techniques.

1. Introduction

This paper describes a novel theory of potential step chronoamperometry (PSCA) for an uncomplicated charge transfer reaction, performed at a single hemispheroidal electrode mounted on an insulator plane. Hemispheroidal electrodes have been considered in the literature as models of mercury microelectrodes obtained by deposition of mercury on inlaid solid metal microdisk electrodes [1], and of modified electrodes obtained by embedding spheroidal particles in a planar substrate [2]. Further examples include hemispheroidal shapes of polymer sensors in polymer entrapped enzyme ultramicroelectrodes [3], and "whisker" electrodes obtained by dendritic growth, or by carbonization of organic compounds [4]. Hemispheroidal electrodes are also interesting from a purely theoretical point of view, as they require an unified theory that includes the theories of inlaid disks and hemispheres as special subcases (which otherwise might seem rather unrelated).

We shall assume a simple reduction reaction

$$O + ne^- \rightleftharpoons R \tag{1}$$

with only species O being initially present. Diffusional transport of O will be considered, under limiting current conditions caused by an electrode potential step to a highly negative value at time $t = 0$ (the theory obtained applies equally well to the reverse reaction with R initially present, after appropriate sign changing). Possible additional complications, such as natural convection, Ohmic drops, or double layer charging, will not be taken into account.

There have been several former theoretical studies related to the PSCA for reaction (1) at hemispheroidal electrodes. Birke [5], Oldham [6], Myland and Oldham [4], Diao et al. [7], and Rajendran and Sangaranarayanan [8] determined and analysed steady state currents that are achieved after sufficiently long time after applying the potential step (or other electrode perturbations). The authors of Ref. [8] observed that the formulae for the steady state current are equivalent to equations derived earlier in soil infiltration studies [9], which was unnoticed by other electrochemists. Myland and Oldham [4] presented two terms of a short-time expansion to the PSCA current, for oblate and prolate hemispheroids. Phillips [10] reported three terms of a long-time current expansion. Qian et al. [11] performed transient digital simulations of the PSCA, by solving the relevant diffusion partial differential equations (PDEs) by the finite-analytic method. The simulations were restricted to oblate hemispheroids. Diao et al. [12] derived a simplified analytical equation describing the PSCA current at oblate hemispheroids. Rajendran [13]

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presented a heuristic all-time approximant to the PSCA current, designed both for the oblate and prolate hemispheroids. Later on, Rajendran and Ananthi [14] proposed another, more elaborate approximant of the Padé type. They also presented four terms (albeit not entirely consistent with Ref. [10]) of the long-time current expansion. The approximations from Refs. [4,10,12-14] are compiled in Appendix A.

The theory to be presented below will be based on the approach previously employed for considering the PSCA at an inlaid microdisk electrode [15]. In Ref. [15] the microdisk was perceived as a limiting case of an oblate hemispheroid, when the smallest of its radii is reduced to zero. By using this property, a rigorous formula was derived, representing a Laplace transform of the concentration distribution around a microdisk. The formula involved a series of spheroidal wave functions [16–22]. A possibility of adopting an analogous formalism for the description of hemispheroidal electrodes was indicated, but the discussion was focused on the microdisk modelling only. In the present work we shall explore the possibility indicated, and we shall derive respective formulae for the Laplace transforms of the Faradaic current density and the Faradaic current at a hemispheroidal electrode. This will be accomplished in an analytical way, without any simplifications. Subsequently, we shall invert the Laplace transforms numerically, to obtain highly accurate values of the current density and the current, in the time domain. Theoretical modelling employing numerical inversion of the Laplace transform has been advocated in electrochemistry by Montella [23,24]. The numerical inversion has also proven successful in the developments of the electrochemical modelling methodology based on integral equations (IEs) [25].

It should be emphasised that no electrochemist has presented thus far complete rigorous and explicit analytical or semi-analytical equations for the transient Faradaic current density and the Faradaic current due to PSCA at a hemispheroid. The equations obtained in Refs. [4-8,10-14] are either not complete, not explicit, or not rigorous. To be rigorous, the equations should not involve heuristic approximations or simplifications. Completeness requires the validity of the equations for any time value, and for any physically justified location in space. For explicitness, a need to solve implicit equations, such as IEs or partial differential equations (PDEs), must be avoided: the Faradaic current density and the Faradaic current should be computable directly as right-hand sides of the equations. In contrast, the semi-analytical equations derived in the present work are simultaneously rigorous, complete, and explicit.

2. Theory

A hemispheroid can be defined as a body resulting from rotating an ellipse around one of its axes, and halving the spheroid obtained along the plane formed by the second, rotated axis. In the case of hemispheroidal electrodes, the cut plane coincides with the insulator plane, on which the electrode is mounted. Such an electrode has a rotational symmetry. This suggests a description using a cylindrical coordinate system (r, z), in which the z axis is the symmetry axis, with $z = 0$ corresponding to the insulator plane (see Fig. 1). The lengths of the two semi-axes of the hemispheroidal electrode can be denoted by a and b, with a equal to the basal radius of the hemispheroid, and b equal to the distance by which the hemispheroid stands above the insulator plane. It is convenient to introduce a shape parameter $\sigma = b/a$. Depending on the value of σ one can distinguish the following special cases (cf. Fig. 1). The case of an inlaid disk electrode corresponds to $\sigma = 0$. When $0 < \sigma < 1$ we have an oblate hemispheroidal electrode. When $\sigma = 1$ the electrode is hemispherical. Finally, $\sigma > 1$ corresponds to a prolate hemispheroidal electrode. In the further discussion we shall assume that any hemispheroid is represented by the parameters a and σ

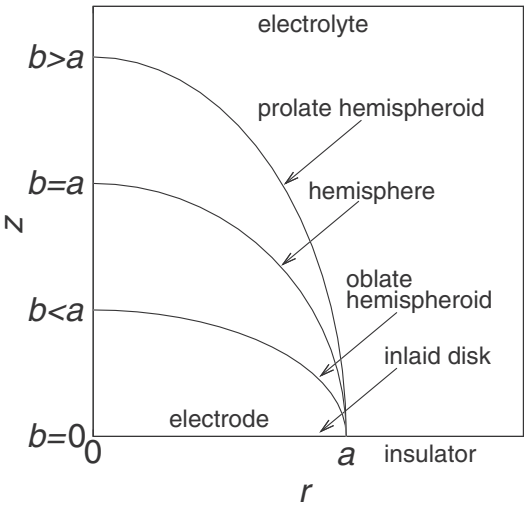

Fig. 1. The various special cases of a hemispheroidal electrode.

(rather than a and b). From the standard equation of an ellipse, it is then easy to find [4] that any point at the surface of a hemispheroidal electrode has coordinates $(r, Z(r))$, where

$$Z(r) = a\sigma\left[1 - \left(\frac{r}{a}\right)^2\right]^{1/2}. \tag{2}$$

Subsection 2.1 provides the initial boundary value problem (IBVP) for the PSCA experiment, formulated using standard cylindrical coordinates. Subsection 2.2 provides alternative formulations, more suited to the particular cases of σ. Known steady state solutions are recalled in Subsection 2.3. Derivations of the transient solutions are addressed in Subsection 2.4.

2.1. The IBVP in cylindrical coordinates

In the cylindrical coordinate system, the two-dimensional diffusion PDE for the concentration $c(r,z,t)$ of species O in the electrolyte is:

$$\frac{\partial c(r,z,t)}{\partial t} = D\left[\frac{\partial^2 c(r,z,t)}{\partial r^2} + r^{-1}\frac{\partial c(r,z,t)}{\partial r} + \frac{\partial^2 c(r,z,t)}{\partial z^2}\right]. \tag{3}$$

The PDE is accompanied by the initial condition

$$c(r,z,0) = c^\star. \tag{4}$$

In Eqs. (3) and (4) D is the diffusion coefficient of O, and $c^\star$ is its initial uniform concentration. The boundary conditions (all holding at $t > 0$) are as follows. At the electrode surface (for $0 \le r < a$)

$$c(r,Z(r),t) = 0, \tag{5}$$

and at the insulator surface (for $r > a$)

$$\left.\frac{\partial c(r,z,t)}{\partial z}\right|_{z=0} = 0. \tag{6}$$

Eq. (5) assumes a zero concentration of O at the electrode surface, as a consequence of maintaining, at $t \ge 0$, a highly negative electrode potential (limiting current conditions). Eq. (6) is a no-flux condition, stating the lack of the consumption of the depolarizer at the insulator