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Theory of Potential Step Chronoamperometry at a Microband Electrode: Complete Explicit Semi-Analytical Formulae for the Faradaic Current Density and the Faradaic Current

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ABSTRACT

Theory of potential step chronoamperometry under limiting current conditions and for purely diffusional transport at a microband electrode has been a subject of several studies. However, no complete and explicit expressions for the Faradaic current density and the Faradaic current have been reported thus far. In the present study such expressions are derived using a novel theoretical approach. The microband is considered as a limiting case of an elliptic cylinder, when the length of the smallest diameter of the elliptic cross-section tends to zero. Solution to the problem of heat conduction around an elliptic cylinder, due to Tranter [Quart. J. Mech. Appl. Math. 4 (1951) 461], is utilised. Following Tranter, the method of separation of variables in the Laplace space is used, resulting in two Mathieu differential equations. The concentration of the depolarizer, the Faradaic current density, and the Faradaic current, are then expressed as inverse Laplace transforms of certain infinite series involving appropriate Mathieu functions. The series are amenable to further analytical examinations. In particular, it is proven that a quasi-steady state develops at large time. It is also demonstrated how the popular idea, of an hemicylinder electrode "equivalent" to a microband, has to be understood to be correct. Numerical evaluation of the series provides unprecedentedly highly accurate solution values. Hence, the present solutions should be preferred over formerly used low-accurate formulae, for the purposes of experimental data analysis, and for the testing of modelling/simulation techniques.

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1. Introduction

This paper is devoted to the theoretical description of potential step chronoamperometry (PSCA) at a single planar microband electrode, embedded flush in an insulator plane. Limiting current conditions and purely diffusional transport are assumed. Complications such as natural convection or double layer charging are not taken into account. The electrode is assumed to be infinitely long, so that the edge effects, in reality present at the ends of the microband, need not be considered. Consequently, the theory does not depend on the spatial coordinate along the axis parallel to the microband. There are at least two reasons why such a theory is important for electrochemistry. First, experiments of this kind are routinely performed in practical applications of microelectrodes. Second, theoretical models of PSCA may serve as challenging benchmark examples for testing various analytical and computational approaches to electroanalytical modelling. This is because of the presence of difficulties typical for the microelectrodes: edge effects characterised by spatial and temporal singularities of the current density. It is therefore not surprising that over the past decades there have been many theoretical and digital simulation studies devoted to such experiments. Readers will find comprehensive lists of the studies in the book by Britz [1], and in two more recent reviews by Rajendran [2], and Britz and Strutwolf [3]. References [1–3] survey also the literature about the modelling of microband array electrodes that are not considered in the present paper.

It is perhaps more surprising that no electrochemist has presented thus far a complete and explicit analytical solution, to the problem discussed. The solutions published can be divided into approximate analytical, semi-analytical, and purely numerical. To the approximate analytical solutions belong those obtained by Aoki et al. [4,5], who used a mathematically intricate Wiener-Hopf technique to deduce approximate expressions for the PSCA

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current, valid for small and large times. The semi-analytical solutions include those reported by Cope et al. [6,7], who formulated the theory in terms of integral equations in the Laplace space. The integral equations were subsequently solved numerically by a sophisticated method accounting for the singularities. Other semi-analytical solutions were obtained by Mirkin and Bard [8,9], by first deriving two-dimensional integral equations for the Faradaic current density in the space-time domain, and next solving them by means of a quadrature-type method. The solutions obtained in Refs. [4–9] are either not complete or not explicit (or both). Completeness requires the validity of the solutions for any time value, and for any relevant location in space. For explicitness, a need to solve some implicit equations (such as integral or differential equations) must be avoided: important quantities of interest, such as the Faradaic current density and Faradaic current, should be computable directly as right-hand sides of appropriate mathematical equations. Finally, as an example of many purely numerical solutions we mention the digital simulation study by Britz et al. [10], who obtained reference values of the PSCA limiting current by means of finite difference methods.

Apart from the above rigorous theoretical models, a number of electrochemists [6,11–13] have presented various heuristic approximations to the PSCA current, mostly in order to cover the intermediate time interval, in which the analytical solutions from Refs. [4,5] were not satisfactory. Such approximations are usually arbitrary and not very accurate. Some comparisons of the heuristic approximations are available in Refs. [2,10]. Further comparisons will be given in the present paper.

A summary of the various formulae for the current, reported in the references listed above, and including the heuristic approximations, is given in Appendix.

In the present work we describe a novel theoretical approach that allows us to obtain previously unknown complete and explicit semi-analytical solutions to the PSCA at a microband electrode. The approach relies on viewing the initial boundary value problem (IBVP) for the PSCA at a microband electrode as a limiting case of a slightly different model of PSCA at a hypothetical infinite elliptic cylinder microelectrode, when one radius of the elliptic cross-section of the cylinder tends to zero. This allows us to utilise the analytical solution to the mathematically equivalent problem of heat conduction around an elliptic cylinder, published in 1951 by Tranter [14].

Complete explicit expressions for the Faradaic current density and the Faradaic current will be obtained in the form of an inverse Laplace transform of certain infinite series, which can be evaluated by applying a numerical inversion of the Laplace transform. The formulae may appear complicated and not enabling an immediate identification of the key variables and their influence on the electrochemical responses. However, we shall demonstrate that further analytical examinations and interpretations of the formulae are possible, leading to interesting and useful conclusions. We shall also see that highly accurate numerical values can be computed, that would be much more difficult or even impossible to obtain by usual 2D digital simulations [1].

Essential elements of the present theory are outlined in Sect. 2. Section 3 describes results of numerical tests, comparing the theory with independently available numerical reference data, and with formulae for limiting cases.

Readers interested in potential extensions of the present theory, to include additional effects such as natural convection or double layer charging, may be guided by Refs. [15,16] (the first reference addresses natural convection at a microband; the second deals with double layer charging at a microdisk electrode). Considering such effects is likely to result in a substantially more complicated formalism, and any attempt to take such effects into account is far outside the scope of the present study.

2. Theory

We begin with the standard presentation of the relevant IBVP in Cartesian coordinates (Subsect. 2.1), then reformulate it using elliptic coordinates (Subsect. 2.2). The Tranter solution [14] is subsequently described (Subsect. 2.3), allowing us to derive explicit formulae for the Faradaic current density and the Faradaic current (Subsect. 2.4). Finally, we discuss the limiting cases of large and small times (Subsect. 2.5-2.7).

2.1. The IBVP in Cartesian coordinates

The IBVP describing the PSCA at a microband electrode is usually formulated in the Cartesian coordinate system (x, y, z), assuming that the electrode and the insulator surfaces form the $x-y$ plane, and that the electrode is located at $-a/2<x<a/2$ and $-\infty<y<\infty$, where a is the electrode width. The insulator is located at $-\infty<x<-a/2$, $a/2<x<\infty$, and $-\infty<y<\infty$. As the electrode band is assumed infinite in the direction of y, the IBVP does not depend on the y coordinate. Owing to the expected symmetry of the IBVP, with respect to the $y-z$ plane, the spatial domain is usually further restricted to the $x>0$, $z>0$ quadrant of the $x-z$ plane.

The diffusion partial differential equation (PDE):

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

is accompanied by the initial condition

$$c(x,z,0)=c^{\star}. \tag{2}$$

In Eqs. (1) and (2) $c(x, z, t)$ denotes the concentration of a depolarizer, D is its diffusion coefficient, and $c^{\star}$ is its initial uniform concentration. The boundary conditions (all holding at $t>0$) are as follows. At the $x-y$ plane the boundary conditions are:

$$c(x,0,t)=0 \tag{3}$$

when $0<x<a/2$ (at the electrode surface), and

$$\left.\frac{\partial c(x,z,t)}{\partial z}\right|_{z=0}=0 \tag{4}$$

when $a/2<x<\infty$ (at the insulator surface). Eq. (3) expresses the concentration drop down to zero, as a result of applying, at $t=0$, a large potential step to the electrode, thereby enforcing limiting current conditions. The no-flux condition, Eq. (4), expresses the lack of the consumption of the depolarizer at the insulator surface. In the electrolyte bulk the boundary conditions are:

$$c(\infty,z,t)=c^{\star}, \tag{5}$$

$$c(x,\infty,t)=c^{\star}. \tag{6}$$

At the symmetry plane $y-z$ one usually assumes the boundary condition

$$\left.\frac{\partial c(x,z,t)}{\partial x}\right|_{x=0}=0. \tag{7}$$

When solving the IBVP (1)-(7), one is primarily interested in obtaining theoretical predictions for the Faradaic current density $j(x, t)$, and the Faradaic current $i(t)$ (per unit length of the microband), since the current is the usual experimental observable. Current density is normally not measurable experimentally, but its detailed knowledge offers insights into the progress of the electrochemical experiment. Knowing exact values of the current density is also useful for validating results of various modelling or simulation approaches. In the case of an electroreduction reaction taking

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