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A new theory, and automatic computation of reversible cyclic voltammograms at a microband electrode

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ABSTRACT

By generalising the recent theory of chronoamperometry [L. K. Bieniasz, Electrochim. Acta 178 (2015) 25], a new, semi-analytical description of reversible cyclic voltammetry at a microband electrode is obtained, assuming equal diffusion coefficients of the species involved in a redox reaction. In contrast to the formerly proposed model [K. Aoki, K. Tokuda, J. Electroanal. Chem. 237 (1987) 163], the new theory does not involve any heuristic approximations. It is based on the formalism of Mathieu equations and functions, and provides rigorous and complete expressions for the voltammetric current, in the form of either a convolution integral or an integral equation. The voltammograms are calculated automatically with a prescribed accuracy, by using either the adaptive integrator dqags from the QUADPACK package, or the adaptive Huber method for integral equations. The two methods are compared, and dqags is found to be more efficient. A highly accurate (relative error about 10^{-16}) procedure for calculating the kernel function of the integral equation, and its moment integrals, is also described.

1. Introduction

The objective of the present paper is to describe novel results concerning the theory and computation of cyclic voltammograms for a reversible redox reaction at a microband electrode embedded flush in an insulator plane. Voltammograms of this type are studied routinely in contemporary electrochemistry, since both cyclic voltammetry and band microelectrodes belong to standard electroanalytical techniques [1]. However, we shall show that despite former modelling studies [2–9] there is still a place for a new, previously unknown mathematical description of such voltammograms.

Among the various modelling approaches to microelectrodes [10], the most straightforward are direct digital simulations [11,12] by numerically solving diffusion partial differential equations (PDEs). Such simulations, employing finite difference or other direct methods, were performed for the present electroanalytical experiment by a number of authors [2,3,7–9]. The microelectrode simulations involve two-dimensional spatial domains and are, in consequence, computationally expensive. The use of various conformal transformations of spatial coordinates can speed up the calculations [11,12], but computational costs nevertheless limit practically achievable relative errors of the numerical solutions to (at best) about $10^{-2}-10^{-5}$. Apart from this limitation, digital simulation returns nothing more than just numerical values of the model solutions. It does not necessarily offer insights into the theoretical relationships. This observation is not a critique of digital simulation which for many complex models is indispensable. However, it is a good scientific practice to look for analytical or semi-analytical solutions of electroanalytical models, whenever there is a chance of obtaining such solutions, even though the use of digital simulation might be easier. Derivations of (semi-)analytical solutions improve our understanding of the models. An availability of various alternative theoretical descriptions of electroanalytical experiments can also help avoiding misinterpretations caused by blind uses of modern electroanalytical hardware and software [13].

One interesting alternative to direct digital simulations of voltammetry at a microband electrode is offered by the two-dimensional integral equation (IE) approach of Mirkin and Bard [5,6]. A partially analytical solution of the diffusion PDEs leads to IEs for the Faradaic current density distribution across the microband. This approach is a natural generalisation of the classical one-dimensional IE method for spatially one-dimensional models [14], and it can be applied to any controlled potential transient experiments, not only to voltammetry. Numerical solution of the resulting IEs should be faster than the aforementioned direct digital simulation, because one spatial dimension is eliminated in the process of deriving the IEs. However, we shall not follow this theoretical route, because satisfactory numerical techniques for solving the Mirkin and Bard IEs still have to be designed.

Instead, we shall explore another theoretical route, similar to that recently applied to obtain a complete rigorous semi-analytical solution for the chronoamperometric limiting current at a microband [15], and a highly accurate approximation to this current [16]. We shall obtain rigorous and complete semi-analytical expressions for cyclic voltammograms in the case of equal diffusion coefficients of the redox couple,

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by using the formalism of Mathieu equations and functions [17]. This will allow us to determine the voltammograms in two alternative ways. One way will be analogous to that used by Aoki and Tokuda [4], who related the voltammetric current with the chronoamperometric limiting current. However, in contrast to Aoki and Tokuda we shall derive a rigorous integral formula for the voltammogram, rather than an approximate heuristic formula obtained in Ref. [4]. The second way will yield the voltammetric current as a solution of a one-dimensional IE similar to those encountered in spatially one-dimensional electroanalytical models [14]. A rigorous formula for the kernel of this IE will be derived. A highly accurate procedure for computing this kernel function (and its moment integrals) will also be presented.

Both ways of deriving the voltammograms will be followed by numerical computations. To comply with the modern standards of scientific computing, we shall utilise adaptive techniques that allow one to automatically achieve a prescribed accuracy. Hence, for evaluating the voltammetric current as an integral we shall use an adaptive quadrature. For solving the IE the adaptive Huber method [14,18–21] for one-dimensional electrochemical IEs will be used, in a way very similar to solving IEs describing transient experiments at a cylindrical (or hemicylindrical) microelectrode [22,23]. The latter microelectrode is often compared to, and regarded similar to the microband [3,24–26]. This will be the first application of one-dimensional IEs to the modelling of transient experiments at a microband, in contrast to the modelling of voltammetry at a microdisk electrode, which has already been accomplished in this way [27–29] (Ref. [29] was based on a previous paper written in Chinese [28], which makes both papers difficult to understand, at least for the present author. One unclear aspect is whether it is correct to replace two-dimensional IEs, that rigorously represent such models [5,6], by one-dimensional IEs, when the electrode reaction is quasi-reversible, as was done in Ref. [29]. Available knowledge suggests that such a replacement is possible when the concentrations of the reactants are uniform along the electrode surface. However, for quasi-reversible redox reactions they cannot be uniform). Since in one-dimensional IEs both spatial dimensions are eliminated, their numerical solution is, of course, faster than the solution of the Mirkin and Bard IEs.

There exists at least one more, potentially applicable, method of calculating the voltammograms. It is the method that relies on the superposition of chronoamperometric responses corresponding to a sequence of discrete potential values [30–32]. This method will not be used here, for reasons that will be given later.

Cyclic voltammograms calculated accurately by either of the above two routes can find application in the analysis of experimental voltammograms at microband electrodes, or they can serve for testing/validating various other modelling methods. The highly accurate procedures for computing the kernel function and its moment integrals can also allow one to perform the so-called convolutive analysis of experimental transients. The convolutive analysis presents a challenge in the case of microelectrodes, due to the still limited knowledge of the kernel functions [33,34].

2. Theory

We retain here the following idealisations adopted in Refs. [2–8,15,16]: an effectively infinite microband (implying a translational symmetry of the mathematical model); an infinite electrode-insulator plane; a semi-infinite electrolyte phase; a single electrochemical reaction uncomplicated by homogeneous or heterogeneous non-electrochemical reactions; purely diffusional transport of the reactants; neglection of additional effects such as natural convection, double layer charging, or ohmic potential drops.

We thus consider the Nernstian redox reaction

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

taking place at the microband, with O and R being the species subject to diffusion in the electrolyte. Any controlled potential transient experiment for this reaction is described by the following initial boundary value problem (IBVP), formulated in the Cartesian coordinate system (x,y,z). Diffusion PDEs are:

$$\frac{\partial c_{\mathrm{X}}(x,z,t)}{\partial t} = D_{\mathrm{X}}\left[\frac{\partial^2 c_{\mathrm{X}}(x,z,t)}{\partial x^2} + \frac{\partial^2 c_{\mathrm{X}}(x,z,t)}{\partial z^2}\right], \tag{2}$$

where X stands for O or R, $c_{\mathrm{X}}(x,z,t)$ denotes the concentration of a species X, and D_{X} is its diffusion coefficient. We assume that the electrode and the insulator surfaces coincide with 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 $-\infty<y<\infty$. The electrolyte phase corresponds to $z>0$. Owing to the translational symmetry in the direction of y, the IBVP does not depend on the y coordinate. Owing to the 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.

For fixing attention, we consider a transient experiment that begins with the electroreduction reaction (1), but the formulae provided below are equally well applicable for oxidation, after appropriate sign changing. Hence, assuming that the reaction product is not initially present, initial conditions are:

$$c_{\mathrm{O}}(x,z,0) = c^\star, \tag{3}$$

$$c_{\mathrm{R}}(x,z,0) = 0, \tag{4}$$

where $c^\star$ is the initial uniform concentration. Boundary conditions (all holding at $t>0$) are as follows. At the electrode surface ($x-y$ plane, $0<x<a/2$) the Nernst equation and the balance of fluxes must be obeyed:

$$c_{\mathrm{O}}(x,0,t)/c_{\mathrm{R}}(x,0,t) = \exp\left\{\frac{nF}{RT}\left[E(t)-E^0\right]\right\}, \tag{5}$$

$$D_{\mathrm{O}}\left.\frac{\partial c_{\mathrm{O}}(x,z,t)}{\partial z}\right|_{z=0} + D_{\mathrm{R}}\left.\frac{\partial c_{\mathrm{R}}(x,z,t)}{\partial z}\right|_{z=0} = 0. \tag{6}$$

In Eq. (5) $E(t)$ is the electrode potential perturbation, E^0 is the conditional potential of reaction (1), and F, R, and T have their usual meaning. At the insulator surface ($x-y$ plane, $a/2<x<\infty$) the no-flux boundary conditions express the lack of consumption of the species at the insulator surface:

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

In the electrolyte bulk the concentrations remain unperturbed from their initial values:

$$c_{\mathrm{O}}(\infty,z,t) = c_{\mathrm{O}}(x,\infty,t) = c^\star, \tag{8}$$

$$c_{\mathrm{R}}(\infty,z,t) = c_{\mathrm{R}}(x,\infty,t) = 0. \tag{9}$$

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

$$\left.\frac{\partial c_{\mathrm{O}}(x,z,t)}{\partial x}\right|_{x=0} = \left.\frac{\partial c_{\mathrm{R}}(x,z,t)}{\partial x}\right|_{x=0} = 0. \tag{10}$$

When solving the IBVP (2)–(10), 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. The unknowns