



Highly accurate, inexpensive procedures for computing theoretical chronoamperometric currents at single straight electrode edges and at single microband electrodes



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ABSTRACT

Theoretical considerations of potential step chronoamperometry for electrochemical systems involving straight electrode edges lead to a number of analytical or semi-analytical expressions, or special functions, describing current-time dependences. Unfortunately the functions are hard to evaluate accurately on a computer, due to numerical difficulties or high computational costs. In this work computationally inexpensive procedures have been developed, for two special functions describing chronoamperometry at a single straight edge and for one special function expressing chronoamperometric current at a single microband electrode (two straight edges). The concept of the minimax approximation has been employed. The procedures are highly accurate, ensuring relative errors close to, or even smaller than 10^{-16} , which is the machine accuracy for standard double precision variables. In addition, computing a single function value requires less than a microsecond of the processor time on currently available personal computers. The procedures can be useful for the purposes of experimental data analysis, and for the testing/validation of diverse mathematical and numerical modelling techniques designed for electroanalytical chemistry.

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1. Introduction

In many electrochemical systems an electrolytic phase is in contact with a solid phase composed partly of an electronic conductor (electrode), and partly of an insulator. Edges separating the conducting and non-conducting areas of the interface between the two phases play an important role in the Faradaic current generation. Distributions of the Faradaic current density along the interfaces usually possess local maxima or even singularities at the edges. Such phenomena are generally termed “edge effects” in the literature.

Theoretical description of the edge effects is of considerable interest, mostly in connection with the widespread use of micro- and submicroelectrodes [1], where such effects are significant, but also in the studies of partially blocked or passivated electrodes. Apart from their physicochemical importance, the edge effects present challenging benchmark situations for digital simulation methods [2] and other mathematical or computational modelling approaches used in electrochemistry. They usually pose significant difficulties to any analytical or numerical approaches.

In view of the above circumstances, it would be useful to have a collection of highly accurate but cheaply computable procedures, or

approximations to various special functions occurring in the theory of the edge effects. Such procedures could be used both for the experimental data analysis, and for validating modelling/simulation methods. By “high accuracy” we mean here the relative accuracy close to, or even better than 10^{-16} , which is the machine accuracy of standard double precision variables [3] used predominantly for scientific calculations. Approximations possessing this level of accuracy have already been developed for several difficult-to-compute special functions of interest to electroanalytical modelling [4–6]. The computation of special functions with the machine accuracy is currently standard in computational science, as is exemplified by numerous libraries provided together with compilers of programming languages or with numerical packages. The machine accuracy is most desirable for researchers developing and testing simulation techniques for electrochemistry. The convergence of any new method has to be demonstrated in a wide range of discretisation errors, down to the level of machine errors. This requires highly accurate reference solutions of benchmark example models. Experimental data analysis is perhaps less demanding, since experimental results usually have errors close to 1%. However, this argument is often overused, resulting in a widespread but anti-progressive opinion that electrochemists do not need theoretical formulae more than 1% accurate. There is no necessity of maintaining this minimalist culture, and there is no harm in designing and using highly accurate formulae for data analysis, if only such formulae can be derived.

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In the present paper we describe highly accurate approximations to three functions occurring in the theory of potential step chronoamperometric currents, in the case of systems involving electrode edges that are straight lines on a planar interface. These are probably the simplest possible arrangements where the edge effects occur. Two of the functions considered originate from the theory of chronoamperometry at a single straight edge, reported by Myland and Oldham [7]. These functions can be expressed in terms of the (known) generalised hypergeometric series, but the series is hard to evaluate reliably and accurately without using a multiprecision environment, such as MATHEMATICA [8]. The third function describes the chronoamperometric Faradaic current at a microband electrode, embedded flush in an insulator plane. In this case there are two closely separated, parallel straight edges. For the latter function a complete, semi-analytical expression has recently been derived by the present author [9]. In contrast to all former theoretical and numerical approaches, the expression is rigorously valid for any time value, and it can also be used for computing highly accurate values of the current. Unfortunately, such calculations are computationally expensive, and again require a multiprecision environment.

The approximations developed in the present work are free from the inconveniences caused by the costly multiprecision calculations, and can therefore be more practical.

Assumptions adopted in Refs. [7,9], referring to the three functions considered here, include: infinite interfaces, edges, and electrolyte phases; translational symmetry of the mathematical models in the direction of the edges; a single electrochemical reaction uncomplicated by homogeneous or heterogeneous non-electrochemical reactions; purely diffusional transport; limiting current conditions; and neglect of additional effects such as natural convection, double layer charging, or ohmic potential drops. For fixing attention, we shall assume that the electrochemical reaction is an electroreduction, but the formulae provided below are equally well applicable for oxidation, after appropriate sign changing.

2. Functions

In this section we present the special functions describing chronoamperometry at straight edges, for which relevant approximations will be given in Section 3.

2.1. The case of a single edge

As was shown by Myland and Oldham [7] the Faradaic current density j depends on the distance d from a single straight edge (measured along the electrode surface), and on time t , according to the formula:

$$j(d, t) = -\frac{nFc^*}{(\pi Dt)^{1/2}} \Phi \left[\frac{d}{(4Dt)^{1/2}} \right], \quad (1)$$

where n is the number of electrons transferred in the electrochemical reaction considered, F is the Faraday constant, and c^* and D denote the initial/bulk concentration and diffusion coefficient of a depolarizer. Function $\Phi(\zeta)$, where $\zeta = d(4Dt)^{-1/2}$, has three alternative mathematical representations, out of which the one most useful for the present study is:

$$\Phi(\zeta) = \frac{1}{2} \left[\left(\frac{\zeta}{2} \right)^{1/2} {}_2F_2 \left(-\frac{1}{4}, \frac{1}{4}; \frac{3}{4}, \frac{3}{4}; -\zeta^2 \right) \frac{\Gamma(3/4)}{\Gamma(3/4)} + \left(\frac{\zeta}{2} \right)^{1/2} {}_2F_2 \left(\frac{1}{4}, \frac{3}{4}; \frac{5}{4}, \frac{3}{4}; -\zeta^2 \right) \frac{\Gamma(5/4)}{\Gamma(5/4)} \right]. \quad (2)$$

In Eq. (2) $\Gamma(\cdot)$ is the Euler gamma function, and

$${}_pF_q \left(\vec{\alpha}; \vec{\beta}; z \right) = \sum_{k=0}^{\infty} \frac{(\alpha_1)_k \dots (\alpha_p)_k}{(\beta_1)_k \dots (\beta_q)_k} \frac{z^k}{k!} \quad (3)$$

with $\vec{\alpha} = [\alpha_1, \dots, \alpha_p]^T$ and $\vec{\beta} = [\beta_1, \dots, \beta_q]^T$ is the generalised hypergeometric function [10]. In Eq. (3), for any real number α , $(\alpha)_k$ denotes the Pochhammer symbol [10]:

$$(\alpha)_k = \alpha(\alpha+1)\dots(\alpha+k-1) = \Gamma(\alpha+k)/\Gamma(\alpha). \quad (4)$$

By integrating Eq. (1) along the variable d , one obtains the Faradaic current $i_{\text{edge}}(d, t)$ generated within the electrode strip of width d , adjacent to the edge, per unit length of the strip:

$$i_{\text{edge}}(d, t) = -nFc^*D \frac{2}{\pi^{1/2}} I_{\Phi} \left[\frac{d}{(4Dt)^{1/2}} \right], \quad (5)$$

where

$$I_{\Phi}(\zeta) = \int_0^{\zeta} \Phi(\lambda) d\lambda \quad (6)$$

is simply the integral of $\Phi(\zeta)$.

Functions $\Phi(\zeta)$ and $I_{\Phi}(\zeta)$ are two special functions for which we shall present relevant approximate procedures. Plots of these functions are shown in Fig. 1a. These functions were originally derived for the theory of a single electrode edge [7], with the intention to clarify the role of the edge effects in the current generation at partially blocked electrodes. In practice, a single edge presents an idealisation of reality, as any real electrode must have a finite size, and hence more than one edge. Therefore, the functions $\Phi(\zeta)$ and $I_{\Phi}(\zeta)$, and the theory of Ref. [7], are expected to provide useful predictions for chronoamperometry only at very short times of the experiments, as long as the currents generated at any particular edge do not interfere with the currents generated at other edges. This property has been demonstrated [9] for a single microband electrode, but a similar utility of the functions $\Phi(\zeta)$ and $I_{\Phi}(\zeta)$ can be expected for dual microband electrodes [11], interdigitated band microelectrode arrays [12], micromesh electrodes [13], thin microring electrodes [14], or band models of the surface geometry of electrochemically heterogeneous surfaces, such as those corresponding to the highly ordered pyrolytic graphite [15].

2.2. The case of two parallel edges (a single microband)

The theory of chronoamperometry at a microband electrode has been considered by many authors (for overviews of the related literature see, in particular, Refs. [2,9,16,17]). However, the only currently available complete and explicit formula for the Faradaic limiting current is the semi-analytical expression from Ref. [9]:

$$\bar{i}_{\text{band}}(\bar{t}) = \mathcal{G}(16\bar{t}), \quad (7)$$

with

$$\mathcal{G}(\tau) = \mathcal{L}^{-1} \left\{ -\frac{2\pi}{s} \sum_{m=0}^{\infty} \left[A_0^{(2m)}(s) \right]^2 \frac{\text{Fek}'_{2m}(0, -s)}{\text{Fek}_{2m}(0, -s)} \right\}. \quad (8)$$

In Eq. (7) \bar{t} is the dimensionless time, defined as

$$\bar{t} = Dt/a^2, \quad (9)$$

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