



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



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ABSTRACT

A novel theory is presented, of potential step chronoamperometry at a microdisk electrode, assuming a purely diffusional transport under limiting current conditions. The theory provides previously unknown, rigorous, complete, and explicit expressions for the concentration, the Faradaic current density, and the Faradaic current. The microdisk is considered as a limiting case of an oblate microhemispheroidal electrode, when the smallest radius of the hemispheroid tends to zero. The method of separation of variables in the Laplace space is used, resulting in two spheroidal differential equations. The concentration of the depolarizer, the Faradaic current density, and the Faradaic current, are then expressed as inverse Laplace transforms of infinite series involving spheroidal wave functions. Numerical Laplace transform inversion, applied to the series, yields highly accurate solution values. The series are also amenable to analytical examinations. Hence, the present solutions should be preferred over formerly used low-accurate and/or heuristic approximations, for the purposes of experimental data analysis, and for the testing of modelling/simulation techniques. The formula derived for the concentration can also be used to develop a theory of chronoamperometry at oblate microhemispheroidal electrodes.

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1. Introduction

In this paper we present a novel theory of potential step chronoamperometry (PSCA) performed at a single planar microdisk electrode, embedded flush in an insulator plane. We assume a simple reduction reaction



with only species O being initially present and subject to a purely diffusional transport under limiting current conditions caused by a step to a negative potential 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, are not taken into account. The paper is to large extent similar to the previous article [1] that described a new theory of PSCA at a microband electrode. The similarity lies in the general aspects of the methodology: we derive exact, explicit, and complete expressions

for the Laplace transforms of the Faradaic current density and of the Faradaic current. This is accomplished in an analytical way, without any simplifications. Subsequently, we 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 [2,3]. The numerical inversion has also proven successful in the developments of the integral equation (IE)-based electrochemical modelling methodology [4].

There are at least two reasons why the theory of PSCA experiments at microdisks is of interest to electrochemistry. First, these experiments have become standard in practical applications of microelectrodes, and microdisk electrodes are even more popular than microbands. Experimental data obtained in such experiments should be analysed using a reliable theory that preferably does not involve unnecessary simplifications or inaccuracies. Second, theoretical models of such experiments may serve as challenging benchmark examples for testing various analytical and computational approaches to electroanalytical modelling. This is caused by the presence of edge effects characterised by spatial and temporal singularities of the current density, which pose severe difficulties for the modelling techniques. The testing requires an availability of

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Nomenclature

c^*	initial/bulk concentration of a depolarizer (species O)
c	concentration of a depolarizer (species O)
D	diffusion coefficient of a depolarizer (species O)
F	Faraday constant
g	parameter of the spheroidal ODE (36); here $g = r_0(s/D)^{1/2}$
Γ	oblate spheroidal coordinate (radial)
Γ_0	location of a hemispheroid surface along coordinate Γ
γ	auxiliary coordinate, defined as $\gamma = \sinh \Gamma$
$i(t)$	dimensional Faradaic current, defined by Eq. (10)
$\tilde{i}(\tilde{t})$	dimensionless Faradaic current, defined as $\tilde{i}(\tilde{t}) = i(t)/i_{ss} = -i(t)/(4nFDc^*r_0)$.
i_{ss}	dimensional steady state current, defined by Eq. (26)
i	imaginary unit
$j(r, t)$	dimensional Faradaic current density, defined by Eq. (9)
$\tilde{j}(\tilde{r}, \tilde{t})$	dimensionless Faradaic current density, defined as $\tilde{j}(\tilde{r}, \tilde{t}) = -j(r, t)r_0/(nFDc^*)$
$\mathcal{L}\{G\} = \hat{G}$	Laplace transform of any expression G (between domains of t and s)
$\tilde{\mathcal{L}}\{G\}$	Laplace transform of any expression G (between domains of $\tilde{t}$ and $\tilde{s}$)
λ	eigenvalue of the spheroidal ODE (36)
m	parameter of the spheroidal ODE (36) (here equal zero)
n	number of electrons transferred in reaction (1)
r	dimensional (radial) cylindrical coordinate
$\tilde{r}$	dimensionless cylindrical coordinate, defined as $\tilde{r} = r/r_0$
r_0	microdisk electrode radius
s	Laplace variable corresponding to time t
$\tilde{s}$	Laplace variable corresponding to time $\tilde{t}$, defined as $\tilde{s} = (r_0^2/D)s$
t	dimensional time
$\tilde{t}$	dimensionless time, defined as $\tilde{t} = Dt/r_0^2$
θ	oblate spheroidal coordinate (angular)
ϑ	auxiliary coordinate, defined as $\vartheta = \sin \theta$
u	auxiliary dependent variable, defined as $u = c^* - c$
z	dimensional cylindrical coordinate
$\tilde{z}$	dimensionless cylindrical coordinate, defined as $\tilde{z} = z/r_0$

highly accurate theoretical predictions (ideally with errors at the level of the error of machine representation, which for predominantly used standard double precision variables is about 10^{-16} [5]). For these reasons, over the past decades there have been many theoretical and digital simulation studies devoted to the modelling of the PSCA at microdisk electrodes. The book by Britz [6], and three more recent reviews [7–9] provide a helpful introduction to the related literature. References [6] and [9] survey also the literature about the modelling of microdisk array electrodes that are not considered in the present paper.

Among the previous studies of the above problem, one can distinguish analytical, semi-analytical, and purely numerical ones. An exact analytical result was the equation for the steady state Faradaic current i_{ss} (see Eq. (26) in Subsect. 2.3 later). The derivation of i_{ss} is sometimes attributed to Saito [10], but the formula for the steady state solution (here the concentration of O) was known earlier in the area of heat conduction studies [11]. The steady state current i_{ss}

presents a limit, to which the transient PSCA current decays when time $t \rightarrow \infty$.

Early theories of the transient PSCA current [12,13] were simplified, and are not currently used. Aoki and Osteryoung [14] tried to derive rigorous analytical series expansions of the current, valid in the limits of small and large time t . They used the mathematically intricate Wiener-Hopf technique. Unfortunately, Ref. [14] contained errors, which has given rise to a number of corrections [15–19]. At present, it seems that Refs. [17,19] contain correct values of a few first coefficients of the current expansion valid for large t , whereas correct three first terms of the expansion valid for small t were obtained by Phillips and Jansons [18] (cf. Eqs. (A.1) and (A.2) in Appendix A that contains a collection of the most important published formulae for the PSCA current at a microdisk).

Among the former semi-analytical solutions, there are those obtained by numerically solving relevant IEs. In one approach the IEs were formulated in the Laplace space [20–22]. Alternatively, they were formulated in the time domain [23]. Numerical solution of such IEs is usually a difficult task, because of the presence of spatial and temporal singularities of the solutions, and the present state of art of the numerical methods used for such calculations is not very satisfactory.

Most of the theoretical studies of the PSCA at a microdisk have been accomplished using transient digital simulations by directly solving the diffusion partial differential equations (PDEs) by numerical techniques such as finite-difference or other similar methods [15,24–43]. Simulations of this kind usually suffer from difficult to eliminate errors associated with the spatial and temporal singularities of the solutions or their derivatives. Hence, several from Refs. [15,24–43] were devoted to various attempts to minimise such errors.

Apart from the rigorous theoretical models, a number of authors [44–48] presented heuristic approximations to the PSCA current, mostly in order to cover the intermediate time interval, in which the series expansions elaborated in Refs. [14–19] were not satisfactory. We list these approximations in Appendix A. Such approximations are usually arbitrary and not very accurate. Some comparisons of the heuristic approximations are available in Refs. [34,49]. Further comparisons will be described in the present paper.

In addition to the literature devoted specifically to the modelling of PSCA at microdisk electrodes, it is pertinent to mention previous works on the modelling of PSCA at hemispheroidal microelectrodes [50–55]. The microdisk electrode can be perceived as a limiting case of an oblate microhemispheroid, when the smallest of its radii is reduced to zero. Hence, the theory for the microdisk electrode should be, in fact, a special case of the more general theory for the oblate microhemispheroidal electrode. The available theory for the microhemispheroidal electrode is, however, less developed than that for the microdisk, being mostly focused on steady state currents [50,51] and heuristic approximations for the transient PSCA current [52,54,55], transient simulations being rare [53].

Finally, we observe that there exists a literature devoted to the mathematically equivalent problems of heat transport around a conducting disk in an insulating plane, and around spheroidal bodies, which has been overlooked in electrochemistry. In particular, large-time and small-time approximations to the solutions of the conducting disk problem were obtained by Norminton and Blackwell [56,57] several years before Aoki and Osteryoung [14]. Simulations by Schneider et al. [58] preceded almost all electrochemical simulation studies [15,24–43], with the exception of those of Flanagan and Marcoux [24]. Works by Blackwell [57] and Marder and Keltner [59] contain important mathematical suggestions that we shall utilise in the present work.

It should be emphasised that no electrochemist has presented thus far complete rigorous and explicit analytical or semi-analytical equations for the Faradaic current density and

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