



# A new theory and automatic computation of reversible cyclic voltammograms at an inlaid disk electrode

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## ABSTRACT

By generalising the recent theory of chronoamperometry [L. K. Bieniasz, *Electrochim. Acta* 199 (2016) 1], a new, semi-analytical description of reversible cyclic voltammetry at an inlaid disk electrode is obtained, assuming equal diffusion coefficients of the electroactive species. In contrast to some former modelling studies, the new theory does not involve simplified or low-accurate approximations to the chronoamperometric current or integral transformation kernel, but it is mathematically rigorous. An explicit expression for the voltammetric current function is derived, in the form of an inverse Laplace transform of an infinite series involving spheroidal wave functions. An equivalent formula involving convolution integrals, more suitable for calculations, is also obtained, as well as an integral equation for the current function. The voltammograms are calculated automatically with a prescribed accuracy, by using either the adaptive integrator INTDE based on double exponential formulas, or the adaptive Huber method for integral equations. INTDE is more efficient, allowing one to compute a current function value with a relative error as close to  $\pm 10^{-16}$  as is possible, in a computing time of ca. 1 ms on a contemporary laptop computer.

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## 1. Introduction

Cyclic voltammetric experiments performed on inlaid disk (micro)electrodes currently belong to the standard arsenal of electroanalytical techniques [1]. Consequently, there is a need for a rigorous theoretical description of such experiments, and for efficient and accurate procedures of computing theoretical voltammograms. From the mathematical point of view, obtaining such a theory is usually a difficult task, because this requires a solution of two-dimensional partial differential equations (PDEs) with complicated boundary conditions [2–4], which typically results in sophisticated formalisms.

The present paper is devoted to the theory and computation of cyclic voltammograms for a single, reversible redox reaction at an inlaid disk, uncomplicated by homogeneous reactions. Although this particular electrochemical system has been considered in many former studies (see, in particular, Refs. [5–22]), we shall present a new, previously unknown mathematical description of reversible voltammograms, and new, automatic procedures of computing

them. This work is to a large extent analogous to the previous study [23] where a novel theory and automatic computation methods of reversible cyclic voltammograms were elaborated for band (micro) electrodes. The emphasis on automatic computations is motivated by the modern standards of computational science, and desired standards of computational electrochemistry [24]. We shall also pay special attention to methods of computing the voltammograms with a high accuracy and efficiency. By “high accuracy” we understand an accuracy comparable (as much as this is possible) with the accuracy of the representation of standard double precision variables [25] which have relative errors close to  $\pm 10^{-16}$ . Obtaining highly accurate theoretical reference voltammograms is of particular interest to those who develop modelling and simulation methods for electrochemistry, and need to verify the correctness of their methods. High efficiency is in turn desirable if one wants to think about real-time theoretical analysis of experimental data, which belongs to the current trends in electroanalytical instrumentation (see, for example, Brett [26]).

Theoretical reversible linear potential sweep and cyclic voltammograms at inlaid disks were calculated in the past predominantly by using digital simulation methods serving for a direct numerical solution of PDEs [3,4]. Mostly finite difference methods were used for this purpose [5,7–10,13–15,19–22], but sporadically

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other methods were employed [11]. Digital simulations are useful and often indispensable, but they yield nothing more than just numerical values of the model solutions. They do not necessarily provide insights into the theoretical relationships (in addition, contemporary digital simulation methods are not very accurate; practically achievable moduli of the relative errors of the numerical solutions are limited to about  $10^{-2} - 10^{-5}$ ). Therefore, it is 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. This often allows one to better understand the models, and can also help avoiding misinterpretations caused by blind uses of modern electroanalytical hardware and software [27].

One can distinguish at least the following five semi-analytical approaches A-E, potentially applicable to the theoretical description of reversible voltammograms at inlaid disks:

(A) If this is feasible, one can try to represent the voltammetric current function as an inverse Laplace transform of an appropriate analytically derived expression. Numerical Laplace transform inversion must subsequently be applied, in general, to calculate the current function [28]. Powerful and automatic numerical algorithms for performing the inversion are currently available, which often operate without any need for numerical integration in the complex plane, or without using complex numbers at all, and can also invert singular transforms without any difficulty [29]. Such calculations can be very accurate, but they are usually computationally expensive and require special multiprecision environments such as MATHEMATICA [30] (see, for example, Ref. [31]). Approach A was not yet applied to reversible voltammograms at inlaid disks. (B) A closely related possibility is to express the voltammetric current function by certain convolution integrals of the limiting chronoamperometric current, which are finally evaluated numerically (for a recent overview of approach B see Ref. [32] and references cited therein). Approach B was used by Aoki et al. [6] to compute reversible linear potential sweep (non-cyclic) voltammograms at an inlaid disk. The approach requires an assumption of uniform concentrations at the electrode, which is fulfilled when diffusion coefficients of the electroactive species are identical (see Sect. 2 for more details). The calculations from Ref. [6] were not very accurate, because of employing a low-accurate approximation to the chronoamperometric current. Similar, also not very accurate calculations were performed by Mahon and Oldham [16]. An advantage of approach B is that efficient and automatic procedures for numerical integration exist [32] and can be employed without a need for special computing environments. Approach B is also expected to be faster than digital simulations by directly solving PDEs, because spatial dimensions are entirely eliminated in the process of deriving the convolution integrals.

(C) Another semi-analytical method, related to that used in Refs. [6,16], and also restricted to the case of uniform concentrations at the electrode, is to convert the initial boundary value problem for PDEs (describing the voltammetric experiment for a reversible charge transfer at a disk electrode), to an appropriate one-dimensional Volterra integral equation (IE) of the first kind. Such an IE is similar to a variety of IEs resulting from spatially one-dimensional electroanalytical models [33]. The IE must subsequently be solved numerically for the unknown voltammetric current function, because the IE itself does not represent the solution of the problem, but only its alternative formulation. This method was used by Jin et al. [12] (although most of the results of Ref. [12] are likely to be incorrect, because the assumption of uniform concentrations at the electrode is not applicable to quasi-reversible charge transfers, which were mainly considered there). They employed a low-accurate approximation to the kernel of the

IE. Similar to approach B, numerical calculations associated with approach C should be faster than digital simulations by directly solving PDEs. Automatic numerical techniques for solving such IEs exist, for example the adaptive Huber method elaborated by the present author [34–38], and can be adopted for calculations.

(D) A more general semi-analytical approach to simulating voltammetry for reversible reactions at inlaid disks (not restricted to uniform concentrations at the electrode) could be the conversion of the PDEs to two-dimensional IEs, introduced to electrochemical modelling by Mirkin and Bard [39,40]. Their approach is a natural generalisation of the classical IE method for spatially one-dimensional models [33], mentioned above in point C. Here again the IEs must be solved numerically, since the IE itself does not represent a solution of the problem but only its alternative formulation. Numerical solution of such two-dimensional IEs is likely to be faster than digital simulations by directly solving PDEs, but to a lesser extent than in the case of one-dimensional IEs. This is because one-dimensional IEs (that depend only on time) correspond to one-dimensional PDE problems (dependent on time and one spatial coordinate). Hence, the spatial coordinate is eliminated in the IEs, which reduces the computational effort of solving the IEs, compared to the solution of the PDEs. But two-dimensional IEs (that depend on time and one spatial variable) correspond to two-dimensional PDE problems (dependent on time and two spatial coordinates). Again one spatial coordinate is eliminated, but the second spatial coordinate remains in the IEs, which implies a higher solution cost of the two-dimensional IEs, compared to the one-dimensional IEs. Unfortunately, satisfactory automatic methods for solving the Mirkin and Bard IEs are not yet available. In the case of reversible charge transfers one obtains Volterra-Fredholm IEs of the first kind, which are inherently ill-conditioned or even ill-posed. This might be one reason why Mirkin and Bard calculated exclusively quasi-reversible voltammograms at inlaid disks [39].

(E) Still another semi-analytical method relies on the superposition of chronoamperometric responses corresponding to the sequence of discrete potential steps [18,41,42]. Molina et al. [18] used this method to calculate voltammograms at inlaid disks, assuming uniform concentrations at the electrode surface, but they used low-accurate approximations to the chronoamperometric currents. In comparison to the approaches A-D, numerical aspects of approach E, such as accuracy, convergence, stability, and efficiency, are almost unknown (Ref. [18] mentions an accuracy of merely 1%), and no automatic algorithms employing the method have been described. However, the method can be interpreted as a variant of approach B, in which the convolution integral is replaced by a rectangle-type quadrature of low accuracy.

In the present work we follow approaches A, B and C, assuming equal diffusion coefficients of the electroactive species. In contrast to the former modelling studies [6,12,16,18] we do not use low-accurate approximations to the chronoamperometric current or to the IE kernel. Instead, by generalising the recent theory of chronoamperometry [43] we derive rigorous mathematical solutions, or use highly accurate approximants developed with the help of such solutions [44].

We repeat once again that the present study is limited to reversible charge transfer reactions between electroactive species having identical diffusion coefficients. The results obtained cannot be used to discuss voltammograms for quasi-reversible or irreversible reactions, nor even for reversible reactions involving electroactive species with unequal diffusion coefficients. They cannot be used for the judgments of the validity of Butler-Volmer or alternative models of electrochemical kinetics for the description of any electrochemical systems.

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