LIST OF PUBLICATIONS BASED ON THIS RESEARCH WORK:


Analytical Expression Of Current-Time Behavior In Rapid Flash Photolytic Processes At A Planar Electrode

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ABSTRACT
Analytical expression of current in rapid photolytic processes at a planar electrode is derived. The model is based on a stationary diffusion equation containing a non-linear term related to flash photolytic processes. The derivation is given for a planar electrode. An excellent agreement with the previous analytical results is noted.

INTRODUCTION
Non-linear reaction-diffusion models and their study arise in various contexts. Among them mention may be made of polymer modified ultramicroelectrodes, homogeneous mediated enzyme catalyzed reactions, electrodes modified with multi layered enzyme systems, and rapid photolytic processes. Therefore these models have been the subject of intense theoretical, numerical and experimental study over the past decades. The above all fields, the dimensionless non-linear reaction diffusion equation is

\[ \frac{\partial C}{\partial \tau} = \nabla^2 C - \varphi(C) \]

where \( C \) represents the dimensionless concentration of the electro active species, \( \tau \) represents the dimensionless time and \( \varphi(C) \) represents the homogeneous reaction term generally polynomial in the concentrations (which is non-linear in concentration). Most non-linear differential equations are difficult to solve in closed form. It is very difficult to obtain the exact solution to most non-linear differential equation. Moreover, even when closed-form solution is known, it may be so complicated that its qualitative properties are obscured. Thus, for most non-linear differential equations it is necessary to have reliable techniques to determine the approximate behavior solutions.

In Michaelis-Menten kinetics, the non-linear term is

\[ \varphi(C) = \frac{KC}{1 + \alpha C} \]

When \( \alpha C < 1 \), the non-linear term in the above equations is approximately equal to \( KC \). When \( \alpha C > 1 \), the non-linear term can be written as \( K/\alpha \). This model is completely discussed in Ref. We have discussed some of the reaction diffusion equations when

\[ \varphi(C) = \alpha C \]

In photolytic processes, the non-linear reaction term is
A COMPARISON OF DIFFUSION-LIMITED CURRENT AT MICROELECTRODES OF VARIOUS GEOMETRIES

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In this paper, we present a critical evaluation of the influence of geometry on the behavior of the transient current at ultramicroelectrodes. The nonsteady-state chronoamperometric diffusion limited current of various microelectrodes (circular disc, circular ring, elliptical disc, elliptical ring, band, hemicylinder, hemisphere, hemispheroid and hemisphere electrodes) are compared. Here, the area of the entire electrode is fixed and time variables are also normalised with respect to area. The chronoamperometric currents for short and long times for all microelectrodes are given in tabular as well as graphical form also.

Keywords: Microelectrode; nonsteady state; steady state; chronoamperometric; transient current.

1. Introduction

One of the major achievements in electroanalytical chemistry in the 1980s was the introduction of microelectrodes, i.e., electrodes of which one of the characteristic dimensions is of the order of a few micrometers (the radius in the case of microdiscs and microhemispheres, band width in the case of microbands, etc.). The characteristic of microelectrodes is the establishment of a cylindrical or hemispherical diffusion flux leading to a large increase in mass transfer. Ultramicroelectrode exhibits several advantageous properties compared with conventional electrodes. Microelectrodes are powerful tools for understanding the mechanism and kinetics of fast reactions. The electrochemical literature of recent years indicates an increasing interest in the development of ultramicroelectrodes for electrochemical measurements in view of their advantages such as smaller cell time constant (a consequence of the very low interfacial area and corresponding low double-layer capacitance), reduced ohmic drop (a consequence of the very small current flow), and enhanced current density (a consequence of convergent diffusion).

Microelectrodes of many shapes have been described. Microelectrodes of simple shapes are experimentally preferable because they are more easily fabricated.
A comparison of diffusion-limited currents at microelectrodes of various geometries for EC reactions

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Abstract
The steady-state and non-steady-state diffusion-limited currents for EC reactions for all ultramicroelectrodes (circular disc, circular ring, elliptical disc, elliptical ring, band, hemisphere, hemicylinder, hemi-oblate and hemi-prolate electrodes) are compared. In this paper we present a critical assessment of the influence of geometry on the behavior of the transient current. In the research presented here, the surface area of all the electrodes was fixed. The chronoamperometric currents for all times and for all $K$ values are given in tabular and graphical form.

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Keywords: Reaction/diffusion; Ultramicroelectrodes; Transient current; Steady-state; EC mechanism

I. Introduction
If the geometric dimensions of a voltammetric working electrode become progressively smaller, then the behavior of the electrode begins to quit diverge from that of a large electrode, which can be approximated by an electrode of infinite dimension. These differences are caused by changing conditions of the mass transport from the bulk of the solution towards the electrode, and have several important practical implications, such as a decreased ohmic drop of potential, $IR$, fast establishment of a steady-state signal, a current increase due to enhanced mass transport at the electrode boundary and an increased signal-to-noise ratio [1,2]. These effects make sufficiently small electrodes advantageous in many areas of electroanalytical chemistry. The application of small-sized electrodes (ultramicroelectrodes) has been further enhanced by increasing demands from analytical chemistry (e.g., the need for electrodes in miniature cells for detection of high-performance separations or in electrochemical sensors) and biochemistry (in situ electroanalytical measurements in living organisms) [1,2].

However, many electrode processes at ultramicroelectrodes are complicated; for example, the catalytic electrode process (EC reaction) is one of them. With the increasing interest in these reactions, there is a need to develop methods for the determination of the kinetics of the coupled chemical reaction and to understand the relationship between the rate constant, $K$, and the limiting current density.

I.1. Previous work

Much work has been carried out to study the EC mechanism at ultramicroelectrodes using analytical approximations [3–14] and numerical methods [15–22]. Space permits us to mention only a few of them below. Delmastro and Smith [4] solved the mass transport equations at a dropping mercury electrode for the pseudo-first-order reaction. Reischmann et al. [5] adapted this to give an expression for a spherical electrode. Dayton et al. [6] also derived the spherical response using Neumann's integral theorem. Denuault et al. [7,8] derived an analytical expression for the steady-state current at a spherical electrode due to a second-order EC process. Oldham [9] has derived the current for pseudo-first-order kinetics at microdisc electrodes using the "equivalent sphere" approximation.

Bender and Stone [10] tackled the problem of finding an exact expression for steady-state current for disc electrodes by means of an integral equation. Zhuang and Chen [11] have derived the current equation for the EC reaction at spherical electrodes for steady-state conditions using the concept of the steady-state reaction-diffusion layer. Phillips [12] derived a pair of asymptotic equations for pseudo-first-order behavior at a microdisc electrode without resorting to a spherical approximation. Most
Analytical Expression for Transient Chronoamperometric Current at Ultramicroband Electrode

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Abstract—Analytical solution of non-steady state chronoamperometric current at ultramicroband electrode is derived. The analytical expression for current (Padé approximant), valid for entire time domain is compared with the analytical and digital simulation data. A satisfactory agreement with the available limiting cases of analytical expressions and digital simulation data is noted.

Key words: Chronoamperometry, ultramicroband electrodes, Padé approximation, band electrode.
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INTRODUCTION

Microelectrodes are powerful tools for understanding the mechanism and kinetics of fast reactions. Microelectrodes, having at least one dimension on the order of micrometers, offer a number of advantages in electrochemical measurements compared to traditional macroelectrodes of millimeter dimension [1]. These advantages include lower interfacial capacitance and, therefore, smaller cell time constants, reduced ohmic drop through the solution, and enhanced current density, a result of convergent diffusion. A number of microelectrode geometries have been explored, including disc, band, ring, cylinder and hemisphere [1].

Microelectrodes of simple shapes are experimentally preferable because they are easily fabricated and generally conform to simpler voltametric relationships. Nevertheless, there is interest in microelectrodes of more complicated shapes, if only because the shapes of small experimental electrodes may not always be quite as simple as their fabricators intended. Moreover, and ironically, complex shapes may sometimes be more easily modeled than simpler ones. Microelectrodes [2] can be used to probe chemical events in macromolecules. For example, in scanning electrochemical microscopy, chemical heterogeneities can be examined on a micrometer scale. Ultramicroelectrodes can be used to provide a real-time view of exocytosis, the secretion arising from fusion of intracellular vesicles with the plasma membrane of individual biological cells [4].

In electrochemical systems, mixed boundary value problems arise in the study of transport phenomena at ultramicroelectrodes, whose dimensions range from 100 Å to 1000 Å [5]. These are employed in analyzing electron transfer reaction mechanisms on account of reduced ohmic resistances which enable elimination of double layer correction to the observed electrochemical response. Apart from this, diverse applications involving biosensors [6, 7] and molecular electronic devices [7-10] are also being envisaged for ultramicroelectrodes. The usual experimental techniques employed are chronoamperometry [7, 11-15] wherein potential step perturbation is applied in cyclic voltammetry [7, 12] involving potential scan at different sweep rates, or steady state voltammetry/amperometry.

Various geometries of these electrodes such as band, disc, hemisphere, ring etc are customarily fabricated. The investigation of transport phenomena at these geometries involves the solution of diffusion equation in appropriate coordinate systems. The concentration of the electroactive species and the flux are specified in two different domains thereby constituting a mixed boundary value problem. The simplest version of this occurs when diffusion is the sole mode of transport and potential step is applied to obtain current response (chronoamperometry). Among several mathematical procedures employed in these contexts, mention may be made of Wiener-Hopf factorization [13], method of matched asymptotic expansions [16, 17], Padé approximant techniques [18, 19], etc.

The purpose of the present communication is to derive a two-point Padé approximation for the non-steady state chronoamperometric current at ultramicroband electrode which shows satisfactory agreement with the available analytical and simulation data. Further the method is of such general validity that it can be applied for other geometries too such as ring, hemisphere, hemi cylinder, tubular band electrodes etc.
Traveling-wave solution of non-linear coupled reaction diffusion equation arising in mathematical chemistry

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Abstract A simple analytical approach to find the traveling-wave solution for a set of two coupled non-linear reaction diffusion equations is reported. An exact analytical solution for traveling-waves of the Fisher equations with a general non-linearity is found. The boundary value, the boundedness and the stability of the solution are discussed. This technique is straight forward to use involving minimal algebra. Use of the method for selected case is demonstrated.

Keywords Traveling-wave solutions • Non-linear reaction diffusion equations • Fisher equations

1 Introduction

Non-linear phenomena play a very important role in physics [1], chemistry and biology (heat and mass transfer, filtration of liquids, diffusion in chemical reactions, etc.). In particular in physics, non-linear waves are encountered in numerous domains such as fluid mechanics [2], solid-state physics [3], plasma physics [4] and chemical physics [5]. New names like solitons, kinks, breathers, etc. are now commonly used in the vast literature [6] dealing with this subject. Unfortunately these topics are treated only in advanced courses and can rarely be found on an introductory level. Therefore, simple techniques and methods are needed to investigate these phenomena and to make them accessible for undergraduate study.

Construction of particular exact solutions for the non linear equations remains an important problem. Finding exact solutions that have a physical, chemical or biological interpretation is of fundamental importance. Linear superposition principle cannot

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Title: System of coupled non-linear reaction diffusion processes at conducting polymer-modified ultramicroelectrodes
Electrochimica Acta

Dear Dr Lakshmanan Rajendran,

I am pleased to inform you that the revised version of your paper "System of coupled non-linear reaction diffusion processes at conducting polymer-modified ultramicroelectrodes" has been accepted for publication in Electrochimica Acta without further modifications. The manuscript will now go to the Production Department of Elsevier for technical editing. You will receive the proofs from Elsevier in due course.

Thank you for submitting your work to this Journal.

With kind regards,

Sergio Trasatti
Editor-in-Chief
Electrochimica Acta

Note
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