Electrochimica Acta 283 (2018) 300–305

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Use of the Saul'yev method for the digital simulation of chronoamperometry at the disk electrode, in the presence of homogeneous chemical reactions

Dieter Britz [a, *], Jörg Strutwolf [b]

[a] Department of Chemistry, Aarhus University, 8000 Aarhus C, Denmark
[b] Institute for Print and Media Technology, Chemnitz University of Technology, 09107 Chemnitz, Germany

ARTICLE INFO

Article history:
Received 3 May 2018
Received in revised form
21 June 2018
Accepted 23 June 2018
Available online 28 June 2018

Keywords:
Computational electrochemistry
Digital simulation
Saul'yev method
Finite differences
Disk electrode simulation
Homogeneous chemical reactions

ABSTRACT

The two-dimensional Saul'yev method of simulating processes at a disk electrode is tested in the presence of homogeneous chemical reactions. The catalytic EC′ reaction can produce a thin reaction layer, which is a test of any simulation method. The second-order Birk/Perone (B/P) reaction is similarly a test because of the nonlinear term appearing in the kinetic equations (although it does not give rise to a thin reaction layer). The Saul'yev method handles these with no special problems and is competitive, in terms of speed, with implicit methods at similar accuracy (and faster in the case of the nonlinear B/P case).

1. Introduction

In a prior paper [1] we described the use of the Saul'yev finite difference method for simulating the behaviour of a disk electrode under diffusion limited chronoamperometry with a potential jump, as well as a reversible system under linear sweep voltammetry. See that paper for details. A question was raised whether Saul'yev is also able to handle a homogeneous chemical reaction (*hcr*) present, particularly one that can produce a thin reaction layer, that is, a sharp concentration gradient near the electrode, and this is addressed here. Additionally, a second-order *hcr* is a test of any simulation method, as the governing transport equation then includes a nonlinear term.

The diffusion limited case, as studied here, is an extreme, and it was felt that the discussion would be needlessly complicated by including quasireversible conditions, without any significant gain.

It is possible these days to perform simulation with simulation packages such as COMSOL Multiphysics® [2], or DigiElch [3], both of which can handle two-dimensional problems. As will be seen, we do use COMSOL, for verification, but we advocate direct programming of simulation, as these packages tend to be expensive, and we promote reasonably simple simulation methods such as what we describe in the present article. Not everyone has the means to purchase one of these commercial packages.

1.1. The disk electrode

We choose, as previously, the two-dimensional problem of a disk electrode embedded flush in an insulating plane. In cylindrical coordinates the diffusion equation is

$$\frac{\partial C}{\partial T} = \left(\frac{\partial^2 C}{\partial Z^2} + \frac{\partial^2 C}{\partial R^2} + \frac{1}{R}\frac{\partial C}{\partial R} \right), \quad (1)$$

where the variables have been normalised for concentration, $C = c/c^*$ (c^* being the bulk concentration); time $T = Dt/a^2$, D being the diffusion coefficient of the diffusing substance, t the time and a the disk radius; the radial distance is $R = r/a$ and the coordinate normal to the electrode $Z = z/a$. The electrode disk then assumes a radius of unity. The chemical kinetic term must be added as

* Corresponding author.
E-mail addresses: britz@chem.au.dk (D. Britz), joerg.strutwolf@mb.tu-chemnitz.de (J. Strutwolf).

https://doi.org/10.1016/j.electacta.2018.06.146
0013-4686/

appropriate.

The dimensionless current is given by [4, p.257]

$$I = \frac{\pi}{2}\int_0^1 R\left.\frac{\partial C}{\partial Z}\right|_{Z=0} \mathrm{d}R\,. \tag{2}$$

As previously, we make use of the convenient coordinate transformation due to Verbrugge and Baker [5] (**VB**),

$$\mathrm{R} = \cos\theta\cosh\left(\frac{\Gamma}{1-\Gamma}\right)$$

$$\mathrm{Z} = \sin\theta\sinh\left(\frac{\Gamma}{1-\Gamma}\right). \tag{3}$$

The diffusion equation then becomes

$$\frac{\partial C}{\partial T} = \frac{1}{F}\left(\frac{\partial^2 C}{\partial\theta^2} + b_\theta\frac{\partial C}{\partial\theta} + a_\Gamma\frac{\partial^2 C}{\partial\Gamma^2} + b_\Gamma\frac{\partial C}{\partial\Gamma}\right) \tag{4}$$

with the coefficients for VB given by

$$\begin{aligned} F &= \sin^2\theta + \sinh^2\left(\frac{\Gamma}{1-\Gamma}\right)\\ b_\theta &= -\tan\theta\\ a_\Gamma &= (1-\Gamma)^4\\ b_\Gamma &= (1-\Gamma)^2\tanh\left(\frac{\Gamma}{1-\Gamma}\right) - 2(1-\Gamma)^3\,. \end{aligned} \tag{5}$$

The dimensionless current I is [4, p.284]

$$I = \frac{\pi}{2}\int_0^{\pi/2}\left.\frac{\partial C}{\partial\Gamma}\right|_{\Gamma=0}\cos\theta\,\mathrm{d}\theta\,. \tag{6}$$

In these coordinates, using an implicit simulation method, an evenly divided spatial grid about 20×20, coupled with, say, five-point approximations to the spatial derivatives provides sufficient accuracy [6] but in the case of the Birk/Perone reaction, where there is no mathematical solution, in order to produce reference values in the following, a finer grid was used, see below. In this work, sufficient accuracy was deemed to be an error not exceeding 0.1% in magnitude from a time $T = 0.1$ onwards. However, this needed to be relaxed to 1% in the case of the Birk/Perone reaction, which does converge but more slowly. For the Saul'yev method, as well, a finer grid must be used as well as smaller time steps, as it is a somewhat less accurate method.

1.2. Choice of homogeneous chemical reactions

We chose, in order to obtain a reaction layer, the catalytic EC' reaction

$$\begin{array}{lcl} \mathrm{A} + e^- & \Leftrightarrow & \mathrm{B}\\ \mathrm{B} & \rightarrow & \mathrm{A} \end{array} \tag{7}$$

in which A is reduced reversibly to B, which reverts to A by a pseudo-first-order reaction with rate constant k. This is a two-species coupled system but if we assume that the two species have equal diffusion coefficients, it reduces to a single transport equation, since then the sum of the two concentrations at any point in the diffusion space is constant, equal to the starting concentration of A. The rate constant is normalised by $K = ka^2/D$. In a more general form the reaction-diffusion equation for A is

$$\frac{\partial A}{\partial T} = \nabla^2 A + KB \tag{8}$$

and since we assume $A + B = 1$, this becomes an equation involving only A

$$\frac{\partial A}{\partial T} = \nabla^2 A + K(1-A)\,. \tag{9}$$

This system, at a disk, has a solution for the current as a function of time, due to Galceran et al. [7], which we combine with Bieniasz' accurate solution for the current [8,9]. The means of computation of this solution is described in Appendix A. It was used to check the accuracy of the Saul'yev method.

Another challenging *hcr* is that described by Birk and Perone [10] (**B/P**), where a substance A is produced instantly by a flash of light in solution and is thus present at an evenly distributed concentration in the cell, and begins to decay with a second-order reaction, while being electrolysed at the same time, at a diffusion limiting potential. Here there is no thin reaction layer, the problem being the second order nature of the homogeneous chemical reaction. The system is described by

$$\frac{\partial A}{\partial T} = \nabla^2 A - 2KA^2\,, \tag{10}$$

K being the second-order reaction rate constant, normalised as $K = kc^* a^2/D$. The factor 2 is there because for every reaction, two molecules are removed, as was argued in Ref. [11], where this case was simulated for some one-dimensional systems. The challenge here is the squared reaction term in the kinetic equation. Saul'yev shares with other implicit methods the problem of the nonlinear term, despite Saul'yev being explicit at every step. One can then either use Newton iteration, or use a linear approximation for the squared term. Both have been tried [4, p.164-] and the approximation version was only slightly less accurate than the Newton alternative, so this was used here. The linearisation approximation is [4, p.164]

$$A'^2 \approx 2AA' - A^2\,, \tag{11}$$

containing only linear terms in the unknown A', A being the present known values. We follow the notation that dashed quantities are future values at time $T + \delta T$, while plain symbols are present knowns at time T.

There is no known solution for the disk case, and in order to provide reference values to compare the Saul'yev method with, the implicit method BDF started with a single backward implicit step, as described in Ref. [4] was used, using a fine 50×50 VB grid and time intervals equal to 0.0001. This will be denoted BI/BDF hereafter. As well, COMSOL Multiphysics® simulations were performed for the B/P system, yielding results very close to BI/BDF, within around 0.5% difference.

1.3. Saul'yev method in two dimensions

Two variants of the Saul'yev method in two dimensions have been described previously [1]. They are **LRDU** (left-right, down-up) and **RLUD** (right-left, up-down). LRDU sometimes produced slightly more accurate current values.

For the grid in VB space, at a given point indexed with (i,j), index i referring to the value Γ_i and j to the value θ_j, the backward implicit