Journal of Electroanalytical Chemistry 682 (2012) 147–157

Contents lists available at SciVerse ScienceDirect

Journal of Electroanalytical Chemistry

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

EChem++ – An object-oriented problem solving environment for electrochemistry. Part 7[1]: Simulation of equilibrium electron transfer processes with implicit Dirichlet boundary conditions

Steffi Benthin, Bernd Speiser *

Universität Tübingen, Institut für Organische Chemie, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

ARTICLE INFO

Article history:
Received 31 May 2012
Received in revised form 19 July 2012
Accepted 21 July 2012
Available online 31 July 2012

Keywords:
Adaptive finite element method
Rosenbrock schemes
Computational electrochemistry
Lagrange multiplier
Nernst equilibrium

ABSTRACT

We present a direct approach to include equilibrium electron transfers into electrochemical simulation models based on the finite element method. This reaction step is described by the Nernst equation combined with a mass flux balance equation. Mathematically, the Nernst equation is an implicit Dirichlet boundary condition with two coupled concentrations. These boundary conditions are imposed within a numerical solver consisting of Rosenbrock schemes and an adaptive finite element method by means of Lagrange multipliers. The algorithm described in this study is integrated into the object-oriented, open source code for the problem solving environment EChem++. Simulations of an equilibrium electron transfer under cyclic voltammetric and chronoamperometric conditions in a one-dimensional cell geometry under semi-infinite linear diffusion show the validity and applicability of this method in the context of molecular electrochemistry.

1. Introduction

Digital simulation [2,3] is an indispensable tool to gain detailed insights into the mechanisms, kinetics and thermodynamics of electrochemical systems, whose dynamics are generally governed by transport (most commonly diffusion) coupled to electron transfer (ET) processes, adsorption and preceding or follow-up chemical reactions (in solution or on the electrode surface) in almost infinitely complex combinations. We call the network of these steps the electrode reaction. Its potential complexity necessitates flexible modeling strategies and simulation algorithms. To integrate modeling (i.e., the physico-chemical and mathematical description of the steps) and simulation (i.e., the numerical solution of the governing equations) with analysis methodology in one single computer program, Bieniasz [4] suggested the development of a ”problem solving environment” (PSE) for electrochemistry. Such software is expected to offer, among other tasks, the potential to describe, simulate and (combined with appropriate data) analyze every possibly conceivable experimental electrochemical system.

In the present series of papers we discuss *one* practical approach for such a PSE: EChem++. This software consists of several object-oriented modules written in the C++ programming language. The modeling component is *Ecco*, a compiler for electrochemistry [5]. Under the assumption of (currently) planar finite or semi-infinite diffusion, Ecco translates an electrode reaction mechanism into the corresponding partial differential algebraic equation (PDAE) system with appropriate initial and boundary conditions. The concentrations of all involved chemical species and electric currents or electrode potentials are the unknowns [1,6]. The actual simulation is implemented in the *Solver* module [1,6,7]. The PDAEs are discretized in time and space coordinates and solved for the concentrations of the chemical species and any other unknowns involved. This is accomplished by the application of Rosenbrock schemes and the finite element method (FEM), for time and space, respectively. Both, the time and the space grid are dynamically controlled and adapted to the complexity of the situation. The solver module copes both with controlled-potential and controlled-current experiments. Each reaction step is described by an appropriate kinetic rate law with associated rate constants. All types of steps mentioned above can be combined arbitrarily. For reversible reactions, i.e. those that proceed in the forward and reverse directions with non-zero rates, the characteristics of the forward *and* the reverse step are defined separately.

If the rate of a particular reversible step is very fast on the time scale of the experiment which in turn is related to mass transfer, the step will be in equilibrium and may alternatively be characterized by the respective equilibrium constant. While equilibrium steps are often approximated by very fast kinetics, a general PSE should also provide the option to include equilibrium reactions in the mechanistic formulation and allow calculations without

---

[1] Part 6, see Ref. [1].

* Corresponding author. Tel.: +49 7071 2976205.
E-mail address: bernd.speiser@uni-tuebingen.de (B. Speiser).

1572-6657/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jelechem.2012.07.024

having to make additional assumptions. When building the model of an electrode reaction, a choice between a kinetic (the particular reaction step has a finite, although possibly large rate) and an equilibrium formulation (the reaction step is in equilibrium at all times during the simulation) would then have to be taken.

In this paper, we will concentrate on equilibrium formulations of electron transfer steps and suggest a corresponding solver algorithm. Equilibria for steps other than ET will be treated separately.

ET steps obey, if kinetically controlled, e.g. Butler–Volmer kinetics [8] (pp. 92–98), if, on the other hand, proceeding infinitely fast (equilibrium electron transfer), they are described by the Nernst equation [8] (p. 31).

The characteristics of electron transfer processes are included into the mathematical model as boundary conditions at the electrode. Mathematically, we distinguish between Dirichlet, Neumann and Robin type boundary conditions [9–14]. A Dirichlet boundary condition specifies a value for an unknown, e.g. a concentration, itself. A Neumann boundary condition, on the other hand, controls the spatial derivative of an unknown. If both, the spatial derivative *and* the unknown itself are combined in the boundary condition, it is of Robin type.[2] If the values of *two or more* unknowns are directly coupled in the boundary condition, we will call this to be of *implicit Dirichlet* type – in contrast to the aforementioned *explicit* Dirichlet boundary conditions [15], which concern only a single unknown. Furthermore, a Dirichlet or Neumann boundary condition is said to be *homogeneous*, if the unknown or the spatial derivative of the unknown, respectively, equals zero [17] (p. 11).

Several approaches have been applied in the literature to include the equilibrium limiting case of reversible electron transfer processes into electrochemical simulations. One obvious attempt is the approximation with Butler–Volmer kinetics and the use of a very large heterogeneous rate constant [7,18,19]. The boundary conditions (e.g. Eq. (4) in Ref. [7]) resulting from Butler–Volmer kinetics are of Robin type, coupling two concentrations with one of their spatial derivatives. Boundary conditions containing a derivative are well supported by the underlying variational principle for the FEM techniques used in EChem++ (see Appendix A of [7], or [20]). However, the limiting value of the heterogeneous rate constant at which reversibility of the electron transfer can be assumed depends on the experimental conditions [18,21], and has to be carefully chosen before every simulation. This is unsatisfactory for a general solver algorithm.

Alternatively, the Nernst equilibrium has been considered *directly*, i.e. without approximation by very fast Butler–Volmer kinetics. The boundary condition resulting from the Nernst Eq. (1)

$$E = E^0 + \frac{RT}{nF} \ln \frac{c_{\mathrm{ox}}}{c_{\mathrm{red}}} \tag{1}$$

is of the implicit Dirichlet type, because the concentrations of the oxidized and reduced species, c_{ox} and c_{red}, are coupled through the electrode potential E (E^0 is the formal potential, R the gas constant, T the absolute temperature, F the Faraday constant, and n the number of transferred electrons). This type of coupling demands more complex numerical methods as compared to explicit Dirichlet boundary conditions [15]. Direct imposition of the Nernst equilibrium was attempted previously with most major simulation methods used in the context of electrochemical simulations.

The seminal paper for cyclic voltammetric curve calculation [22] already used Eq. (1) directly for the reversible electron transfer case in the context of the Laplace transform methodology. More recent applications of this analytical or semi-analytical [23] solution technique approached much more complex mechanisms [24–27]. However, it appears that the solution process then becomes tedious [24,25] and may not be generally applicable [23].

In the context of finite difference algorithms [2,3], the Nernst equation and the mass flux balance at the electrode surface have been combined to eliminate one of the concentrations at the boundary and to simplify the PDE system [28–30]. This use of Eq. (1) as a boundary condition seems to have only been applied without coupled chemical reactions.

In FEM simulations, a similar approach has been used [31], however, again, only for simple electron transfers without coupled complexities. More complicated systems, without constraints to the mechanism, have been treated by reformulating the boundary conditions at the electrode to be of explicit Dirichlet type. Thus, the concentrations at the electrode are calculated just before every FEM step. This is accomplished by either iteratively solving recursion formulae [32] or by solving an equation system consisting of the Nernst equation and the mass flux balance equation, where the derivatives are approximated by difference quotients [33,34]. These additional calculations in every FEM step have an adverse effect on the simulation time. In the former approach [32] the accuracy of the concentrations at the electrode depends on the tolerances of the termination condition in the solution of the recursion formulae. A smaller tolerance increases the accuracy, however, the simulation duration also increases. If, on the other hand, the derivatives in the mass flux balance equation are approximated by difference quotients [33,34], the accuracy of the calculated concentrations at the electrode depends on that of the difference quotient. Thus, in both cases additional numerical errors are introduced into the simulation.

Here, we propose an algorithm to include the Nernst equilibrium into the FEM framework without additional calculations or approximations. We will use "Lagrange multipliers", introduced by Babuška [35] into the FEM methodology. Lagrange multipliers provide a classical approach to optimize a function subject to constraints [15]. In the context of FEM, the functional of the underlying variational approach is minimized subject to the boundary conditions. Essentially, the implicit Dirichlet boundary condition is included as an additional equation and coupled to the PDE through the Lagrange multiplier [10], which becomes an additional unknown. The Lagrange multiplier has been shown to be the spatial derivative of the unknown described by the Dirichlet boundary condition [20,36,37]. Thus, no approximation is introduced.

The Lagrange multiplier method was earlier established to impose *explicit* Dirichlet boundary conditions onto FEM and is well-studied for model problems [35–43]. The method is also suitable for problems with *implicit* Dirichlet boundary conditions [15], if e.g. a moving front within the solution space [44] is characteristic. Examples appear in heat-conduction [45], resin transfer molding [10], in aero-acoustic or elasto-acoustic wave propagation [46] and electron scattering [20] simulation. Modeling of polyelectrolyte swelling and deformation by a polarizing potential was supported by enforcing an incompressibility constraint through Lagrange multipliers [47]. To the authors' knowledge applications of FEM calculations with the use of Lagrange multipliers in electrochemistry have been reported previously only in contexts different from the modeling of equilibrium electron transfers emphasized in the present work: for example, tasks related to optimization with respect to constraints and for systems in electrochemical equilibrium [48], or accurate flux calculations [49]. The latter reference is also an example for the use of the COMSOL Multiphysics commercial software that is not restricted to electrochemical simulations. COMSOL uses Lagrange multipliers to treat Dirichlet boundary conditions [50]. Calculation of fluxes and currents in an electrochemical context [49] is a special application of this technique.

---

[2] The Robin and similar types of boundary conditions are sometimes called Cauchy boundary conditions [15,16].