



Computer simulations of electrodiffusion problems based on Nernst–Planck and Poisson equations

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ABSTRACT

A numerical procedure based on the method of lines for time-dependent electrodiffusion transport has been developed. Two types of boundary conditions (Neumann and Dirichlet) are considered. Finite difference space discretization with suitably selected weights based on a non-uniform grid is applied. Consistency of this method and the method put forward by Brumleve and Buck are analysed and compared. The resulting stiff system of ordinary differential equations is effectively solved using the RADAU5, RODAS and SEULEX integrators. The applications to selected electrochemical systems: liquid junction, bi-ionic case, ion selective electrodes and electrochemical impedance spectroscopy have been demonstrated. In the paper we promote the use of the full form of the Nernst–Planck and Poisson (NPP) equations, that is including explicitly the electric field as an unknown variable with no simplifications like electroneutrality or constant field assumptions. An effective method of the numerical solution of the NPP problem for arbitrary number of ionic species and valence numbers either for a steady state or a transient state is shown. The presented formulae – numerical solutions to the NPP problem – are ready to be implemented by anyone. Moreover, we make the resulting software freely available to anybody interested in using it.

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1. Introduction

Mass and charge transport processes play an important role in different areas of science. In electrochemistry they are extensively used for the description of membrane potentials and concentration profiles. Particular application of this description is the field of ion selective electrodes (ISEs) and molten salts. In engineering problems the behaviour of porous materials is affected by the transport of ions due to concentration gradients. These mechanisms of ionic diffusion in porous media which appear, for example in the filtration by ion exchange membranes and the transport of pollutants in soils, have received a great deal of attention from chemical and geological engineers. The process of ionic diffusion remains of primary importance in many civil engineering problems since the long-term durability of many building materials, such as concrete, is directly effected by the transport of chemical species [1]. In semiconductor field the transport of charged species was considered from the very beginnings of this discipline. Workers in this

field developed many powerful techniques but usually directed to solve its specific problems (two species and steady-state). The membrane processes involving charge transport are also of vital importance in cell biology since they support homeostasis of living organisms.

All these processes (ionic diffusion in porous media, electrochemical and biological membranes as well as electrons and holes transport in semiconductors) can be described using Nernst–Planck and Poisson (NPP) system of partial differential equations with suitable initial and boundary conditions. Although, tools for modelling individual applications are described in literature yet, they are not easy to get. Some of them are commercial (e.g., COMSOL), some use commercial computation environments (e.g., Mathematica, Mathcad, MATLAB), and others require to buy the commercial specialised numerical libraries (like DiffPack, NAG, IMSL, etc.).

In this paper we will promote the use of full form of NPP equations, i.e., including explicitly the electric field as an unknown variable. We will present an effective method of numerical solution of NPP problem for arbitrary number of ionic species and valence numbers, both for steady and transient states. A new discretization

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scheme is presented and its consistency is analysed. Two types of boundary conditions are considered: (1) Neumann-like boundary conditions for fluxes—known in electrochemistry as Chang–Jaffé boundary conditions and (2) Dirichlet boundary condition for concentrations. Obtained formulae – expressions for numerical solution to NPP problem – can be used by anyone interested to implement them on their own. Moreover we make the resulting software available to anybody interested in using it.

The plan of this paper is as follows. We start from the short introduction to NPP equations with Dirichlet and Neumann-like boundary conditions. A method of lines using new space discretization scheme is described and used for obtaining numerical solution of initial-boundary value problem for the NPP system. This method is tested for a binary electrolyte case, where an analytical solution for transient state is available. The use of the software for solving liquid junction and bi-ionic cases is also demonstrated. Application to ion-selective electrodes are shown and compared with experimental results. Generation of impedance spectra based on the time dependent solution of NPP problem is also presented.

2. Mathematical model

The multi-layer NPP model describes a system consisting of α layers, each corresponding to a different phase Fig. 1. This transient model of electrodiffusion allows a description of the evolution of ionic concentrations and electric potential profiles in time, and is often used in modelling of transport in liquid and solid electrolytes, melted salts, oxide scales, etc. In this model, diffusion and migration of ions are governed according to the Nernst–Planck (NP) flux expression, while the Poisson (P) equation describes the electrical interaction of the species. However, it is convenient to replace the Poisson equation by the displacement current equation as described by Cohen and Cooley [2]. All these equations form the following system of evolutionary nonlinear partial differential equations (PDEs) for r components and α layers:

$$\begin{cases} \frac{\partial c_i^j}{\partial t}(x, t) = -\frac{\partial j_i^j}{\partial x}(x, t) & \text{for } i = 1, \dots, r, \\ \frac{\partial E^j}{\partial x}(x, t) = \frac{1}{\epsilon_j} I(t) - \sum_{i=1}^r z_i j_i^j(x, t), \\ x \in [\lambda_{j-1}, \lambda_j] & \text{for each layer } j = 1, \dots, \alpha, \\ t \in [0, t_{END}], \end{cases} \quad (1)$$

where the expression for the Nernst–Planck flux (*constitutive relation*) is

$$j_i^j(x, t) = -D_i^j \frac{\partial c_i^j}{\partial x}(x, t) + \frac{F}{RT} D_i^j z_i (c_i^j E^j)(x, t). \quad (2)$$

In the above equations c_i^j – the molar concentration of i -th component in j -th layer, E^j – the electric field in j -th layer, $I(t)$ – the electrical current density, ϵ_j – dielectric constant of j -th layer, λ_{j-1}, λ_j – the boundaries of j -th layer, z_i – the valence number of

i -th component, t_{END} – duration of the process, and F, R, T have their usual meanings (the Faraday constant, gas constant and absolute temperature).

For completeness, the above system of PDE must be accompanied by boundary and initial conditions. The initial conditions consist of given concentration profiles and electric field:

$$\begin{aligned} c_i^j(x, 0) = c_{0,i}^j(x), \quad E^j(x, 0) = E_0(x), \quad \text{for } x \in [\lambda_{j-1}, \lambda_j], \\ i = 1, \dots, r, \quad j = 1, \dots, \alpha. \end{aligned} \quad (3)$$

$E_0(x)$ is assumed to be zero for all x except in the case of impedance spectra simulations. In simulations we used electroneutral initial profiles, although it is not necessary.

The boundary conditions may be of various types. In this paper we use two types of boundary conditions. The first are the Neumann-like boundary conditions for fluxes [3], known in electrochemistry as Chang–Jaffé boundary conditions. The first order heterogeneous rate constants \bar{k}_i^j, \bar{k}_i^j are used to describe the kinetics at the interface $x = \lambda_j$ between the layers j and $j + 1$:

$$j_i^j(\lambda_j, t) = j_i^{j+1}(\lambda_j, t) = \bar{k}_i^j c_i^j(\lambda_j, t) - \bar{k}_i^j c_i^{j+1}(\lambda_j, t). \quad (4)$$

The above equation is a special case of Butler–Volmer equation, when the overpotential equals zero [4].

The second possibility (basically for single-layer problems, $\alpha = 1$) is the standard Dirichlet boundary conditions for concentrations

$$\begin{aligned} c_i^1(\lambda_0, t) = c_{i,L} = \text{const}, \\ c_i^1(\lambda_1, t) = c_{i,R} = \text{const} \quad \text{for } i = 1, \dots, r, \end{aligned} \quad (5)$$

where $c_{i,L}, c_{i,R}$ are the left and right bulk concentrations [5,6]. The use of both types of boundary conditions will be presented for liquid junction case.

Scaling and dimensionless variables The presented problem contains many physical parameters. By introducing dimensionless variables, the number of these parameters can be reduced. Moreover, by finding the proper scaling factors it is possible to identify the relative contribution of the various terms in the equations. This may be used to obtain better accuracy in numerical procedures. Thus, the Eqs. (1)–(5) may now be converted into a dimensionless form [7] through the following transformations:

$$\begin{aligned} \bar{x} := x/x_s, \quad \bar{t} := t/t_s, \quad \bar{c}_i^j(\bar{x}, \bar{t}) := c_i^j(x_s \bar{x}, t_s \bar{t})/c_s, \\ \bar{E}^j(\bar{x}, \bar{t}) := E^j(x_s \bar{x}, t_s \bar{t})/E_s, \end{aligned} \quad (6)$$

where x, t, c_i^j, E^j and $\bar{x}, \bar{t}, \bar{c}_i^j, \bar{E}^j$ are physical and dimensionless values of distance, time, concentration and electric field respectively; x_s, t_s, c_s, E_s are their characteristic values (scaling factors). Dimensionless parameters take the form: $\bar{D}_i^j = \frac{t_s}{x_s^2} D_i^j$, $\bar{k}_i^j = \frac{t_s}{x_s} k_i^j$, $\bar{k}_i^j = \frac{t_s}{x_s} k_i^j$, $\bar{\lambda}_j = \lambda_j/x_s$.

From this point on, we use the rescaled variables in all equations and the overbars are dropped to ease the burden of notation.

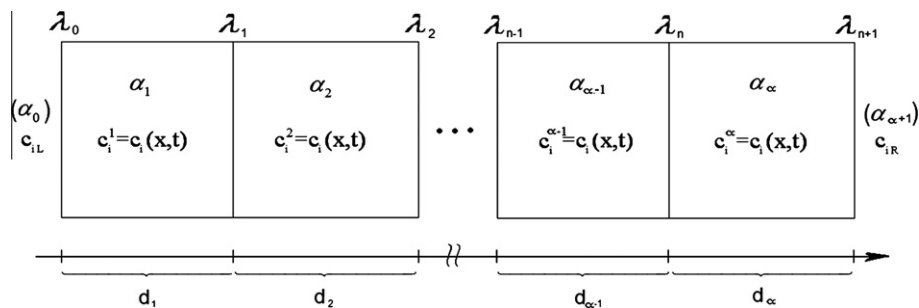


Fig. 1. Schematic representation of the system for NPP model of electrodiffusion.

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