EIS simulations for ion-selective site-based membranes by a numerical solution of the coupled Nernst–Planck–Poisson equations

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Abstract

The numerical simulations of steady-state potentials and impedance spectra of ion-selective membranes electrodes (ISEs) with ionic sites are presented. The set of Nernst–Planck–Poisson and continuity equations is solved numerically by means of the finite difference method and the Rosenbrock solver. Transient and steady-state solutions for ion-selective electrodes under open- or closed-circuit conditions are calculated. The Fourier transformation of the potential-time response to a current perturbation is used for determination of complex impedances. The paper presents simulations of ISEs as a function of varying the ionic concentrations in the “bathing” solution or the rates of ion transfer across the membrane/solution interfaces. It is shown that the non-Nernstian behaviour of passive membrane electrodes is a result of kinetic constraints at the interfaces, which are manifested in the appearance of an additional arc between the high-frequency bulk and the low-frequency (Warburg) arcs. The presented approach directly relates the transport properties of the bulk and interfaces (ionic diffusivities and heterogeneous rate constants of transport across interfaces) to the characteristic features of complex impedances (dimensions and characteristic radial frequencies), and allows non-linear effects to be simulated.

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1. Introduction

Electrochemical impedance spectroscopy (EIS) is a powerful tool for characterizing various electrochemical systems because it allows the separation and characterization of individual kinetic processes. The theoretical treatment of EIS is typically based upon the Nernst–Planck flux equations coupled to Poisson’s equation (NPP). The NPP equation system can be solved analytically only under idealized conditions, usually assuming steady state and electroneutrality. More realistic models, such as the NPP in real time and space domains, require numerical simulations [1].

Moreover, according to Macdonald, instead of using a physical model for interpreting EIS, which could provide a valid physico-electrochemical accounting for the mechanisms in the systems, the equivalent electrical circuits are predominantly used. The latter, being the analogs of the systems, simply reproduce the properties and represent an incomplete analysis of the data [2]. The application of the NPP model for interpreting EIS was initially presented by Macdonald and co-workers [3–6]. Unfortunately, even for the very idealized cases considered by these authors, complex algebraic equations were obtained.

The first numerical solution of the NPP equations was provided by Cohen and Cooley [7], who introduced a system of reduced units and space charge expressed by the displacement current equation (implemented also in this work). The milestone in the field of the NPP numerical modelling is the paper by Brumleve and Buck [8]. Their approach is free from approximate assumptions and directly relates the impedance spectra to the physical parameters (concentrations, heterogeneous rate constants and diffusivities). Unfortunately, their program written in unpublished FORTRAN codes was “frozen” at a limited
number of points and was never developed further. Recently, Sokalski and Lewenstam [9] extended NPP simulations for liquid junctions and ISE membranes for transient states using C++ codes and cumulative libraries. This group showed further [10] that the Henderson and Nikolowski–Eisenman equations, used widely in potentiometry with ion-selective electrodes (ISE), are special cases of the NPP model. However, they did not comment on the application of their NPP implementation for the simulation of EIS. Very recently an elegant investigation of ion-selective membrane electrodes with passive plastic membranes by EIS was presented by Gabrielli et al. [11,12]. These authors showed that non-Nernstian behaviour of ISEs is influenced by transport limitations inside the membranes and across the interfaces, as seen by EIS. However, in their approach the NPP problem was simplified by the use of electroneutrality, steady state, and arbitrary summation to calculate the total membrane impedance.

The aim of this work is to present impedance spectra derived from the NPP model by means of a simple numerical method. We follow the approach presented by Brumleve and Buck and extended by Sokalski and Lewenstam. However, in order to avoid self-made coding, we use the programming facilities and integrators of the mathematical program Mathcad 12 (by Mathsoft). As an illustration of the power of the method, we study ISE in typical configurations. The first case (A) is an ISE membrane in contact with a multi-ionic bathing solution with different concentrations of primary divalent cation (10−10−1 M). In the second example (B), the influence of cationic transfer rates across the interfaces (heterogeneous rate constants are 10−8−102 m s−1) in a bionic system is analyzed.

2. Theory

We consider the one-dimensional NPP problem in a symmetric system of a single planar plastic membrane bathed with two solutions. The governing transport equations are the Nernst–Planck flux formula, the Poisson equation and the continuity equation. The Nernst–Planck equation for an ionic component in a dilute solution is given by

\[ J_i(x, t) = -D_i \frac{\partial c_i(x, t)}{\partial x} - \frac{F}{RT} z_i c_i(x, t) E(x, t) \]  

where \( J_i \) denotes the flux, \( c_i \) the concentration, \( D_i \) the diffusivity, and \( z_i \) the valence of the \( i \)-th specie. \( E \) denotes the electric field and \( F, R, T \) denote the Faraday constant, the gas constant and the temperature, respectively.

Following Cohen and Cooley [7], we replace the Poisson equation by the total current equation, which conveniently introduces total current density (\( I \)) as a parameter of the model:

\[ \frac{\partial E(x, t)}{\partial t} = \frac{1}{\varepsilon} \left( I(t) - F \sum_i z_i J_i(x, t) \right) \]

where \( \varepsilon \) is the electric permittivity.

The continuity equations express the conservation law of each component:

\[ \frac{\partial c_i(x, t)}{\partial t} = -\frac{\partial J_i(x, t)}{\partial x} \]  

(3)

The interfacial fluxes depend on the heterogeneous rate constants and concentrations at each side of the interface:

\[ J_{i,p+1}^p(t) = k_{i,L}^p c_{i,L}^p(t) - k_{i,R}^{p+1} c_{i,R}^{p+1}(t) \]  

(4)

where \( c_{i,L} \), and \( c_{i,R} \) denote concentrations on the left and right side of the interface \( p/p + 1 \), respectively, and \( k \) denotes the forward and backward heterogeneous rate constants of transition across the interface.

The constant ionic concentrations in the bathing solutions and Eq. (4) form the Chang-Jaffe boundary conditions [13] that are employed in this paper. The initial concentrations obey the electroneutrality condition, and consequently there is no space charge in the membrane for \( t = 0 \).

The use of a multilayer system and chemical reactions inside each layer are equally permitted in our program, but for simplicity they are not considered here.

The above equations are converted to a finite difference form with the space grid containing closely spaced points near the interfaces and a much wider spacing inside the bulk. The concentrations are defined inside each node, while the electric field and fluxes are computed between nodes. This formulation is consistent with the mass and charge conservation as required by the continuity and displacement-current equations [8–10]. Consequently two separate space grids for computations of the concentrations and the electric field are used, for details concerning discretization see Ref. [8]. The obtained set of equations is solved in Mathcad 12 using the implicit Rosenbrock algorithm, which was found to be more effective in computing than other algorithms, e.g. Radau5.

3. Simulations of complex impedances

In this paper, we follow the two-step approach proposed by Brumleve and Buck for EIS simulations [8]. At first, under zero total current density (open-circuit) simulations are carried out until the desired transient or steady state is obtained (\( t_1 = 10^5 \) s). Then the system is closed and perturbed by a step current signal:

\[ I(t > t_1) = I_0 \]  

(5)

where \( I_0 \) is the amplitude of the current signal (in present calculations we used the small value of 10−4 A m−2, in order to retain the semi-linearity of the response).

Computations are carried out until the new steady state is reached (\( t_2 = 10^6 \) s). The Fourier transformation of the potential-time response, \( V(t_k) \), allows the complex impedances to be determined:

\[ Z'(\omega) = -\left( \sum_k \Delta V'_k + \Delta V_0\omega \right) I_0^{-1} \]  

(6)

\[ Z''(\omega) = \sum_k \Delta V'_k \frac{\omega I_0}{I_0} \]  

(7)
where

\[
\Delta V'_k = \frac{V(t_{k+1}) - V(t_k)}{\omega k} \left[ \cos \omega t_{k+1} - \cos \omega t_k \right] / \omega^2 (t_{k+1} - t_k) 
+ \left[ (V(t_{k+1}) - V_\infty) \sin \omega t_{k+1} - (V(t_k) - V_\infty) \sin \omega t_k \right] / \omega 
\]

\[
\Delta V''_k = \frac{V(t_{k+1}) - V(t_k)}{\omega k} \left[ \sin \omega t_{k+1} - \sin \omega t_k \right] / \omega^2 (t_{k+1} - t_k) 
+ \left[ (V(t_{k+1}) - V_\infty) \cos \omega t_{k+1} - (V(t_k) - V_\infty) \cos \omega t_k \right] / \omega
\]

(8)

(9)

Average simulations last 160 and 600 s for steps one and two, respectively, on a computer with a 3.2 GHz P4 processor and 1 Gb RAM.

Presented below are the EIS simulations for ion-selective membrane in contact with a bathing solution of different concentration of a primary ion (case A), or a system of different cationic transfer rates at the membrane interfaces (case B). For simplicity we assume full dissociation in the homogenous membrane. The physical parameters shared in both cases are the layer thickness \( L = 10^{-4} \) m and the relative dielectric permittivity of \( \varepsilon_r = 10 \). The discretization parameters involve the closest spacing, \( 5 \times 10^{-10} \) m, and the total number of nodes, 71 (20 at each interface with a width of \( 5 \times 10^{-10} \) m, and 31 inside the bulk). Other parameters and initial concentrations are listed in Tables 1 and 2 for cases A and B, respectively.

### 3.1. Multi-ionic case (A)

An ISE membrane sensitive for primary divalent ion in the presence of a weakly interfering monovalent ion is considered. The initial ionic concentrations in the left and the right bathing solutions \( (c_{i,L}, c_{i,R}) \) as well as in the membrane \( (c_{i,M}) \), diffusion coefficients and heterogeneous rate constants at the left interface (at the right interface the values are symmetrical) are given in Table 1.

In order to validate the present “kinetic” model, the protocol proposed previously [9,10] is used, i.e. the ISE steady-state membrane potentials, calculated after the

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**Table 1**

<table>
<thead>
<tr>
<th>Ion</th>
<th>( c_{i,L} ) (M)</th>
<th>( c_{i,M} ) (M)</th>
<th>( c_{i,R} ) (M)</th>
<th>( D_{i,M} ) (m² s⁻¹)</th>
<th>( k_{i,L} ) (m s⁻¹)</th>
<th>( k_{i,L} ) (m s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma^2+ )</td>
<td>( 10^{-10} )</td>
<td>( 5 \times 10^{-4} )</td>
<td>1</td>
<td>10⁻¹¹</td>
<td>10⁻³</td>
<td>10⁻³</td>
</tr>
<tr>
<td>( J^+ )</td>
<td>0.15</td>
<td>0</td>
<td>0</td>
<td>10⁻¹¹</td>
<td>4.472 × 10⁻⁷</td>
<td>10⁻³</td>
</tr>
<tr>
<td>( R^- )</td>
<td>0</td>
<td>( 10^{-3} )</td>
<td>0</td>
<td>10⁻¹¹</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>Ion</th>
<th>( c_{i,L} ) (M)</th>
<th>( c_{i,M} ) (M)</th>
<th>( c_{i,R} ) (M)</th>
<th>( D_{i,M} ) (m² s⁻¹)</th>
<th>( k_{i,L} ) (m s⁻¹)</th>
<th>( k_{i,L} ) (m s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma^+ )</td>
<td>( 10^{-3} )</td>
<td>( 10^{-3} )</td>
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<td>10⁻¹⁰</td>
<td>10⁻⁸–10²</td>
<td>( k_{\Gamma^+} )</td>
</tr>
<tr>
<td>( J^+ )</td>
<td>0</td>
<td>0</td>
<td>( 10^{-3} )</td>
<td>10⁻¹¹</td>
<td>( k_{J^+} )</td>
<td>( k_{J^+} )</td>
</tr>
<tr>
<td>( R^- )</td>
<td>0</td>
<td>( 10^{-3} )</td>
<td>0</td>
<td>10⁻¹¹</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

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![Fig. 1. Steady-state membrane potentials for different concentrations of primary ion [I²⁺] in a bathing solution. The inset shows the differences of potentials calculated from the Morf model [14] and the present method.](image_url)
equilibration time $t = 10^4 \text{s}$, are compared with predictions by the “thermodynamic” model presented by Morf [14]. As can be seen in Fig. 1, very good agreement between the predictions of these two models is found, thus proving the applicability of the present numerical method for modelling the potentiometric responses of ISEs.

Simulated EIS spectra for case (A) are presented in Fig. 2. For all concentrations there are two arcs of characteristic frequencies $\omega = 10^5$ and $3 \times 10^{-5}$ Hz for the left arcs and the right arcs, respectively. The high-frequency arcs are attributed to the bulk properties of a plastic membrane (in terms of equivalent circuits they are interpreted as the charging of the bulk capacitance in parallel with the resistance [8,11]). The low-frequency arcs are distorted semicircles; at higher frequencies they exhibit the $\pi/4$ slope, characteristic for the Warburg impedance.

The obtained spectra overlap for $[I^{2+}] \geq 10^{-4} \text{M}$ and for $[I^{2+}] \leq 10^{-9} \text{M}$ and change gradually in the intermediate region. In similar concentration ranges, a linear (for $[I^{2+}] \geq 10^{-4} \text{M}$ and for $[I^{2+}] \leq 10^{-9} \text{M}$) and nonlinear potentiometric responses were predicted, Fig. 1.

### 3.2. Bi-ionic case (B)

This case depicts the kinetics of cationic transfer across the interfaces as a factor influencing the potential response in a bi-ionic system, as suggested by Gabrielli et al. [11]. The initial ionic concentrations, diffusivities and heterogeneous rate constants at the left interface (at the right interface these values are symmetrical) are presented in Table 2.

In the computations we use the same value for the forward and backward heterogeneous rate constants for cations at both interfaces, $k = k_{f-L} = k_{b-L} = k_{f-L} = k_{b-L}$.

The calculated steady-state membrane potentials (after time $t = 10^4 \text{s}$) for different interfacial kinetics are presented in Fig. 3. For the heterogeneous rate constant $k \geq 10^{-3} \text{m s}^{-1}$, the simulated value of the membrane potential is very close to the Nernstian response (59.1 and 59.2 mV, respectively). For $k < 10^{-3} \text{m s}^{-1}$, the slower the interfacial kinetics is assumed, the bigger the departure from the Nernstian value is predicted.
The EIS spectra for \( k = 10^{-6} - 10^{-7} \) and \( k = 10^{-8} \text{ m s}^{-1} \) are presented in Figs. 4-6, respectively. As in case (A), also in this case the simulated complex impedances exhibit the same trend as the open-circuit potential responses. For \( k \geq 10^{-4} \text{ m s}^{-1} \), the interfacial kinetics is sufficiently fast (in comparison to other transport-limiting processes) and only two, high- and low-frequency, arcs are predicted [11,15]. For lower values of \( k \), an additional intermediate frequency arc attributed to the interface impedance develops. It starts for \( k = 10^{-5} \) and grows further with decreasing \( k \) in Fig. 5. For \( k = 10^{-8} \text{ m s}^{-1} \), the interfacial arc totally dominates the impedance spectrum in Fig. 6 (the steady-state membrane potential then approaches zero, as seen in Fig. 3). By coincidence, the same type of correlation was empirically observed in recent studies comparing potentiometric response of ISEs and their electrochemical characteristics as given by EIS spectra [16,17]. This suggests the validity of applying EIS as a simple diagnostic tool for testing the functional property of passive ISEs. A similar conclusion, for the ISEs with ionophore-based membranes, was recently presented by Gabrielli et al. [11]. However, while these authors attribute the non-Nernstian behaviour also to the existence of the Warburg (diffusional) arc, this paper suggests that, in the framework of the NPP model used here, it is not a necessary condition.

4. Conclusions

The numerical solution of the Nernst–Planck–Poisson equations with the Chang-Jaffe boundary conditions has been described. A finite difference method and the Rosenbrock solver have been used in Mathcad 12. The presented model is general and allows the determination of transient and steady-state solutions to the NPP problem. Thus, modelling of steady-state potentials and complex impedances becomes accessible with the same tool. It is worth noting that the model relates complex impedances directly to the kinetic properties of bulks and interfaces, and no equivalent circuits are needed to interpret the EIS spectra of electrochemical systems. An advantage of the present numerical method is the feasibility of NPP simulations by means of commercially available software with a user-friendly, Windows-type interface, namely Mathcad 12.

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References