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# Electro-Diffusion at Different Length Scales

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**Abstract.** The modelling of electro-diffusion in the multicomponent system in open space and time domains has been only recently addressed and made numerous applications in biology, fuel cells, electrochemical sensors and reference electrodes possible. In this work we show the numerical simulations of electrical potential over time and resulting electrochemical impedance spectra of ion-selective membrane electrodes (ISE's). The numerical results are obtained by use of the coupled Nernst-Planck, Poisson and continuity equations (forming the NPP model). The equations are solved by means of the finite difference method, the Rosenbrock solver with the use of Matlab (by MathWorks) platform. The potential-time response of the ISEs in open- and closed-circuit conditions as a function of varying heterogeneous rate constants, ionic concentrations and membrane thickness are computed. The potential-time response to small-current perturbation is applied for simulations of the impedance spectra. The results obtained show that the membrane with Nernstian response presents only one capacitive arc in the impedance spectra, related to conductivity and dielectric properties of the membrane material. Non-Nernstian behaviour is related to slow ionic transport through the membrane|solution interfaces and is manifested by the appearance of an additional (capacitive) arc between the high-frequency bulk and the low-frequency (Warburg) arcs. The presented approach directly relates the diffusivities in the membrane and the interface properties (heterogeneous rate constants determining the transport across interfaces) to the characteristic properties of the impedance spectra (characteristic radial frequencies). It is concluded that the Matlab platform allows solving the NPP problem and simulating the non-linear effects in electro-diffusion in a convenient way.

## 1 Introduction

Electrochemical impedance spectroscopy (EIS) is of great importance in the analysis of electrochemical systems, such as sensors and biomembranes, batteries and fuel cells, as well as in dedicated studies of charge transfer and corrosion mechanisms, electrode kinetics or a double-layer. This technique is based on the disturbance of the electrochemical reaction from its steady-state by applying a small perturbation to the system. The relaxation of the system to reach the another steady-state allows analyzing its time response with respect to the time constant of each elementary process [1].

Mass conservation laws, the Nernst-Planck flux formulae and Poisson equation form fundamental system of equations (NPP) that allows calculating full time response of the ion-selective electrode (ISE) and impedance spectra without approximate assumptions, *e.g.*, linear dependence of potential and concentrations on position. The second great advantage of the NPP is that it relates directly simulated impedance spectra to physico-chemical parameters of the system. Thus, the usual analysis of equivalent circuit gets new possibilities.

This work presents simulated impedance spectra calculated on the basis of NPP problem for two different systems, multi- and bi-ionic case.

# 2 Theory

## 2.1 Model

The considered system consists of two bathing solutions and the membrane, Fig. 1. The membrane is assumed to be flat, isotropic and of thickness $d$ [2]. These assumptions are equivalent the one-dimensional NPP problem. Diffusivities, dielectric permittivity and thickness are assumed to be constant. The convection of the solvent in membrane is ignored.

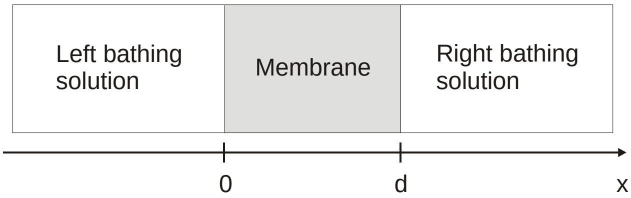

**Fig. 1:** Schematic representation of the considered system.

The initial-boundary value problem for one dimension is given by the set of equations known as the Nernst-Planck-Poisson problem. Ionic fluxes are expressed by [3-6] (list of symbols is included in Appendix):

$$J_i(t,x) = -D_i\left[\frac{\partial c_i(t,x)}{\partial x} - z_i c_i(t,x)\frac{F}{R\cdot T}E(t,x)\right] \tag{1}$$

The evolution of the electric field is represented by the Poisson equation:

$$\frac{\partial E(t,x)}{\partial x} = \frac{\rho(t,x)}{\varepsilon} \tag{2}$$

where

$$\rho(t,x) = F\cdot\sum\nolimits_i z_i c_i(t,x)$$

denotes the charge density. The mass conservation law describes the evolution of concentrations:

$$\frac{\partial c_i(t,x)}{\partial t} = -\frac{\partial J_i(t,x)}{\partial x} \tag{3}$$

In this work, the Poisson equation is replaced by its equivalent form, the total current equation in the form proposed by Cohen and Cooley [7]:

$$I(t) = F\cdot\sum_{i=1}^{r} z_i J_i(t,x) + \varepsilon\frac{\partial E(t,x)}{\partial t} \tag{4}$$

Fluxes of ions at the membrane interfaces are given by Chang-Jaffe boundary conditions [8]:

$$\begin{aligned} J_i(t,0) &= k_{i,\mathrm{fL}} c_{i\mathrm{L}} - k_{i,\mathrm{bL}} c_i(t,0) \\ J_i(t,d) &= -k_{i,\mathrm{fR}} c_{i\mathrm{R}} + k_{i,\mathrm{bR}} c_i(t,d) \end{aligned} \tag{5}$$

Initial concentrations obey the electro-neutrality condition and consequently initially there is no space charge in the membrane [2]:

$$c_i(0,x) = c_i^0(x),\, E(0,x) = 0 \text{ for } x \in [0,d].$$

The membrane potential, $V(t)$, is given by [9]:

$$V(t) = -\int_0^d E(t,x)\,dx \tag{6}$$

Eqns. (1) to (5) were converted into a finite difference form with the space grid containing closely spaced points near the interfaces and a distinctively wider spacing inside the membrane. Above initial boundary-value problem was solved numerically in Matlab 7.1 using implicit Rosenbrock algorithm (*ode23s* in Matlab).

### 2.2 Electrochemical Impedance Spectroscopy

The impedance of a system can be determined from the linear response of the system to a small-current perturbation. In this work:

$$I(t) = \begin{cases} 0 & \text{for } t \in [0,t_k] \\ I_0 & \text{for } t \in (t_k,\infty] \end{cases}.$$

From eqns. (7) the potential–time response, $V(t)$, and impedance $Z(t) = V(t)/I(t)$ are computed. The Fourier transforms of the current perturbation and of the impedance are given by:

$$I^*(\omega) = I'(\omega) + jI''(\omega),$$

where $I'(\omega) = 0$ and $I''(\omega) = -I_0/\omega$, and

$$Z^*(\omega) = Z'(\omega) + jZ''(\omega),$$

where $Z'(\omega) = -V''(\omega)\cdot\omega/I_0$ and $Z''(\omega) = V'(\omega)\cdot\omega/I_0$

Following Brumleve and Buck [9] we transform $V(t)$ by evaluating cosine and sine integrals:

$$V'(\omega) = \int_0^\infty \left(V(t) - V_\infty\right)\cos(\omega t)\,dt,\; V''(\omega) = \int_0^\infty \left(V(t) - V_\infty\right)\sin(\omega t)\,dt + \frac{V_\infty}{\omega} \tag{7}$$

## 3 Results

### 3.1 Multi-Ionic Case

In this case the system of three ions is considered. Namely, the system consists of main ion $J^{2+}$, weakly interfering ion, $I^+$, that is partially blocked at the interfaces and charged ionic site $R^-$, which is restricted only to the membrane and is blocked at interfaces. The impedance spectra, Fig. 4, were calculated on the basis of data as presented in Table 1.

**Table 2.** Initial concentrations, diffusivities and heterogeneous rate constants for multi-ionic case

| | $c_{i\mathrm{L}}$ [M] | $c_{i\mathrm{M}}$ [M] | $c_{i\mathrm{R}}$ [M] | $D_i$ [m$^2$s$^{-1}$] | $k_{i,\mathrm{fL}}$ [ms$^{-1}$] | $k_{i,\mathrm{bL}}$ [ms$^{-1}$] | $k_{i,\mathrm{bR}}$ [ms$^{-1}$] | $k_{i,\mathrm{fR}}$ [ms$^{-1}$] |
|---|---|---|---|---|---|---|---|---|
| $J^{2+}$ | $10^{-10}\div 1$ | $5\times10^{-4}$ | 1 | $10^{-11}$ | $10^{-3}$ | $10^{-3}$ | $10^{-3}$ | $10^{-3}$ |
| $I^{+}$ | 0.15 | 0 | 0 | $10^{-11}$ | $4.472\times10^{-7}$ | $10^{-3}$ | $10^{-3}$ | $4.472\times10^{-7}$ |
| $R^{-}$ | 0 | $10^{-3}$ | 0 | $10^{-11}$ | 0 | 0 | 0 | 0 |

Fig. 4 shows that the resistance of the system decrease when concentration of main ion increase. This behavior is obviously a result of increased conductivity. This plot shows the presence of two arcs: a high-frequency bulk arc (related to the properties of the membrane) and the characteristic finite Warburg impedance arc at low frequencies (due to diffusion in the membrane). It is worth notice that for the highest and lowest concentrations of primary ion arcs overlap.

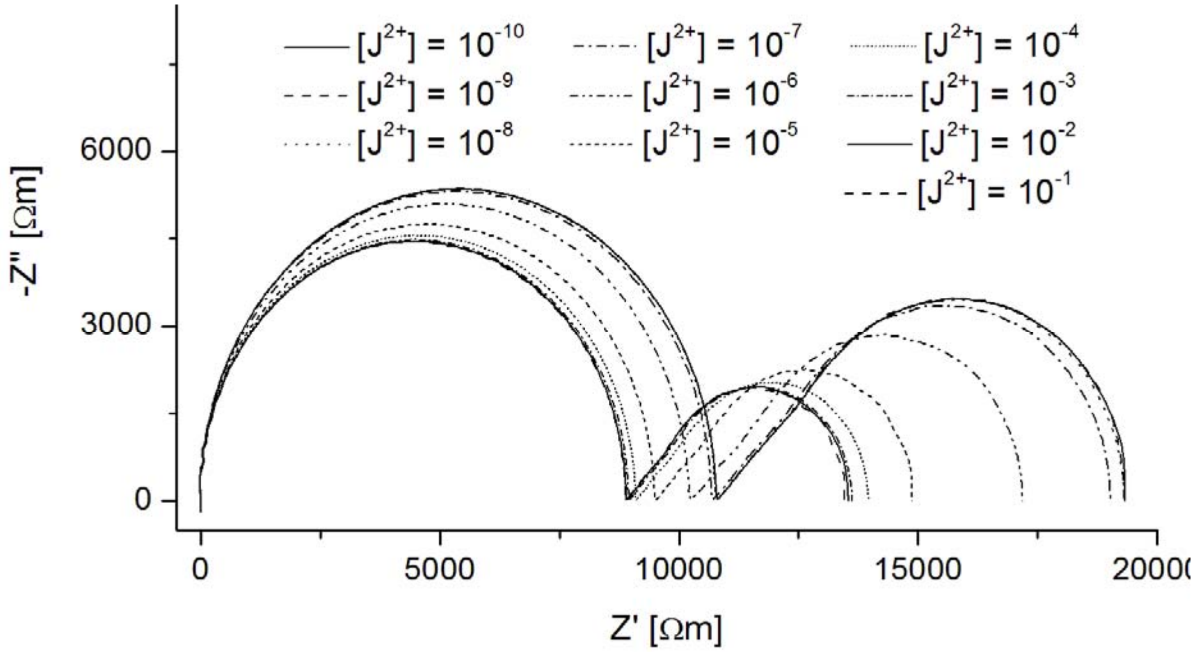

**Fig. 4.** Simulated complex impedances for different concentrations of primary ion [$J^{2+}$] in left bathing solution. Radial frequency range: $\omega = 10^{-4} - 10^{8}$ [Hz], $I_0 = 10^{-4}$ [Am$^{-2}$].

### 3.2 Bi-Ionic Case

Bi-ionic case has a practical importance in determining selectivity of the ISE. In this case system of two cations, $J^+$, $I^+$, and one anion, $R^-$. is considered. The value of diffusion coefficient for main ion, $J^+$, exceeds by one order of magnitude the diffusivity $I^+$. It was assumed that heterogeneous rate constants for both cations are equal, $k = k_{i,\mathrm{fL}} = k_{i,\mathrm{bL}} = k_{i,\mathrm{fR}} = k_{i,\mathrm{bR}}$. Charged ionic site, $R^-$, is restricted only to the membrane phase. The influence of heterogeneous rate constants and membrane thickness on impedance spectra is showed below.

Fig. 5 presents the impedance spectra calculated for bi-ionic case, according to the conditions given in Table 3.

**Table 3.** Initial concentrations, diffusivities and heterogeneous rate constants for bi-ionic case. $k = k_{i,\mathrm{fL}} = k_{i,\mathrm{bL}} = k_{i,\mathrm{fR}} = k_{i,\mathrm{bR}}$

| | $c_{i\mathrm{L}}$ [M] | $c_{i\mathrm{M}}$ [M] | $c_{i\mathrm{R}}$ [M] | $D_i$ [m$^2$s$^{-1}$] | $k$ [ms$^{-1}$] |
|---|---|---|---|---|---|
| $J^+$ | $10^{-3}$ | $10^{-3}$ | 0 | $10^{-10}$ | $10^{-6}\div10^{-4}$ |
| $I^+$ | 0 | 0 | $10^{-3}$ | $10^{-11}$ | $10^{-6}\div10^{-4}$ |
| $R^-$ | 0 | $10^{-3}$ | 0 | $10^{-11}$ | 0 |

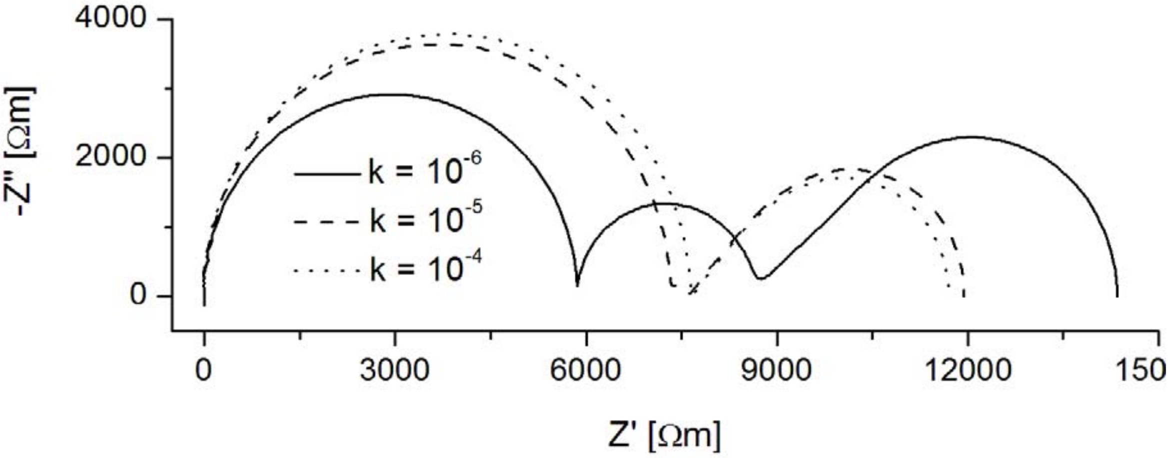

**Fig. 5.** Simulated complex impedances for different heterogeneous rate constants. Radial frequency range: $\omega = 10^{-4} \ldots 10^{8}$ Hz, $I_0 = 10^{-4}$ Am$^{-2}$.

The impedance diagram shows that in the case of low values of the heterogeneous rate constants a slow interfacial transport invokes additional arc in an intermediate frequency range. This additional arc is attributed to the interface impedance [10].

Fig. 6 and Fig. 7 present impedance arcs simulated for different values of membrane thickness. The heterogeneous rate constants equal: $k = k_{i,\mathrm{fL}} = k_{i,\mathrm{fR}} = k_{i,\mathrm{bL}} = k_{i,\mathrm{bR}} = 10^{-4}$ [ms$^{-1}$] for all cations. One can see that in thick membranes only two arcs arte present, the high-frequency bulk arc and the low-frequency Warburg arc, Fig. 6. When the thickness of the membrane decreases, arcs become smaller (impedance of the system decreases). For values of membrane thickness in the range 250 nm $< d <$ 5 µm an additional, middle frequency range arc appears. When $d \leq 250$ nm again, only two arcs are present, the high-frequency arc, connected with properties of bulk of the membrane and the middle- and low-frequency arc, which is related to interfacial properties of the membrane, Fig. 7. This behaviour is in good agreement with Ohm's law.

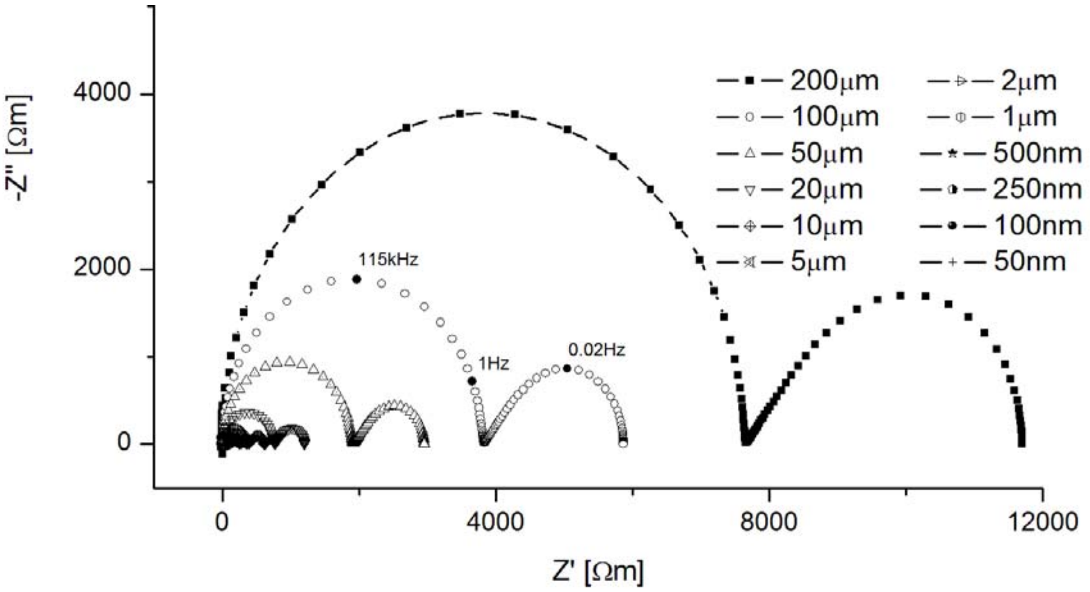

**Fig. 6.** Simulated impedance spectra for different values of membrane thickness. Radial frequency range: $\omega = 10^{-4} \ldots 10^{8}$ Hz, $I_0 = 10^{-4}$ Am$^{-2}$.

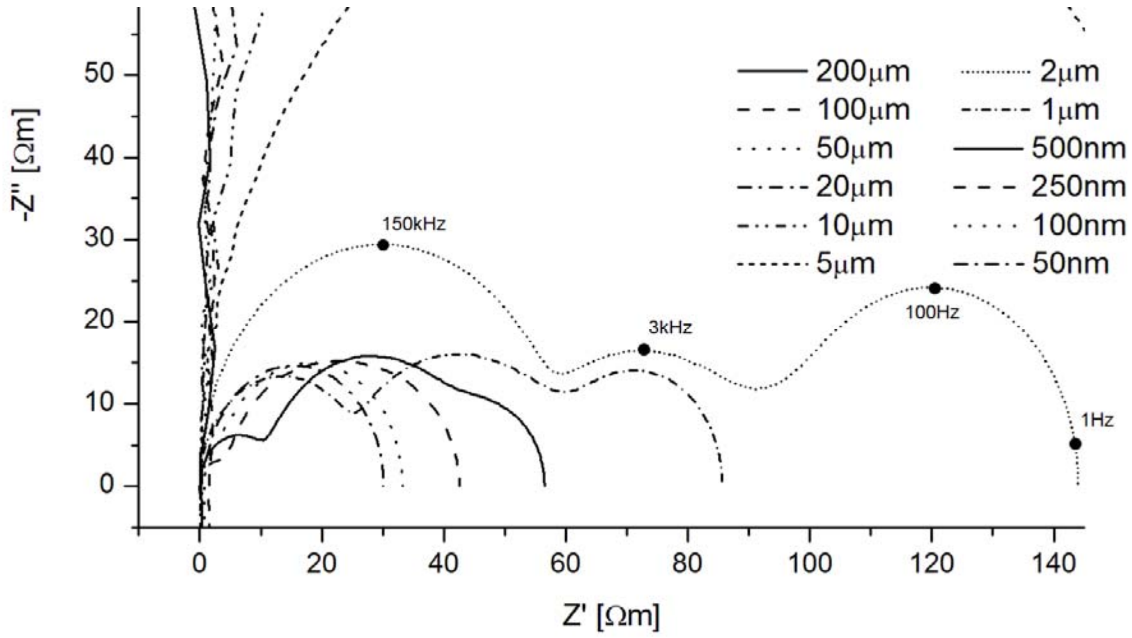

**Fig. 7.** Simulated impedance spectra for different values of membrane thickness. Bi-ionic case. Radial frequency range: $\omega = 10^{-4} \ldots 10^{8}$ Hz, $I_0 = 10^{-4}$ Am$^{-2}$.

## 4 Conclusions

The numerical solution of the system of coupled Nernst-Planck-Poisson equations is presented. The method directly relates the diffusivities in the membrane and the interface properties (heterogeneous rate constants of transport across interfaces) to the characteristic features of impedance spectra (dimensions and characteristic radial frequencies). Consequently, the equivalent circuit is not necessary to interpret the impedance spectra of electrochemical systems. Instead it can be useful in inverse problems. It was found that qualitatively similar effects on impedance spectra are a result of different physico-chemical parameters.

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### Appendix: Symbol legend

| | |
|---|---|
| $c_i$ | concentration of *i*-th ion |
| $c_{i\mathrm{L}}, c_{i\mathrm{R}}$ | concentrations of *i*-th ion in left and right bathing solution |
| $c_{i0}, c_{i\mathrm{d}}$ | concentrations of *i*-th ion in the membrane at $x = 0$ and $x = d$ |
| $E$ | electric field |
| $J_i$ | flux of *i*-th ion |
| $k_{i,\mathrm{fL}}, k_{i,\mathrm{bL}}, k_{i,\mathrm{fR}}, k_{i,\mathrm{bR}}$ | heterogeneous rate constants at interfaces, where subscripts *i*, *f* (or *b*) and *L* (or *R*) denote the component, direction of ion permeation (toward or from the membrane) and left (or right) side of the membrane, respectively. |
| $D_i$ | self diffusion coefficient |
| $z_i$ | valence of *i*-th ion |

| | |
|---|---|
| $\rho$ | electric charge density |
| $V$ | membrane potential |
| $Z^*$ | complex impedance |
| $Z'$ | real part of impedance |
| $Z''$ | imaginary part of impedance |
| $V'$ | real part of complex potential |
| $V''$ | imaginary part of complex potential |
| $V_\infty$ | potential at $t = \infty$ |
| $F$ | Faraday constant |
| $R$ | gas constant |
| $T$ | temperature |
| $\varepsilon$ | dielectric permittivity |
| $I_0$ | amplitude of the current signal |
| $j$ | $\sqrt{-1}$ |
| $\omega$ | radial frequency |

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