

INVERSE PROBLEMS IN MASS AND CHARGE TRANSPORT

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Abstract - Inverse problems have been becoming an important method for determination of materials properties, size and shape design, identification of the proper boundary and/or initial conditions. In this work we show the application of the inverse method to multi-component electrochemical systems. The basic process operating in these systems is electrodiffusion which can be described by the full form of the Nernst-Planck and Poisson equations for arbitrary initial conditions and Neumann-like boundary conditions. No simplifications like electroneutrality or constant electric field assumption are used. Results for several examples are demonstrated: determination of chloride diffusion coefficient in concrete, optimization of detection limit for ion selective electrodes and determination of EIS spectra using NPP model.

Résumé – Problèmes inverses pour le transport de matière et de charge. Les problèmes inverses sont devenus une méthode importante pour la détermination des propriétés des matériaux, pour la conception de leur taille et forme ou pour l'identification des conditions limites et/ou initiales. Dans ce travail, nous montrons l'application de la méthode inverse à des systèmes électrochimiques à plusieurs composants. Le processus de base opérant dans ces systèmes est l'électrodiffusion qui peut être décrite par la forme complète des équations de Nernst - Planck et de Poisson pour les conditions initiales arbitraires et les conditions aux limites de type de Neumann. Aucune simplification comme l'électroneutralité ou l'hypothèse de champ électrique constant ont été utilisés. Les résultats pour plusieurs exemples sont donnés : la détermination du coefficient de diffusion du chlorure dans le béton, l'optimisation de la limite de détection pour les électrodes sélectives d'ions et la détermination des spectres EIS en utilisant le modèle NPP.

1. THE INVERSE METHOD - INTRODUCTION

The inverse method is very useful in determination the physical parameters of any mathematical model by comparing its prediction with experimental data. It allows calculating the optimal values of model parameters p_1, \dots, p_m by performing computer simulations which give the solution for these values. The idea is to define the proper goal function, $GoalFun(p_1, \dots, p_m)$, which measures the difference between results produced by real world experiment and model predictions, and then to seek its global minimum. Let us denote by $y_i^M(x, t; p_1, \dots, p_m)$ the solution of the mathematical model (*Model*) as a function of $x \in \mathbf{R}^3$ and time $t > 0$. The values obtained from experiment (*Exp*) shall be denoted as $y_i^{Exp}(x, t)$, where we do not show “dependence” on parameters

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p_1, \dots, p_m , because there is only one set of their values selected by nature. One possible measure of difference is

$$GoalFun(p_1, \dots, p_n) := \sum_i \int_0^{t_{end}} \int_{\Omega} |y_i^{Model}(\mathbf{x}, t; p_1, \dots, p_n) - y_i^{Exp}(\mathbf{x}, t)|^2 dx dt, \quad (1)$$

where $\Omega \subset \mathbf{R}^3$ is a domain in space where the process occurs, and $t_{end} > 0$ is duration of the process. In the case when we measure the results only after some time (i.e. at the particular time t_{end} only) the goal function will be defined rather as

$$GoalFun(p_1, \dots, p_n) := \sum_i \int_{\Omega} |y_i^{Model}(\mathbf{x}, t_{end}; p_1, \dots, p_n) - y_i^{Exp}(\mathbf{x}, t_{end})|^2 dx \quad (2)$$

The assumption that we know the experimental data $y_i^E(\mathbf{x}, t)$ in the whole domain, $\mathbf{x} \in \Omega \subset \mathbf{R}^3$ is rather optimistic. In most case the function is known in selected points, $y_i^E(\mathbf{x}_k, t)$. In this case the goal function is usually considered as

$$GoalFun(p_1, \dots, p_n) := \sum_i \sum_k |y_i^{Model}(\mathbf{x}_k, t_{end}; p_1, \dots, p_n) - y_i^{Exp}(\mathbf{x}_k, t_{end})|^2 \quad (3)$$

A procedure based on the inverse method ultimately requires the optimization function (goal function) be passed to some minimum seeking algorithm such as Hierarchical Genetic Strategy (HGS) or Sequential Quadratic Procedure (SQP) to find the global optimum. This is purely a mathematical/numerical problem and there are many possible choices [1].

2. MULTILAYER NERNST-PLANCK-POISSON MODEL

In this paper we demonstrate using of inverse method for electrochemical systems. Thus, we briefly present Nernst-Planck-Poisson (NPP) system of equations which is multidisciplinary and appearing in many fields of science and technology where mass and charge transport occurs. It is general and rich enough in a physical sense to describe the effects occurring in semiconductors [2,3], building materials (such as concrete) [4], synthetic and biological charged membranes [5] and colloids [6]. Let us consider a system that consists of n layers, each representing different phase, inside of which concentration changes of r components c_i^j (ions or uncharged chemical species, $i = 1, \dots, r$) and a change of the electrical field E^j in space and time takes place. The scheme of the n -layer system is presented in figure 1.

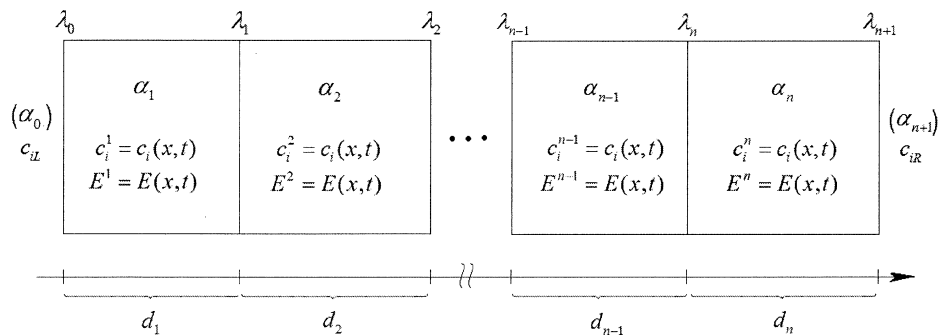


Figure 1. The scheme of the n -layer system between two solutions with i -th component concentration c_{iL} on the left, and c_{iR} on the right side of the system.

Each layer has its own thickness d_j and dielectric permittivity ε_j , is flat and isotropic, so it can be assumed as a continuous environment. On the right side and on the left side of that system, respectively, the bulk solutions with constant concentrations of each component i , c_{iR} and c_{iL} , are assumed. The charge z_i of each ion i and diffusion coefficients D_i^j in each layer α_j , are known. An external current density $I(t)$ can be applied to the system. The Nernst-Planck flux expression describes the flux of ions in space and time:

$$J_i^j(x,t) = -D_i^j \frac{\partial c_i^j}{\partial x}(x,t) - \frac{F}{RT} D_i^j z_i (c_i^j E^j)(x,t) + (c_i^j v^j)(x,t), \quad (4)$$

The above equation connects the flux with three processes: diffusion ($-D_i^j \frac{\partial c_i^j}{\partial x}$), migration ($-\frac{F}{RT} D_i^j z_i c_i^j E^j$), and convection ($+c_i^j v^j$). Moreover, Gauss's law (or the Poisson equation) in the form:

$$\frac{\partial E^j(x,t)}{\partial x} = -\frac{\partial^2 \varphi^j(x,t)}{\partial x^2} = \frac{F}{\varepsilon_j} \sum_i z_i c_i^j(x,t), \quad (5)$$

can be substituted with the displacement current equation, as shown by Cohen and Cooley [7]:

$$I(t) = F \cdot \sum_{i=1}^r z_i J_i^j(x,t) + \varepsilon_j \cdot \frac{\partial E^j(x,t)}{\partial t}. \quad (6)$$

To connect concentrations evolution in time with flux of components mass balance equation is used

$$\frac{\partial c_i^j}{\partial t} = -\frac{\partial J_i^j}{\partial x}. \quad (7)$$

These equations with proper initial and boundary conditions form a set of partial differential equations PDEs. Solution of these equations [8] gives the concentration and electrical fields as the functions of space and time. Finally, the overall electrical potential of the j -th layer (as a function of time) is calculated by the integral of electric field over space:

$$\Delta \varphi^j(t) = - \int_{\lambda_{j-1}}^{\lambda_j} E^j(x,t) dx, \quad (8)$$

where λ_{j-1} and λ_j represent the phase boundaries.

For the above problem without simplifications (e.g., constant electric field) a numerical method was derived and effectively solved using C++ programming language [8].

3. DETERMINATION OF CHLORIDE DIFFUSION COEFFICIENT IN CONCRETE – TWO COMPARTMENTS AND TIME DEPENDENT DIRICHLET BOUNDARY CONDITIONS.

In this section we present the application of inverse method to determine a chloride diffusion coefficient in concrete – the parameter which describes the rate of chloride ingress into the concrete matrix and consequently effects corrosion of rebars in concrete. The classical approach is the so called two chamber experiment in which a sample of usually cylindrical concrete is placed between two chambers containing solution. One chamber may contain the concentrated salt with Cl^- ions while the second may be free of it (at the beginning). By measuring the time dependent change of concentration in both chambers and using the inverse methodology we can determine the diffusion coefficient. The classical method assumes the chloride concentration in the first chamber is practically constant (because it contains the concentrated salt and the depletion is relatively small) and takes into account only changing concentration in the second chamber. Here we present a result when this simplifying assumption is dropped.

Let us assume the stationary state in the concrete. The balance equation in 1D

$$\frac{\partial c}{\partial t}(x,t) = -\frac{\partial J}{\partial x}(x,t) \quad \text{for } 0 < x < d, \quad t \geq 0 \quad (9)$$

gives $\partial J / \partial x = 0$, hence $J(x,t) = J(t)$. Thus the flux $J(t)$ is determined by its value on the boundary $x = d$, which can be expressed as

$$J(t) = \frac{V_2}{A} \frac{dc_2}{dt}(t), \quad (10)$$

where V_2 is the volume of chamber 2 and A is the cross-section area. On the other hand we have $J = -D\partial c / \partial x$, so $c(x,t)$ is linear with respect to $x \in [0, d]$: $\partial c / \partial x = (c(d,t) - c(0,t)) / d$. Taking into account the Dirichlet boundary conditions $c(0,t) = c_1(t)$, $c(d,t) = c_2(t)$, and equations (10) and (11) together with $J = -D\partial c / \partial x$, we obtain the equation

$$\frac{V_2}{A} \frac{dc_2}{dt}(t) = -D \frac{c_2(t) - c_1(t)}{d}. \quad (11)$$

for the evolution of concentration in the chamber 1. The unknown is $c_2 = c_2(t)$, but the function $c_1 = c_1(t)$ is given (measurement). The solution of equation (11) is

$$c_2(t, D) = c_2(0) e^{-\frac{DA}{V_2 d} t} + \frac{DA}{V_2 d} \int_0^t c_1(s) e^{\frac{DA}{V_2 d} (s-t)} ds. \quad (12)$$

The determination of the diffusion coefficient is now converted to the minimization of the following goal function

$$GoalFun(D) = \int_0^{t_{end}} \left| c_2^{Exp}(t) - e^{-\frac{DA}{V_2 d} t} \left(c_2^{Exp}(0) + \frac{DA}{V_2 d} \int_0^t c_1^{Exp}(s) e^{\frac{DA}{V_2 d} s} ds \right) \right|^2 dt, \quad (13)$$

or $GoalFun(\alpha) = \int_0^{t_{end}} \left| c_2^E(t) - \alpha e^{-\alpha t} \int_0^t c_1^E(s) e^{\alpha s} ds \right|^2 dt$, where $\alpha = \frac{DA}{V_2 d}$ is a rescaled diffusion coefficient and $c_2^{Exp}(0) = 0$ (a usual experimental condition). Thus the problem was turned into finding the minimum, $\min_{\alpha > 0} GoalFun(\alpha)$. As an illustration let us consider the data measured in two chambers over the period 60 h with sampling interval 6 h. The values of concentration $c_1^{Exp}(t)$, c_2^{Exp} are given in *table I*.

Table I. Experimental data in two chamber setup. Change of concentration in both chambers over time are taken into account.

| t /h | 0 | 6 | 12 | 18 | 24 | 30 | 36 | 42 | 48 | 54 | 60 |
|---------|---|------|------|------|------|------|------|------|------|------|------|
| c1(t)/M | 3 | 2.93 | 2.75 | 2.66 | 2.53 | 2.3 | 2.21 | 2.07 | 1.94 | 1.89 | 1.75 |
| c2(t)/M | 0 | 0.03 | 0.12 | 0.2 | 0.29 | 0.45 | 0.49 | 0.56 | 0.67 | 0.74 | 0.82 |

The goal function for this data defined by (13) is plotted in *Figure 2*. The plot is not detailed enough to reveal that there is in fact one global minimum for dimensionless diffusion coefficient, namely $\alpha_{min} = 0.034$.

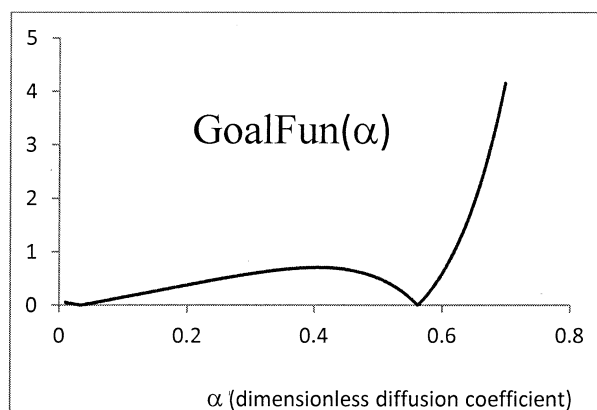


Figure 2. Plot of the goal function for the two chamber problem with both concentrations changing over time. This particular plot is for data in *table I*.

4. DETECTION LIMIT OF ION-SELECTIVE ELECTRODES

In this section optimization of measurement conditions, i.e., improving of the detection limit of potentiometric ion sensors is presented. Potentiometric ion sensors based on ion-selective electrodes (ISEs) are a very important subgroup of electrochemical sensors [9]. They allow potentiometric determination of the activity of one ion in the presence of other ions. They are very attractive for practical applications due to their features, such as small size, portability, low-energy consumption, and relatively low cost.

The detection limit is one of the constitutive parameters of an ISE. Typically, the detection limit of ISE lies in a micromolar (μM) range [10,11] but can be engineered to vary by several orders of magnitude depending on the inner solution concentrations or the time of measurement. It can be lowered, even down to a picomolar (pM) range, by using inner solutions whose concentrations of analyte ions are kept at the low level as was shown by Sokalski *et al.* [12,13,14].

Basing on NPP model and using hierarchical genetic algorithm (HGS) as procedure for finding the optimal parameters we obtained the inverse method [15] for optimal detection limit. The problem is to find the concentration of the preferred ion ($c_{1,IS}$) in the inner solution and the measuring time (t_{end}) providing the *best detection limit* (*DetLim*) of an ISE. In the NPP-HGS method the goal function is defined as the value of the detection limit obtained using the NPP model for two variable parameters, $c_{1,IS}$ and t_{end} . Thus, using the NPP model the calibration curve for given $(c_{1,IS}, t_{end})$ is computed (simulated)

$$\text{CalibrationCurve}: [-13, -3] \ni \log c_{1,Sample} \mapsto \varphi(c_{1,Sample}; c_{1,IS}, t_{end}) \in \mathbf{R}, \quad (14)$$

and next, according to some procedure (the IUPAC or Sokalski's definition), we can extract from it the detection limit. Putting these two steps together we have a desired optimization function

$$\text{GoalFun}(c_{1,IS}, t_{end}) := \text{DetectionLimit}(\text{CalibrationCurve}(c_{1,IS}, t_{end})) \in \mathbf{R}. \quad (15)$$

For presentation we selected two examples, first with two optimization parameters (Figure 3a) and second with three parameters (Figure 3b).

HGS optimized this function for the individuals represented by the values of these two parameters. Figure 3a shows the time-concentration-detection limit map (isolines) obtained using the NPP model with overlaid points obtained with NPP-HGS method. The detection limit is depicted by the contour map with different colour intensities (the darker the colour, the lower the

detection limit). The local/global minima can be read from the plot. In order to obtain such a contour plot, 1200 calibration curves were calculated [15].

To further demonstrate the effectiveness of NPP-HGS method the optimization of three parameters, concentration of the primary ion in the inner solution ($c_{1,IS}$), measuring time (t_{end}), and the diffusion coefficient of the preferred ion in the membrane (D_1^{mem}) was made. The results, presented in Figure 3b. shows that the lowest detection limit is obtained in two regions:

1) $\log(c_{DetLim}) < -11.5$ when the diffusion coefficient of the preferred ion is in the range $5.1 \cdot 10^{-11}$ to $5.9 \cdot 10^{-11} \text{ m}^2/\text{s}$, its internal solution is in the range $8.8 \cdot 10^{-9}$ to $9.6 \cdot 10^{-9} \text{ M}$ and measuring time is around 27 s.

2) $\log(c_{DetLim}) < -10.5$ when the diffusion coefficient of the preferred ion is in the range $1.0 \cdot 10^{-11}$ to $1.2 \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$, its internal solution is in the range $2.2 \cdot 10^{-6}$ to $2.4 \cdot 10^{-6} \text{ M}$ and measuring time is around 482 s.

This result would be very unfeasible to obtain by the “brute force” approach. 12 000 calibration curves (132 000 points) would take around 150 days. The computational effort using NPP-HGS method was around 20 times smaller.

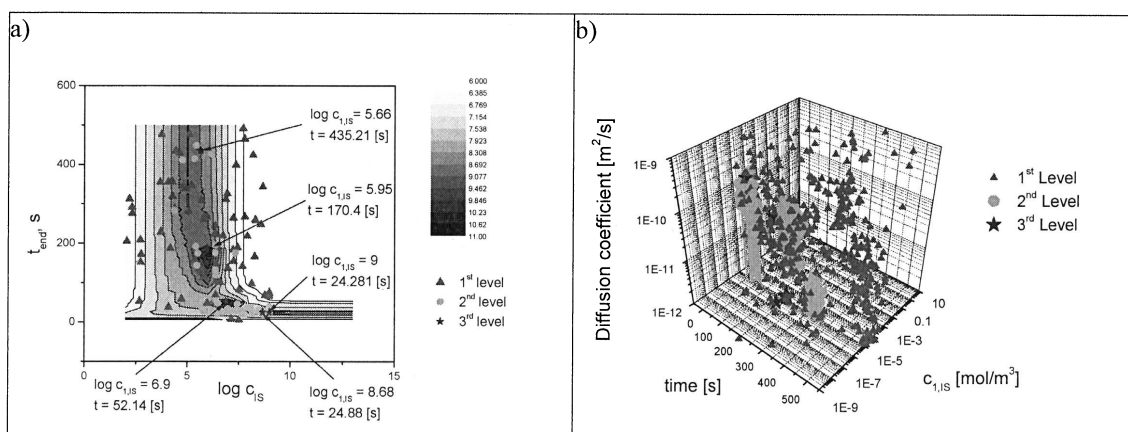


Figure 3. a) Example 1: detection limit as a function of time and concentration (two parameters). The darker the area the better detection limit. The contours were calculated only for visualization of the detection limit function. But the points show several stages of HGS algorithm which approaches the minimum. b) Example 2: the picture shows calculated points by HGS in ($c_{1,IS}, t_{end}, D_1^{mem}$) space (three parameters). The red, green and blue colours denote the individuals of the first, second and third populations, respectively.

The presented calculations show a great future potential for the NPP model combined with the HGS to facilitate the design of ISEs with a lower detection limit and in particular provide recommendations concerning analytical robustness for measurements in low concentrations.

5. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

In this section we demonstrate the application of the inverse method to model the frequency perturbation response of the system. Electrochemical impedance spectroscopy (EIS) is a useful tool for analyzing various electrochemical systems because it allows the separation and characterization of individual kinetic processes [16]. It has become established as one of the most popular analytical

tools in material research. Its broad area of application includes corrosion studies and corrosion control; monitoring of properties of electronic and ionic conduction polymers, colloid and coatings, measurements in energy storage, batteries, and fuel cells systems, biological analysis and biomedical sensors; measurements in semiconductors and solid electrolytes; studies of electrochemical kinetics, reactions and processes [17]. It allows to study such processes as adsorption, charge and mass transport, and kinetics of coupled sequential and parallel reactions. Of special interest here is its application for investigation of ISE – or more precisely – for ion selective membranes which form the main part of such electrodes.

The standard treatment in EIS is based on the electrical equivalent circuit method which is convenient and easy to implement. But equivalent circuits – according to Macdonald [18] – are mere “*analogs, which do not pretend to describe the physico-electrochemical properties of the system, but simply reproduce the properties.*” One of the consequences is non-uniqueness of such representation (different circuits can give the same impedance spectra). Thus, we prefer using more fundamental physico-chemical description (e.g., NPP model) [19].

Another approach in EIS is based on the description of the system by the fundamental and constitutive laws which take the form of PDEs (dynamical systems). Simulations based on these equations allow to obtain the impedance spectrum of the analyzed system, $\{Z(\omega)\}_{\omega>0} \subset \mathbb{C}$, where \mathbb{C} denotes the complex number field. Such physical models not only reproduce the impedance spectrum, but can also elucidate the mechanism of the processes occurring at the interface in terms of physical concepts. The ultimate goal of EIS is to characterize the mechanism of the charge transfer reaction and transport modes, so we have to go beyond the equivalent circuits. In the case of electro-diffusion processes this treatment of EIS can be based on the NPP equations. In special cases the NPP system can be handled to give analytically expressed $Z(\omega)$, but in general it requires numerical simulations [20].

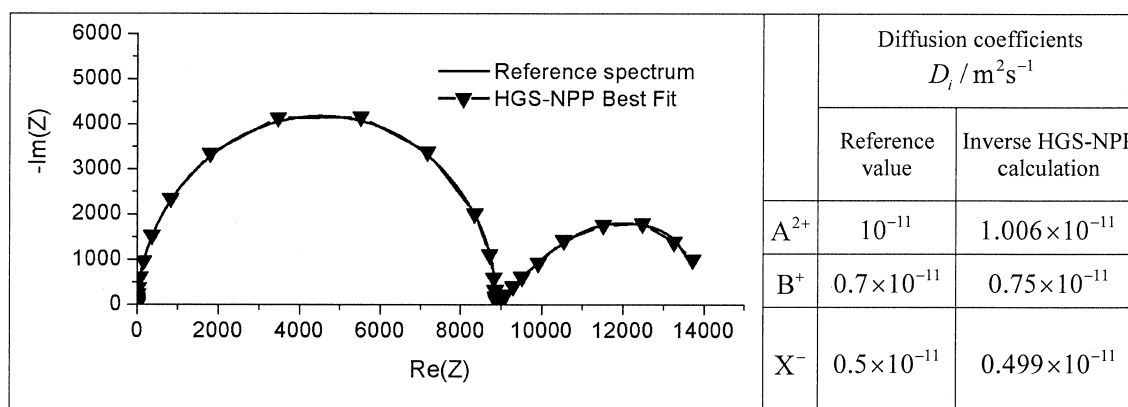


Figure 4. The results of the inverse HGS-NPP compared with the reference spectrum calculated for different values of diffusion coefficients for each ion. The reference and computed diffusion coefficients by the inverse HGS-NPP method.

As an illustration of the inverse method in EIS without the equivalent circuits we present an example of the HGS strategy to find the optimal parameters (diffusion coefficients) in a membrane system containing three movable ions (A^{2+} , B^+ , X^-). The presented method can be used to find parameters such as membrane thickness, dielectric permittivity, heterogeneous rate constants, and concentrations (reference or sample solution). The problem is to find the NPP parameters which minimize the difference between the reference (experimental) and calculated (model) impedance spectra (Figure 4), i.e. to minimize the following function:

$$GoalFun := \sum_k g_k |\operatorname{Re}(Z_k^{Model}) - \operatorname{Re}(Z_k^{Exp})|^2 + \sum_k h_k |\operatorname{Im}(Z_k^{Model}) - \operatorname{Im}(Z_k^{Exp})|^2 \quad (16)$$

where g_k , h_k are weight functions, Z_k^{Model} , Z_k^{Exp} are calculated and experimental complex impedance values for the k -th frequency. Optimization was performed with constraints $D_i / \text{m}^2 \text{s}^{-1} \in [10^{-13}, 10^{-9}]$. The simulations show that the diffusion coefficient of the B^+ ion has little effect on the shape of the impedance spectrum. The results of HGS-NPP simulations are presented in *Figure 4*.

6. CONCLUSIONS

The above examples illustrate the power and flexibility of the inverse method. It can be effectively used for the description of multicomponent electrodiffusion problems such as impedance spectra, detection limit of ISEs and generally determination various model parameters. In each case a goal function for optimization is defined and then a procedure for finding extrema is applied. As we seek the global extremum some care with the method selection is recommended. Here we used method based on genetic algorithms which are known for good performance in finding global extrema. Obviously the presented methodology is as good as the model used for the description of the real process. In particular, future applications will concern reaction terms in NPP model (e.g., complexation), 2D and 3D geometries (e.g., non-planar interfaces, ionic channels), or various complex boundary conditions.

7. ACKNOWLEDGEMENT

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