

Computer modeling of CHEMFET sensors for data fusion in environmental water monitoring systems*

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* This work was supported by the 5th Framework Programme of European Commission SEWING ([http](http://www.sewing-project.org), 2002)

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Abstract

CHEMFET sensors are important devices for online monitoring of ionic contents of environmental water. In automated monitoring systems chemical data fusion from electrical signals of sensors needs an efficient way of sensors modeling. Furthermore a sensor model should be dedicated to a data fusion algorithm. In this paper we present a technological model based on Van den Berg theory of chemical phenomena in the CHEMFET. Its main features are: arbitrary ion valencies and linearity with respect to ion activities. The latter is especially valuable in the data fusion algorithm.

Keywords

CHEMFET sensors; modeling; data fusion; ions detection, water monitoring systems

INTRODUCTION

CHEMFET sensors technology

In field effect transistors the channel conductance is a function of electrical field perpendicular to the gate oxide surface. In the n-channel MOSFET, a p-type silicon substrate (bulk) contains two n-type diffusion regions (source and drain). The structure is covered by a silicon dioxide insulating layer on top of which a metal gate electrode is deposited.

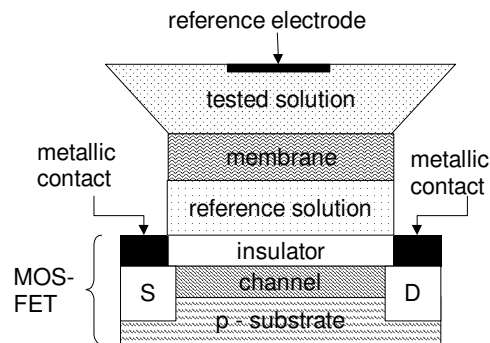


Figure 1. A schematic cross-section through a CHEMFET sensor

If the insulating layer is covered not by the metal gate but by an ion-selective polymeric membrane we obtain a device sensitive to different cations or anions, so-called, CHEMFET (Bakker, 1997). However, in order to establish a reversible electron transfer at the membrane/insulator interface, the deposition of an intermediate layer is required. A polyHEMA hydrogel layer allows us to obtain the well-defined mechanism of charge transfer between the ion-selective membrane and the transistor,

by means of the immobilized inner solution. Moreover, introduction of such a hydrogel layer, in which an aqueous buffered solution of salts can be absorbed, eliminates influence of CO₂ on the CHEMFET response and stabilizes a potential across the sensing membrane. A structure of this device is shown in Fig. 1. The ion-sensitivity of the deposited membranes of CHEMFETs allows us to measure the mole activity of one kind of ions (metal cations, anions and neutral molecules) from many kinds dissolved in a solution.

Data fusion problem

In this work we are focused on water monitoring by means of a probe containing a set of r CHEMFET sensors sensitive to r different ions. This probe, dipped in a tested water produces a vector of electrical signals $\mathbf{E}_B = [E_{B1}, \dots, E_{Br}]^t$. The problem is how to extract from these signals activities $\mathbf{a} = [a_0, a_1, \dots, a_r]^t$ of r tested ions contained in the tested water (Forster *et al*, 1991). Solution of this data fusion problem is simple if a relation between \mathbf{E}_B and \mathbf{a} is linear or can be transformed into the linear form, e.g. $\mathbf{e}_B = \mathbf{H} \mathbf{a}$, where $\mathbf{e}_B = \exp[-(\mathbf{E}_B - \mathbf{V}_{offs})/\psi_0]$. After simple calibration the ionic activities can be calculated from $\mathbf{a} = \mathbf{H}^{-1} \mathbf{e}_B$.

In this paper we present a Super-Nikolski model which is nonlinear with respect to \mathbf{e}_B but linear with respect to \mathbf{a} , so has the form $\mathbf{H}(\mathbf{e}_B) \cdot \mathbf{a} = \mathbf{1}$. Its advantage is a wider range of activity extraction than it was in the linear case. Data fusion based on this model will be a subject of a separate publication. In what follows we explain principal properties of the model: its technological character, availability of arbitrary ion electrovalencies and linearity with respect to \mathbf{a} .

Empirical model of Nikolski and Eisenmann (NkEis)

The membrane potential E_M is found to be the fundamental part of the measured signal since it describes the whole performance of the CHEMFET. Because the ion-sensitive membrane is interposed between the sample and the reference electrolyte, the membrane potential is divided into four potential contributions: the phase boundary potentials at both interfaces, potential across the electrolyte and the diffusion potential within the membrane. Assuming, that the potential at the membrane/reference solution interface is independent of the sample and that the diffusion potential is negligible, the membrane potential is governed by the phase boundary potential at the membrane/sample interface.

From basic thermodynamical considerations, assuming that interfacial ion transfer and complexation processes are relatively fast and that the equilibrium holds at the interface (so that the electrochemical potentials for both phases are equal) the phase boundary potential and thus the membrane potential can be described by the well-known Nernst equation:

$$E_M = V_{offs} + \frac{\psi_0}{z_i} \ln a_i, \quad (1.1)$$

where: z_i is the valency and a_i the activity of the uncomplexed ion in the sample, V_{offs} includes all sample-independent potential contributions, $\psi_0 = RT/F$, R , T and F are the universal gas constant, the absolute temperature and the Faraday constant. The potential of ion-selective membranes in solution containing different potential generating ions has been the subject of many experimental works. Investigations of the behavior of glass electrodes in mixtures of monovalent and multivalent cations, as well as studies of electrodes with liquid membranes led to formulation of a semi-empirical equation describing the membrane potential of an ion-selective electrode:

$$E_M = E^o + \frac{\psi_0}{z_i} \ln \left[a_i + K_{ij} a_j^{z_i/z_j} \right], \quad (1.2)$$

known as Nikolski-Eisenmann equation (Nikolski, 1937; Eisenmann, 1957), where: z_i and z_j are valencies of primary and interfering ions, a_i and a_j are activities of the i th and j th ions in the mixed sample, K_{ij} is selectivity coefficient representing a measure of the sensor selectivity towards interfering ions.

Despite differences between theoretical and experimental values of the selectivity coefficients the Nikolski-Eisenmann (NkEis) model has been commonly accepted and used for the description of properties of ion-selective potentiometric sensors. However, if ions of different charge are taken into account ($z_i \neq z_j$) the NkEis equation is inconsistent i.e. exchanging the indices i for j does not give identical analytical expressions. Therefore, the predicted signal of a sensor depends on which ion is treated as the primary and which as the interfering ion. This is a serious limitation of the model and can lead to substantial errors in practice. Several works pointed out that describing the sensor properties using NkEis equation, K_{ij} should be treated as a function e.g. of studied ions activities. Moreover, the temperature dependence of activity coefficients of ions should be considered when modeling the response of sensors in different temperature using the NkEis equation. These limitations of the NkEis model encouraged us to look for other models, sufficiently simple and accurate for data fusion applications in water monitoring systems. One of the models recently proposed is Super-Nikolski developed in what follows.

DEVELOPMENT OF SUPER-NIKOLSKI MODEL

Technological model of Van den Berg

According to works of Van den Berg (1988) and Ogrodzki *et al* (2000), Ogrodzki (2002) let us assume that an aqueous electrolyte solution contains several kinds of cations C_j^+ and anions A_i^- of respective mole concentrations c_j^+ , c_i^- , valencies z_{C_j} , z_{A_i} and activities a_{C_j} , a_{A_i} . We take into account Boltzmann Law describing activities \bar{a}_{C_j} , \bar{a}_{A_i} of C_j^+ , A_i^- in the membrane as linearly dependent on activities of these ions in the bulk electrolyte a_{C_j} , a_{A_i} and exponentially dependent on the voltage E_B between the membrane surface and the solution bulk, with division constants k_{C_j} , k_{A_i} electro-thermal potential $\psi_0 = n_i kT / q$, Boltzmann constant k , absolute temperature T , electron charge q and nonideality index n_i . Then we take into account the membrane filled with the ionophore containing ligands L , which are able to create charged complexes $C_j L$ with cations. Let the ionophore be strongly sensitive to the primary cation C_1^+ and weakly sensitive to interference cations C_j^+ , $j = 2, \dots, m$. Complexation of cations is proportional to activity of these cations in the membrane \bar{a}_{c_j} and on activity of free ligands \bar{a}_L , with complexation coefficients β_j . Of course balance of the ionophore components must hold. The ionophore contains also anions Y of a lipophilic salt, which associates with complexes $C_j L$ producing complexes $C_j LY$. Their activity is proportional to activity of free lipophilic ions \bar{a}_Y and to concentration of complexes $C_j L$ with association parameters K_{aj} . Balance of association and of all charged molecules also holds.

In this paper we extend results of Ogrodzki *et al* (2000), Ogrodzki (2002) by assuming that a sensor is sensitive to a certain ion (cation or anion) and the electrolyte moreover contains $m-1$ other ions of the same sign (we call them ions) and n ions of opposite sign (we call them counter-ions). Let

z_0, z_1, \dots, z_m be arbitrary valencies of ions while $z_0^A, z_1^A, \dots, z_n^A$ let be respective valencies of counter-ions. Moreover, z_Y is a valency of counter-ions of the lipophilic salt. The final technological model of the ion-selective membrane based on the above summarized theory of Van den Berg (1988) can be written in the compact form:

$$\frac{\bar{a}_{Ltot} C_1^w}{1 + C_1} + C_0^w + C_A^w + \frac{z_Y \bar{a}_{Ytot} (1 + C_1)}{1 + C_3} = 0, \quad (2.1)$$

where: $e_B = \exp\left(-\frac{E_B - V_{offs}}{\psi_0}\right)$, $\psi_0 = nRT/F$, E_B is a potential of the membrane, a_j, a_j^A are the j th ion and counter-ion activities and

$$\begin{aligned} C_0^w &= z_0 b_0 a_0 e_B^{z_0} + \sum_{j=1}^m z_j b_j K_{j a_j} e_B^{z_j}, \quad C_3 = C_1 + C_2 \bar{a}_{Ltot}, \\ C_1 &= a_0 e_B^{z_0} + \sum_{j=1}^m K_{j a_j} e_B^{z_j}, \quad C_2 = k_{a0} a_0 e_B^{z_0} + \sum_{j=1}^m k_{aj} K_{j a_j} e_B^{z_j}, \\ C_1^w &= z_0 a_0 e_B^{z_0} + \sum_{j=1}^m z_j K_{j a_j} e_B^{z_j}, \quad C_A^w = \sum_{j=1}^n z_j^A K_j^A a_j^A e_B^{z_j^A}. \end{aligned} \quad (2.2)$$

The parameters of this model were explained in details by Ogrodzki *et al* (2003). The technological Van den Berg model (VDB), unfortunately is difficult in practical application due to considerable numerical complexity and difficult extraction of parameters. There are two reasons of such a problem. The first reason is that extraction of parameters is performed on the basis of measured device responses: sensor voltage (mainly dependent on the membrane voltage E_B) versus ions activity. Measurements of these responses are always of small accuracy because of a nature of chemical measurements. The second reason is that the model is ill-conditioned and impossible is accurate extraction of those parameters which weakly influence the response even if measurements were performed accurately. To bridge a gap between inaccurate empirical models and an ill-conditioned physical one a Super-Nikolski model has been proposed for data fusion.

Super-Nikolski model

We introduce a new model suitable for ions with different valencies. Since in the charge balance (2.1) charged complexes of the ionophore (the 1st term) and lipophilic complexes (the 4th term) are dominating then we create a Super-Nikolski (SNk) model by neglection of the 2nd component and the 3rd component responsible for counter-ions influence. The same approach was used by Ogrodzki (2002) in the case of all valencies equal 1 or -1. In the case of nonunit valencies, after some algebra, we yield the general SNk model:

$$C_1 = \frac{1}{w} \quad (2.3)$$

where:

$$w = -\frac{1}{2} \left[\beta + 2 \pm \beta \sqrt{1 - \frac{4 \bar{a}_{Ltot} \bar{K}_a}{\gamma}} \right], \quad \bar{K}_a = \frac{C_2}{C_1} \quad (\text{average association constant}) \quad (2.4)$$

In the above the sign + or - should be chosen to gain a positive value of w . Since all ions are of the same sign, while z_Y is of the counter-ion sign, hence

$$\gamma = \alpha \frac{\bar{z}}{z_Y} \quad (\text{where } \alpha = \frac{\bar{a}_{Ltot}}{\bar{a}_{Ytot}}) \quad (2.5)$$

is negative. Moreover typically $\alpha \approx 2$, so we take the sign +.

Now we assume that influence of the mean lipophilic constant \bar{K}_a is negligible. Our experience shows that its influence on the model response is infinitesimal in fact. Then (2.3) reduces to $w = -(\gamma + 1)$ and we get the linear data fusion equation $-(\gamma + 1)C_1 = 1$, which after substitution of γ from (2.5) can be rewritten in the form $\bar{a}_{Ltot} \bar{z}C_1 + \bar{a}_{Ytot} z_Y C_1 = -\bar{a}_{Ytot} z_Y$. If we take into account that $\bar{z}C_1 = C_1^w$ and substitute symbols from (2.4) then a data fusion equation takes the linear form:

$$a_0 e_B^{z_0} \left(\alpha \frac{|z_0|}{|z_Y|} - 1 \right) + \sum_{j=1}^m K_j a_j e_B^{z_j} \left(\alpha \frac{|z_j|}{|z_Y|} - 1 \right) = 1 \quad (2.6)$$

where $\alpha |z_0| / |z_Y| - 1 \neq 0$. Since sensor parameters are specific for one particular ion, we can introduce factors in parentheses additively into V_{offs} and multiplicatively into selectivity K_j obtaining the reduced SNk model (RSNk):

$$a_0 \tilde{e}_B^{z_0} + \sum_{j=1}^m \tilde{K}_j a_j \tilde{e}_B^{z_j} = 1 \quad (2.7)$$

where $\tilde{e}_B = \exp[-(E_B - \tilde{V}_{offs}) / \psi_0]$. This model is especially convenient for extraction during the sensor calibration process.

CONCLUSION – COMPARISON OF MODELS - EXAMPLE

The introduced RSNk model has several nice features. The first advantage is its physical character, based on Boltzman Law, complexation, association and charge balance, so parameters of the model are technological. Such technological models are especially valuable in CAD, since optimization in technological parameters space directly indicates how the technological process should be modified. Next great advantage of the SNk model is its linearity with respect to ion activities, which is the feature especially applicable in the data fusion equations which can be efficiently solved. Another advantage of SNk model is its application to ions of arbitrary valencies. All these advantages do not hold in the NkEis model. Its great disadvantage is inconsistency and bad interpretation of selectivity coefficient, not reflecting the real selectivity when we have ions of different nonunit valencies. This problem was reported e.g. by Umezawa *et al* (1995) and several modifications have been proposed.

If we have several ions of different valencies so far preferable was VDB model. However due to its very complicated character and difficult identification, we propose SNk model. In this paper we compare its accuracy with VDB. Comparison of these two models for the same values of parameters was the first stage of the SNk model verification and a main purpose of this paper.

We have performed simulation experiments with SNk and VDB models of the same parameters extracted from a set of typical measurements obtained from automatic CHEMFET measuring equipment available in Warsaw University of Technology. We do not list values of extracted parameters but only show that a relative discrepancy between responses from SNk and VDB models usually is not greater than 2 - 3% in activity range $10^{-8} - 10^{-1}$ mole/l. In an example shown below the electrolyte contained main ions NH_4 of valency +1 and interfering ions Ca of concentration 10^{-2} mole/l and valency +2. As it is seen in Fig. 3 an error between SNk and VDB responses is less than 1% and in Fig 2 these two responses are almost indistinguishable. Interesting is observation that the higher ion valencies, the smaller is relative error of the SNk model with respect to VDB model. Since SNk model has been obtained by neglecting straight influence of ions and counter-ions, we note that the higher valency of ions in the electrolyte, the less important is role of this influence.

On the opposite side we observe in Fig. 2 that discrepancy between NkEis and VDB/SNk models for the same parameters is huge, of course if ion valencies are not unit. For unit valencies it was shown (Ogrodzki, 2002) that models differ less than 1.5%.

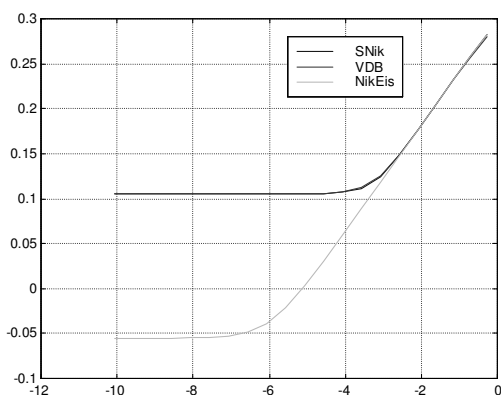


Figure 2. Voltage response of the sensor as a function of main ion activity calculated from SNk and VDB models (the upper, black curve) and NkEis model (the lower, gray curve)

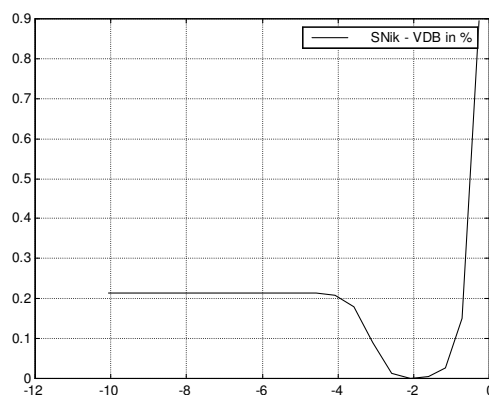


Figure 3. Relative error in % between SNk and VDB models

In this paper we do not show how SNk model can fit practical measurements. Problem of the model extraction and verification will be a subject of another publications.

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