

STRUCTURAL CHARACTERISTICS OF GAS SENSOR BASED ON CONDUCTING POLYMER

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It was shown recently that it is possible to improve the characteristics of a chemical sensor by means of adequate processing of the adsorption-desorption noise, which normally occurs in microminiature sensors. The main idea is to subject the noisy output signal produced by a small-size sensor to a kind of threshold discrimination. Mathematical analysis made in [5] for an ideal adsorption-desorption noise allows one to conclude that selectivity of a sensor can be highly improved due to discrimination. In order to apply this idea to a concrete sensor, one needs to know its structural and functional characteristics, which govern the noise statistical properties. First of all, it is necessary to determine to what extent the process of analyte reception can be modeled by a pure surface absorption-desorption process. This is a structural characteristic. Among functional characteristics are the total number of analyte-binding sites, n_s , the binding-releasing rate constants, k^\pm , and others. In this paper, we use sensor response kinetic curves to determine the above characteristics for a chemoresistive sensor based on polyaniline.

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1. Introduction

Detecting of chemical substances (analytes) dissolved in a gas or liquid can be made by chemical sensors able to adsorb reversibly molecules of analyte in amounts that depend on its concentration and specificity of adsorbing sites in the sensor. Selectivity of adsorption of molecules on the sites normally determines the selectivity of the whole sensor.

The size of industrial sensors can be very small. As a result, the stochastic nature of the adsorption-desorption process becomes visible as a noise in sensor's output signal (see Fig. 1). This makes difficult clear discrimination between signals produced by different analytes.

Adsorption-desorption noise has been studied experimentally and theoretically in connection with phase and frequency stability in quartz resonators [1,2]. Its consequences for small sensors operating properties are discussed in [3].

On the other hand, in natural biological sensory systems, such as taste and olfaction, the size of primary receptor units (receptor neurons) is so small that the number of binding sites per neuron does not exceed $\sim 5000-100000$ for different species [4]. With such a relatively small number of receptor sites one can expect a substantial noise level and a poor signal/noise ratio, and, as a result, a low quality discrimination between different smells. However, the natural systems demonstrate reliable discrimination between smells. Here, it is worth to notice that a noisy signal about the number of occupied receptors is subjected to a type of threshold discrimination due to specifics of functioning of biological neurons. We expect that this way of processing of a primary signal, if

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applied in a small industrial chemical sensor, can improve its discriminating ability. Such a possibility was analyzed theoretically in [5]. For this purpose, the temporal characteristics of the adsorption-desorption stochastic process (noise) were obtained. Namely, if W_b and W_a (see Fig. 1) denote the mean time which the number of receptors occupied by analyte spends continuously below and above a definite threshold, then one can estimate the portion of time which the process is above the threshold during the measurement:

$$q = \frac{W_a}{W_b + W_a}. \quad (1)$$

For two different analytes A_1 and A_2 , the portion may be different, q_1 and q_2 . This allows one to introduce the threshold sensor selectivity with respect to the A_1 and A_2 :

$$\nu = \log\left(\frac{q_1}{q_2}\right). \quad (2)$$

It is proven in [5] that ν can be much higher than the selectivity of individual receptors, μ , which is determined as

$$\mu = \log\left(\frac{p_1}{p_2}\right), \quad (3)$$

where p_1 , p_2 are the probabilities that any single receptor is occupied by analyte if A_1 , A_2 is applied, respectively.

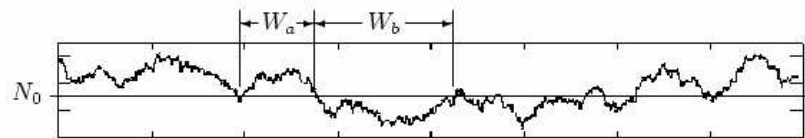


Fig. 1. Example of the adsorption-desorption stochastic process.

As a result, the threshold chemical detector design was proposed [6]. In this detector (Fig. 2), the row signal, which gives the amount of receptors occupied with an odor at the primary sensory unit, is subjected to threshold discrimination, and the result is averaged over a temporal window. It is shown mathematically [5] based on the exact description of adsorption-desorption statistics that the threshold detector of this type can be much more selective than its primary receptor sites.

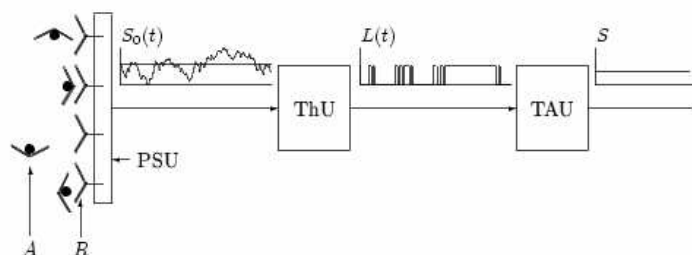


Fig. 2. Schematic picture of a threshold chemical detector. A - analyte molecules; R - adsorption sites; PSU — primary sensing unit; ThU — threshold unit; TAU — temporal averaging unit. For details, see [5, 6].

All processing stages can be realized in a single wafer, which we believe brings about a new functionality to chemical sensors. This kind of design can be considered as a new type of on chip signal conditioning [7].

In order to apply this design to a real chemical sensor, we use a chemoresistive sensor based on polyaniline [8]. First of all, it is necessary to determine to what extent the process of analyte

reception can be modeled by a pure absorption-desorption process. This is a structural characteristic. Also, for making estimations for quantities like q in (1), we need the functional characteristics that govern the adsorption-desorption process. Among those characteristics are the total number of analyte-binding sites, N , or n_r below, the binding-releasing rate constants, k_r^+ , k_r^- , and others. In this paper, we use sensor response kinetic curves to determine the above characteristics for a chemoresistive sensor interacting with acetone dissolved in argon.

2. Materials and methods

2.1. Sensor design

The chemoresistive sensors were manufactured in the Physical Chemistry Institute of NAS, Ukraine [8]. The sensor array was fabricated by photolithography of 150 nm thick gold on standard glass-ceramic substrate and then wafer was diced in 6-element chips. The chips were mounted on small printed circuit board and were connected by wire bonding. Each element contained 20 pairs of raster electrodes of 15 μm width separated by 25 μm distance with a common area of 2 mm^2 (Fig. 3). In this paper we use the data obtained from a single element. The films were synthesized by electrochemical oxidative polymerization of monomer. Polyaniline was obtained from a 1 M aqueous solution of various acids with 0.15 M of the corresponding anilinium salt. Films synthesis was performed in a three-electrode nonpartitioned cell. The polymerization was conducted in a cyclic potential mode. The final thickness of the polyaniline film was ~ 150 nm. The films were doped with heteropolyacids ($\text{PMo}_{12}\text{O}_{40}^{3-}$, $\text{PMo}_{11}\text{VO}_{40}^{4-}$).

2.2. Kinetic curves

The kinetic curves have been obtained in the Institute of Semiconductor Physics of NAS, Ukraine. Measurement of the films responses towards the vapors of organic solvents (analytes) was performed following the procedure described in [8] and using acetone as an analyte. The sensor array response was measured at a fixed concentration of acetone in argon, which was obtained by streaming pure argon through a well with liquid acetone at room temperature. The argon flow rate was 30 ml/min . The acetone concentration was determined by weighing the well before and after the experiment. The concentration exact value is 5.043×10^{18} molecules of acetone per ml . The effect of the analyte on the electric characteristics of the polyaniline films was recorded as the variation of the direct current through an array of polyaniline resistors. After each measurement, the array of polyaniline resistors was blown with argon to remove the vapor of the analyte until the value of the current had returned to its base value. Kinetic response curves were measured for about 200 s with a step of 2 s.

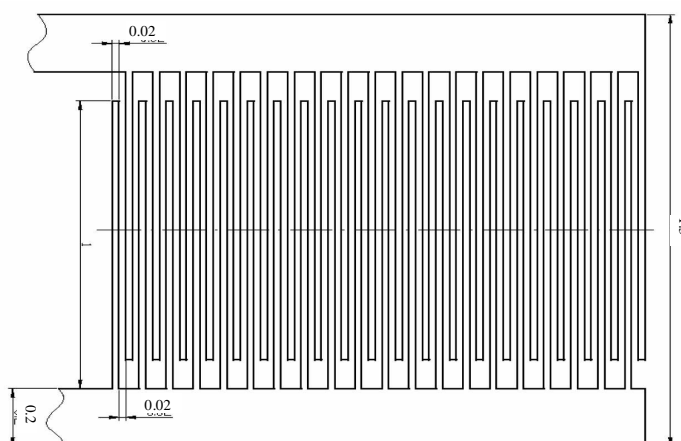


Fig. 3. Chemoresistive sensor construction.

2.3. Numerical methods

We looked for a set of physical parameters, which gives a theoretical curve optimally describing the experimental one. Standard programs of optimization require to specify initial values of the optimizable physical parameters. If these initial values considerably differ from exact ones, then the problem of determination of optimizable parameters becomes essentially more complicated and often its solutions is fairly problematic even in the case of optimization of a function of single parameter. In the case of several parameters, programs of optimization are efficient provided that the domains of definition of all parameters do not essentially differ. For the considered problem, possible values of unknown parameters either vary in a wide range (the rate constants k_r^\pm) whose limits may differ by 10^{19} times [9] or are unknown at all (k_p^\pm , and i). For this reason, these programs cannot be directly used for the solution of this problem.

The procedure of optimization proposed in the present paper involves two stages. At the first stage, approximate initial values of the unknown quantities are determined by the method of minimization of a function of several variables based on the Hooke–Jeeves procedure of direct search [10, 11] using the algorithm presented in [12]. Since the obtained initial values of the required quantities belong to different ranges, we propose a special procedure for determination of these values. At the second stage, we determine the optimizable parameters of the required quantities (a local minimum is determined) and, then, numerically solve the system of equations for these values and compare its solution with the experimental data.

3. Results

The typical kinetic curve obtained shows the slowest current rise at the moment of application of analyte (Fig. 4).

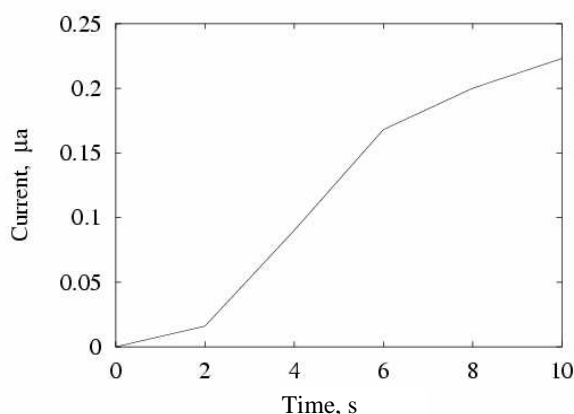


Fig. 4. Typical time dependence of the initial part of kinetic curve.

This cannot be explained by a pure adsorption-desorption process. Indeed, the adsorption-desorption process can be described by the following scheme:



where Z , R denote a molecule of acetone and an adsorption site, respectively, and k^+ , k^- are the corresponding rate constants. The corresponding kinetic equation is as follows:

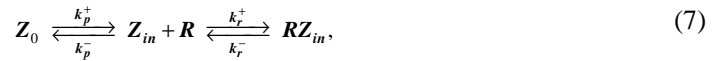
$$\frac{d}{dt}[RZ] = k^+[Z] - k^-[RZ], \quad (5)$$

and its solution for the initial condition $[RZ]=0$ is as follows:

$$[RZ](t) = \frac{k^+[Z]}{k^-} (1 - e^{-k^-t}). \quad (6)$$

This kinetics has the fastest rate at $t=0$, which disagrees qualitatively with what is observed experimentally.

The idea of more realistic paradigm, which could describe qualitatively the time course of the experimental curves can be offered if one takes into account the relative sizes of the polymer film thickness (150 nm) and an acetone molecule, which is 0.3 nm. This means that there is enough room in the film for the acetone to migrate transversally. In this case, we must describe separately the molecules of analyte that are in the film but not bound at the receptor sites and those bound. This also introduces an additional process of acetone exchange between the polymer bulk and the external gas. The simplest scheme for these processes is as follows:



where Z_0 , Z_{in} denote acetone molecules in the outside gas and those in the polymer but not bound, respectively; k_p^+ , k_p^- are the constants characterizing acetone exchange rate between the polymer bulk and the outside gas¹; k_r^+ , k_r^- are the acetone Z_{in} binding-releasing rate constants², respectively. In this scheme, we have two unknown functions, namely $[Z_{in}]$ (the concentration of free acetone in the polymer bulk) and $[RZ_{in}]$ (the concentration of acetone in the polymer bulk, which is bound at the receptor sites end ensures their conductivity). The second one determines the current-time course through the sensor. The corresponding kinetic equations are as follows:

$$\frac{d}{dt}[Z_{in}] = k_p^+[Z_0] + k_r^-[RZ_{in}] - k_p^-[Z_{in}] - k_r^+(r - [RZ_{in}])[Z_{in}], \quad (8)$$

$$\frac{d}{dt}[RZ_{in}] = k_r^+(r - [RZ_{in}])[Z_{in}] - k_r^-[RZ_{in}], \quad (9)$$

where r is the total concentration of (free and bound) receptor sites in the polymer bulk. Exact solution of this pair of nonlinear equations is unknown. At the same time, comparison of its numerical solutions with the experimental data can bring about information concerning values of physical constants, such as, k_p^\pm , k_r^\pm , r as well as the current through a single bound receptor site, i , which are required for correct interpretation of noise in the measured data.

If we take as a volume measuring unit the polymer volume in the sensor, $V = 0.25 \times 10^{-6}$ ml, then concentrations $[Z_{in}]$, $[RZ_{in}]$, r will be equal to the numbers of molecules of free and bound acetone, and the total amount of receptor sites in the sensor. Denote them as a_i , a_r , n_r , respectively. The amount of molecules of acetone in the V ml of the outside gas is a_o , $a_o = [Z_o]V = 1.25 \times 10^{12}$. Then from Eqs. (8), (9) we have

$$\frac{d}{dt}a_i = k_p^+a_o + k_r^-a_r - k_p^-a_i - \frac{k_r^+}{V}(n_r - a_r)a_i, \quad (10)$$

$$\frac{d}{dt}a_r = \frac{k_r^+}{V}(n_r - a_r)a_i - k_r^-a_r. \quad (11)$$

¹Here, we expect, for the sake of simplicity, that free acetone is distributed homogeneously in the polymer bulk.

²Here, we adopt the simplest paradigm: a receptor site gets its maximum conductivity after binding of a single acetone molecule.

Here, dimension of k_r^+ is ml/s . The quantity which is measured experimentally is $i \times a_r$, where i is the current through a single bound site.

To probe the applicability of the paradigm presented in (7) and determine possible values for the unknown constants k_p^\pm , k_r^\pm , n_r , and i , we numerically solve the system of nonlinear differential equations (10), (11) with initial conditions

$$a_i(t=0)=0, \quad a_r(t=0)=0 \quad (12)$$

using the procedure of minimization based on the least-squares method. To this end, the deviation of the sum of squares of differences of the theoretical ($a_r(t=t_m) \cdot i$, $t_m = 2m$ s, $m = 1, 2, \dots, N_p$) and experimental values of the current through a sensor at the corresponding times is minimized.

The sets of optimal parameters found are presented in the Table 1, and comparison of the corresponding theoretical curve with the experimental one is shown in Fig. 5.

Table 1. Sensor's characteristics obtained by fitting. Here, N_p is the number of experimental points from the start taken into account.

N_p	$k_p^+, 1/s$	$k_p^-, 1/s$	$\frac{k_r^+}{V}, 1/s$	$k_r^-, 1/s$	n_r	i, nA
10	0.448×10^{-7}	0.493a	0.127×10^{-5}	0.0369	3.912×10^4	0.0097
20	0.208×10^{-6}	0.794	0.100×10^{-6}	0.0931	2.267×10^5	0.0056
30	0.178×10^{-7}	0.794	0.156×10^{-5}	0.0686	2.041×10^4	0.0431
50	0.423×10^{-9}	0.781	0.151×10^{-3}	0.0718	6.631×10^3	0.0907

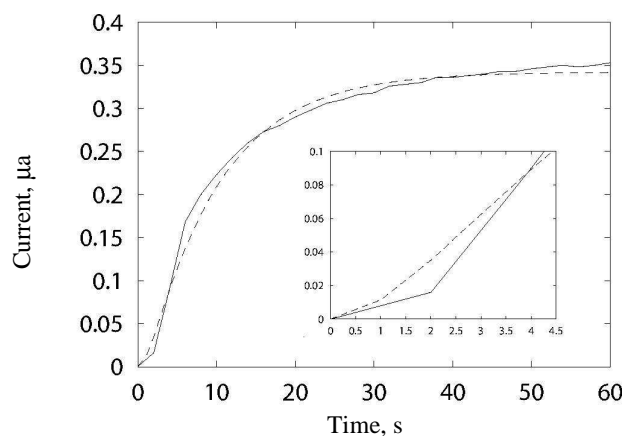


Fig. 5. Comparison of experimental (continuous line) and theoretical (dotted) curves. The number of experimental points used is $N=30$. On the insert – the initial part of the curves.

4. Discussion and conclusions

Obtained results suggest that taking into account of free analyte in the sensor polymer can give satisfactory qualitative description of the kinetics of the initial stage of interaction of analyte with sensor (Fig. 5). Also, the physical characteristics obtained by fitting (Table 1) are in the frame of physical intuition. Thus, this approach can be fruitful for studying sensors with absorption of

analyte. The information about the physical characteristics can be utilized at the stage of synthesis of a polymer film and for choosing an optimal doping method. At the same time, the approach can be improved in several ways. Among those is to consider a situation when the receptor must bind more than a single analyte molecule before it starts conducting, as well as to use for fitting not only the rising part of kinetic curve but also the falling part obtained after removing analyte from the external gas. Also we must say that the fluctuation statistics of the sensor read will differ from the pure adsorption-desorption statistics, therefore, before exploiting the method developed in [5] for improving selectivity it is necessary to perform additional mathematical or numerical analysis of noise in this case.

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