Nonlinear chemical sensors

Studies of electrolyte diodes and catalytic resistors

Ph.D. thesis

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The summary of the Ph.D. dissertation

I. Introduction

The motivation of my research work is tightly connected to the research on the field of non-linear dynamics conducted at the Department of Chemical Physics at BUTE[1]. During my work I've been mainly engaged in the research on the field of acid-base diodes and transistors. Reaction, diffusion and ionic migration of chemical components take place in these systems. During such experiments an exotic behavior has been discovered that the mathematical model could not explain.

Thus the first set of objectives of my Ph.D. research was the investigation of the acid-base diode to determine the cause of the deviation of the current-voltage characteristics (CVCs) from the analytical model. For this purpose the modification of the existing apparatus was necessary and for certain measurements new apparatuses have been designed. Furthermore I also aimed to automatize the measurements. I have also been working with numerical calculations that have been adapted to the actual problems, in order to revise and check the validity of the analytical model of the electrolyte diode measurements. It has always been a target to shrink the active part of the apparatus for the purpose of reducing the time constants. During my years as a Ph.D. student came the opportunity from Prof. Ronald Siegel of using a MEMS[2] device as the reduced sized active part of

[1] Budapest University of Technology and Economics

[2] Micro-Electro-Mechanical Systems

our apparatus. Tthe possibility and effects of the size reduction have been investigated with this MEMS device. This has been made possible in the meantime by the change of electrolyte in our apparatus, since instead of the "harsh" strong acid - strong base electrolyte environment a milder, weak acid - weak base has been applied.

The second set of objectives of my research work have been shaped when we started to investigate the applicability of the principles of complex dynamics - that is so simply exhibited by oscillating chemical systems [Noszticzius et al. (2005)] - on a simple physical system. This investigation was based on the fact that systems with oscillating and complex behavior are highly sensitive to certain parameters and this sensitivity can be exploited to measure that parameter.

A hybrid automaton has been created where a simple physical system is controlled by a computer and the complex dynamics is originated from the unstable nature of the control system. In the preliminary experiments the Logistic map was chosen as the algorithm and a catalytic platinum wire as the physical system, which detects combustible gases in the ambient air with a change in its resistance. The hybrid automaton changes its dynamics as a result of the change of the combustible gas concentration in the ambient air.

II. New scientific results

1.

It has been shown with results of experimental measurements that the applied PVA gel (glutardyaldehyde crosslinked polyvinyl alcohol hydrogel) contains fixed negative ionic groups [Iván et al. (2002)].

a) Experimental apparatus

For this purpose an experimental apparatus (Fig. 1) has been constructed where electric current can flow through a gel strip immersed in aqueous electrolyte

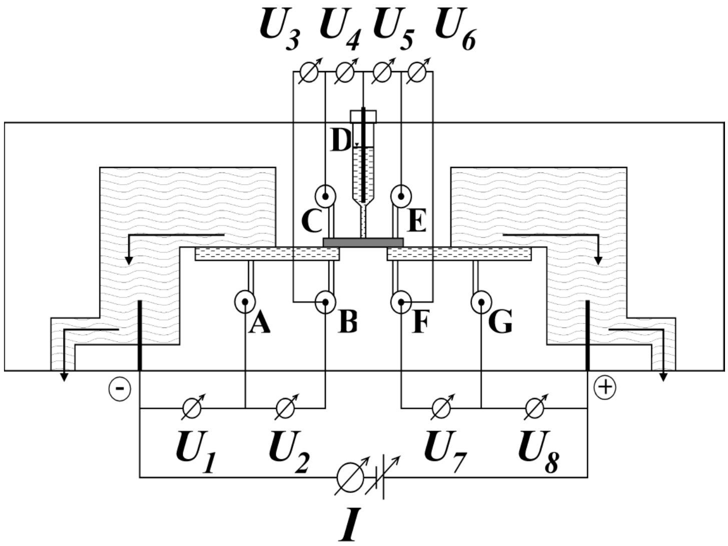

Figure 1: Schematic of apparatus "B". The gel strip (grey rectangle) in the middle of the apparatus. The gel connects two glass fibre layers. The electrolyte flows are marked with arrows. The measuring electrodes are labeled with capital letters A-G. The eight symbolic voltmeters U_1-U_8 represent eight channels of the multimeter.

solutions. Electrodes and salt bridges were placed on top of and around the gel. It was then possible to investigate the current induced concentration polarization phenomena in the different zones inside the gel and also in the cathodic and anodic boundary layers.

b) Measurements

Electric potential distributions have been measured with a PVA strip and dilute aqueous KCl solutions in the apparatus. The changes of the relative resistance of each zone could be calculated from these results. Based on my measurements and calculations It has been shown that while both in the cathodic boundary and in the gel the concentration of the salt is increasing thus it is decreasing in the anodic boundary. This kind of concentration polarization can be induced only by the fixed negative charges inside the PVA gel.

2.

CVCs of PVA hydrogel cylinders have been measured and interpreted based on model calculations [Iván et al. (2002)].

a) Measurements

An apparatus has been designed for the measurements where a gel cylinder inserted into a narrow bore (0.8 mm in diameter and 3.2 mm long) was connecting two aqueous KCl solutions of equal concentrations. The inflow of the fresh electrolytes were maintained by peristaltic pumps. The measured characteristics are not straight lines but curves with a positive second derivative. Furthermore, it has been found that the conductivity of the gel in 0.01 molar KCl solution is smaller, in 0.001 molar solution it is approximately equivalent, and in 0.0001 molar solution it is measurably higher than the conductivity of the hole (which is filled only with electrolyte).

b) Model calculations

The above results have been simulated with numerical model calculations based on the fixed charge and the Nernst-Planck equations. The upcurved CVCs can be modeled with the concentration polarization in the unstirred cathodic boundary layer, since in the cathodic boundary layer - and therefore the inner part of the gel also - the concentration of the conductive salt is increasing with the increasing current. We have to assume, though, that the anodic boundary layer is stirred by the electroconvection - a well known phenomena among ion-exchange membranes. This assumption was necessary since without the electroconvective stirring in the anodic boundary layer the concentration polarization would cause such an increase in the impedance that would result in a declining CVC in contrast with the experimental results.

3.

An apparatus has been constructed and a measurement technique has been elaborated that facilitates the quantitative determination of the fixed ionic groups of weakly charged hydrogels [Iván et al. (2004)], because in the measurements described in the first two theses the unstirred boundary layers caused uncertainties that prevented a quantitative evaluation of the experimental results.

a) Apparatus

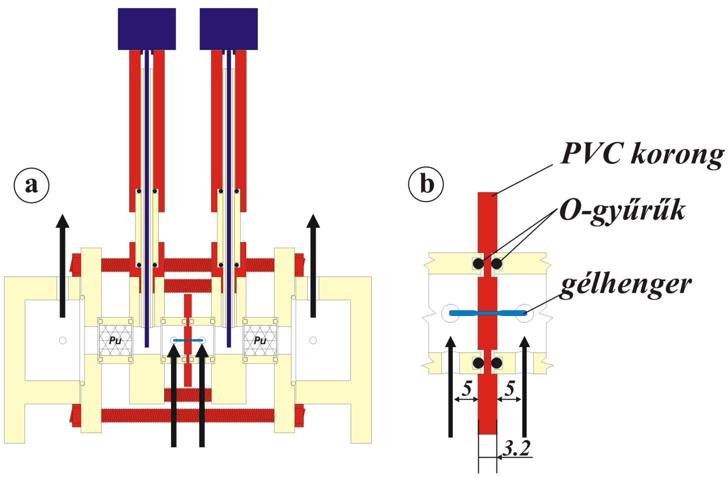

Figure 2: (a) Cross-sectional view of the Plexiglas apparatus. Arrows indicate the continuous flow of electrolytes. Pu: polyurethane foam. DC motors driving the stirrers are placed on the top of the two plexiglas tubes. (b) Enlarged view of the PVC disk with the gel cylinder.

An apparatus has been designed (Fig. 2) that is capable of minimizing the width of the cathodic and anodic gel-liquid boundary layers and the associated polarization phenomena with strong stirring. Furthermore, a data logger software has been written that simplified the evaluation of the measurements.

b) Measurements

CVCs of 0.001 and 0.01 molar KCl solutions have been measured with the electrolyte filled narrow bore of the new apparatus and with a gel cylinder inserted into the narrow bore.

c) Correction

A correction method has been developed that can determine the parasitic voltage drops on the electrolyte solutions around the gel from the experimental results using model calculations and can be subtracted from the measured values. This way I could plot such CVCs where the potential difference on the gel cylinder was free of the parasitic voltage drops.

d) Correlation

The following relationship has been derived for the determination of the concentration of the fixed anions, a_F, present in the gel, taking into consideration the Donnan equilibrium as well

$$\alpha = \frac{\sqrt{1 + \left(\frac{2c_{02}}{a_F}\right)^2} + R}{\sqrt{1 + \left(\frac{2c_{01}}{a_F}\right)^2} + R}, \tag{1}$$

where α is the ratio of the initial slopes of the CVCs measured with the gel cylinder with two different KCl concentrations (c_{02} and c_{01}), and R is calculated from the diffusion coefficients of the ions K^+ and Cl^-:

$$R = \frac{D_{K^+} - D_{Cl^-}}{D_{K^+} + D_{Cl^-}} = -0.02. \tag{2}$$

4.

A measurement and a calculation method have been worked out that can be used to determine not only the concentration but also the pK value of the fixed weakly acidic groups present in hydrogels [Iván et al. (2004)]. Furthermore, it has been confirmed with model calculations that the error of the above applied approximate analytical formula of the acid - base diode is negligible.

a) Formula

Acid-base diode measurements have been made where the gel cylinder was connecting 0.1 molar HCl with 0.1 molar KOH solutions using the apparatus in thesis 3 a). The concentration of the fixed anions, a_F, present in the middle zone can be calculated from the relative slope, s_R, of the characteristics of the reverse biased diode using the following formula:

$$a_F = 2 \cdot \left(1 + \frac{D_{OH}}{D_H}\right) \cdot c_0 \cdot s_R \tag{3}$$

b) Simplifications

The analytical formula (3) contains three important simplifications:

- electroneutrality,
- equilibrium of the reaction between the H^+ and OH^- ions, and
- the gel can be divided into three distinct regions.

It has been shown with numerical model calculations not containing these simplifications that the approximations under the applied experimental conditions do not cause errors exceeding the experimental error.

c) Calculation of the pK

The pK of the fixed weak acid was calculated with the following formula using the two fixed anion concentrations (a_{F1} and a_{F2}) obtained with the different measurements, a_{F1} from the measurements with KCl solutions (1), and a_{F2} from the measurements with the acid-base diode (3):

$$pK = \log\left(a_{F1} - a_{F2}\right) - 2\log\left(a_{F2}\right) \tag{4}$$

5.

Electrolyte diodes with asymmetric stirring have been created where different stirring was applied on the two boundaries of the gel [Iván et al. (2004)]. It has been shown that the salt accumulation or the salt depletion in the unstirred boundary layers causes conductivity changes in the gel that produces the asymmetric characteristics.

6.

The theory of acid-base diodes for weak acids and bases has been extended [Iván et al. (2005a)]. Its analytical approximation contains the following 3 simplifications of the full mathematical model:

- quasi-electroneutrality,
- quasi-equilibrium of the chemical reactions, and
- the gel of the reverse biased diode can be divided into three zones.

7.

Exact model calculations have been made using the full mathematical model of the weak acid - weak base diode. Weak acid - weak base experiments have been conducted to verify the analytical and numerical results. Comparing these three results it has been shown that the analytical model can describe the experimental results in a satisfactory way [Iván et al. (2005b)].

a) Optimal analytical solution

Comparing the numerical results with the analytical results the concept of the optimal analytical solution has been introduced where the concentration profile of the fixed charges does not contain simplifications other than quasi-equilibrium and quasi-electroneutrality. It has been shown with the numerical results that the two "quasi" approximations cause negligible errors in the analytical model.

b) Comparison of the results

Examining the analytical and numerical results it can be said that the slope of the reverse biased analytical CVC approximates very well the slope of the numerical results, on the other hand the intercept can deviate even 5–10% which deviation roots in the simplifying assumptions of the analytical derivation. A good agreement can be found with the numerical and analytical results as compared to the experimental results.

8.

A new thin MEMS chip has been tested by inserting it into the apparatus in thesis 3 a). The chip contains bores of 80 μm in diameter which were considered small enough to increase the speed of the measurements of the electrolyte diode arrangement.

a) MEMS chip

A MEMS chip designed for drug delivery has been inserted into the weak acid - weak base measurement system described in thesis 7. The MEMS chips were provided by Prof. Ronald Siegel (Dept. of Biomed. Eng., University of Minnesota, Minneapolis).

b) Results

The aim to assemble a faster experimental arrangement was successful since according to the experimental results with the integrated MEMS chip the time required for the concentration profiles to reach asymptotic state was of orders of magnitude shorter. Nevertheless, voltage instabilities and a drift of the current could be observed during the measurements that were caused by the material of the chip. These effects can be eliminated later by the insulation of the MEMS chip.

9.

It has been demonstrated on a physical model system that the principle of a new type of dynamical measurement method - which has only been used in chemical reaction kinetics for its highly specific nature - can be applied in a more general way.

a) The principle of the measurement

A control algorithm has been created that maintains an oscillatory or a chaotic asymptotic state - instead of the one stable stationary state which is usual in process control - by connecting a simple analogue physical system (a catalytic resistor) and a digital system (computer). These asymptotic states respond very sensitively to a change in the parameter value and thus this change can be detected.

b) Measurements with the heat conductivity of the gas mixture

The feasibility of the principle has been demonstrated with measurements based on the heat conductivity changes of the ambient air surrounding the platinum wire.

c) Experimental apparatus

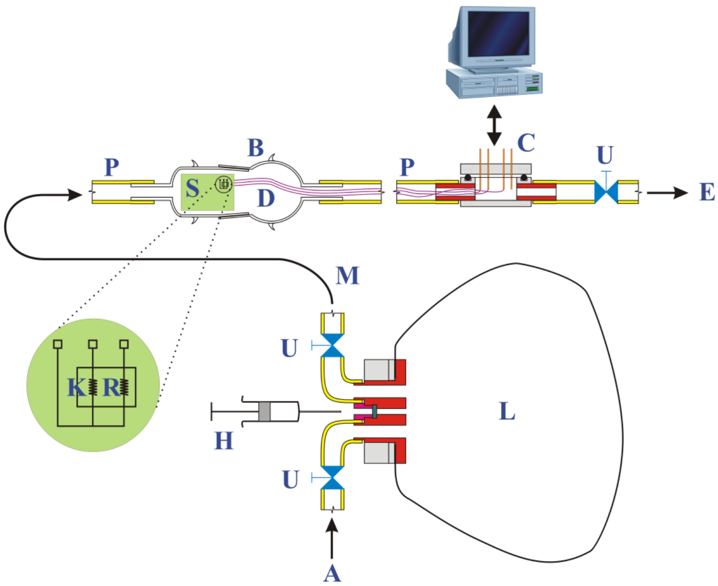

Figure 3: The apparatus designed for the combustible gas measurements. **L**: balloon for the hexane-air mixture, **L** to **E**: hermetically sealable gas space, **S**: the MEMS chip with the platinum wire. For further details and key see Fig. 10.6 of dissertation.

An apparatus has been constructed (Fig. 3) that can be used to make a gas mixture of a given composition (e.g. hexane - air) and this mixture can be kept inside an airtight compartment where the catalytic platinum wire is placed. To carry out the measurements a program has been written that is responsible for the control of the measuring instrument and the generation of the complex dynamics.

d) Determination of the concentration of combustible gases

It has been shown with the use of a combustible gas (hexane) that a certain dynamic behavior can be configured so - based on the above principle - that the concentration of the combustible gas can be determined using a calibration curve.

III. Perspectives and practical adaptability

The two main topics of the dissertation, the electrolyte diodes and the hybrid automaton are special chemical sensors with non-linear behavior. The possible applications utilizing this specific feature are the following:

Electrolyte diode

a. since the reverse biased diode is capable of sensitive detection of contaminating ions thus it could be useful as the detector of an ion chromatography device, such experiments were already started in our laboratory,

b. different gels, polymer dispersions, membranes and porous materials can be examined with the use of the weak acid - weak base diode system, since this mild chemical environment does not damage these materials,

c. further measurements can be made with the insulated MEMS chip and this way the diode could be fast enough to be used as a detector;

Hybrid automaton

a. the sensitivity of the developed measuring technique can be increased greatly,

b. the model system applied here could evolve into a device that can detect the combustible gas appearing in the ambient air,

c. since the aim of my experiments was only to demonstrate the principle on a model system, this principle can be used in such cases where the dynamics of the measurement is advantageous over the standard static measuring methods.

Publications on the subject of the dissertation

1. K. Iván, N. Kirschner, M. Wittman, P. L. Simon, V. Jakab, Z. Noszticzius, J. H. Merkin, and S. K. Scott. Direct evidence for fixed ionic groups in the hydrogel of an electrolyte diode. *Phys. Chem. Chem. Phys.*, 4:1339–1347, 2002.

2. K. Iván, M. Wittman, P. L. Simon, Z. Noszticzius, and Jürgen Vollmer. Electrolyte diodes and hydrogels: Determination of concentration and pK value of fixed acidic groups in a weakly charged hydrogel. *Phys. Rev. E*, 70:061402, 2004.

3. K. Iván, P. L. Simon, M. Wittmann, and Z. Noszticzius. Electrolyte diodes with weak acids and bases I. Theory and an approximate analytical solution. *Journal of Chemical Physics*, 123:164509, 2005.

4. K. Iván, M. Wittmann, P. L. Simon, Z. Noszticzius, and D. Šnita. Electrolyte Diodes with Weak Acids and Bases II. Numerical model calculations and experiments. *Journal of Chemical Physics*, 123:164510, 2005.

5. R. Siegel, K. Iván, Z. Noszticzius, et al. *Journal of Nanoscience and Nanotechnology*, Special Issue for the International Symposium on Soft-Nanotechnology, manuscript in preparation.

Popular publication on the subject of the dissertation

1. Z. Noszticzius, K. Kály-Kullai, and K. Iván. Non-linear dynamics in chemistry. *Természet Világa*, 136. évf.:67–73, I. különszám 2005. (*in Hungarian*)

Posters related to the dissertation

1. K. Iván, M. Wittman, P. L. Simon, Z. Noszticzius, and Jürgen Vollmer. A novel type of electrolyte diode, 4th ESF REACTOR workshop: "Nonlinear phenomena in chemistry" Budapest, 24–27 jan., 2003.

2. K. Iván, M. Wittman, P. L. Simon, Z. Noszticzius, and Jürgen Vollmer. Electrolyte diodes and hydrogels. Determination of concentration and pK value of fixed acidic groups in a weakly charged hydrogel 5th ESF REACTOR workshop, Prague, 2–6 September, 2004.