

Modeling of Transferring Processes in the Planar Electrochemical Sensors

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Abstract

Planar ECTs (electrochemical transducers) are the new type of sensors, which are very effective for measuring pressure and motions (velocity and acceleration). These sensors are characterized by an exceptionally high sensitivity to mechanical action due to high rate of transducing of the mechanic signal into electric current. In this work, we develop a mathematical model of a planar electrochemical system, which detects mechanical signals. We simulated the processes of mass and charge transfer in planar electrochemical transducer, obtained the main system characteristics and investigated the dependence on geometric parameters. Copyright © VBRI Press.

Keywords: Planar electrochemical systems, microelectronic technology, electrochemical transducer, mass and charge transfer, computational model.

Introduction

Currently, microelectronic technologies allow the creation of a variety of electrochemical microsystems, which are very perspective for the design of modern motion and pressure sensors. In our paper, we considered planar ECT (electrochemical transducer) [1]. This is a new type of transducers based on planar microelectronic technologies.

Planar ECTs have a variety of advantages over MEMS and piezoelectric sensors in the infrasonic and subhertz ranges.

ECTs with metal mesh electrodes are well-studied [2]. Simulation of mesh structures [3, 4] resulted in a number of important qualitative conclusions, which are confirmed experimentally. Further development of technology led to the study of planar systems.

The planar ECTs were first modeled in [5, 6]. A very simplified model was investigated; in particular, the simplest condition of the limiting current at the electrodes was used. Nevertheless, a number of qualitative results have been obtained in those studies. In [7], much more complex model was studied, the Navier-Stokes and Nernst-Planck equations were solved and the Butler-Volmer condition was applied at the electrodes. The results obtained in the work [7] were verified using the sensors with metal mesh electrodes. We based our model on the Navier-Stokes equation and

convection-diffusion equation, and used the Butler-Volmer condition on the electrodes.

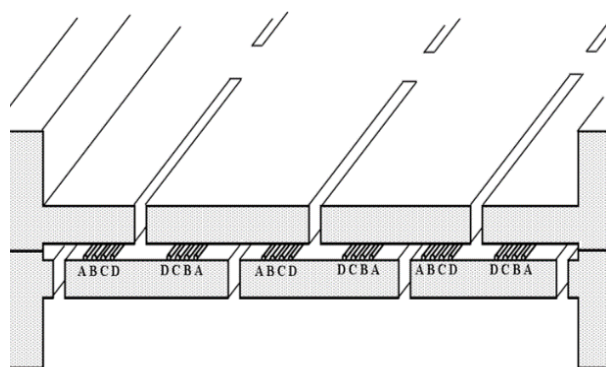
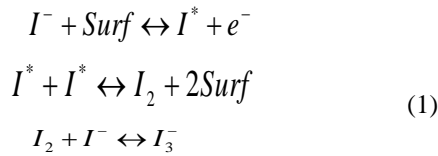


Fig. 1. Schematic view of microelectronic structure.

The ECT's transducing element comprised of a set of electrodes immersed in a solution of a three-component electrolyte (Fig. 1). The electrolyte is a water-based KI solution with a small addition of excess I₂. In aqueous solution potassium iodide dissolves, forming positive K⁺ and negative I⁻ ions, and additional iodine forms an excess of I₃⁻ ions.

When a reference voltage is applied to the electrodes, a reversible reaction begins on the electrodes [2]:



As a result of the electrochemical reaction, a nonequilibrium concentration of ions occurs near the electrodes, and a stationary concentration distribution and a constant electric current are established in the system under the influence of diffusion. Electromigration in the system is strongly suppressed due to the screening of the main ions by an excess of ions of the background electrolyte.

Transducing electrodes are placed in a channel with electrolyte. Flexible membranes are mounted on the ends of the channel. As a result of external mechanical influence, the electrolyte starts to move. An additional convective ion flux appears in the electrolyte volume and increases or decreases the flow of the ions to the electrode.

Additional ions are delivered to the electrodes and participate in the electrochemical reaction, and as a result, the output current from the electrodes changes. Thus, in present of stationary background current caused mainly by diffusion, an additional alternating current arises, due to convective ion transfer. Herewith, this additional current is proportional to the amplitude of the external mechanical signal, which caused perturbation of the mechanical system.

Main equations

There are three main processes inside the ECTs: diffusion, convection and electromigration. The main processes of transducing in ECTs are described by the convective-diffusion equation:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_I) + \mathbf{u} \cdot \nabla c_i = R_i \tag{2}$$

where i — index of the corresponding ion, c_i — ion concentration; D_i — diffusion coefficient; z_i — ion charge; $u_{m,i}$ — velocity in the specific direction $m(x, y)$; ϕ_I — electric potential of the electrolyte; R_i — changing of the concentration in the value per time (mol/m³s).

Component « $-\nabla(D_i \Delta c_i)$ » describes the diffusion transfer impact, which is the main in that system type. Component « $-\nabla(z_i u_{m,i} F c_i \nabla \phi_I)$ » describes the impact of electromigration transfer in ion flow. This component is relatively small because of the screening effect of the main carriers by the ions of the background electrolyte K⁺, which do not participate in the reaction at the electrodes. Nevertheless, we take into account the electromigration effect in our works, because the dynamic range of electrochemical transducers reaches 165 dB [2], and the effect of electromigration can be significant on the boundary of the range. Component « $-\nabla(z_i u_{m,i} F c_i \nabla \phi_I)$ » describes the convection transfer of ions by the mechanical flow of the electrolytic liquid.

This contribution determines the effectiveness of external mechanical signal registration.

Electroneutrality condition is valid in the electrolyte volume:

$$\sum_i z_i c_i = 0 \tag{3}$$

The mechanical motion of a liquid electrolyte is described by the Navier-Stokes equation:

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot [-\mathbf{p} + \mu \nabla \mathbf{u}] + \mathbf{F} \tag{4}$$

where $\rho = 1473 \text{ kg/m}^3$ — density of the electrolyte; $\mu = 1.4 \text{ mPa} \cdot \text{s}$ — dynamic viscosity of the electrolyte; \mathbf{F} — vector of the additional force density (contains with the electric forces and so on); p — pressure; \mathbf{u} — electrolyte velocity;

The continuity equation is valid in the volume of the liquid:

$$\rho \nabla \cdot (\mathbf{u}) = 0 \tag{5}$$

We used the Butler-Volmer boundary condition to describe the electrochemical processes on the electrodes:

$$i_{loc} = i_0 (C_R \exp(\frac{\alpha_a F \eta}{RT}) - C_0 \exp(\frac{\alpha_c F \eta}{RT})) \tag{6}$$

where C_R — is the dimensionless concentration of the input ions in the forward reaction; C_0 — dimensionless concentration of the output ions in the reverse reaction; $i_0 = 500 \text{ A/m}^2$ — the exchange current density limit; F — Faraday constant, $\alpha_{a,c}$ — electrodes efficiency in the reaction; $\eta = \Phi_{ref} - \Phi_I - E_{eq}$ — the effective potential between the electrode and the electrolyte ($\Phi_{ref} = 0.3 \text{ V}$ — potential between the electrode; Φ_I — potential of the electrolyte on the boundary of a double layer; $E_{eq} = 0.564 \text{ V}$ — equilibrium potential); $T = 293.15 \text{ K}$ — temperature of the system; R — universal gas constant.

No-slip boundary condition set on the solid walls:

$$\mathbf{u}_{electrodes} = 0 \tag{7}$$

The surfaces of the channel are dielectric:

$$-\mathbf{n} \cdot \mathbf{N}_i = 0 \tag{8}$$

Modeling

We modeled transducing element of the planar microstructure (Fig. 2).

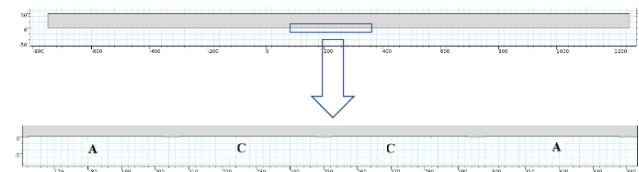


Fig. 2. Geometry parameters of electrode structure: channel height = 50 μm; channel length = 2000 μm; electrode’s length = 40 μm; distance between the anode and cathode = 5 μm; electrode’s thickness = 200 nm. A — anodes, C — cathodes.

Strictly speaking, all particles participate in charge transfer. The potassium ions do not participate only in electrodes reactions. We demonstrate the ion distributions of I_3^- ions for the example, the distributions of the other ions are related to it through the electroneutrality equation. Actually, I_3^- ions determine the charge transfer in our system.

We considered the basic distributions obtained by modeling of our system. **Fig. 3** shows the velocity field, the concentration, the concentration gradient and the total I_3^- flow in the presence of a convective flow directed to the right at a given time.

The fluid flow inside the device is laminar, and the Reynolds number is much less than one. **Fig. 3A** shows the velocity field in the working range of our device. **Fig. 3B** shows the distribution of ion concentration I_3^- . Between the cathodes there is a region with a lower concentration of ions, and the size of this region determines the time of transition into the operating mode. The concentration gradient (**Fig. 3C**) actually determines the region in the volume where the main charge transfer occurs. The magnitude of the maximum concentration gradient near the electrodes determines the sensitivity of the system. **Fig. 3D** shows the module of the total flux of I_3^- ions in the system in the presence of the convective flow directed to the right at a given time.

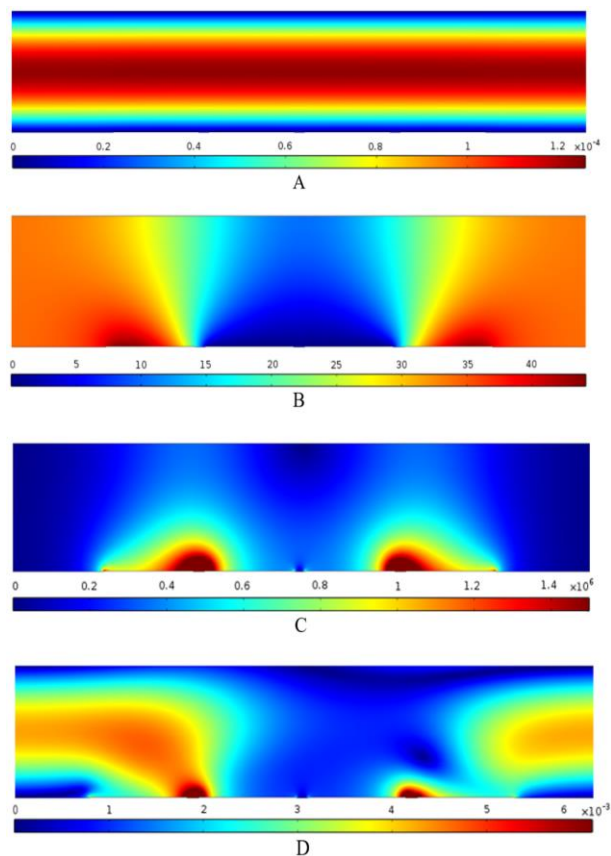


Fig. 3. Main distributions. A — velocity field (m/s), B — concentration (mol/m³), C — concentration gradient (mol/m⁴), D — total flow in the presence of a convective flow directed to the right at a given time. (mol/m²s).

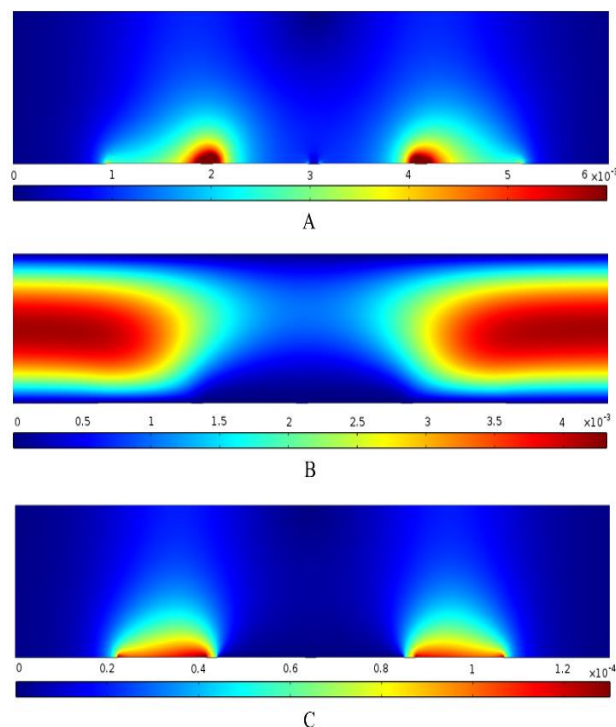


Fig. 4. Modules of diffusion (A), convection (B) and electromigration (C) fluxes (mol/m²s).

We consider the transport processes (2) separately. The components of the total ion flux are shown in **Fig. 4**.

Fig. 4A shows the module of diffusion flux of I_3^- ions in the system. The flux reaches a maximum in the region between the anode and the cathode; this is because the concentration gradient is the largest at the shortest distance between the place of formation and decay of I_3^- ions. **Fig. 4B** shows the module of the convective flow, it is maximal at the intersection of the maximum of the concentration gradient with the maximum of the velocity. The convective flow does not directly affect the ion flux through the surface of the electrode. Instead, it changes the ratio of the concentrations in the regions above the electrodes, from where additional ions (that are brought by the convection flow) reach the electrode under the action of diffusion. **Fig. 4C** shows the electro migration flow module. The electro migration flow over the cathode is close to zero, because it includes composition of concentration and the gradient of the electric field, and the ion concentration I_3^- tends to zero in this region. This flux is small in the anode region, of the order of $1.2 \cdot 10^{-4}$ mol/m²s, which is about 1% relative to the total flux. Nevertheless, the electromigration can not be completely neglected, because electromigration ion fluxes are asymmetric and give an essential contribution to nonlinearity.

We calculated CV-curve and transfer function of our system (**Fig. 5**).

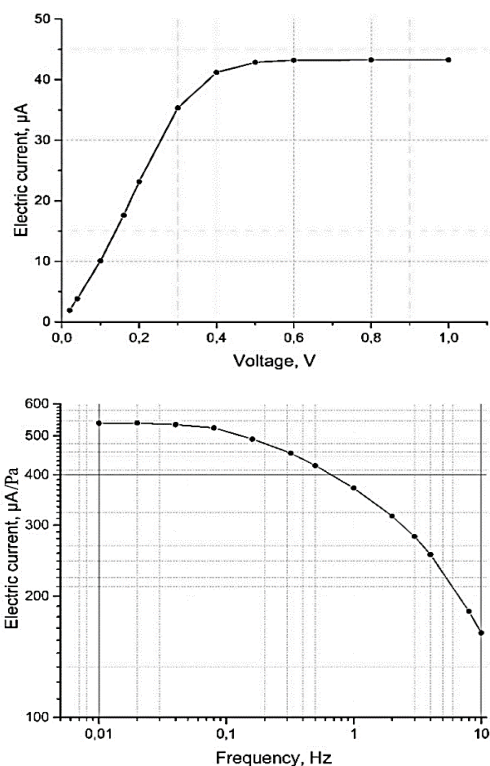


Fig. 5. CV-curve and transfer function.

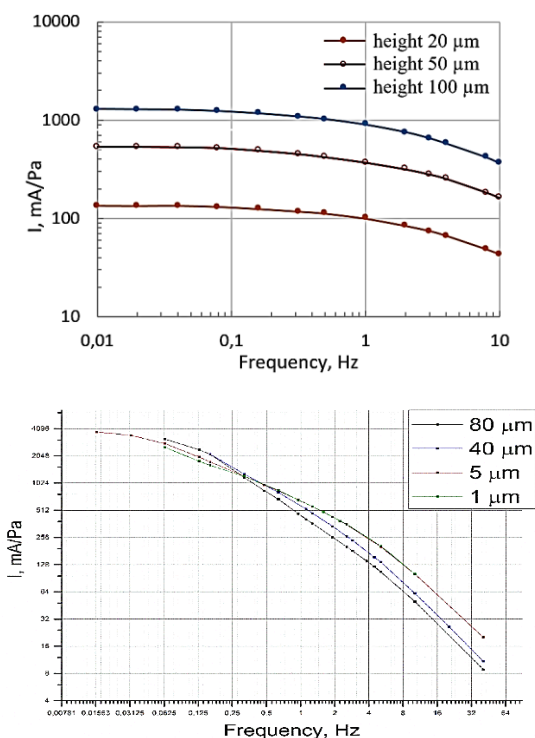


Fig. 6. Example of the relationship of the channel height [9] and the distance between the electrodes [10] to the transfer function of planar ECT.

Also, we studied the relationship between the geometrical parameters and transfer characteristics of the system (Fig. 6). We have established the main regularities:

- (1) The slope of transfer function does not change with increasing channel size. The efficiency of pressure conversion increases.
- (2) The slope of transfer function changes with decreasing the distance between the electrodes; the smaller the distance, the higher the conversion factor at low frequencies. At the same time, the effective part of the electrode surface decreases, because the region of the maximum concentration gradient is "attracted" to the electrodes.

Conclusion

We developed a new simulation model for planar electrochemical transducer, based on numerical solution of Navier-Stokes equation and convection-diffusion equation. We set the correct boundary conditions under the presence of fluid flow and background voltage. We took into account all three types of ions and their mutual influence. We investigated the influence of all main transfer processes, including the electromigration process, which is traditionally neglected.

We calculated the velocity field, ions concentration distribution and concentration gradient, the signal current through the surface of electrodes at various frequencies under the influence of external mechanical signals. We obtained quantitative estimates of hydrodynamic flow and fluxes of all ions and described their impact in system characteristics in presents of external mechanical signal. We calculated the transfer function and CV-curve for the various geometry. We summarized our results and defined the basic relationships between geometry and main system characteristics.

Acknowledgements

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