

Technological Principles of Motion Parameter Transducers Based on Mass and Charge Transport in Electrochemical Microsystems

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Abstract—The most important advantage of motion parameter transducers based on mass and charge transport in electrochemical systems is exceptionally high rate of mechanical signal conversion to electric current. Devices of this class are based on the principle of diffusion charge transport under the conditions of forced convection appearing as a result of external acceleration. This work shows the possibility of development of modern high-technology devices based on an electrochemical transducer developed using up-to-date microelectronic technologies.

Keywords: electrochemical transducer, electrochemical cell, molecular–electronic transport, solid–liquid microsystems, convective diffusion

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1. PHYSICAL PRINCIPLES OF OPERATION OF MOTION SENSORS BASED ON MASS AND CHARGE TRANSPORT IN ELECTROCHEMICAL MICROSYSTEMS

An electrochemical transducer (ECT) with the operation principle based in the phenomenon of molecular–electronic transport is a set of electrodes placed into the solution of electrolyte (Fig. 1).

As a rule, a solution used contains a high concentration of background (not participating in the electrode reactions) electrolyte with a slight additive of the active component for charge transfer through the liquid/metal interface on the electrode surface. It is known that in this case, it is sufficient to consider only the fluxes of the active component to account only for diffusion and convective transport to calculate the current in the system. The role of the background electrolyte is limited to screening the electric field in the liquid and thus suppression of migration charge transport. Operation of the sensor is based on the fact that the rate of the electrochemical reaction on the electrodes is much higher than the rate of supply of the reacting substances.

The principle of ECT operation can be easily explained using the approximation of planar permeable (for liquid but not the charge) electrodes first developed in [1]. When electric voltage is applied to

the system, electrochemical current appears (the so called “background current”) independent of the presence of mechanical motion (Fig. 2a). In this case, electrochemical reactions cause the development of the concentration gradients of the solution components and charge transport in stationary electrolyte occurs through diffusion of ions from one electrode to another.

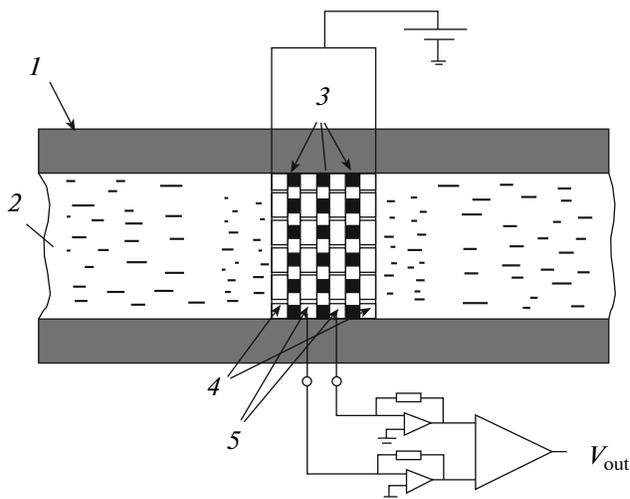


Fig. 1. Electrochemical transducer. (1) Ceramic or glass casing; (2) electrolyte; (3) porous ceramic walls; (4) anodes; (5) cathodes.

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In the presence of a mechanical signal, electrolyte starts moving as a result of inertia and additional convective transport of ions to the electrodes appears alongside with the diffusion, which drastically changes the rate of supply of the reacting substances to the electrodes and thus the current through the sensor changes dramatically. Additional (to the “background” value) electric current appears in the system; herewith, this current is proportional to the external mechanic signal.

In other words (Fig. 2b), the liquid flow resulting from the mechanic motion distorts the established “stationary” distribution of the charge carrier concentrations in the interelectrode space, which leads to a drastic change in the concentration gradient near the electrode surface and the electric current through the electrode, in its turn, depends on the concentration gradient near the electrode surface as follows:

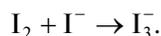
$$I = -Dq \int_S (\nabla c ds), \quad (1)$$

where D is the diffusion coefficient, c is the concentration of charge carriers, q is the charge of carriers, S is the electrode surface area.

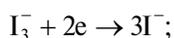
Herewith, such a system is characterized by an exceptionally high sensitivity towards mechanic exposure due to high rate of conversion of the mechanic signal to electric current.

Various redox reactions can be used in a transducer, for example: iodine/iodide, ferricyanide/ferrocyanide etc. Herewith, ECT electrodes are made of a metal that does not participate in the cation exchange but carries out only the electron exchange, which theoretically allows the device to operate infinitely long without changes in the operating parameters.

At present, iodine/iodide systems with platinum electrodes are most widespread. The electrolyte of such a system consists of a highly concentrated aqueous solution of potassium iodide KI (the lower temperature limit is -15°C) or lithium iodide LiI (the lower temperature limit is -55°C) and a small amount of molecular iodine I_2 . In the presence of an excess of iodide, iodine passes into a well-soluble complex compound, triiodide, according to the following scheme:



When current passes through ECT, the following electrochemical reactions occur on the electrodes: reduction of triiodide on the cathode:



oxidation of iodide on the anode:



Herewith, potassium or lithium ions play the role of the background electrolyte and take no part in the reactions.

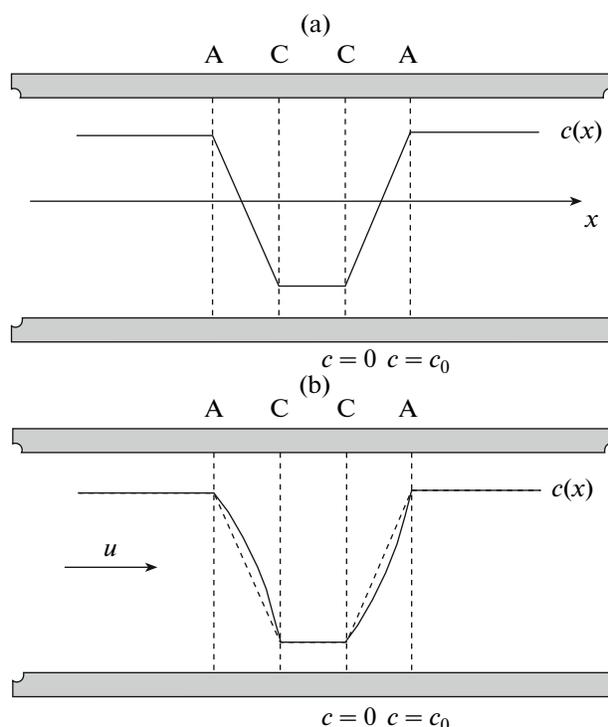


Fig. 2. Distribution of the concentration of electrolyte in an electrode assembly with planar permeable electrodes. $c(x)$ is the concentration established in the presence of a voltage shift; (a) concentration distribution in the absence of mechanical motion; (b) it is shown how the distribution of concentration $c(x)$ is changed under the effect of the incident liquid flow; u is the velocity of the liquid flow, the electrode designations: A are anodes, C are cathodes (similar to the designations in the further figures).

Under an increase in the interelectrode potential difference, the intensity of electrochemical reactions grows gradually, until the state is achieved when all triiodide ions reaching the electrode take part instantly in the electrochemical reaction. Herewith, the mode of current saturation is implemented and the further increase in the potential difference causes no change in its value. In this mode, the current saturation value is determined by the bulk rate of supply of the active component to the electrodes. In a stationary electrolyte, the supply rate is determined by the diffusion of ions. Additional convective mechanism appears when the solution is moving that changes the saturation current dramatically. Voltammetric characteristics of an electrode system in a stationary and moving electrolyte are shown in Fig. 3. The characteristic feature of the conversion process is its high efficiency, which consists in a high electric response that exceeds significantly the noises of the relevant electronics even at low input mechanic exposure. Ultimately, this provides the high signal/noise ratio for the whole measurement path.

At present, there is an experimental production of transducers for microceramic ECTs with gauze elec-

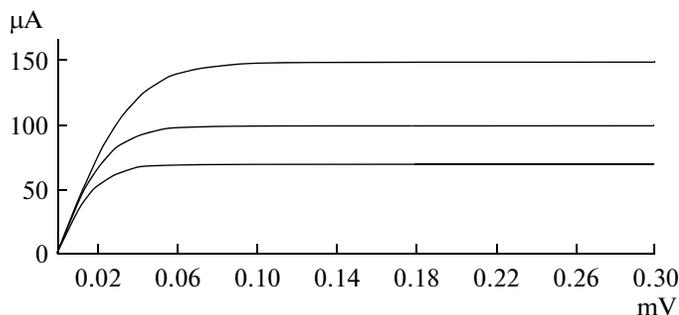


Fig. 3. Voltammetric characteristics of the transducer electrode system in the stationary electrolyte (middle curve) and in electrolyte moving from the anode to the cathode (upper curve) and in the reverse direction (lower curve).

trodes. A number of original experimental devices and systems for solutions for diverse problems is developed on the basis of these transducers in the Center of Molecular Electronics of Moscow Institute of Physics and Technology. Some of the small-batch devices are shown in Fig. 4, the total number of the developed devices and modifications is several tens. These include unique ones, e.g., a device for determining the direction to the geographical north or six-component systems for monitoring of the state of high-rise buildings and complex engineering structures capable of registering both linear and rotary vibrations.

2. CHARGE AND MASS TRANSPORT IN ECT

To describe the processes of transport and signal conversion and calculation of the frequency, dynamic, and noise characteristics of ECT, it is necessary to solve a system of equations of hydrodynamics and convective diffusion under the conditions of a variable flow of electrolyte through the electrochemical cell. The main equation describing the transport of the active component in the transducer system under consideration is the general equation of nonsteady-state convective diffusion:

$$\frac{\partial c}{\partial t} = D\Delta c - \mathbf{V}\nabla c, \quad (2)$$

where c is the concentration of active ions, \mathbf{V} is the hydrodynamic velocity of the flow of electrolyte against the transducer casing, D is the diffusion coefficient, t is the time.

Velocity distribution required for solution of (2) can be obtained on the basis of the Navier–Stokes equations (it is enough to use in the calculation of the linear response approximation of small Reynolds numbers) and conditions of incompressibility of liquids:

$$\frac{\partial \mathbf{V}}{\partial t} = \nu \Delta \mathbf{V} - \frac{\nabla P}{\rho}, \quad (3)$$

$$\operatorname{div} \mathbf{V} = 0, \quad (4)$$

where ν is the viscosity coefficient of electrolyte, P is the pressure, ρ is the density.

In the case of low velocities of the electrolyte flow, the solution of the equation of convective diffusion can be searched for in the form of a series, where each next addend is proportional to the amplitude of the electrolyte flow velocity u with a higher power exponent. In the studies of the linear system response, it is sufficient to take into consideration only the first two expansion terms:

$$c = c_0 + c_1 e^{i\omega t}, \quad (5)$$

where c_0 is the concentration distribution in a stationary liquid, c_1 is a small additive to the concentration linear by hydrodynamic velocity and changing harmonically. Then equation (5) is transformed into the following system:

$$\Delta c_0 = 0, \quad (6)$$

$$\frac{\partial c_1}{\partial t} = D\Delta c_1 - \mathbf{V}\nabla c_0. \quad (7)$$

In the linear approximation, the system consisting of equations (3), (4), (6), and (7) determines completely the processes of convective diffusion occurring in the cell. Usually the boundary conditions applied for its solution represent natural physical conditions of the absence of the flow of active ions on dielectric surfaces, constancy of concentrations on conducting electrodes, standard hydrodynamic conditions of liquid adhesion on solid walls, and also conditions of the known pressure drop at the inlet and outlet of the transducer channels.

The amplitude of the differential cathodic current is considered as the output signal for the most widely used four-electrode system (two anodes and two cathodes positioned symmetrically):

$$I(t) = I_{\text{cathode2}}(t) - I_{\text{cathode1}}(t) = Dq \left(\oint_{S_{\text{cathode2}}} (\nabla c_1(t) ds) - \oint_{S_{\text{cathode1}}} (\nabla c_1(t) ds) \right), \quad (8)$$

where I is the output signal, t is the time, I_{cathode1} , I_{cathode2} are the currents through the surface of the corresponding electrodes, S_{cathode1} , S_{cathode2} are the surface areas of the corresponding electrodes.

From the viewpoint of the output sensor parameters, the main faults of the seismic sensors are related to the regularities of the behavior of its characteristics in the high-frequency range. Earlier, a number of works on analysis of the transducer response to high-frequency signals was published. Papers [2, 3] considered a system of cylindrical electrodes corresponding to gauze transducer structures used in serial ECT devices. The obtained results describe rather well the frequency behavior of the characteristics of real transducers and show in particular that there is a high-frequency limit for the sensitivity of transducer with

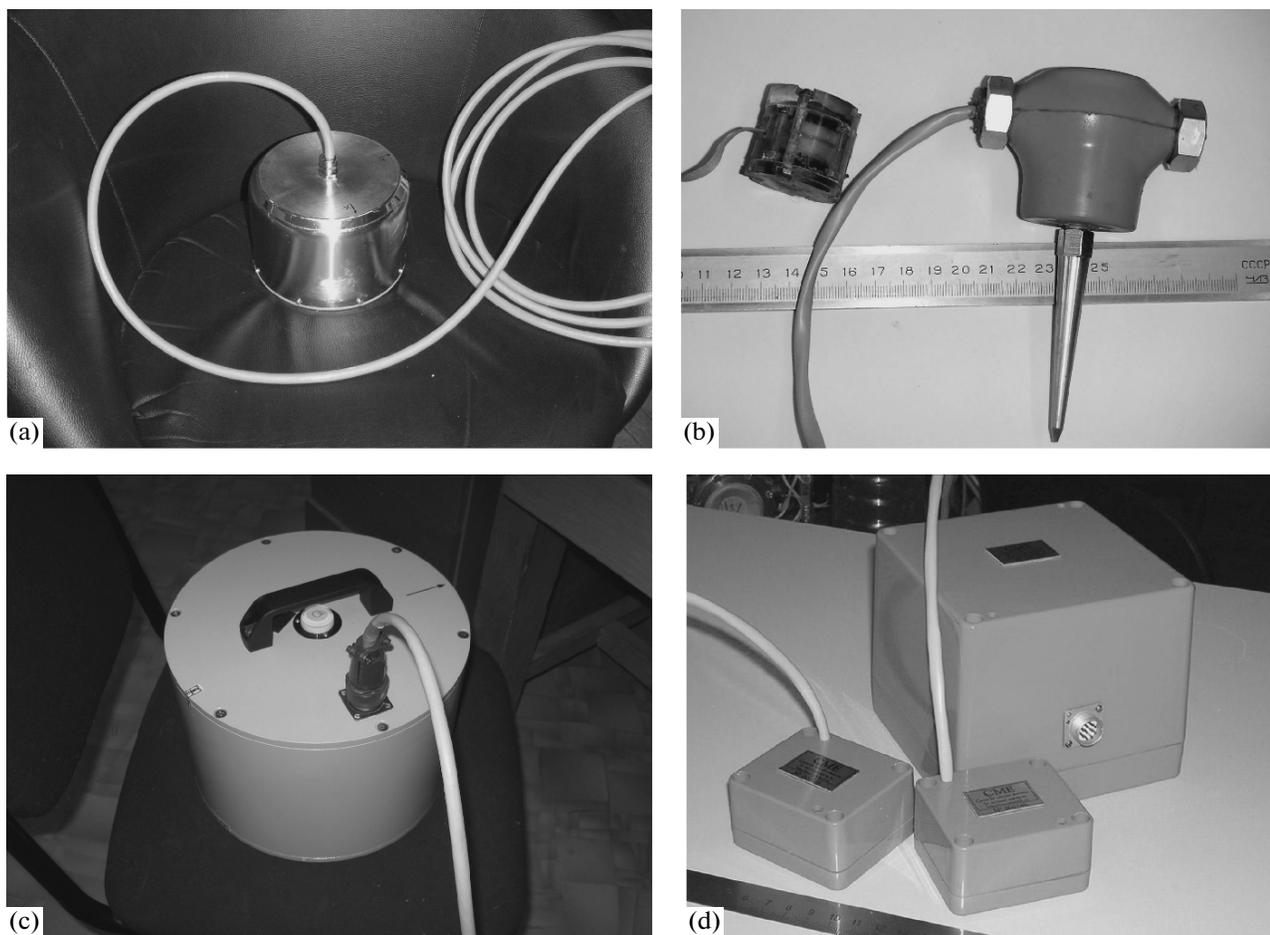


Fig. 4. Some of the modern devices and setups developed in the Center of Molecular Electronics of Department of Physical and Quantum Electronics of Moscow Institute of Physics and Technology: (a) offshore seismic detector; (b) geophone; (c) precision seismic detector with power feedback; (d) rotary transducers for various applications.

gauze electrodes that cannot be overcome by variation of geometric parameters. (Here and further, the “high frequencies” are high frequencies from the viewpoint of long–period seismology and transport processes in ECT. This is the range from several Hz to several hundreds of Hz. In this respect, low frequencies are several thousandths (!) to tenths of Hz).

To improve the high–frequency transducer response, it was suggested to use gauze electrodes of extremely thin fibers. There is a practical necessity to reach the maximum operating frequencies of above 800 Hz for seismic sensors, which corresponds for devices with feedback to the necessity of shifting the corresponding characteristic frequency to about 3–4 kHz. Herewith, the temperature range in the negative region must reach -40°C , which corresponds to $D \sim 10^{-10} \text{ m}^2/\text{s}$. The fiber radius in this case must be:

$$R \leq \sqrt{D/\omega} \approx 70 \text{ nm.} \quad (9)$$

Practical implementation of gauze structures of this type appears rather difficult at the present level of

technology. At the same time, planar structures of the corresponding size can well be obtained.

Theoretically, transducers with planar electrodes were studied using numeric–analytical [4, 5] and numeric [6–8] methods. Main interest in the publications under discussion was directed to the studies of the low–frequency behavior of the transducer systems. Accordingly, structures with the size above $1 \mu\text{m}$ were studied. Nevertheless, a number of the results obtained is directly related to the discussed subject. Thus, one can state on the basis of the comparison of the results of [2] and [4] that just a transition to the ring electrode geometry from that with cylindrical ones while preserving the characteristic size of the key microsystem parameters allows achieving an increase in the frequency, at which the characteristic starts decaying at high frequencies and also a more favorable character of the characteristic decrease, which makes it possible to avoid the high–frequency sensitivity limit of the gauze electrode assembly that is shown to exist in [2]. In [6, 7], the structure with planar electrodes was studied and it was shown that such a struc-

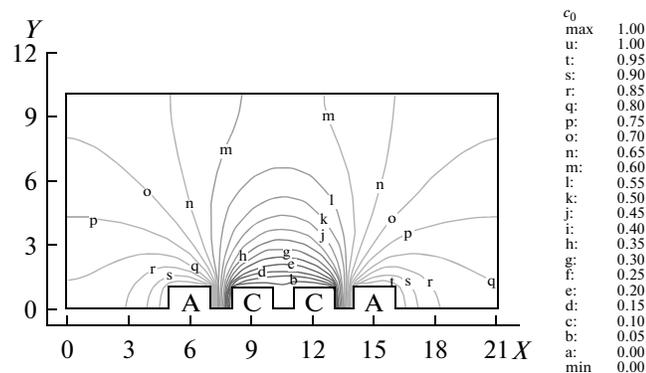


Fig. 5. Steady-state profile of concentration c_0 . Constant concentration lines are denoted by Latin letters, axis X and Y show the dimensions of the calculated structure in μm , the electrodes are made in the form of rectangular tabs. The highest concentration gradient (highest line density) is obtained in the interelectrode space.

ture is even more promising as regards manufacturing of the transducer as compared to that with ring electrodes. The results of [7] also point to a slower rate of decrease of the amplitude–frequency response of miniature planar electrochemical cells at an increase in the frequency as compared to those used at present. In [6], the process of signal transduction was considered in a cell with electrodes applied on the channel walls and the following figures are presented in particular. Figure 5 shows the steady-state concentration distribution in the absence of electrolyte movement. This value corresponds to c_0 from equations (5) and (6) above. Figure 6 shows the characteristic distribution of velocities in the channel. The correction to concentration c_1 linear by the velocity is presented in Fig. 7. The outer circuit in the above figures shows the boundaries of the model region, herewith the electrodes correspond to small rectangles in the lower part of the fig-

ures. The outer electrodes are anodes, the inner ones are cathodes.

As follows from the presented figures, the maximum concentration gradient ∇c_0 corresponds to the region in the gap between the electrodes. The maximum of concentration c_1 (Fig. 7) proves to be removed from this region, so that as the exposure frequency increases, ions from this region fail to reach the electrode surface in the time corresponding to the period of signal variation. Accordingly the transducer sensitivity starts decreasing much faster, as soon as diffusion length λ_D appears to be lower than the characteristic dimensions of the electrode structure. Herewith, the highest value is characteristic of the region between the anode and cathode, as it is here that a concentration perturbation linear by the measured velocity is developed that is ultimately responsible for the output signal value.

At the same time, a decrease in the characteristic dimensions of the electrode structure and geometric size of the working channel filled by electrolyte causes a decrease in the level of intrinsic noise of the transducer. In particular, this concerns the mechanism of nonequilibrium hydrodynamic noise related to convective instability in the liquid in the transducer studied in [8].

The following conclusions can be formulated:

(1) The electrode system with planar electrodes has a number of advantages as compared to other discussed electrode configurations even when the characteristic dimensions of the transducer microstructures remain at the former level.

(2) A decrease in the characteristic dimensions of the main transducer elements allows extending the transduction frequency range, increasing linearity and in many cases also providing higher sensitivity.

(3) One of the most important parameters of the planar structure that largely determines the ECT char-

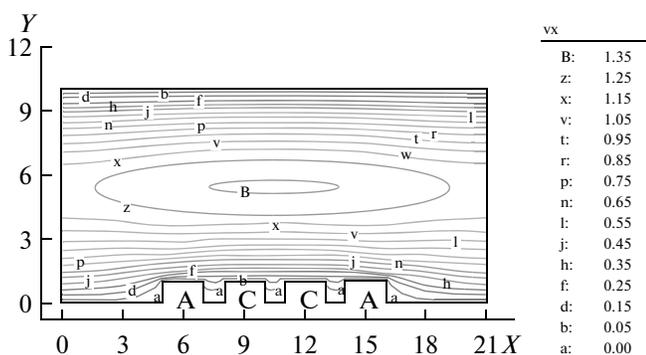


Fig. 6. Distribution of the horizontal velocity component in the cell. Lines with a similar horizontal rate component are denoted by Latin letters, axis X and Y show the dimensions of the calculated structure in μm , the electrodes are made in the form of rectangular tabs.

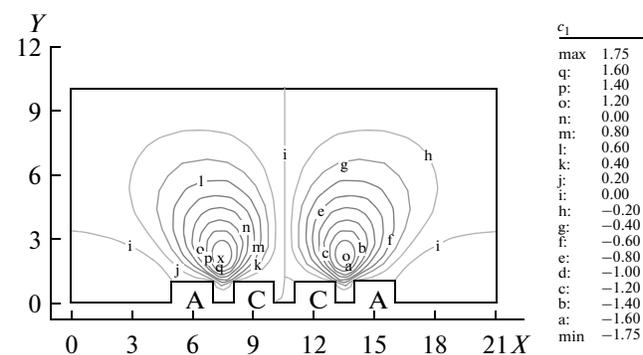


Fig. 7. Velocity-linear correction to the steady-state distribution of concentration c_1 . Lines with a similar velocity-linear correction to the concentration are denoted by Latin letters, axis X and Y show the dimensions of the calculated structure in μm , the electrodes are made in the form of rectangular tabs.

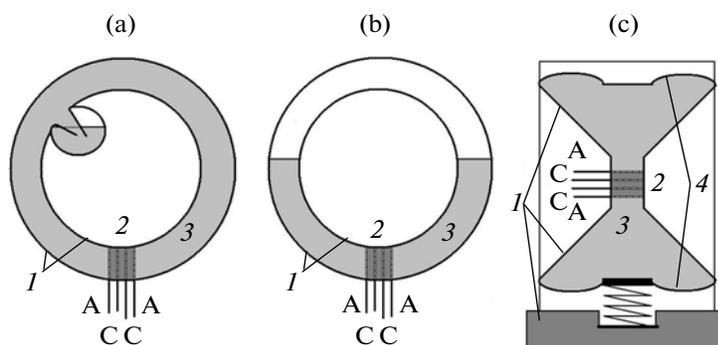


Fig. 8. Types of ECT-based sensors. (a) rotary transducer; (b) horizontal section; (c) vertical section. (1) Casing, (2) transducer, (3) channel filled by electrolyte, (4) membranes.

acteristics is the distance between the cathode and anode.

Thus, one of the main directions for development of electrochemical motion parameter sensors is the further decreasing the characteristic dimensions of the ECT transducer microstructure as much as can be done at the present stage of development using the up-to-date microtechnologies, as the existing gauze ceramic technology can be of no more help in this direction. Using standard microelectronic technologies allows significantly miniaturizing the electrode assembly, minimizing the scatter of the transducer parameters, decreasing the power consumption, and considerably decreasing the cost of the ready-to-use sensors. ECT manufactured on the basis of microtechnologies can have the characteristic dimensions of the key structural elements down to 100 nm, i.e., it becomes possible to decrease the characteristic dimensions of the transducers by 2–3 orders of magnitude.

3. TECHNOLOGICAL APPROACH TO DEVELOPMENT OF ECT

In manufacturing of a seismic detector, the sensor is placed across the dielectric channel confined on both sides between flexible membranes and filled by the working liquid. At present, ECT electrode assemblies are manufactured from metallic gauze with the wire diameter of 30–100 μm . The schematic drawing of seismic sensors and the layout of transducer electrodes is shown in Figs. 8 and 9.

The output amplitude–frequency characteristic of the series-produced transducer is presented in Fig. 10 (curve 1). The further formation of the output characteristic is provided by using deep negative electrodynamic feedback. As dependent on the method of the feedback signal formation, one can obtain the output proportional to velocity or to acceleration. Ultimately, the output amplitude–frequency response has quite a standard planar structure characteristic of devices for such applications with characteristic nonuniformity in the working frequency range of at least 1 dB. Simulta-

neously, using feedback allows providing high device response linearity, temperature and timing stability of the output parameters.

Despite the obtained rather high output parameters, the devices developed and produced at present have a number of faults that ultimately limit their application range. The main of these are as follows:

- (1) high cost of transducer manufacturing,
- (2) rather high scatter of parameters of manually produced transducers resulting in the necessity of individual tuning of the corresponding electronics for each sensor, which also increases the cost of the device;
- (3) early decrease in sensitivity of the sensor in the high-frequency range (see Fig. 10, curve 1).

The above difficulties can be easily overcome at the modern technical level if planar transducers are used. In particular, the possibility of implementation of a sensor with the characteristic electrode structure dimension of 7 μm is shown in [9].

On the basis of the results of analytical and numeric models described above, we developed and manufactured transducer sensors with the characteristic electrode dimensions of 3 μm . A schematic drawing of the transducer structures is shown in Fig. 11.

The flow sheet includes the following set of main technological operations: the dielectric device casing surface and gap channel in the silicon plate are obtained using oxidation in a diffusion furnace; the electrode microstructure is formed using explosive photolithography and electron-beam deposition; through cuts in the support plates are formed using laser cutting with a tunable pulsed pico-/femtosecond laser; pin assignment and pinout of the device is carried out using the methods of ultrasonic welding, precision contact soldering, and contact gluing using a conducting paste. On the whole, the process represents a set of process operations quite widespread in semiconductor microelectronic industry, however, the experience in application of these methods for manufacturing motion-parameter transducers based on mass and charge transport in electrochemical micro-

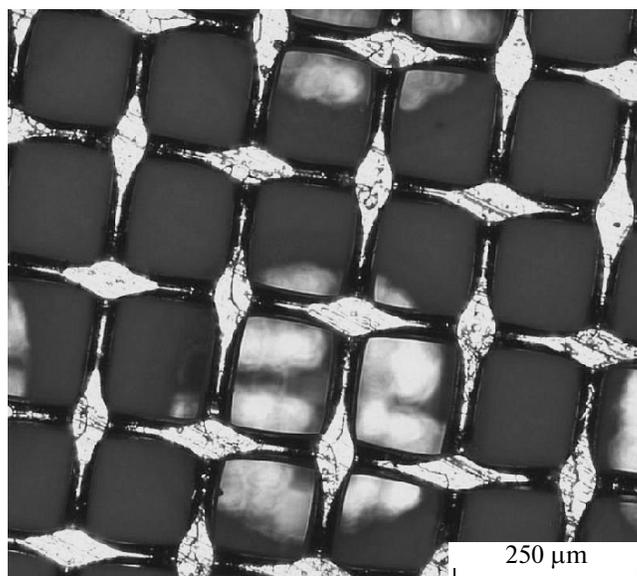


Fig. 9. Image of the internal design of an electrode stack of modern ECT obtained using a Nikon Eclipse LV150 microscope. The image is obtained in the direction of the sensitivity axis (in the direction of liquid flow). One can distinctly see the gauze of the outer electrode, anode 4 (Fig. 1) twister of cylindrical wires flattened at their intersections. The gauze spacing is 150 μm , the wire thickness is 30 μm . One can see under the gauze indistinct light round spots with the radius of about the gauze spacing: perforated holes in ceramic wall 3 (Fig. 1) separating the electrodes.

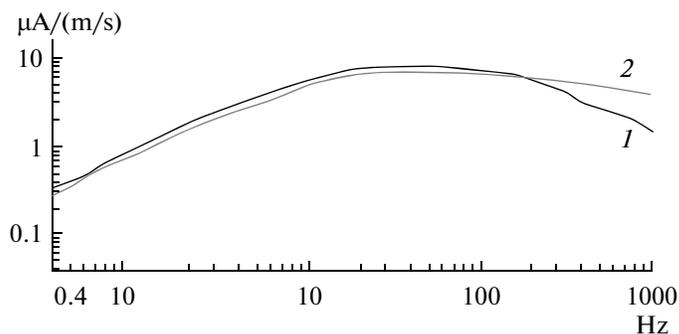


Fig. 10. Amplitude–frequency characteristic of the sensor of (1) a seismic detector with a gauze–type transducer cell (1) and (2) a seismic detector manufactured using planar technologies.

systems has as yet been quite limited. Photographs of the manufactured samples are shown in Fig. 12.

Figure 12 shows distinctly scaled-up transducer electrode structures (groups of 4 light parallel bands)

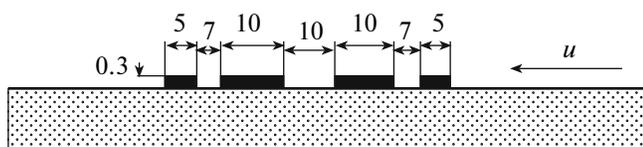


Fig. 11. Schematic representation of the transducer electrode structure (cross–section). u is the direction of the electrolyte flow.

and through holes in a silicon plate with applied electrodes providing access of the working liquid to the transducer electrode system.

Details in the geometry of the transducer electrode system were studied using a Nikon Eclipse LV150 high resolution microscope equipped with a BWH-501 3D surface profiler with a high precision piezoelectric actuator and the corresponding software. According to its technical specifications, the device allows studying surface profiles with the height variations of 100 nm to 40 μm . In particular, this device allows obtaining layer–by–layer photographs of the studied surface regions with the step of 25 nm and constructing on their basis 3D models and profiles of the studied struc-

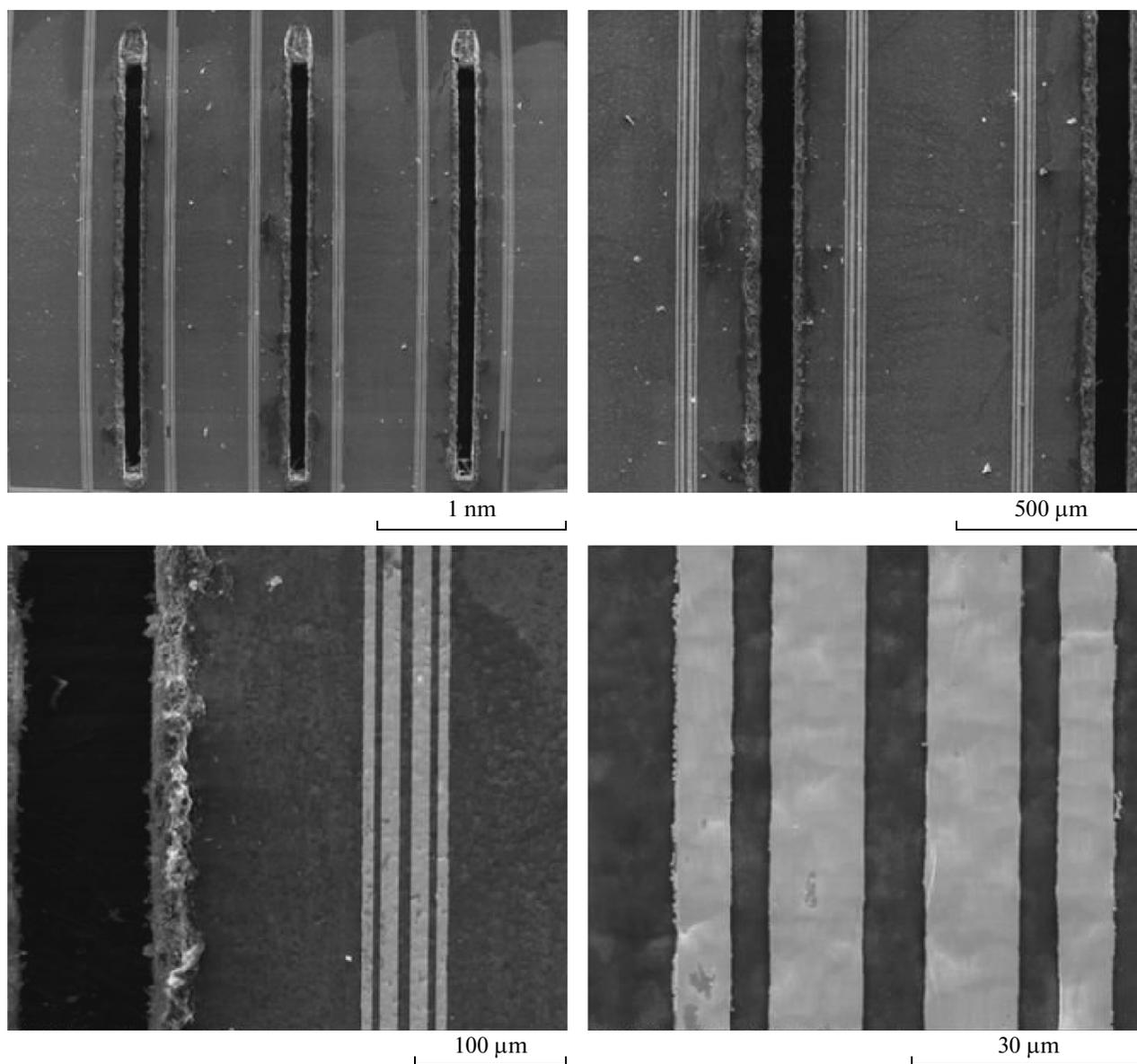


Fig. 12. Images of the electrode structure of ECT sensors. The images were obtained using a FEI Quanta 200 scanning electron microscope.

tures. The results of such a study are presented in Figs. 13 and 14.

Figure 14 shows positions and profiles of the two neighboring electrodes, anode and cathode, and also the nonconducting gap between them. Thin vertical lines show the boundaries between the electrodes and nonconducting gaps. The electrode surface height relative to the nonconducting gap is 100 nm. A certain rise in the electrode surface profile at the edges is created by the mask when it is removed from the surface after the electrodes are applied using explosive photolithography.

Figure 10 shows the amplitude–frequency characteristic of the seismic sensor with a new type sensor (curve 2) as compared to the conventional device (curve 1). As seen from the obtained results, sensitivity of the high–frequency new sensor decreased much less as compared to that in the conventional device, which, firstly, is quite in line with the theoretical predictions and numeric calculations discussed above; and secondly, it is a convincing proof that the new transducer developed using microelectronic technologies exceeds significantly the modern EPM devices as regards the operating frequency range.

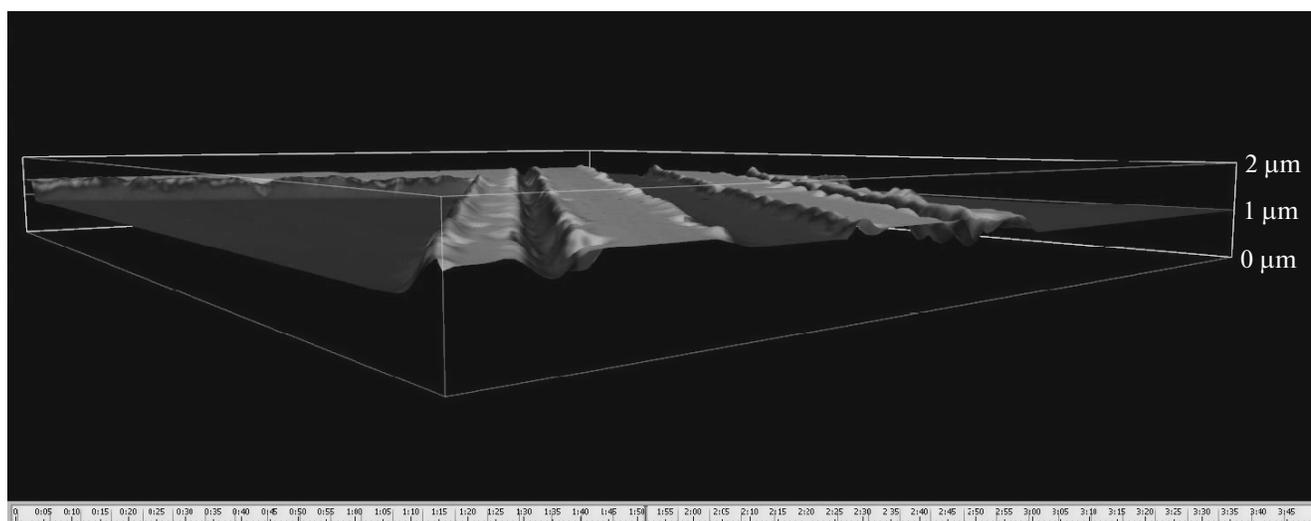


Fig. 13. 3D model of the transducer electrode structures constructed using a Nikon Eclipse LV150 microscope equipped with a BWH-501 3D surface profiler.

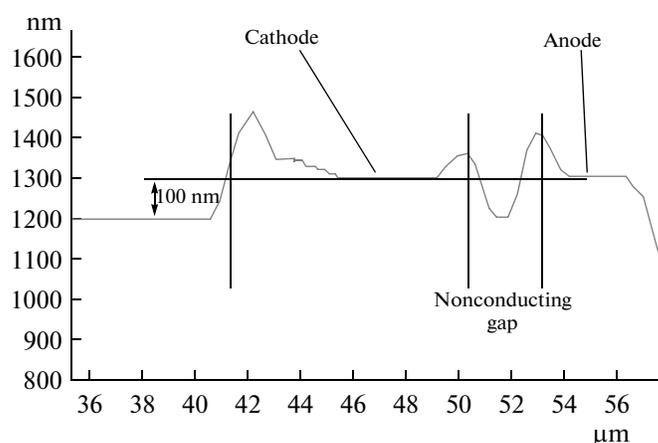


Fig. 14. Profile of the electrode structure obtained using a Nikon Eclipse LV150 microscope equipped with a BWH-501 3D surface profiler. The profile section shown corresponds to two electrodes and a gap between them.

Motion parameter gauges based on molecular–electronic transfer in ECT with their low prime cost in mass production and using modern microelectronic technologies and a qualitative step forward in technical parameters, are characterized by quite a wide application sphere including seismic exploration (particularly, 2D and 3D, including vector seismics), navigation systems (including portable personal ones and designed for small off-line equipment), systems for vibration control and seismic monitoring of the state of buildings and facilities, some medical applications (such as portable cardiac monitor systems, systems for orthopaedics and sports medicine), car safety systems, robotics, and many others.

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REFERENCES

1. Larkam, C.W., *J. Acoustical Soc. America*, 1965, vol. 37, no. 4, p. 664.
2. Agafonov, V.M. and Krishtop, V.G., *Russ. J. Electrochem.*, 2004, vol. 40, p. 537.
3. Agafonov, V.M. and Krishtop, V.G., *Mikrosist. Tekh.*, 2004, no. 9, p. 40.
4. Kozlov, V.A. and Terent'ev, D.A., *Russ. J. Electrochem.*, 2002, vol. 38, p. 992.
5. Kozlov, V.A. and Terent'ev, D.A., *Russ. J. Electrochem.*, 2003, vol. 39, p. 401.
6. Agafonov, V.M. and Orel, A.A., *Nano- Mikrosist. Tekh.*, 2008, no. 5, p. 50.
7. Agafonov, V.M., Bugaev, A.S., and Orel, A.A., *Nano- Mikrosist. Tekh.*, 2009, no. 5, p. 32.
8. Safonov, M.V., *Electronic Journal “Issledovano v Rossii”*, 2004, p. 2433.
9. Agafonov, V.M., Krishtop, V.G., and Safonov, M.V., *Nano- Mikrosist. Tekh.*, 2010, no. 6, p. 47.