

SHORT  
COMMUNICATIONS

## Dynamic Characteristic of an Electrochemical Cell with Gauze Electrodes in Convective Diffusion Conditions

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**Abstract**—A frequency dependence of the transfer function of an electrochemical cell is studied experimentally in the frequency span 0.02 to 40 Hz under conditions of controlled convective diffusion. Above the diffusion frequency, experimental data nicely conform to theoretical calculations, but below it the function's decay cannot be explained within existing theoretical notions.

*Key words:* transfer function, convective diffusion, accelerometer

Studying dynamic characteristics of an electrochemical cell, besides of being of purely scientific interest, is of utmost import for practice because this cell is widely employed as a sensor in molecular electronic converters of motion parameters and wave fields. This is precisely the reason for many a theoretical work devoted to the transfer function (TF) of these systems, which sought for the electrode geometry that would ensure an analytical frequency dependence of TF in a broad frequency range [1–9]. A study [1] of TF of a cell with parallel plate electrodes in the framework of a one-dimensional convective diffusion equation showed that, starting with diffusion frequency  $\omega_D = D/d^2$  ( $D$  the diffusion coefficient,  $d$  the interelectrode gap) and up to the very high frequencies, TF must fade as  $\omega^{-1/2}$ . A spherical electrode geometry was studied theoretically in [2, 3]; a system of ring electrodes in a dielectric channel, in [4–6]; and a set of cylindrical electrodes, in the framework of a numerical analysis, in [7–9]. As follows from the works cited, at  $\omega > \omega_D$ , TF decays as  $\omega^{-1}$ . An experimental check on the notions and theoretical conclusions stated in those works is a daunting task, for any attempt to impose a harmonic change on a fluid flow in a cell has unavoidably to do with a mechanical oscillatory system. In practice this means that an experiment determines the system's net TF

$$W(\omega) = W_1(\omega)W_2(\omega). \quad (1)$$

Here,  $W_1(\omega)$  and  $W_2(\omega)$  are TFs of the cell and the mechanical system. As follows from (1), to determine  $W_1(\omega)$ , which is the subject under analysis, it is necessary to know  $W_2(\omega)$  to a high accuracy. Actually, standard oscillatory systems have been studied well enough and an expression for  $W_2(\omega)$  in the general form may be computed sufficiently accurately [10], but in our case

the electrochemical cell is in essence just a component of a mechanical oscillatory system, whose hydrodynamic resistance  $R_h$  defines the system's decay. As  $R_h$  is impossible to measure accurately, the data obtained by different methods differ nearly tenfold. Hence the need to develop a procedure for measuring TF of a cell, which would not involve measuring  $W_2(\omega)$ . Studying TF of an electrochemical cell in a pure shape is precisely the aim of this work.

A way to solve this problem is to measure TF of a molecular electronic accelerometer of rotational motion [11] whose mechanical system has no return force, which simplifies the shape of  $W_2(\omega)$ . The linear speed of an electrolyte flow in the channel of an angular accelerometer obeys the equation

$$\dot{V} - \frac{R_h S}{2\pi r \rho} V = -a_{ex}. \quad (2)$$

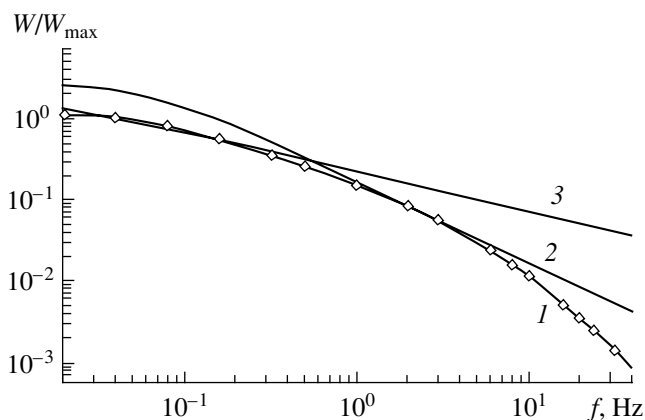
Here,  $S$  the channel's cross-section area,  $r$  the radius of a ring channel,  $\rho$  the electrolyte's density, and  $a_{ex}$  the tangential acceleration of rotation of the accelerometer body. From (2) we easily obtain

$$W_2(\omega) = \frac{1}{\omega_h + i\omega}, \quad (3)$$

where  $\omega_h = R_h S / 2\pi r \rho$ . The system's  $R_h$  is so great that  $W_2(\omega)$  starts fading at frequencies of about a few tens of hertz. At  $\omega \ll \omega_h$ ,  $W_2(\omega) = \text{const}$  and TF for an angular accelerometer coincides with that for the cell, which gives us a chance to measure the latter directly.

Figure 1 shows TF for an angular molecular electronic accelerometer obtained as a result of measurements at 0.02–40 Hz on a calibration stand (Fig. 2) that was capable of imposing sine rotational oscillations with a distortion factor below 1%. It follows that at 0.04–0.16 Hz the TF the decays as  $\omega^{-1/2}$ ; at higher fre-

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**Fig. 1.** (1) Experimental TF for electrochemical cell, (2) plot for  $W = \text{const}(1 + \omega^2/\omega_D^2)^{-1/2}$ , and (3) plot for  $W = \text{const}\omega^{-1/2}$ .

frequencies, as  $\omega^{-1}$ ; starting with 6 Hz, as  $\omega^{-3/2}$ ; and after 20 Hz, as  $\omega^{-2}$ . The TF decay as  $\omega^{-1}$  at  $\omega > \omega_D$  (for our cell,  $\omega_D \sim 0.06$  Hz) is hardly surprising, for according

to results of [2–9], TF must be approximated with the expression

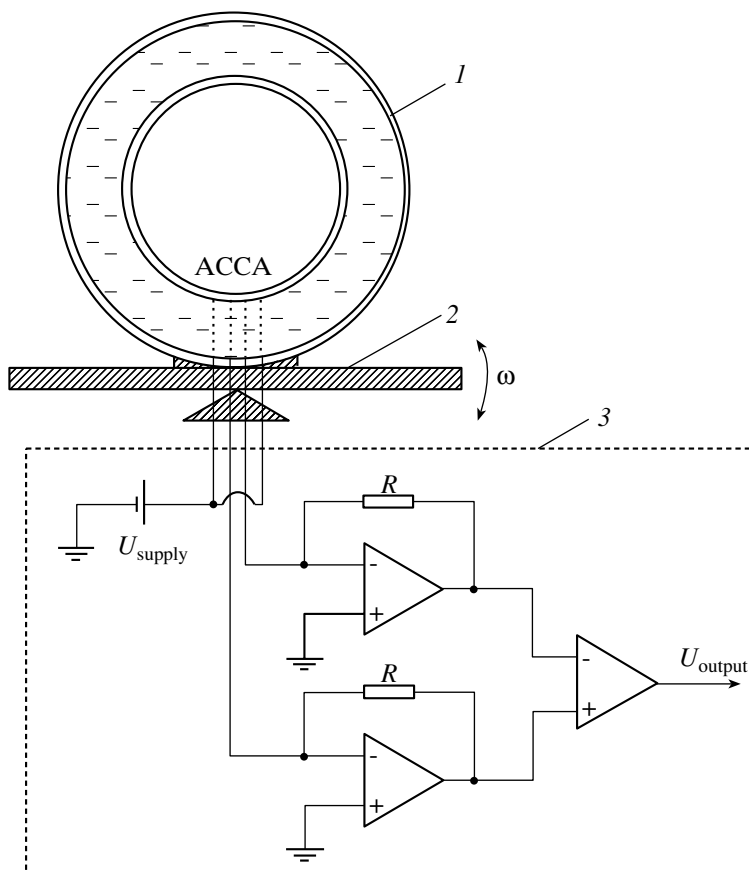
$$W_1(\omega) \sim \frac{1}{\sqrt{1 + \omega^2/\omega_D^2}}, \quad (4)$$

starting with a zero frequency. At 1–4 Hz, experimental TF nicely obeys (4) indeed (Fig. 1).

The TF decay as  $\omega^{-3/2}$  may be explained theoretically by assuming that the diffusion length  $l_D = (D/\omega)^{1/2}$ , which defines the number of ions that reach the electrode within an oscillation period, decreases with increasing  $\omega$ . Hence, in the frequency range where  $l_D$  becomes smaller than the diameter of the gauze wire, there emerges an additional TF decay mechanism, which is connected with a fine structure of electrodes [12].

The further increase in the TF decay at frequencies in excess of 20 Hz is connected with distortion of the profile of the electrolyte flow speed upon nearing  $\omega_h$ ;  $W_2(\omega)$  stops being a constant and the characteristic obtained is not TF of the cell in a pure form any longer.

Of special interest from the general physics standpoint is the TF portion below 0.16 Hz, where TF decays as  $\omega^{-1/2}$  and severely differs from expected curve (4). A



**Fig. 2.** Experimental setup: (1) accelerometer, (2) platform of calibration stand, (3) input schematics of relevant electronics.

frequency dependence of TF of this sort can be interpreted theoretically neither in view of results reported in [2–9] nor in the one-dimensional model [1], for the TF decay as approximately  $\sim \omega^{-1/2}$  begins at  $\omega > \omega_D$ .

Thus, the TF we obtained for an electrochemical cell at ultralow frequencies cannot be described adequately by any existing theoretical model for transport phenomena in diffusion systems.

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