

# Electrochemical impedance in ac diagnostics of weakly conducting media

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Impedance ac diagnostics is regularly used to study the transport phenomena in conducting systems of different dimensionalities. A common reason for using ac methods that are more complex than dc methods is the possibility to exclude the influence on the current-voltage ( $I$ - $V$ ) characteristic of contact phenomena accompanying dc measurements. In some cases ( $2d$  electron systems over helium) dc transport measurements are impossible. In weakly doped semiconductors (diluted electrolytes), the situation is less critical, but problems with the ohmic properties of the conducting contacts remain. The analysis of the details of the formalism that determines the reaction of a conducting medium to an external disturbance depends largely on the form of Ohm's law for a conductor introduced into the impedance circuit. If there is a reason to define this law by the formula  $\mathbf{j} = \sigma \mathbf{E}$ , where  $\mathbf{j}$ ,  $\sigma$ ,  $\mathbf{E}$  correspond to local values of current density, conductivity, and transport electric field, the structure of complex resistance  $\hat{Z}_F(\omega)$  is considered as a force one. If there is a diffusion component in Ohm's law then the structure of complex resistance  $\hat{Z}_\mu(\omega)$  is considered as an electrochemical one. We describe a standard electrolytic capacitor in series  $RC$  with a step load in terms of force or complex electrochemical impedance. Comparison with experiment shows the electrochemical structure of the complex resistance.

Keywords: transport phenomena, current density, conductivity, electrochemical impedance, Ohm's law.

## Introduction

The behavior of conducting systems of different dimensionalities in an alternating exciting field is regularly studied using impedance ac diagnostics. A common reason for this method, more complicated than methodological possibilities in the dc regime, is the possibility to exclude the influence of contact phenomena accompanying dc measurements on the current-voltage ( $I$ - $V$ ) characteristic. In some cases ( $2d$  electron systems over helium [1–3]) dc transport measurements are impossible. In semiconductor structures, the situation is less critical, but problems with the ohmic properties of the conducting contacts remain [4, 5].

The complex resistance  $\hat{Z}(\omega)$ , which determines the reaction of a conducting medium to an external perturbation, essentially depends on the form of Ohm's law for a con-

ductor introduced into an impedance circuit. If there are reasons for writing it as  $\mathbf{j} = \sigma \mathbf{E}$ , we call the structure of complex resistance  $\hat{Z}_F(\omega)$  the force one. If there is a diffusion component in Ohm's law, then we call this structure of  $\hat{Z}_\mu(\omega)$  electrochemical.

For weakly doped semiconductors and dilute electrolytes, the force interpretation of ohmic conductivity is generally accepted. Homogeneous electric field  $\mathbf{E}$  in Ohm's law  $\mathbf{j} = \sigma \mathbf{E}$  does not violate the constancy of the average density of charge carriers in the volume of a three-dimensional conducting medium. This property allows linear transport calculations, taking the field  $\mathbf{E}(t)$  as the initial perturbation (in practice, the perturbation is the potential difference  $V_g(t)$  between the control electrodes). The local current density  $\mathbf{j}(t)$  caused by the external field is also homogeneous [5]. Recent measurements of  $\hat{Z}_F(\omega)$  in dilute

colloidal solutions are discussed in [6, 7] (in [6], the Wayne Kerr bridge 6425A was used, in [7], it was the LCR meter, HP484A at  $\omega \sim 150$  kHz, at which the imaginary part of the impedance disappears).

Experimental data [8–10] shows that in the mode of step loading  $V_g(t) = V_0 \theta(t)$  [ $\theta(t \leq 0) = 0$ ,  $\theta(t > 0) = 1$ ] the characteristic relaxation times  $\tau_\infty$  are much higher than expected  $\tilde{\tau}_{\text{out}}$  in the force interpretation  $\hat{Z}_F(\omega)$  [definitions of times  $\tilde{\tau}_{\text{out}}$  and  $\tau_\infty$  are given below, formulas (3) and (11)]. The statement  $\tau_\infty \gg \tilde{\tau}_{\text{out}}$  also arises in the study of relaxation phenomena accompanying the loss of stability of a charged liquid surface in an external electric field and is discussed separately [11]. The experimental behavior of a standard electrolytic capacitor in a stepwise loading regime in terms of force  $\hat{Z}_F(\omega)$  or electrochemical  $\hat{Z}_\mu(\omega)$  structures of complex resistances is considered in this work.

### 1. Impedances $\hat{Z}_F(\omega)$ and $\hat{Z}_\mu(\omega)$ for an electrolytic capacitor under a stepwise load

The complex resistance in Ohm's law  $V_g(t) = \hat{Z} J(t)$  is usually called impedance  $\hat{Z}$  [12]. If the perturbation  $V_g(t)$  is harmonic with a frequency  $\omega$ , the Ohm's law takes the form

$$V_g(\omega) = \hat{Z}(\omega) J(\omega), \quad (1)$$

where  $\hat{Z}(\omega)$  is the complex impedance of the conducting structure. In the general case of nonharmonic perturbations, the concept of impedance keeps its meaning as a linear relationship between  $V_g(t)$  and  $J(t)$ .

A. Let us consider an impedance circuit shown in Fig. 1, containing a voltage source  $V_g(t) = V_0 f(t)$  [ $V_0$  is the amplitude of the disturbance,  $f(t)$  is the time dependence of this perturbation, stepwise or harmonic], external resistances  $R_i$  and a flat capacitor  $C_d$  which can be filled with a dilute electrolyte.

The experimental data for the total displacement charges  $Q_i(V_0, t)$  ( $i = A, B, C$  in Fig. 2), getting on the capacitor electrodes in Fig. 1 under step perturbation  $V_g(t) = V_0 \theta(t)$  allows to verify the theory predictions in zones “1” and “2” marked in Fig. 3 and Table 1. Index “ $i$ ” denotes the values of external resistances  $R_i$  used when performing the time cycles  $0 < t < \infty$ .

The RC impedance equation for  $Q_F(t)$  in the “force approximation” has the form [12]

$$R_0 \frac{dQ_F}{dt} + \frac{Q_F}{C_d} = V_g(t). \quad (2)$$

Here  $R_0$  is one of the resistances  $R_i$  of the circuit in Fig. 1,  $C_d \propto d^{-1}$  is the geometric capacitance of an empty capacitor,  $d$  is the distance between its plates and  $V_g(t)$  is the voltage applied to the circuit. The term “force approximation” introduced above means that the transport component (first term) of Eq. (2) follows the Ohm's law in the form  $E_R = R_0 J$ , where  $J = dQ_F / dt$ . We are looking for a solution of Eq. (2) first in the case of an empty capacitor, and

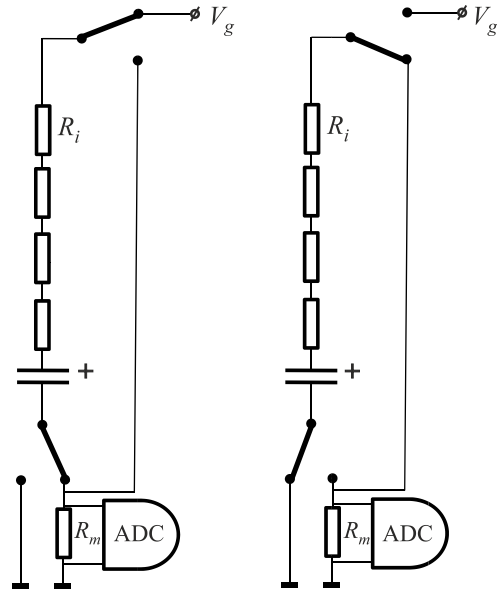


Fig. 1. Circuit diagram with electrolytic capacitor  $C_d$  and calibrated external resistances  $R_i$  (precision resistors of the C2-29 type, high-precision with a low-temperature coefficient of resistance) for measuring the RC constant by short-circuiting the corresponding resistors. The left side circuit corresponds to charging the capacity  $C_d$  from the voltage source  $V_g(t)$ , the right side one corresponds to its discharge (the contact position changes). The time-dependent values of the total charge  $Q(t)$  on the capacitor plates are calculated using the data on current flow through the reference resistance  $R_m = 24.9$  Ohm and their subsequent ADC (Analog-to-Digital Converter) processing (the abbreviation is explained in the text of the work). The obtained values of  $Q(t)$  are presented in Fig. 2.

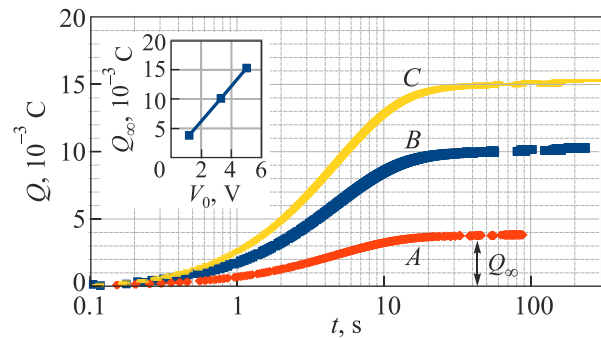


Fig. 2. Dependence of the charge  $Q(t)$  [C] on the logarithm of time [s] in the cell Fig. 1 under the stepwise loading of the capacitor with different voltage gates:  $V_0 = 1.2$  (A), 3.3 (B), 5.0 (C) V; external circuit resistance is 1592.9 Ohm. Vertical arrows explain the  $Q_\infty$  definition used in the text to construct dimensionless quantities. The inset shows the dependence of  $Q_\infty$  on  $V_0$ , emphasizing the linearity of the considered relaxation processes in this region (nonlinear effects start for this type of capacitors in the region  $V_0 > 10$  V). Each line  $Q(t)$  at a fixed voltage gate  $V_0$  is recorded 4 times in 2 charge-discharge cycles, so the points on the graphs belong to 4 curves. The hysteresis of characteristics in the charge-discharge cycle was not observed.

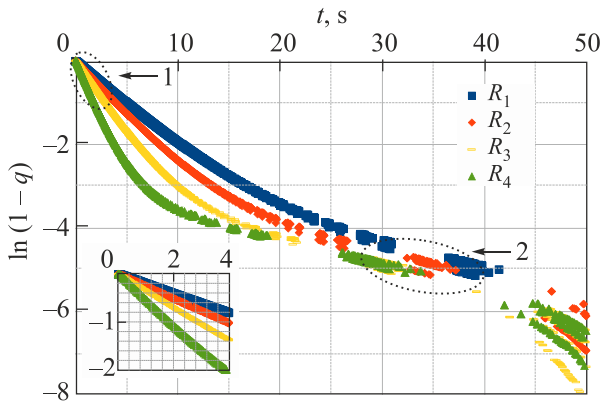


Fig. 3. Representation of the function  $Q_i(V_0, t)$  (Fig. 2) in the coordinates  $(\ln [1 - q_i(t)], t)$  (13), voltage gates  $V_0 = 1.2$  V. External resistance value  $R_i$ :  $R_1 = 1592.9$  (squares),  $R_2 = 1260.9$  (rhombuses),  $R_3 = 928.9$  (stars),  $R_4 = 569.9$  (triangles) Ohm. The curves indicate the formation of two regimes corresponding to the relaxation behavior of  $Q_i(V_0, t)$  function. Scenario (9) takes place in zone “1”. Scenario (11) — in zone “2”. The parameters:  $\tau_\lambda^i$ ,  $C_\lambda^i$ ,  $\tau_\infty^i$  are obtained by processing the linear parts of the graphs using a numerical procedure for determining the derivatives (see text for the details). The corresponding numbers are gathered in the Table 1.

then its generalization to a filled with dilute electrolyte one. Two types of external perturbation of a system with a dilute electrolyte are discussed: stepwise and sinusoidal. These forms of external perturbation are appropriate for showing the difference between two approximations [“force”  $\hat{Z}_F(\omega)$  and “electrochemical”  $\hat{Z}_\mu(\omega)$ ] describing the impedance properties of a dilute electrolyte.

The solution  $Q_F^0(t)$  of the Eq. (2) defines the impedance  $\hat{Z}_F(t)$ . Without electrolyte it reads

$$Q_F^0(t) = C_d V_0 [1 - \exp(-t / \tau_{out})], \quad Q_F^0(0) = 0, \quad \tau_{out} = R_0 C_d. \quad (3)$$

To show the difference between the impedances of  $\hat{Z}_F(\omega)$  and  $\hat{Z}_\mu(\omega)$  in a capacitor filled with electrolyte, it is convenient to know the relaxation time  $\tau_{out}$  (3).

Table 1. Data processing of Figs. 3 and 4, corresponding to different values of control gates:  $V_0 = 1.2$  and 3.3 V [ $R_i$  is the values of the external resistances, the times  $\tau_\lambda^i$  represented by formulae (9), the values of  $C_\lambda^i$  determined by the formula  $C_\lambda^i = \tau_\lambda^i / R_i$ , the times  $\tau_\infty^i$  defined by formulae (11)]

$V_0 = 1.2$ V				
$R_i$ , Ohm	569.9	928.9	1260.9	1592.9
$\tau_\lambda^i$ , s	$1.797 \pm 0.015$	$2.800 \pm 0.012$	$3.817 \pm 0.020$	$4.848 \pm 0.029$
$\tau_\infty^i$ , s	$17.4 \pm 2.1$	$14.8 \pm 1.7$	$14.2 \pm 1.7$	$15.6 \pm 3.8$
$C_\lambda^i$ , $10^{-3}$ F	$3.15 \pm 0.03$	$3.01 \pm 0.03$	$3.03 \pm 0.02$	$3.04 \pm 0.02$
$V_0 = 3.3$ V				
$R_i$ , Ohm	569.9	928.9	1260.9	1592.9
$\tau_\lambda^i$ , s	$1.829 \pm 0.010$	$2.873 \pm 0.022$	$3.905 \pm 0.016$	$4.987 \pm 0.045$
$\tau_\infty^i$ , s	$43.7 \pm 9.7$	$44.7 \pm 8.0$	$46.8 \pm 12.0$	$51.5 \pm 20.0$
$C_\lambda^i$ , $10^{-3}$ F	$3.21 \pm 0.02$	$3.09 \pm 0.02$	$3.10 \pm 0.02$	$3.13 \pm 0.03$

Filling the capacitor with electrolyte changes the problem. First, its volume is filled with a dielectric with a constant  $\epsilon$ , which is the real part of the dielectric constant of the electrolyte at low frequencies (formally, at a frequency tending to zero). This almost instantaneous change of capacity can be easily taken into account by the replacement  $C_d \rightarrow C_d^e = \epsilon C_d$ . Secondly, simultaneously with the voltage drop in the outer section of the circuit, a similar process occurs in the volume of the electrolyte. Taking it into account leads to corrections of the form  $R_{in} dQ/dt$  to Eq. (2), where  $R_{in}$  is the internal resistance of the electrolyte volume. Third, from the moment the external disturbance  $V_g(t)$  is switched on, the process of its screening by electrolyte ions begins, which changes the capacity  $C(t)$  with time. With the replacements  $R_0 \rightarrow R(t)$  and  $C_d^e \rightarrow C(t)$ , problem (2) becomes more complicated, turning into a system of equations. The definitions that control the behavior of  $R(t)$  and  $C(t)$  arise depending on the amplitude of the external perturbation  $V_g(t)$ . The resulting changes in the behavior of  $Q_F(t)$  in comparison with  $Q_F^0(t)$  (3) give an idea about the transport properties of the electrolyte in the force approximation.

The definition of the capacitance  $C(t)$  has the following structure [12]:

$$C(t) \tilde{V}_g^2(t) / 2 = \int_{-d}^{+d} \frac{\tilde{E}^2(x, t)}{8\pi} dx, \quad \tilde{V}_g(t) = V_g(t) - R_{out}(t) \frac{dQ_F}{dt}, \quad (4)$$

where  $\tilde{E}(x, t)$ ,  $\tilde{V}_g(t)$  are the electric field distribution and perturbation in bulk electrolyte. In the force approximation, the behavior of  $\tilde{E}(x, t)$  follows from the definitions [10, 11]

$$d\sigma_F(t) / dt + \sigma_{eff} [\tilde{E}(t) - 4\pi\sigma_F(t)] = 0, \quad \sigma_{eff} = (\sigma_+ + \sigma_-), \quad \sigma_F(t) = en_s(t), \quad (5)$$

and using the force approximation simplifications

$$en_s^\pm - j(0) = 0, \quad n_s^\pm = \int_0^d \delta n_\pm(x) dx, \quad j(0) \propto (\tilde{E} - 4\pi en_s), \quad (6)$$

$$\sigma_{\text{eff}} \simeq \tau_{\text{Maxw}}^{-1}, \quad \tilde{E}(t) = \tilde{V}_g(t) / \varepsilon d, \quad t > 0, \quad Q_F(t) = en_s(t)S. \quad (7)$$

In the force scenario of relaxation, the ion current in the volume of the capacitor does not depend on coordinates; therefore, its value  $j(x)$  can be taken at any point, for example, in the center of the cell, where  $x = 0$ , i.e.,  $j(0) \equiv j(x = 0)$ . The external field is screened by the electrolyte ions so the charge density  $\delta n_\pm(x)$  at the edges of the cell increases forming so-called accumulation layers with surface ion density  $n_s^\pm$ .  $S$  is the surface of the gate electrodes,  $\sigma_{\text{eff}}$  is the effective electrolyte conductivity with contributions  $\sigma_+$  and  $\sigma_-$  ions of different charges.  $\tau_{\text{Maxw}}$  is so-called Maxwell relaxation time characterizing the rate of relaxation phenomena in bulk electrolyte (see, e.g., [14]). The current definition  $j(0) \propto (\tilde{E} - 4\pi en_s)$  corresponds to the force approximation of relaxation kinetics.

Equation (5) requires the boundary conditions. Let us consider two cases:

(i) The dependence of voltage on time has the form  $V_g(t) = V_0\theta(t)$ , then the filling of accumulation layers starts.

(ii) The dependence of voltage on time has the form  $V_g(t) = V_0 \exp(i\omega t)$ , where  $\omega$  is the excitation frequency.

The asymptotics of the derivative  $d\sigma(t)/dt$  at large times:  $t/\tau_{\text{Maxw}} \gg 1$  or  $\omega t \gg 1$ , in these two cases are qualitatively different.

In the case (i), the charge  $Q(t)$  is determined by two flows: the arrival of charges in the capacitor from the outer part of the circuit with the relaxation time  $\tau_{\text{out}} = R_0 C_d$  (3) and the internal flows in the cell with electrolyte conductivity following the law (8) [10, 11]:

$$\sigma_F(t) \int_0^t \frac{d\sigma_F}{(\tilde{E}(t) - \sigma_F / 4\pi)} = t / \tau_{\text{Maxw}}, \quad \sigma_F(0) = 0, \quad 0 \leq t \leq \tau_{\text{Maxw}} \quad (8)$$

with a relaxation time of the order of  $\tau_{\text{Maxw}}$ .

If  $\tau_{\text{Maxw}} \ll \tau_{\text{out}}$ , the process of filling the capacitor by mobile charges is controlled by the time  $\tau_{\text{Maxw}}$ , the function  $\tilde{E}(t)$  (7) transforms to  $\tilde{E}(t) \rightarrow E = V_0 / (\varepsilon d)$  and formula (8) takes the form

$$\sigma_F(t) = E [1 - \exp(-t / \tau_{\text{Maxw}})] / 4\pi, \quad \sigma_F(0) = 0, \quad 0 \leq t \leq \tau_{\text{Maxw}}. \quad (8a)$$

Under conditions (8), (8a), the function  $C(t)$  (4) can be approximated by the effective capacity  $C_\lambda$  having the scale  $C_\lambda \propto C_d^\varepsilon d / \lambda$ , where  $\lambda$  is the Debye screening length (we assume  $d \gg \lambda$ , typical for electrolyte capacitor).

For evaluating  $C_\lambda$ , it is necessary to go beyond the force approximation, since formally the force limit for the effective capacity  $C(t \rightarrow \infty)$  turns out to be divergent. Thus, the evolution of  $Q_F(t)$  in the area  $\tau_{\text{Maxw}} \leq t \leq \tau_\infty$  is determined by the expression

$$\sigma_F(t) = \tilde{E} [1 - \exp(-t / \tau_\lambda^i)] / 4\pi, \quad \sigma_F(0) = 0, \quad (9)$$

$$\tau_\lambda^i = R_i C_\lambda, \quad C_\lambda \simeq C_d^\varepsilon d / \lambda, \quad \tilde{\tau}_{\text{out}}^i \ll \tau_\lambda^i \ll \tau_\infty.$$

Here  $\tilde{\tau}_{\text{out}}^i$  is the effective relaxation time from (3) taking into account the replacement  $C_d \rightarrow C_d^\varepsilon$ ,  $\tau_\infty$  is the time of electrochemical relaxation (discussed below, see (11)). The relaxation time  $\tau_{\text{Maxw}}$  does not appear in the equations of this scenario, but it determines the transition  $C(t) \rightarrow C_\lambda$ .

The general definition of the capacitance  $C(t)$  (4) depends on the filling rate of the accumulation layers at the edges of the cell. Under the conditions  $0 \leq \tau_{\text{Maxw}} \ll \tilde{\tau}_{\text{out}}$ , the capacitance  $C(t)$  grows rapidly in the interval  $C_d \leq C(t) \leq C_\lambda$ . Subsequently, the growth of the capacitance stops, and the time dependence of Eq. (4) is reduced to its presence in the factors  $\tilde{V}_g^2(t)$  on both sides of definition (4), while the problem of the behavior of the fields  $\tilde{E}(x, t)$  from (4) in the volume of the cell is linear in  $V_g(t)$ . Verification of this important property is presented in the inset of Fig. 2.

The time  $\tau_{\text{Maxw}}$  is an important parameter for the definition of ADC regime activity. If, e.g., we have  $\theta$ -like excitation [regime (i)], the time intervals  $\Delta t_i$  into which the current experiment time is divided to perform intermediate integrations  $\delta Q_i \propto \int j_i dt$ , performed by the ADC, is selected in our case from considerations of  $\Delta t_i \gg \tau_{\text{Maxw}}$ . Thus starting from the zero moment  $t = 0$ , the information about the current value of  $\sigma_F(t)$  is not recorded in the measurements.

In the case (ii) with an oscillating external voltage  $V(t) = V_0 \exp(i\omega t)$ , the possibility of converting  $C(t) \rightarrow C_\lambda$ , allowing serious simplifications (9), is absent. In each cycle, the electrolyte in the cell changes its polarization, as a result the density  $n_s(t)$  of the accumulation layers fluctuates around zero. The situation resembles the problem of the frequency dispersion of the dielectric permittivity of polar dielectrics [13]. In this case, the case (i) corresponds to switching on a permanent electric field in order to determine the static dielectric constant of a molecular liquid (for example, water). The dipole moments of water molecules, initially in chaotic positions, are polarized by an external electric field within a characteristic time  $\tau_{\text{rot}}$ . This time cannot be accurately measured in a stepwise mode. For the liquids with polar molecules and Debye screening length [14], the experiment leads to estimations:  $\tau_{\text{rot}} \sim 10^{-11}$  s. This time determines the position of the observed frequency dispersion of the dielectric constant of polar liquids on the frequency axis.

**B.** The difference in the behavior of functions  $Q_F^0(t)$  (3) and  $Q_F(t)$  (9) gives an understanding of the phenomenon of

the force relaxation in electrolytes. The predictions can be checked for the cells filled with either cryogenic [8] or conventional (pure water) [9, 10] electrolytes with high internal resistance.

It becomes evident, that the relaxation process  $Q_i(t) \rightarrow Q_\infty$  is not finished around the times  $\tau_{\text{Maxw}}$  [or  $\tau_\lambda^i \gg \tau_{\text{Maxw}}$ , where  $\tau_\lambda$  is from (9)]. According to Fig. 2 and their special representation (for clarity) by Figs. 3 and 4, the processes in the “1” zones correspond to the force approximation. But the relaxation process does not decay at long times of the “1” zones, moving to the “2” zones with the characteristic time  $\tau_\infty \tau_\lambda \geq \tilde{\tau}_{\text{out}} \tau_{\text{Maxw}}$ . The reasons for this transformation indicating a significant contribution of the diffusion component of flows to the relaxation process are discussed below. One of the disadvantages of the force interpretation of relaxation process is the simplified concept of the structure of the accumulation layers  $n_s^\pm$ . These two-dimensional formations retain the structure of  $\delta$ -functions along the edge of the cell at all stages of the relaxation process, what was used calculating (6) [10, 11]. In fact, the layers must have a finite thickness of the order of the Debye length  $\lambda_D$  for a given conducting medium. It seems that the force simplification makes sense in any case in the presence of the inequality  $\lambda_D \ll d$ , where  $d$  is the distance between the capacitor electrodes. This consideration makes sense in electrostatics, but it is qualitatively incorrect for an expression for the current density containing the derivatives  $dn_\pm/dx \neq 0$ . To avoid these divergences, it is necessary to use the “electrochemical” approximation instead of the “force” one.

According to the electrochemical approach [10, 11, 15]

$$\begin{aligned} |e|^{-1} j_\pm(\mathbf{r}, t) &= \sigma_0^\pm \nabla \mu_\pm, \\ \mu_\pm(x) &= \pm |e| \varphi(x) + T \ln(n_\pm), \\ \sigma_0^\pm &= |e| n_\pm \zeta_\pm, \end{aligned} \quad (10)$$

where  $\zeta_\pm$  is the ion mobility.

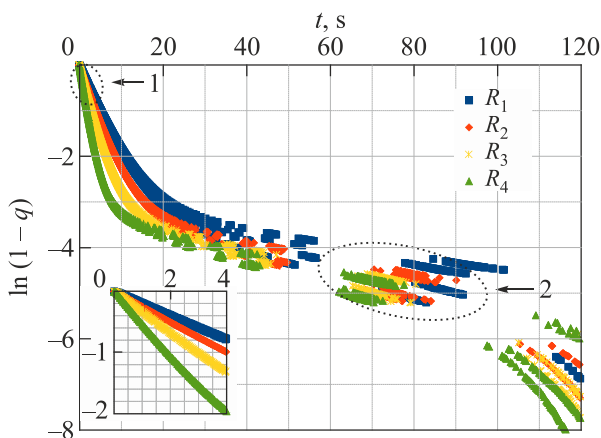


Fig. 4. A set of graphs  $\ln[1 - q_i(t)]$  with formation of regimes: “1” and “2” — at control gate  $V_0 = 3.3$  V. The inset explains the details of the “1” zone (similar to Fig. 3). The center of the zone “2” is oriented towards the saddle points, at which  $d^2Q_i/dt^2$  changes sign (the details are in the Appendix).

The smallness of the fluxes  $j_\pm(t)$  in the ohmic mode agrees with the finiteness of the derivatives  $dn_\pm/dx \neq 0$  if the combination  $\nabla \mu_\pm$  tends to zero near a stationary solution arising at the end of the relaxation process. The same property ensures the finite thickness of the accumulation layers.

The general system of equations that determine the properties of the electrochemical impedance  $\hat{Z}_\mu(\omega)$  consists of the continuity equation for the current  $j_\pm(\mathbf{r}, t)$  and the Poisson–Debye equation, connecting the local values of  $n_\pm(\mathbf{r}, t)$  and the electric potential  $\varphi(\mathbf{r}, t)$  together with the boundary and initial conditions.

These conditions should be sufficient to formulate the problem of electrolyte relaxation in the cell (Fig. 1) from the initial homogeneous state to the final state corresponding to the complete screening of the external perturbation  $V_g(t) = V_0\theta(t)$  in the central part of the cell by the fields of the formed accumulation layers.

Formulation of this problem and its detailed discussion (mainly at the numerical level) is presented in a review work [15], an approximate analytical solution is proposed in [11]:

$$dj/dt = -j/\tau_\infty, \quad j(t \rightarrow \infty) \rightarrow 0, \quad (11)$$

$$\tau_\infty = \frac{e}{\zeta_{(+)} T} \int_0^d ds \int_0^s \exp\left[+\frac{|e| \Phi_\infty(s, \xi)}{T}\right] d\xi, \quad \frac{e}{\zeta_+ T} = \frac{1}{D_+},$$

$$\Phi_\infty(x, s) = [\varphi_\infty(x) - \varphi_\infty(s)].$$

At long times the expression  $\Phi_\infty(x, s)$  can be simplified by replacing  $\varphi(x, t) \rightarrow \varphi_\infty(x)$ .

The relation following from dimensional analysis [15] and verified numerically in the region  $eV/T \leq 1$

$$\tau_\infty / \tau_{\text{Maxw}} \sim L/\lambda \quad (12)$$

illustrates the role of diffusion in the formation of the time  $\tau_\infty$  in comparison with  $\tau_{\text{Maxw}}$ . Obviously, characteristic times (12) emphasize the necessity to take into account the force and diffusion components in the complex solution of problem (10), but the time structure  $\tau_\infty(V_g)$  (11) cannot be suggested by the dimensional analysis.

In the calculations accompanying definitions (11), it was noted that they were obtained in agreement with Einstein’s rules. Expecting manifestations of the diffusion effect on the current density, one could limit ourselves to replacing (8), (9) by (11), leaving further formal calculations. But the conductivity of electrolytes is considered a nonlinear function of the density of mobile charges since the work of Debye, Onsager, Kohlrausch [16–18]. This complication does not affect the picture of evolution (6)–(9), since in structure (8) only the formula  $j(0) \propto (E_\perp - 4\pi en_s)$  is important, which makes sense without any requirement for the properties of conductivity as a function of density. In electrochemistry, this part of the formalism becomes critically important.

The force term  $\pm\sigma|e|\nabla\varphi$  in (10) should be a linear function of the density of mobile particles. These are Einstein's rules relating the coefficients of mobility and diffusion of statistically classical charges. The discord with [16–18] is obvious. The details of the relationship between the  $\hat{Z}_F(\omega)$  and  $\hat{Z}_\mu(\omega)$  regimes take on a meaning beyond the purely “electrolytic” subject. And the correspondence (or not) to the observations of the details of formula (11) allows us to speak about the fulfillment of Einstein's rules in far from gas conditions.

C. Let's process the data  $Q_i(V_0, t)$  [where  $V_g(t) = V_0\theta(t)$ ] in Fig. 2 for comparison with the predictions (3), (9) or (8), (11). The “ $i$ ” index denotes the values of the external resistances used when starting time cycles,  $\tau_\lambda^i < t < \infty$ . For short periods of time in zones “1” (Figs. 3 and 4) appears the influence of the effective capacity  $C_\lambda$ . The last stage of the accumulation layers formation corresponds to zones “2”.

Processing  $Q_i(V_0, t)$  data in coordinates

$$(\ln[1 - q_i(t)], t), \quad q_i(t) = Q_i(V_0, t) / Q_i(V_0, t \rightarrow \infty) \quad (13)$$

is shown in Figs. 3 and 4. In these variables the values of  $\ln[1 - q_i(t)]$  with different external resistances  $R_i$  and the same capacitance values at short times  $t$  have the form of a cluster of straight lines depending on the index “ $i$ ” with the origin at zero. The slope of these lines gives (as expected) an idea of the time scales  $\tau_\lambda^i = R_i C_\lambda$ , where the capacity  $C_\lambda$  is defined by formulas (9). The quality of the estimation of these slopes depends on the observed length of the linear segments of the function  $\ln[1 - q_i(t)]$  (the details of this data processing are discussed in the Appendix). The final results are summarized in the Table 1:

$$C_d^e \ll C_\lambda \simeq C_{\text{pass}} = 3000 \mu\text{F}. \quad (14)$$

It is easy to see from the data in the Table 1 that the reduction general equations (2)–(8) to formula (9) does indeed take place. The measured values of  $C_\lambda$  are close to the passport value  $C_{\text{pass}} = 3000 \mu\text{F}$ , which is much higher than the nominal geometric capacitance of  $C_d^e$ .

At large times when

$$q_i(t) = (1 - \Delta q_i), \quad \Delta q_i \rightarrow 0, \quad \ln \Delta q_i \rightarrow -\infty, \quad (15)$$

the cluster of lines is gathered into a set of asymptotics:  $\ln[1 - q_i(t)] \rightarrow \ln \Delta q_i$  uniformly tending to the region of small values of the logarithm [times over 50 s (Fig. 3) and over 120 s (Fig. 4)].

The asymptotics (15) are preceded by the most important for our work zones “2” in Figs. 3 and 4 (approximately linear areas in the vicinity of 35 s in Fig. 3 and 80 s in Fig. 4; they are marked with dashed ellipses). The times  $\tau_\infty$  are gathered in the Table 1.

Under the conditions  $\lambda_D \ll d$ , accumulation layers are practically formed. The resistance of the medium is predominantly diffusional, which characterizes the proximity of

the electrochemical potential to its stationary value  $\nabla\mu \rightarrow 0$ . Internal resistance begins to exceed all input values  $R_i$ , and therefore the times  $\tau_\infty^i$  cease to depend on  $R_i$  (unlike the zone “1”). From the data of Figs. 3 and 4 one can see the predicted by formulae (11) inequality  $\partial\tau_\infty / \partial V_0 > 0$ .

## 2. Impedances $\hat{Z}_F(\omega)$ and $\hat{Z}_\mu(\omega)$ for the electrolyte in a periodic external perturbation

The Debye–Huckel–Onsager theory [16, 17] contains two corrections to the mobilities of  $\zeta_\pm^{(0)}$  ions in an infinitely dilute electrolyte: relaxation  $\zeta_\pm^{\text{rel}}$  and electrophoretic  $\zeta_\pm^{\text{foret}}$ .

$$\zeta_\pm^{\text{rel}} = -\zeta_\pm^{(0)} \frac{e^2 |z_1 z_2| q}{3\varepsilon T \lambda (1 + \sqrt{q})}, \quad q = \frac{(\zeta_+^{(0)} z_+ - \zeta_-^{(0)} z_-)}{(z_+ - z_-)(\zeta_+^{(0)} + \zeta_-^{(0)})}, \quad (16)$$

$$\zeta_\pm^{\text{foret}} = -\zeta_\pm^{(0)} R_\pm / \lambda. \quad (17)$$

Here  $\zeta_\pm^{(0)}$  is the ions Stokes mobility with the effective radiuses  $R_\pm$ . Formulae (16), (17) are taken from [18], where the results of [16, 17] are reproduced using the correlation properties of the ion system in a charged liquid.

Definitions (16), (17) suggest a nonlinear structure of electrolyte conductivity  $\sigma_\pm = \pm e \zeta_\pm n_\pm$  and, on this basis, a prerequisite for violating Einstein's rules in the argument of Sec. 1. On the other hand, the entire electrochemical literature, represented by the encyclopedic book [5], says that formulae (16), (17) correspond to experimental data on transport in dilute electrolytes. It remains to assume that the discrepancies between the predictions [16, 17], the numerous confirmations of their validity [5] and the contradiction of formulae (16), (17) to Einstein's rules are of a methodological nature. One can talk about Ohm's law in the form  $\sigma_\pm = \pm e \zeta_\pm n_\pm$  but it has to be measured correctly.

As noted in the Introduction, the dc possibilities for transport measurements in dilute electrolytes disappear. The ac methods taking into account (16), (17) correspond to the force interpretation of the impedance  $\hat{Z}_F(\omega)$ . In fact, all impedance circuits provide information about the electrochemical impedance  $\hat{Z}_\mu(\omega)$ , for which the diffusion component is important, as shown above for the step disturbance example. It remains to verify this for the case  $\hat{Z}_\mu(\omega)$  with periodic perturbation.

A. The case of periodic external perturbation  $V_g(t) = V_0 \exp(i\omega t)$  corresponds to the operation mode of the above mentioned standard devices [6, 7] for measuring the ohmic resistance of liquid conductors. Within the framework of approximation (5), in the force approximation for  $\hat{Z}_F(\omega)$  in the region  $eV_0 \ll T$  we have

$$i\omega\sigma = \omega_*[\sigma_0 - \sigma], \quad \omega_* = 4\pi\sigma_{\text{eff}}, \quad \sigma_0 = E_0 / 4\pi,$$

$$(i\omega + \omega_*)\sigma(\omega) = \omega_*\sigma_0, \quad \sigma(\omega) = \frac{\omega_*\sigma_0}{(i\omega + \omega_*)}. \quad (18)$$

The oscillating density  $\sigma(\omega)$  has a familiar relaxation dispersion. Its processing in terms of

$$\operatorname{Re} \sigma(\omega) = \frac{\omega_*^2 \sigma_0}{\omega^2 + \omega_*^2}, \quad \operatorname{Im} \sigma(\omega) = -\frac{\omega \omega_* \sigma_0}{\omega^2 + \omega_*^2} \quad (19)$$

suggests the existence of a relaxation maximum at the frequency  $\omega = \omega_*$ . It follows from the requirement  $\partial \operatorname{Im} \sigma(\omega) / \partial \omega = 0$ .

The equation of motion of a free charged particle in an alternating field is

$$M \left( \frac{dv}{dt} + \frac{v}{\tau} \right) = eE_0 \exp(i\omega t), \quad (20)$$

formally similar to (18), where  $M$  is the effective mass of the charged particle,  $e$  is its charge,  $\tau$  is the appropriate relaxation time. But the constants included here differ in meaning.

Naturally, solutions (18), (20) are used in different areas of physics. The equation of motion (20) is, for example, the fundamental one in the description of the details of a one-particle Brownian motion [19]. On its basis, there is a method for determining the effective mass including the temperature dependence of the effective mass of cations (positive ions) in liquid helium [20]. This phenomena, containing in the interpretation [21, 22] Stokes' predictions made a century ago (see [23], § 20), was experimentally discovered only when studying the dynamic properties of helium ions.

**B.** Simplifications (replacing  $j(x, t) \rightarrow j(t)$  [11]) in the derivation of formula (11) can be avoided in the case of  $eV_0 \ll T$  by writing the solution of Eq. (10) with respect to  $n_+(x, j_+)$  in a more general form:

$$n_+(x, j_+) = n_+^0 \exp\left(+\frac{e\varphi}{T}\right) + \frac{1}{\zeta_+ T} \int_0^x \exp\left[+\frac{|e|\Phi(x, s, t, j)}{T}\right] j_+(s, t) ds, \quad (21)$$

$$\Phi(x, s, t, j) = [\varphi(x, t, j) - \varphi(s, t, j)], \quad 0 \leq x \leq +d.$$

Taking into account (21) in the limit  $e\varphi \ll T$  for the density differences  $\delta n = (n_+ - n_-)$ , we find

$$\delta n \simeq 2n_{\pm}^0 \frac{e\varphi}{T} + \frac{1}{T} \left( \frac{1}{\zeta_+} + \frac{1}{\zeta_-} \right) \int_0^x j_{\pm}(s, t) ds, \quad (22)$$

$$n_+^0 = n_-^0, \quad j_+ = j_-.$$

In the general definition (21), all exponentials are expanded in terms of the small parameter  $e\varphi \ll T$ , in the difference  $\delta n = (n_+ - n_-)$  the terms linear in this parameter are preserved. Substituting (22) into the three-dimensional continuity equation  $\dot{n}_{\pm} + \operatorname{div} \mathbf{j}_{\pm} = 0$  leads to an inhomogeneous parabolic equation with respect to the function  $y(x, t)$ :

$$\frac{\partial}{\partial t} \left[ 2n_{\pm}^0 \frac{e\varphi}{T} + \frac{1}{T} \left( \frac{1}{\zeta_+} + \frac{1}{\zeta_-} \right) y(x, t) \right] = -\frac{\partial^2 y(x, t)}{\partial x^2}, \quad j_{\pm}(d, t) = 0, \quad (23)$$

$$y(x, t) = \int_0^x j_{\pm}(s, t) ds$$

with inhomogeneity  $\propto \partial \varphi / \partial t$  and two boundary conditions: oddness of the function  $y(x, t)$  and  $dy(x = \pm d, t) / dx = 0$ , corresponding to no current flowing through the boundaries  $x = \pm d$ . To solve the problem self-consistently, its analysis should be continued, complementing (23) with the solution of the Poisson equation taking into account (22). This problem again reduces to a second-order differential equation with constant coefficients linking [as in (23)] the functions  $y(x, t)$  and  $\varphi(x, t)$ . General recommendations for solving a system of differential equations are to proceed from an existing pair of second-order equations to one fourth-order equation (see, e.g., [24]). The question of fulfilling the necessary boundary conditions when following [24] remains and is rather complicated. In our case, it is more convenient to keep the system of two equations.

Assuming all functions to be oscillating  $\propto \exp(i\omega t)$  and

$$\int_0^x j_{\pm}(s, t) ds = y(x, t) = \sum_l y_l(t) \sin\left(\frac{\pi l}{2d} x\right), \quad (24)$$

$$\varphi(x, t) = \sum_l \varphi_l(t) \sin\left(\frac{\pi l}{2d} x\right),$$

$$dy(x, t) / dx|_{x=\pm d} = 0, \quad l = 1, 2, 3, \dots; \quad \varphi_l(t) = \sum_{\omega} \varphi_l(\omega) \exp(i\omega t)$$

we get for  $y_l(\omega)$

$$i\omega \left[ 2n_{\pm}^0 \frac{e\varphi_l(\omega)}{T} + \frac{1}{T} \left( \frac{1}{\zeta_+} + \frac{1}{\zeta_-} \right) y_l(\omega) \right] = (\pi l / d)^2 y_l(\omega),$$

or

$$y_l(\omega) = \frac{2i\omega n_{\pm}^0 e^2 \varphi_l(\omega) / T}{i\omega / \tilde{D} + (\pi l / d)^2}, \quad \tilde{D} = \frac{D_+ D_-}{(D_+ + D_-)}. \quad (25)$$

Here the Fourier components  $\varphi_l(\omega)$  have still to be determined. Poisson's equation with  $\delta n$  (22) has the form

$$\Delta \varphi = \frac{\varphi}{\lambda^2} + \tilde{y}(x, t), \quad \tilde{y} = \frac{4\pi e}{\varepsilon T} \left( \frac{1}{\zeta_+} + \frac{1}{\zeta_-} \right) y(x, t), \quad (26)$$

$$\lambda^2 = \frac{\varepsilon T}{8\pi e^2 n_+^0}, \quad \varphi(x, t) = -\varphi(-x, t), \quad \varphi(\pm d, t) = \pm V_g(t). \quad (27)$$

Here  $y(x, t)$  is from (24), (25).

The solution (26), (27) formally has the structure

$$\varphi(x, \omega) = \varphi_0 \sinh(x / \lambda) + \frac{\lambda}{2} \int_0^x \sinh[2(x-s) / \lambda] \tilde{y}(s, t) ds, \quad (28)$$

where the coefficient  $\varphi_0$  is arbitrary and can be obtained from the second of the boundary conditions (27):

$$\varphi_0 \sinh(d/\lambda) + \frac{\lambda}{2} \int_0^d \sinh[2(d-s)/\lambda] \tilde{y}(s,t) ds = V_g(t). \quad (29)$$

Finally, to estimate the coefficients of  $\varphi_l(\omega)$ , we have to use the Fourier transform for the function  $\varphi(x,t)$  (24):

$$\varphi_l(\omega) = \frac{1}{d} \int_0^d \varphi(x,\omega) \sin(2l+1) \frac{\pi x}{d} dx. \quad (30)$$

Here  $\varphi(x,\omega)$  is from (28),  $\tilde{y}(x,t)$  is from (26),  $y(x,t)$  is from (24),  $y_l[\omega, \varphi_l(\omega)]$  is from (25). Equation (30) looks like non-uniform integral equation respectively coefficients  $\varphi_l(\omega)$ .

The partial solution (21)–(30) of the problem of the electrolytic capacitor behavior with variable voltage  $V_g(t) = V_0 \exp(i\omega t)$  on its metal plates [Eq. (30) is not solved], allows to see the qualitative difference in the self-consistent solution details of this problem and the approximation applied in [16, 17]. Scenario (21)–(30) shows that what happens in the capacitor volume depends on the potential difference at the control electrodes. The fluxes  $j_{\pm}(x,t)$  (10) in the electrolyte volume, the charge densities  $n_{\pm}(x,t)$  and the self-consistently calculated screening fields are spatially inhomogeneous near the capacitor edges, especially in the limit  $d \gg \lambda$ . The homogeneous part of the problem, which occupies the middle part of the capacitor, practically does not participate in the transport, being screened from external influence by the fields of the accumulating layers. For the formalism [16, 17] without self-consistent consideration of the external perturbation with the final formulae (16), (17) the homogeneity of the external field leading to the electrolyte ions motion is essential. The transport field is homogeneous in the force scenario of ionic relaxation (18), (19), but this approximation is not consistent with the data in Figs. 3 and 4, where it can be seen that it does not describe the case of dilute electrolytes.

The agreement of the experimental data [5] with predictions [16, 17] cannot be a serious argument in favor of the force scenario of transport phenomena in electrolytes [formulae (16), (17) do not fit with Einstein's rules]. In the electrochemical formalism, the question of how to extract mobility data (diffusion coefficients) from impedance measurements remains open [the possibility (19) disappears]. To get the answer, it is necessary to solve for the beginning the integral equation (30).

### 3. Discussion of the results and conclusion

The impedance formalism allows one to formulate relaxation equations for  $Q(t)$  in two cases: either “force” (3)–(9) for  $Q_F(t)$ , or  $Q_{\mu}(t)$  (10), (11) for electrochemical one. The effective “force” relaxation time (9) turns out to be much shorter than the corresponding electrochemical one  $\tau_{\infty}$  from (11). The experimental data (Figs. 3 and 4) confirm these predictions. Comparison of the times  $\tau_{\infty}$  for  $V_0 = 1.2$  and 3.3 V suggests that the dependence of  $\tau_{\infty}$  on  $V_g$  has an electrochemical character.

The conductivity of electrolytes is a nonlinear function of the mobile charges density. This complication does not affect the reasoning (5)–(9) of the force approach, since in their structure only the condition  $j(0) \propto (E_{\perp} - 4\pi en_s)$  (6) is important, but turns out to be unacceptable in the case of the electrochemical approach [details around formulae (10), (11)].

The force component  $j_{\pm}^{\text{force}} = \pm \sigma \nabla \varphi$  is also present in the electrochemical determination of the current density, and its properties must remain identical in both scenarios. However, in the electrochemical approach, this contribution must be linear with respect to the density of mobile charges. This follows from Einstein's rules relating the mobility and diffusion coefficient of statistically classical charges. The disagreement with [16–18] is obvious. The details of the transition between the  $\hat{Z}_F(\omega)$  and  $\hat{Z}_{\mu}(\omega)$  regimes are beyond the scope of electrolyte theory and verification of the information contained in formula (11) serves as a criterion for the existence of Einstein's rules.

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## Appendix

### Definition of the function $dQ_{\mu}(t)/dt$ slope in the time zones “1”, “2” (Fig. 3)

The graphs in Fig. 5 show the standard deviations  $\sigma$  (a logarithmic scale) of the function  $Q_{\mu}(t)$  as a function of time for the measurements Figs. 3 and 4 with the control gate  $V_0 = 1.2$  V. The slope of the plots  $\ln(1 - q_i)(t)$  (numerical differentiation) was determined by a least-squares method with a window of  $n = 20$  measurement points sliding in time. For each point  $j$  a set of measurement points  $[j - n/2; j + n/2]$  was created, for which the linear regression coefficients and the standard deviation  $\sigma$  were calculated. The points where the standard deviation of  $\sigma$  is minimal are taken as the middle of linear sections. The minimum values of  $\sigma$  (deviation from the linear mode) are observed in the region of  $< 10$  s (zone “1”), the next minimum is in the region of 30–40 s (zone “2”).

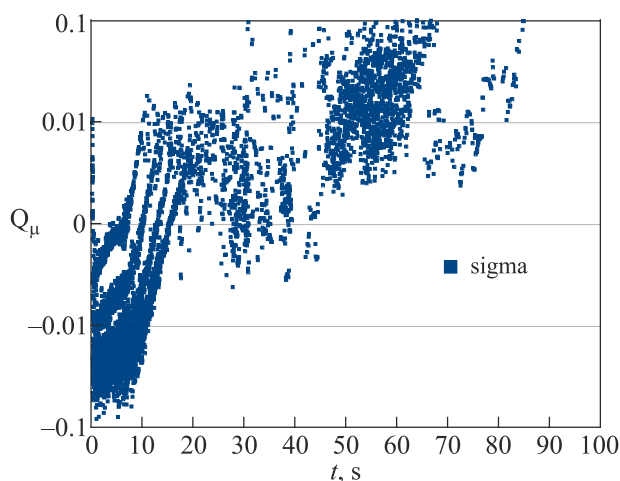


Fig. 5. The standard deviations  $\sigma$  (a logarithmic scale) of the function  $Q_{\mu}(t)$  as a function of time for the measurements Fig. 3. Minima are observed in the region of  $< 10$  s (zone “1”) and in the region of 30–40 s (zone “2”).

## Електрохімічний імпеданс в ас-діагностиці слабопровідних систем

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Імпедансна ас-діагностика регулярно залучається до дослідження транспортних явищ в провідних середовищах різної мірності. Загальною причиною, яка змушує вдаватися до ас-ускладнень на тлі порівняно простих методичних можливостей в dc-режимі, є бажання виключити вплив на вольтамперні ( $I$ - $V$ ) характеристики контактних явищ, що супроводжують dc-вимірювання. У деяких випадках ( $2d$ -електрони над гелієм) dc транспортні вимірювання є принципово неможливими. У слаболегованих напівпровідниках (розбавлених електролітах) ситуація менш критична, але проблеми з омичністю контактів зберігаються. Аналіз деталей імпедансного формалізму, що визначає реакцію провідного середовища на зовнішнє збурення, у значній мірі залежить від форми закону Ома для провідника, що впроваджується в імпедансний ланцюг. Якщо є підстави для його визначення формулою  $\mathbf{j} = \sigma \mathbf{E}$ , де  $\mathbf{j}$ ,  $\sigma$ ,  $\mathbf{E}$  відповідають локальним значенням густини струму, провідності й транспортного електричного поля, структура комплексного опору  $\hat{Z}_F(\omega)$  вважається силовою. При наявності в законі Ома дифузійної складової, мова йде про електрохімічний імпеданс  $\hat{Z}_{\mu}(\omega)$ . У даній роботі на простому прикладі — стандартний електролітичний конденсатор у послідовному  $RC$  ланцюжку при ступінчатому навантаженні — обговорюються можливості опису спостережуваних ефектів із залученням  $\hat{Z}_F(\omega)$  або  $\hat{Z}_{\mu}(\omega)$ . Порівняння з експериментом свідчить на користь  $\hat{Z}_{\mu}(\omega)$ .

Ключові слова: транспортні явища, густина струму, провідність, електрохімічний потенціал, закон Ома.