ASYMMETRY OF ELECTRODE ARRANGEMENT AS THE REASON FOR THE SCATTER IN THE MEASURED ELECTROCHEMICAL IMPEDANCE

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An asymmetric electrode arrangement can cause significant errors in measurements of the electrochemical impedance, as was first pointed out by Grahame [1]. Damaskin and Nikolaeva-Fedorovich [2] offered a qualitative treatment of this effect for a system of electrodes consisting of two regions having different electrolyte resistivities; however, no quantitative analysis was given for real electrochemical cells. Below, we examine the suppression of the scatter in measurements of the input impedance of a system consisting of a cylindrical test electrode and an auxiliary electrode parallel to it. Figure 1 shows a horizontal view of this system.

For simplicity we assume that the boundary effects at the ends of the electrodes can be neglected and that the plane electrode and electrolyte are infinite; in addition we assume the current lines are uniform along the height of the cylinder and plate. Under these conditions, the problem reduces to that of finding the current lines in the plane of the diagram; i.e., ultimately to the familiar solution of the two-dimensional equation for an electrostatic field [3, 4]. Then the current lines are circles passing through a point with the coordinates $(\sqrt{l^2-a^2}, 0)$, whose centers are on the y axis. Then the intersection of the current lines gives the position of the electrical axis of the cylinder.

If the electrode–electrolyte interface has no electrical resistance, the total impedance of the system is equal to the electrolyte resistance, and can be calculated. For this purpose, we use the expression obtained by Kadaner [3] for the conductivity of a current tube emanating from a surface element hds of the cylindrical electrode, where ds is an element of the circular arc of the cylinder:

$$dG = \frac{A}{a}\cdot\frac{ds}{x}, \tag{1}$$

where $A = h\varkappa\sqrt{l^2-a^2}/\ln[(l+\sqrt{l^2-a^2})/a]$; h is the height of the cylinder, and $\varkappa$ is the conductivity. Writing the differential equation for the cylinder circle in these coordinates as $ydy = (l-x)\,dx$, we find $ds = a[a^2-(l-x)^2]^{-1/2}dx$; from this we find

$$dG = \frac{A\,dx}{x\sqrt{a^2-(l-x)^2}}. \tag{2}$$

Integrating (2) from $x = l-a$ to $x = l+a$, and taking half the result, we find the familiar expression for the conductivity of the medium between a cylinder and a plane:

$$G = 2A\int_{l-a}^{l+a}\frac{dx}{x\sqrt{a^2-(l-x)^2}} = \frac{2A}{\sqrt{l^2-a^2}}\arcsin\frac{a^2+lx-l^2}{ax}\Bigg|_{l-a}^{l+a} = \frac{2\pi A}{\sqrt{l^2-a^2}} \tag{3}$$

The same result can be obtained by writing the conductivity of the current tube emanating from a surface element hdy of the plane electrode in the form [3]

$$dG = 2A\frac{dy}{y^2+l^2-a^2} \tag{4}$$

and integrating this expression from $-\infty$ to $+\infty$.

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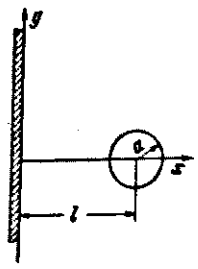


Fig. 1

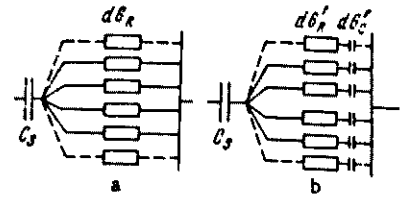


Fig. 2

Fig. 1. Electrode arrangement: a) radius of the cylindrical electrode; 1) distance from the plane electrode to the cylinder axis.

Fig. 2. Equivalent circuits: a) without a double-layer capacitance for the plane electrode; b) with such a capacitance.

Equations (2) and (4) can be used to analyze the behavior of a system of ideally polarizable electrodes in an alternating current. We first assume that there is a double layer with a capacitance per unit area C_d (we assume the plane electrode has no capacitance). Assuming also that the double layer does not affect the shape of the current lines, we can represent each current tube at an element hds of the cylinder surface as a series-connected capacitance

$$c_s = C_d h ds$$

and resistance

$$r_s = ax / A ds.$$

The cotangent of the phase shift in the tube is

$$\omega r_s c_s = \omega a C_d h x / A = \gamma x,$$

where

$$\gamma = \omega a C_d h / A.$$

From this it is not difficult to calculate the capacitive and resistive components of the tube conductivity, on the basis of the equations for transforming from a series to a parallel RC-circuit [5]:

$$dG_C = \frac{\omega C_d h ds}{1+\gamma^2 x^2} = A\gamma \frac{dx}{(1+\gamma^2 x^2)\sqrt{a^2-(l-x)^2}}, \qquad (5)$$

$$dG_R = \frac{A\gamma^2}{a}\frac{x\,ds}{1+\gamma^2 x^2} = A\gamma^2 \frac{x\,dx}{(1+\gamma^2 x^2)\sqrt{a^2-(l-x)^2}}.$$

To integrate Eq. (5), we introduce the notation

$$\lambda = l-a, \qquad \mu = l-a,$$

$$p = \frac{1+\gamma^2\lambda\mu}{1+\gamma^2\mu^2}, \qquad q = \frac{1+\gamma^2\lambda^2}{1+\gamma^2\mu^2} \qquad (6)$$

and make the replacement $x = (t^2\mu+\lambda)/(t^2+1)$. Expanding the fractions by the undetermined-coefficient method [6] and integrating, we find the conductivity components to be

$$G_C = \omega C_p = \frac{4A\gamma}{1+\gamma^2\mu^2}\int_0^\infty \frac{(t^2+1)\,dt}{t^4+2pt^2+q} = \frac{\pi\sqrt{2}\,\gamma A}{1+\gamma^2\mu^2}\cdot\frac{1+\sqrt{q}}{\sqrt{q}\sqrt{p+\sqrt{q}}}, \qquad (7)$$

$$G_R = 1/R_p = \frac{4A\gamma^2\mu}{1+\gamma^2\mu^2}\int_0^\infty \frac{(t^2+\lambda/\mu)\,dt}{t^4+2pt^2+q} = \frac{\pi\sqrt{2}\,\gamma^2\mu A}{1+\gamma^2\mu^2}\cdot\frac{\lambda/\mu+\sqrt{q}}{\sqrt{q}\sqrt{p+\sqrt{q}}}. \qquad (8)$$

Determining the tangent of the phase shift,

$$\omega C_p R_p = \frac{1+\sqrt{q}}{\sqrt{q}+\lambda/\mu}\cdot\frac{1}{\gamma\mu} \qquad (9)$$

and converting from a parallel (R_p, C_p) equivalent circuit to the series one (R_s, C_s) [5], we find the input-impedance components to be

$$C_s = \frac{\pi\sqrt{2}\,ahC_d}{1+\gamma^2\mu^2}\cdot\frac{(\gamma\sqrt{q}+1)^2+\gamma^2\mu^2(\gamma\sqrt{q}+\lambda/\mu)^2}{(\gamma\sqrt{q}+1)\gamma\sqrt{q}\,\gamma\sqrt{p+\gamma q}}, \tag{10}$$

$$R_s = \frac{\mu(1+\gamma^2\mu^2)}{\pi\sqrt{2}\,A}\cdot\frac{(\gamma\sqrt{q}+\lambda/\mu)\gamma\sqrt{q}\,\gamma\sqrt{p+\gamma q}}{(\gamma\sqrt{q}+1)^2+\gamma^2\mu^2(\gamma\sqrt{q}+\lambda/\mu)^2}. \tag{11}$$

The measured capacitance and resistance C_s and R_s thus in principle depend on the frequency. The limiting values of these quantities are the most interesting: as $\omega\to 0$, when $\gamma\ll 1$; $p = 1$; $\sqrt{q} = 1$, we have

$$C_s = 2\pi ahC_d \tag{12}$$

$$R_s = l/2\pi A$$

as $\omega\to\infty$, with $\gamma\gg 1$, $\sqrt{q} = \lambda/\mu$, $p = \lambda/\mu$, we have

$$C_s = 2\pi ahC_d\sqrt{l^2-a^2}/l \tag{13}$$

$$R_s = \sqrt{l^2-a^2}/2\pi A.$$

In other words, the range over which the input capacitance and resistance of the system vary is governed by the difference l^2-a^2. If $\sqrt{l^2-a^2}\simeq l$, we see that C_s and R_s do not depend on the frequency and are given by

$$C_s = 2\pi ahC_d \tag{14}$$

$$R_s = l/2\pi A;$$

i.e., the asymmetry of the electrode arrangement in this case does not affect the measured input impedance, and the equivalent circuit is that shown in Fig. 2a. It is not difficult to see that the condition $\sqrt{l^2-a^2}\simeq l$, is equivalent to the inequality $l \geq 10\,a$ and is thus essentially always satisfied in real cells.

We can use this result to take into account the presence of a double layer on the auxiliary (plane) electrode. For this purpose we represent the overall cell circuit as shown in Fig. 2b and assume that the impedance of each current tube can be written, on the basis of Eq. (4), as a series-connected resistance

$$r_s' = \frac{l^2+y^2}{2A\,dy} \tag{15}$$

and capacitance

$$c_s' = hC_d'\,dy, \tag{16}$$

where C_d' is the double-layer capacitance per unit area for the interface between the plane electrode and the electrolyte. Repeating the calculation procedure above, we find

$$dG_c' = \frac{2A}{\delta}\cdot\frac{dy}{y^4+2l^2y^2+(l^4+\delta^{-2})} \tag{17}$$

$$dG_s' = 2A\cdot\frac{(l^2+y^2)\,dy}{y^4+2l^2y^2+(l^4+\delta^{-2})}, \tag{18}$$

where

$$\delta = \omega hC_d'/2A.$$

After integrating from 0 to ∞ and taking half the result, we easily find (converting to the series RC circuit)

$$C_s' = 2\pi A\cdot\frac{1+\delta^2(l^2+s)^2}{\omega\delta s\sqrt{2\sqrt{l^2+s}}},$$

$$R_s' = \frac{s\sqrt{2\sqrt{l^2+s}}}{2\pi A\,(l^2+s)}\cdot\frac{\delta^2(l^2+s)^2}{1+\delta^2(l^2+s)^2}, \tag{19}$$

$$\omega C_s'R_s' = \delta(l_2+s)$$

where

$$s = \frac{\sqrt{1 + \delta^2 l^4}}{\delta}.$$

As $\omega \to 0$ and for $\delta \ll 1$, we have $s = 1/\delta, \sqrt{l^2 + s} = 1/\sqrt{\delta}$, and

$$C_s' = \frac{2\pi}{\sqrt{\omega}} \sqrt{hC_d A}, \qquad R_s' = \frac{1}{2\pi\sqrt{\omega}} \cdot \frac{1}{\sqrt{hC_d A}} \tag{20}$$

In other words, at sufficiently low frequencies this system has the properties of a line with uniformly distributed parameters (a Warburg impedance). If C_S' is much larger than the double-layer capacitance C_s of the cylindrical electrode, the capacitive component of the input impedance will be governed entirely by the latter; i.e., the capacitance measured will be equal to C_S. On the other hand, the resistive component of the measured impedance is equal to R_S' in this case; i.e., it depends strongly on the frequency. This frequency dependence has been noted several times in the literature [7, 8] for a system of electrodes in which a mercury pool was the auxiliary electrode. At sufficiently high frequencies, when $\delta \gg 1$ and $s = l^2$ and $\sqrt{l^2 + s} = l\sqrt{2}$, the measured capacitance and resistance acquire the limiting values

$$C_s' = 2\pi h l C_d', \qquad R_s' = l / 2\pi A. \tag{21}$$

Here C_S' remains much larger than C_S and as before can be neglected, while the resistance reaches its value in the absence of a capacitive impedance at the interfaces.

An asymmetry in the electrode arrangement thus does not lead to large errors if the purpose of the measurement is to determine the capacitance of the electrical double layer on an ideally polarizable electrode. It is only necessary that the test electrode be sufficiently small in comparison with the auxiliary electrode. However, the situation is complicated considerably if it is necessary to analyze the frequency dependence of the impedance (in a study of the kinetics of chemical reactions or of adsorption), since in this case the scatter in the resistance measurements due to the asymmetry superimposed on that due to the electrode processes makes it essentially impossible to analyze these processes. This is evidently true not only of the cylinder–plane system but also of analogous systems, e.g., the sphere–plane system.

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