INFLUENCE OF LEADS IN MEASUREMENTS OF ELECTROCHEMICAL-CELL IMPEDANCE

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In measuring electrochemical impedance, it is necessary to take into account the distortions introduced by the impedance of the connecting leads and conductors. It is generally assumed that this impedance can be treated as a concentrated inductance connected in series with the cell [1, 2], but this does not always reflect the actual situation. In measurements at high frequencies and with large electrolyte resistances (e.g., in working with solid electrolytes, nonaqueous solutions, etc.), reduction of the lead impedance to an inductance results in pronounced errors. The best way to eliminate the distorting influence of the leads is obviously to shorten them and to use special compensating circuits [3, 4]. However, this cannot always be done. It is therefore important to have reliable methods for estimating the distortions introduced.

Two parallel leads separated by a sufficiently short distance can be treated as a homogeneous two-conductor line (Fig. 1). A segment of this line at a distance x from its origin and having a length dx can be characterized by the interlead capacitance c_0dx, active conductivity g_0dx, and inductance l_0dx, and the active resistance r_0dx, where c_0, g_0, l_0, and r_0 are the parameters of a unit line length. The equivalent circuit in Fig. 1 provides a good description of real two-conductor lines so long as the distance between the two leads remains materially less than the wavelength of the fluctuations in the electromagnetic field. This condition is usually satisfied up to frequencies of several tens of MHz. The differential equations for a homogeneous line have the form

$$-\frac{d\dot{U}}{dx} = (r_0 + j\omega l_0)\,\dot{I},$$
$$-\frac{d\dot{I}}{dx} = (g_0 + j\omega c_0)\,\dot{U}, \tag{1}$$

where $\dot{U}$ and $\dot{I}$ are the complex amplitudes of the voltage and current during harmonic oscillations (see, e.g., [5]). The solutions of these equations are well known and have the form [6]:

$$\dot{U}_b = \dot{U}_e \operatorname{ch}\gamma s + \dot{I}_e Z_в \operatorname{sh}\gamma s,$$
$$\dot{I}_b = \frac{\dot{U}_e}{Z_в}\operatorname{sh}\gamma s + \dot{I}_e \operatorname{ch}\gamma s, \tag{2}$$

where the subscripts b and e indicate the beginning and end of a line of length s. In addition,

$$\gamma = [(r_0 + j\omega l_0)(g_0 + j\omega c_0)]^{1/2},$$
$$Z_в = [(r_0 + j\omega l_0) / (g_0 + j\omega c_0)]^{1/2}. \tag{3}$$

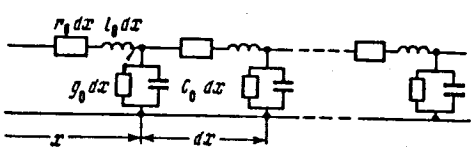


Fig. 1. Equivalent circuit of homogeneous line.

The input impedance of the line $Z_{in} = U_b/I_b$, if its end is connected to an electrochemical cell with an impedance $Z_c = U_e/I_e$, is

$$Z_{in} = Z_в \frac{Z_c + Z_в \operatorname{th}\gamma s}{Z_в + Z_c \operatorname{th}\gamma s}. \tag{4}$$

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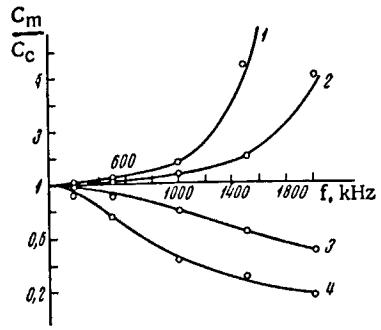


Fig. 2. Influence of lead impedance on measured capacitance of RC model; $L_1 = 0.565\ \mu H$, $C_1 = 23$ nF; 1) $C_c = 2 \cdot 10^4$ nF, $R_c = 50\ \Omega$; 2) $C_c = 10^4$ nF, $R_c = 50\ \Omega$; 3) $C_c = 1630$ nF, $R_c = 450\ \Omega$; 4) $C_c = 1630$ nF, $R_c = 930\ \Omega$. The dots represent experimental data, while the curves were calculated from Eq. (11).

With the end of the line disconnected ($Z_c = \infty$) or short-circuited ($Z_c = 0$), we obtain the open-circuit or short-circuit impedances:

$$Z_{oc} = Z_0 / \operatorname{th} \gamma s, \qquad Z_{sc} = Z_0 \operatorname{th} \gamma s. \tag{5}$$

Thus,

$$Z_{in} = Z_{oc} \frac{Z_c + Z_{sc}}{Z_c + Z_{oc}}. \tag{6}$$

Under practical conditions, the leads to the cell should have strictly fixed characteristics. Specifically, there should be no change in the distance between the leads or their relative positions during the measurements. Coaxial cables or other systems of conductors that make contact through a layer of solid dielectric are therefore generally used for this purpose. If leads with a sufficiently ideal insulation (polyethylene, polystyrene, etc.) are used, the specific conductivity remains very low even at high frequencies ($g_0 = 10^{-6}$-10^{-7} mho/m). In most cases, it is also possible to disregard the active resistance of the leads r_0. When the frequency is increased, r_0 rises as a result of the spin effect [6]. It is therefore best to employ multistrand leads with a small individual strand cross section.

When definite prerequisites are satisfied, a two-conductor line thus has a purely reactive impedance and is characterized solely by its inductance and capacitance. The former can reach 0.3-1 μH/m, while the latter can reach 30-100 nF/m. For two parallel round conductors, we have the approximate expressions [6]:

$$l_0 \simeq 0.92 \log [(b-a)/a], \quad \mu H/m$$
$$C_0 \simeq 12.1\varepsilon / \log [(b-a)/a], \quad nF/m$$

where ε is the dielectric constant of the insulation, b is the distance between the leads, and a is the cross-sectional radius of one lead. Since the quantities b_0 and C_0 are sufficiently small,

$$\operatorname{th} \gamma s = j \operatorname{tg} (\omega s \sqrt{l_0 C_0}) = j \left[\omega s \sqrt{l_0 C_0} + \frac{1}{3} (\omega s \sqrt{l_0 C_0})^3 + \ldots \right] \simeq j \omega s \sqrt{l_0 C_0} \tag{7}$$

and, moreover,

$$Z_0 = \sqrt{l_0 / C_0}. \tag{8}$$

Thus, according to Eq. (4),

$$Z_{in} = \frac{Z_c + j\omega s l_0}{1 + j\omega s C_0 Z_c}. \tag{9}$$

Representing Z_{in} in the form $R_{in} + 1/j\omega C_{in}$ and Z_c in the form $R_c + 1/j\omega C_c$ (i.e., using a series circuit), we find

$$\left.\begin{aligned} \frac{1}{\omega C_{in}} &= \frac{m}{m^2+n^2} \frac{1-\omega^2 l_0 s C_c}{\omega C_c} + \frac{n}{m^2+n^2} R_c \\ R_{in} &= \frac{m}{m^2+n^2} R_c - \frac{n}{m^2+n^2} \cdot \frac{1-\omega^2 l_0 s C_c}{\omega C_c} \end{aligned}\right\}, \tag{10}$$

where $m = 1 + C_0 s/C_c$ and $n = \omega C_0 s R_c$.

These equations enable us to take into account with sufficient accuracy the influence of the lead impedance at frequencies of up to 10 MHz. However, they are rather cumbersome and inconvenient for practical calculations. We therefore introduce still another equation, assuming that we can neglect the difference between the parameter m and 1 (which means that the measured capacitance must be rather large in comparison with the lead capacitance). Then

$$C_{in}=\frac{1+(\omega C_1 R_c)^2}{1-\omega^2 L_1 C_c+\omega^2 C_1 C_c R_c^2}C_c$$
$$R_{in}=\frac{R_c}{1+(\omega C_1 R_c)^2} \qquad (11)$$

where $C_l = c_0 s$ and $L_l = l_0 s$.

As can be seen from Eq. (11), R_{in} depends on the factor $\delta_R = \omega^2 C_l^2 R_c^2$. If $C_l = 100$ nF and $R_c = 10^3\ \Omega$, the difference between R_{in} and R_c, which is governed by δ_R, exceeds 1% when $\omega \geq 10^6$ sec^{-1}, i.e., at frequencies of more than 160 kHz. The input capacitance includes two additional correction factors: $\delta_L = \omega^2 L_1 C_c$ and $\delta_C = \omega^2 C_1 C_c R_c^2$. Since $C_c \gg C_1$ under normal conditions, $\delta_C \gg \delta_R$. Because the corrections δ_L and δ_C have different signs in the expression for C_{in}, the final result depends on R_c. At large cell resistances, $\delta_C > \delta_L$ and C_{in} remains less than C_c, decreasing with frequency. Conversely, if $\delta_C < \delta_L$, C_{in} exceeds C_c and increases with the frequency. In ordinary measurements, the correction δ_R remains rather small (no more than a few percent). We can therefore treat the quantities R_{in} and R_c as equal in calculating δ_R without introducing any major error, i.e., assume $\delta_R = (\omega C_l R_c)^2 \simeq (\omega C_1 R_{in})^2$. Equation (11) can then be rewritten in a form convenient for calculation of C_c and R_c from experimental data:

$$C_c=\frac{C_{in}'}{1+\omega^2 L_1 C_{in}'-\omega^2 C_1 C_{in}' R_c^2}$$
$$C_{in}'=C_{in}[1+(\omega C_1 R_{in})^2]^{-1}$$
$$R_c=R_{in}[1+(\omega C_1 R_{in})^2] \qquad (12)$$

The relationships thus derived were checked with the aid of series RC models composed of mica condensors and metal-film resistors. The leads were two wires in polyethylene insulation joined by adhesive tape. The capacitance and inductance of the leads were measured with an E12-1A resonance C-L gage. In accordance with Eqs. (5), (7), and (8), $Z_{oc} = 1/j\omega C_l$ and $Z_{sc} = j\omega L_l$, so that the capacitance was determined under open-circuit conditions and the inductance under short-circuit conditions. They amounted to 23 nF and 0.565 μH, respectively. The input impedance of the "lead-model cell" system was measured with an E10-2 transformer bridge, a G4-18A external generator, and an S1-19B oscillograph as the null indicator. In order to expand the range of the capacitance measurements, the bridge was equipped with an additional air capacitor having a capacitance of 1100 nF. The measurements were made at frequencies between 100 kHz and 2 MHz with a cell voltage of 30 mV. The measurement results were in the form of the parallel components C_p and $1/R_p$ and were then converted to the corresponding figures for a series RC circuit.

As can be seen from Fig. 2, Eq. (11) satisfactorily described the influence of the leads on the measured impedance.

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