MEASURING THE POLARIZATION RESISTANCE OF A METAL UNDER A THIN LAYER OF ELECTROLYTE

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Success in using the polarization resistance method depends on the accuracy with which the possible errors are estimated [1-3].

In this article we attempt to estimate the errors arising in measurements under a thin layer of electrolyte [4-6] and to determine the permissible parameters of the transducers, including bifilar ones [7-10]. The electrodes 1 and 2 of these transducers (Fig. 1) are made in the form of insulated wires double-wound on a frame 3 and freed from the insulation on the side facing the test medium.

In measuring the polarization resistance R_p of a two-electrode circuit it is necessary to take account of the resistance R_s of the electrolyte between the electrodes. In contrast with parallel electrodes [2, 3, 11], with coplanar electrodes the ohmic resistance of the electrolyte between the parts of the electrodes remote from the insulation layers can cause departures from their measurements and corresponding errors in determining the corrosion rate i_c.

There are no literature data on calculation of R_s between coplanar electrodes.

Suppose that a layer of electrolyte with thickness h is present on the surface of a bifilar transducer with electrodes of length l with a working surface of width q and an insulating layer of thickness p. The potential difference between the electrodes is U, and the resistivities of the metal ρ_0 and electrolyte ρ are such that $\rho_0 \ll \rho$. We shall neglect the voltage drop along the electrodes, and to determine the potential distribution within the electrolyte we shall use Laplace's equation [12]

$$\Delta U = 0. \tag{1}$$

We shall assume that the charge is uniformly distributed over the working surfaces of the electrodes. Solving Eq. (1) with these assumptions, we find the resistance of the electrolyte between the electrodes of the bifilar transducer:

$$R_s = \frac{\rho\left[q\ln\left(1+\frac{2p}{q}\right)+2p\ln\left(1+\frac{q}{2p}\right)\right]}{4l\left[h\ln\sqrt{\frac{\left(\frac{q}{2}+\frac{p}{2}\right)^2+h^2}{\left(\frac{p}{2}\right)^2+h^2}}+\frac{q+p}{2}\operatorname{arctg}\frac{2h}{q+p}+\frac{p}{2}\operatorname{arctg}\frac{2h}{p}\right]}. \tag{2}$$

Since the inequalities $q \gg p$ and $h \ll p$ are fairly well satisfied for a bifilar transducer with a thin layer of electrolyte, we get

$$R_s = \frac{\rho p\left(\ln\frac{q}{2p}+1\right)}{2lh\ln\frac{q}{p}}. \tag{3}$$

In the bulk of the electrolyte, we again have $q \gg p$, but $h \gg (q+p)/2$, so that Eq. (2) becomes

$$R_s' = \frac{2\rho p\ln\left(\frac{q}{2p}+1\right)}{\pi lq}. \tag{4}$$

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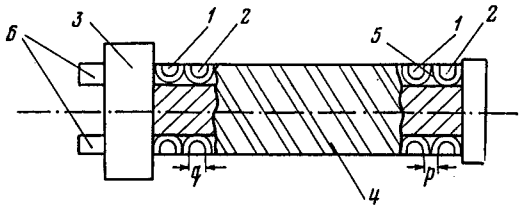

Fig. 1. Bifilar transducer. 1, 2) Electrodes of truncated wire (diameter exaggerated tenfold); 3) frame; 4) electrical insulation layer (thickness exaggerated a hundredfold); 5) epoxy resin; 6) current leads.

Hence we can determine the resistivity of the electrolyte,

$$\rho = \frac{\pi l q R_s'}{2p \ln\left(\frac{q}{2p} + 1\right)}. \tag{5}$$

Suppose that ρ is the same in the electrolyte layer as in the bulk; then from (3) and (5) we get

$$h = \frac{\pi q}{4 \ln \frac{q}{p}} \cdot \frac{R_s'}{R_s}. \tag{6}$$

We experimentally verified Eq. (2) in two ways. Firstly, on five copper bifilar transducers with different parameters we determined the resistance* of a 0.01 N solution of KCl at 20°C with the transducers entirely immersed in the bulk of the electrolyte. From the results we calculated ρ for each transducer by means of Eq. (5) (see Table 1). The mean value of ρ agrees with the tabulated values of this quantity [14], within the experimental error.† This confirms the validity of Eq. (2) in the limiting case of the bulk of the electrolyte ($h \to \infty$).

In the second method, Eq. (2) was checked experimentally by immersing the same transducers in distilled water and measuring R_s (Fig. 2). At the moment marked with an arrow, the transducers were taken out into an atmosphere saturated with water vapor at 25°C. Runoff and evaporation of moisture from the surfaces of the transducers were accompanied by an increase in R_s for all the transducers (curves 1-5).

From the data, by means of Eq. (6) we calculated the thickness of the film of moisture on the surface of the transducers at various times after removal from the bulk of the water (see Table 1). Within the experimental error (10%) the thicknesses of the films of moisture on the different transducers were the same at the same time. In fact, the processes of runoff and evaporation of liquid from the vertical surface of a transducer, and consequently also h, should not depend on the parameters of the transducer. This conclusion also follows from [15]. At the initial moment of time, the values of h calculated by us agree with those predicted in [15].

To determine the range of applicability of coplanar electrodes, let us divide up the surface of each electrode into n parts. The simplest equivalent electrical circuit of the metal–electrolyte boundary in the k-th part can be represented in the form of parallel-connected polarization resistance R_{pk} and polarization capacitance C_{pk} [16].

In ac measurements at a sufficiently high frequency, the C_{pk} shunt R_{pk}, and the whole of the voltage drop is across the ohmic resistance of the transducer,

$$\frac{1}{R_s} = \sum_{k=1}^{n} \frac{1}{R_{sk}}. \tag{7}$$

*We measured R_s with an ac bridge [9] at 4.4 kHz (voltage amplitude 10 mV).
†The mean values were compared with the tabulated values with the aid of the t criterion at the 95% significance level [13].

TABLE 1. Resistivity of 0.01 N Solution of KCl and Thickness of Film of Distilled Water, Calculated from Eqs. (5) and (6)

Transducer No.	ρ at 20°C, Ω·cm	Values of h at various times (in minutes) after extraction of transducers, in μm				
		1	5	10	20	40
1	860	44	23,6	8,6	2,5	0,33
2	730	69	31,0	13,5	3,0	0,38
3	880	62	29,6	12,2	2,6	0,36
4	650	57	27,4	11,0	2,0	0,33
5	510	78	33,0	9,7	1,8	0,29
Mean value and confidence interval	726±191	58±12	30±4	11±2	2,4±0,6	0,34±0,04

If we made dc measurements, on the other hand, the R_{pk} will shunt the polarization capacitances C_{pk}, and the total impedance R_0 of the transducer will be

$$\frac{1}{R_0}=\sum_{k=1}^{n}\frac{1}{2R_{pk}+R_{sk}}. \tag{8}$$

If all n parts of the electrode are perfectly equivalent, i.e., if all the R_{pk} and R_{sk} are equal,* from (7) and (8) we get a simple expression for the total polarization impedance of the electrode,

$$R_p=\frac{R_0-R_s}{2}. \tag{9}$$

In the case of uniform corrosion, the condition of equality of the R_{pk} is satisfied. If the electrodes are coplanar, the values of the R_{sk} depend on the position of the k-th part on the surface of the electrode. Therefore, relation (9) can only hold approximately for a bifilar transducer.

For fixed n, the maximum value of R_{sk} is reached when k = n/2. Therefore, to determine the conditions in which Eq. (9) holds, it is evidently advantageous to compare the sums of the polarization and ohmic impedances in the first and n/2-th sections according to the following inequality:

$$\frac{2R_{pk}+R_{sn/2}}{2R_{pk}+R_{s_1}}\leqslant 1+\delta. \tag{10}$$

The quantity δ characterizes the error in determining R_p by means of Eq. (9) from measurements of R_0 and R_s on the bifilar transducer. Since as well as $R_{sn/2}$ and R_{s_1} there are another (n/2 − 2) ohmic resistances in the gap between the first and n/2-th parts of the electrode surfaces, the real error will be less than δ.

On the basis of the theory of the polarization resistance method [17-19] and Eq. (2), from inequality (10) we get a general relation for the critical parameter of the bifilar transducer,

$$q_{\text{crit}}=\sqrt{\frac{8Kh\delta n}{i_c\rho\ln 2n}}, \tag{11}$$

where K is a coefficient of proportionality between i_c and R_p. If we assume that the systematic and random errors of the method R_p are equal to 10% [20], we can put δ = 0.1, n = 100, and from (11) we then get

$$q_{\text{crit}}=\sqrt{\frac{15Kh}{i_c\rho}}. \tag{12}$$

This relation enables one to get an approximate estimate of the critical parameters ($p_{\text{crit}}\approx 0.1q_{\text{crit}}$) of the bifilar transducer, and with the aid of these we can determine R_p from the experimental data by means of Eq. (9) with an error of less than 10%.

Calculations reveal that in the conditions of the above experiment (Fig. 2), $q_{\text{crit}}\approx 1$ mm. Since at any moment of time the thicknesses of the moisture films on the different trans-

*This case is realized if the working surfaces of the electrodes are parallel and opposite one another.

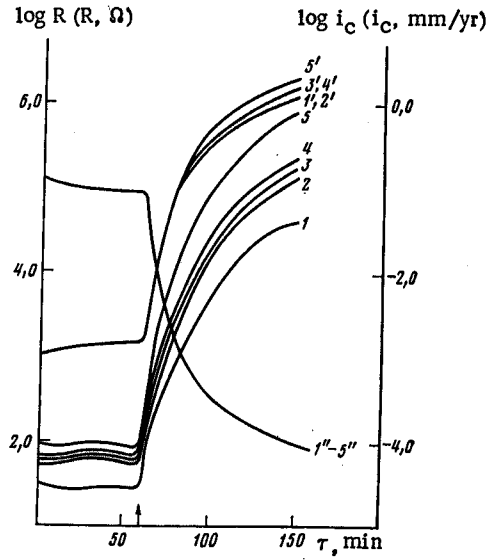

Fig. 2. Corrosion behavior of bifilar copper transducers with various parameters in distilled water and after being taken out (↑) into an atmosphere saturated with water vapor at 25°C. 1-5) log R_s; 1'-5') log R_o; 1"-5") log i_c.

ducers are equal (see Table 1) and do not exceed 0.73 mm, the rates of corrosion of copper on them must also be equal. In fact, by measuring the total impedances of the transducers in direct current* (Fig. 2, curves 1'-5') and calculating R_p by means of Eq. (9), we obtained equal values of i_c for all the transducers (curves 1"-5").

According to Tschapek et al. [22, 23], electrolytes (0.01 N KCl or NaCl solutions, $\rho < 1 \cdot 10^3$ Ω·cm) retain their bulk electrical properties only in layers not less than 0.1 μm thick. We shall take these values of ρ and h as critical. According to our own data [7-10] and those of other authors [4, 24, 25], in films of neutral electrolytes more than 0.1 μm thick, i_c for copper and steel does not exceed 0.1 mm/yr. Substituting these values of i_c, h, and ρ into Eq. (12), we find that bifilar transducers with the parameters $q \leqslant 0.4$ and $p \leqslant 0.04$ mm can measure R_p of copper or steel with an error of less than 10% in practically all cases of atmospheric corrosion.

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*Here R_o was measured with the aid of the device described in [21].

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