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STUDY OF THE RATE OF CORROSION OF METALS BY A FARADAIC DISTORTION METHOD, II

EFFECT OF THE OHMIC RESISTANCE AND CAPACITY OF THE DOUBLE
LAYER ON THE MEASUREMENT OF THE HARMONIC COMPONENTS OF
THE FARADAIC CURRENT

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In our previous communication [1] the theory of a faradaic distortion method has been presented for the study of the rate of corrosion. In the present communication we investigated the applicability of this method to measuring cells employed in practice, namely the effect of the capacity of the double layer and the ohmic resistance of the solution have also been considered in addition to that of the faradaic impedance. The ohmic resistance of the solutions can readily be compensated by a potentiostat permitting the compensation of the total ohmic drop in the cell. The effect of the capacitive current flowing through the double layer can be eliminated by performing measurements at least at two different frequencies and by extrapolating the data to $\omega = 0$ frequency. The capacitive current appears in the fundamental harmonic component of the current only.

In our previous communication [1] a method has been presented for the determination of the rate of corrosion of metals by faradaic distortion assuming that the faradaic impedance only consisted of a resistance having characteristics corresponding to the charge transfer reaction of the anodic and cathodic partial processes. The method is based on the measurement of the harmonic components of the current flowing through the electrode under the effect of a potentiostatically controlled sinusoidal alternating voltage superimposed on the polarizing direct voltage.

The electrochemical parameters of the metal (such as corrosion current and the slopes of the Tafel's equations of the cathodic and anodic processes, respectively) have been calculated on the basis of the measurement of the first three harmonic components of the faradaic alternating current at two potentials, one is the anodic and the other is the cathodic Tafel range, respectively. The electrochemical parameters can also be calculated by the measurement of the harmonic component at the corrosion potential. In the calculation previously reported, the effect of the capacity of the double layer of the electrode and that of the solution resistance between the working electrode and the reference electrode have been left out of consideration.

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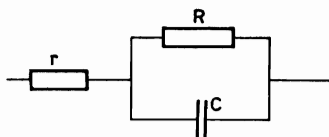


Fig. 1. Equivalent circuit of the electrode

Without these assumptions, the electrode behaviour or actually the cell impedance can be characterized by the equivalent circuit shown in Fig. 1, where r is the constant solution resistance mentioned above, while the electrode impedance consists of faradaic impedance, R and capacity C of the double layer. In the present case the former is equal to a resistance corresponding to the charge transfer reaction which depends on the potential but is independent of the frequency of the a.c. component, while the latter is the capacity of the double layer which, as a first approximation is assumed to be independent of the electrode potential, *i.e.* it is assumed to be a linear circuit element. This assumption is generally valid for small amplitudes of the alternating voltage.

In our earlier works [2-4], the effect of the ohmic resistance and that of the capacity of the double layer have been calculated in the case of a.c. polarography, *i.e.* diffusion polarization. The ohmic resistance and the capacity of the double layer have been found to modify the theoretical relationships to an extent depending on the frequency and the concentration of the solution.

This effect was found to be smaller when the frequency was low (the capacitive current was negligible as compared to the faradaic current) and/or concentration of the species determining the potential was low (*i.e.* the ohmic resistance is negligible as compared to the faradaic impedance). The above theoretical calculations have also been verified experimentally.

In the present communication, the application of the faradaic distortion method is studied for the case of an electrode impedance corresponding to the equivalent circuit of Fig. 1.

The impedance of the circuit shown in Fig. 1 is given by the following formula:

$$Z = \frac{1}{\frac{1}{R} + i\omega C} + r = \frac{(r + R) + i\omega rRC}{1 + i\omega RC}, \quad (1)$$

where ω is the angular frequency of the sinusoidal alternating voltage, and i is the imaginary unit. As the method is based on the study of the alternating current density proportional to the electrode admittance, the reciprocal of Eq. (1) has to be written

$$\frac{1}{Z} = \frac{1 + i\omega RC}{(r + R) + i\omega r RC} = \frac{1}{r + R} \frac{1 + i\omega RC}{1 + i\omega \frac{rR}{r + R} C} = \frac{1}{r + R} \times$$

$$\times \frac{1 + \omega^2 R^2 C^2 \frac{r}{r + R}}{1 + \omega^2 R^2 C^2 \left(\frac{r}{r + R}\right)^2} + i\omega \frac{1}{r + R} \frac{RC \frac{R}{r + R}}{1 + \omega^2 R^2 C^2 \left(\frac{r}{r + R}\right)^2} \quad (2)$$

The discussion of Eq. (2) is rather cumbersome, therefore the admittance was studied three special cases.

1) When $\omega \rightarrow \infty$, the second term of Eq. (2) tends to zero and

$$\lim_{\omega \rightarrow \infty} \frac{1}{Z} = \frac{1}{r}, \quad (3)$$

i.e. at very high frequencies the impedance of the double layer tends to zero and the admittance is determined by the ohmic resistance.

2) When $\omega \rightarrow 0$, the imaginary term of the admittance disappears again and

$$\lim_{\omega \rightarrow 0} \frac{1}{Z} = \frac{1}{r + R}, \quad (4)$$

and thus the admittance is unaffected by the capacity of the double layer.

3) When ω is sufficiently small, the terms containing ω^2 are negligible as compared to unity and

$$\frac{1}{Z} = \frac{1}{r + R} + i\omega \frac{R^2 C}{(R + r)^2}. \quad (5)$$

Writing the square of the absolute value of Eq. (5)

$$\left| \frac{1}{Z} \right|^2 = \left(\frac{1}{r + R} \right)^2 + \omega^2 C^2 \left(\frac{R}{R + r} \right)^4 \quad (6)$$

it becomes evident that the square of the admittance is a function of the second power of the frequency, when ω is small.

The dependence of the square of the admittance on the frequency is shown in Fig. 2. Thus $\left| \frac{1}{Z} \right|^2$ assumes values between $\left(\frac{1}{r + R} \right)^2$ and $\left(\frac{1}{r} \right)^2$, depending on frequency ω .

In other words the ohmic resistance and the parallel RC circuit act as a voltage divider to a degree depending on the frequency and, consequently, only a fraction of the constant amplitude of the alternating voltage applied to the cell appears on the electrode impedance.

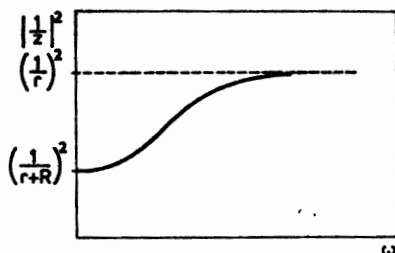


Fig. 2. The frequency dependence of the admittance

The fundamental harmonic component of frequency ω of the measured alternating current is proportional to the absolute value of the admittance given by the following expression

$$\left| \frac{1}{Z} \right| = \frac{1}{r+R} \sqrt{1 + \omega^2 R^2 C^2 \left(\frac{R}{r+R} \right)^2} \quad (7)$$

It is apparent that the fundamental harmonic component of the current depends on the frequency, in contrast to the case when the electrode behaviour is only characterized by resistance R [1].

The frequency dependent voltage division between the ohmic resistance and the electrode impedance has a larger effect on the second and third harmonic components, which are functions of the second and third power, respectively, of the alternating voltage appearing across resistance R or across the electrode impedance in the present case [1].

The higher harmonic components generated on the faradaic impedance also flow through resistance r . As an undistorted sinusoidal alternating voltage was imposed on the cell impedance, the higher harmonic voltages appearing across resistance r also appear with opposite phase across the electrode impedance. The higher harmonic currents flowing under the effect of the above voltages decrease the intensity of the measured higher harmonic components on account of their phase relations and thus they cause an error in the evaluation of the experimental data.

Consequently, when the faradaic distortion method is employed in such cases when the ohmic resistance of the solution is considerable, it is advisable to impose the alternating voltage on the electrode by means of a potentiostat compensating the voltage drop on the above constant resistance in order to ensure that the voltage appearing on the faradaic impedance be undistorted and have the desired amplitude. In this case the electrode admittance is given by the following expression

$$\frac{1}{Z} = \frac{1}{R} + i\omega C. \quad (8)$$

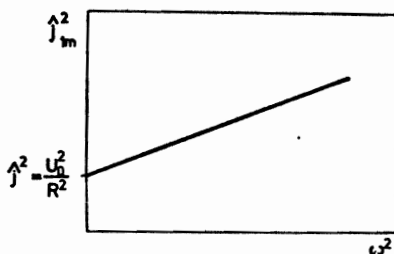


Fig. 3. Extrapolation of the measured first harmonic current

This equation still reflects the shunting effect of the capacity of the double layer on resistance R . However, the square of the amplitude of the experimentally measured fundamental harmonic current density (j_{1m}) is a linear function of ω^2 , as it can be readily shown if the square of j_{1m} is calculated using the square of the absolute value of the admittance. Then the following equation is obtained

$$j_{1m}^2 = j_1^2 + \omega^2 C^2 U_0^2 = \frac{U_0^2}{R^2} + \omega^2 C^2 U_0^2, \quad (9)$$

where j_1 is the amplitude of the fundamental harmonic current density of the faradaic current and U_0 is the amplitude of the alternating voltage applied to the electrode (Fig. 3).

Thus j_1 , i.e. the fundamental harmonic current component independent of double layer effects, can be obtained from measurements performed with alternating voltages at various frequencies and by linear extrapolation of j_{1m} to $\omega = 0$.

This value can readily be employed to calculate the corrosion current density according to the method reported in our previous communication [1].

The capacity of the double layer can also be evaluated according to Eq. (9) and Fig. 3.

These data may also provide valuable information e.g. in the case of the adsorption of inhibitors.

The measured values of the second and third harmonic current components can be employed for the evaluation of the corrosion current density without further correction provided that the effect of r is eliminated by the use of an adequate potentiostat since the double layer capacity — being a linear circuit element — does not generate higher harmonic components and thus the source of the latter is only the faradaic impedance.

The above results lead to the conclusion that the effect of r should be compensated by using an adequate potentiostat and the measurements should be carried out applying at least two alternating voltages having different

frequencies but equal amplitudes in order to permit extrapolation for the elimination of the effect of C .

The current densities of the second and third harmonic components are equal in the case of two applied voltages of different frequencies when the effect of r is properly compensated and the capacity of the double layer can really be assumed to be independent of the electrode potential in the potential range corresponding to the investigation.

The experimental results related to the above method will be published later.

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