SHORT COMMUNICATIONS

FARADAIC ADMITTANCE OF ELECTROCHEMICAL PROCESSES*

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Ershler (1947) and Randles (1947) showed that the behaviour of micro-electrodes under the action of a small alternating potential gives a powerful tool for measuring the rates of fast electrode reactions. It was shown that :

(i) The change in the concentration of the oxidant lags behind the anodic faradaic current by $\frac{1}{4}\pi$.

(ii) The phase angle φ between the alternating components of the voltage and the faradaic current is given by the relation

$$\cot \varphi = 1 + \frac{1}{K_s}\sqrt{(\tfrac{1}{2}\omega D)}, \qquad (1)$$

so that φ is always $\leqslant \frac{1}{4}\pi$.

Breyer, Bauer, and Hacobian (1955) have derived an expression for the phase angle between the concentration of the oxidant and the alternating voltage which leads to the relation

$$\cot \varphi = 1 - \frac{1}{K_s}\sqrt{(\tfrac{1}{2}\omega D)}. \qquad (2)$$

This obviously differs from equation (1). Bauer, Smith, and Elving (1960) have pointed out that " the reported experimental results have on occasion appeared to support equation (1) (Randles 1947 ; Randles and Somerton 1952 ; Rosenthal and Ershler 1948) and at other times equation (2) (Buchanan and Werner 1954 ; Breyer, Bauer, and Hacobian 1955 ; Bauer and Elving 1958) ". It seems (Bauer and Elving 1960) that either of the two equations can be used depending on whether $\varphi \gtrless \frac{1}{4}\pi$. The derivation of Breyer, Bauer, and Hacobian (1955) has been examined and it will be shown in the present paper that equations (1) and (2) become identical on correcting an error due to inconsistency of sign conventions, which has crept into the derivation of the latter equation.

The relation

$$\Delta i_{(E)} = nFAD\frac{\partial(\Delta c_{(0,\tau,E)})}{\partial x_{x\to 0}}$$

(Breyer and Hacobian 1954) implies that $\Delta i_{(E)}$ is to be considered positive when $\partial \Delta c_{(0,\tau,E)}/\partial x_{x\to 0}$ is negative, i.e. when the concentration gradient of the oxidant is negative in the immediate vicinity of the electrode. In other words, the net

current is termed positive when it is anodic in character. Hence Breyer and Hacobian's (1954) equation

$$\Delta i_{(E)} = nFA \Delta c_{0(0, E)} \sqrt{(\omega D)} \cos (\omega \tau + \theta' + \tfrac{1}{4}\pi) \tag{3}$$

conveys that the *anodic* current *leads* the concentration polarization of the oxidant by $\frac{1}{4}\pi$. (This is perfectly true and is equivalent to the statement: "the concentration of the oxidant leads the *cathodic* current by $\frac{3}{4}\pi$.) While developing the derivation in the latter paper, Breyer, Bauer, and Hacobian (1955) have started with the rate equation,

$$i_{t(E_s)} = nFA [K_f c_{(0, \tau, E_s)}^{Ox} e^{-(\alpha nF\varepsilon)/RT} - K_b c_{(0, \tau, E_s)}^{Red} e^{(1-\alpha)(nF\varepsilon)/RT}]. \tag{4}$$

Obviously, $\Delta i_{(E_s)}$ as defined above is " net cathodic " current. They have further put

$$i_{t(E_s)} = i_{(E_s)} + \Delta i_{(E_s)}, \tag{5}$$

here, $\Delta i_{(E_s)}$ is the contribution of the a.c. towards the total current (the contribution being taken as positive when it is cathodic), and

$$i_{(E_s)} = nFA (K_f' \tfrac{1}{2}°_B - K_b' \tfrac{1}{2} c_B).$$

It is thus seen that the sign conventions used in equations (3) and (5) as regards $\Delta i_{(E_s)}$ are not consistent. It can be appreciated that $\Delta i_{(E_s)}$ (of eqn. (5)) $= -\Delta i_{(E_s)}$) (of eqn. (3)). On making the correction, cot θ' turns out to be

$$\cot \theta' = -2K_e Z - 1 \quad \text{and} \quad \cot \varphi = -\cot (\theta' + \tfrac{1}{4}\pi) = -\left(1 + \frac{1}{K_e}Z\right),$$

φ being the phase angle between the voltage and the current and $Z = \sqrt{(2/\omega D)}$ which is identical with equation (1) if one takes into account the different sign conventions used for the potential.

    This difference can be explained by the fact that Randles in his derivation considers the phase difference between the current and the potential of the solution whereas in the present derivation, the phase angle considered is between the current and potential of the electrode. The two phase angles naturally would differ by π. It is to be further pointed out that since φ here represents the phase angle by which the potential of the *electrode leads* the cathodic current whereas the corresponding quantity of Randles (say φ_R) represents the phase angle by which the cathodic current *leads* the potential of the *solution*, the relation between φ_R and φ is given by $\varphi_R = -\varphi + \pi$, whence we get $-\cot \varphi_R = \cot \varphi$.

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