POTENTIODYNAMIC CURRENT/POTENTIAL RELATIONS FOR FILM FORMATION UNDER OHMIC RESISTANCE CONTROL

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Abstract—Theoretical potentiodynamic current/potential curves for a film formation process under an ohmic resistance control are given. Results are compared with experimental data involving the formation of insoluble parathiocyanogen on platinum and the precipitation of a solid CuCl layer during copper dissolution in aqueous HCl solution.

INTRODUCTION

The effect of ohmic polarisation on the potentiodynamic E/I curves derived for simple activation polarisation processes recently reported[1], suggested the convenience of evaluating the potentiodynamic E/I relationships for a film formation process under ohmic resistance control, where the change of the ohmic resistance is produced by the spread of the reaction product as a layer on the electrode surface[2]. Mueller's theory of current transients for this type of processes[3] is based on two types of layer growth which initially consist of the random spread of the solid layer of low conductivity at constant thickness across the electrode surface until only small pores in the layer remain, followed by the increase of the layer thickness with constant pore area. It assumes that the solution and diffusion of the solid species formed at the electrode at a high current density is negligible as well as any concentration polarisation contribution. The resistance of the layer-pore system is relatively small until about 99 per cent of the surface is covered. When this state is reached, the resistance increases abruptly and becomes rate controlling for the current flow. Mueller's theory was applied to potentiostatic current/time transients in various reactions[4, 5].

The present paper refers to the derivation and test of the potentiodynamic E/I relations obtained for the ideal system obeying Mueller's model. The theoretical voltammograms are compared with those obtained for (i) the electrochemical formation of an insoluble $(SCN)_x$ film on platinum with acetonitrile–KSCN solutions at 76°C and (ii) the electrochemical formation of an insoluble layer of CuCl during copper dissolution in 6 N HCl aqueous solution.

THEORETICAL DERIVATION

According to Mueller's model for passivity, the insoluble film starts to crystallise out at certain points

and extends outwards over the surface as a layer of uniform thickness, δ. If the total area of the electrode is A_0 and θ is the degree of coverage of the electrode, the resistance of the pores threading the layer, R', is:

$$R' = \frac{\delta}{\kappa A_0 (1 - \theta)} \tag{1}$$

κ is the specific conductivity of the electrolyte solution in the pores. When an external potential, E, is applied to the electrolysis cell and a current I is flowing, at any instant it results:
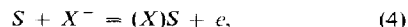
$$I(R' + R_0) = E. \tag{2}$$

The resistance of the cell is the sum of R' and R_0, the latter being the ohmic resistance of the system without film formation. Combining (1) and (2) gives:

$$I = \frac{E}{R_0 + \dfrac{\delta}{\kappa A_0 (1 - \theta)}}. \tag{3}$$

Equation (3) is, therefore, the rate equation for the electrochemical process.

Let us consider a simple fast electrode reaction:

$$S + X^- = (X)S + e, \tag{4}$$

involving the formation of an insoluble species (X) of low electrical conductivity on the electrode surface. The concentration of the ionic species is assumed to be constant from the outer Helmholtz plane throughout the bulk of the solution. When a potential sweep is applied both E and θ in equation (3) change with time. If δ is independent on the potential sweep rate, v, the current can also be expressed in terms of θ as follows:

$$I = \frac{zF\rho\delta A_0}{M}\frac{d\theta}{dt} = k_0 \frac{d\theta}{dt} \tag{5}$$

where ρ is the specific gravity of the film formed and M its molecular weight. The ratio $zF\rho\delta A_0/M$ corre-

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sponds to the charge k_0 required to cover the electrode area with a layer of an homogeneous thickness equal to δ. Since the current for film formation is assumed to be carried by all ionic species except the reacting one, the transference number is taken as unity. Combining equations (3) and (5) and taking into account that the potential E changes linearly with time t, one obtains:

$$\frac{E_i + vt}{k_0\left[R_0 + \dfrac{\delta}{\kappa A_0(1 - \theta)}\right]} = \frac{d\theta}{dt} \qquad (6)$$

where $v = dE/dt$ and E_i is the initial potential. Equation (6) can be numerically solved yielding the $\theta = \theta(t)$ relationship. Since the latter is known, the E/I curve is obtained from equation (3). The E/I curve exhibits a maximum current, I_m, at a potential E_m, which is immediately determined from the condition $(\partial^2\theta/\partial t^2) = 0$. Thus, from (6) one obtains:

$$\frac{d^2\theta}{dt^2} = \frac{1}{(zF\rho\delta)^2\left[R_0 + \dfrac{\delta}{\kappa A_0(1 - \theta)}\right]^2}$$
$$\times \left\{MvzF\rho\delta\left[R_0 + \frac{\delta}{\kappa A_0(1 - \theta)}\right]\right.$$
$$\left. - M(E_i + vt)\frac{zF\rho\delta^2}{A_0(1 - \theta)^2}\frac{d\theta}{dt}\right\} = 0. \quad (7)$$

Equation (7) is fulfilled if:

$$\left[R_0 + \frac{\delta}{\kappa A_0(1 - \theta_m)}\right] = \frac{E_m\delta}{A_0(1 - \theta_m)^2}\frac{d\theta}{dt}. \qquad (8)$$

The subscript m refers to the values of θ and E at the current peak.

At the current peak equation (3) results:

$$R_0 + \frac{\delta}{\kappa A_0(1 - \theta_m)} = \frac{E_m}{I_m}. \qquad (9)$$

Then, from equation (8), (9) and (5) one obtains:

$$I_m = \left(\frac{zF\rho\kappa A_0}{M}\right)^{1/2}(1 - \theta_m)v^{1/2}. \qquad (10)$$

According to equation (10), if θ_m is independent of v, the current peak height should increase linearly with the square root of the potential sweep rate, the slope depending on the properties and thickness of the film.

Finally, from equations (3) and (10), the following relationship is derived:

$$E_m = \left[R_0 + \frac{\delta}{\kappa A_0(1 - \theta_m)}\right]\left(\frac{\kappa A_0 M}{zF\rho\delta^2}\right)^{1/2}(1 - \theta_m)v^{1/2}. \qquad (11)$$

Then, at a constant R_0, the peak current potential should also increase linearly with the square root of the potential sweep rate.

EXPERIMENTAL TECHNIQUE

Parathiocyanogen film formation

$(SCN)_x$ films were deposited on platinum electrodes by anodising a saturated KSCN–acetonitrile solution at 76°C. Solution preparation was made as recommended in the literature[6]. The tight Pyrex glass electrolysis cell consisted of the usual three electrode compartment arrangement, including a reflux condenser to avoid solvent losses. The surface of the platinum wire working electrode was mechanically polished before each run. The potential of a platinum wire immersed in the solution with the usual Luggin–Haber capillary arrangement was used as reference. It was very reproducible and kept constant during the duration of each run. A platinum sheet of large area served as the counterelectrode. The electrical conductance of the electrolytic solution and the solubility curve of KSCN in acetonitrile were also determined.
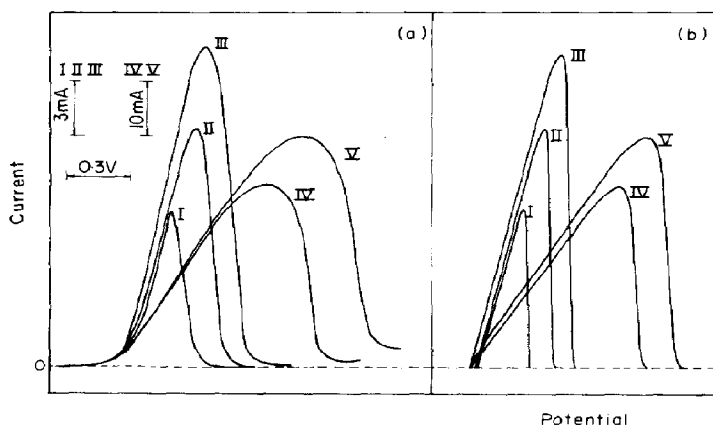

Fig. 1. Potentiodynamic E/I curves run at different potential sweep rates. (a) Experimental curves for parathiocyanogen film formation (with R_0). Electrode area: 0·0974 cm². (b) Theoretical curves calculated with data assembled in Table 2. (I) 5 mV/sec; (II) 10 mV/sec; (III) 15 mV/sec; (IV) 50 mV/sec; (V) 80 mV/sec. The origin of the theoretical curves are located to correspond the experimental curves.

Insoluble CuCl film formation

Insoluble CuCl films were made at $19.5°C$ with a 6 N HCl aqueous solution employing shielded horizontal copper anodes to avoid convection effects. The experimental procedure, the electrode treatment and solution preparation were the same already described in the literature[4, 5]. Runs were made with cathodically cleaned electrode surfaces. Between each run the solution was stirred for the homogeneous dissolution of the CuCl layer.

In both cases the potentiodynamic E/I curves were recorded with the electronic circuit described elsewhere[7].

RESULTS AND INTERPRETATION

When a solution of KSCN in ACN is anodised at a temperature near the boiling point of the solvent, an insoluble film of $(SCN)'_x$ is formed on the platinum anode according to the overall reaction:

$$xSCN^- + Pt(xe) = (SCN)_xPt. \qquad (12)$$
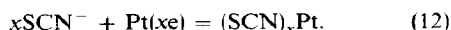
The corresponding potentiodynamic E/I curves swept towards anodic potentials at different v (Fig. 1a) comprise an ohmic polarisation due to the potential drop between the working electrode and the reference electrode. The anodic reaction starts at about 0.3 V with respect to the initial potential. Both the current peak, I_m, and its potential, E_m, increase linearly with $v^{1/2}$. The shift of E_m towards anodic potentials as v increases is so large that, for instance, at $v = 150$ mV/sec, (Fig. 1a), a potential region is reached where a different electrochemical process takes place. The charge, Q, related with the formation of the passive film, within the range of v covered, is constant ± 9 per cent (Table 1).

Figure 2a shows a set of voltammograms run at a constant v with different ohmic resistors, R, in series with the internal cell resistance. Now, the anodic peak height decreases as R increases and the apparent peak potential shifts towards more anodic potentials. As R increases the initial straight line portion of the E/I display extends over a larger anodic potential range and the slope of the line decreases as R increases.

The experimental E/I records shown either in Figs. 1a or 2a are satisfactorily compared with those computed through equations (3) and (6) (Figs. 1b and 2b) using the parameters assembled in Table 2. From this
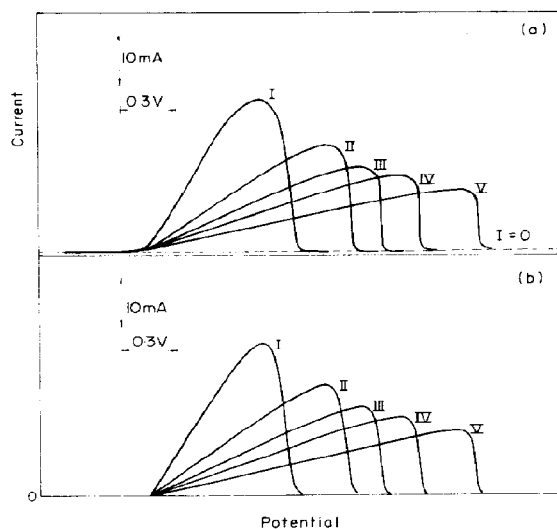

Fig. 2. Potentiodyanamic E/I curves run at 40 mV/sec and different ohmic resistances, R. (a) Experimental records for parathiocyanogen film formation. (b) Theoretical curves calculated with equations (3) and (6). (I) $R = R_0$ (R_0 is estimated from the slope of the experimental curve); (II) $R = R_0 + 20$; (III) $R = R_0 + 40$; (IV) $R = R_0 + 60$; (V) $R = R_0 + 100$.

result one concludes that θ_m is independent of v but it depends on R.

Anodic potentiostatic transients for the dissolution of shielded horizontal copper anodes in aqueous HCl are known and were already quantitatively compared to Mueller's theory of passivation[4, 5]. The anodic transient exhibits a first current plateau which is related to the following reaction:

$$Cl^- + Cu = CuCl + e, \qquad (13)$$
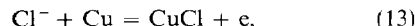
where the anodic layer of CuCl passivates the electrode. The process is convection free for rapid transients. The Cu/HCl system exhibits also a second current plateau related to a new electrode process and complex ion formation, since CuCl is dissolved as $CuCl_2$ and $CuCl_3^{2-}$. The solubility of CuCl also depends strongly upon the HCl concentration[8].

Table 1. Charge related to parathiocyanogen film formation at $76°C$

v (mV/sec)	Q (C/cm²)
5	3.05 ± 0.40
10	3.47
15	3.94
30	3.91
50	4.14
80	3.85
100	3.92

Table 2. Parameters employed for calculation of E/I curves of Fig. 1b

v (mV/sec)	R_0 (Ω)	Q (mC)	δ (cm)
5	22	230	7.10×10^{-4}
10	22	270	8.33×10^{-4}
15	21.5	310	9.56×10^{-4}
50	18.5	310	9.56×10^{-4}
80	17.5	325	1.00×10^{-3}

Electrode area 0.0974 cm². $\kappa = 0.025$ Ω^{-1} cm^{-1}. R_0 was obtained from the slopes of the experimental E/I curves.

Figure 3 shows a set of voltammograms run with a constant ohmic resistance and changing v. They are more complex in shape than those reported for the formation of the parathiocyanogen film. Thus, the initial portion is slightly curved, approaching at higher anodic potentials a straight line region which goes up to near the current peak. Then, the current decreases rather abruptly and at the end of the sweep the E/I display presents a clear distortion. The slope of the straight line portion of the voltammograms run at a constant v but with different values of R (Fig. 4) decreases as the latter increases.

Due to the complexity of CuCl film formation the comparison of the experimental and theoretical voltammograms requires at least two corrections on the experimental records. The first one refers to the initial charge required for saturating the electrode/electrolyte interface, which, in principle, does not contribute to any appreciable resistance change at the interface. This charge can be evaluated from the voltammograms run at a constant v with different R, by integration of the E/I curve from 0 to t (Table 3). The estimated charge is 330 mC/cm^2. The reaction product accumulates within a volume defined by the electrode area and a solution layer thickness equal to 2×10^{-3} cm, taking into account that the solubility of CuCl in aqueous 6 N HCl, at 19°C, is 1·7 M[8].

The second correction is made from the voltammograms run with a constant R and changing v. In this case, the $I_m/v^{1/2}$ straightline relationship is no longer obeyed at large v (Fig. 5), the effect being more marked when the ohmic resistance is low, indicating that the saturation charge depends on v. This dependence arises because as v increases the accumulation of the reaction product is more rapid and simultaneously its rate of dissolution, which is determined by the Cl$^-$ ion diffusion, competes to a lesser extent. Then, as v increases a smaller amount of saturation
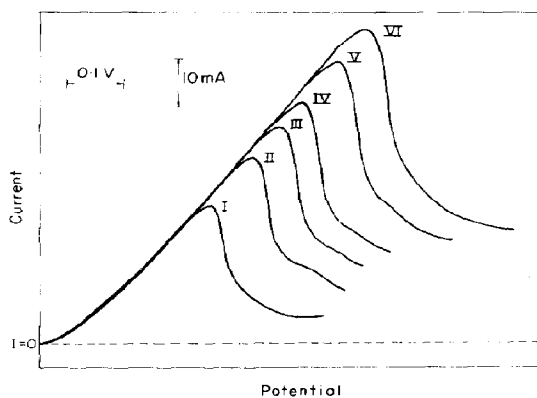
Fig. 4. Potentiodynamic E/I curves at 200 mV/sec and different ohmic resistances, R for CuCl film formation in 6 N HCl. Electrode area 0·086 cm^2. (I) $R = R_0$; (II) $R = R_0 + 2$; (III) $R = R_0 + 5$; (IV) $R = R_0 + 10$; (V) $R = R_0 + 15$.

charge is required. The effect is equivalent to that reported in the anodic potentiostatic transients where the total charge for passivation became smaller when the process occurred faster (smaller transition times)[4]. This competing dissolution process introduces a baseline correction which has been made to voltammograms shown in Fig. 6. After all these corrections the experimental displays can be compared with the theoretical voltammograms computed with data assembled in Table 4. There is coincidence over a large range of potential (Fig. 6), discrepancies being observed at the end of each voltammogram due to the occurrence of a new reaction involving the partial dissolution of the metal as Cu(II) ions.

DISCUSSION

The voltammetric equations derived from Mueller's model for film formation at electrodes reproduce with

Fig. 3. Potentiodynamic E/I curves at different potential sweep rates for CuCl film formation in 6 N HCl (with R_0). Electrode area 0·086 cm^2. (I) 50 mV/sec; (II) 100 mV/sec; (III) 150 mV/sec; (IV) 200 mV/sec; (V) 300 mV/sec; (VI) 400 mV/sec.
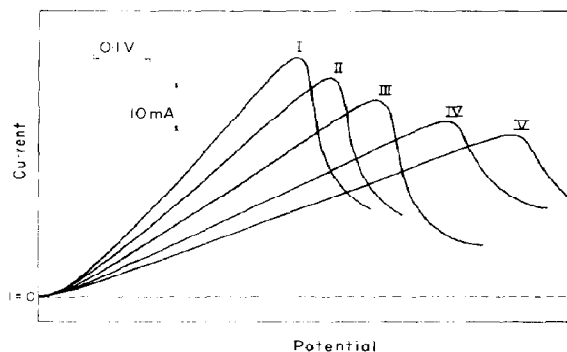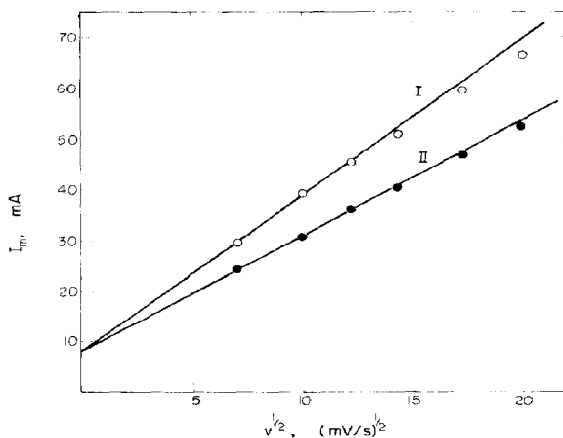
Fig. 5. Dependence of I_m on $v^{1/2}$ for CuCl film formation in 6 N HCl. (I) $R = R_0$; (II) $R = R_0 + 5$.
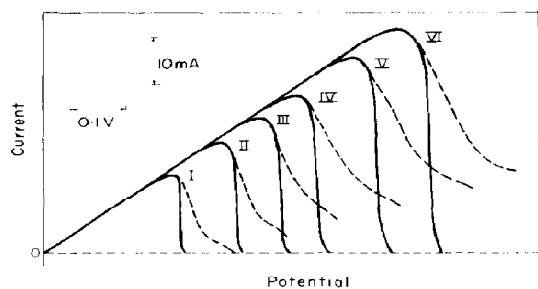
Fig. 6. Comparison of the experimental E/I curves after baseline correction (dotted lines) with E/I curves calculated with equations (3) and (6) (full lines).

a reasonable good approximation the shape of the voltammograms obtained for the two electrode reactions referred above. The best agreement extends from the initial potential up to a potential exceeding about 50 mV the potential of the peak current. A complete quantitative agreement between theory and experiment within the whole potential range covered by those reactions is certainly unexpected since both processes imply a more complex behaviour. The larger discrepancy appears at high anodic potential.

The electrochemical formation of the parathiocyanogen film on platinum occurs together with a partial ànodic dissolution of the metal. Therefore, one should expect the experimental voltammogram involves a charge larger than the theoretical one. Furthermore, the magnitude of the charge required for passivation indicates that a more elaborated reaction model is required to account for this process[9], including con-

Table 3. Saturation charge for CuCl film formation obtained from Fig. 4

t (sec)	$I_{t=t}$ (mA)	Q (mC)
1·20	22·50	27·00
1·35	21·25	28·69
1·50	18·75	28·12
1·75	16·50	28·87
1·95	14·75	28·76

Electrode area: 0.086 cm^2.

Table 4. Parameters employed for calculation of E/I curves of Fig. 6

$$R_0 = 12.7 \, \Omega$$
$$Q = 45.15 \text{ mC}$$
$$\kappa = 9.3 \times 10^{-3} \, \Omega^{-1} \text{ cm}^{-1}$$
$$\delta = 1.53 \times 10^{-4} \text{ cm}$$
$$A_0 = 0.086 \text{ cm}^2$$
$$\rho = 3.53 \text{ g cm}^{-3}$$
$$M = 99$$

ductivity, film thickness and porosity changes. These considerations also apply to the CuCl film formation. Nevertheless, the partial agreement between experimental and theoretical data reveals the extent of ohmic polarisation contribution in both film formation processes.

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