MATHEMATICAL MODELLING OF CURRENT-POTENTIAL CURVES FOR THE Pb/H₂SO₄ SYSTEM

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Introduction

In previous work [1], voltammetric studies have been conducted to determine the influence of the potential sweep rate on:

(i) the electrode processes taking place during the anodic dissolution of lead in concentrated (~ 5 M) sulphuric acid solutions;

(ii) the formation of the lead sulphate insoluble film;

(iii) the cathodic reduction of the passivating layer.

Using these results, the work reported here attempts a theoretical computation of the current/potential curves. Other investigations have been undertaken on the electrode processes involved with the passivation of metals through the formation of insoluble films [2, 3].

In the present work, the electrode process was considered to be controlled only by the charge transfer and the change in the free active surface $(1 - A)$ of the electrode, where A represents the degree of coverage by an insoluble film. The theoretical approach was based on Müler's theory [4, 5] of passivation. The theoretical computation of the current/potential curves was carried out using the Srinivasan–Gileadi mathematical model [6] when extended to two-electron transfer reaction of the type:

$$M \rightleftharpoons N^{2+} + 2e^- \tag{1}$$

where M is a metal. The model relies on the assumption that the lead sulphate film is insoluble and cannot be removed from the electrode surface except by electrochemical reduction.

The Srinivasan–Gileadi model refers to the adsorption on the electrode surface of a monolayer of an electrochemically active species from the solution. An attempt has been made here to extend the model to cover the formation of an insoluble film of constant and much higher thickness than a monolayer (*i.e.*, of the order of 0.1 μm). Apart from this, all assumptions of the Srinivasan–Gileadi model are maintained in this analysis.

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Anodic process: reversible reaction at quasi-equilibrium

Theoretical background

For a reversible anodic reaction with a two-electron transfer of the type:

$$Pb \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Pb^{2+} + 2e \tag{2}$$

the faradaic current, i_F, can be expressed as [6]:

$$i_F = k_1(1 - A) \exp(2\alpha EF/RT) - k_{-1}A \exp(-2(1 - \alpha)EF/RT) \tag{3}$$

where: k_1 and k_{-1} are the specific rate constants for the forward and backward reactions, respectively, when the potential difference, E, at the metal/solution interface is zero; A is the coverage of the electrode surface with reaction product; the other terms are well known. Both E and A are time-dependent.

Since, in our case, for eqns. (2) and (3) above:

$$i_F \ll k_1(1 - A) \exp(2\alpha EF/RT)$$

$$|i_F| \ll k_{-1}A \exp(-2(1 - \alpha)EF/RT)$$

it follows that $i_F = 0$, hence:

$$A = \frac{K_1}{\exp(-2EF/RT) + K_1} \tag{4}$$

where $K_1 = k_1/k_{-1}$ and is an equilibrium constant. The net faradaic current, i_F, may also be expressed as:

$$i_F = Q_{0,a}\left(\frac{dA}{dt}\right) \tag{5}$$

where $Q_{0,a}$ is the specific amount of electricity required to form, on the electrode surface, a layer of reaction product of constant thickness. Substituting eqn. (4) in eqn. (5) yields:

$$i_F = \left(\frac{2Q_{0,a}F}{RT}\right)\left(\frac{K_1 \exp(-2EF/RT)}{(\exp(-2EF/RT) + K_1)^2}\right)v \tag{6}$$

where:

$E = (E_i + vt)$ and $E_i = 0$; E_i is the initial potential; v is the sweep rate; E is the potential at time t.

The condition for a maximum in the current/time curve is:

$$\left(\frac{di_F}{dt}\right) = 0 \quad \text{or} \quad \left(\frac{d^2A}{dt^2}\right) = 0 \tag{7}$$

This gives the maximum anodic current ($i_{F,M}$) and the peak potential (E_M)

$$E_M = -\frac{RT}{2F} \ln K_1 \tag{8}$$

$$i_{F,M} = \left(\frac{Q_{0,a}F}{2RT}\right)v \tag{9}$$

Numerical computation

The theoretical computation of the potential/current curves for the anodic process of lead dissolution, with the formation of an insoluble lead sulphate layer, was carried out by computer processing of eqn. (6). This procedure was conducted for 15 potential sweep rates experimentally tested in the authors' laboratories. Parameters K_1 and $Q_{0, a}$ were estimated using eqns. (8) and (9), respectively.

Equation (8) shows that K_1 is independent of v, but is strongly dependent on E_i. As others have pointed out [6], however, E_i can be chosen arbitrarily. Here, it is taken as the potential at which the experimentally determined anodic current is zero. The equilibrium constant corresponding to this potential is: $K_1 = 0.933 \times 10^{-2}$. According to eqn. (9), $Q_{0, a}$ is a function of the potential sweep rate. Table 1 gives the dependence on v of both the experimentally determined ($Q_{0, a}^{exp}$) and theoretically calculated ($Q_{0, a}^{theor}$) amounts of electricity for reaction (2). Analysis of the data shows that there is good agreement between the values.

With knowledge of the K_1 and $Q_{0, a}^{theor}$ parameters, the theoretical potential/current curves were obtained by computer processing of eqn. (6). These curves are compared with the experimental curves, for different potential sweep rates, in Fig. 1. The results show that there is extremely good correlation between the two types of curve, irrespective of the sweep rate. Hence, the dissolution process of lead with the formation of a lead sulphate

TABLE 1

Dependence on potential sweep rate of the amounts of electricity involved in the anodic oxidation of lead

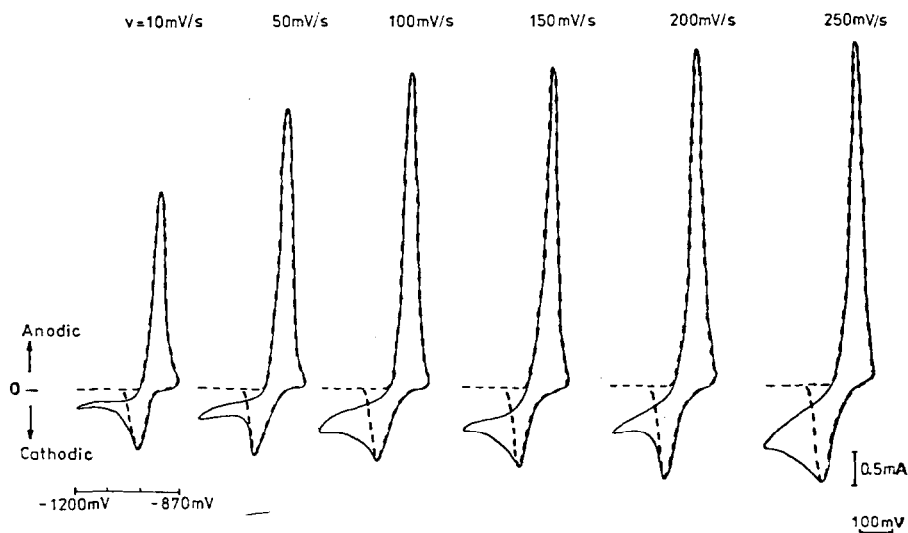| v (mV s^{-1})	$Q_{0, a}^{exp}$ (10^3 C cm^{-2})	$Q_{0, a}^{theor}$ (10^3 C cm^{-2})	$Q_{0, c}^{exp}$ (10^3 C cm^{-2})	$Q_{0, c}^{theor}$ (10^3 C cm^{-2})
5	61.3	69.50	59.30	55.50
10	43.4	54.86	42.40	35.79
15	33.3	42.00	29.70	14.48
20	25.5	32.25	22.80	11.10
25	21.8	27.47	18.40	9.00
35	16.4	20.76	13.70	6.70
50	12.4	15.66	10.03	4.90
75	9.0	11.43	7.09	3.46
100	7.0	8.83	5.67	2.77
125	5.7	7.18	4.86	2.37
150	4.8	6.00	4.00	2.06
175	4.1	5.17	3.75	1.83
200	3.7	4.69	3.55	1.73
225	3.3	4.20	3.28	1.60
250	3.0	3.79	3.00	1.50

Fig. 1. Experimental (——) and theoretical (– – –) current/potential curves for different potential sweep rates.

passivating layer is controlled by the charge-transfer kinetics and the development of the insoluble film. Using eqn. (4), the coverage A_a of the electrode surface with insoluble film was estimated for different values of the potential, E. It was found that A_a increases with increase in the potential and becomes equal to 0.5 at the peak potential. A_a is independent of the sweep rate and reaches a maximum value of 0.99 at the end of the positive-going scan. This fact is in agreement with the observed decrease in the electricity amounts involved in the anodic process with increase in sweep rate. Thus, at the end of the potential sweep, the electrode surface is completely covered with an insoluble film, but the thickness of the latter becomes smaller and smaller Hence, the lead electrode surface may be passivated by different amounts of lead sulphate [1].

Cathodic process: irreversible reaction

Theoretical background

In this case, only the reverse of reaction (2) is considered. Equation (3) reduces to:

$$|i_F| = k_{-1}A \, \exp(-2(1-\alpha)EF/RT) = k_{-1}A \, \exp(2(1-\alpha)vtF/RT) \qquad (10)$$

since

$$E = E_i - vt \quad \text{and} \quad E_i = 0$$

the net faradaic current is:

$$|i_F| = -Q_{0,c}\left(\frac{dA}{dt}\right) \qquad (11)$$

where $Q_{0,c}$ is the specific amount of electricity required to remove (by reduction) the insoluble film from the electrode surface. Further, proceeding as in the case of the anodic process, the following calculating relations are obtained:

$$|i_{F,M}| = \frac{2Q_{0,c}(1-\alpha)F}{eRT} v \qquad (12)$$

$$E_M = -\frac{RT}{2F(1-\alpha)} \ln \frac{2Q_{0,c}(1-\alpha)F}{k_{-1}RT} - \frac{RT}{2F(1-\alpha)} \ln v \qquad (13)$$

$$\ln A - -\frac{k_{-1} \cdot RT}{2Q_{0,c}(1-\alpha)vF}[\exp(-2(1-\alpha)EF/RT) - 1] + \frac{2(1-\alpha)EF}{RT} \qquad (14)$$

$$\ln |i_F| = \ln k_{-1} - \frac{k_{-1} \cdot RT}{2Q_{0,c}(1-\alpha)Fv}\left[\exp\left(-\frac{2(1-\alpha)EF}{RT}\right) - 1\right] - \frac{2(1-\alpha)EF}{RT} \qquad (15)$$

Numerical computation

The theoretical computation of the potential/current curves for the irreversible cathodic reduction of a lead sulphate insoluble layer, was achieved by computer processing of eqn. (15) for 15 potential sweep rates conducted experimentally [1]. The parameters $Q_{0,c}$ and k_{-1} were estimated using eqns. (12) and (13), respectively. From the data presented in Table 1, it can be seen that the experimental values for both $Q_{0,c}^{exp}$ and $Q_{0,c}^{theor}$ are higher than those calculated using eqn. (12). This suggests that, during the cathodic process, a sequence of secondary reactions occurs in addition to the main process of the reduction of the $PbSO_4$ layer.

Using eqn. (14), the rate constant k_{-1} was estimated for each sweep rate; the average value was 2.4×10^{-4} A cm^{-2}. The theoretical cathodic potential/current curves were obtained by computer processing of eqn. (15) and are given in Fig. 1 together with the corresponding experimental curves. Analysis of the curves shows that, in contrast to the anodic situation, the theoretical and experimental data deviate from each other at potentials close to the cathodic maximum. At more negative potentials, for example, the experimental cathodic currents, in absolute value, are higher than those calculated theoretically. Indeed, the latter decline rapidly to zero. These results are in accordance with the behaviour of $Q_{0,c}^{exp}$ and $Q_{0,c}^{theor}$ (see Table 1) and with the values of A_c calculated using eqn. (14). It was found that A_c depends on v and, for a given v, decreases as the potential moves towards more negative values. A_c becomes equal to 0.37 at the peak potential, and then rapidly falls to zero at the end of the negative-going potential sweep. These findings demonstrate clearly the complexity of the cathodic process.

Conclusions

It has been shown that the Srinivasan–Gileadi model can be extended to the anodic dissolution of metals with insoluble film formation. In the case of a cathodic process, the extension of the model is restricted (by the complexity of the process) to a limited potential range. The latter, however, does include the peak potential. An accurate analysis of this case, taking into account the diffusion and the potential ohmic drop in the pores of the passivating film, will be reported in a future paper.

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