Short Communication

Analysis of the oxidation process of anodic Pb(II) films on lead in sulfuric acid solution

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Abstract

Electro-oxidation of the anodic Pb(II) film formed on lead at 0.6 V in H_2SO_4 solution for 20 min is analysed using non-linear regression, chrono-amperometry and linear sweep voltammetry. It is shown that the overall current transient of the oxidation at 1.4 V can be separated into the following contributions: (i) oxidation of the Pb(II)-containing phases into PbO_2 which involves mainly an instantaneous nucleation and two-dimensional growth mechanism under charge-transfer control (2DIC); (ii) oxidation of the lead substrate into PbO under the diffusion control of oxygen ions, and (iii) evolution of oxygen on the electrode. The plumbous phases that participate in the oxidation process include an inner layer of $(PbO + PbO \cdot PbSO_4)$ together with an adjacent part of an outer layer of $PbSO_4$. Several electrochemical quantities of significance with respect to this oxidation process have been calculated, such as the thickness of the PbO_2 formed, the degree of oxidation of the Pb(II)-containing phases, as well as the diffusion coefficient of O^{2-} in the concurring oxidation process of Pb to PbO.

Keywords: Lead/sulfuric acid system; Electro-oxidation; Anodic lead(II) films

1. Introduction

Lead electrode reactions in sulfuric acid medium have been studied extensively by using different stationary and transient techniques [1–6]. Since the pioneering work by Fleischmann and Thirsk [7] on the nucleation and growth process of PbO_2 during the oxidation of pure anodic $PbSO_4$ film, many researchers have exploited different electrocrystallization models to explain various kinds of phase transformation of the anodic films on lead [8–19]. The most common method used to analyse the current transient in the chrono-amperometry measurements is to compare their fit with theoretical curves in a reduced variable plot, i.e. j/j_m versus t/t_m or $(j/j_m)^2$ versus t/t_m, where j_m and t_m denote, respectively, the maximum current density and its corresponding time. The method cannot give any quantitative information, however, about the nucleation and growth process. Moreover, even the qualitative conclusion cannot be unambiguously drawn when the severe deformation of current transients occurs due to other subsidiary reactions or (and) double-layer charging. Non-linear fitting, which is utilized the least, is a powerful tool to deconvolute the complex current transients and pro-

vide insight into the significant parameters of each process involved.

The anodic Pb(II) film on lead in H_2SO_4 solution can be divided into two types: one is formed during the cycling process and the other is formed at a potential between −0.4 to +0.95 V (versus Hg/Hg_2SO_4), or the 'PbO formation potential window' [20,21]. The oxidation of the first kind of film was suggested by Hampson et al. [8] to follow an instantaneous nucleation and two-dimensional growth mechanism under charge-transfer control (2DIC). On the other hand Valeriote and Gallop [9] considered it to contain at least two different electrocrystallization processes at different times. Such a dispute may be due to the fact that the cycled film is not well-defined. In the case of oxidation of the second kind of anodic Pb(II) film, Pavlov and Dinev [22], who mainly exploited linear sweep voltammetry (LSV) and scanning electron microscopy to investigate such a process, proposed that α-PbO in the sub-layer of the film was oxidized to α-PbO_2 first, followed by the conversion of $PbSO_4$ in the outer layer to β-PbO_2. Fletcher and Matthews [11] assigned the current transient in a potential-step measurement to the oxidation of α-PbO in the anodic Pb(II) film to α-PbO_2, according to their simultaneous observation of a transient photocurrent. To the authors' knowledge, however, any quan-

titative analysis of this oxidation process has not yet been reported in the literature.

In this communication, the non-linear fitting method, in conjunction with chrono-amperometry and LSV measurements, is used to analyse the current transient at 1.4 V for the oxidation of the anodic Pb(II) film formed on lead at 0.6 V in sulfuric acid solution. This is undertaken in order to obtain a more detailed picture about the pertinent process, especially to clarify the oxidation kinetics and to determine to which extent each plumbous phase is oxidized.

2. Experimental

Chrono-amperometry and LSV measurements were performed using an EG&G PARC 273 potentiostat/galvanostat interfaced to a computer with an EG&G PARC Model 270 electrochemistry analysis software. The parametric identification procedure of the current transient was home-written according to a Marquardt–Levenberg non-linear least-squares algorithm, to fit a non-linear mathematical model to data points.

Formation and subsequent oxidation of the anodic Pb(II) film were carried out in 4.5 M H_2SO_4 solution prepared from AR H_2SO_4 and distilled water. Lead rod (99.999% pure) was used as the working electrode and had a geometric surface of 0.28 cm^2. A platinum foil served as the counter electrode. An Hg/Hg$_2$SO$_4$ electrode with the same solution as in the electrochemical cell was used as the reference electrode. All potentials are reported with respect to this electrode.

The surface of the working electrode was ground flat with emery paper of successively decreasing grain size down to about 10 μm. Afterwards, the electrode was rinsed thoroughly with distilled water and then placed in the cell. Before anodizing, a cathodic polarization at a potential of − 1.2 V for 20 min was performed in order to remove any oxidation products formed by aerial oxidation during preliminary treatment. The anodic Pb(II) films were grown for 20 min at 0.6 V, and followed by a potential step to 1.4 V for the oxidation, or a negative LSV to a hydrogen-evolution potential for the

determination of the phase composition. All experiments were run at a temperature of 25 ± 2 °C.

3. Results and discussion

The current–time profiles for the formation of an anodic Pb(II) film on lead at 0.6 V for 20 min (curve (A)) and its subsequent oxidation at 1.4 V (curve (B)) in 4.5 M H_2SO_4 are given in Fig. 1. It is well accepted that the emergence of the rising and falling transient current in curve (B) indicates the nucleation and growth of PbO$_2$. In order to estimate the possible mechanism for this solid-phase transformation, the data points in curve (B) were compared with the well-known formalism of electrocrystallization models in a reduced variable test plot, j/j_m versus t/t_m (see Fig. 2) or $(j/j_m)^2$ versus t/t_m (see Fig. 3) [23]. (Note: the time domain here and below is referred to the time of 1200 s, i.e. the start of oxidation at 1.4 V.)

From Figs. 2 and 3, it can be seen none of the theoretical models fit well, although the 2DIC trace appears relatively close to the experimental results. This indicates that the overall transient current at 1.4 V cannot be attributed solely to the nucleation and growth process of PbO$_2$ from the oxidation of
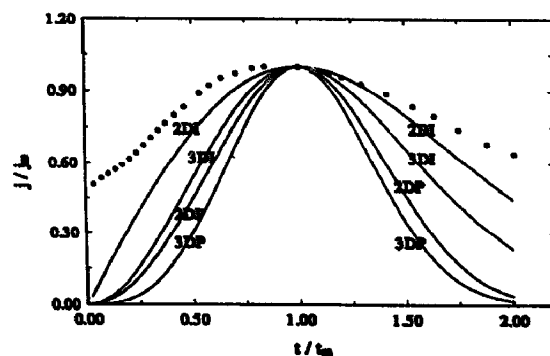
Fig. 2. Comparison of j/j_m vs. t/t_m plots. Solid lines (2DI/P, 3DI/P) correspond to the instantaneous/progressive nucleation and (two and three)-dimensional growth process under charge-transfer control, respectively. Points are taken from curve (B) in Fig. 1. (The time domain is referred to the time of 1200 s both here and below.)
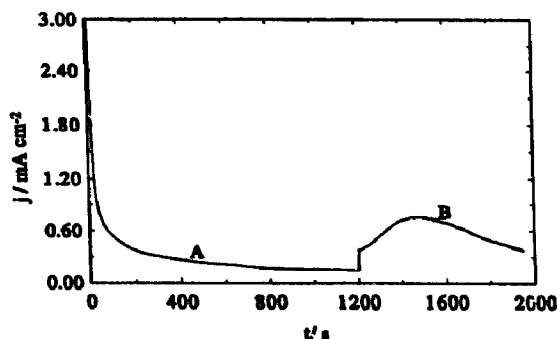
Fig. 1. Current transients recorded for (A) the formation of the anodic Pb(II) film on lead at 0.6 V for 1200 s and (B) the subsequent oxidation of this film at 1.4 V for 750 s, in 4.5 M H_2SO_4.
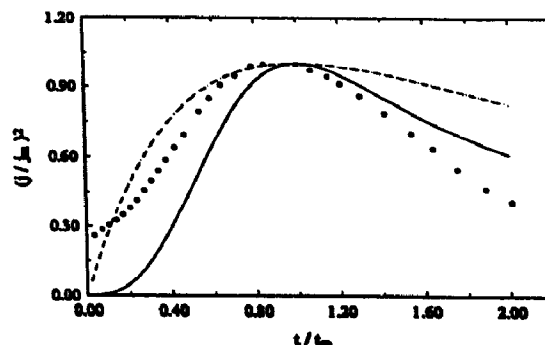
Fig. 3. Comparison of $(j/j_m)^2$ vs. t/t_m plots. (– · –)/(———) corresponds to the instantaneous/progressive nucleation and three-dimensional growth process under diffusion control. Dots are taken from curve (B) in Fig. 1.

the plumbous phases on lead formed at 0.6 V. One subsidiary contribution, namely, oxygen evolution at 1.4 V, should be taken into account given the gas bubbling at the electrode. The other is the concurrent oxidation of the lead substrate to a Pb(II)-containing phase, i.e., PbO (v.i.) as the direct oxidation of lead to PbO_2 is not dynamically preferable. The existence of an inner layer of PbO, even at a positive potential of 1.35 V, has been confirmed by Bullock and Butler [24]. They found also that an adjacent outer layer of PbO_2 hinders the diffusion of $SO_4{}^{2-}$ ions from the bulk solution, thus it is reasonable to rule out the formation of basic lead sulfates in the inner layer. Based on the above consideration, the following equation is proposed to describe the oxidation current transient

$$j = P_1 t^{-1/2} + P_2 + P_3 t \exp(-P_4 t^2) \tag{1}$$

where P_1, P_2, P_3 and P_4 are parameters to be identified.

In Eq. (1), the first term is related to the oxidation of substrate, with a rate that is determined by the diffusion of oxygen ions. Thus [25]

$$P_1 = (F^2 DcZ/V_m)^{1/2} \tag{2}$$

where F denotes the Faraday constant, V_m is the molar volume of PbO, c represents the O^{2-} concentration on the surface of the PbO, which can be assumed to be $1/V_m$; D is the diffusion coefficient of O^{2-}, and Z is the number of electrons passing through the circuit as one atom of lead is oxidized to one molecule of PbO.

The second term in Eq. (1), which is regarded to be constant within the time domain of regression, represents the oxygen-evolution current as well as a possible residual diffusion current at $t \to \infty$.

The third term in Eq. (1) corresponds to an instantaneous nucleation and two-dimensional growth process of PbO_2 under charge-transfer control (2DIC). Growing nuclei are considered to be discs instantaneously formed on a planar electrode surface. In this case [23]

$$P_3 = 2n\pi F M h N_0 k^2/\rho \tag{3}$$

and

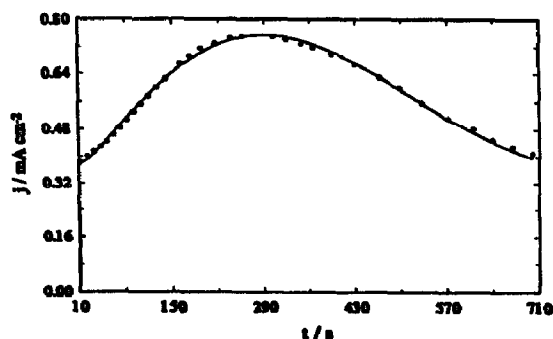$$P_4 = \pi N_0 M^2 k^2/\rho^2 \tag{4}$$

Fig. 4. Fitting of current transient data taken from curve (B) in Fig. 1 according to Eq. (1) (———).

where h is the height of the discs or the thickness of the PbO_2 layer, N_0 the nuclei density, k the lateral electrocrystallization constant of the PbO_2 nuclei, n the number of electrons consumed as one molecule of PbO_2 is formed; M and ρ are the molecular mass and mass density of PbO_2, respectively.

Through the proposed mathematical model (e.g. Eq. (1)), the experimental current transients that result from the oxidation process at 1.4 V can be reproduced satisfactorily within a wide span of time, as is shown in Fig. 4. The four parameters thus obtained are listed as follows:

(i) $P_1 = 0.28$ mA cm^{-2} s$^{-1/2}$
(ii) $P_2 = 0.27$ mA cm^{-2}
(iii) $P_3 = 2.65 \times 10 - 3$ mA cm^{-2}s^{-1}
(iv) $P_4 = 5.93 \times 10^{-6}$ s^{-2}

In addition, the replacement of the third term in Eq. (1) with any other well-known nucleation and growth kinetics will result in a failure of regression or unreasonable parametric values. This favours the feasibility of the proposed model. Using the above regression results, several electrochemical quantities of importance regarding the oxidation process can be estimated for the first time. From Eqs. (3) and (4), the thickness of the PbO_2 layer formed, h, can be deduced as follows

$$h = \frac{MP_3}{2nF\rho P_4} \tag{5}$$

By using the following values, $F = 9.65 \times 10^7$ mC mol^{-1}, $n = 2$, $M/\rho = V_m = 25$ cm^3 mol^{-1}, the value of h is calculate from Eq. (5) to be about 0.29 μm. From the integral of the third term in Eq. (1), it is possible to estimate at a certain time the conversion quantity of PbO_2 from the plumbous phases previously formed on lead, that is

$$Q_t = \int_0^t P_3 t \exp(-P_4 t^2) \, dt$$

$$= -(P_3/2P_4) \exp(-P_4 t^2)|_0^t \tag{6}$$

For an ideal situation in which the proposed model is assumed to be always correct regardless of the oxidation period, the limiting quantity of PbO_2 thus formed could be $Q_{t \to \infty} = P_3/(2P_4) = 223$ mC cm^{-2}. According to the 2DIC model, the PbO_2 layer would grow most densely upon limitation. Practically, for an oxidation period of 600 s ($\sim 2t_m$), the conversion quantity is 197 mC cm^{-2}. As the oxidation time surpasses 700 s ($Q_t = 210$ mC cm^{-2}), the discrepancy between the experimental and theoretical current is positive and increases with time, which may be due to some change of kinetics and mechanism and is beyond the scope of the present discussion.

In order to determine those plumbous phases on lead that take part in the oxidation process, it is first necessary to elucidate the phase composition of the anodic Pb(II) film. The anodic Pb(II) film on lead at 0.6 V was assigned to an outer perm-selective layer of $PbSO_4$, an inner layer of PbO,
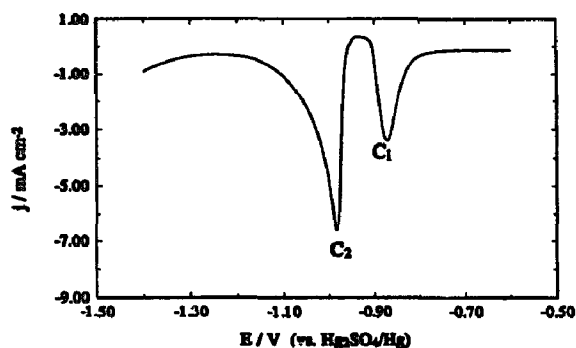
Fig. 5. Linear sweep voltammogram at a scan rate of 2 mV s⁻¹ from −0.6 to −1.4 V for the analysis of the phase composition of the anodic Pb(II) film on lead formed at 0.6 V for 20 min.

and some $PbO \cdot PbSO_4$ [20,21,26,27]. An LSV analysis of the composition of the anodic Pb(II) film formed on lead at 0.6 V for 20 min in a 4.5 M H_2SO_4 solution is shown in Fig. 5. The charge quantities under the cathodic peaks C_1 (−0.85 V) and C_2 (−1.0 V) are 100 and 240 mC cm⁻², which correspond to the reduction of $(PbO + PbO \cdot PbSO_4)/Pb$ and $PbSO_4/Pb$, respectively. For the oxidation of the plumbous phases to PbO_2 through electrocrystallization, a high over-potential is required. Recalling that the main oxidation process can be depicted by Eq. (1), it is reasonable to assume that upon oxidation at 1.4 V, PbO_2 discs with a thickness of 0.39 μm nucleate instantaneously at places close to the substrate. This is followed by a lateral growth of the nuclei and results in a rising and falling transient current. By comparing the quantities of the plumbous phases previously formed at 0.6 V and the converted quantity at 1.4 V, it is found for 600 s of oxidation that more than 97 mC cm⁻² of $PbSO_4$ in the anodic Pb(II) film was transformed to PbO_2 and, in addition, that most of the $(PbO + PbO \cdot PbSO_4)$ was oxidized. The PbO_2 layer thus formed is mainly the α-polymorph, which is more stable in an alkaline environment. Nevertheless, the outermost part of the PbO_2 layer adjacent to the remaining $PbSO_4$ may convert to β-PbO_2 since the reconstruction of the $PbSO_4$ layer may decrease its semi-permeability, or, increase the acidity inside the anodic film [22,28].

Another electrochemical quantity of interest that can be calculated from the fitting results is the solid-phase diffusion coefficient, D, of oxygen ions that controls the concurrent oxidation the lead substrate to PbO.

According to Eq. (2), with $F = 9.65 \times 10^7$ mC mol⁻¹, $M/\rho = V_m = 23.4$ cm³ mol⁻¹, $c = 1/V_m$, $Z = 2$, $P_1 = 0.28$ mA cm⁻² s^{1/2}, the value of D is about 2.4×10^{-15} cm² s⁻¹.

4. Conclusions

The electro-oxidation at 1.4 V of the anodic Pb(II) film anodically grown on a lead electrode in sulfuric acid solution involves three distinguishable processes that comprise the conversion of the plumbous phases to PbO_2, the oxidation of the substrate lead to PbO, and the evolution of oxygen. The

formation of a PbO_2 layer conforms to mainly an instantaneous nucleation and two-dimensional growth mechanism under charge-transfer control. Based on the proposed kinetics for the analysis of the oxidation current transient, several related electrochemical quantities of interest have been computed for the first time, such as the thickness of the PbO_2 layer the quantity of PbO_2 formed, and the diffusion coefficient of O^{2-} ions that controls the oxidation process of substrate lead to PbO. In conjunction with the LSV analysis of the phase composition of the anodic Pb(II) film, the results have also shown more convincingly the extent to which the plumbous phases are transformed to PbO_2. Furthermore, the kinetic model proposed in this communication can be extended to describe the oxidation process of the anodic Pb(II) film on Pb–1at.%Sb or Pb–1at.%As electrodes, and the influence of antimony or arsenic as an alloying agent on such an oxidation process will be presented elsewhere [29].

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