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Fundamentals of lead-acid cells. VIII. Potential step studies on the oxidation of porous lead electrodes in sulphuric acid

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Using the potential step technique, the oxidation of lead to lead sulphate is compared for solid and porous lead electrodes. Similarities and differences are observed between the behaviour of the two types of electrode and are explained in the light of current porous electrode theory.

1. Introduction

We have already investigated the solution region for the anodic oxidation of lead in H_2SO_4 [1] and our results confirmed the findings of other workers [2–10]. In this paper, the behaviour of planar and porous lead electrodes in the solid phase region is investigated.

Brennan and Hampson [11] have investigated in detail certain aspects of the system and have postulated that the development of solid phase $PbSO_4$ on a lead anode is governed by a two-dimensional nucleation and growth process. However, Archdale and Harrison [3] postulated that the development of solid phase $PbSO_4$ on a lead anode should be governed by a three-dimensional nucleation and growth process. Unfortunately, observed data for the initial part of the i–t transient conformed to $i \propto t$ which is indicative of a two-dimensional process. The work of Fleming and Harrison [7] confirmed the observations and these authors suggested that some type of progressive nucleation of solid state $PbSO_4$ was taking place. However, Archdale and Harrison [3], and Fleming and Harrison [7], have observed that because of the initial solution reaction, the development of a really satisfactory kinetic interpretation for this electrocrystallization cannot be achieved.

In our work on porous electrodes, we have shown [1] that the reaction in the solution region, which is controlled by factors affecting the diffusion layer in a direction away from the porous face, is insignificant in comparison with reactions occurring within the porous matrix. In this paper we compare the responses of planar and porous lead electrodes to potential step experiments.

2. Experimental

The manufacture and preparation of planar and porous lead electrodes, and the design of the electrochemical cell, has been described previously [1]. Solutions were made up using Analar grade reagents with tridistilled water. Deoxygenated 5 M H_2SO_4 was used and all measurements were made at room temperature, 25° C ± 2° C; potentials were measured with respect to the Hg/Hg_2SO_4 reference electrode in 5 M H_2SO_4.

Potentiostatic pulse measurements were obtained using a potentiostat (Chemical Electronics, type TR70/2A), and a function generator (J. Dawson, Newcastle-upon-Tyne), while the electrode response was recorded using an X–Y–t recorder (Bryans Series 26 000).

3. Results and discussion

Fig. 1 shows a typical i–t transient resulting from an anodic potential step on a planar lead electrode in deoxygenated 5 M H_2SO_4. This result is similar to results obtained previously by Harrison and

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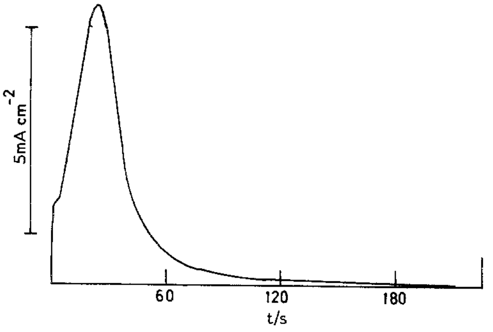

Fig. 1. The oxidation transient formed by anodically pulsing a mechanically polished stationary planar Pb electrode from – 1200 mV to – 920 mV in deoxygenated 5 M H_2SO_4, showing the growth of $PbSO_4$.

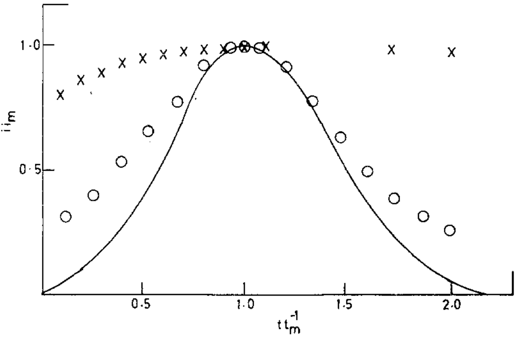

Fig. 2. ii_m^{-1} versus tt_m^{-1} for potential steps on stationary planar and porous lead electrodes from – 1200 mV to – 920 mV in deoxygenated 5 M H_2SO_4. (o) planar electrode and (X) porous electrode. The theoretical curve shown is for the progressive nucleation and growth of two- or three-dimensional processes.

co-workers [3, 7] in deoxygenated 1 M H_2SO_4. The response consists of a rapidly falling current which reaches a minimum, then rises, and eventually falls; in Fig. 1 the initial fall is partially masked by the subsequent rise at the potential depicted. This rising portion is $i \propto t$ and the subsequent falling part of the curve, owing to thickening of the $PbSO_4$ layer, approximately follows the well-known $i \propto t^{-1/2}$ dependence.

The response to a potential step is qualitatively similar at varying potentials for the planar lead electrode. However, as the magnitude of the potential step increases, the magnitude of the maximum current achieved (i_m) increases, and the time (t_m) to reach i_m falls; typical results are shown in Table 1.

Fig. 2 shows the reduced plot ii_m^{-1} versus tt_m^{-1} for the i–t response of the planar lead electrode. On the same axes is drawn the theoretical curve for the progressive nucleation and growth of two- or three-dimensional processes (cylinders and pyramids, respectively). The fit suggests that the transient represents the progressive nucleation and growth of a two- or three-dimensional layer of lead sulphate. However, this observation is in direct contradiction with the observation of $i \propto t$ dependence for the first part of the transient exemplified by Fig. 1. Harrison and co-workers [3, 7] also found the nucleation of $PbSO_4$ to be progressive in deoxygenated 1 M H_2SO_4. However, these authors were of the opinion that the growth process should be three-dimensional, despite the lack of experimental evidence. Thus, we are forced to the conclusion that the solution state process interferes seriously with the observation of the true electrocrystallization kinetics of the solid state process. This conclusion agrees with that of Harrison and co-workers [3, 7].

Table 1. The potential dependence of the i–t *response of a planar electrode in deoxygenated 5 M H_2SO_4 to an anodic potential step from – 1200 mV*

E (mV)	i_m (mA cm^{-2})	t_m (s)
–940	1	250
–930	2	70
–920	7	22

The same general features of the i–t transient are observed for porous electrodes as for smooth electrodes. An abrupt rise in current is followed by a rapid fall (0·1 s) as the double layer is charged, followed by the expected rise and fall in current characteristic of a nucleation and growth process. These features are apparent in Figs. 3 and 4. Fig. 3 has an expanded time scale showing the effect of double-layer charging, whilst Fig. 4 illustrates the falling behaviour of the transient.

The first rise and fall may also contain elements present owing to the need to saturate electrode reaction layers with $PbSO_4$ prior to the commencement of the solid phase reaction. Reactions in which both solid state and liquid processes occur simultaneously are not particularly uncommon [12]. We have analysed the first parts of these i–t transients from porous lead electrodes, and the linear rise in current with time demonstrated by the smooth lead electrode was not observed. Nor,

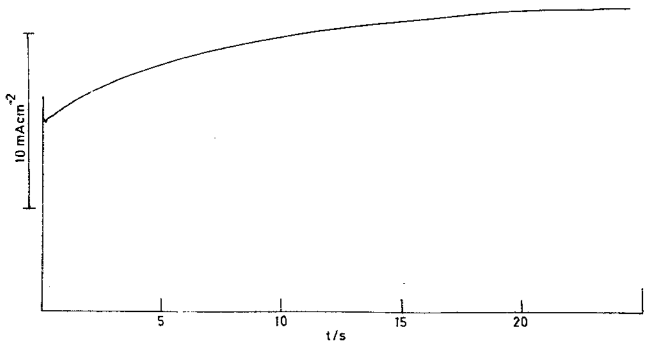

Fig. 3. The rising part of the oxidation transient formed by anodically pulsing a stationary porous Pb electrode from − 1200 mV to − 920 mV in deoxygenated 5 M H_2SO_4.

however, did the data conform to a t^3 relationship observed by Casson *et al.* [13] for related reactions on PbO_2 with porous electrodes. A possible interpretation of this complex *i–t* relationship arises because of the complications imposed by the porous matrix. We have discussed in another context [14] how the penetration depth of the porous matrix can be used to describe porous electrode behaviour qualitatively. In that case we were dealing with a simple solid phase reaction (any solution phase reaction was apparently insignificant). In the present case we have the possibility of both solution and solid phase reactions. Here, as the reaction is driven progressively deeper into the electrode, owing to the nucleation and growth of solid phase lead sulphate at the front, new areas of the electrode are subjected first to the solution reaction, where the characteristic current would fall with time, and finally to the solid phase reaction with the rising current characteristics. The resultant behaviour is a composite *i–t* transient. The time (t_m) of the occurrence of i_m in the *i–t* transient will be controlled predominantly by the front of the electrode down to the penetration depth, since this region of the electrode forms the major part. Moreover, the response of this region conforms to that of a planar electrode of enhanced area. Thus, we might expect t_m for the porous electrode to be the same, or very slightly increased, compared to that of a planar electrode under similar conditions. This is well illustrated by Table 2 which shows the dependence of i_m and t_m on potential for a porous lead electrode. Comparison with Table 1 shows that, within the bounds of experimental error, t_m for porous and planar lead electrodes is similar.

Analysis of the *i–t* transients from porous lead electrodes indicates that there is no correlation with any of the theoretical models for the nucleation and growth process. We must here conclude that the porous matrix of the electrode,

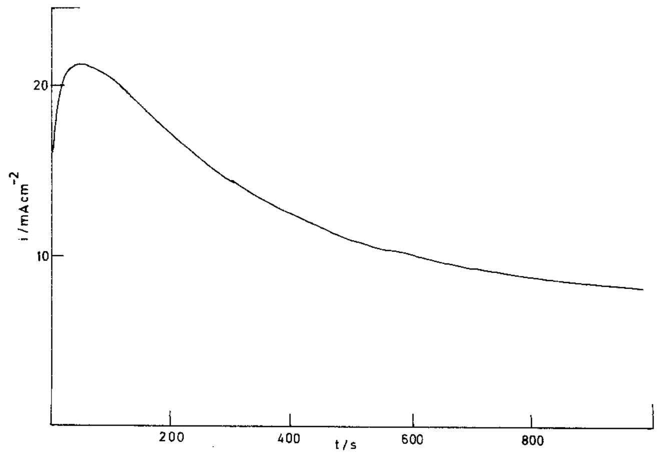

Fig. 4. The oxidation transient formed by anodically pulsing a stationary porous Pb electrode from − 1200 mV to − 920 mV in deoxygenated 5 M H_2SO_4.

Table 2. The potential dependence of the i–t *response of a porous lead electrode in deoxygenated 5 M H_2SO_4 to an anodic potential step from − 1200 mV*

E (mV)	i_m (mA cm^{-2})	t_m (s)
−940	9·5	280
−930	13·5	80
−920	21·0	40
−910	31·5	25
−900	50·0	20
−850	113·0	1

coupled with the solution reaction, completely obscures electrocrystallization kinetics (see Fig. 2).

This is different from the case of porous PbO_2 discussed by this laboratory [15]. In the PbO_2 case, the solution reaction could be neglected, also the conductivity of the PbO_2 porous matrix was significantly lower than that of the porous lead matrix. Thus, we would expect the penetration depth to be much larger in the case of PbO_2, and the extent of porous electrode penetration, as the reaction proceeds, to be proportionally less in the case of PbO_2 than in the case of lead. In other words, porous PbO_2 would be expected to behave more like a planar electrode than would the porous lead electrode.

4. Conclusions

The following conclusions were reached:

(a) The *i–t* oxidation transients of lead to lead sulphate on planar and porous electrodes have the same general features.

(b) The time (t_m) to attain maximum current (i_m) is similar for planar and porous electrodes.

(c) There is some evidence that the nucleation and growth process of lead sulphate on the planar lead electrode is progressive and either two- or three-dimensional. This evidence is contradicted by an $i \propto t$ dependence of the rising part of the transient. It is concluded that this $i \propto t$ dependence is an artefact due to the dissolution reaction, which obscures the first part of the curve and prevents a true kinetic interpretation of the data.

(d) The *i–t* response of the porous lead electrode to an anodic potential step is complex and obscures the true kinetics of the nucleation and growth of lead sulphate. This complex *i–t* response is due to complications imposed by the porous matrix and the possible intrusion of the dissolution reaction.

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