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Reactions at lead electrodes in 5 mol dm^{-3} H_2SO_4 near the equilibrium potential

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The nature of the anodic reactions of lead near the $PbSO_4$/Pb equilibrium potential depends strongly upon the state of the metal. By an electrochemical etching process a lead surface is produced which participates in a solution controlled dissolution process; a simple chemical etching process results in a solid state process. The natures of these processes are investigated and discussed. The addition of expander materials to the electrolyte solution apparently inhibits both the solution and the solid state processes.

1. Introduction

In our laboratories we have been, from time to time, concerned with the participation of lead solution species in the operational reactions of lead acid cells. There is no doubt that in dilute sulphuric acid solution the lead negative electrode reaction involves solution Pb^{2+} species provided that the electrode is not driven too far positive into the potential region where solid phase $PbSO_4$ is thermodynamically stable at the electrode. Confirmation of this has been provided by a number of investigations due to Harrison *et al.* [1], Armstrong and Bladen [2] and ourselves [3, 4]. The existence of reaction participating Pb^{2+} aqueous species and the kinetic interpretation of the electrochemical measurements concerned with the solution reaction has led to the suggestion of a rather complex electrode reaction [4] involving a binuclear lead species.

We have had considerable difficulty in extending the detection of Pb^{2+} species to concentrations of H_2SO_4 corresponding to the operating conditions of a lead acid cell. It has been suggested that the reasons for this include the lower solubility of $PbSO_4$ in the concentrated acid and the increased sulphate activity. These are undoubtably complicating factors which will reduce the lead dissolution region by 30 mV for each tenfold decrease in solubility, but, even so, it should be possible to detect a 'free dissolution' window even at very low solubilities. The possible effects of expander materials (which are conventionally added to lead negatives in order to improve low temperature behaviour) on this solution reaction are of considerable interest. This paper records the results of an investigation of these effects using a rotating disc technique.

2. Experimental details

The Teflon shrouded lead electrode ($\phi = 0.2$ cm) has already been described [5]. The electrode was rotated at a uniform speed using a rotating disc assembly (Kemitron electronics RD1). The electrode was driven by a high precision motor-generator using a special belt drive which obviated speed fluctuations. Rotation speed was estimated by an opto-electronic shaft encoder to an accuracy of ± 0.02 r.p.s. The motor-generator could be either manually controlled or automatically controlled by a Z80 based microcomputer via a D to A interface. A box girder construction in stainless steel reduced vibration and eccentric movement of the electrode to an absolute minimum.

Potential control of the working electrode with respect to a Hg_2SO_4/Hg reference electrode in the same electrolyte solution was achieved using a precision potentiostat (Hitek DT 2101).

All solutions were prepared from analytical

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grade chemicals. Expander material used was Indulin C supplied by J. Lucas Ltd.

Electrodes were introduced into the 5 mol dm^{-3} H_2SO_4 electrolyte solution with a potential in the hydrogen region imposed on the electrode before electrode/electrolyte contact was made. In this way any film development on an uncontrolled electrode was avoided.

3. Results and discussion

Experiments with a large number of electrode surface preparation methods indicated that the subsequent behaviour of the electrode in the vicinity of the equilibrium potential was crucially dependent upon the surface characteristics. It was apparent that it was difficult to prepare an electrode which would provide evidence of a solution reaction in which Pb^{2+} ions freely leave the electrode. Moreover once a film of $PbSO_4$ had been produced at the electrode it was not possible to demonstrate a solution Pb^{2+} reaction by any *in situ* treatment that we could devise. The best method of obtaining the solution reaction was by electrolytically etching in a complex solution of perchloric acid, ethanol and ether ($HClO_4$ – 60%, 45 parts; C_2H_5OH, 50 parts; $(C_2H_5)_2O$, 5 parts). Most of the usual methods of electrode pretreatment did not result in evidence for a solution Pb^{2+} reaction irrespective of the *in situ* treatment of the electrode following the initial electrode/electrolyte contact. A simple chemical etch based on nitric acid (10%) generated an electrode free of any evidence for Pb^{2+} in the sulphuric acid electrolyte. This latter chemical treatment represented the extreme of complete solid state $PbSO_4$ formation

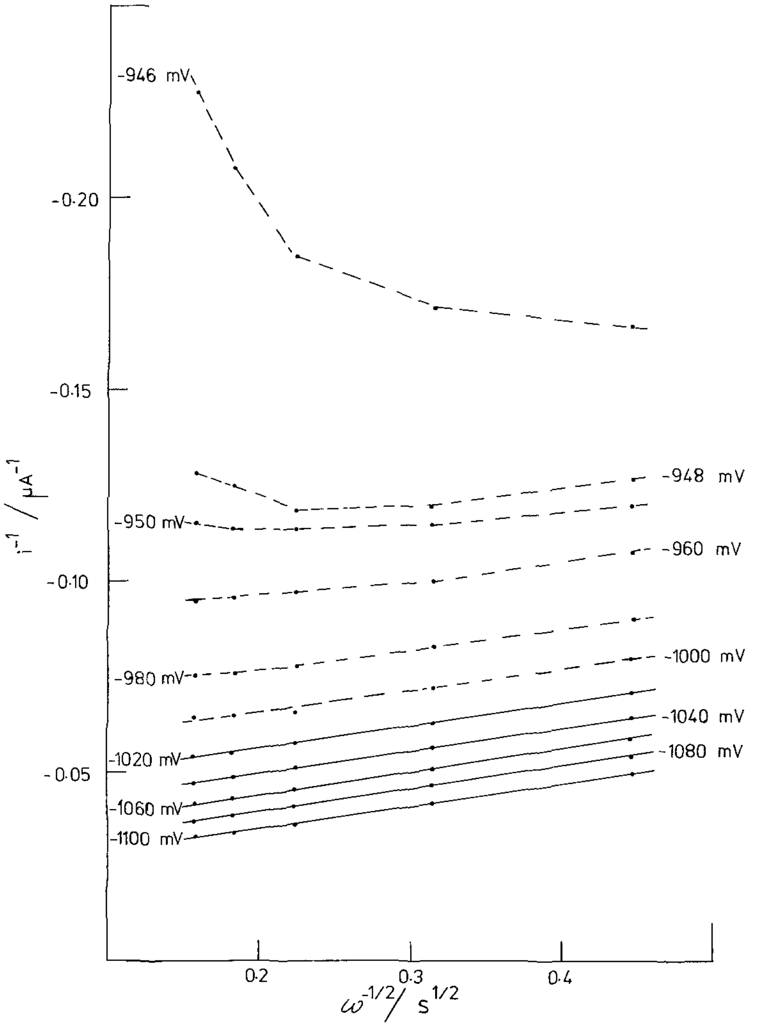

Fig. 1. Relationship between current and rotation speed at a series of potentials. Pb electrode, 5 mol dm^{-3} H_2SO_4, 23° C. Electrochemical etch (see text).

in contrast to that of a limited solution behaviour resulting from the non-aqueous electrolytic process. These two extremes were chosen for experimental study.

3.1. *Experiments with* $HClO_4$–C_2H_5OH–$(C_2H_5)_2O$ *etch*

Contrary to our previous experience with 1 mol dm^{-3} electrolytes [4], it was not found possible to completely eliminate the reduction current due to hydrogen ion at the rotating disc electrode (RDE). This reduction current arises due to the high hydrogen ion concentration. The presence of traces of oxygen enhances the total reduction current [2, 4] and generally it was found expedient to reduce these currents to very low values by purging nitrogen over a long period. It was not possible to completely eliminate the (cathodic) reduction current. This complicated the electrochemistry since the hydrogen reduction intruded into the lead dissolution process.

Fig. 1 shows the results of our experiments in which lead RDE's were rotated at carefully controlled potentials close to the rest potential. The measurements at potentials more negative than the lead dissolution region form a series of parallel straight lines which have intercepts corresponding to infinite rotation speed currents (i_∞) which increase exponentially with potential. The change in i_∞ with potential (Fig. 2a) leads to a Tafel slope in excess of 200 mV dec^{-1} which is not uncommon for the hydrogen ion reduction reaction at an electrocatalyst of only fair activity [6].

By extrapolation of the hydrogen reduction lines back into the lead dissolution region the net currents observed were corrected at each rotation speed in order to obtain the lead dissolution current i_{Pb} assuming that

$$i_{net} = i_{Pb} + i_{H_2} \tag{1}$$

where i_{H_2} is the cathodic current for hydrogen evolution. This correction when applied to the upward curving lines of Fig. 1 allowed the cal-

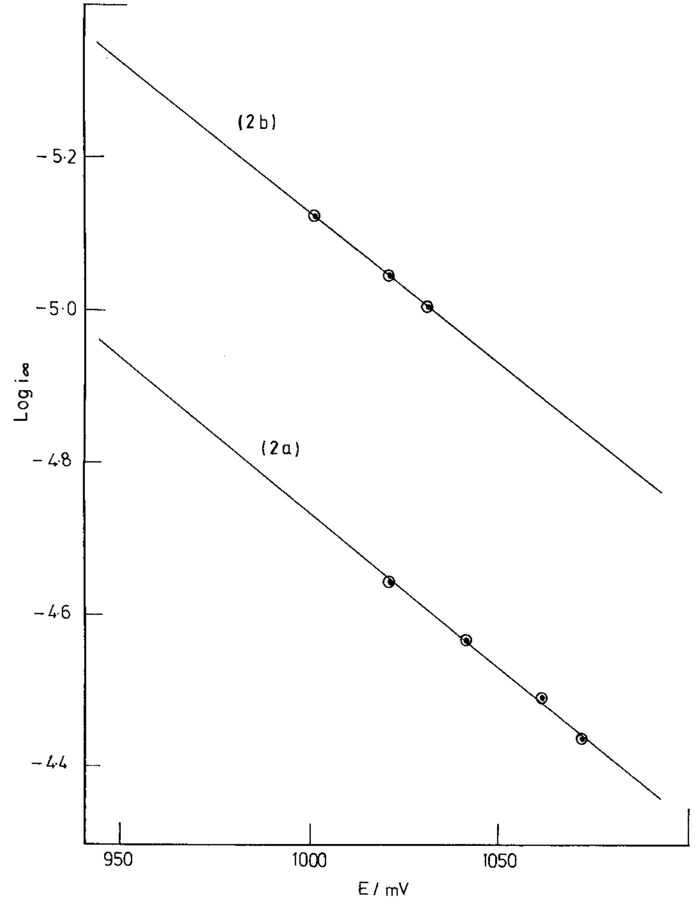

Fig. 2. (a) Tafel line for the hydrogen evolution process on electrodes of Fig. 1. (b) Tafel line for the hydrogen evolution process on electrode of Fig. 6.

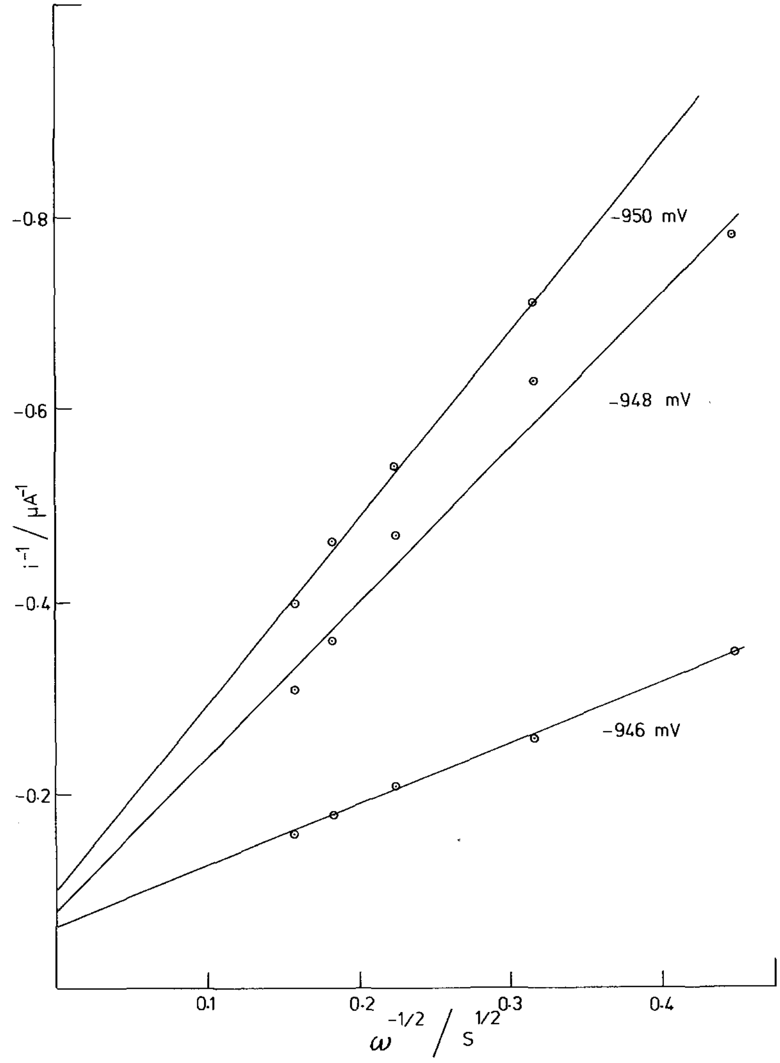

Fig. 3. Lead dissolution currents from the data of Figs. 1 and 2.

culation of the rotation speed dependence of i_{Pb} as shown in Fig. 3. It is clear that these lines are sufficiently rectilinear to confirm that the lead dissolution current observed in the potential region bounded by — 950 and — 946 mV corresponds to a solution controlled dissolution reaction. At more positive potentials the current increased enormously and became rotation speed independent. The Tafel line in Fig. 4 represents the charge transfer controlled current i_∞, for lead dissolution (at infinite rotation speed) into 5 mol dm^{-3} sulphuric acid. The Tafel slope here is rather lower than was obtained for 1 mol dm^{-3} H_2SO_4 [4]. This is probably due to the adsorption of Pb^{2+} (or a species based on Pb^{2+}) at the electrode; at any rate the potential is such that we are almost under conditions where no Pb^{2+} leaves the electrode so that the reaction becomes completely solid state. Attempts to calculate the slope dependency $(\partial i^{-1}/\partial \omega^{-1/2})_E$ as a function of the potential E gave very low values (Fig. 5) indicating the likelihood that conditions were on the edge of almost complete adsorption.

We can conclude that there is a solution controlled lead dissolution reaction in 5 mol dm^{-3} H_2SO_4 and that this occurs in a very narrow range of potentials between — 950 to — 946 mV. Within this narrow window the reaction at the electrode under battery conditions (5 mol dm^{-3} H_2SO_4) involves a simultaneous reduction of solution H^+ to form H_2 together with a lead dissolution process.

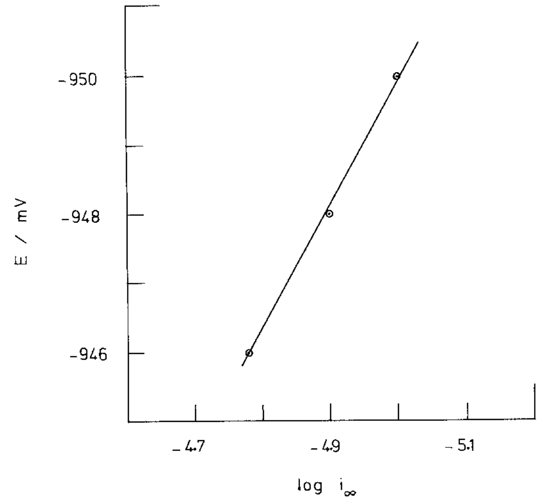

Fig. 4. Tafel line connecting the limited data for the lead dissolution process isolated in Fig. 3.

3.2. *The effect of an expander material in the solution*

The addition of an expander material (Indulin C) was made in order to see the effect on the solution reaction. Fig. 6 records the data from the RDE experiments. In the hydrogen region a family of straight lines similar to that observed in the absence of expander was obtained. Subtraction in accordance with Equation 1 showed that there was, within experimental limits, considerably less current due to lead dissolution at any potential in the (original) dissolution range up to the limit of the $PbSO_4$ region (Fig. 2b). Moreover as shown in Fig. 7 the rotation speed dependence was not characteristic of a solution reaction and it is clear that we were on the threshold of a solid state process. The current calculated for the case of the indulin C saturated solution did not form well-defined i^{-1} —$\omega^{-1/2}$ lines, in fact the correlations exhibited an opposite gradient to that expected for a solution process. Moreover the $PbSO_4$ phase deposition potential was found to be more positive by $\simeq$ 25 mV than in the pure sulphuric acid solution. The existence of this positively shifted region in the case of the expander indicated that not only is the solution process suppressed but the solid state electrocrystallization process is inhibited. These observations suggest that the expander acts via an adsorbed electrode film which both inhibits nucleation of $PbSO_4$ and hinders the progress of Pb^{2+} ion across the interphase possibly by combination of Pb^{2+} with the adsorbed film.

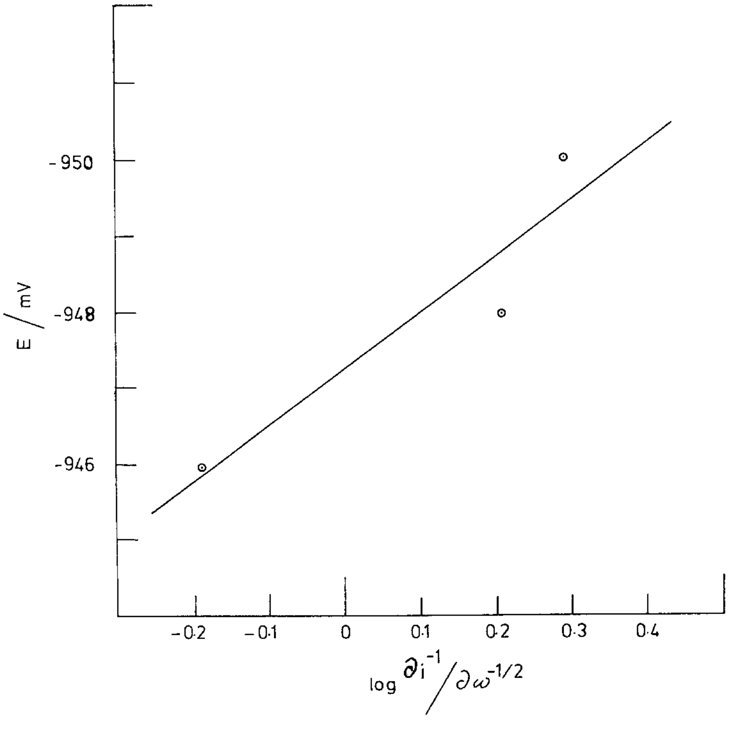

Fig. 5. The dependence of $(\partial i^{-1}/\partial \omega^{-1/2})_E$ on potential from Fig. 3.

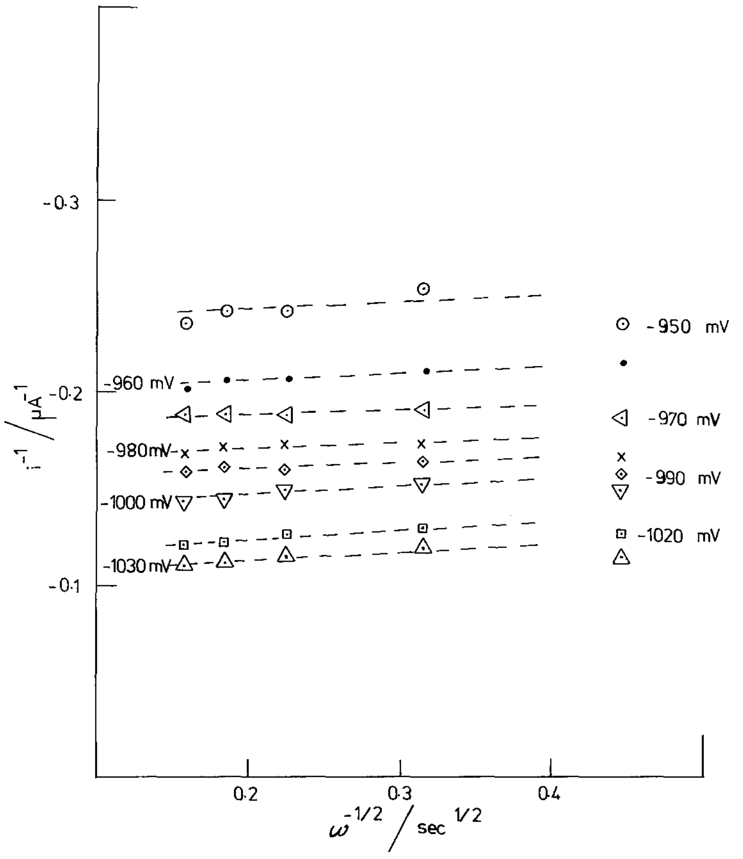

Fig. 6. As Fig. 1 but with electrolyte solution saturated with Indulin C.

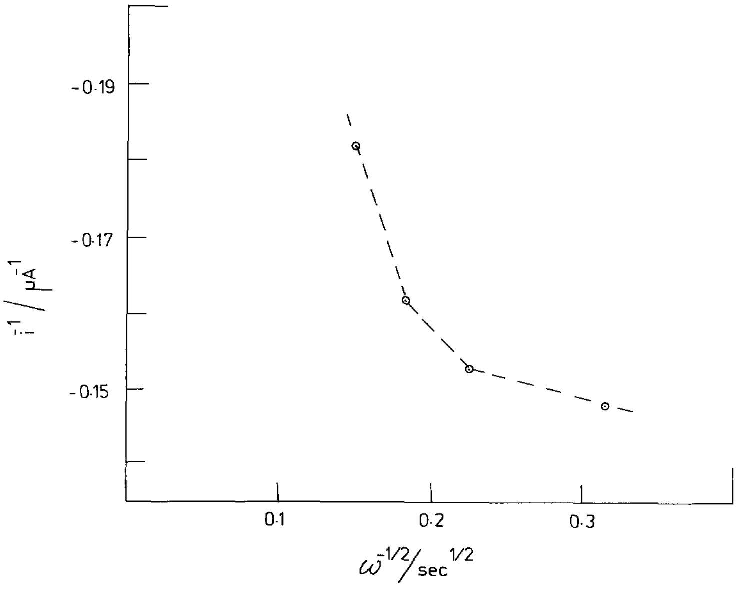

Fig. 7. Residual anodic currents after the removal of the estimated hydrogen current (Fig. 2b) from the data of Fig. 6.

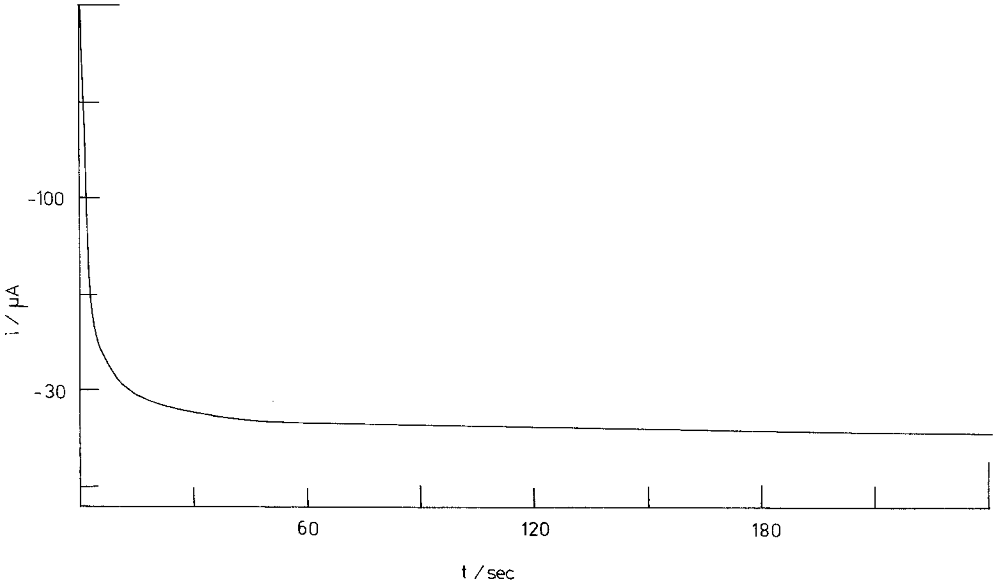

Fig. 8. Electrode as Fig. 1 but chemically etched (10% HNO_3). Current on electrode/electrolyte contact at — 1150 mV (8.5 rps).

3.3. *Experiments with chemically etched lead (10% HNO_3 – 1.67 mol dm^{-3})*

In order to avoid any possibility of solid phase formation due to intruding reactions, the etched electrode was introduced into the cell (after washing) with the polarizing circuit maintained in the hydrogen region. This avoided the production of any surface films due to the initial electrode/electrolyte contact. The current flowing on this initial contact is shown in Fig. 8; an initially high current as the electrode is covered with H_2 species gives way to a steady state indicating absence of films. Steady state measurements were made at a series of potentials in the range — 1150 to — 946 mV as shown in Fig. 9. The strong influence of the etching process is shown by comparison of Figs. 9 and 10 where the shorter etch engenders a more reactive electrode. Tafel plots in this region obtained by extrapolating the data of Figs. 9 and 10 to infinite rotation speed are shown in Fig. 11. The Tafel slopes approximate to the 120 mV dec^{-1} region at the more anodic potentials. In general the Tafel slopes are high, these have been discussed [6].

At potentials more positive than — 946 mV it was not possible to obtain steady state currents. This is shown convincingly in the data of Fig. 12. The curve is a well-developed crystallization transient and although the hydrogen evolution process intrudes significantly in the early stages (— ve currents) the form of the transient is unequivocal [7]. The deconvolution of the hydrogen and $PbSO_4$ reaction cannot be made accurately enough to decide the dimensionality of the process, but to a first approximation it seems to conform to a two-dimensional instantaneous nucleation and growth process. The shorter etch produces the higher current transient and must have given rise to the larger surface population of active centres.

We can conclude that the etching process engenders a film (possibly oxide or hydroxide) which on contact with the electrolyte at — 946 mV forms a thermodynamically stable film of $PbSO_4$ over a period of about 1 h. This film is formed by a process of growth and overlap giving rise to a rising and falling current response. The early stages are complicated by the hydrogen reaction.

The process of the post etch film is likely to arise from the high exchange current when lead dissolves. This probably produces pH conditions high enough to form a monolayer film of a basic salt (or hydroxide/oxide).

4. Conclusions

1. If film free surfaces of lead are available, a

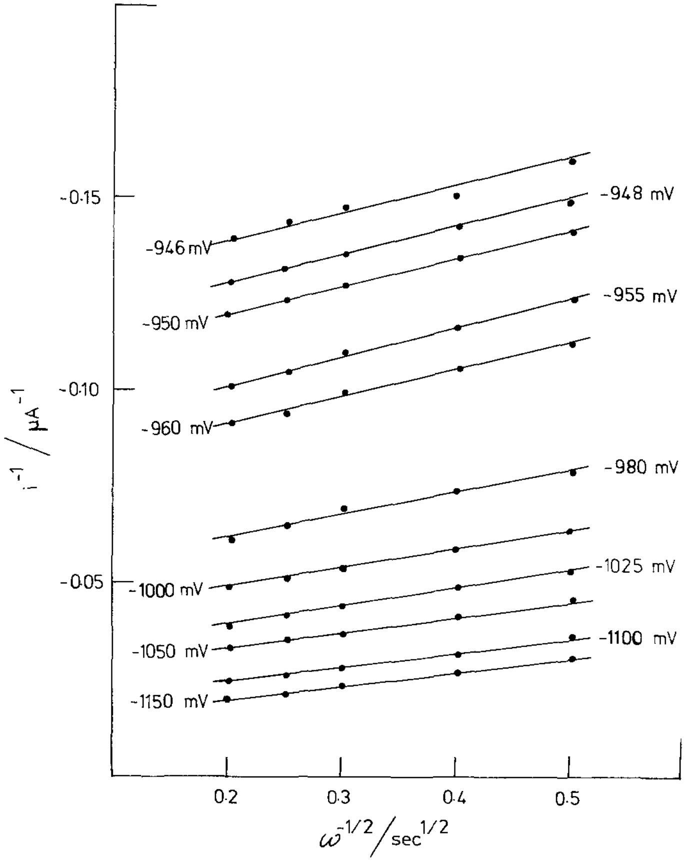

Fig. 9. The dependence of current and rotation speed in the potential region — 1150 to — 946 mV. Electrode details as Fig. 8 – 60 s etch.

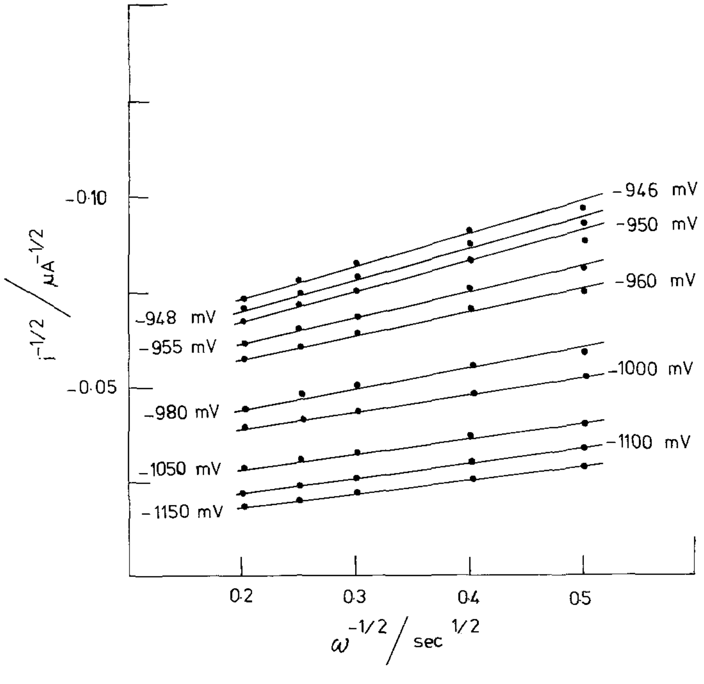

Fig. 10. As Fig. 9 but 5 s etch.

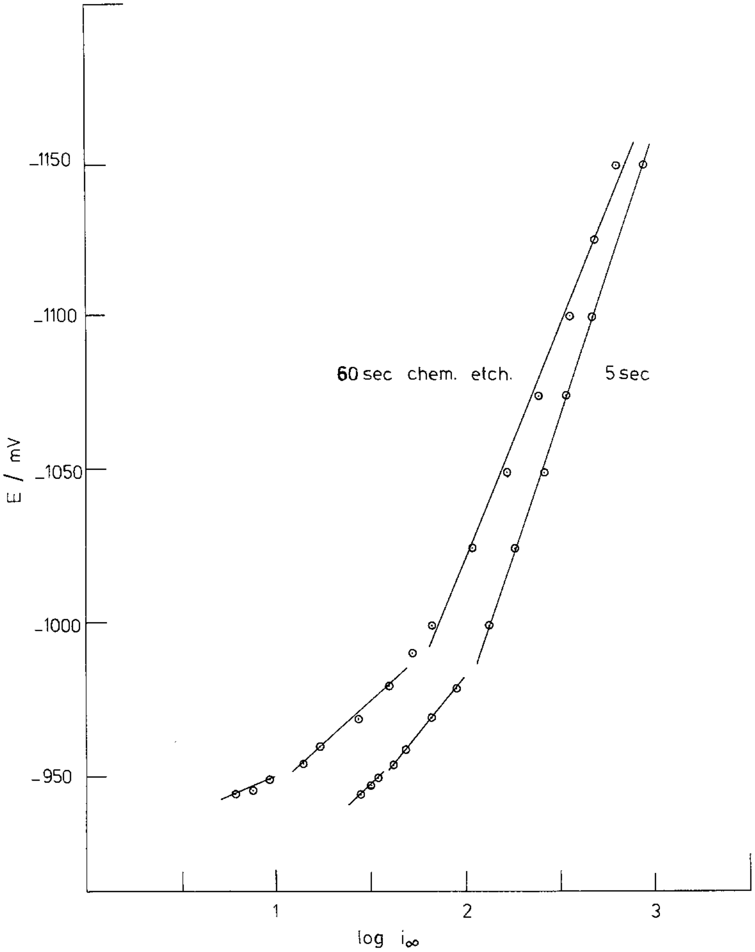

Fig. 11. Tafel plots corresponding to Figs. 9 and 10.

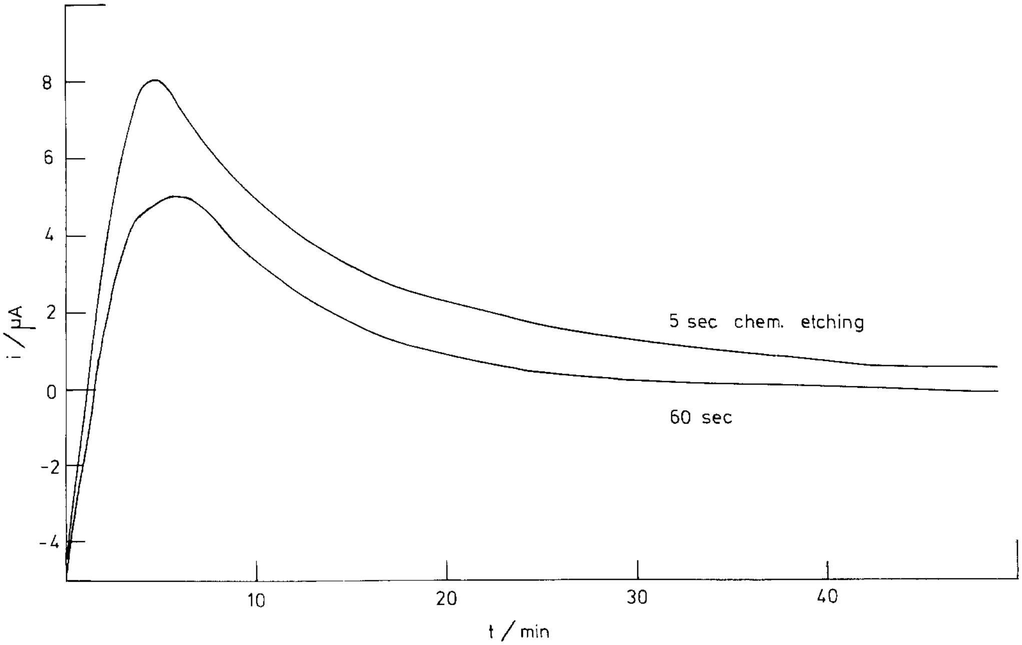

Fig. 12. As Fig. 8 but — 944 mV.

solution dissolution window is present at ~ − 946 to − 950 mV.

2. If the etching process produces a film, this cannot be removed and ultimately a $PbSO_4$ film is formed on the surface which obscures the dissolution process. This is the generally observed behaviour.

Work is continuing on this topic.

Acknowledgements

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