

THE OXIDATION OF POROUS LEAD ELECTRODES IN SULPHURIC ACID SOLUTIONS

N. A. HAMPSON and J. B. LAKEMAN

Chemistry Department, University of Technology, Loughborough, Leicestershire (Gt. Britain)

(Received March 30, 1978; in revised form July 11, 1978)

Summary

The electrochemical oxidation of porous lead electrodes is compared and contrasted with that of solid lead. Significant differences between the behaviours of the two electrode types are observed and interpreted in terms of the major component of the oxidation of the porous electrode arising from the "inner" porous electrode structure. This "inner" contribution is not affected by the geometry of the electrode hydrodynamic layer.

Introduction

The electrochemistry of the lead-acid battery has been reviewed by a number of workers [1]. In spite of its long history, it is clear from the large volume of work recently published in this area that interest in the electrochemical science and technology of this device is increasing. The basic electrochemistry of the Pb-PbSO₄ electrode has only been satisfactorily studied relatively recently. This was partly due to the fact that progress has been slow in the development of suitable electrical circuits for the investigation of very fast electron transfer reactions, and partly because the investigations of the kinetics of an electrode of the second kind (anionic electrode), at which a solid phase is being formed, is daunting.

The electrochemical oxidation of solid lead to form lead sulphate has been investigated by the Newcastle group [2 - 8]. Harrison and his co-workers [2 - 6] have shown that lead dissolves electrochemically in sulphuric acid to produce a soluble Pb(II) species. An insoluble PbSO₄ layer may also be formed when the concentration of soluble Pb(II) species exceeds the solubility limit. It has also been suggested by Fleming and Harrison [7] that a precipitation mechanism to form PbSO₄ occurs under some conditions prior to the solid state reaction. A more recent paper by Armstrong and Bladen [8] confirms much of the earlier work of Harrison [2 - 7] and some of the findings of Carr *et al.* [9, 10]. The Armstrong work [8] confirmed that anions were adsorbed and that this adsorption inhibited the oxygen reduction

on the lead electrode. Moreover, impedance measurements were used to indicate that the active dissolution of lead takes place by a fast, reversible, diffusion-controlled reaction to produce Pb(II) species which diffuse away from the electrode surface. In the electrode potential region where a solid reaction product is formed, an anodic voltage step results in a rising, transient current response. Such rising transients have been noted by Brennan and Hampson [11 - 13] who used them to test the theory that "negative expanders" of lead cells acted by suppressing the solid state oxidation of lead in favour of the dissolution-precipitation process [2, 11].

The study of porous lead electrodes has received relatively little attention, although this aspect of the electrochemistry of lead is highly relevant to the modern lead-acid battery industry. The industrial processes by which porous lead electrodes 0.1 - 0.3 cm thick are produced are usually specific for each manufacturer. In essence, the process consists of reducing a mixture of lead oxide, hydroxide, sulphate, and lead in dilute sulphuric acid. (The main raw material for this process is leady oxide, or grey oxide, which is tetragonal PbO admixed with about 40% lead.) In order to improve performance, various expanders are added (*e.g.*, BaSO₄, C, lignosulphonates). The resulting product has a porosity of about 40%.

It is of considerable interest to extend the study of the electrochemistry of lead to porous electrodes. This paper describes experiments made with solid and porous electrodes in order to compare the behaviours. In particular, the existence of an identifiable "solution" reaction at the porous electrode was investigated.

Experimental

The solid lead rotating disc electrodes were discs of 0.071 cm² cut and machined from metal rod supplied by Koch-Light (5N purity), set in a Teflon holder. The electrodes were pretreated by polishing on roughened glass using tridistilled water as a lubricant in order to remove any embedded material. Immediately prior to an experiment the electrode was etched (60 s; HNO₃ 1.58M) in order to produce a surface free from oxides. It was then rinsed several times with tridistilled water and immersed in the electrolyte solution while still wet from the final rinse water. As soon as the rest potential had been attained the electrode was held at a cathodic potential close to the onset of hydrogen evolution, in solutions deoxygenated with nitrogen (BOC 'white spot'), to minimise the chances of the development of any sulphate film. For experiments using aerated solutions, washed air was introduced into the cell using a rotary pump *via* a fine sintered frit.

Porous electrodes were prepared in the same format as the solid electrodes by arranging that the lead rod terminated beneath the surface of the Teflon shrouding. By forcing a conventional battery negative paste into the cavity a porous layer was produced ($\phi = 3$ mm; 0.76 mm deep) which terminated the lead electrode. The paste (0.2% C, 0.4% BaSO₄, 0.02% organic

expander) was galvanostatically transformed to porous lead at 50 mA until a steady potential (-1.5 V *vs.* $\text{Hg}_2\text{SO}_4/\text{Hg}$, $0.1\text{M H}_2\text{SO}_4$) was obtained and hydrogen was being freely evolved. In this way a porous deposit was produced similar to that associated with a conventional automotive negative (~ 1.52 mm thick but both sides utilised). It should be noted that galvanostatic charging was carried out in the upward facing position to prevent hydrogen gas retention in the porous matrix. After formation, the electrode was washed in tridistilled water and fitted into the electrolytic cell.

Measurements were carried out in a Pyrex cell of conventional form with a glassy carbon rod, as subsidiary electrode, situated in a separate compartment. The reference electrode, also in a separate compartment, was connected to the working solution, 2 mm away from the working electrode, *via* a Luggin capillary and a closed, liquid-seal tap. Potentials are referred to the $\text{Hg-Hg}_2\text{SO}_4$ reference electrode in H_2SO_4 of the same molarity as the working solution. Solutions were made up using AnalaR grade reagents with tridistilled water; working solutions were either 1.0M or $5.0\text{M H}_2\text{SO}_4$, and all measurements were made at room temperature, 25 ± 2 °C.

Potential step, linear potential sweep, and stationary measurements were obtained using a potentiostat (Chemical Electronics, Type TR 70/2A) and a function generator (J. Dawson, Newcastle upon Tyne), the electrode response being recorded either with an XYt recorder (Bryans series 26700) or a digital multimeter (Hewlett Packard 3490A).

Results and discussion

Solid electrodes

Cyclic potential sweep experiments

If the positive limit of the potential sweep was limited to ~ -930 mV (corresponding to an overpotential of 40 mV), then, for the sweep speeds employed (≤ 135 mV s^{-1}), the charges in the positive- and negative-going sweeps on either side of the equilibrium potential were equal. This indicates that the anodic electrode products were able to leave the electrode as required by the production of solution soluble Pb^{2+} only.

At more positive potential limits charge not recovered in the positive excursion was recorded at potentials negative of E_{rev} . This indicates the development of a solid phase, PbSO_4 , at the electrode at potentials more positive than -930 mV. Figure 1 shows that this limit depends on the sweep speed; at the higher sweep speed the positive limit is increased, as indicated in Table 1. The limit was quite reproducible and could be detected to a precision of 1 mV with our experimental set-up. It seems likely that solid lead sulphate is developed on the electrode by a dissolution-precipitation mechanism and that at the slower sweep speeds time is available for PbSO_4 deposition at a smaller overpotential.

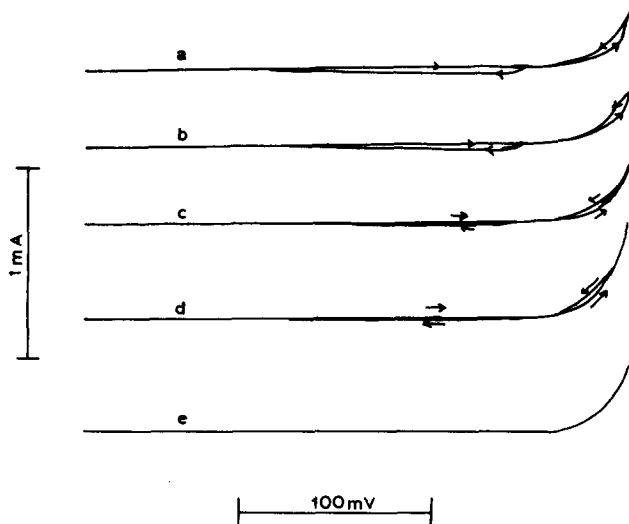


Fig. 1. LSV curves for a solid lead electrode between -1200 mV and -916 mV in $1M$ H_2SO_4 at varying sweep rates. (a) 1.25 $mV s^{-1}$, (b) 4.05 $mV s^{-1}$, (c) 13.1 $mV s^{-1}$, (d) 42.5 $mV s^{-1}$, (e) 135 $mV s^{-1}$.

TABLE 1

Maximum anodic potential limit before the onset of solid phase deposition at different sweep rates

Sweep speed ($mV s^{-1}$)	Maximum anodic potential (mV)
1.25	-926
13.10	-922
42.50	-913

Rotating disc experiments

In order further to investigate the kinetics of the dissolution process within the "dissolution region", the effect of rotation speed on the steady-state current was investigated in the limited potential range -947 - -957 mV. The rotation speed dependence of the current at constant potential for a metal disc electrode freely dissolving at a rate controlled by charge transfer and mass transport in solution has been discussed by Armstrong and Bulman [14]. In the present case for a Pb dissolution current, i , which is much less than the limiting diffusion current, i_d , due to H^+ and HSO_4^- diffusion, and a first order removal of Pb^{2+} from the lattice, we have:

$$i = i_{\infty} - nFk_b C_o \quad (1)$$

which can be inverted to give:

$$\frac{1}{i} = \frac{1}{i_{\infty}} + \frac{k_b 1.61 D_o^{-2/3} \nu^{1/6} \omega^{-1/2}}{i_{\infty}} \quad (2)$$

At infinite speed of rotation, the current passing across the electrode is controlled only by the process of charge transfer, and this current depends on the potential according to

$$\frac{i_{\infty}}{nFk_b} = C_o = C_o^{E^{\ominus}} \exp(E - E^{\ominus})nF/RT. \quad (3)$$

Therefore, plots of i^{-1} vs. $\omega^{-1/2}$ should have an intercept of i_{∞}^{-1} and a slope showing a 30 mV/decade Nernstian dependence on potential. Also, plots of $\log i_{\infty}$ vs. potential are Tafel curves corresponding to the charge transfer reaction.

Figure 2 shows typical i^{-1} vs. $\omega^{-1/2}$ plots for a solid lead electrode in deoxygenated 1M H_2SO_4 . These plots were extrapolated to give i_{∞} , and $\log i_{\infty}$ vs. potential is plotted in Fig. 3. The slope of the Tafel curve in Fig. 3 was approximately 32 mV/decade. This is somewhat surprising for a two electron charge transfer reaction, $Pb(0) \rightarrow Pb(II)$, and indicates a value of the charge transfer coefficient which approaches zero. Abnormal values of charge transfer coefficients have been observed [15]. However, in the absence of

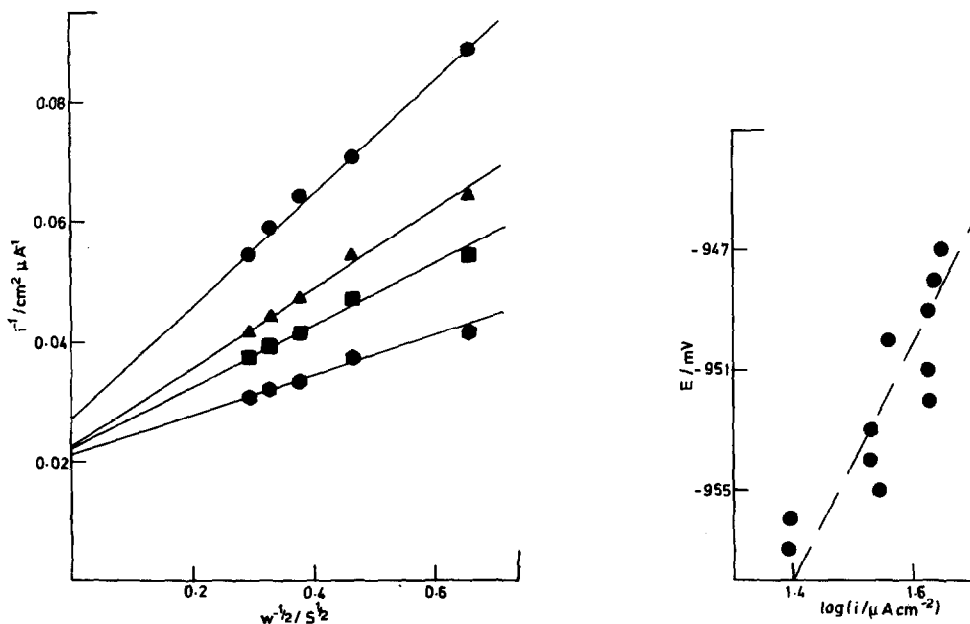
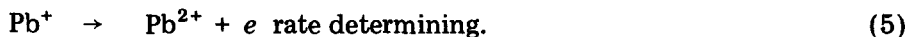


Fig. 2. Typical i^{-1} vs. $\omega^{-1/2}$ plots for a solid lead rotating disc electrode in 1M H_2SO_4 at various potentials. \circ , -955 mV; Δ , -952 mV; \blacksquare , -951 mV; \bullet , -947 mV.

Fig. 3. Semilogarithmic plot of $\log_{10} i$ at infinite rotation speed vs. potential for a solid lead electrode in 1M H_2SO_4 . Broken line indicates a slope of 40 mV/decade.

adsorption [8] it seems at least plausible to suggest that the process being studied is two consecutive one-electron transfers although the matter is by no means settled



With a charge transfer coefficient of 0.5 this would predict a Tafel slope of 40 mV per decade. The dotted line in Fig. 3 is drawn with this slope and indicates that the above mechanism is a possibility.

The potential dependence of the slope (σ) of the i^{-1} vs. $\omega^{-1/2}$ lines follows from the potential dependence of the concentration of Pb^{2+} species in equilibrium with the electrode. For a fast reaction, as is confirmed by our value of the exchange current, this would predict a slope dependency of 30 mV per decade. This slope is shown dotted in Fig. 4 which also contains the salient data and from these it is obvious that the actual slope is lower than 30 mV. It is possible that the results are still affected by PbSO_4 back precipitation, even in this limited range. It seems that the data are scattered rather than being progressively affected at the more positive potential, which suggests that irreproducibility in electrode pretreatment and preparation may be the primary cause. In this connection Harrison *et al.* [2 - 6] have emphasised that for lead in sulphuric acid the surface conditions of the lead may be crucial in determining the response. Thus, it has been reported [2] that the solution region was absent in the case of mechanically polished electrodes. We do not find this if care is taken to remove oxide films. However, the influence of electrode topography cannot be disputed, and it is considered that this factor contributes significantly to experimental variation.

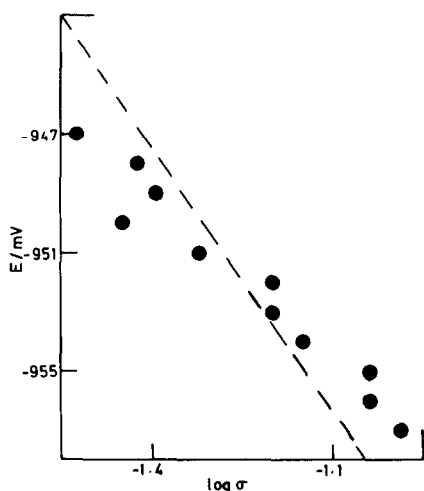


Fig. 4. Semilogarithmic plot of $\log_{10} \sigma$ [$\sigma = di^{-1}/d\omega^{-1/2}$] vs. potential for a solid lead electrode in 1M H_2SO_4 . Broken line indicates a slope of 30 mV/decade.

Potential step experiments

In order to confirm the rotating disc measurements, potential step experiments were made by stepping from a potential in the polarizable region to one in the "dissolution region" and observing the transient current.

Potential step measurements, comparable with the steady-state ones, obtained by stepping into the lead dissolution region, do not result in reproducible data. The pulse response of a stationary solid lead electrode in deoxygenated 1M H₂SO₄ was examined.

For an electrode reaction under potentiostatic control, the current density, i , with charge transfer and diffusion rate control, is a function of time according to the relationship [16]

$$i = i_{\infty} \exp(\lambda^2 t) \operatorname{erfc}(\lambda\sqrt{t}) \quad (6)$$

where

$$\lambda = \frac{i_{\infty}}{nF} \left[\frac{1}{C_R D_R^{1/2}} \exp\left(\frac{\alpha nF}{RT} \eta\right) + \frac{1}{C_O D_O^{1/2}} \exp\left(\frac{-(1-\alpha)nF}{RT} \eta\right) \right] \quad (7)$$

and i_{∞} , the current density at $t = 0$, is given by

$$i_{\infty} = i_o \left[\exp\left(\frac{\alpha nF}{RT} \eta\right) - \exp\left(\frac{-(1-\alpha)nF}{RT} \eta\right) \right]. \quad (8)$$

Under potentiostatic conditions, λ is a constant which depends on the electron exchange and mass transfer parameters, whereas i_{∞} is independent of mass transfer.

In the limit of very small time, the current density is proportional to \sqrt{t} according to

$$i = i_{\infty} (1 - 2\lambda t^{1/2}/\pi^{1/2}) \quad \text{for } \lambda t^{1/2} \ll 1. \quad (9)$$

Thus, a plot of i vs. $t^{1/2}$ should give a straight line with an intercept of i_{∞} , the charge transfer current.

Figure 5 shows typical i vs. $t^{1/2}$ plots taken from pulses into the lead dissolution region from a potential of -1300 mV, and Fig. 6 shows the plot of $\log_{10} i_{\infty}$ vs. E . The dotted line in Fig. 6 is drawn with a slope of 40 mV for comparison with Fig. 3, and it is clear that the data conform to a somewhat lower Tafel slope. This could be due to the extrapolation not being quite satisfactory for such a fast reaction, due to the approximation (eqn. (7)) not holding over the time scale employed. Some confirmation of this is provided by the data of Fig. 7 in which the slope of the $i - t^{1/2}$ lines are correlated in the form corresponding to an exponential dependence on potential. The expected slope, 30 mV per decade as in Fig. 4, shown by the dotted line, is greater than the actual values obtained and suggests that this extrapolation of the transient data may not lead to a very precise value of i_{∞} . On the other hand, at long times eqn. (6) predicts a correlation of i with $t^{-1/2}$ which passes through the origin, and the slope of which shows a 30 mV dependence on potential. In our experiments this was observed, in agreement with the data already obtained by Harrison [2].

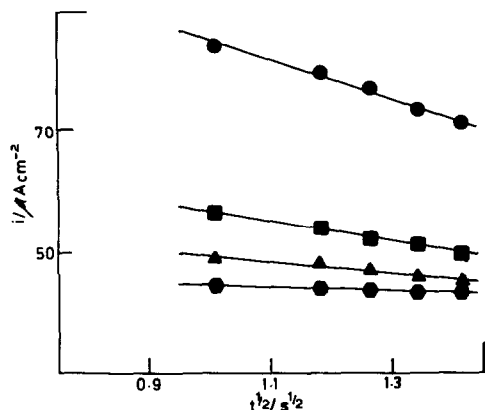


Fig. 5. Typical i vs. $t^{1/2}$ plots for a solid lead electrode in 1M H_2SO_4 . ●, -949 mV; ■, -951.5 mV; ▲, -953 mV; ◆, -958 mV.

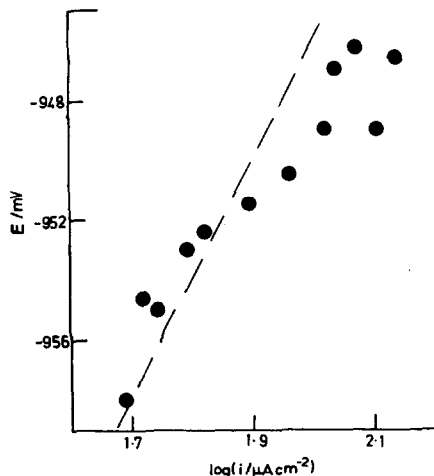


Fig. 6. Semilogarithmic plot of $\log_{10} i$ at $t = 0$ vs. potential for a solid lead electrode in 1M H_2SO_4 . The broken line indicates a slope of 40 mV/decade.

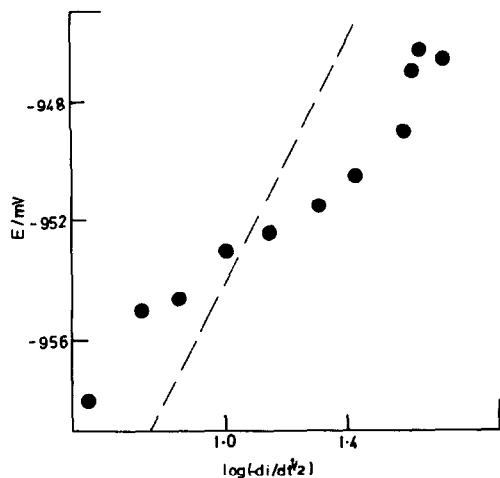


Fig. 7. Semilogarithmic plot of $\log_{10} (-di/dt^{1/2})$ vs. potential for a solid lead electrode in 1M H_2SO_4 . The broken line indicates a slope of 20 mV/decade.

Experiments with 5M H_2SO_4

The results of a number of experiments made with 5M H_2SO_4 indicated that the potential range in which only a solution reaction could be observed was much smaller than with 1M H_2SO_4 . This is in agreement with a lower solubility of $PbSO_4$ at the higher concentration. In the higher concentration, the driving force for the development of solid $PbSO_4$ at the electrode is increased considerably. The solid phase process intruded into the rotation

speed dependence of current and it was difficult to obtain good i^{-1} vs. $\omega^{-1/2}$ plots, although it was confirmed that current increased with ω . Reliable i_{∞} values in 5M H_2SO_4 were found to be very difficult to obtain. However, there is no doubt that i_{∞} is smaller in 5M than in 1M H_2SO_4 .

Porous electrodes

Rotating disc experiments

Figure 8 shows that there is a considerable difference in current obtained from the same nominal diameter electrode, and it is clear that the difference between the magnitudes of the currents is due to the porous structure on the "inside" of the electrode. Attempts were made with both 1M and 5M H_2SO_4 to obtain a rotation speed dependence for the porous electrode. It was found, however, that with these two electrolytes none could be detected with our experimental set-up. We can explain this behaviour if the rotation of the electrode were only to affect the flow of ions from the material on the surface of the electrode, in accordance with Levich [17]. The observation of no rotation speed dependence of current follows from a recognition that the electrode/electrolyte situation within the pores is unaffected by rotating the electrode, since the majority of the current comes from "inside" the electrode, and rotation modifies only the diffusion layer thickness.

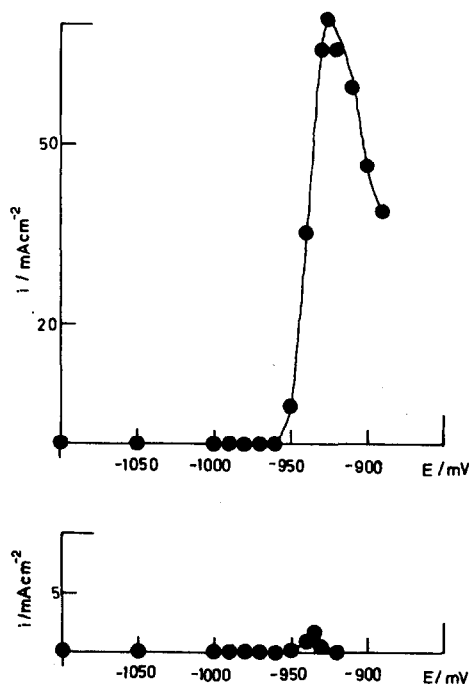


Fig. 8. Steady state current-voltage curves for rotating electrodes in 1M H_2SO_4 at 16.7 Hz with a sampling time of 45 s. Upper figure is for the porous lead rotating electrode, and the lower figure is for a solid lead rotating disc electrode.

This hypothesis was tested by investigating the rotation speed dependence of a thin layer of porous Pb, obtained by the reduction of a layer of lead sulphate formed on solid lead. Linear relationships were obtained by plotting i^{-1} against $\omega^{-1/2}$, indicating that the diffusion layer geometry was affected as predicted by Levich [17]. Table 2 shows the characteristics of these plots over a range of potential which indicate that, in this case, i_{∞} is larger, and the slope $di^{-1}/d\omega^{-1/2}$ less, than with solid electrodes. These data confirm that the effect of the porosity is to reduce the relative rotation speed dependence of the current due to the extra current contribution from the porous structure beneath the surface, which is unaffected by the hydrodynamic flow. The layer of porous material was thickened by cycling and it was observed that this resulted in an increase in i_{∞} and a decrease in the slope, σ . Thus, the rotation speed dependence is reduced as the layer is thickened.

TABLE 2

Rotation speed dependency of thin, porous- (reduction of single layer of PbSO_4 formed at -850 mV) and solid lead electrodes in deoxygenated 1M H_2SO_4 .

Electrode	E (mV)	σ ($di^{-1}/d\omega^{-1/2}$)	i_{∞} ($\mu\text{A cm}^{-2}$)
Thin porous	-945	0.003 4	127.5
Thin porous	-950	0.007 0	67.0
Solid	-945	0.028 2	76.5
Solid	-950	0.035 4	36.0

That a porous electrode behaved in a similar manner to a solid one as far as the existence of a well-defined diffusion layer is concerned [17] was tested using the well-known oxygen reduction reaction [8] at a lead surface. Oxygen is reduced at the lead electrode at a sufficiently negative potential at a fast rate, controlled only by mass transport in solution, as a four electron process. In Fig. 9 we compare the rotation speed dependence of reduction current for air-saturated 1M H_2SO_4 . Since the reaction is very fast, oxygen must be supplied to the electrodes only *via* the solution and we would expect a similar effect of rotation on the hydrodynamic layers of both electrodes. This is observed from our data. A similar potential dependence for the solution reaction is observed with both electrodes, as shown in Fig. 9(a), which shows steady-state current-voltage curves for porous and solid lead electrodes at potentials cathodic to E_{rev} in oxygenated 1M H_2SO_4 . One curve is shown for the porous electrode at a rotation speed of 16.7 Hz, and the solid electrode is shown at rotation speeds of 8.3 and 50 Hz. Figure 9(b) shows plots of i^{-1} vs. $\omega^{-1/2}$ for porous and solid electrodes in oxygenated 1M H_2SO_4 at a potential of -1100 mV and a rotation speed of 16.7 Hz. The mechanism (4e reversible reduction) is clearly the same on both electrodes.

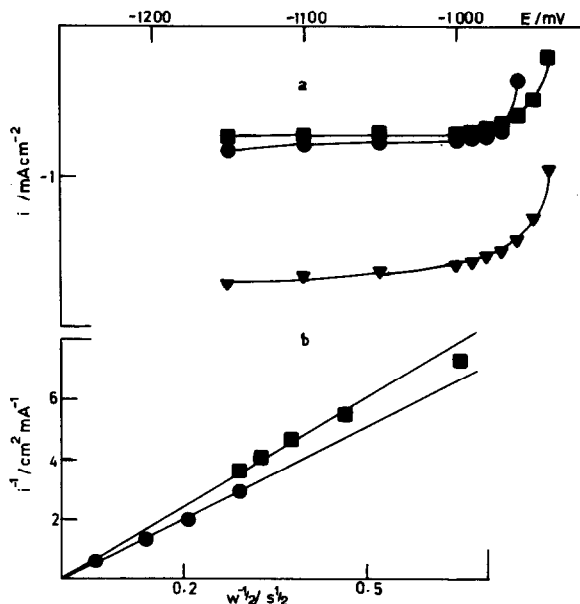


Fig. 9. The rotation speed dependence of the lead electrode for the oxygen reduction reaction. (a) Steady-state current-voltage curves at cathodic potentials for 45 s sampling time. ■, solid lead electrode at 8.3 Hz; ●, porous electrode at 16.7 Hz; ▼, solid electrode at 50 Hz. (b) i^{-1} vs. $\omega^{-1/2}$ plots at -1100 mV. ■, porous electrode; ●, solid electrode.

Conclusions

(1) The existence of a potential region in which lead dissolves freely in 1M and 5M H_2SO_4 is confirmed. The positive limit of this region is lower in 5M H_2SO_4 than in 1M H_2SO_4 .

(2) The rotation speed dependence of steady-state currents suggests that the charge transfer reaction might be two, single electron transfers, the second $[\text{Pb(I)} \rightarrow \text{Pb(II)}]$ being the rate determining step.

(3) A porous electrode in the form of a shrouded RDE does not show a rotation speed dependence. This is interpreted in terms of the major current source being the porous structure beneath the face of the electrode.

Acknowledgements

We thank Joseph Lucas Limited for financial support (to J.B.L.), and R. Taylor, A. N. Fleming and J. Smith for informative discussions.

List of symbols

C_o, C_R	Equilibrium concentrations of oxidised and reduced species.
C_o^E	Equilibrium concentration of oxidised species at E^\ominus .
D_o, D_R	Diffusion coefficients of oxidised and reduced species.
E, E^\ominus, E_{rev}	Potential, standard potential and reversible potential.
F	Faraday.
i	Current density.
i_d	Diffusion limited current.
i_o	Exchange current density.
i_∞	Current density after elimination of mass transport effects.
k_b	A reduction rate constant.
R	Gas constant.
t	Time.
T	Absolute temperature.
α	Transfer coefficient.
η	Overpotential.
ν	Kinematic viscosity.
ω	Frequency, radians s^{-1} .

References

- See, for example, (i) L. Jumeau, *Les Accumulateurs Electriques*, Dunod, Paris, 1904; (ii) G. Vinal, *Storage Batteries*, Wiley, New York, 1955; (iii) P. Ness, *Electrochim. Acta*, 12 (1976) 161; (iv) P. Ruetschi, *J. Power Sources*, 2 (1977/78) 3.
- G. Archdale and J. A. Harrison, *J. Electroanal. Chem.*, 34 (1972) 21.
- G. Archdale and J. A. Harrison, *J. Electroanal. Chem.*, 39 (1972) 357.
- G. Archdale and J. A. Harrison, *J. Electroanal. Chem.*, 43 (1973) 321.
- G. Archdale and J. A. Harrison, *J. Electroanal. Chem.*, 47 (1973) 93.
- A. N. Fleming, J. A. Harrison and J. Thompson, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, New York, 1975, p. 1.
- A. N. Fleming and J. A. Harrison, *Electrochim. Acta*, 21 (1976) 905.
- R. D. Armstrong and K. L. Bladen, *J. Appl. Electrochem.*, 7 (1977) 345.
- J. P. Carr, N. A. Hampson and R. Taylor, *J. Electroanal. Chem.*, 33 (1971) 109.
- J. P. Carr, N. A. Hampson, S. N. Holley and R. Taylor, *J. Electroanal. Chem.*, 32 (1971) 345.
- M. P. J. Brennan and N. A. Hampson, *J. Electroanal. Chem.*, 48 (1973) 465.
- M. P. J. Brennan and N. A. Hampson, *J. Electroanal. Chem.*, 52 (1974) 1.
- M. P. J. Brennan and N. A. Hampson, *J. Electroanal. Chem.*, 54 (1974) 263.
- R. D. Armstrong and G. M. Bulman, *J. Electroanal. Chem.*, 25 (1970) 121.
- T. F. Sharpe, in A. Bard (ed.), *Encyclopedia of Electrochemistry of the Elements*, Vol. 1, Ch. 5, Dekker Inc., New York, 1973.
- K. J. Vetter, *Electrochemical Kinetics. Theoretical Aspects*, English edn., Academic Press, New York, 1967, p. 365.
- V. G. Levich, *Physicochemical Hydrodynamics*, Prentice-Hall, New York, 1962.