

THE HYDROGEN EVOLUTION REACTION ON LEAD-BISMUTH ALLOYS

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Summary

Investigations into the hydrogen evolution reaction on lead-bismuth alloys (0 - 5 wt %) show that Bi does not lower the overpotential

Introduction

In the final stages of the recharging process of the lead-acid battery, the hydrogen overpotential determines the potential of the negative electrode. If the hydrogen overpotential is low due to the presence of impurities (Sb is a well-known example), open circuit losses occur due to hydrogen evolution from impurity centres, in parallel with the transformation of PbSO_4 to porous lead. For low-maintenance batteries cessation of the use of Sb would be desirable. As antimony is known to extend the cycle life, however, its use in batteries seems likely to continue.

The addition of alloying ingredients to battery support grids is a conventional process for obtaining properties required by the battery manufacturer, both for production and end product performance. Bismuth is a naturally occurring impurity in a number of lead ores and its effect on the electrotechnology of the lead-acid system is, thus, of some import. For a metal impurity to be tolerable it must affect neither the negative nor the positive plates. When studying the recharge characteristics of a particular alloy, the effect on the hydrogen evolution over-potential is important. This paper reports our research into the hydrogen evolution reaction (h.e.r.) on lead-bismuth alloy negative electrodes.

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Characteristics of the hydrogen evolution reaction on lead

A large number of investigations into the h.e.r. on lead and lead alloy electrodes, in sulphuric acids of different strengths, has been reported. The results of these investigations were, in general, published prior to 1960 and have been reviewed by Aguf and Dasoyan [1]. It can be concluded that the kinetic data conform to a process of rate control by the charge-transfer step. Jafa [2] has shown that the hydrogen overpotential on pure lead in a range of sulphuric acid solutions ($\sim 0.05 \text{ M} - 0.005 \text{ M}$) conforms to the Tafel equation

$$\eta = a + b \log i \quad (1)$$

where $a = 1.52$ and $b = 0.118$ against a standard hydrogen electrode (S.H.E.) taking a cathodic overpotential as positive. Kolotyrykin [3] looked at the h.e.r. on pure lead in $0.01 \text{ M H}_2\text{SO}_4$, and the values for a and b , 1.56 V and 0.12 V , respectively, agree closely with those of Jafa. The technique used by Kolotyrykin shows the so-called "potential instability" where measurements obtained rapidly were somewhat higher than ones obtained slowly over many hours. The "fast" technique, starting at the most positive part of

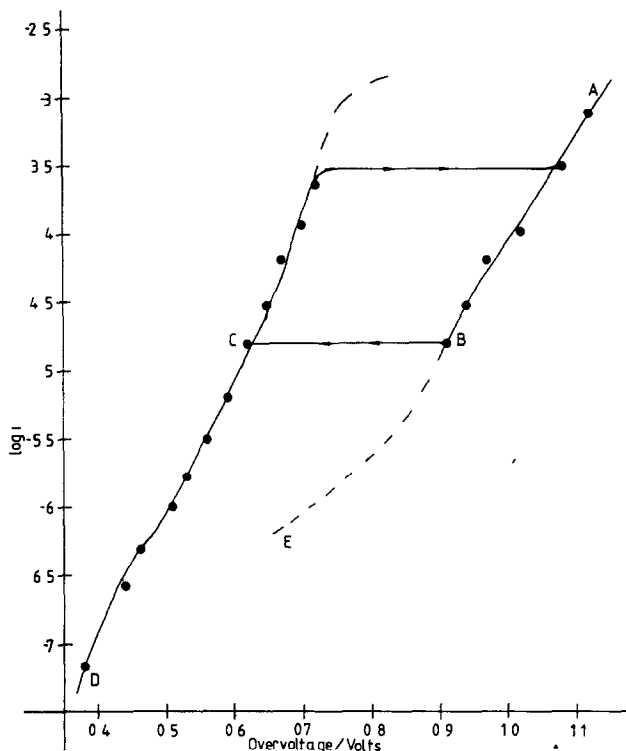


Fig 1 η vs $\log i$ curves for lead in $1.0 \text{ N H}_2\text{SO}_4$. Solid line slow measurements, dashed line fast measurements (from Kolotyrykin [3])

the experimental region, gives one line (ABE) on Fig. 1, while the lower branch (DCA) is shown if sufficient time is allowed for the value of η to decrease, apparently indicative of adsorption. Starting from the least negative potentials the lower branch was observed from the fast experiments so that, under favourable conditions, a hysteresis loop was generated by a cyclic experiment. It is clear from these results that care must be taken in order to obtain reproducibility with the lead electrode, especially at low current densities.

Investigations were also carried out into the effect of bismuth addition on the grain structure of lead in an attempt to correlate the change in η with surface structure.

Experimental

Experiments were undertaken using a potentiostat in conjunction with a ramp generator, the response of the electrode to the potential sweep was recorded on a conventional X-Y recorder. The electrodes were cast to form rods of polycrystalline Pb and Pb-Bi alloys (Table 1), and then machined to 3 mm dia rods and encased in PTFE to form electrodes suitable for a rotating disc assembly (Velodyne circuit constructed in the laboratory). The electrodes were fitted into a conventional 3-limb electrolytic cell. All potentials were measured with reference to the Hg/Hg₂SO₄/electrolyte solution electrode and the solution's i - R drop was reduced by employing a Luggin capillary.

A carbon rod (99.999%, B D H) counter electrode was employed in order to exclude the possibility of the intrusion of unwanted metal ions. Electrodes were prepared by polishing on 600 and 1200 grit emery paper and then etching in 10% HNO₃. Etching was continued until there were no traces of any adhering SiC visible on microscopic examination of the working electrode surface. The acid etch also facilitated removal of any smeared lead oxide film. After washing in triply-distilled water the electrode was fitted into the cell and the electrochemistry carried out at 22 ± 1 °C.

Voltage sweeps were made between -1200 mV and -2300 mV at a range of sweep rates using a supported electrolyte 1 M with respect to Na₂SO₄ and 0.05 M with respect to H₂SO₄ (higher acid concentrations resulted in early bubble formation and reduced the obtainable experimental data). The electrolyte was chosen on the basis of the previously noted work [1-3] and remained our standard electrolyte for the complete comparison. The rate of change of potential was varied within wide limits in order to find the most useful sweep rate. If the sweep rate was too fast then the electrode reaction was unable to keep up with the applied potential, if it was too slow then hydrogen evolution from the electrode surface, in the form of bubbles, interfered with the current flow and "noisy" transients resulted. It was found that sweeping in the range 50-100 mV s⁻¹ gave excellent responses with no signs of gas interference. The adequacy of our conditions

TABLE 1

Metal electrode composition

Pure Pb (%)		"Base" Pb (%)		"Pure" Bi (%)	
Pb	> 99 999	Pb	> 99 973	Bi	> 99 9
	(Aldrich, Gold Label)	Bi	$= 5 \times 10^{-4}$		(Johnson-Mathey, Mathey Reagent)
		Cu	< 0 003		
		Fe	< 0 001		
		Sb	< 0 001		
		As	< 0 001		
		Ag	< 0 0025		
		Mn	< 0 001		

Alloy composition

Alloy No	Pb (%) $\pm 0 008$	Bi (%) $\pm 0 008$
1	99 725	0 275
2	99 455	0 565
3	98 937	1 063
4	97 891	2 109
5	96 413	3 587
6	95 091	4 909

for the establishment of satisfactory and reproducible overpotential-current data was confirmed by the conformity of our data with those of the generally accepted Russian workers [4]

For the investigation into the grain structure of the alloys, polycrystalline lead and lead alloy rods of approximately 10 mm dia were cast in poly(methyl methacrylate) blocks. After machining these to a suitable size, surface polishing consisted of 600 and 1200 grit emery paper followed by mechanical polishing with a svelte-type cloth disc and 0.3 μm alumina using water as the lubricant. After polishing, the sample was washed with triply-distilled water and acetone before being stored in a desiccator to reduce the chance of oxy-hydroxide film formation. Etching of the samples was carried out using a 10% HNO_3 solution, followed by a triply-distilled water wash and then ethanol. Photomicrographs revealed the change in grain structure on the addition of bismuth.

Results and discussion

Figure 2 shows the potential-current density data for lead. The Tafel slope, i_e , the value of b in eqn (1) was found to be -0.13 V and the

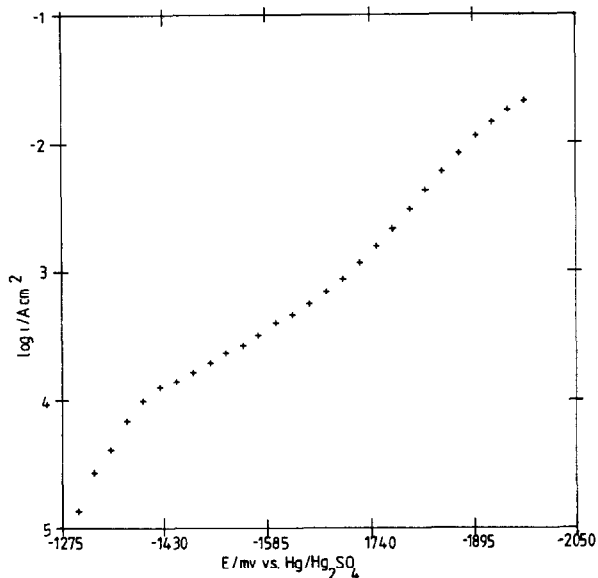


Fig 2 Potential-current density data for lead in 0.05 M H_2SO_4 and 1.0 M Na_2SO_4 , 22 °C

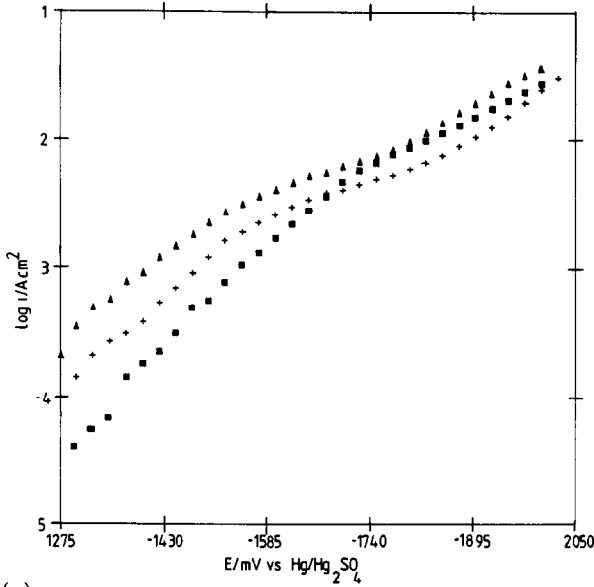
value of the ordinate at the reversible potential (referred to the E_h) was 1.31 V. These values agree fairly well with the Russian work (in H_2SO_4 of equivalent sulphate concentrations to the supported electrolyte of the present study) where the values of a and b were only slightly changed by sulphate concentration changes.

In Fig 3(a) and (b) current density-potential curves are shown for typical alloys of Pb and Bi from the series above. Values of i_0 and b were calculated from the straight, lower sections of the curves. In Table 2 we give values of i_0 referred to the hydrogen electrode for the alloy, together with a and b values, for comparison with the earlier published data we have expressed a and b in terms of an overpotential defined by

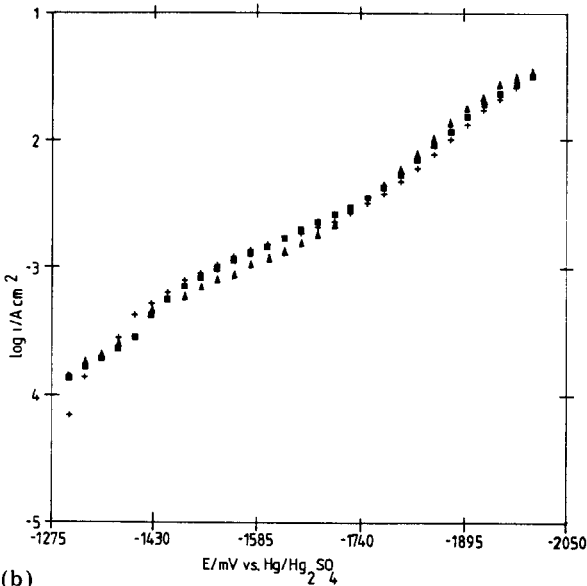
$$\eta = (E_{i=0} - E_i) \quad (2)$$

Our data show the lower portion of the hysteresis loop produced by the slow establishment of an adsorption equilibrium as discussed by earlier workers [4]. Figure 4 illustrates a closed loop potential-current density plot for pure Pb. On the same axes are plotted the data points for the upward sweep on the 4.91% Bi alloy. In our experiments the higher potential data may be expected to exhibit a decreased dependence of current on the potential due to the intrusion of current control by mass transport.

The values in Table 2 show that the presence of Bi in lead alloy does not increase the rate of the hydrogen reaction. An indication that the hydrogen reaction on Pb-Bi alloys might be slow arises from the work of Kılımnık *et al* [5] on Bi, who report that a and b Tafel coefficients of the order of 1.1 V and



(a)



(b)

Fig 3 (a) Potential-current density data for lead-bismuth alloys in 0.05 M H_2SO_4 and 1.0 M Na_2SO_4 , 22 °C +, Alloy 1, ■, alloy 2, ▲, alloy 3, (b) potential-current density data for lead-bismuth alloys in 0.05 M H_2SO_4 and 1.0 M Na_2SO_4 , 22 °C +, Alloy 4, ■, alloy 5, ▲, alloy 6

TABLE 2

The kinetic constants for the h e r on various Pb-Bi alloys in 0.05 M H₂SO₄ and 1.0 M Na₂SO₄ at 22 °C

Bi (%)	<i>b</i> (V)	Log ₁₀ <i>t</i> ₀	<i>a</i> (V)	<i>i</i> ₀ (10 ⁻¹¹ A cm ⁻²)
0	-0.13	-9.80	-1.31 ± 0.04	15.8
0.275	-0.14	-10.96	-1.58 ± 0.04	1.10
0.565	-0.15	-10.37	-1.59 ± 0.04	4.27
1.063	-0.14	-10.68	-1.53 ± 0.04	2.09
2.109	-0.15	-10.41	-1.51 ± 0.04	3.89
3.587	-0.16	-9.83	-1.54 ± 0.04	14.8
4.909	-0.14	-10.91	-1.51 ± 0.04	1.23

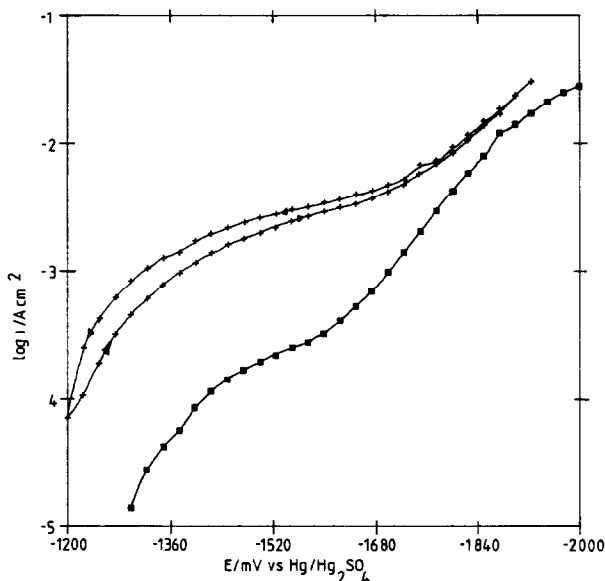
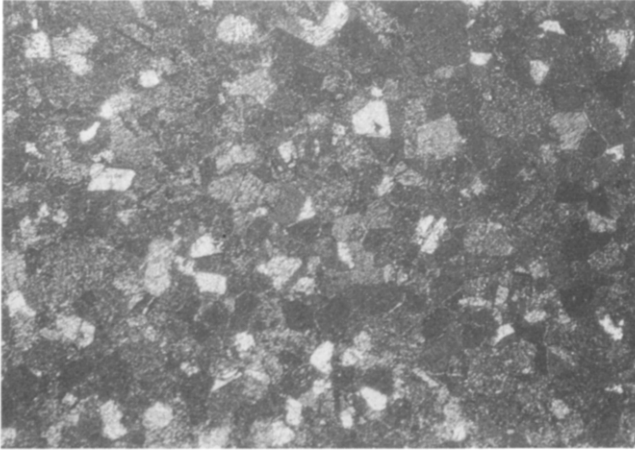


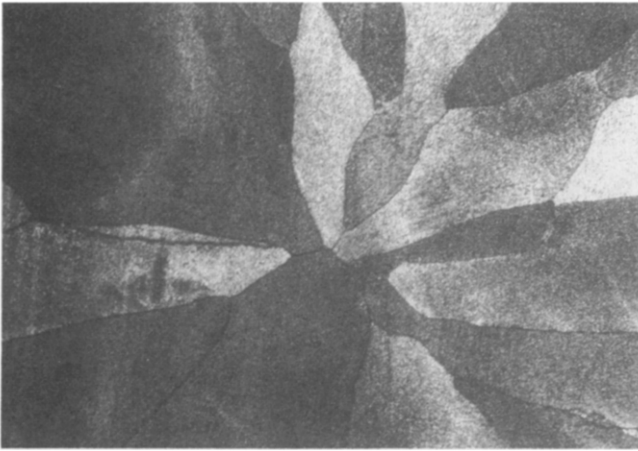
Fig. 4 Potential-current density data in 0.05 M H₂SO₄ and 1.0 M Na₂SO₄, 22 °C
+, Pure Pb, ■, alloy 6

0.12 V, respectively, have been found for the metal [6]. The value of *a* is close to the values obtained for the alloys in the present study, although the Tafel slopes reported here are generally increased by the addition of Bi to the metal (Investigations into the electrochemistry of pure Bi in 5 M H₂SO₄ electrolyte showed hydrogen evolution beginning 50 mV more cathodic than for pure lead.)

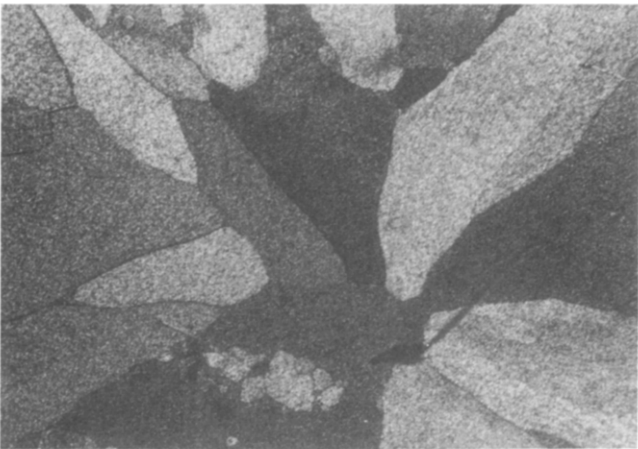
The addition of small amounts of Bi gives rise to a significant change in both Tafel constants. Subsequent addition of Bi, however, appears to have little if any effect on either *a* or *b*. It seems likely that the small differences



(a)



(b)

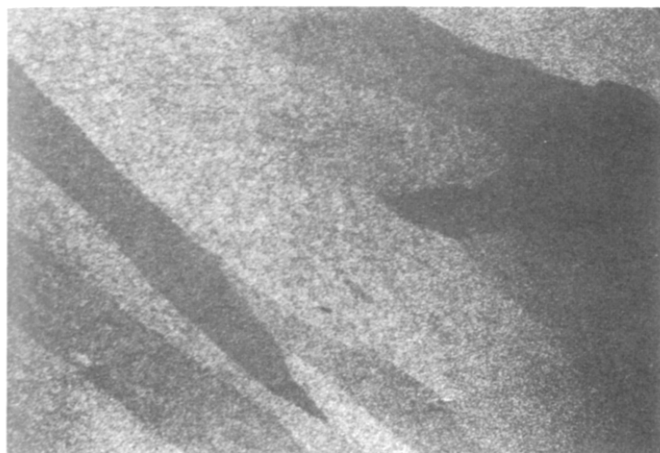


(c)

Fig 5(a) - (c) (continued)



(d)



(e)

Fig. 5 (a) Base lead, 10% HNO₃ etch, ×45 magnification (b) Pb-Bi alloy (0.061% Bi), 10% HNO₃ etch, ×45 magnification (c) Pb-Bi alloy (0.21% Bi), 10% HNO₃ etch, ×45 magnification (d) Pb-Bi alloy (0.21% Bi), 10% HNO₃ etch, ×45 magnification (e) Pb-Bi alloy (2.11% Bi), 10% HNO₃ etch, ×45 magnification

observed are due either to surface preparations of different specimens or they reflect differences in adsorption of hydrogen and anions on different alloy surfaces

Examination of the freshly etched sample surface reveals the change in grain structure with addition of Bi. Figure 5(a) shows a sample of base lead polished and etched. All subsequent alloys were made from bismuth (99.9%) and base lead. Thus, the small and regular shaped grains shown are due to a combination of the effects of the base lead and the other impurities listed in Table 1. The change in grain structure with increasing bismuth content is quite marked. Figure 5(b) and (c) shows the centre of two samples containing 0.061% and 0.21% bismuth, respectively. The change is dramatic,

from small, regular-shaped grains to large, rectilinear grains radiating out from the centre. Further out, the shape of the grains becomes more varied, Fig 5(d) On increasing the bismuth level to 2.11%, Fig. 5(e), there is little change except that the radial type of grain structure extends over the whole sample

As all the alloys were slow cooled, it is obviously the effect of the bismuth content which dictates the grain structure As none of the metals used was a perfect solid solution, the difference in surface heterogeneity, rather than the grain structure, seems to be the likely reason for variations in the Tafel values

Conclusion

We can say from the data in Table 2 that the addition of bismuth does not increase the rate of hydrogen evolution. This may be somewhat unexpected from a theoretical standpoint, particularly bearing in mind the very rapid acceleration of the h.e.r. that Sb (which is in the same periodic group as Bi) has on lead. As the variation in h.e.r. is small after the initial addition of 0.21% Bi and the change in the grain structure is minor, it would seem that the mechanism of the h.e.r. is dependent not upon the amount of Bi present but upon the presence of bismuth

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