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HYDROGEN EVOLUTION ON LEAD–TIN ALLOYS

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Summary

The cathodic evolution of hydrogen from a series of lead–tin alloys (below 1.7% Sn) has been studied with a range of concentrations of aqueous sulphuric acid and, where possible, comparisons are made with previous work. The presence of tin in the alloy decreases the exchange current density. In the α-solid solution phase the Tafel coefficient is unaffected, but is decreased by the presence of β-solid solution. The effect on the technology of the lead cell is discussed.

Introduction

The hydrogen overpotential on lead has been investigated in sulphuric acid [1], giving a range of values for the Tafel coefficients a and b in the equation

$$|\eta| = a + b \log_{10} i \quad (1)$$

Values for lead of a of about 1.3 V and of b in the range 0.11 - 0.16 V have been reported. The value of b is of great importance and has consequently been the subject of much investigation [1]. The adsorption of anions and the state of the electrode surface have a major influence on the h.e.r. The interplay of these features results in hysteresis of the current density–potential polarisation characteristics and accounts for the spread of reported experimental results and the curvature of Tafel lines.

Tin has only been studied minimally in the hydrogen region. Russian authors have reported the evolution of hydrogen on polycrystalline tin from a 1 M solution to be a slow reaction with a b value of 0.13 V [2] from the Tafel slope.

The search for a substitute for antimony as an alloying agent for lead in the grids of lead–acid batteries has been important because of the need to exclude all low hydrogen overpotential depositable materials. This has become more important with the development of low loss, recombination cells for sealed batteries. Many of the alloys used in this connection contain tin. Especially worthy of mention are those where tin is used in combination

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with lead–calcium alloys; more recently with lead–strontium–aluminium: lead–cadmium and lead–arsenic alloys have also found favour. Further results have shown that the formation of tin dioxide from a tin alloy is beneficial in positive battery plate operation [3]. It was therefore considered important to investigate the effect of tin on the h.e.r. at the lead electrode in aqueous sulphuric acid solutions in the range of concentrations of interest to current battery technology. This concentration rarely exceeded 1.5% Sn, and this paper describes the results of experiments made with binary alloys in this range.

Experimental

Electrodes were made from machined cylinders of metal (ϕ = 5 mm) shrouded in PTFE so that the end formed the working electrode surface. Table 1 shows the compositions of the electrode alloys.

TABLE 1

Compositions of electrodes

"Pure Pb"	
Bi	0.018%
Cu	<0.003%
Fe	<0.001%
Sb	<0.001%
As	<0.001%
Ag	<0.0025%
Mn	<0.001%

Alloy no.	"Pure Pb" (%)	"Pure Sn" (%)
1	99.947	0.053
2	99.522	0.478
3	99.13	0.87
4	98.61	1.39
5	98.37	1.63

Electrodes were polished with 600 and 1200 grit SiC paper and then etched in 10% nitric acid solution for 5 s. The electrode was finally washed with triply-distilled water and fitted into the cell. At the end of the procedure the electrode was judged, by microscopic examination, to be free from embedded impurities.

Electrochemistry was carried out using a conventional 3-limb electrolytic cell with a Luggin reference (Hg_2SO_4/Hg electrode in the electrolytic solution) aligned directly beneath the working electrode and 0.5 cm distant. The counter electrode was carbon (99.999%) — (platinum is to be avoided in h.e.r. work with dilute sulphuric acid in which it is soluble).

Experiments were performed between −1.2 V and −2.3 V (−1.0 V and −2.1 V for 5 M sulphuric acid) at a sweep rate of 0.1 V s^{-1} to obtain the current–time data as rapidly as experimentally possible. This minimised the effect of potential on the metallurgical state of the electrode, but it was also important that the potential sweep was not so fast as to force the system

from the reversible state, otherwise imposed irreversibility would affect the results.

All experiments were carried out in an initially-N_2-purged solution at 22 °C which were then run repeatedly until consistent results were obtained, thus ensuring that equilibrium with H_2 had been achieved. Sulphuric acid strengths of 0.01, 0.05, 0.1, 0.5 and 5 M were used to determine the constants *a* and *b* for the alloys in Table 1.

Figure 1 shows a typical plot of current *versus* potential from which the Tafel plot relating $\log_{10} i$ *versus* potential shown in Fig. 2 is obtained. Figure 1 shows the repeatability of consecutive sweeps, co-linearity being obtained typically over a number of sweeps. The appearance of the sweeps at high currents was undulating, due to excessive hydrogen evolution, and these potentials were avoided for Tafel data isolation. The Tafel plots over an extended potential range are actually curves; however, the region at relatively low overpotential contains a range of 150 - 200 mV over which well defined linear regions can be drawn. This agrees with earlier work on lead [1]. Table 2 shows the values for all the alloys at the experimental concentrations.

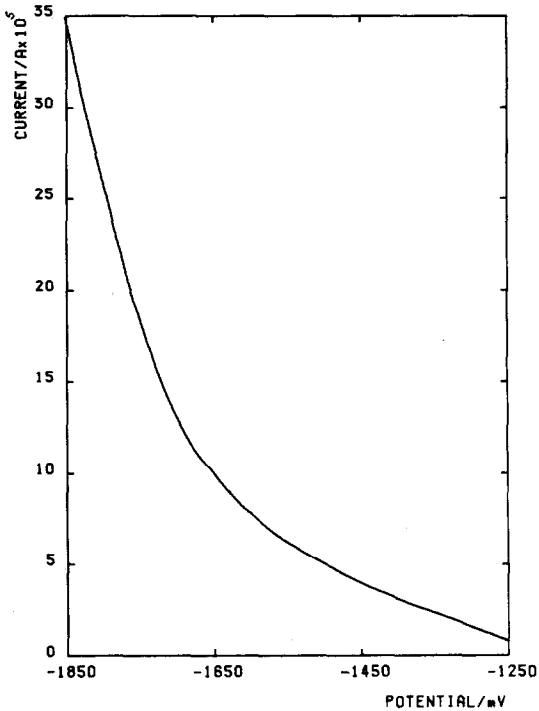

Fig. 1. Typical repetitive (5) linear sweep voltammogram for pure lead in 0.01 M H_2SO_4 and 1 M Na_2SO_4 at 22 °C (electrode area 0.07 cm^2).

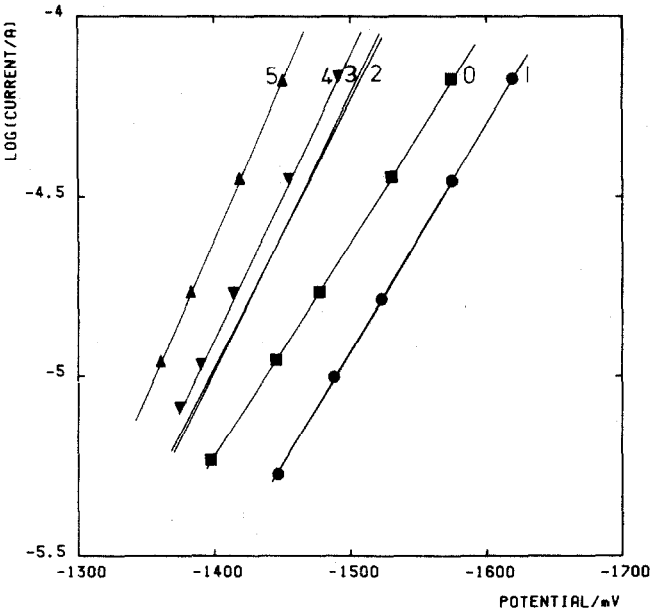

Fig. 2. Tafel lines for 0.01 M H_2SO_4 and 1 M Na_2SO_4 at 22 °C (numbers on lines represent alloy no. — see Table 1 — 0 being pure lead).

TABLE 2

Tafel slopes (b mV^{-1}) for the systems investigated

Sn (%)	H_2SO_4 conc. (M)				
	5	0.5	0.1	0.05	0.01
0.0	159	153	156	157	160
0.053	161	150	156	152	155
0.478	142	138	132	132	125
0.87	127	129	133	131	121
1.39	125	131	118	109	111
1.63	111	125	105	107	107

Discussion

The results obtained indicate that the hydrogen overpotential is increased by the presence of 0.053% tin and is decreased at higher concentrations of tin.

The overpotential on lead in sulphuric acid solutions is known to depend on solution conditions and metallurgical preparation. The value obtained in the present investigation, however, is representative of many in the literature [4] and is in reasonable agreement with the value obtained in a recent investigation in this laboratory. Slight differences in hydrogen over-

potential may be caused by a number of factors in which polycrystalline metals are concerned. The hydrogen overpotential on tin is not as certain as lead. Early Russian workers reported values of 0.13 V of the Tafel slope [2] but experimental difficulties have been found in the preparation of tin electrodes due to the crystal structure of the metal.

When small amounts of tin are added the rate of hydrogen evolution on lead is retarded, the effect being constant throughout the electrolyte concentration range. It seems likely, therefore, that this is the effect of tin on lead in a homogeneous solid solution. As the thermodynamic solubility of tin in the α-phase of lead at room temperature amounts to 1.3% (±0.5%) [5] it is more than likely that the nominal 0.5% alloy used contained a significant quantity of the β-phase tin-rich solid solution at the surface (arising from the rapid chilling which occurs when metals are cast). This would explain the more rapid evolution rate on the tin alloys at the 0.5% tin level and above. The rate of hydrogen evolution is retarded very significantly in the range up to and at 0.05% tin and this appears to suggest that an increase in the tin content, resulting in a monotonic increase in hydrogen evolution rate, is due to an increase in surface heterogeneity caused by the progressive appearance of the β-solid solution in the remainder of the range of alloy compositions. This argument is verified by the magnitudes of the Tafel slopes, *i.e.*, additions of tin to lead in the homogeneous α-phase region leave the slope unaffected, whereas the appearance of β-phase affects the slope due to changes in the value of the charge transfer coefficient, α, in the Tafel region.

$$i = i_0 \exp \frac{\alpha n F}{RT} |\eta| \tag{2}$$

where i_0 is the exchange current density and α the charge transfer coefficient.

In the solid solution region the effect of tin is to reduce the apparent exchange current density. This may be, in part, a surface area effect, the lower melting alloy having a greater surface mobility than pure lead. The lower roughness factor, associated with the lower melting alloy, and consequently greater surface area, accounts for the higher overpotential or lower reaction rate.

From the data in Tables 2 and 3 it is apparent that alloying with tin below ~0.05% does not significantly reduce the hydrogen overpotential. Hence, it is clear that in modern lead–acid batteries tin additions to the negative grid in moderate amounts (up to 0.15%) will not unduly affect the rate of hydrogen evolution.

The exchange current densities shown in Table 3 corresponding to each of the systems tested were calculated by mathematical interpolation. Two trends emerge from these values:

(i) the exchange current densities on lead and lead–tin alloys are not affected by the sulphuric acid concentration (a statistical analysis of our results indicates that the reported effect of adsorption at very low H_2SO_4

TABLE 3

Exchange current densities (i_0 (A cm^{-2})$^{-1}$) for the systems investigated

Sn (%)	H_2SO_4 conc. (M)				
	5	0.5	0.1	0.05	0.01
0.0	5.66×10^{-7}	3.38×10^{-8}	2.83×10^{-7}	1.26×10^{-8}	6.00×10^{-5}
0.053	1.02×10^{-7}	1.89×10^{-9}	1.02×10^{-7}	3.06×10^{-7}	3.11×10^{-6}
0.478	1.48×10^{-8}	6.01×10^{-10}	1.80×10^{-8}	2.04×10^{-10}	5.08×10^{-8}
0.87	8.03×10^{-10}	6.41×10^{-11}	5.08×10^{-8}	2.55×10^{-7}	6.52×10^{-9}
1.39	1.59×10^{-9}	1.26×10^{-9}	1.72×10^{-9}	2.29×10^{-9}	5.44×10^{-10}
1.63	2.11×10^{-11}	1.47×10^{-11}	2.51×10^{-11}	5.62×10^{-10}	5.36×10^{-10}

concentrations [1] is not apparent in the present experimental concentration range);

(ii) the exchange current densities decrease by approximately two orders of magnitude as the concentration of tin is increased to 1.6%. It thus appears that as the β-phase material reduces the Tafel slope for the h.e.r., the intrinsic exchange rates on the richer tin alloys are significantly less than on pure lead and alloys containing 0.05% tin. The exchange current density values reported are subject to considerable error due to the long extrapolation needed; however, the trend shown is unequivocal — the presence of increasing amounts of tin in lead progressively lowers the exchange current density. The Tafel coefficient b, on the other hand, decreases with increasing tin content. In considering the rate of hydrogen evolution at any particular potential these two factors, a and b, therefore clearly offset each other to some extent. This is demonstrated by the order of the reaction rates shown in Fig. 2, which conforms to the industrially significant potential region.

Conclusions

The concentration of sulphuric acid does not affect the Tafel slope for the h.e.r. on lead and lead–tin alloys.

Alloying with tin affects the rate of hydrogen evolution on lead in aqueous sulphuric acid.

The effect of the addition of tin within the experimental range (up to 1.6%) is to decrease the exchange current density.

The effect of tin (0.05% - 1.6%) is to decrease the Tafel coefficient b (mV).

The two factors a and b are antagonistic when considering the effect of tin at a particular current density; however, in the range of charging potentials of interest to battery technologists we conclude that at tin concentrations in the range 0.05 - 1.6%, the rate of hydrogen evolution increases with increasing tin content. Below 0.05% the evolution rate is retarded.

The effect of tin on the h.e.r. can be explained by the development of β-phase solid solution in the α-phase solid solution.

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