

## ELECTROCHEMICAL INVESTIGATION OF LEAD-CALCIUM ALLOYS IN SULPHURIC ACID

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### Summary

The hydrogen evolution reaction from, and the cycle life ( $\text{Pb} \rightarrow \text{PbSO}_4$ ) of, a series of lead-calcium alloys (0 - 0.2 wt.% Ca) in sulphuric acid have been studied.

The exchange current density and Tafel slope for the H.R.E. increase with Ca content up to 0.05 wt.% then decrease to a value approaching that of pure lead. The alloys with <0.075 wt.% Ca show an initial capacity *versus* cycle number similar to pure lead. From 0.075 to 0.15 wt.% the rate of increase in capacity increases with Ca content. The 0.2 wt.% alloy's capacity decreased on cycling.

The observed results are explained by :

- (i) preferential adsorption of calcium ions at the electrode surface;
- (ii) incorporation of Ca, to form a supersaturated solution, with alloys containing < 0.075 wt.% Ca;
- (iii) formation of an insoluble, non-conducting layer of calcium sulphate on the high content alloy.

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### Introduction

The recent advances in lead-calcium battery technology, particularly maintenance-free cells, has increased the interest in non-antimonial alloys which alleviate hydrogen evolution and prevent formation of toxic metal hydrides. To maintain the mechanical properties required for mass production, a ternary alloy containing Pb, Ca, and Sn with rigid control of the Ca content between 0.07 and 0.1 wt.% [1, 2] is now commonly employed.

There are few reported investigations into the electrochemistry of Pb-Ca binary alloys and these are limited to the Ca content [3, 4]. It was therefore considered important to study the hydrogen evolution reaction on, and 'Pb to  $\text{PbSO}_4$ ' cycling of, Pb-Ca binary alloys with 0 to 0.2 wt.% Ca. This paper reports the results obtained from this investigation.

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## Experimental

### *Hydrogen evolution reaction*

Electrodes were constructed from alloy rods set in Teflon so that one end formed the surface of the 0.2 cm<sup>2</sup> disc electrode. The surface was prepared by a three stage polishing routine involving 600 and 1200 grit emery paper followed by roughened glass. Etching in 10% nitric acid removed the cold worked surface and any embedded particles.

The electrode was rinsed with triply-distilled water then placed in a standard three-limbed cell containing the electrolyte solution (0.1 M H<sub>2</sub>SO<sub>4</sub> and 1 M Na<sub>2</sub>SO<sub>4</sub>), a reference electrode (Hg/Hg<sub>2</sub>SO<sub>4</sub>), and lead counter electrode.

Linear sweep voltammograms were obtained between -1.3 V and -2.4 V at 40 mV s<sup>-1</sup> using an *iR* compensating potentiostat and a ramp generator. The experiments were run at 21 ± 2 °C and the solution was purged with nitrogen for 15 min before each experiment.

Several sweeps were made with each alloy to ensure the reproducibility of the results and equilibrium with hydrogen.

### *Optical microscopy*

Samples from the alloy rods were set in 'Perspex', manually lapped on 120, 600 and 1200 grit emery paper, and mechanically polished using 5 μm alumina on Selvyt polishing cloth. A second stage of preparation involved alternate mechanical (0.3 μm alumina) and chemical polishing (lactic acid/hydrogen peroxide/methanol solution), followed by a 2 - 3 min etch in 10% nitric acid and a final rinsing in triply distilled water then absolute alcohol. The micrographs were taken at ×70 magnification.

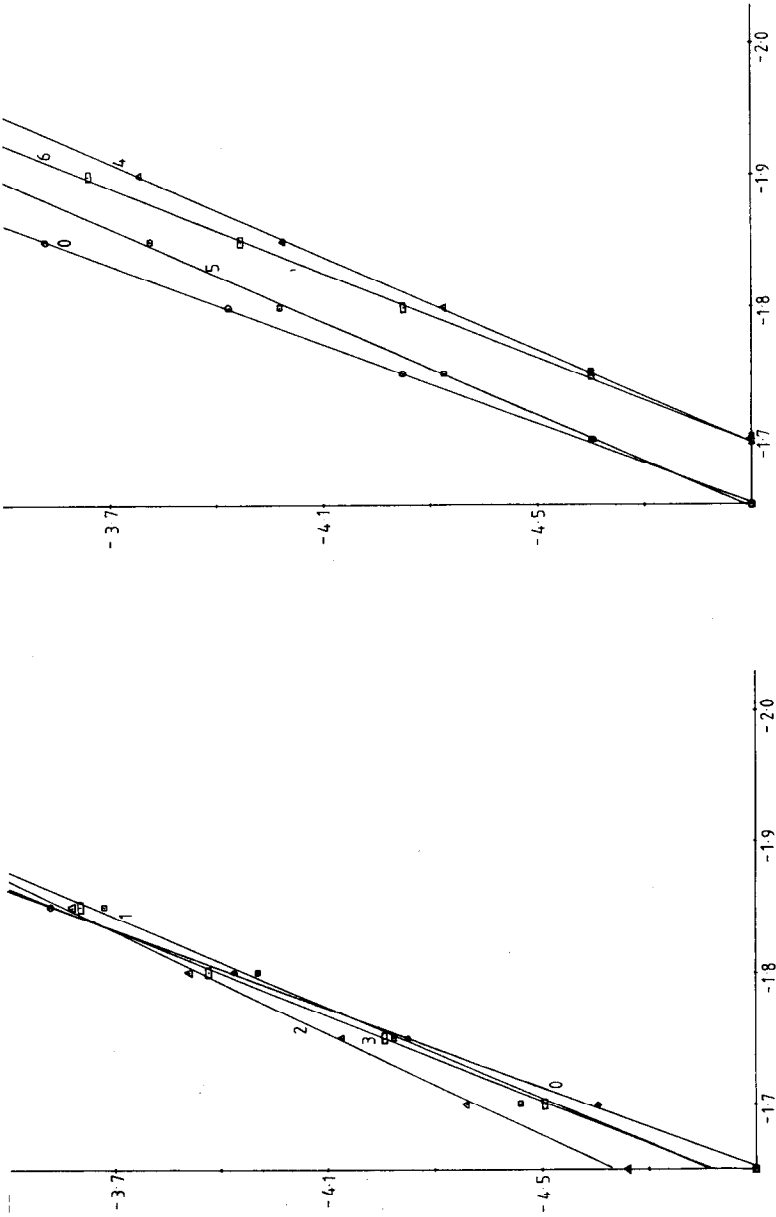
### *Potentiodynamic chronocoulometry*

The electrode preparation and cell were as described above. The electrolyte solution was 5 M H<sub>2</sub>SO<sub>4</sub>, and sweep limits -1300 to -500 mV with a sweep rate of 40 mV s<sup>-1</sup>. The current was monitored, and the charge passed (coulombs cm<sup>-2</sup>) during PbSO<sub>4</sub> formation was calculated by computer (using Simpson's rule). The data were then stored, together with the cycle number, on disc.

## Results and discussion

### *Hydrogen evolution reaction*

Figures 1 and 2 show Tafel plots ( $|\eta| = a + b \log i$ ;  $\eta$  = overpotential,  $i$  = current density) which were obtained from potentiodynamic sweeps of the Pb-Ca alloys. Tafel coefficients ( $b$ ), from these plots, are displayed in Table 1 with the corresponding exchange current densities ( $i_0$ ) which were calculated by extrapolation to 0 mV with reference to the hydrogen electrode.



Figs. 1, 2. Tafel slopes for alloys studied (see Table 1 for alloy numbers). Abscissa V (wrt Hg/Hg<sup>+</sup>); ordinate log |i|.

TABLE 1

Exchange current densities ( $i_o$ ) and Tafel slopes ( $b$ ) for the alloys studied

Alloy	Ca (wt.%)	$i_o$ ( $A\ cm^{-2} \times 10^{-11}$ )	$b$ (m V)
0	0	1.0	152
1	0.025	1.5	179
2	0.05	44.1	191
3	0.075	5.1	166
4	0.1	5.4	178
5	0.15	8.9	176
6	0.2	1.8	165

These results clearly show that in Pb-Ca alloys with <0.075 wt.% Ca the exchange current density and Tafel slope increase with Ca content. Alloys with Ca content >0.075 wt.% have  $i_o$  and  $b$  values higher than, but approaching, those obtained with pure lead.

These results can be explained by the presence of a second exchange reaction in the form of calcium incorporation [5, 6]:



$Na_2SO_4$  was used to enhance the conductivity of the electrolyte solution but the incorporation of Na into Pb under these conditions is insignificant. The Tafel slope and exchange current density for pure Pb in 0.1 M  $H_2SO_4$  without  $Na^+$  are, within experimental error, the same as those with  $Na^+$ .

At calcium levels up to 0.07 wt.% the more negative potentials involved with hydrogen evolution will give a supersaturated solution of Ca in Pb at the electrode surface which would, with time, form the stable intermetallic compound  $Pb_3Ca$ . This increases the apparent exchange current density,  $i_o$ , while the preferential adsorption of calcium ions (preferred to protons) reduces the hydrogen evolution, hence an increase in the  $b$  values.

At higher Ca concentrations the Ca-rich areas, *e.g.*, grain boundaries, will be covered by an insoluble, non-conducting layer of calcium sulphate, hence the observed electrochemistry approaches that of pure lead.

### Microscopy

Figures 3 - 8 show the micrographs taken of alloys containing 0.025 - 0.2 wt.% Ca. These results show that the grain size falls with addition of Ca (as previously reported by Caldwell *et al.* [4]). This decrease is most apparent in the higher content alloys. However, as it is continuous it cannot account for the maxima observed in the  $i_o$  and  $b$  values (Table 1).

### Potentiodynamic chronocoulometry

Figure 9 shows the charge *versus* cycle number for all the alloys investigated. There is a clear separation between three sets of alloys:

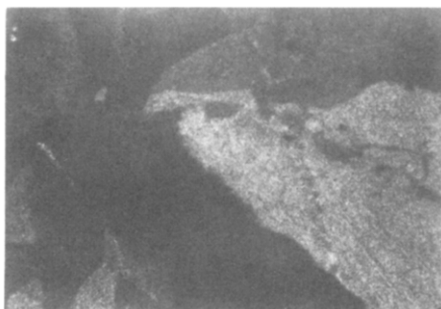


Fig. 3.

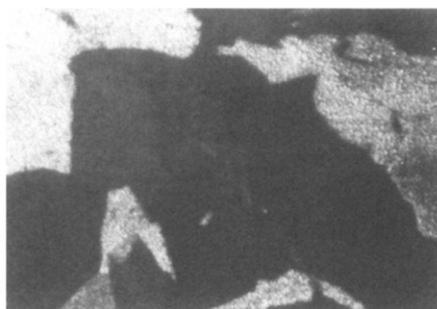


Fig. 4.

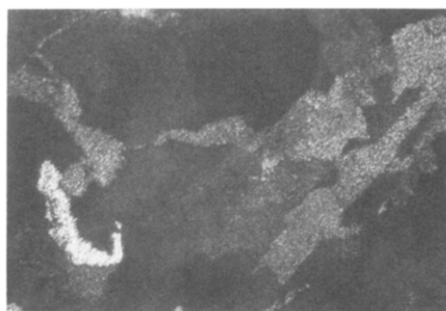


Fig. 5.



Fig. 6.

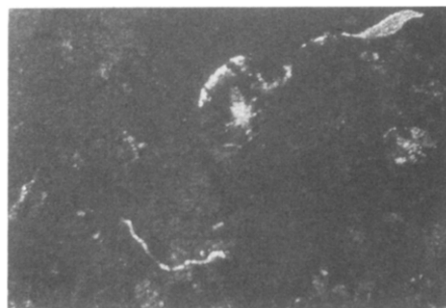


Fig. 7.

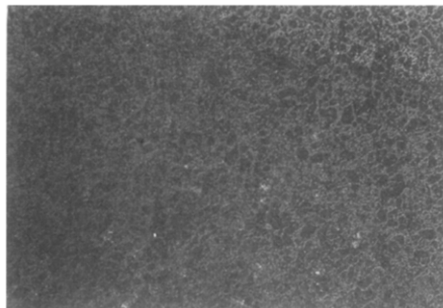


Fig. 8.

Figs. 3 - 8. Micrographs of alloys 1 - 6, respectively. Magnification  $\times 30$ .

- (i)  $< 0.075$  wt.% Ca
- (ii)  $0.075 - 0.15$  wt.% Ca
- (iii)  $0.2$  wt.% Ca.

The alloys with low or zero Ca content show a similar gradual increase in capacity during the first few thousand cycles. With the higher Ca content alloys, the formation of calcium sulphate will prevent formation of the porous structure and insulate the electroactive material (Pb). The intermediate content alloys show a faster formation of the porous structure and insufficient calcium sulphate to block the pores.

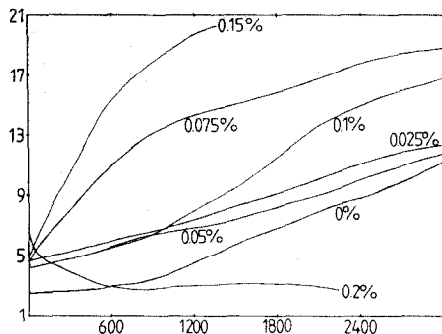


Fig. 9. Capacity vs. cycle number for alloys 0 - 6. Abscissa: cycle number; ordinate: charge coulomb<sup>-1</sup> cm<sup>-2</sup> ( $\times 10^{-2}$ ).

## Conclusions

These results support the industrial choice of 0.07 - 0.1 wt.% Ca in Pb-acid battery negatives. The addition of Sn to form ternary Pb-Ca-Sn alloys may, however, produce synergic effects and therefore no conclusions can be drawn about the optimum level of Ca in this case.

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