

Hydrogen evolution on lead-antimony-cadmium alloys in gelled and flooded sulphuric acid electrolyte

G Vanmathi and P V Vasudeva Rao

Central Electrochemical Research Institute, Karaikudi - 623 006, INDIA

The electrochemical behaviour of lead and its alloys has been studied in flooded as well as gelled H_2SO_4 electrolytes. By applying LSV technique, the potential is scanned between 0 V and -1.85 V to find the applicability of these alloys as grid materials for negative plates in lead acid battery. It is found that the alloys under study have higher hydrogen overpotential in gelled electrolyte than in flooded electrolyte.

Key words: Hydrogen overpotential, lead-acid battery, gelled electrolyte, Pb-Sb-Cd alloy

INTRODUCTION

The electrochemical behaviour of various alloys of lead has been studied in flooded H_2SO_4 electrolyte [1]. But very little information is available on the hydrogen evolution reactions in gelled sulphuric acid electrolyte [2]. In this work, the electrochemical behaviour of lead and its alloys, viz. Pb-Sb, Pb-Cd, Pb-Sb-Cd alloys, has been studied with particular reference to H_2 evolution reactions.

EXPERIMENTAL

Electrodes were cast from high purity metals. They were mechanically polished. Analytical grade H_2SO_4 of various concentrations were prepared with triple distilled water. Pyrogenic silica was used for preparing the gel [3]. A Wenking potentiostat Model PoS 73 with three electrode cell assembly was used for the study. The potentials are all referred with respect to $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode.

RESULTS AND DISCUSSION

Figure 1 shows the LSV curves for pure lead, Pb-Sb, Pb-Sb-Cd and Pb-Cd in 7.5N gel. From the voltammograms, the characteristic peaks of various constituents of alloys are observed and the corresponding potentials are given in Table I. In Fig. 1(a), the $\text{PbO} \cdot \text{PbSO}_4 \rightarrow \text{Pb}$ reaction peak current is recorded at -760 mV. The $\text{PbSO}_4 \rightarrow \text{Pb}$ reaction takes place at -1010 mV followed by H_2 evolution at potential $E > -1300$ mV [2]. For Pb-Sb alloy (Fig. 1b), in addition to the peaks characteristic of lead, $\text{Sb}_2\text{O}_3 \rightarrow \text{Sb}$ reaction occurs at -650 mV. At -900 mV, $\text{Sb}_2(\text{SO}_4)_2 \rightarrow \text{Sb}$ reaction occurs. In between the $\text{PbSO}_4 \rightarrow \text{Pb}$ and H_2 evolution reactions, a peak due to $\text{Sb} \rightarrow \text{SbH}_3$ is also seen [2]. For Pb-Sb-Cd alloy, no peak characteristic of cadmium is observed (Fig. 1c), because all the Cd (1.8%) present forms solid solution with Sb and the alloy contains excess Sb over and above the solid solution. The cadmium

peak, however, is exhibited for the Pb-Cd alloy (Fig. 1d) as $\text{CdSO}_4 \rightarrow \text{Cd}$ at -1200 mV [4].

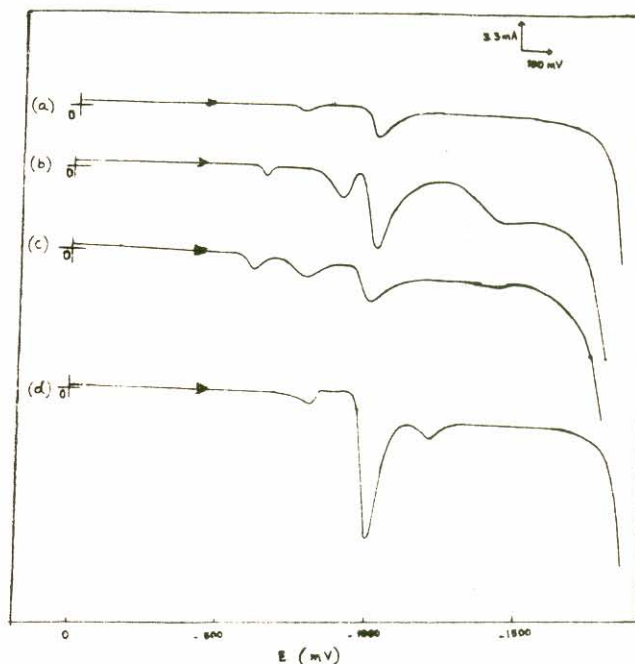


Fig. 1: LSV for (a) Pb - 99.99% (b) Pb-Sb 4.5% (c) Pb-Sb (2.3%) - Cd (1.8%) (d) Pb-Cd 2% alloys in 7.5N gelled H_2SO_4 electrolyte at 20mV sec^{-1}

It is found that the η_{H_2} increases with decreasing acid concentration [1] (vide Table II). The increase in hydrogen overpotential in the flooded electrolyte is due to the increase in pH at the interface. Following the $\text{PbSO}_4 \rightarrow \text{Pb}$ reaction, the replenishment of SO_4^{2-} ions at the interface is faster in flooded electrolyte than in gelled electrolyte; the diffusion of ions is also slowed down by the denser nature of the gel leading to a higher pH at the interface and hence higher hydrogen overpotential.

TABLE-I: Peak potentials of various alloys

Sweep rate = 20 mV sec⁻¹ [H₂SO₄] = 7.5N

Alloy comp.	PbSO ₄ → Pb		η _{H₂}	
	Acid (mV)	Gel (mV)	Acid (mV)	Gel (mV)
Pb 99.99%	-1100	-1010	-1680	-1770
Pb-Sb 4.5%	-1110	-1030	-1570	-1630
Pb-Cd 2%	-1020	-1050	-1710	-1790
Pb-Sb (2.3%)- Cd (1.8%)	-1015	-1010	-1610	-1670

REFERENCES

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TABLE-II: Pure lead in various concentrations of sulphuric acid

Sweep rate = 20 mV sec⁻¹

Concentration (N)	PbSO ₄ → Pb (mV)	η _{H₂} (mV)
5	-990	-1710
7.5	-1100	-1680
25	-1140	-1510

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