

## KINETICS OF HYDROGEN EVOLUTION REACTION ON LEAD/ACID BATTERY NEGATIVE ELECTRODES WITH SILICATE AND ANTIMONY ADDED TO THE ELECTROLYTE

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### Introduction

The modern trend in lead/acid battery design is towards the maintenance-free (MF) type. The latter includes vented cells with excess electrolyte as well as pressure-regulated valve cells with either gelled or absorbed electrolyte [1]. In these cells, the loss of oxygen produced during charge or overcharge at the positive electrode is minimized either by oxygen-hydrogen recombination on a suitable catalyst contained in the vent plug, or by oxygen reduction on the porous lead of the negative electrode.

Technologies for producing MF batteries for float applications are well established [2]. Attempts have also been made by a few companies to produce MF batteries for deep-discharge applications. A deep-cycle battery with hybrid type grid alloy composition gives the best life and field service [3, 4]. In these cells, the positive grid usually contains about 1 wt.% antimony (together with small quantities of certain other metals such as cadmium, tin, selenium, and arsenic), while the negative grid is made from an antimony-free alloy. The cells are closed under pressure with vent caps having provision for the escape of gases in the event of pressure build up; the vents can be resealed.

Hydrogen evolution in MF lead/acid batteries is minimized by using antimony-free, or at least low-antimony, grids for the electrodes [5, 6]. A constant, but slow, evolution of hydrogen gas [5-8] has frequently been observed in systems operating for long periods. It is difficult, however, to prevent a loss of the hydrogen produced by overcharge, corrosion of the negative grid material, or during storage of these systems. A progressive loss of hydrogen from the cell causes electrode imbalance and eventual cell or battery failure.

In the hybrid-type alloy configuration, the rate of poisoning of the negative plate by Sb(III) species is much less than that in a conventional cell

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with antimonial grids [9]. Such hybrid construction should be effective in deep-discharge service, although a release of antimony from the positive plate is unavoidable.

This work is directed towards examining the effects of both sodium silicate, used in gelled electrolyte MF cells, and dissolved antimony species Sb(III) in the electrolyte (which could arise due to corrosion of low-antimony grid supports) on the kinetics of hydrogen evolution occurring on lead/acid battery negative electrodes with different grid materials.

## Experimental

Positive and negative electrodes manufactured with different grid materials, namely, Pb-0.08wt.%Ca-0.5wt.%Sn, Pb-3wt.%Sb, and pure lead, were obtained from UB-MEC batteries in a factory cured-and-formed condition. Negative-limited test cells with excess electrolyte were assembled with two positive counter electrodes arranged on both sides of the working electrode. The grid material was the same for both positive and negative electrodes in any given test cell in order to exclude possible interaction effects by corrosion products. Similarly, whenever the composition of the electrolyte was changed (in order to introduce additives), a new set of positive and negative electrodes was used. This procedure eliminated possible interaction by any impurities carried over from preceding tests.

The electrodes were first given an initial soak time of 10 h in the electrolyte containing the chosen additives. The electrodes were subjected to a charge/discharge cycle at the  $C/10$  rate and then returned to a full state-of-charge before polarization measurements were commenced.

The potential of the test electrode was measured against an Hg/Hg<sub>2</sub>SO<sub>4</sub>, 4.8 M H<sub>2</sub>SO<sub>4</sub> reference electrode. All potentials are quoted with regard to this reference electrode. The latter was connected to the test cell via a glass capillary bridge filled with 4.8 M H<sub>2</sub>SO<sub>4</sub>. The bridge terminated in a Luggin tip aligned close to the centre of the test electrode. The electrode potential was measured to  $\pm 0.1$  mV, using a Keithley Electrometer, under both galvanostatic and steady-state conditions (about 2 min after setting a given current). The electrolyte was gently stirred throughout the experiment. All measurements were carried out at  $30 \pm 1$  °C.

Preliminary studies showed that well-defined, steady-state Tafel lines for the hydrogen evolution reaction (HER), extending over about two decades of current in antimony-free electrolyte, are obtained only if the polarization measurements are made in the direction of decreasing current, starting from about  $0.1 \text{ A cm}^{-2}$  (apparent area). This procedure probably removes a major part of the dissolved Pb<sup>2+</sup> in the vicinity of the test electrode by electrodeposition, so that the distortion of the polarization curve for HER is minimized.

The exchange current density ( $i_0$ ) for HER was measured by extrapolation of the HER Tafel line (at or beyond  $-1000$  mV) to the reversible

potential of HER ( $-612$  mV) in the electrolyte, assuming the partial pressure of hydrogen to be 1 atm.

A stock solution of  $4.80$  M  $\text{H}_2\text{SO}_4$  was prepared from AR grade acid and distilled water. Antimony powder ( $5 \text{ g l}^{-1}$ ) and/or sodium silicate ( $5 \text{ g l}^{-1}$ ) were added to separate portions of this solution and the mixture thoroughly stirred to effect complete dissolution. Sodium silicate is known to exist as a polymeric species that, at low pH value, is termed polysilicic acid [10].

## Results and discussion

Polarization curves for the HER, obtained with different types of charged negative electrodes with/without polysilicic acid and antimony (III) additives to the electrolyte, are shown in Figs. 1-3.

Significant features of the curves are:

(i) an initial arrest of potential close to the open-circuit potential of the electrode in all cases;

(ii) a limiting current behaviour at about  $0.5 \text{ mA cm}^{-2}$  in two cases of antimony-free electrolyte;

(iii) a well-defined Tafel region for HER at potentials cathodic to about  $-1000$  mV over about two decades of current density in two cases of antimony-free electrolyte;

(iv) a longer initial arrest of potential, a fade-out of the limiting-current behaviour at low current densities, and an ill-defined Tafel region cathodic to about  $-1000$  mV occurring at relatively high current densities in the antimony-containing electrolyte (with/without polysilicic acid); the ill-defined Tafel regions may be partly due to the occurrence of two cathodic reactions, namely, hydrogen and stibine evolution [11].

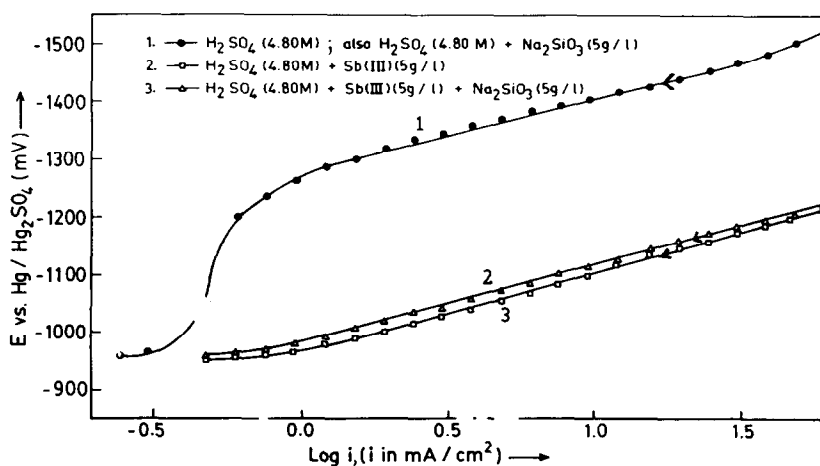


Fig. 1. Steady-state galvanostatic current-density/potential curves for cathodic hydrogen evolution reaction on negative lead/acid electrode. Base grid Pb-0.08wt.%Ca-0.5wt.%Sn.

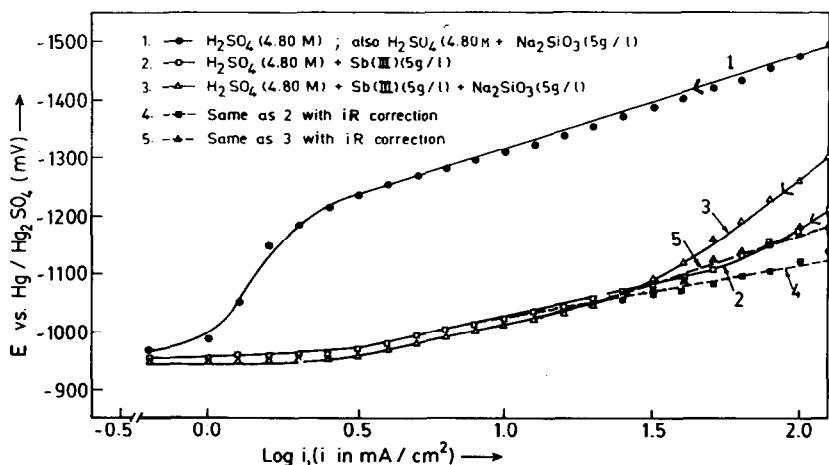


Fig. 2. Steady-state galvanostatic current-density/potential curves for cathodic hydrogen evolution reaction on negative lead/acid electrode. Base grid: pure Pb.

The initial arrest of potential in the polarization curves is attributable to the  $Pb^{2+}/Pb$  reaction at the electrode, since the potential is in the region close to the reversible potential of the  $Pb/PbSO_4$  electrode, *i.e.*,  $-0.976$  V. Further, the  $Pb/PbSO_4$  electrode reaction is kinetically reversible (fast reaction), as is evidenced by the fact that it is used as an electrode in the secondary lead/acid battery. Apparently, the negative active material undergoes spontaneous dissolution (corrosion) under open-circuit conditions to generate sufficient  $Pb^{2+}$  in the electrolyte to sustain a reaction current in this region of potential, and eventually causes a small, limiting current to flow.

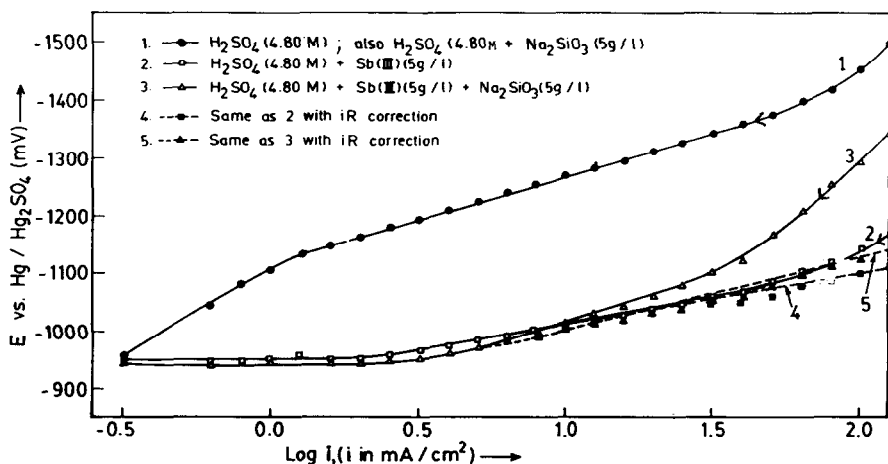


Fig. 3. Steady-state galvanostatic current-density/potential curves for cathodic hydrogen evolution reaction on negative lead/acid electrode. Base grid: Pb-3wt.%Sb.

The occurrence of the well-defined Tafel region at sufficiently cathodic potentials on spongy lead in antimony-free electrolyte is in accord with known facts of HER on pure lead [5 - 8]. Similarly, the large electrocatalysis of HER by dissolved Sb(III) in the electrolyte, as demonstrated by curves 2 and 3 in Figs. 1 - 3, is in agreement with the known deleterious effect of antimony in lead/acid cells, namely, enhancement of the gassing rate.

Exchange current densities ( $i_{o,H}$ ) and Tafel slopes ( $b_H$ ) for HER derived from the Tafel lines beyond about  $-1000$  mV in Figs. 1 - 3 are listed in Tables 1 and 2, respectively. The distortion of the Tafel lines in Figs. 2 and 3 (curves 2 and 3) is due to  $iR$  drop caused by  $H_2$  bubbles, the HER being catalysed by the Sb(III) additive, as could be verified by the fact that the deviation from the corrected Tafel line is linear with  $i$  and passes through the origin.  $iR$ -corrected Tafel lines were therefore used in these cases to evaluate  $i_{o,H}$ ,  $b_H$  and  $i_{cor}$  values.

TABLE 1

Exchange current densities ( $i_{o,H}$ ) for hydrogen evolution reaction on negative electrode of lead/acid cell with  $Na_2SiO_3$  and Sb(III) added to the electrolyte

| Electrolyte composition  | $i_{o,H}$ (A cm <sup>-2</sup> (apparent area))/grid material |                    |
|--|--|--------------------|
|  | Pb-Ca-Sn and Pb (average value)                              | Pb-Sb              |
| H <sub>2</sub> SO <sub>4</sub> (4.8 M)<br>or<br>H <sub>2</sub> SO <sub>4</sub> (4.8 M) + Na <sub>2</sub> SiO <sub>3</sub> (5 g l <sup>-1</sup> ) | $2 \times 10^{-7}$   | $5 \times 10^{-7}$ |
| H <sub>2</sub> SO <sub>4</sub> (4.8 M) + Sb(III) (5 g l <sup>-1</sup> )  | $2 \times 10^{-6}$   | $5 \times 10^{-6}$ |
| H <sub>2</sub> SO <sub>4</sub> (4.8 M) + Na <sub>2</sub> SiO <sub>3</sub> (5 g l <sup>-1</sup> ) + Sb(III) (5 g l <sup>-1</sup> )                | $3 \times 10^{-6}$   | $3 \times 10^{-7}$ |

TABLE 2

Tafel slopes ( $b_H$ ) for hydrogen evolution reaction on negative electrode of lead/acid cell with  $Na_2SiO_3$  and Sb(III) added to the electrolyte

| Electrolyte composition  | $b_H$ (mV/decade)/grid material |       |
|--|---------------------------------|-------|
|  | Pb-Ca-Sn and Pb (average value) | Pb-Sb |
| H <sub>2</sub> SO <sub>4</sub> (4.8 M)<br>or<br>H <sub>2</sub> SO <sub>4</sub> (4.8 M) + Na <sub>2</sub> SiO <sub>3</sub> (5 g l <sup>-1</sup> ) | 138                             | 140   |
| H <sub>2</sub> SO <sub>4</sub> (4.8 M) + Sb(III) (5 g l <sup>-1</sup> )  | 130                             | 115   |
| H <sub>2</sub> SO <sub>4</sub> (4.8 M) + Na <sub>2</sub> SiO <sub>3</sub> (5 g l <sup>-1</sup> ) + Sb(III) (5 g l <sup>-1</sup> )                | 125                             | 95    |

TABLE 3

Corrosion current density ( $i_{\text{cor}}$ ) of fully charged negative electrode of lead/acid cell with  $\text{Na}_2\text{SiO}_3$  and  $\text{Sb(III)}$  added to the electrolyte

| Electrolyte composition   | $i_{\text{cor}}$ ( $\text{A cm}^{-2}$ )/grid material |                    |
|---|---|--------------------|
|   | Pb-Ca-Sn and Pb<br>(average value)                    | Pb-Sb              |
| $\text{H}_2\text{SO}_4(4.8 \text{ M})$<br>or<br>$\text{H}_2\text{SO}_4(4.8 \text{ M}) + \text{Na}_2\text{SiO}_3 (5 \text{ g l}^{-1})$ | $3 \times 10^{-5}$                                    | $9 \times 10^{-5}$ |
| $\text{H}_2\text{SO}_4(4.8 \text{ M}) + \text{Sb(III)} (5 \text{ g l}^{-1})$  | $2 \times 10^{-3}$                                    | $3 \times 10^{-3}$ |
| $\text{H}_2\text{SO}_4(4.8 \text{ M}) + \text{Na}_2\text{SiO}_3 (5 \text{ g l}^{-1}) + \text{Sb(III)} (5 \text{ g l}^{-1})$           | $2 \times 10^{-3}$                                    | $2 \times 10^{-3}$ |

The corrosion current densities ( $i_{\text{cor}}$ ) obtained from HER Tafel line intercepts at open-circuit potentials of the electrodes are shown in Table 3.

In any given electrolyte,  $i_{\text{cor}}$ ,  $i_{\text{o, H}}$  and  $b_{\text{H}}$  values should be more or less independent of the nature of the grid material (electrode substrate) as long as there is no antimony in the grid material, since the active material exposed to the electrolyte in these cases is pure, spongy lead. Accordingly, average values of  $i_{\text{o, H}}$ ,  $b_{\text{H}}$  and  $i_{\text{cor}}$  for electrodes with Pb-Ca-Sn and Pb grid materials are shown in Tables 1 - 3. As can be seen, the presence of antimony in the grid material causes a significant electrocatalysis of the HER.

It follows from the average  $i_{\text{o, H}}$  and  $i_{\text{cor}}$  values in Tables 1 and 3, that while  $\text{Sb(III)}$  additives substantially electrocatalyse the HER on lead, as well as the open-circuit corrosion of lead, the polysilicic acid additive has no effect on  $i_{\text{o, H}}$  and  $i_{\text{cor}}$  when present on its own, but causes a small, detectable electro-retardation of the HER, and inhibition of the corrosion rate, when  $\text{Sb(III)}$  is also present in the electrolyte. The last result is rather unexpected, since polysilicic acid is not expected to become adsorbed on metallic surfaces and retard interfacial reactions such as corrosion. A probable explanation for the existence of such an electroretardation effect is that in a strongly acid medium, such as in the present case, the colloidal polysilicic acid produced by acid hydrolysis of sodium silicate [10] facilitates (by virtue of its large specific surface) adsorption of  $\text{Sb(III)}$  species from the solution. This process may be similar to the adsorption of  $\text{Sb(III)}$  and other ions on other oxide dispersions in  $\text{H}_2\text{SO}_4$  [12].

The implication of these results with regard to sealed lead/acid cells is that a gelled-electrolyte approach is likely to be beneficial for sealed cells with absorbed electrolyte and low-antimony positive grids (required for deep-cycle applications), since the deleterious effects on the negative electrode by  $\text{Sb(III)}$  migrating from the positive electrode is offset, at least partly, by polysilicic acid in the electrolyte. An additional advantage that could arise is an accelerated transport of oxygen by surface diffusion on the polysilicic acid molecules.

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