

## ANTIMONY POISONING IN LEAD-ACID BATTERIES

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### Summary

Linear potential sweep measurements were conducted using rotating lead-disc electrodes in sulfuric acid electrolyte containing antimony. Within the range investigated hydrogen evolution at the negative electrode is shown to be a monotonic function of the quantity of antimony deposited on the electrode surface. In the potential range  $-950\text{ mV}$  to  $-1150\text{ mV}$  *uersus*  $\text{Hg}/\text{Hg}_2\text{SO}_4$  the antimony deposition on lead electrodes is time dependent only; at more negative potentials the deposition rate decreases with over-voltage. At potentials  $<-1320\text{ mV}$  antimony purging occurs. Various additives to the electrolyte were investigated to determine their ability to suppress the hydrogen evolution; aromatic aldehydes and wood flour were found to be effective. A possible mechanism is discussed.

### Zusammenfassung

Linear-Potential-Sweep Messungen unter Verwendung rotierender Bleischiebenelektroden wurden in antimonfreier und antimonhaltiger  $\text{H}_2\text{SO}_4$  durchgeführt. Es wird gezeigt, dass im untersuchten Bereich die Wasserstoffentwicklung an der negativen Elektrode eine monotone Funktion der auf der Elektrodenoberfläche abgeschiedenen Antimonmenge ist. Im Potentialbereich  $-950\text{ mV}/-1150\text{ mV}$  *versus*  $\text{Hg}/\text{Hg}_2\text{SO}_4$  ist die Antimonabscheidung auf Bleielektroden ausschliesslich eine Funktion der Zeit; bei negativeren Potentialen verringern sich die Abscheidungsraten mit der Überspannung und bei Potentialen  $<-1320\text{ mV}$  ist sogar eine Antimonreinigung zu beobachten. Verschiedene Additive zum Elektrolyten wurden auf ihre Fähigkeit, die Wasserstoffentwicklung zu unterdrücken, untersucht; aromatische Aldehyde und Holzmehl wurden als wirksam identifiziert. Ein möglicher Mechanismus wird diskutiert.

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### Introduction

Antimony is widely used as an alloying element for electrode grids in lead-acid cells. In addition to beneficial effects, mainly in the production

of lead-acid cells, antimony also lowers the hydrogen-overvoltage at the negative electrode — a known disadvantage.

Antimony, which is found in negative active masses, comes primarily from the positive electrodes [1]. Antimony(V) anions are released into the electrolyte by anodic corrosion of the positive grids and can then be transferred to the negative electrode, where they are reduced first to Sb(III) and subsequently to metallic antimony deposited on the electrode [2].

Depending on the negative electrode potential, antimony is released from the negative electrode as  $\text{SbH}_3$  [3-10]. The aim of this work was to investigate the purging of deposited antimony from the negative lead electrodes by applying negative potentials. The influence of the presence of organic substances on the hydrogen evolution current was also investigated.

## Experimental

For all measurements a linear potential sweep technique using rotating disc electrodes was applied.

### (i) Test equipment

The electrolyte in the test cell was 40% sulfuric acid. The working electrode was an insulated lead rod of 6.35 mm dia. A commercial  $\text{Hg}/\text{Hg}_2\text{SO}_4$  electrode in the same electrolyte served as reference and an oversized sheet of pure lead (Merck No. 7365) served as counter electrode. The reference and counter electrodes were separated from the electrolyte of the working electrode by electrolyte bridges to prevent them from influencing the measurements, especially by oxidation.

### (ii) Preparation of the electrolytes and the working electrode

**The electrolytes.** Electrolyte A was commercial sulfuric acid (Merck No. 9286;  $d = 1.3 \text{ g cm}^{-3}$ , 5.3 M). Electrolyte B had  $15 \text{ mg l}^{-1}$  of Sb(III) added as  $\text{Sb}_2(\text{SO}_4)_3$ . Electrolytes  $C_n$  contained various additives in defined amounts and were stored for 20 h in a water bath at  $70 \pm 1$  °C.

**The working electrode.** Immediately before each measurement the working electrode surface was polished with fine abrasive paper under running water, then rinsed with methanol and deionized water.

### (iii) Test procedures

All measurements were carried out at room temperature using 10 ml of electrolyte and with the working electrode rotating at  $600 \pm 6$  rpm. In each case the scan rate was  $10 \text{ mV s}^{-1}$ .

**Procedure I.** The working electrode was held at a preset potential of -1200 mV for 15 min. The potential was then increased at a constant rate to -700 mV.

**Procedure II.** The working electrode was held at  $-1200\text{ mV}$  until a preset current flowed. A linear potential sweep within the range  $-450\text{ mV}$  to  $-250\text{ mV}$  was then carried out.

**Procedure III.** The working electrode was held at  $-1100\text{ mV}$  for 5 min, followed by 5 min at a second potential. Immediately thereafter a linear sweep from  $-450\text{ mV}$  to  $-250\text{ mV}$  was performed.

**Procedure IV.** The working electrode was held at a preset potential for 15 min using antimony containing electrolyte B.

**(iv) Evaluation of the quantity of antimony dissolving from the working electrode**

The quantity of antimony on the working electrode was evaluated by integration of the antimony dissolution peaks obtained by procedures II or III in the potential range  $-450\text{ mV}$  to  $-250\text{ mV}$ . Multiplying these areas, expressed as charge, by the electrochemical equivalent (assuming 3 charge transfers for each antimony atom) gave the quantity of antimony dissolved from the working electrode.

## Results and discussion

### (i) Antimony on negative electrodes

Figure 1(a) and (b) compares linear potential sweeps, according to procedure I, for electrolytes A and B, respectively. The main difference due to the antimony in electrolyte B is the hydrogen evolution current value (current after 15 min rest at a potential of  $-1200\text{ mV}$ ), which is approximately 50 times greater than that in pure sulfuric acid.

To study the influence of the quantity of antimony deposited on the working electrode, procedure II using electrolyte B was employed. Figure 2 presents the results obtained with this test. The hydrogen evolution current is nearly proportional to the quantity of antimony deposited on the working electrode.

Procedure IV was used to observe the development of the hydrogen evolution current with time. Figure 3 shows, in a 3-dimensional plot, the current curves obtained for potentials in the range  $-950\text{ mV}$  to  $-1600\text{ mV}$  (the values for  $t = 0$  have been extrapolated).

A current increase with time is observed for each potential, presumably due to the increasing antimony deposition on the working electrode.

The currents increase with overvoltage in the range  $-950\text{ mV}$  to approximately  $-1200\text{ mV}$ , a behaviour similar to that of a pure antimony electrode, followed by a decrease between  $-1200\text{ mV}$  and  $-1450\text{ mV}$ . For potentials more negative than  $-1450\text{ mV}$ , the current increases again, a behaviour similar to that of a pure lead electrode.

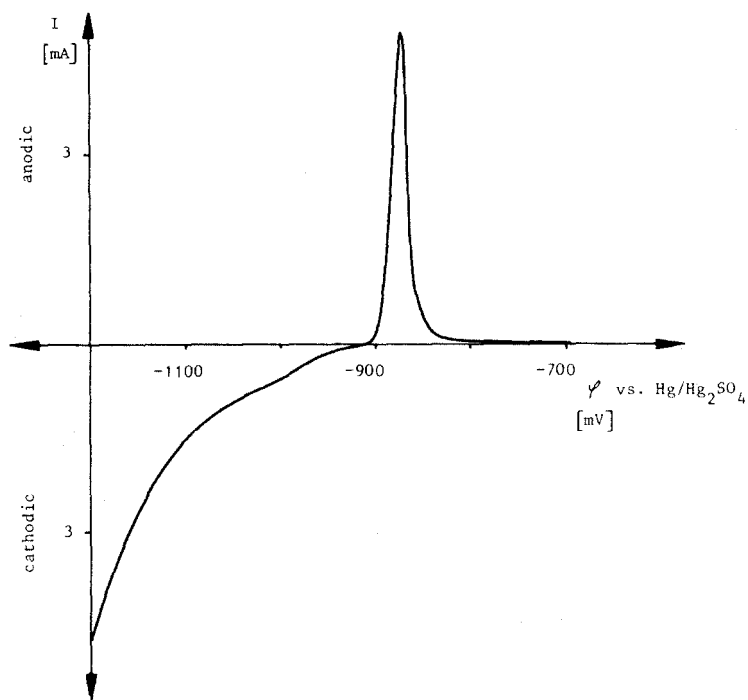
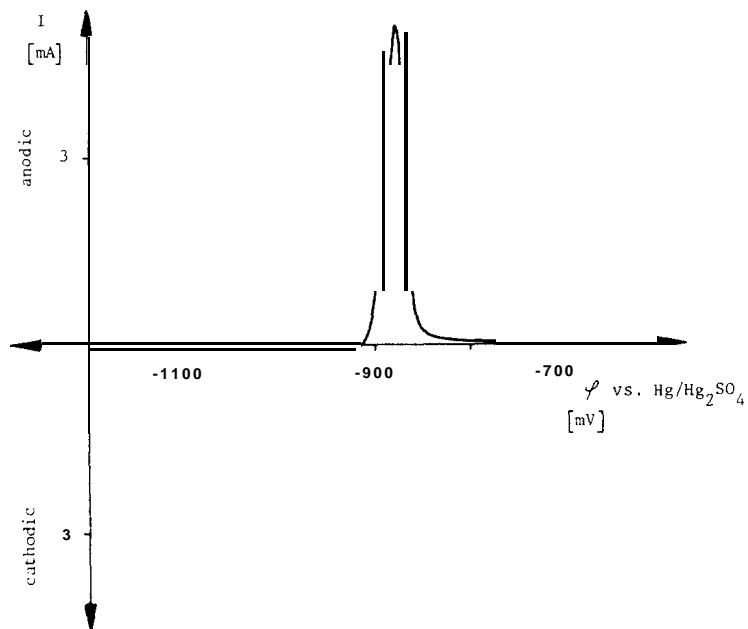


Fig. 1. (a) Linear potential sweep of a lead-disc electrode in  $\text{H}_2\text{SO}_4$ . (b) Linear potential sweep of a lead-disc electrode in  $\text{H}_2\text{SO}_4$  containing  $15 \text{ mg l}^{-1}$  of  $\text{Sb(III)}$ .

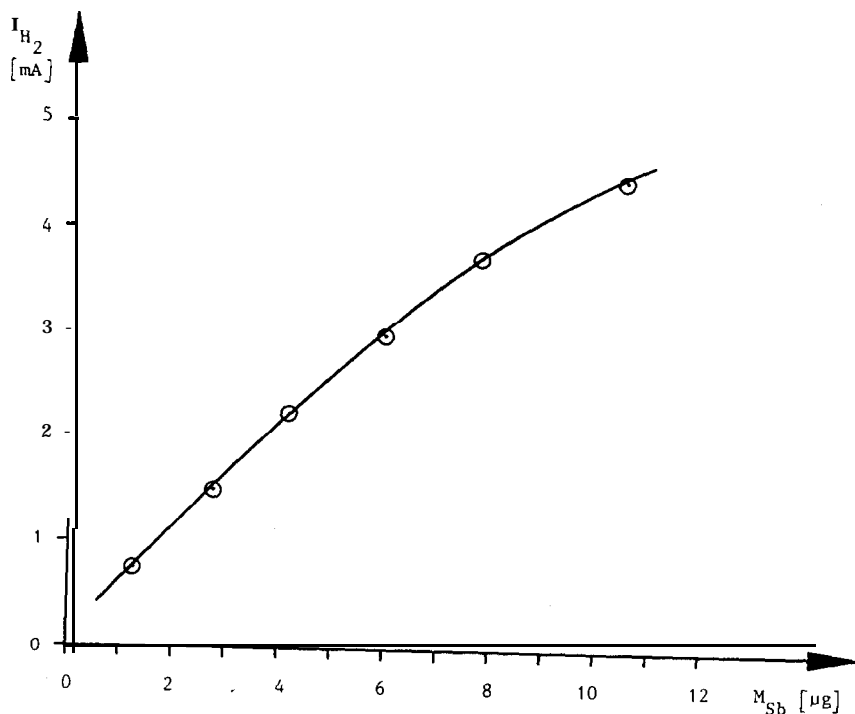


Fig. 2. Hydrogen evolution current as a function of the quantity of antimony deposited on the rotating lead-disc electrode surface.

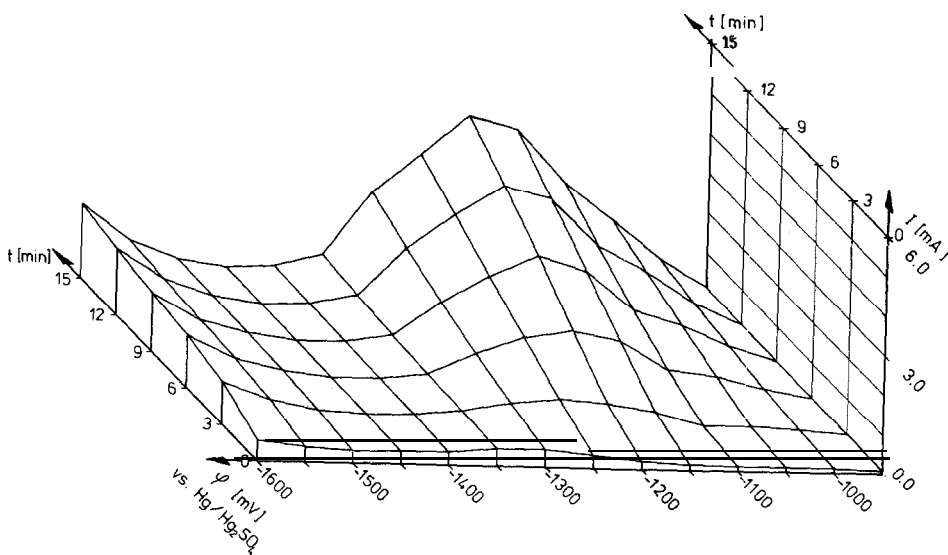


Fig. 3. Current at a rotating lead-disc electrode in  $\text{H}_2\text{SO}_4$  containing  $15 \text{ mg l}^{-1}$  of Sb(III) as a function of potential and time.

Procedure III was employed, using electrolyte B containing antimony, to study the relationship between the quantity of antimony found on the working electrode and the potential applied. During the first 5 min, at a working electrode potential of  $-1100$  mV, antimony is deposited reproducibly, while during the second 5 min period, at a different (constant) potential, the quantity of antimony on the working electrode varies.

The total amount of antimony on the electrode surface at the end of these tests was measured. The difference between this value and the value after the first 5 min is a function of the potential applied during the second 5 min period. (See Table 1 and Fig. 4.)

The quantity of antimony deposited on the working electrode surface in the potential range  $-900$  to  $-1150$  mV is almost independent of the potential and depends only on the time, which was constant. As the

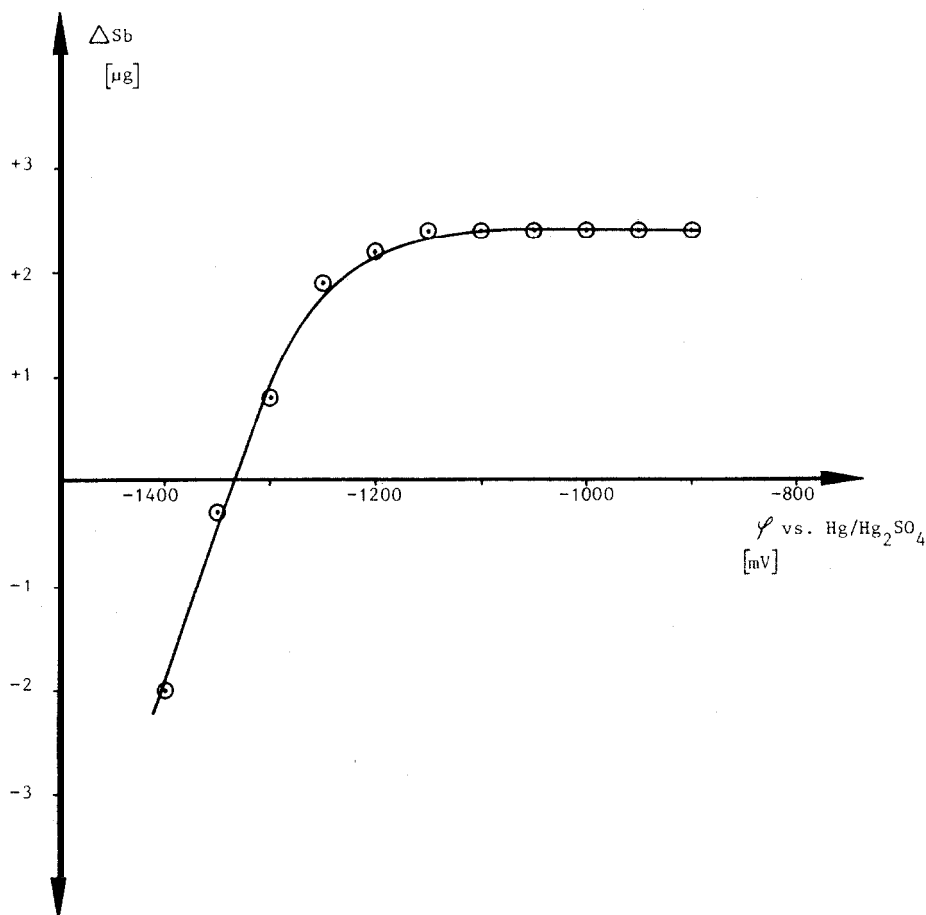


Fig. 4. Variation of the quantity of antimony on the rotating lead-disc electrode surface as a function of potential.

TABLE 1

Variation of the quantity of Sb on a rotating lead-disc electrode surface as a function of potential

$t_1 = 5 \text{ min}$ $\varphi \text{ vs. Hg/Hg}_2\text{SO}_4$ (mV)	$t_2 = 5 \text{ min}$ $\varphi \text{ vs. Hg/Hg}_2\text{SO}_4$ (mV)	$Q_{\text{Sb}}$ (mA s)	$M_{\text{Sb}}$ ( $\mu\text{g}$ )	$\Delta M_{\text{Sb}}$ ( $\mu\text{g}$ )
-1100	—	5.76	2.4	—
-1100	-900	11.51	4.8	+2.4
-1100	-950	11.48	4.8	+2.4
-1100	-1000	11.44	4.8	+2.4
-1100	-1050	11.48	4.8	+2.4
-1100	-1100	11.51	4.8	+2.4
-1100	-1150	11.44	4.8	+2.4
-1100	-1200	11.04	4.6	+2.2
-1100	-1250	10.32	4.3	+1.9
-1100	-1300	7.68	3.2	+0.8
-1100	-1350	5.04	2.1	-0.3
-1100	-1400	0.96	0.4	-2.0

potential falls below  $-1200 \text{ mV}$  significantly smaller quantities of antimony are found on the electrode surface and at  $-1320 \text{ mV}$  no additional antimony is deposited on the electrode; the deposition and dissolution rates are in equilibrium. At potentials more negative than  $-1320 \text{ mV}$ , even antimony deposited during the first 5 min was removed from the electrode surface within the second period of time.

The reason for this decreasing antimony deposition is believed to be due to stibine evolution. According to Dasoyan and Aguf [10] the potential of stibine generation calculated for  $\text{H}_2\text{SO}_4$  electrolyte ( $d = 1.3 \text{ g cm}^{-3}$ ) is  $-1050 \text{ mV}$  ( $\approx -480 \text{ mV}$  versus NHE). With the test procedure used, significantly diminished antimony deposition rates could be observed for potentials  $< -1150 \text{ mV}$ . It is important to note that stibine evolution can result in a purging of antimony from the negative electrode, as indicated by the tests showing that antimony already deposited was removed in a later, second reaction.

#### (ii) Influence of organic chemical compounds in the electrolyte

Historically, separator materials for lead-acid cells consisted of specially treated wood veneers. After the introduction of synthetic separators a large number of negative active mass additives were tested [11, 12], because such separators failed to show some of the beneficial influences on the lead-acid battery performance which were obtained from wood separators. Today, additives to the active masses, called expanders, usually consist of mixtures of  $\text{BaSO}_4$ , lamp black, wood flour and/or organics extracted from wood, especially lignin, lignin sulfonates, etc.

Mahato [13] reported the influence lignosulfonate cations have on the hydrogen overvoltage, and Azim [14] reported the change in the hydrogen evolution caused by expander action.

As the structure of lignin is very complicated and not yet completely understood, Simon [15] attempted to investigate the influence of well-defined aromatic compounds on battery performance. He reported that the pure substances were ineffective, and only after preceding oxidation with subsequent reduction did they become effective as inhibitors.

We have tested aromatic alcohols, aldehydes, and acids as electrolyte additives to determine their influence on the hydrogen evolution current (electrolytes  $C_n$ ). Test procedure I was used and oxidation of the tested substances could be excluded by linking the positive electrode via an electrolyte bridge.

A "selectivity" value,  $S$ , was defined to quantify the effectiveness of an additive as a suppressor of the hydrogen evolution current:

$$S = \frac{I_{H_2}}{I_{H_2, \text{add.}}} \frac{Q_{Pb, \text{add.}}}{Q_{Pb}}$$

where  $I_{H_2}$  represents the hydrogen evolution current after 15 min at  $-1200$  mV *versus* the reference electrode in electrolyte B,  $I_{H_2, \text{add.}}$  is the same, but refers to electrolytes  $C_n$ ,  $Q_{Pb}$  is the discharge capacity of the negative electrode in a linear potential sweep curve for the Pb/PbSO<sub>4</sub> reaction (area under peak) in electrolyte B, and  $Q_{Pb, \text{add.}}$  is the same, but refers to electrolytes  $C_n$ . The second factor in the above definition is necessary to exclude pure "surface reducers" from selectivity merits.

Selectivity values,  $S$ , are presented in Table 2(a) and (b), while Fig. 5(a), (b), (c) gives typical current-voltage curves for the methoxybenzene group. They show that these substances do not negatively influence the discharge reaction (compared with Fig. 1(b) the area under the lead/lead sulphate peak remains nearly constant). The aldehydes suppress the hydrogen evolution current. Table 2(a) shows that, of the group of substances tested, only the aldehydes have selectivity values significantly greater than 1.


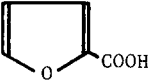
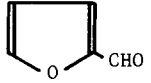
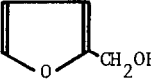

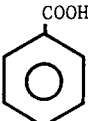
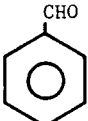
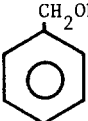
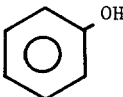
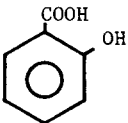
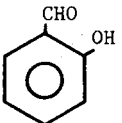
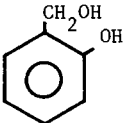
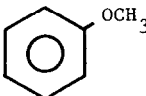
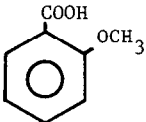
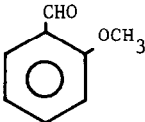
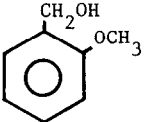
In Table 2(b) isomers of the methoxybenzaldehydes are compared; only 2- and 4-methoxybenzaldehydes suppress the hydrogen evolution current significantly, while 3-methoxybenzaldehyde has a low selectivity value. It is well known that aromatic compounds substituted at the 2- or 4- position are more reactive than those substituted at the 3-position. Additionally, Table 2(b) shows selectivity values for dimethoxybenzaldehyde isomers and for 2,3,4-trimethoxybenzaldehyde.

The commercially available expander Indulin AT was tested as an additive at  $1 \text{ g l}^{-1}$  of electrolyte. It was used as received as well as in purified form, *i.e.*, all water soluble components were removed prior to use. The purified Indulin AT did not significantly suppress the hydrogen evolution current, while the original expander (with approximately 5% water-soluble components) had a selectivity value of 84. Neither lamp black nor BaSO<sub>4</sub> influenced the hydrogen evolution.



TABLE 2(a)

Selectivity values,  $S$ , for some organic compounds

	Acids COOH	Aldehydes CHO	Alcohols CH <sub>2</sub> OH
 Furan	$S = 1$  Furan-2-carboxylic acid	$S = 3$  Furan-2-aldehyde	$S = 1$  Furan-2-alcohol
 Benzene	$S = 1$  Benzoic acid	$S = 11$  Benzaldehyde	$S = 1$  Benzylalcohol
 Phenol	$S = 1$  2-Hydroxy benzoic acid	$S = 75$  2-Hydroxy benzaldehyde	$S = 1$  2-Hydroxy benzylalcohol
 Methoxy benzene	$S = 2$  2-Methoxy benzoic acid	$S = 40$  2-Methoxy benzaldehyde	$S = 1$  2-Methoxy benzylalcohol

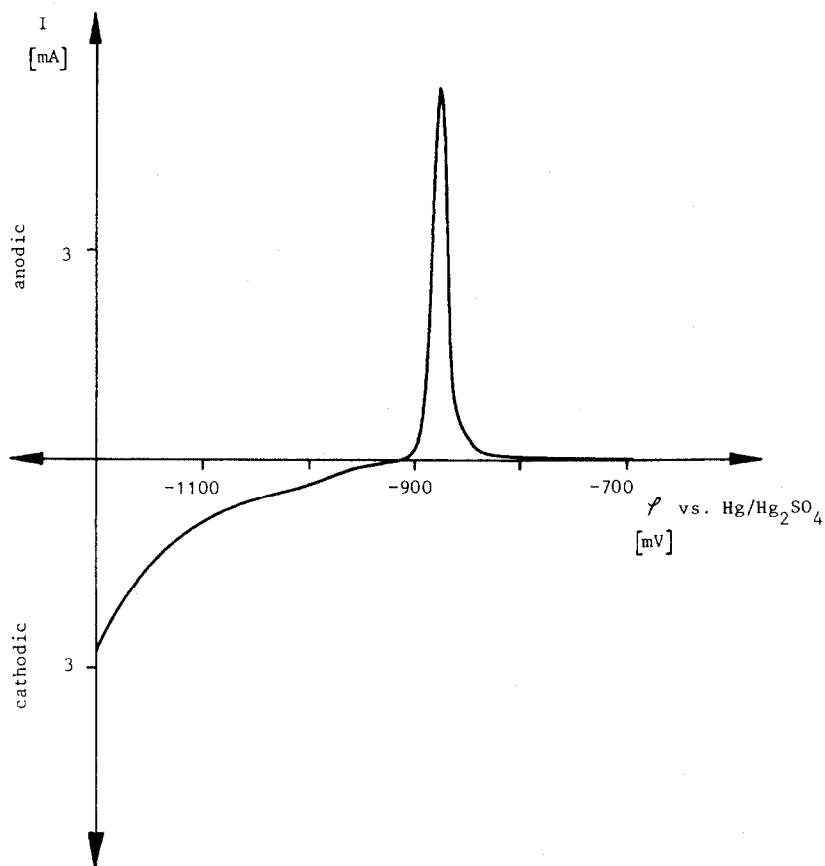
Oak wood flour, used as an additive for negative active masses, was evaluated at  $1 \text{ g l}^{-1}$  of electrolyte. The selectivity value was high ( $S = 33$ ), see Fig. 6.

Wood consists basically of cellulose, hemicelluloses and lignins; the hemicelluloses consist of pentosans and hexosans. In acidic media the hexosans become hexoses and are converted to 5-hydroxymethylfurfural,

TABLE 2(b)

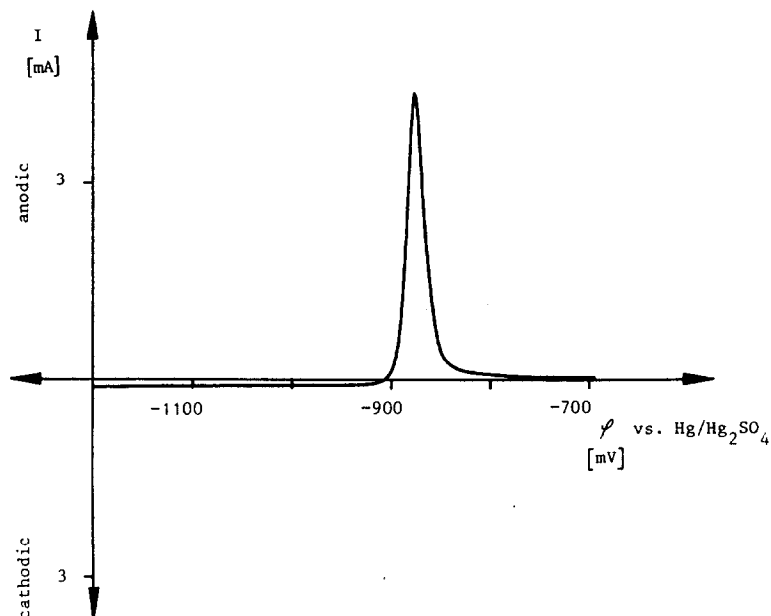
Selectivity values,  $S$ , for some methoxybenzaldehydes

Substance	Selectivity, $S$
2-methoxybenzaldehyde	40
3-methoxybenzaldehyde	5
4-methoxybenzaldehyde	47
2,4-dimethoxybenzaldehyde	44
2,5-dimethoxybenzaldehyde	31
3,4-dimethoxybenzaldehyde	4
3,5-dimethoxybenzaldehyde	10
2,3,4-trimethoxybenzaldehyde	66



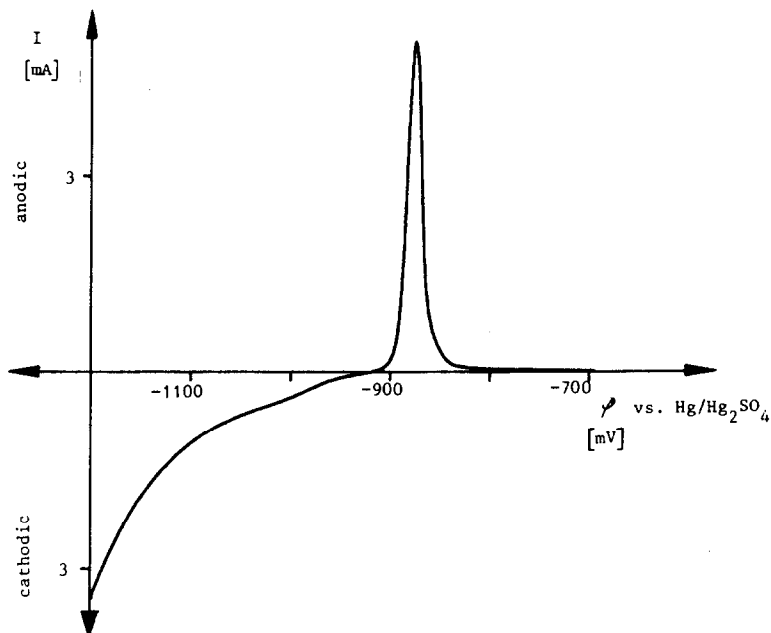
(a)

Fig. 5. (a) Linear potential sweep of a rotating lead-disc electrode in  $\text{H}_2\text{SO}_4$  containing  $15 \text{ mg l}^{-1}$  of  $\text{Sb(III)}$  and  $10^{-4} \text{ mol l}^{-1}$  of 2-methoxybenzoic acid.



(b)

Fig. 5. (b) Linear potential sweep of a rotating lead-disc electrode in  $\text{H}_2\text{SO}_4$  containing  $15 \text{ mg l}^{-1}$  of Sb(III) and  $10^{-4} \text{ mol l}^{-1}$  of 2-methoxybenzaldehyde.



(c)

Fig. 5. (c) Linear potential sweep of a rotating lead-disc electrode in  $\text{H}_2\text{SO}_4$  containing  $15 \text{ mg l}^{-1}$  of Sb(III) and  $10^{-4} \text{ mol l}^{-1}$  of 2-methoxybenzylalcohol.

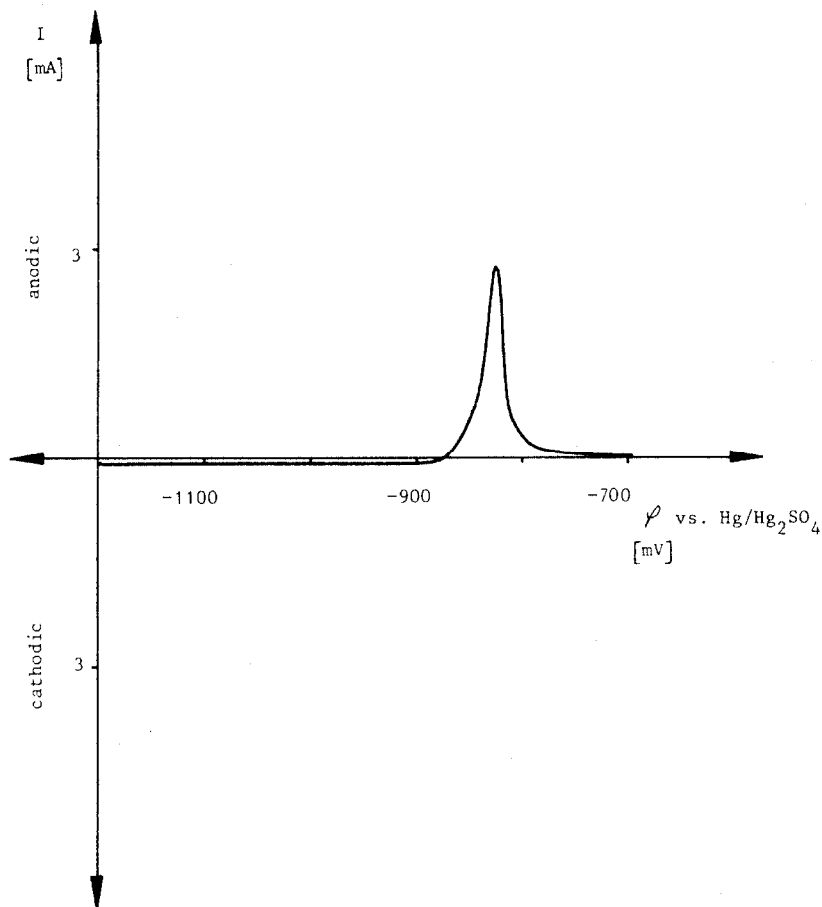


Fig. 6. Linear potential sweep of a rotating lead-disc electrode in  $\text{H}_2\text{SO}_4$  containing  $15 \text{ mg l}^{-1}$  of  $\text{Sb(III)}$  and  $1 \text{ g l}^{-1}$  of oak wood flour.

the pentosans to pentoses and to furfural [16]. Furfural can be reduced at the negative electrode to furfuryl alcohol which is known to polymerize in sulfuric acid media [17]. This would explain the positive results obtained with furfural (see Table 2(a)) and with oak wood flour (see Fig. 6), which suppresses hydrogen evolution significantly. It also diminishes the lead discharge peak, however, most probably due to partial coverage of the electrode's lead sites.

A conceivable model for the manner in which the specific adsorption of aromatics at the negative electrode could occur, and thereby suppress hydrogen evolution, is given in Fig. 7.

During normal operation of a lead-acid battery the negative electrode remains in a potential range in which the lead areas of the electrode surface are positively charged while the antimony sites are negatively charged

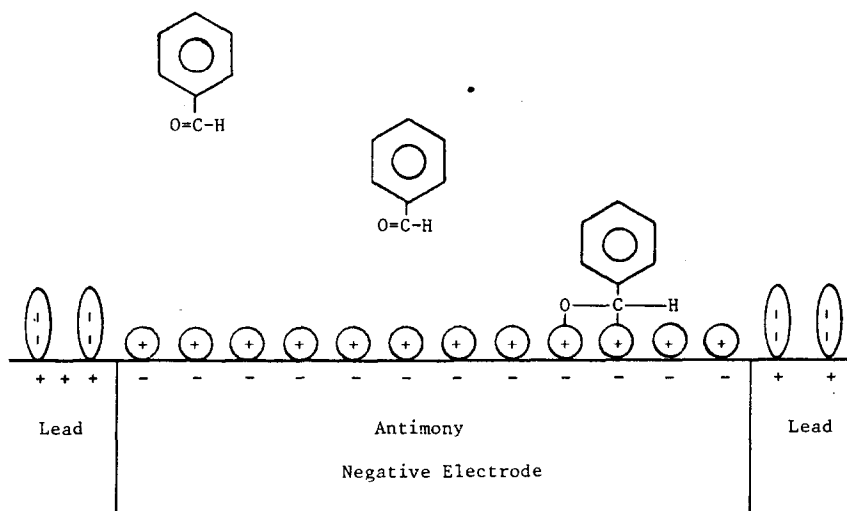


Fig. 7. Adsorption of aromatic aldehydes at the electrode surface (model).

(potential of zero charge:  $\text{Pb} \approx -1250$  mV;  $\text{Sb} \approx -750$  mV). Therefore,  $\text{SO}_4^{2-}$  species will be preferentially adsorbed at the lead areas of the electrode, while  $\text{H}^+$  species will cover the antimony sites. According to Damaskin *et al.* [18] aldehydes are better adsorbed at cathodic polarized electrode surfaces compared with the corresponding alcohols.

The beneficial effects of the suppression of hydrogen evolution in lead-acid batteries will be provided by additives which are able to maintain a high selectivity value over a long period of time and over a great number of charge/discharge cycles. With constant current charging regimes, the effect of hydrogen suppression by an additive is that the negative electrode potential increases and antimony purging becomes possible.

### Acknowledgements

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