

EFFECT OF ORGANIC ADDITIVES ON THE LEAD/ACID NEGATIVE PLATE

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Introduction

Additives to the negative mass of lead/acid batteries are commonly known as 'expanders'. These are composed of carbon black, barium sulphate, and lignosulphonate. Lignin, which is a wood derivative, is the common name for large macromolecules. Lignin dissolves in sulphuric acid to form lignosulphonate and this is the form in which lignin expander is commonly used in negative plates. The lignosulphonate adsorbs onto both lead and lead sulphate and influences the formation of the latter by reducing the crystal growth rate so that the crystals are smaller and the film more porous [1]. On charge, this effect causes a partial charge inhibition, whereas on discharge it decreases the electrode polarization and suppresses the solid-state passivation [2]. The formation of a transient lead lignosulphonate complex that leads to a greater depth-of-discharge was suggested by LeMehaute [3]. The overall effect of lignin is to impart a higher capacity (especially at low temperatures) to the negative plate throughout its life.

Claims have been made in the literature that certain commercial lignins can also maintain a high overvoltage for hydrogen in the presence of antimony [4]. When comparing lignins from different sources, the effect of structure differences is not known. This has led to conflicting results concerning the ability of lignin to maintain hydrogen overvoltages.

A new area of research for the lead/acid battery industry involves valve-regulated cell technology. Non-antimonial alloys are used successfully in applications that do not require cycling. On the other hand, batteries built for traction applications cannot achieve the same level of performance as high-antimony (>8 wt.%) batteries. An alternative approach to that of complete antimony removal may be through the use of low-antimony alloys (2.5 wt.%) plus the addition of various compounds that can reduce the poisoning effect of antimony at the negative.

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The work reported here has followed that of Böhnstedt *et al.* [5] in which a comparison was made of the effectiveness of a variety of organic compounds on suppressing the hydrogen evolution reaction. From that study, two of the most effective compounds were found to be 2-hydroxybenzaldehyde (Hyd) and 2-methoxybenzaldehyde (Met). In the experiments described below, the performance of these two compounds is compared with that of Vanisperse A, a commercial product from Borregaard Industries Ltd. that contains sodium lignosulphonate.

Experimental

All experiments were carried out in 4.5 M H_2SO_4 (Merck) solutions. The working electrode was a lead rod (diameter 5 mm) fabricated in the form of a rotating disc. The reference electrode, against which all potentials were measured and reported, was $\text{Hg}/\text{Hg}_2\text{SO}_4$. The counter electrode was a lead sheet with a large surface area and was separated from the working-electrode compartment by a glass frit. Stock solutions of the following compounds were prepared as follows:

- (i) Vanisperse A (Borregaard), 15 mg l^{-1} (Van);
- (ii) 2-hydroxybenzaldehyde (Fluka AG), $10^{-4} \text{ mol l}^{-1}$ (Hyd);
- (iii) 2-methoxybenzaldehyde (Fluka AG), $10^{-4} \text{ mol l}^{-1}$ (Met).

The structure of the benzaldehydes is shown in Fig. 1 along with a model of lignin which is based on the Freudenberg formula [6]. Antimony was used at a concentration of 20 mg l^{-1} .

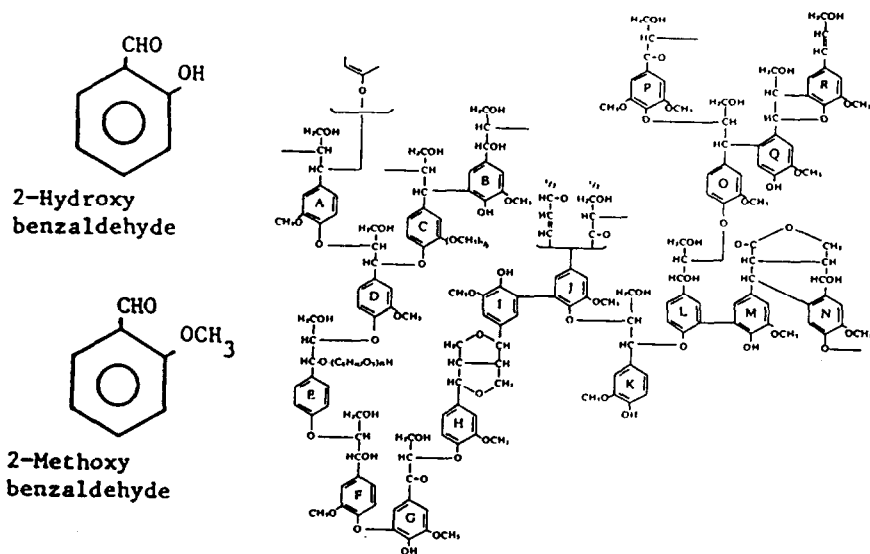


Fig. 1. Structure of benzaldehydes used in this study (left), and of lignin (right).

Voltammetric studies were conducted with a Hi-Tek Instrument's DT 2101 potentiostat in conjunction with a Hi-Tek PPRI function generator and Tacussel EDI rotating disc equipment. The working electrode was held at -1200 mV for 15 min prior to all experiments. The potential was then stepped to -970 mV and swept in the positive direction to -700 mV at a scan rate of 10 mV s^{-1} and a revolution rate of 1000 rpm. Current densities were based on the geometric surface area of the electrode.

Results and discussion

General characteristics of voltammograms

The general features of the voltammograms and the effect of the benzaldehydes on the charge and discharge processes are illustrated in Figs. 2 and 3. In each experiment, 10 cycles were recorded. The first cycle in each solution yields the largest peak. Subsequent cycling results in a broadening and reduction in the size of the peak, as well as a shift in potential. The marked influence of the additives on hydrogen evolution is clearly seen in Fig. 3. The 2-methoxybenzaldehyde (Sb + Met) reduces both the hydrogen evolution and the total amount of charge passed. Quantitative comparison of

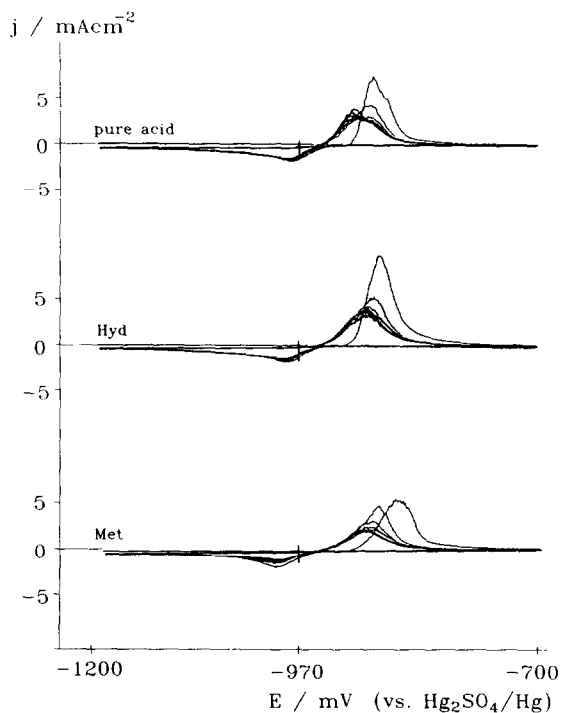


Fig. 2. Voltammograms for a lead disc electrode in pure acid and with benzaldehyde addition.

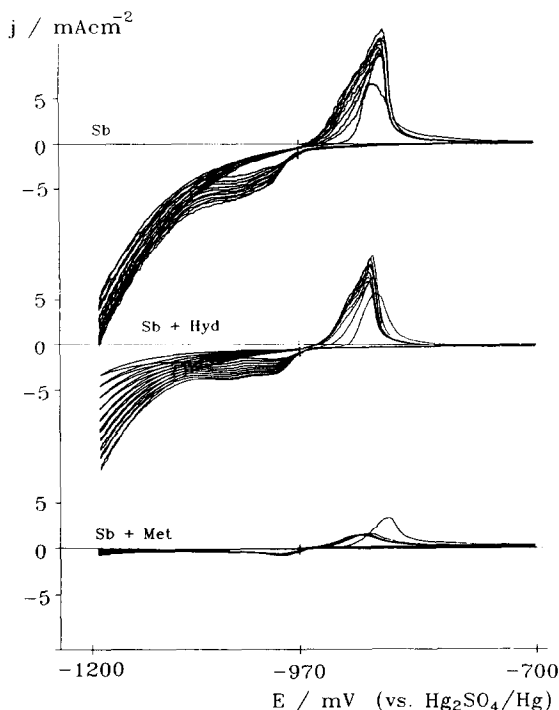


Fig. 3. Voltammograms as in Fig. 2 but with antimony also present.

the curves is presented in the next section, but it should be emphasized here that hydrogen evolution can be greatly reduced in the presence of antimony through the choice of the proper additive.

Charge passed

The area under the curves for the oxidation of lead to lead sulphate (*i.e.*, the charge passed, Q) is presented in Figs. 4 and 5 as a function of cycle number. In Fig. 4, which includes data for Vanisperse A, the strong synergistic effect of antimony and Vanisperse A can be clearly seen: the charge passed increases considerably faster than in solutions containing only Vanisperse A. This indicates that a dramatic increase in porosity of the electrode has taken place. With Vanisperse A alone, the surface area after 10 cycles is exhibiting a gradual increase in value. These results are in sharp contrast to the solution containing all three components (Sb + Van + Met). The methoxybenzaldehyde has a striking effect on the electrode surface area, as seen in the bottom curve of Fig. 4.

Figure 5 shows results for mixtures of antimony with, and without, the organics, and also for the organics alone. The solution containing the methoxybenzaldehyde does not exhibit as dramatic a decrease as that observed when Vanisperse is present (Fig. 4). The effect of antimony alone on the surface area of the electrode is to increase the charge passed.

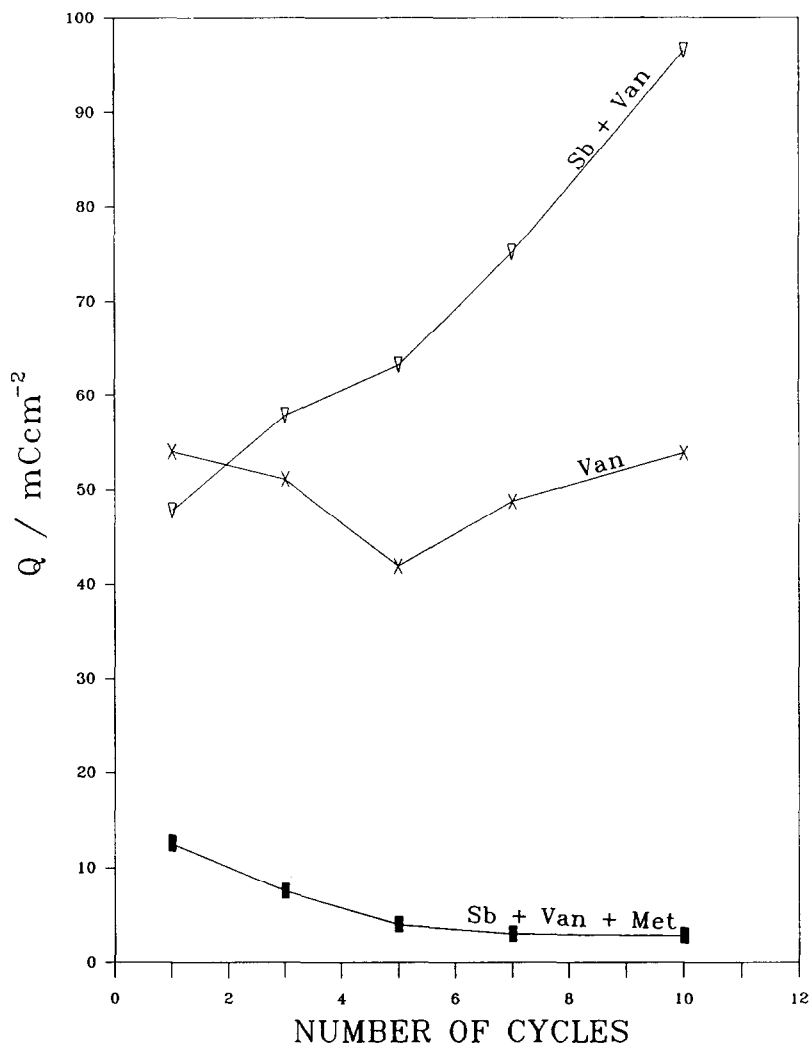


Fig. 4. Charge passed during formation of PbSO_4 , as a function of cycle number.

Hydrogen overvoltage

Further demonstration of the effect of the benzaldehydes is shown in Figs. 6 and 7. The overvoltage required to produce a current density of 0.10 mA cm^{-2} was measured. In pure acid, this overvoltage is -1.45 V ; antimony addition reduced the value to -1.19 V . From a comparison of Figs. 6 and 7, it is noted that Vanisperse A addition has no effect on the hydrogen overvoltage. On the other hand, a shift of 100 mV to more negative potentials is found when methoxybenzaldehyde is added to the electrolyte.

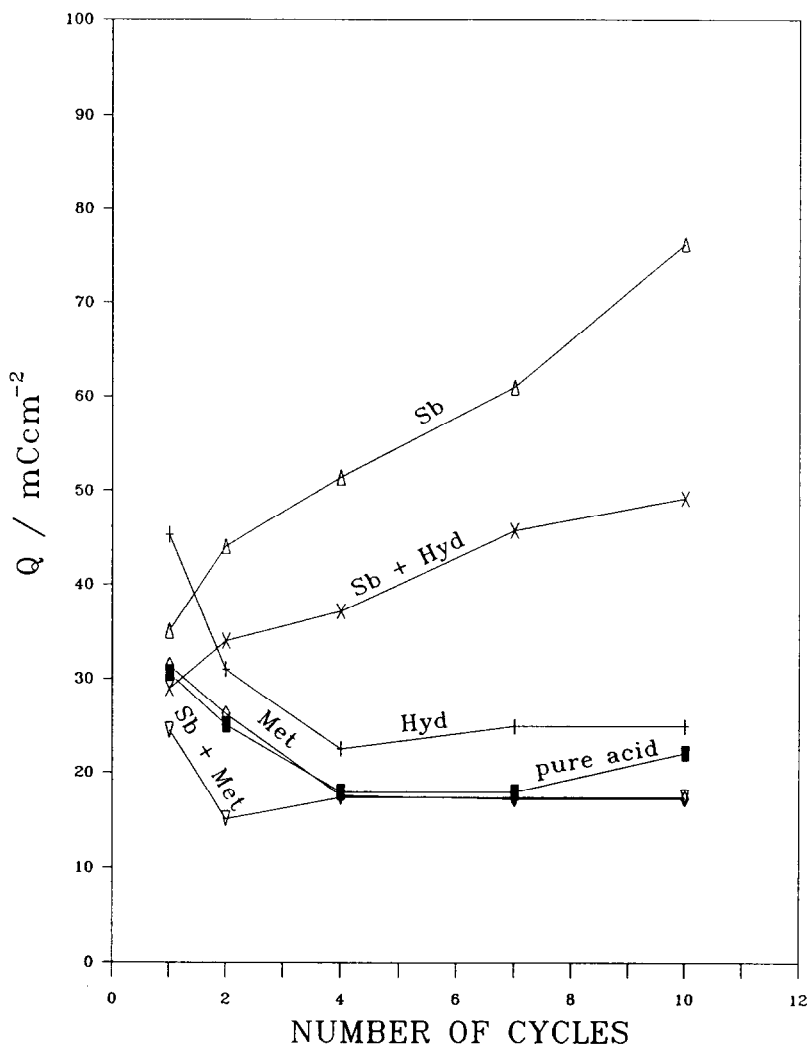


Fig. 5. Charge passed during formation of PbSO_4 as a function of cycle number.

Antimony deposition

It has been suggested [5] that the decrease in hydrogen evolution in solutions containing antimony and benzaldehydes is due to the preferential adsorption of the organic material on sites containing antimony. To determine if benzaldehydes could also act as complexing agents for antimony and thereby prevent, or retard, its deposition an ESCA analysis of the electrode surface was conducted. Solutions without benzaldehyde were found to give the largest value for antimony. By contrast, when the potential of the electrode was held at -1200 mV, no antimony could be found. Some

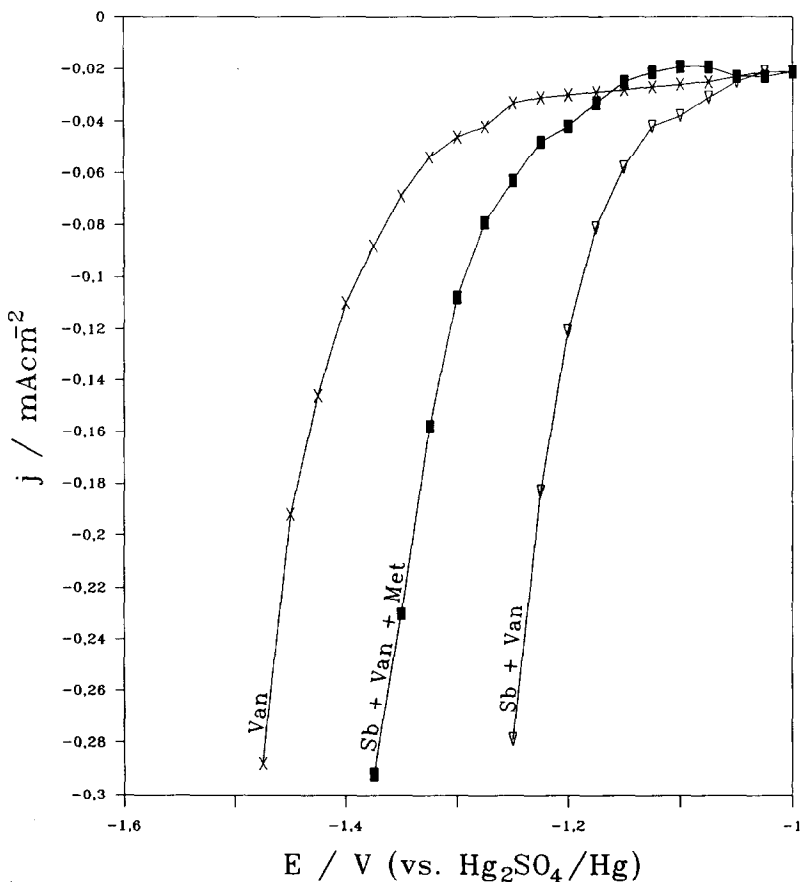


Fig. 6. Hydrogen evolution current on lead in presence of Vanisperse A and antimony.

antimony was detected in experiments where the potential was swept between -1200 and -700 mV; the amount increased with cycle number.

Conclusions

From the above studies, the following general conclusions can be drawn:

- (i) Vanisperse A has negligible effect on hydrogen overvoltage;
- (ii) 2-methoxybenzaldehyde has a large effect on both the hydrogen overvoltage and the discharge capacity of lead;
- (iii) 2-methoxybenzaldehyde can impede the deposition of antimony on lead.

Although the mechanism for the action of 2-methoxybenzaldehyde cannot be unequivocally deduced from this work, it is clear that the addition of certain organic compounds to the electrolyte can affect profoundly the rate

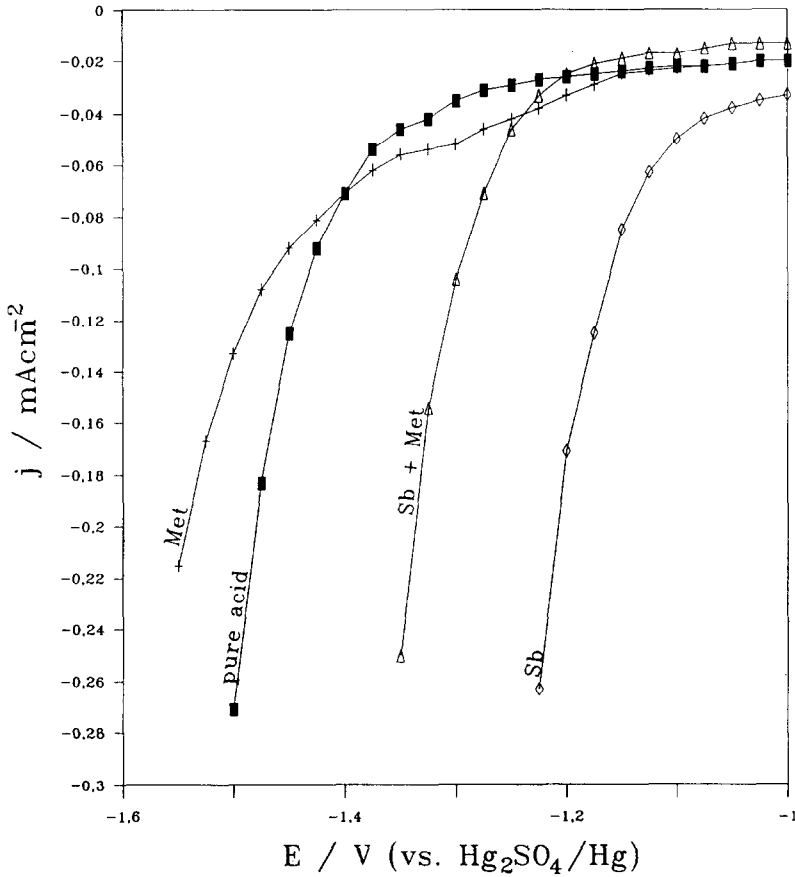


Fig. 7. Hydrogen evolution on lead in the presence of antimony and benzaldehydes.

of hydrogen evolution. This opens up the possibility of manufacturing valve-regulated cells with low levels of antimony.

References

- 1 G. Hoffman and W. Vielstich, *Prog. Batteries Solar Cells*, 5 (1984) 170.
- 2 B. K. Mahato, *J. Electrochem. Soc.*, 127 (1980) 1679.
- 3 A. LeMehaute, *J. Appl. Electrochem.*, 6 (1976) 543.
- 4 B. K. Mahato, J. L. Strebe, D. F. Wilkinson and K. R. Bullock, *J. Electrochem. Soc.*, 132 (1985) 19.
- 5 W. Böhnstedt, C. Radel and F. Scholten, *J. Power Sources*, 19 (1987) 301.
- 6 G. J. Szava, *J. Power Sources*, 23 (1988) 119.