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Influence of substituted benzaldehydes and their derivatives as inhibitors for hydrogen evolution in lead/acid batteries

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Abstract

The influence of substituted benzaldehydes and their derivatives as inhibitors for hydrogen evolution on smooth and porous negative electrodes of the lead/acid system is investigated by cyclic voltammetric measurements. The experiments have been carried out with and without the presence of antimony. The effect of the inhibitors can be distinguished by a moderate and a strong inhibiting action. Use of these inhibitors in flooded lead/acid batteries can reduce water loss during cycling by 50%.

1. Introduction

In addition to the main electrochemical charging and discharging reactions in lead/acid batteries, especially during overcharging and shelf life, other undesirable side reactions take place. As a result, both decomposition of water and a change in electrolyte composition and electrolyte volume occur. The formation of hydrogen gas is particularly undesirable. In general, the hydrogen has to be removed from the battery because its re-combination inside the battery is very slow [1]. Therefore in lead/acid batteries with immobilized electrolytes valve regulation is necessary. A further opportunity to over-come this is problem is to use a special catalyst in the gas room of the battery to provide recombination of hydrogen with oxygen, but this procedure is not popular. The best approach to solve the problem is to suppress any hydrogen evolution in the battery. This appears to be impossible from the thermodynamic point of view.

One way to suppress hydrogen evolution, or to diminish it to a very low value, is to use inhibitors that may shift the hydrogen overvoltage to a more negative electrode potential. The effect of a wide variety of inorganic and organic substances on hydrogen evolution has been described in the literature, e.g. Refs. [2–12,14]. Organic additives that show a substantial inhibition

effect have been found to be derivatives of benzaldehyde [8–10], benzoic acid [7,11] and benzene [12]. The structures of these additives are similar to the sub-structures of the expander lignin. Indeed, expanders sometimes are reported to exhibit a slight inhibition effect on hydrogen evolution [7,8], but this appears to be true only for substances in an unpurified state [8].

Both expanders and the so-called hydrogen-evolution inhibitors are adsorbed on the surface of the negative electrode, but act rather differently. The advantageous effect of expanders on the electrode structure during discharge is achieved by their adsorption on lead and lead sulfate particles. Hydrogen-evolution inhibitors exhibit a structure that is adsorbed at the protons that are mainly present on the antimony sites of the electrodes surface. The mechanism of the specific adsorption of aromatic aldehydes on these sites has been explained primarily by the model of Böhnstedt [8], see Fig. 7. Thus, hydrogen-evolution inhibitors can help to complete the beneficial expander effect (i.e., increase in porosity and mass utilization) by efficient suppression of hydrogen evolution. Such hydrogen-evolution inhibitors may be used in flooded batteries to improve maintenance-free operation, and in valve-regulated lead/acid (VRLA) batteries to decrease the hydrogen pressure.

Though recent experiments have confirmed the beneficial effect of hydrogen-evolution inhibitors [12,14] only a limited amount of information on their utility

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in commercial batteries is available. The aims of the work discussed here are:

(i) to gain a better understanding of the inhibitor effect on both hydrogen evolution and charge/discharge reactions at the negative electrode;

(ii) to improve knowledge on the overall inhibitor effect in industrial batteries.

2. Results

2.1. Basic investigations on the effect of hydrogen-evolution inhibitors

For characterization, and as a first screening test, of substituted benzaldehydes and of their derivatives as hydrogen-evolution inhibitors, cyclic voltammetric studies were performed on smooth and porous lead electrodes. The inhibitor was added to the sulfuric acid electrolyte.

All measurements were carried out in a double-walled glass vessel with the well known three-electrode arrangement (i.e., working electrode, reference electrode, counter electrode). The temperature was 25 °C and an Hg/Hg_2SO_4 reference electrode was used. All potentials are reported with respect to this electrode. The basic electrolyte in all experiments was 1.28 g cm^{-3} (4.93 M) sulfuric acid, the common electrolyte solution in lead/acid batteries.

Fig. 1 shows the effect of vanillin added to the electrolyte on the behaviour of a smooth lead electrode. The voltammogram reveals the different electrode reactions that take place at the electrolyte/electrode interface. The anodic peak at −0.88 V and the cathodic

current peak at −0.98 V are characteristic for the main reactions of lead oxidation and lead sulfate reduction, respectively. The increase in cathodic current at more negative potentials beginning from −1.30 V is attributed to the evolution of hydrogen, i.e.,

$$2H^+ + 2e^- \longrightarrow H_2 \qquad (1)$$

An ideal hydrogen inhibitor should suppress the hydrogen evolution during the cathodic run completely and should have no negative influence on the main electrode reactions. This situation is observed (Fig. 1) if we use the inhibitor vanillin in low concentration (4×10^{-6} mol/l sulfuric acid (sp. gr. = 1.28)). In this case, the hydrogen evolution is suppressed slightly and no influence on the current maxima can be seen.

For porous electrodes and vanillin at a concentration of 1×10^{-4} mol/l (Fig. 2(a)), the cathodic hydrogen evolution reaction is increasingly suppressed with increasing cycle number. Surprisingly, a small expander effect can be additionally observed. An expander effect means that the peak areas of lead oxidation and lead sulfate reduction increase as a consequence of an increase in porosity.

When the vanillin concentration is raised to 5×10^{-4} mol/l (Fig. 2(b)), a strong inhibition of the hydrogen evolution takes place. Simultaneously, an inhibition of the charge transfer of the main reactions can be recognized by the shifting of the maximum of the anodic lead oxidation to the positive direction and by the shifting of the cathodic lead sulfate reduction to the negative direction. The consequence of this effect in the practical use of lead/acid batteries could be that, in the case of constant-voltage charging, the charge voltage has to be increased slightly in order to ensure the chargeability of the negative electrode.

The influence of the vanillin concentration on both hydrogen evolution and the main reaction is presented schematically in Fig. 3. The following observations can be made.

● With increasing concentration of vanillin, the hydrogen evolution at the negative electrode is more and more suppressed, even with increasing cycle number (Fig. 3(a)).

● At low concentrations, vanillin appears to have no influence on the main reaction. For both the anodic and cathodic reactions, the ratios related to the intensity of the maxima without additive are close to one (Fig. 3(b),(c)).

● A concentration of about 5×10^{-4} mol/l is typical for the expander action of the vanillin while, in parallel, the hydrogen evolution is further diminished.

● With a further increase of the vanillin concentration, a partial blocking of the main reaction occurs in parallel with a strong suppression of the hydrogen evolution.

● During the transition from expander action to the partial blocking of the main reaction with increasing
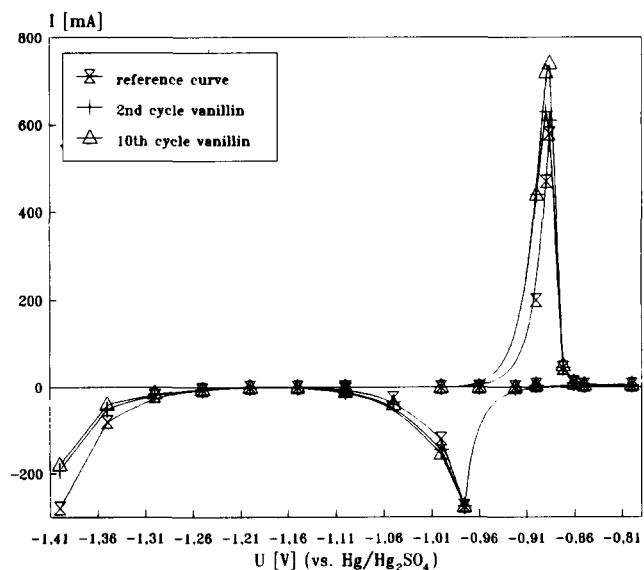

Fig. 1. Voltammogram for smooth lead electrode; 4×10^{-6} mol/l vanillin in 1.28 sp. gr. sulfuric acid. Scan rate: 0.5 mV s^{-1} (reference curve: without vanillin).
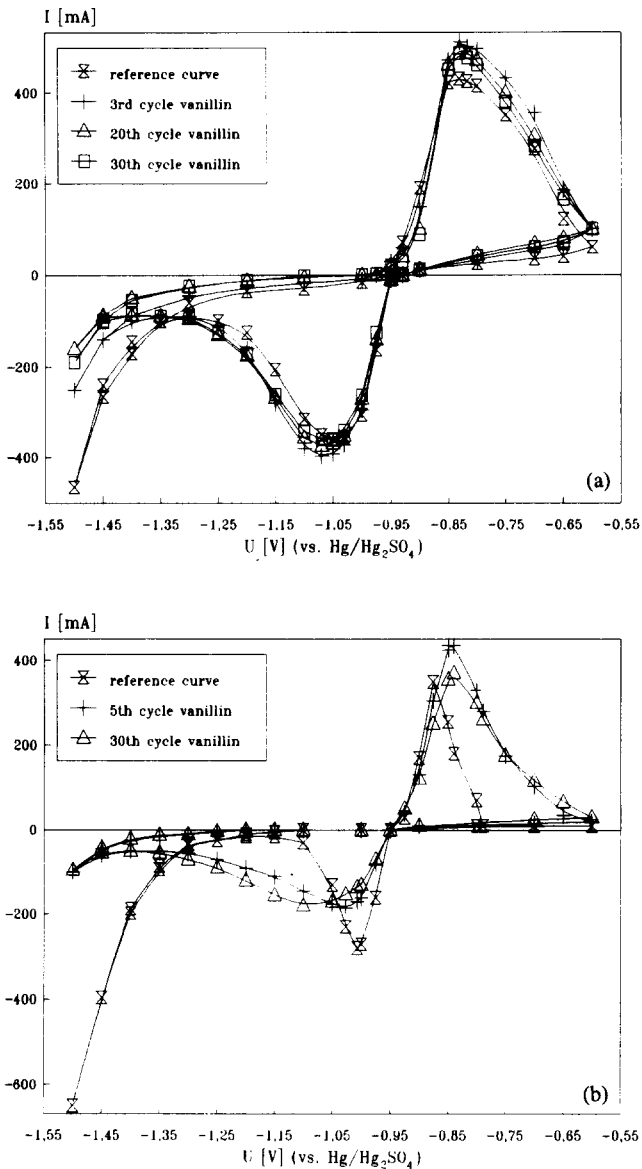
Fig. 2. Voltammogram of a porous lead electrode in 1.28 sp. gr. H_2SO_4: (a) 1×10^{-4} mol/l vanillin; (b) 5×10^{-4} mol/l vanillin. Scan rate: 0.5 mV s^{-1} (reference curve: without vanillin).

vanillin concentration, the coefficient Q_v/Q_0 must reach one again at a certain vanillin concentration. This working condition is of interest in practical applications, because the positive and negative effects of the vanillin on the main electrode reactions are just compensated. That is, the hydrogen evolution is strongly inhibited and there is no impairment from any action of the additional amount of expander above that normally used.

In VRLA batteries, it is most important that the oxygen evolved at the lead dioxide electrode during the overcharge process reacts without kinetic hindrance at the negative electrode. Usually this process is limited by diffusion only. Now the question arises as to whether vanillin as an inhibitor adsorbed at the lead electrode influences this reaction. The data of Fig. 4 demonstrate
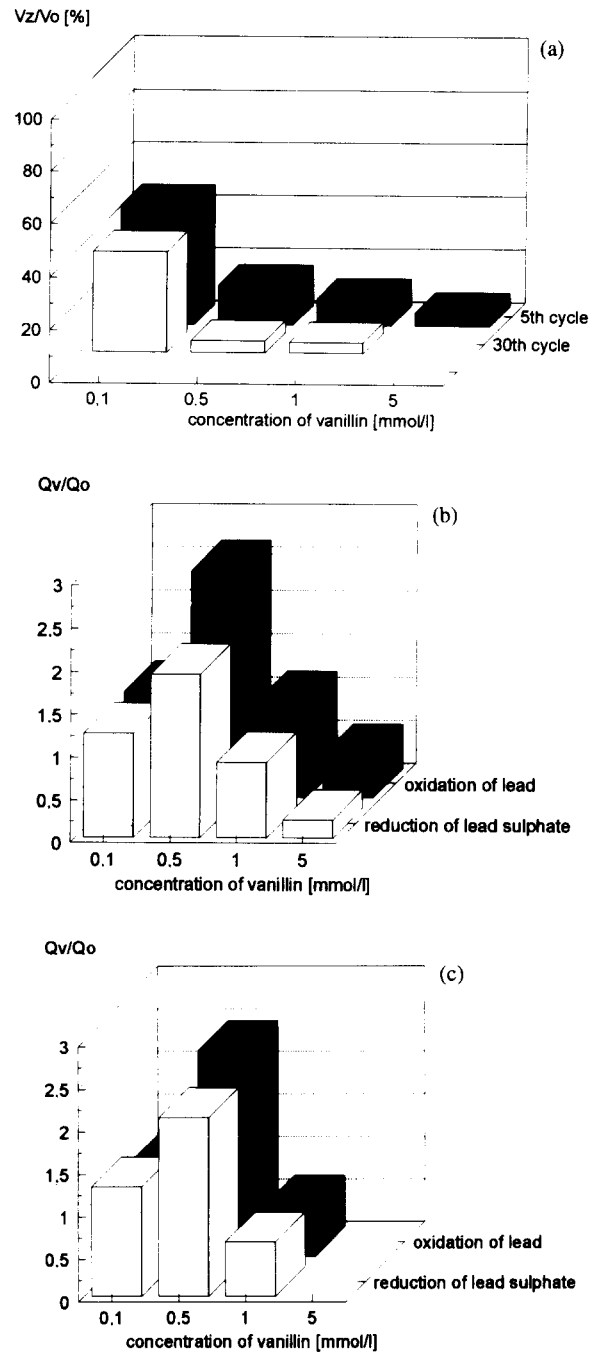

Fig. 3. (a) Influence of vanillin concentration on hydrogen evolution at porous lead electrode; $V_z/V_0 =$ quotient of hydrogen evolution of one cycle with and without additive. (b) Influence of vanillin concentration on Pb/PbSO$_4$ conversion; $Q_v/Q_0 =$ quotient of charge amount with and without vanillin in 5th cycle. (c) $Q_v/Q_0 =$ quotient of charge amount with and without vanillin in 30th cycle.

that there is no negative action of the vanillin on oxygen recombination. While at a vanillin concentration of 5×10^{-4} mol/l in the electrolyte at smooth electrodes the main reactions are hindered, surprisingly the oxygen reduction is supported. It begins at a more positive potential compared with experiments where no vanillin is present.
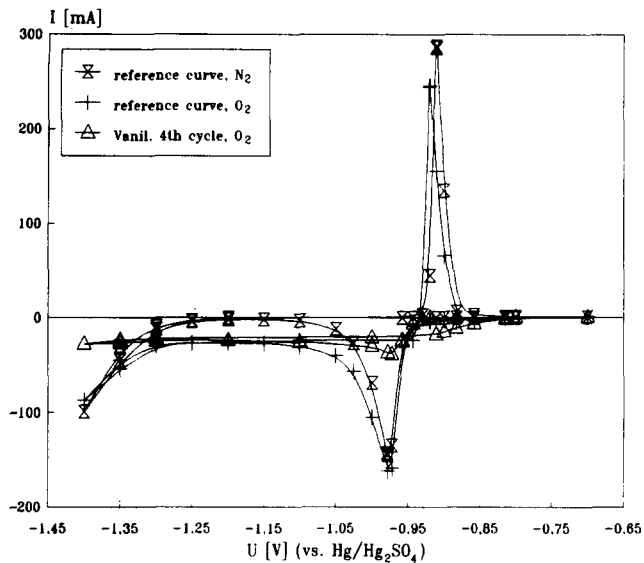
Fig. 4. Voltammogram for smooth lead electrode; 5×10^{-4} mol/l vanillin in 1.28 sp. gr. sulfuric acid. Scan rate: 0.5 mV s^{-1} (reference curves without inhibitor, electrolyte rinsed by nitrogen respectively oxygen).

For practical use of substituted benzaldehydes as inhibitors in lead/acid batteries, it is important to know to what extent the antimony-poisoning effect can be diminished by this additive. By addition of 66 mg/l Sb^{3+} electrolyte the basic voltammogram of the lead electrode in sulfuric acid without any additive is changed drastically (Fig. 5(a), (b)). The hydrogen evolution potential is shifted by more than 300 mV in the positive direction compared with the antimony-free electrolyte. The negative electrode cannot be recharged completely, as is demonstrated by the following anodic run, where the available capacity of the lead electrode is greatly diminished, resulting in a lowered anodic maximum. With 5×10^{-4} mol/l vanillin, the negative effect of the antimony can be almost compensated without any negative influence on the main reactions. This effect is stable for a large number of cycles. Obviously, the inhibitor molecules interact with the protons of the acid that are preferentially adsorbed at the antimony sites of the electrode. This is typical for inhibitors of the moderate type like vanillin.

In the case of simultaneous application of vanillin as an inhibiting additive to the electrolyte and of expander in the usual concentration of 0.15 wt.% in the negative active mass, no negative effect on the performance of the porous lead electrode can be detected (Fig. 6). Though no additional expander effect occurs, if vanillin is added to an expander-containing mass, the inhibitor effect of vanillin on hydrogen-evolution is kept stable in the presence of the expander at typical concentrations.

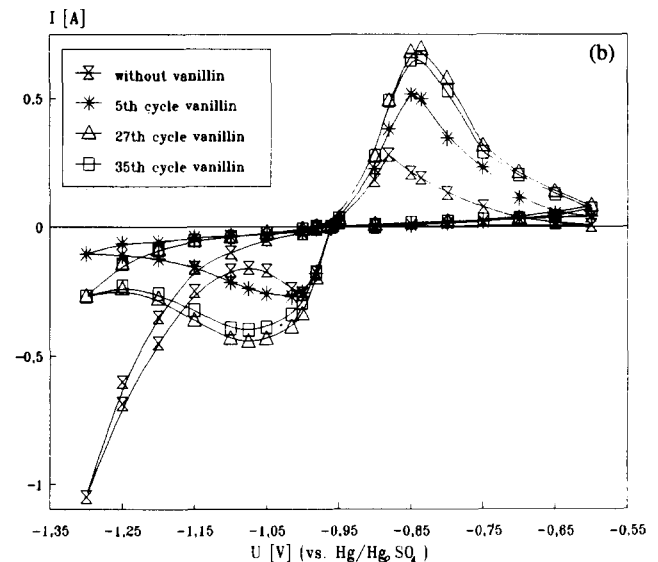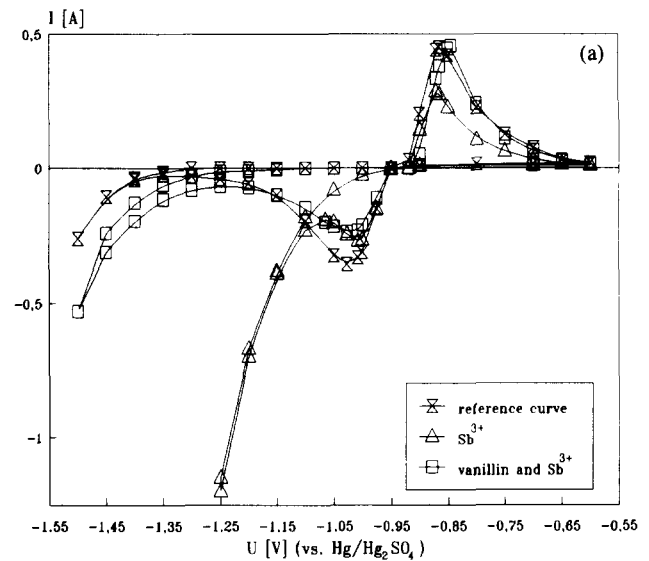On the basis of former investigations [9,12,13], especially the modified model [12] of the inhibition of

Fig. 5. (a) Voltammogram for porous lead electrode; 5×10^{-4} mol/l vanillin and additionally 66 mg/l Sb^{3+} in 1.28 sp. gr. sulfuric acid; (b) later stages with increasing cycle number with same additions of vanillin and antimony. Scan rate: 0.5 mV s^{-1} (reference curve: without any additives).

cathodic hydrogen evolution in lead/acid batteries, it is possible to distinguish between moderate and strong hydrogen-evolving inhibition, as follows.

● Moderate inhibition does not hinder the oxygen reduction and the Pb/PbSO$_4$ conversion directly. This implies selective adsorption of the inhibitor at the antimony sites of the electrode surface, i.e., in accordance with the model of Böhnstedt [8] (Fig. 7(a)). This behaviour enables a decrease in oxygen pressure in the battery, and an improvement in the oxygen recombination efficiency.

● In the case of strong inhibition, the inhibitor is not only adsorbed at the antimony sites of the electrode surface, but also at the free-lead areas (Fig. 7(b)).
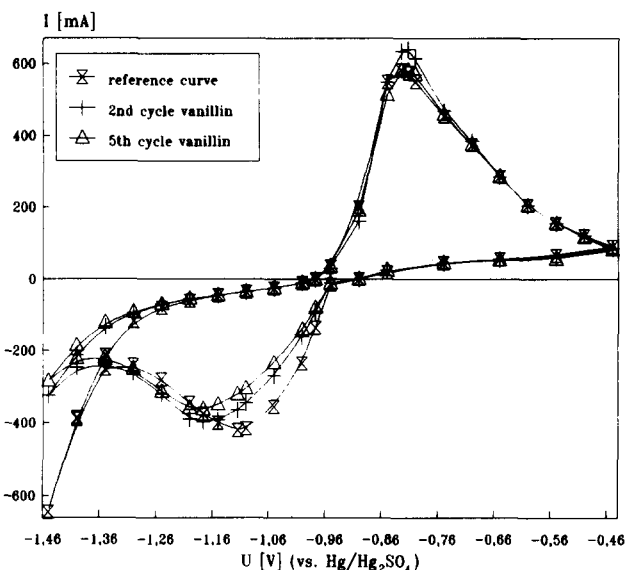
Fig. 6. Voltammogram for porous lead electrode with 0.15 wt.% expander in the active mass; 5×10^{-4} mol/l vanillin in 1.28 sp. gr. sulfuric acid. Scan rate: 0.5 mV s^{-1} (reference curve: without vanillin).
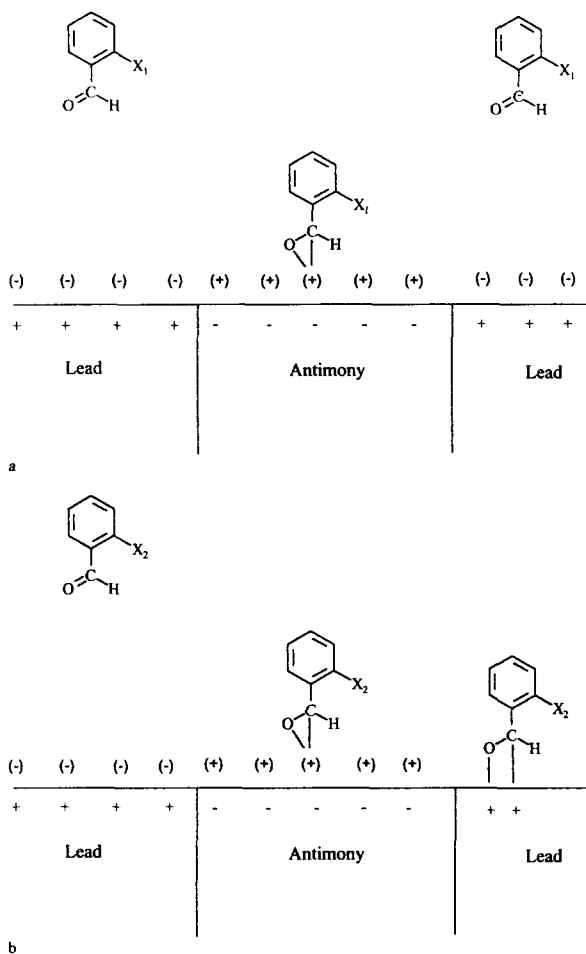

Fig. 7. Modified model of the adsorption of differently substituted benzaldehydes at the negative electrode (free-lead sites covered by sulfate ions, antimony sites covered by hydrogen ions): (a) moderate effect according to Böhnstedt et al. [8]; (b) strong effect.

Thus, oxygen reduction and possibly $Pb/PbSO_4$ conversion — in addition to a strong suppression of the hydrogen evolution — are all inhibited.

The degree of inhibition of an additive is known to correlate with its force of adsorption. Recent impedance measurements have shown a linear relationship between a decrease in double-layer capacity and a suppression in hydrogen evolution [14]. The degree of inhibition is therefore influenced by the strength of the negative charge centre in the organic molecule, which is interacting with the positive charge carriers at the electrode/electrolyte interface. The latter are the protons from the acid that are adsorbed preferentially at the antimony sites or the less positive lead surface. The strength of the negative charged centre of the aromatic organic molecule is influenced by the structure of this centre itself ($-CHO$, $-COCH_3$ or $-COOH$) and by side groups on the benzene ring ($-OCH_3$, $-OH$, $-OC_3H_7$). Electron-shifting side groups, e.g., a methoxy group in the *meta* position, should intensify the strength of the negative centre.

In order to evaluate these effects, an investigation has been made of some derivatives from vanillin. The latter were supplied by Borregaard Industries Ltd., Sarpsborg, Norway. The structures of these compounds are given in Fig. 8. In addition to the vanillin family, the veratraldehyde family has been used. In each family, the use of the aldehyde, the acetophenone and the acid was examined. Additionally, measurements were performed with the very strong inhibitor *p*-propoxy acetophenone.

The results of the cyclic voltammetric and the hydrogen-evolution measurements are summarized in Fig. 9. The following information is obtained.

● Veratraldehyde as an inhibiting agent shows a very similar influence to that of vanillin. An intensive lowering of the cathodic hydrogen evolution (referred to the value without inhibitor) results while, simultaneously,
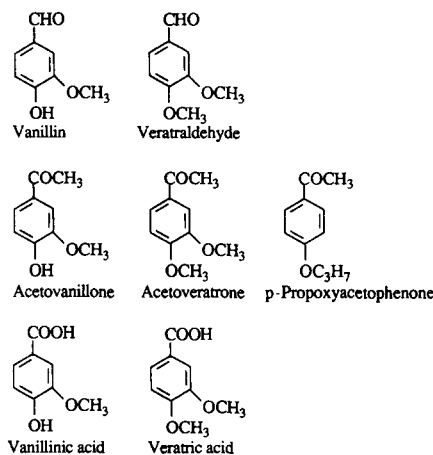

Fig. 8. Structures of the substituted benzaldehydes and their derivatives tested as hydrogen-evolution inhibitors at the lead electrode.
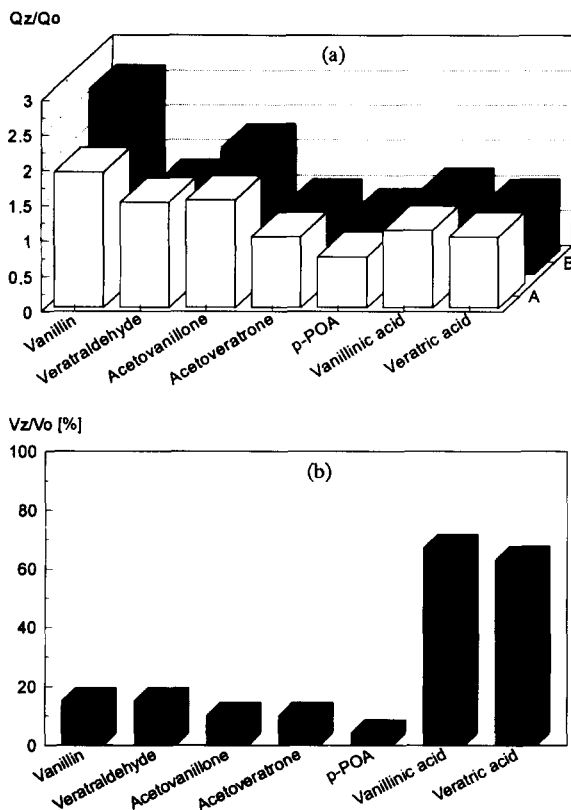
Fig. 9. (a) Influence of the various organic additives on Pb/PbSO$_4$ conversion. Q_v/Q_0 = quotient of charge amount with and without vanillin in the 5th cycle. A: reduction of lead sulfate; B: oxidation of lead. (b) Influence of various organic additives on the hydrogen evolution at porous lead electrode. V_z/V_0 = quotient of hydrogen evolution of one cycle with and without additive.

the available capacity of the electrode is increased. This means that an expander effect also occurs.

● From the cathodic hydrogen evolution, it is found that both vanillin acid and veratric acid have the poorest effect, since the hydrogen evolution is diminished by less than 50% and there is no major influence on the charging and discharging reaction of the lead electrode.

● A very intensive suppression of the hydrogen evolution occurs when the acetophenone compounds are applied as electrolyte additives. An expander effect also exists but is less than that obtained with the aldehydes. On the basis of these cyclic voltammetric measurements, this category of substances seems to be practical, if it is required to have an inhibition action and no influence on the expander behaviour of the electrode.

● When considering the effect of variation in the chemical structure of the substituted benzaldehydes on its inhibition properties, the main influences appear to result from the structure of the negative charge centre. A positive influence of the methoxy substituent in the *meta* position is also discerned. Substituents in the *para* position are less effective.

2.2. Investigations in batteries

The efficiency of vanillin was tested in traction cells (3 PzS 300 type) of both the flooded and gelled type. The positive and negative grid alloys of the flooded cells contained 9.2 and 4.15 wt.% Sb, respectively. Lead–calcium alloy was used for the grids of the gel cells. All cells were sealed with vent plugs. Vanillin was added to the electrolyte at a concentration of 1×10^{-3} mol/l. Two sample groups of six flooded and and six gelled cells were examined. Two further groups without addition of vanillin served as references. All the cells were subjected to a cycling test. After 50 cycles with a depth-of-discharge of 66% at 47 °C, the C/5 capacity was measured at 30 °C. During cycling, as well as after capacity tests, the cells were recharged at: (i) constant current up to a voltage of 2.35 V/cell; (ii) constant voltage at 2.35 V/cell until the current dropped below $0.08 \times I_5$; (iii) constant current at $0.08 \times I_5$ for 3 h (see Fig. 10). Within this cycling procedure, the mean charging factor was about 1.05. This is too low to avoid acid stratification in flooded cells in practical operations. Nevertheless, acid agitation was not applied, since the target here was determination of the water loss that was influenced by vanillin solely without the contribution of other parameters.

There was no topping up of water during the test. The water loss was obtained by recording the weight of the cells. Fig. 11 shows the water consumption during life cycling. The water loss of the flooded cells containing vanillin is reduced significantly by about 50%. By contrast, the consumption of water in the gel cells is not influenced by vanillin. Due to the oxygen reduction cycle, the potential of the negative electrode is elevated and, consequently, evolution of hydrogen is suppressed compared with electrodes in flooded cells. Thus, the
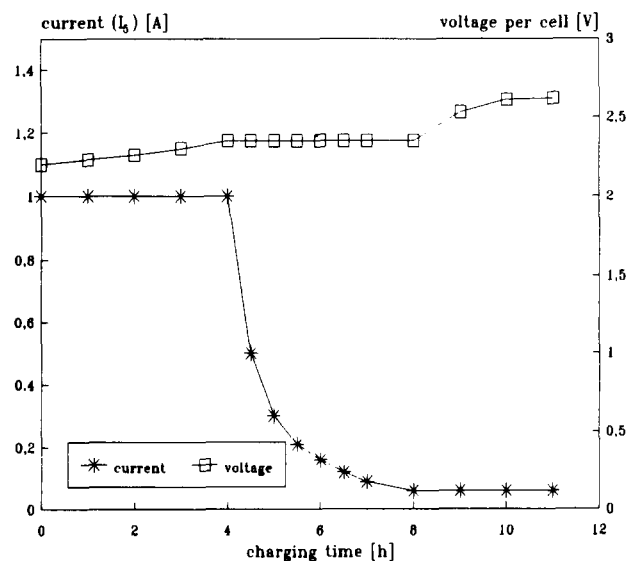

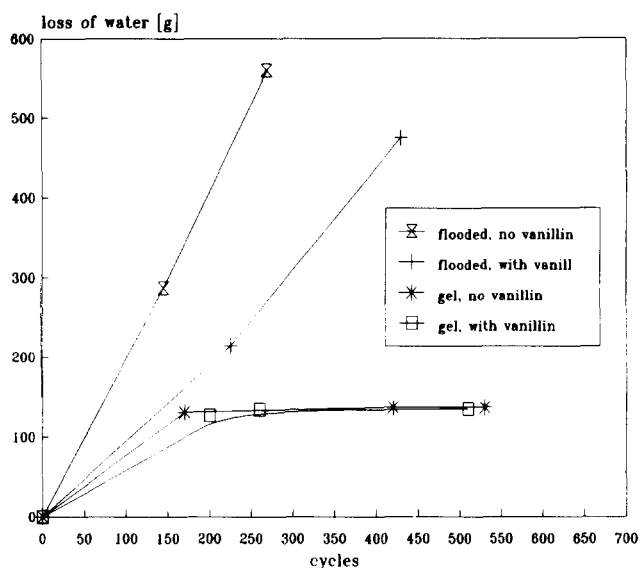Fig. 10. Charging conditions during life cycling.

Fig. 11. Water consumption during life cycling. Effect of vanillin in 3 PzS 300 cells.

effect of vanillin on the negative electrode potential is obviously overwhelmed by the oxygen reduction reaction.

3. Conclusions

With respect to practical applications in lead/acid batteries, aldehydes and acetophenone are promising compounds for the inhibition of hydrogen evolution without influencing expander action in the negative electrode.

Acknowledgement

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