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On the hydrogen balance in sealed lead/acid batteries and its effect on battery performance

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Abstract

An overview is provided on the basic principles of decreasing hydrogen pressure in sealed lead/acid batteries. Approaches that are based on present technology, as well as other possibilities for suppressing hydrogen evolution and oxidizing hydrogen, are studied and discussed. The results emphasize the relevance of so-called hydrogen-evolution inhibitors for industrial applications.

Introduction

In the lead/acid battery, besides the charging/discharging processes, undesirable side reactions also occur (Fig. 1). During overcharging at the end of charging and during open circuit, water is decomposed and results in gas evolution. The basic design principles for sealed lead/acid (SLA) batteries are, therefore, measures for gas removal (Fig. 2) and the suppression of gas evolution (Fig. 3).

Gas recombination in SLA batteries is mainly based on an efficient oxygen cycle. Oxygen reduction at the negative electrode proceeds at a sufficiently high rate, provided there is a rapid transfer of oxygen from the positive to the negative electrode. This can be achieved by immobilizing the electrolyte and by limiting the amount of electrolyte (see a in Fig. 2).

By contrast, the rate of hydrogen oxidation is extremely low in the potential region of $PbO_2/PbSO_4$ due to kinetic hindrances caused by sulfate adsorption at the

Lead Acid Battery

Main reactions:

(+) $PbSO_4 + 2H_2O \rightleftharpoons PbO_2 + HSO_4^- + 3H^+ + 2e^-$

(−) $PbSO_4 + H^+ + 2e^- \rightleftharpoons Pb + HSO_4^-$

Overcharge reactions:

(+) $H_2O \longrightarrow 0{,}5O_2 + 2H^+ + 2e^-$

(−) $2H^+ + 2e^- \longrightarrow H_2$

Selfdischarge reactions:

(+) $PbO_2 + H_2SO_4 \longrightarrow PbSO_4 + 0{,}5O_2 + H_2O$

(−) $Pb + H_2SO_4 \longrightarrow PbSO_4 + H_2$

Fig. 1. Reactions in lead/acid batteries.

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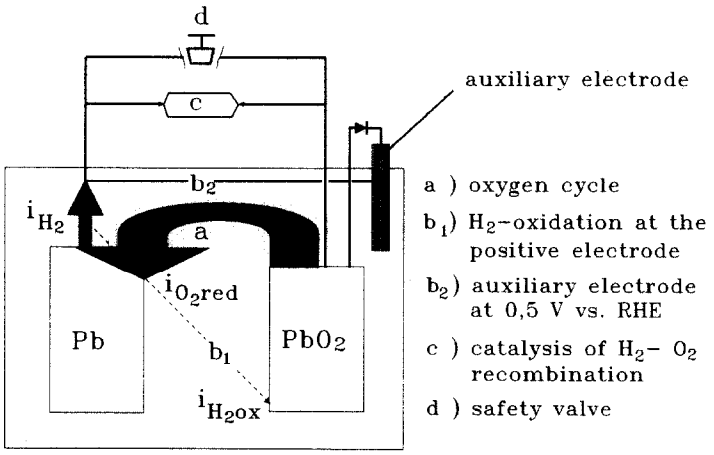


Fig. 2. Means for gas removal in sealed lead/acid batteries.

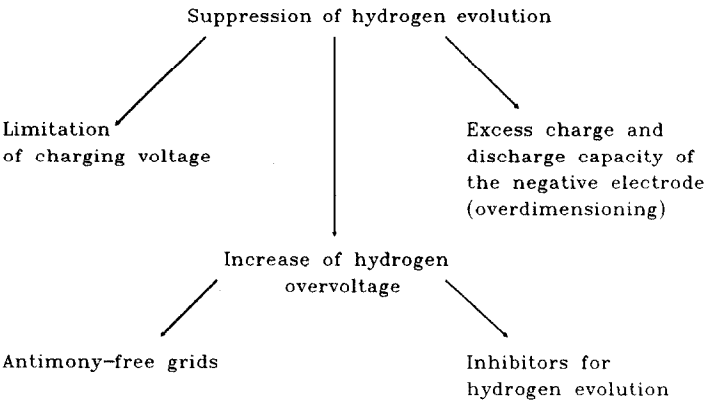


Fig. 3. Means for decreasing hydrogen evolution in sealed lead/acid batteries.

electrode surface (see b_1, in Fig. 2) [1–3]. It has been well documented [e.g., 4, 5], however, that the electrochemical oxidation of hydrogen can be achieved by using a catalyzed auxiliary electrode (see b_2 in Fig. 2). This electrode has to be connected to the $PbO_2/PbSO_4$ electrode via diodes and held in a specific voltage range of ~0.5 V versus RHE to overcome sulfate adsorption.

A further method for removal of the gases is the catalysis of the H_2/O_2 recombination reaction (see c, Fig. 2). The use of nobel metal catalysts for this purpose has been proposed frequently for batteries with flooded electrolyte in order to achieve maintenance-free operation.

For SLA batteries, nobel metal catalysts, regardless of their price, present some problems, e.g., risk of explosion, poisoning of catalyst and electrolyte (i.e., self-discharge). An alternative is the application of a nobel metal-free catalyst. Recent experiments [6, 7] have confirmed that composite catalysts based on tungsten carbide enable efficient removal of excess gases in sealed batteries that use immobilized as well as flooded

electrolytes. As gas evolution in SLA batteries does not occur stoichiometrically and, with high yields, problems arise at the catalyst surface, the use of catalysts for currentless H_2/O_2 recombination is important mainly as an additional recombination method to the oxygen cycle in order to remove excess hydrogen [7]. Obviously, all procedures of gas recombination, including safety-venting (see d in Fig. 2), add to the cost of the battery.

Measures for minimizing hydrogen gas evolution (Fig. 3) appear to be easy to put into practice. In valve-regulated batteries (VRLA), hydrogen evolution is usually suppressed by limiting the charging voltage (i.e., 2.30 to 2.40 V) and by using materials of the highest purity, especially antimony-free lead alloys. In principle, the hydrogen pressure can be also decreased by:

- provision of excess charge capacity at the negative electrode ($PbSO_4$ reserve)
- improvement in the oxygen-recombination conditions (e.g., increase in free-lead sites by incorporating excess negative material and exposed negative electrode surfaces, optimization of separator properties with respect to oxygen transfer, etc.)
- increase in the hydrogen overvoltage by means of H_2-evolution inhibitors

In order to advance the technology of gas recombination and to suppress hydrogen evolution, it is necessary to gather information about the mechanism, efficiency, expense and commercial feasibility of all the factors that influence the hydrogen balance in SLA batteries.

Given that: (i) the principles of efficient oxygen recombination are well-known e.g., [8–14] and have been utilized in recombinant technology, and (ii) studies of hydrogen oxidation by means of auxiliary electrodes and catalysts for H_2/O_2 recombination have recently been reported [5–7], this paper presents both an overview of the balance of hydrogen evolution/oxidation and aims to stimulate ideas on further possibilities to decrease the hydrogen pressure in SLA batteries to levels below those experienced in present technology.

Experimental

Investigation of the processes of hydrogen evolution and hydrogen oxidation were conducted mainly in sealed test cells that comprised one positive (3 A h) electrode, two negative electrodes of the same dimension, and gelled electrolyte, as described in ref. 14. The gas pressure during overcharging and cycling was recorded and served as a criterion for the oxygen-cycle efficiency and the extent of hydrogen evolution [14]. The following investigative techniques were also employed: linear sweep voltammetry (LSV); A h capacity determination; special testing procedures, e.g., for characterizing H_2/O_2 recombination catalysts, as described in ref. 7.

Results and discussion

H_2 oxidation at working potential of positive electrode

From theoretical considerations, the main problems of SLA batteries are:

- continuously occurring H_2 evolution that cannot be completely avoided and, as a consequence
- water loss in VRLA batteries or hydrogen accumulation in hermetically sealed SLA cells, because hydrogen oxidation is kinetically limited

The situation is reflected by the data of Fig. 4 that relate to overpressure curves during cycling in hermetically SLA cells. The pressure maximum (p_{max}) correlates to the sum of p_{O_2} and p_{H_2}, whereas the pressure minimum (p_{min}) is virtually equivalent to p_{H_2}. As expected, if antimony-free grids are used, the hydrogen pressure is substantially lower than in the presence of antimony.

From Fig. 4, it is further observed that, with increasing cycle time, both cell pressure and p_{H_2} achieve a characteristic limit at a level that depends on the grid type used, and its hydrogen overvoltage. The possible causes for reaching a pressure limit are: (i) leakage loss; (ii) improved oxygen recombination efficiency; (iii) a lowered rate of hydrogen evolution; (iv) an increased rate of hydrogen oxidation. As the leakage loss is small (Fig. 4), and after venting, nitrogen-rinsing and repeated cycling the same pressure limit is achieved, the causes (iii) and possibly (iv) appear to be relevant. This is an interesting result because hydrogen oxidation is usually assumed to be immeasurable [15] or negligible [1–3] in industrial VRLA batteries at low hydrogen pressure. Nevertheless, various authors have investigated hydrogen oxidation at positive electrodes e.g., [1–4, 16] and measurable rates of 50 μA cm^{-2} per 10^5 Pa have been calculated [16].

Inspired by these findings and by the lack of complete information on the mechanism of hydrogen oxidation, we have been interested in evaluating if, and to what extent, parameters such as electrolyte medium, hydrogen pressure and overcharging potential influence the rate of hydrogen oxidation at the positive electrode in SLA batteries. The initial results of these studies are given in Figs. 5 and 6.

The anodic current–voltage characteristic in the potential region of hydrogen oxidation at positive electrodes is given in Fig. 5 for flooded and the gelled sulfuric acid both in the presence and the absence of hydrogen. Assuming that the difference

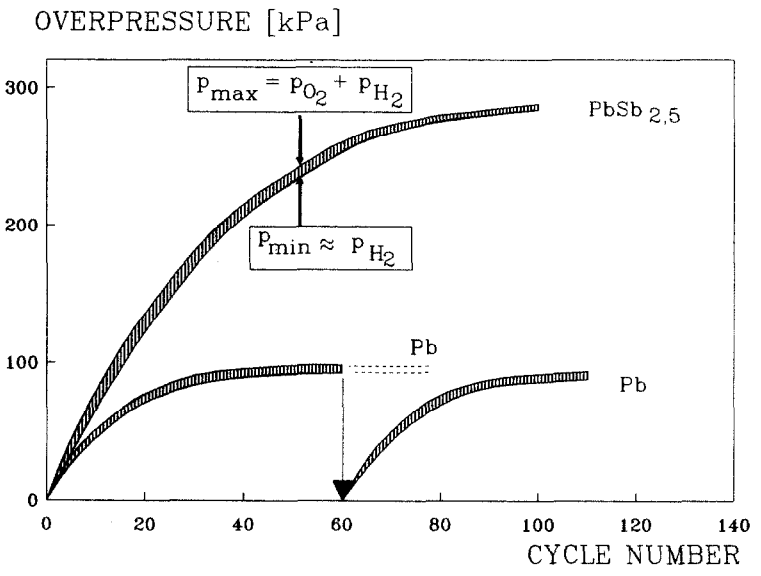


Fig. 4. Change in pressure during cycling of 2 V, 3 A h, sealed lead/acid cells using H_2SO_4 gel (6% Aerosil) and different grid types; cycling regime: discharge current = 0.170/h × C_{20} for 3 h, and charge current = 0.065/h × C_{20} for 9 h; leakage loss at p_{H_2} = 100 kPa is lower than 3 kPa/10 cycles.

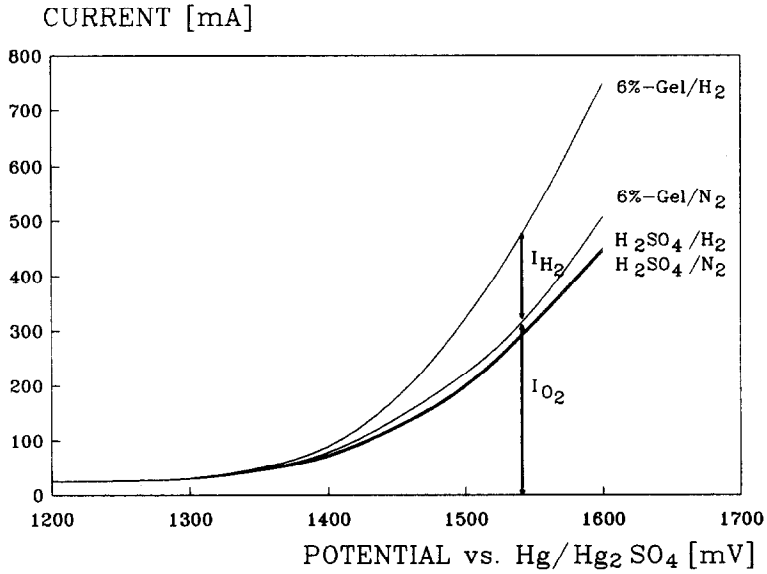


Fig. 5. Influence of hydrogen on potentiostatically-generated current–voltage curves at porous $PbO_2/PbSO_4$ electrodes (3 A h) in H_2SO_4 solution (1.28 sp.gr.) and H_2SO_4 gel with 6% Aerosil. Electrolytes are saturated with pure nitrogen or hydrogen.

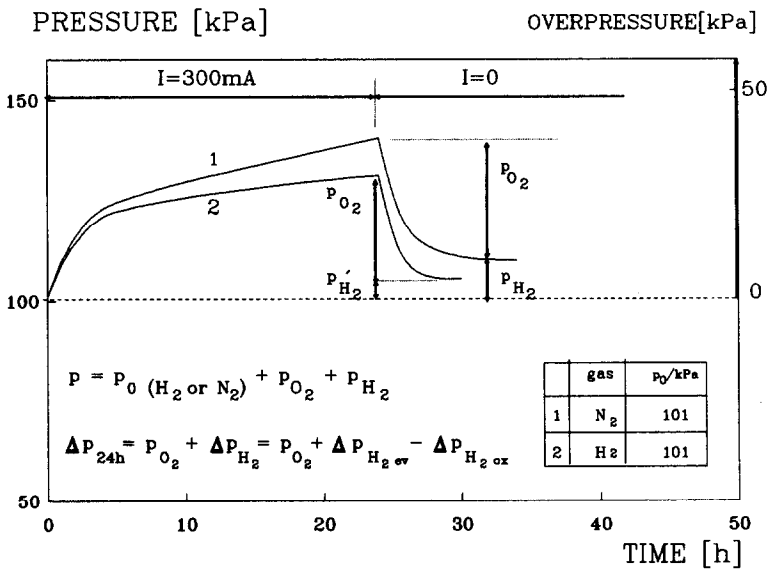


Fig. 6. Influence of initial gas atmosphere on cell overpressure during galvanostatic overcharging of 2 V, 3 A h, sealed lead/acid cells. Grid: pure lead; electrolyte: H_2SO_4 gel (6% Aerosil); gas space: rinsed with nitrogen or hydrogen.

in current for the curves under hydrogen and nitrogen corresponds to hydrogen oxidation, it can be deduced that:

- hydrogen oxidation in H_2SO_4 solution is negligible and is virtually independent of the presence of hydrogen
- the conditions for hydrogen oxidation in H_2SO_4 gel are better than in H_2SO_4 solution, as already reported by Mahato *et al.* [1]
- the hydrogen oxidation rate in gelled electrolyte depends on the potential of the positive electrode and increases on increasing the anodic polarization

Figure 6 shows the influence of hydrogen gas on overpressure versus time curves during galvanostatic overcharging (I_{10}) of hermetically SLA cells. The gas space was filled with pure nitrogen (curve (1)) and pure hydrogen (curve (2)). In general, it can be concluded that:

- the pressure drop after circuit interruption is equal to p_{O_2} at the end of overcharging [14]
- the remaining overpressure corresponds to the resultant amount of hydrogen p_{H_2} given by hydrogen evolution and, possibly, hydrogen oxidation

Under the conditions of case (1), the remaining overpressure p_{H_2} only corresponds to $p_{H_2\,ev}$ and is a quantitative measure for hydrogen evolution [14], as hydrogen oxidation is assumed to be negligible.

The data in Fig. 6 show that, at the end of overcharging, both the increase in p_{H_2} and p_{O_2} are significantly lower in the cell that contains hydrogen compared with measurements under nitrogen. This means that a substantial increase in p_{H_2} up to 101 kPa leads to: (i) increased (measurable) hydrogen oxidation rates and/or suppression of hydrogen evolution and, as a consequence, (ii) lowered oxygen evolution rate and/or improved oxygen recombination efficiency.

Similar experiments performed with a lower overcharging current (I_{20}) did not show this influence of p_{H_2}. These results imply that measurable rates of hydrogen oxidation can be observed under specific conditions in SLA cells, but not in general. Further investigations are necessary to gain complete information on the role of hydrogen oxidation in SLA batteries and the effect of various technological parameters on its rate.

Suppression of hydrogen evolution at the negative electrode

Influence of the processes of oxygen reduction and $PbSO_4$ reduction

The rate of hydrogen evolution is influenced by the rates of both the competing reactions at the negative electrode, oxygen reduction and $PbSO_4$ reduction. As shown recently [14], the oxygen-recombination rate can be increased by increasing p_{O_2} and improving the oxygen-recombination conditions, both these result in suppression of hydrogen evolution. The substantial influence of the oxygen-recombination conditions, primarily a measure for the reactive contact area lead/electrolyte film/oxygen [17], is confirmed by the following measurements.

Figure 7 shows the influence of the state-of-charge of the negative electrode. It is clear that a decrease in the state-of-charge leads to coverage of the surface by discharge products and diminishes the area of free-lead sites. This favours the $PbSO_4$ reduction reaction and hinders oxygen recombination. Consequently, with decreasing state-of-charge, the oxygen pressure increases more and more during galvanostatic (over)charging.

It is interesting to note that the rate of hydrogen evolution is the least at a state-of-charge of 67%. This can be explained as follows:

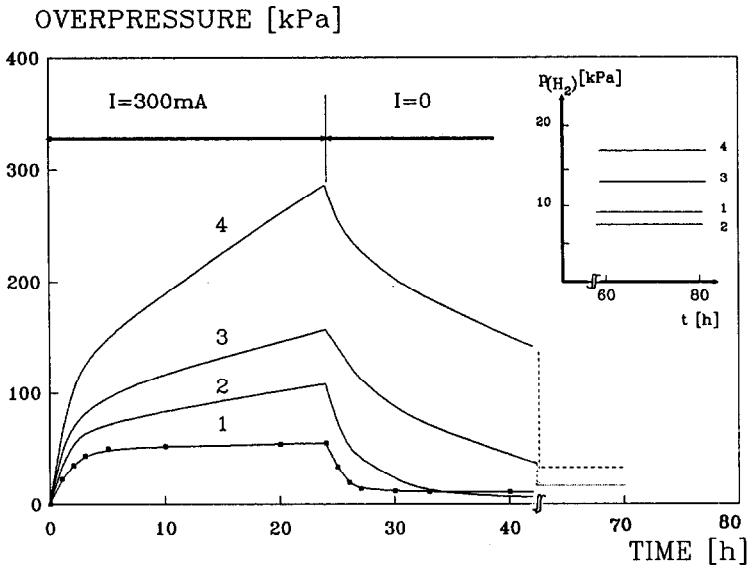


Fig. 7. Influence of state-of-charge of negative electrode on overpressure vs. time curves during galvanostatic overcharging of 2 V, 3 A h, sealed lead/acid cells: (1) nearly 100%; (2) 67%; (3) 50%; (4) 30%. Grid type: pure lead; electrolyte: H_2SO_4 gel (6% Aerosil); gas space: purged with pure nitrogen.

(i) Below this value, the rate of oxygen reduction is extremely low. If passivating layers are formed, $PbSO_4$ reduction is also kinetically hindered. Nevertheless, hydrogen evolution is found to proceed even in the presence of passivating layers [18], as the latter are permeable to protons [19].

(ii) At a slightly discharged state, the oxygen recombination is still efficient, and thus allows an excess charge capacity ($PbSO_4$ reserve) to be utilized for suppressing hydrogen evolution.

(iii) At the fully-charged state, the $PbSO_4$ reduction reaction does not occur and cannot be utilized to suppress hydrogen evolution.

The commercial feasibility of this method is still questionable. This is because the optimal state-of-charge depends on the actual oxygen recombination conditions and these differ from cell to cell and vary during operational life.

Influence of hydrogen evolution inhibitors

Contrary to the antimony-poisoning effect (see Fig. 4, ref. 10), there are many additives that are able to increase the hydrogen overvoltage at the negative electrode. The effect on hydrogen evolution of a wide variety of inorganic and organic substances has been described in the literature, e.g., refs. [20–29]. Organic additives that show a substantial inhibition effect have been found to be derivatives of benzaldehyde [26–28] and benzoic acid [25, 29]. The structure of these additives is similar to that of the substructure of the expander lignin. Indeed, expanders are sometimes reported to exhibit a slight inhibition effect [25, 26], but this appears to be true only for the unpurified state [26].

Expanders, as well as the so-called hydrogen-evolution inhibitors, adsorb on the surface of the negative electrode, but act rather differently. The positive effect of

expanders on the electrode structure during discharge is achieved by adsorption on lead and lead sulfate particles. Hydrogen-evolution inhibitors are designed to adsorb at the protons that are mainly present on antimony sites of the electrode surface. The mechanism of the specific adsorption of aromatic aldehydes on these sites has been satisfactorily modelled by Böhnstedt *et al.* [26], see Fig. 9(a) later. 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. Therefore, such hydrogen-evolution inhibitors may be utilized in flooded batteries to improve maintenance-free operation, and in SLA batteries to decrease the hydrogen pressure.

Hitherto, investigations on aromatic hydrogen-evolution inhibitors has been conducted mainly in H_2SO_4 solution that contains antimony species [26–28]. Little information [25, 29] is available on the effect of such inhibitors in SLA batteries. Therefore, the following experiments have been performed with SLA cells containing antimony species in order to: (i) evaluate the effect of H_2 evolution inhibitors on all competing reactions at the negative electrode; (ii) evaluate their ability to inhibit the antimony-poisoning effect.

Figure 8 shows the effect of two hydrogen-evolution inhibitors on overpressure during overcharging of SLA cells using: (i) Pb–2.5wt.%Sb grids; (ii) an electrolyte prepoisoned by addition of Sb_2O_3. Conclusions on oxygen-recombination efficiency and the amount of hydrogen evolution were drawn from an analysis of pressure decay after circuit interruption and the assumption that hydrogen evolution is negligible. In particular, the following can be deduced:

(i) Both types of hydrogen-evolution inhibitors can decrease hydrogen evolution and also influence the competing reactions of oxygen reduction and $PbSO_4$ reduction. This is because p_{H_2}, as well as p_{O_2}, is affected and, moreover, to a different extent, i.e., deviation from a ratio of 2:1.

(ii) The extent of the influence of the different kinds of inhibitor on the three cathodic reactions at the negative electrode depends on the test conditions, especially the inhibitor type (and/or concentration), the degree of antimony poisoning, etc.

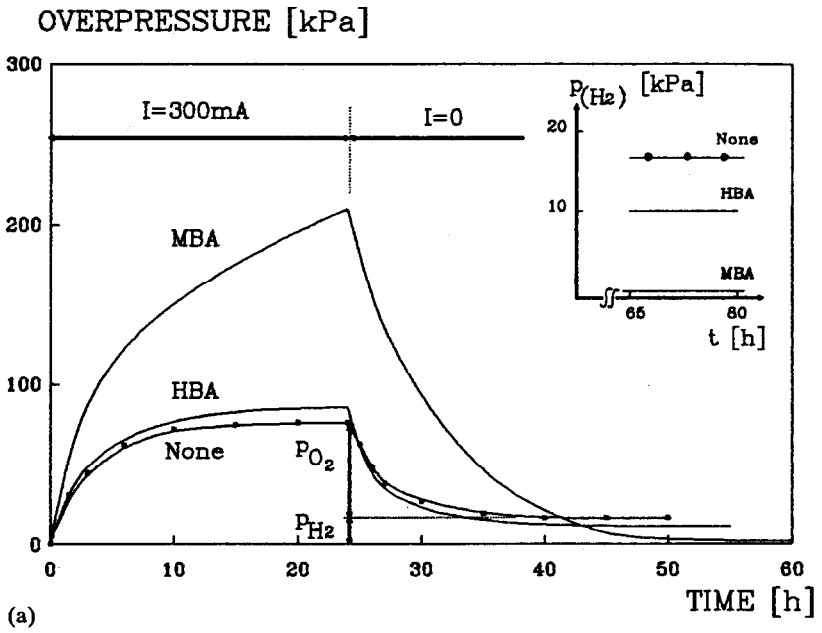
(iii) From Fig. 8, it is clear that 2-hydroxybenzaldehyde (HBA) is able to cause a slight decrease in both p_{H_2} and p_{O_2}, whereas 2-methoxybenzaldehyde (MBA) is a stronger hydrogen-evolution inhibitor but also promotes a considerable increase in p_{O_2}.

The observed deviation in inhibition strength of the benzaldehydes investigated has been explained recently in terms of differences in the electron donor properties of the ring substituents [26, 27]. The general inhibition effect on hydrogen evolution implies that the sum of the current fractions $I_{O_2\,red}$ and $I_{PbSO_4\,red}$ of the competing reactions must increase.

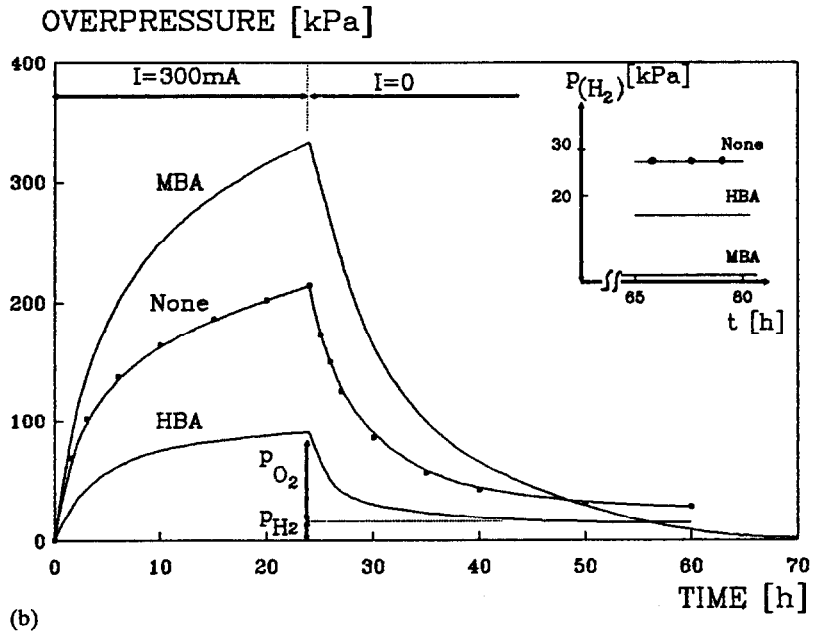
On principle, however, it seems also plausible that a strong inhibitor of hydrogen evolution can directly hinder the oxygen reduction reaction, as well as the $PbSO_4$ reduction process. From the results discussed above, the following may be therefore concluded:

(i) Moderate hydrogen-evolution inhibitors such as (HBA) (type a) do not hinder oxygen reduction and $Pb/PbSO_4$ conversion directly. This implies selective adsorption at the antimony sites of the electrode surface, i.e., in accordance with the model of Böhnstedt [26], see Fig. 9(a). This behaviour enables a decrease in p_{O_2}, i.e., an improvement in oxygen-recombination efficiency (Figs. 8(a) and (b)).

(ii) Strong hydrogen-evolution inhibitors like MBA (type b) are able to adsorb not only at the antimony sites of the electrode surface, but also at free-lead areas



(a)



(b)

Fig. 8. Influence of hydrogen evolution inhibitors on overpressure vs. time curves during galvanostatic overcharging of 2 V, 3 A h, sealed lead/acid cells and dependence on mode of antimony poisoning: (a) grid: Pb–2.5wt.%Sb; (b) grid: Pb; electrolyte prepoisoned by 66 mg l^{-1} Sb^{3+}. Electrolyte: gel (6% aerosil); gas space: purged with pure nitrogen; inhibitor concentration: 3.8×10^{-4} mol l^{-1}.

(Fig. 9(b)). Thus, oxygen reduction and, possibly, $Pb/PbSO_4$ conversion is also inhibited, as indicated by the heavy increase in p_{O_2}, Figs. 8(a) and (b).

The influence of the degree of antimony-poisoning on the overpressure characteristic and inhibitor effect can be deduced from a comparison of Figs. 8(a) and (b). It is found that the stronger the antimony-poisoning effect, the higher is the total overpressure as well as p_{H_2} and p_{O_2}. Furthermore, the more beneficial is the effect of the additive towards suppression of hydrogen evolution, in particular.

Pressure measurements in SLA cells during cycling that employs galvanostatic charging steps confirm the previous findings (Fig. 10). It can be seen that:

- both inhibitor types decrease substantially p_{H_2}, and thus lead to a decrease in the overpressure level
- the inhibition effect on hydrogen evolution was maintained up to at least 70 cycles (Figs. 10(a), (b))
- the antimony-poisoning effect due to antimony erosion in the grids can be compensated by means of moderate inhibitors such as HBA, or even overcompensated if strong inhibitors such as MBA are used (Fig. 10(a))
- in contrast to moderate inhibitors of type a, universal type b inhibitors such as MBA are able to decrease oxygen-recombination efficiency, as indicated by the broadening of the pressure graph

The latter results emphasize the risk associated with the industrial application of type b inhibitors. In fact, feasibility under industrial test conditions has yet to be

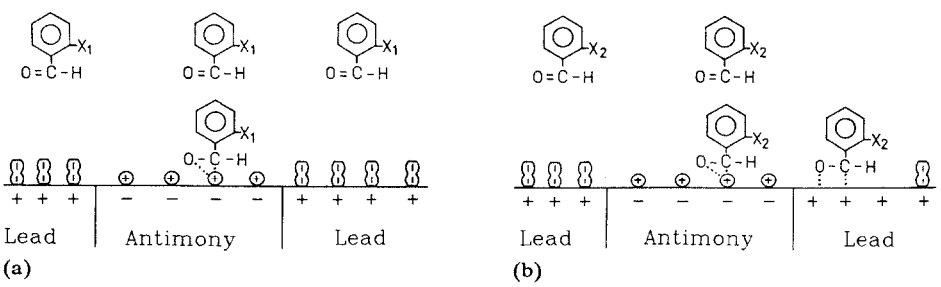


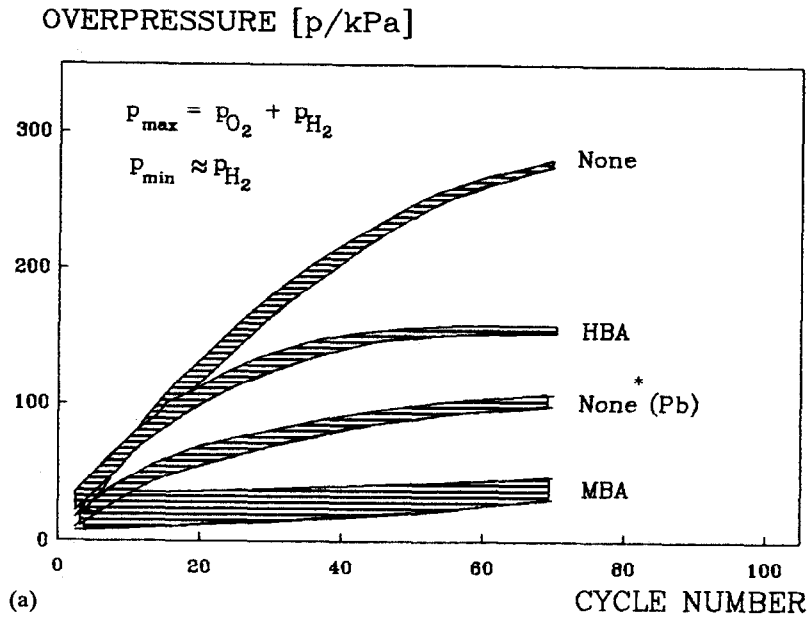
Fig. 9. Modified model of the type of adsorption of differently substituted benzaldehydes at the negative electrode following the pattern of Böhnstedt *et al.* [26], (free-lead sites covered by sulfate ions, antimony sites covered by hydrogen ions): (a) moderate effect (type a); (b) strong effect (type b).

TABLE 1

A h capacity (% theoretical)

Cycle	Negative electrode					Positive electrode		
	None	O-HBA		O-MBA		None	O-HBA	O-MBA
		$(c_1)^a$	$(c_2)^b$	$(c_1)^a$	$(c_2)^b$		$(c_1)^a$	$(c_1)^a$
0	50	49.5	(50)	45	(40)	50	50	48.5
60	49.5	50	(49.5)	47	(38)	51	51.5	49

$^a c_1 = 3.7 \times 10^{-4}$ mol/l H_2SO_4, values corrected to ± 1.
$^b c_2 = 5.5 \times 10^{-4}$ mol/l H_2SO_4, values corrected to ± 1.



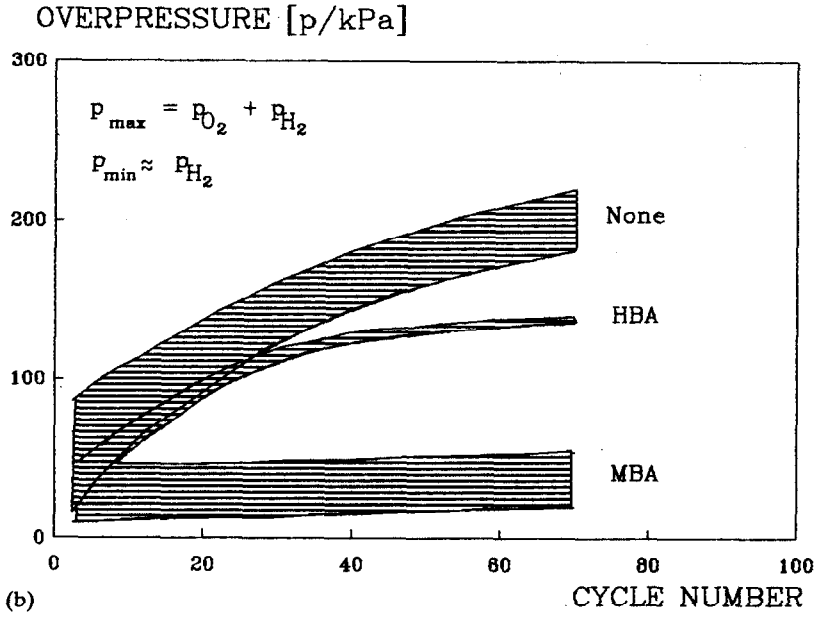


Fig. 10. Influence of hydrogen-evolution inhibitors on overpressure during cycling of 2 V, 3 A h, sealed lead/acid cells and dependence on the mode of antimony poisoning: (a) grid: Pb–2.5wt.%Sb (including additional reference curve based on pure lead); (b) grid: Pb; electrolyte, prepoisoned by 66 mg l^{-1} Sb^{3+}. Electrolyte: gel (6% Aerosil); gas space: purged with pure nitrogen; inhibitor concentration: 3.8×10^{-4} mol l^{-1}.

determined. Therefore, the influence of hydrogen-evolution inhibitors on the process of $Pb/PbSO_4$ conversion was investigated using simple discharge experiments. Table 1 shows the A h capacities of both negative and positive electrodes.

It is evident that the moderate hydrogen-evolution inhibitor, HBA, acts selectively, and does not influence the $Pb/PbSO_4$ oxidation process. By contrast, the universal inhibitor, MBA, impairs the discharge reaction, particularly at the negative electrode. This latter behaviour depends on the concentration of inhibitor.

Conclusions

The following conclusions can be drawn from our studies on various approaches towards decreasing hydrogen pressure in SLA batteries.

1. Under industrial test conditions of SLA batteries, where excess gases are vented and charging is performed at low constant voltage, hydrogen oxidation at the positive electrode does not play an important role. Substantially, higher oxidation rates can be found only under favourable conditions, i.e., gelled (immobilized) electrolyte, high p_{H_2}, and high anodic polarization.

2. An appropriate method to remove excess hydrogen is the currentless catalysis of H_2/O_2 recombination by means of nobel metal-free composite catalysts such as tungsten carbide on active carbon [7].

3. The hydrogen-evolution rate can be affected by influencing the conditions of all cathodic reactions at the negative electrode. Feasible means to further the suppression of hydrogen evolution are: (i) improvement in the rate constant of oxygen reduction [14]; (ii) increase in hydrogen overvoltage by means of hydrogen-evolution inhibitors.

4. The use of hydrogen-evolution inhibitors has commercial importance for flooded, valve-regulated and sealed batteries. The ability of the additives to compensate the poisoning effect caused by antimony, or even to provide for an absolute increase in hydrogen overvoltage opens new perspectives for the construction of VRLA batteries with low-antimonial grids, or possibly, for hermetically-sealed cells. The efficiency of a hydrogen-evolution inhibitor does not depend only on its concentration and the interaction between the additive and the electrode, but also on the rate of hydrogen evolution (e.g., degree of antimony poisoning). The benzaldehyde derivatives are found to behave differently towards the inhibition of hydrogen evolution, and can be grouped into two modes of action.

From the viewpoint of industrial applications, the appropriate type of hydrogen inhibitor is a selectively acting additive such as 2-hydroxybenzaldehyde that does not hinder oxygen reduction and $Pb/PbSO_4$ conversion. A h capacity measurement and cycle-life tests have confirmed that this inhibitor type does not impair discharge reactions at either the negative or the positive electrodes, and is still effective after more than 60 cycles under the test conditions used in this work.

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