================ APPLIED ELECTROCHEMISTRY ================
AND CORROSION PROTECTION OF METALS

Effect of Benzaldehyde Derivatives on the Rate of Hydrogen Evolution in a Sealed Lead–Acid Battery

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Abstract—The influence exerted by a number of benzaldehyde derivatives on the rate of hydrogen evolution from a lead–acid battery was studied.

The market of sealed lead–acid batteries shows a steady rising tendency [1]. Use of batteries of this kind makes it possible to virtually rule out any gas evolution and to dramatically diminish the amount of maintenance work. The last factor is of primary importance, because, for some batteries, the maintenance cost during the service life is comparable with the initial price of the battery itself [2]. The possibility of sealing the lead–acid battery is based on the fact that virtually the whole amount of O_2 evolved at the positive electrode in charging is reduced at the negative electrode (closed oxygen cycle). Performing a similar hydrogen cycle is impossible without using additional catalytic systems because of the extremely low rate of H_2 oxidation at the positive electrode. According to [3], the rate of H_2 oxidation at the PbO_2 electrode is lower than that of O_2 reduction on Pb by a factor of 10^3. Thus, sealing the lead–acid battery requires that the rate of H_2 evolution should be minimized.

The scheme shows the sequence of operations carried out to diminish the rate of H_2 evolution in the sealed battery. It can be seen that the task of inhibiting H_2 formation in the battery is integrated and involves solutions related to the design and the composition of the components of the electrode block (1.1, 1.3, 2.1), to use of external, with respect to the block, devices (2.2, 2.3, 2.4), and to optimization of the charging mode (1.3).

Apparently, the most efficient are the operations intended to diminish the H_2 evolution rate, rather than those aimed to oxidize the gas that has already evolved within the battery, because the former operations control the causes, and the latter, the consequences of the negative phenomenon.
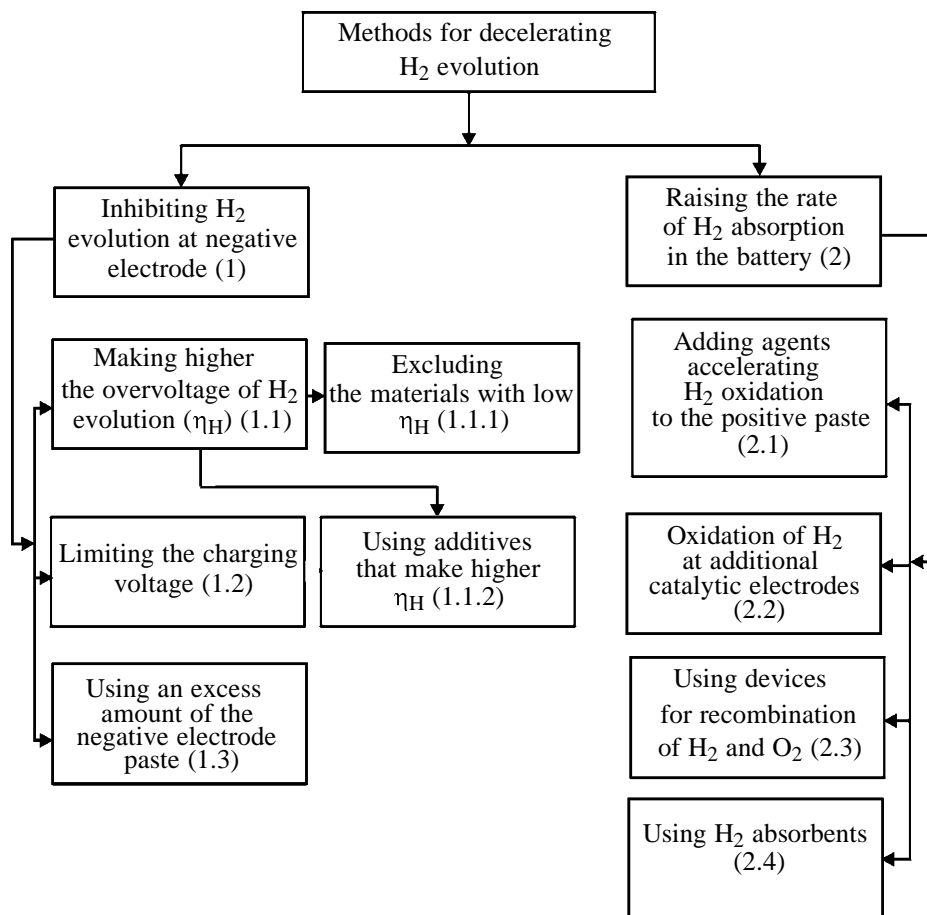
The rate of H_2 evolution can be markedly diminished by (i) excluding elements with low hydrogen overvoltage (Sb, Cu, Ag, As, Fe, Mn, Ni, Co) from the composition of the active paste and structural materials [4], (ii) using additives that make higher the overvoltage of H_2 evolution at the negative electrode, (iii) optimizing the relative amounts of the active pastes [5, 6], and (iv) optimizing the charging mode [7].

At present, neither catalytic electrodes made of platinum or carbon materials nor H_2 absorbents find use in the world practice. Their use, on the one hand, is inefficient and unreliable (catalyst poisoning, low absorption of H_2 because of its low partial pressure within the battery), and on the other, makes higher the cost of batteries.

Additives are widely used in lead batteries to improve their energy-storage and resource parameters. An important role of additives as expanders of negative active pastes, which slow down the rate of recrystallization of spongy lead and preserve its large specific surface area, is well known [8]. Additives are also used as inhibitors of self-discharge [9]. The mechanism of their action commonly consists in that the overvoltage of H_2 evolution on lead and phase impurities increases, which makes slower the rate of the conjugated reaction of Pb oxidation. Additives are also introduced into positive active pastes to improve their mechanical strength and preclude their sagging [10]. Additives of this kind can be introduced in the form of fibers, powders, or suspensions. A considerable progress has been made in all of these areas. However, the specific features of operation of a sealed battery, on the one hand, impose restrictions on additives used in ordinary batteries, and on the other, require that new types of additives should be developed.

The aim of this study was to examine additives that inhibit H_2 evolution in a lead–acid battery.

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│  Methods for decelerating │
│      H₂ evolution         │
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General scheme of operations showing two branches:

Inhibiting H₂ evolution at negative electrode (1)
- Making higher the overvoltage of H₂ evolution (η_H) (1.1)
  - Excluding the materials with low η_H (1.1.1)
  - Using additives that make higher η_H (1.1.2)
- Limiting the charging voltage (1.2)
- Using an excess amount of the negative electrode paste (1.3)

Raising the rate of H₂ absorption in the battery (2)
- Adding agents accelerating H₂ oxidation to the positive paste (2.1)
- Oxidation of H₂ at additional catalytic electrodes (2.2)
- Using devices for recombination of H₂ and O₂ (2.3)
- Using H₂ absorbents (2.4)

General scheme of operations aimed to diminish the rate of H₂ evolution in a sealed battery.

It is known that Pb belongs to metals with a high overvoltage of H_2 evolution. The constant *a* in the Tafel equation for lead is 1.52–1.56 V. However, phase impurities composed of metals with a low H_2 overvoltage can be formed in a working battery on the surface of the negative current lead. To elements of this kind primarily belong Sb and Cu, for which *a* is 0.9 and 0.8 V, respectively. Antimony finds its way to the negative electrode through corrosion of the current lead (made of lead–antimony alloys) of the positive electrode, and lead-plated copper current leads of the negative electrode serve as a source of Cu. During the service life of a battery, the protective properties of the lead coating are impaired and Cu appears on the surface of the negative active paste. Thus, an additive that would make higher the overvoltage of H_2 evolution on Sb and Cu but would not affect the course of the main current-producing processes at the negative and positive electrodes is necessary. With account of the fact that the mechanism by which the gas evolution is hindered is associated with adsorption of additives (surfactants) onto the metal surface, an efficient

additive that would inhibit gas evolution must exhibit a high adsorption selectivity with respect to Cu and Sb, on the one hand, and Pb, on the other. As possible additives were studied benzaldehyde derivatives. In [11, 12], it was shown that aromatic aldehydes, which are characterized by clearly pronounced polarity with high dipole moment and, therefore, exhibit an increased adsorption capacity, exert an inhibiting influence on H_2 evolution. However, their adsorption capacity largely depends on a substituting group, which determines the electron distribution between the benzene ring and this group. The choice of an inhibitor is determined by the following: it should exhibit a selective adsorption on Sb and Cu impurities, without decelerating the current-producing reaction or O_2 reduction. The following benzaldehyde derivatives were examined in this study: 2-hydroxybenzaldehyde $C_7H_6O_2$ (2-HB) and 2-methoxybenzaldehyde $C_8H_8O_2$ (2-MB).

The study was carried out with Sb of SU1 brand, copper foil, and Pb of S1 brand in specially purified

5 M H_2SO_4. The performance of the additives was estimated by analyzing the polarization curves measured at current in the range 0.5–50 mA cm^{-2} at $25 \pm 0.1°C$.

Figure 1 shows the polarization curves obtained on Sb and Cu in an H_2SO_4 solution with addition of 0–1.30 g l^{-1} of 2-MB and 0–1.17 g l^{-1} of 2-HB. The table lists the efficiency factors K_{eff}, defined as the ratio of H_2 evolution rates at a potential of 0.6 V in solutions with and without an additive, for the additives studied.

Figure 1 shows that 2-MB and 2-HB are exceedingly efficient in hindering the H_2 evolution on both Sb and Cu. At their concentration in the electrolyte equal to 9.6×10^{-3} M, K_{eff} is 11.6–22.9 on Sb and 48–50 on Cu. It also follows from Fig. 1 that the inhibiting effect of 2-MB and 2-HB grows as their concentration in solution increases, to become the most pronounced at a concentration of 9.6×10^{-3} M. However, the results obtained give no reason, as yet, to recommend 2-MB and 2-HB as inhibitors of H_2 evolution for lead batteries. For this purpose, it is necessary to make sure that these additives do not affect simultaneously the current-producing reactions and the reactions of the closed oxygen cycle.

Figure 2 shows the polarization curves obtained on a porous lead cathode in a 5 M H_2SO_4 solution with addition of 0–0.9 g l^{-1} of 2-MB and 0–0.8 g l^{-1} of 2-HB. It can be seen that addition of 2-MB leads, in the entire range of concentrations, to an increase in the overvoltage of H_2 evolution. This indicates that the additive can be adsorbed on the Pb surface and can thereby affect the main current-producing processes. At the same time, addition of 2-HB affects the rate of H_2 evolution on Pb only slightly, suggesting its low adsorption capacity with respect to the Pb surface.

It is known that the zero-charge potentials for Pb, Cu, and Sb are -0.69, -0.04, and 0.0 V, respectively (relative to a standard hydrogen electrode). Thus, the surface of Pb is charged positively, and that of Cu and Sb, negatively, at potentials of the negative electrode. Therefore, the surface of Pb is covered in H_2SO_4 with an adsorption layer of HSO_4^- ions, and that of Sb and Cu, with H^+ ions [13]. It is also known that introduction of various substituent groups into the structure of benzaldehyde changes its electronic configuration and the dipole moment of the molecule [14].

The concept of moderate and strong inhibitors of H_2 evolution, which are derivatives of aromatic hydro-
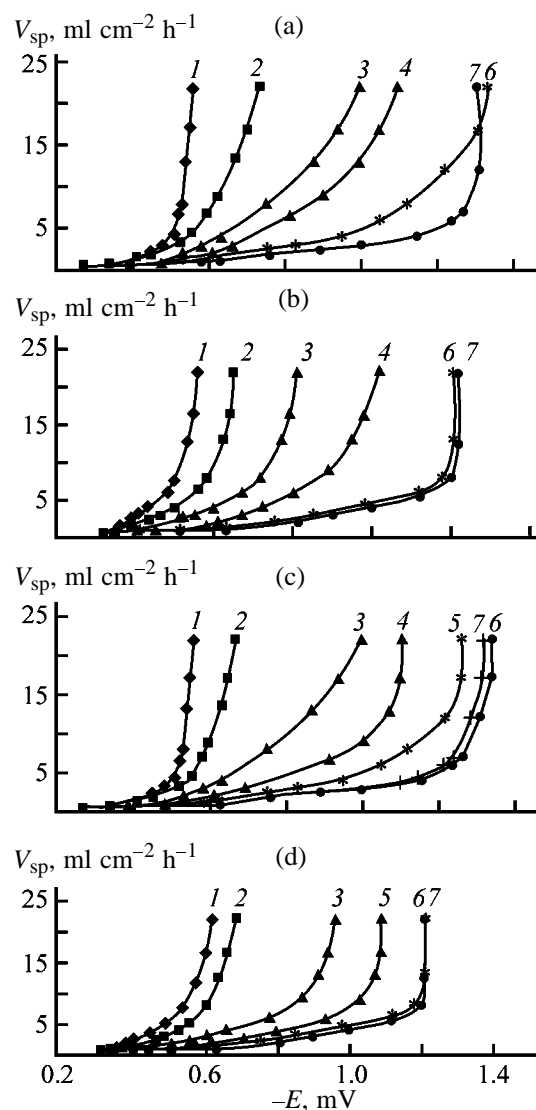
Fig. 1. Specific rate of hydrogen evolution, V_{sp}, on (a, b) antimony and (c, d) copper in a 5 M H_2SO_4 solution with addition of (a, c) 2-MB and (b, d) 2-HB vs. the polarization potential E. Concentration (g l^{-1}): 2-MB: (*1*) 0, (*2*) 0.05, (*3*) 0.17, (*4*) 0.34, (*5*) 0.65, (*6*) 0.83, and (*7*) 1.30; 2-HB: (*1*) 0, (*2*) 0.23, (*3*) 0.47, (*4*) 0.58, (*5*) 0.70, (*6*) 0.88, and (*7*) 1.17.

carbons [13], can be used to account for the experimental data obtained. It should be assumed that strong inhibitors hinder not only the H_2 evolution on Sb and Cu through their adsorption on the surface of these metals, but also the processes on the surface of Pb because of the ability of such inhibitors to displace HSO_4^- ions and be adsorbed on the surface. As a result, the current-producing reaction is hindered.

It was shown that the 2-MB additive has a high adsorbability not only on Sb and Cu, but also on Pb. The latter is strongly undesirable because of the de-

Efficiency factors of 2-MB and 2-HB additives

2-MB		2-HB	
c, g l^{-1} (M)	K_{eff}	c, g l^{-1} (M)	K_{eff}
Antimony cathode			
0.05 (3.7×10^{-4})	1.8	0.23 (1.9×10^{-3})	2.3
0.17 (1.2×10^{-3})	4.0	0.47 (3.8×10^{-3})	5.9
0.34 (2.5×10^{-3})	6.6	0.58 (4.7×10^{-3})	12.8
0.83 (6.1×10^{-3})	8.7	0.88 (7.2×10^{-3})	18.7
1.30 (9.6×10^{-3})	11.6	1.17 (9.6×10^{-3})	22.9
Copper cathode			
0.05 (3.7×10^{-4})	2.9	0.23 (1.9×10^{-3})	2.7
0.17 (1.2×10^{-3})	12.5	0.47 (3.8×10^{-3})	10.5
0.34 (2.5×10^{-3})	16.7	0.70 (4.7×10^{-3})	24.0
0.65 (4.8×10^{-3})	45.0	0.88 (7.2×10^{-3})	42.0
0.83 (6.1×10^{-3})	50.0	1.17 (9.6×10^{-3})	48.0
1.30 (9.6×10^{-3})	50.0	–	–

creasing rate of the main current-producing process at the negative electrode. Thus, the 2-MB inhibitor cannot be recommended for use in lead batteries despite its high performance. In the opinion of Böhnstedt and Radel [13], moderate inhibitors cannot displace HSO_4^- and be adsorbed on Pb, which predetermines the high degree of their selective adsorption. In-

hibitors of this kind are mainly adsorbed on detrimental impurities (Sb, Cu) and suppress H_2 evolution on these elements. At the same time, they are not adsorbed on Pb and do not exert any negative influence on the processes that occur on this element. Consequently, the 2-HB inhibitor can be classed with moderate inhibitors and recommended for use in lead batteries.

However, prior to recommending 2-HB for use in lead batteries, it is necessary to find out whether or not it has an effect on the operation of the positive electrode and, primarily, on the rate of O_2 evolution, which characterizes the efficiency of utilization of the charging current, as well as on the kinetics of the current-producing reaction. An influence of this kind is, in principle, possible because of the contact between the inhibitor introduced into a solution with the positive active paste. For this purpose, polarization curves were measured on a PbO_2 electrode in the anodic potential range in a solution containing the 2-HB inhibitor (Fig. 3a). Figures 3a and 3b show that 2-HB has no effect on the rate of O_2 evolution at the PbO_2 electrode and on its discharge characteristics.

The performance of the 2-HB inhibitor was tested in stationary batteries with a rated capacity of 12 000 A h. At the end of the service life of these batteries, the rate of H_2 evolution was 600 (battery no. 1) and 700 cm^3 min^{-1} (battery no. 2). A 2-HB
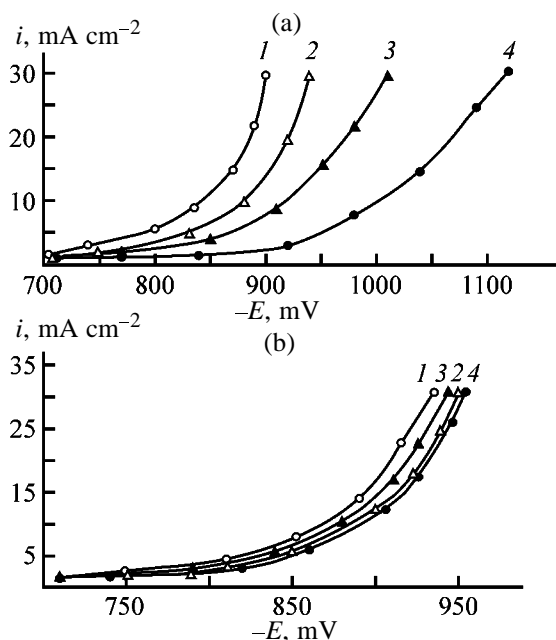
Fig. 2. Polarization curves obtained on a porous lead cathode in a 5 M H_2SO_4 solution with addition of (a) 2-MB and (b) 2-HB. (*i*) Current density and (*E*) potential. Concentration (g l^{-1}): 2-MB: (*1*) 0, (*2*) 0.01, (*3*) 0.09, and (*4*) 0.9; 2-HB: (*1*) 0, (*2*) 0.01, (*3*) 0.1, and (*4*) 0.8.
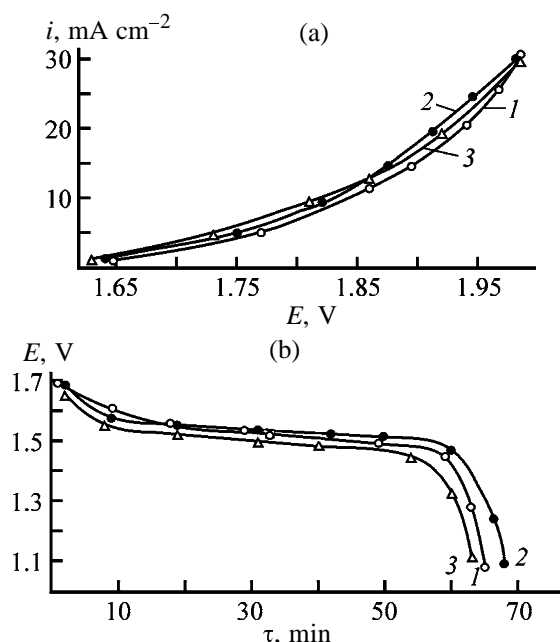
Fig. 3. (a) Polarization and (b) discharge curves obtained on a PbO_2 electrode in a 5 M H_2SO_4 solution (*1*) without additives and with addition of (*2*) 2-MB and (*3*) 2-HB. Concentration (g l^{-1}): 2-MB, 0.9; 2-HB, 0.8. (*i*) Current density, (*E*) potential, and (*τ*) time.

additive was introduced into battery no. 2, with the result that the rate of gas evolution decreased to 200 cm^3 min^{-1} in the subsequent cycle. In battery no. 1, into which no additive was introduced, the gas evolution rate increased to 670 cm^3 min^{-1}.

CONCLUSIONS

(1) According to our results, 2-hydroxybenzaldehyde can be recommended as an additive effectively inhibiting the evolution of H$_2$ in sealed lead–acid batteries.

(2) This inhibitor can diminish the rate of H$_2$ evolution on Sb and Cu by factors of 10–12 and 15–29, respectively, with the discharge characteristics of the electrodes and the efficiency of the closed oxygen cycle remaining virtually unaffected.

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