

INVESTIGATION OF THE EFFECT OF ANTIMONY ON THE NATURE OF LEAD PASSIVATION IN SULFURIC ACID SOLUTIONS

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In a series of works [1 - 3] it has been shown that during the operation of a lead-acid battery, antimony accumulates on the negative electrode due to corrosion of the lead-antimony lattice of the positive electrode. The stationary potential of antimony is much more positive than that of lead in sulfuric acid and the hydrogen overvoltage on antimony is extremely low. Therefore antimony deposited on the negative electrode hinders discharge and considerably increases the rate of self-discharge of the electrode, promoting its "sulfatization"*

A sharp fall in the practical capacity of the negative electrode (when it is poisoned with antimony), by virtue of all that has been said above, is usually only connected with the impossibility of sufficiently complete discharge of the electrode.

The purpose of the present investigation was to determine how the presence of antimony on the negative electrode affects its passivation on discharge. To exclude the effect of the degree of charge on the discharge time, the experiments were carried out with smooth electrodes with a freshly cleaned surface.

MEASUREMENT PROCEDURE

All the measurements were made on flat electrodes, cast from SV grade lead and 8% lead-antimony alloy. The apparent surface of the electrode was 6 cm². Before immersion in the solution, the electrode surface was renewed with a sharp steel chisel. The sulfuric acid solution was prepared from chemically pure sulfuric acid and distilled water, then purified for many hours by passage of a current between smooth electrodes of SV grade lead and diluted to concentrations of 2, 6.68, 9.8 and 11.37 N. The electrode potential was measured against a mercurous sulfate electrode, covered with sulfuric acid solution of the same concentration as that in which the electrode was polarized. As the first experiments showed that after removal of the external layer the electrode surface was oxidized by atmospheric oxygen at room temperature, all subsequent experiments were carried out with preliminary cathode polarization for 20 minutes at a current density of $2 \cdot 10^{-4}$ a/cm² of the apparent surface. For experiments on passivation of lead and lead-antimony electrodes we used anode polarization in four different sulfuric acid concentrations (see above) at the same current density of $2 \cdot 10^{-4}$ a/cm² at 30°.

RESULTS OF MEASUREMENTS

The results of the measurements are shown in Fig. 1. The time (in min) is plotted along the abscissa and the voltage (in volts relative to a mercurous sulfate electrode) along the ordinate. As Fig. 1 shows, the

* The term "sulfatization" is used here to denote the phenomenon beginning most frequently of all when the battery stands for quite a long period in a discharged state and consisting of the fact that such a battery cannot be charged as lead sulfate is not converted to lead on the passage of a cathode current. As was recently shown [4], sulfatization is produced by a number of organic substances which either reduce the rate of solution of lead crystals by being adsorbed on their surface or hamper the discharge of lead ions (Pb⁺⁺) by being adsorbed on the lead.

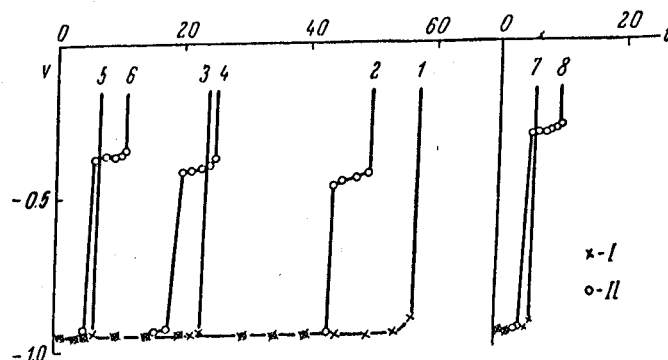


Fig. 1. Change in potential V (in v) of lead and lead-antimony electrodes at an anode polarization current of $2 \cdot 10^{-4}$ a/cm^2 with time t (in min.) in sulfuric acid solutions of various concentrations. H_2SO_4 concentration (normality): 1, 2 — 2; 3, 4 — 6.68; 5, 6 — 9.8; 7, 8 — 11.37. Electrodes: I) lead, II) lead-antimony.

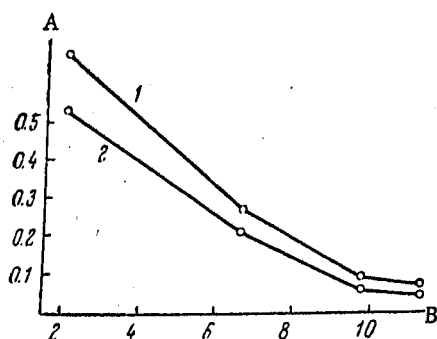


Fig. 2. Relation between the thickness of the passivating $PbSO_4$ layer and the sulfuric acid concentration for lead and lead-antimony electrodes. A) Amount of electricity (in coul / cm^2), B) H_2SO_4 concentration (normality). Electrodes: 1) lead, 2) lead-antimony.

tion leads to a sharp displacement of potential to the positive side at the moment when a small part of the original true surface of the electrode remains free. The true current density (at a constant polarization current strength) at this moment reaches the region of current densities (above 10^{-3} a/cm^2) where the lead ionization overvoltage assumes a considerable value [5].

An increase in the sulfuric acid concentration (under otherwise equal conditions of anode polarization) leads to a decrease in the amount of lead sulfate passivating the electrode due to a decrease in the diffusion coefficient and the solubility of this salt [7]. Figure 2, which was obtained from data given in Fig. 1, shows the nature of the relation we obtained between the thickness of the lead sulfate layer on the passivated electrode and the sulfuric acid concentration. Curve 1 gives the thickness of the $PbSO_4$ layer for lead electrodes and curve 2, that for lead-antimony electrodes. The layer thickness was determined from the amount of electricity passing through the electrode up to the sharp change in potential in a positive direction (in the case of the antimony electrode, up to the first sharp change in potential in a positive direction). Fig. 2 shows that the curve for lead-antimony electrodes lies below that for lead electrodes so that the amount of $PbSO_4$ formed on a lead-antimony electrode is less than that formed on a lead electrode (at the same H_2SO_4 concentration) always by the same proportion, which is on the average 27%, regardless of the sulfuric acid concentration. This may be explained by the fact that part of the surface of the lead-antimony electrode is occupied by antimony.

presence of antimony in the electrode accelerated passivation of the latter. In addition, with anode polarization of lead-antimony electrodes the time-potential curves showed a plateau at a potential close to the equilibrium value for the electrode reaction $Sb + H_2O = SbO^+ + 2H^+ + 3e$. The length of this plateau remained almost constant with a change in sulfuric acid concentration (from 2 N to 11.37 N), while the plateau corresponding to the oxidation of lead to lead sulfate decreased by a factor of approximately 10.

DISCUSSION OF RESULTS

At the beginning of our experiments the anode current density was $2 \cdot 10^{-4}$ a/cm^2 , i.e., in the region of current densities (10^{-5} — 10^{-3} a/cm^2) where the overvoltage of the process $Pb \rightarrow PbSO_4$ is determined by the supersaturation of the sulfuric acid solution with lead sulfate [5]. It is known [6] that passivation of lead due to covering of its surface by a layer of crystals of insoluble and nonconducting $PbSO_4$ under anode polarization

The melting point diagram of the lead-antimony system shows that antimony hardly forms any compounds with lead. When an 8% (with respect to antimony) alloy is cooled, coarse crystals of lead are first deposited. When, as a result of this, the antimony content reaches 13% the melt crystallizes, forming fine crystals of antimony and lead. Calculation shows that in an 8% antimony electrode, antimony crystals occupy about 15% of the surface. Since antimony in sulfuric acid is oxidized at a potential which is several tenths of a volt more positive (~ 0.5 v) than for anode oxidation of metallic lead to lead sulfate and occupies a considerable part of the true surface of the electrode, passivation of a lead-antimony electrode begins correspondingly earlier than for a lead electrode. For the same reason, the true current density from the very beginning of anode polarization will be higher on an 8% antimony electrode by a factor of ~ 1.2 and as lead crystals lying on the surface are consumed, it will increase, and thus must also accelerate passivation of the electrode*. Up to the beginning of passivation, the working lead surface on lead and lead-antimony electrodes has such a size relative to the initial one that the true current density is increased by 1 – 2 orders. As a result, the electrode is passivated and the potential of the lead electrode is displaced in a positive direction before the oxidation of lead sulfate to lead dioxide begins and the potential of the lead-antimony electrode is displaced before the oxidation of antimony begins. The oxidation products of antimony $[\text{Sb}_2(\text{SO}_4)_3$ and $(\text{SbO})_2\text{SO}_4]$ are quite readily soluble in sulfuric acid and therefore the amount of electricity consumed in oxidation of antimony must correspond to the amount of antimony crystals lying on the surface.

At first glance it would seem natural to assume that parallel with the oxidation of antimony at these potentials (lying 0.5 – 0.55 v above equilibrium for the Pb/PbSO₄ system), i.e., with a high overvoltage, the lead crystals liberated must be oxidized to lead sulfate. However, the results of our experiments showed that the amount of electricity consumed in the oxidation of lead at potentials corresponding to the second plateau on the potential-time curve is only an insignificant fraction of that consumed in the oxidation of antimony. This is seen from the fact that the length of the plateau, corresponding to the antimony oxidation potentials (Fig. 1), changes only insignificantly with an increase in the sulfuric acid concentration from 2 to 11.37 N. In addition, if, at the end of the plateau corresponding to the oxidation potentials of antimony, the anodically polarized electrode is immediately polarized cathodically (with preliminary washing with sulfuric acid solution) in a cell with an acidified normal solution of Na₂SO₄, then the potential-time curve shows only one plateau, corresponding to the process $\text{PbSO}_4 \rightarrow \text{Pb}$. The size of this plateau is equal to the size of the first plateau, corresponding to the process $\text{Pb} \rightarrow \text{PbSO}_4$, which occurred during anode polarization of the same lead-antimony electrode.

Apparently, at such positive potentials (0.5 v) there is adsorption passivation of lead crystals liberated by solution of antimony crystals, i.e., passivation requires an amount of electricity less than 10^{-3} coul./cm².

It is reported in the literature [8] that even a slight increase of 40 mv (potentiostatic method) in the potential at which lead is oxidized to lead sulfate leads to a sharp fall in the amount of lead sulfate formed (the amount of it formed at a potential 40 mv more positive is 28% of the amount of PbSO₄ formed at the usual low potential for oxidation of lead to lead sulfate). These data agree well with the results of our measurements.

SUMMARY

It was shown that antimony is capable of passivating a lead electrode. From this it follows that the fall in the practical capacity of the negative electrode of a lead-acid battery due to its poisoning by antimony is not only connected with the fall in degree of charging of the negative electrode.

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* Calculation by the empirically derived equation of Peikert, which was recently shown [7] to reflect the properties of a passivated lead electrode, showed that with an increase in current density by a factor of 1.2 the practical capacity of the electrode falls by 15%. In the calculation by Peikert's equation: $\tau I^n = \text{const.}$, where τ is the discharge time, I is the current density, and n is a constant, we used the value $n = 1.2$ as this was found experimentally for a lead electrode in 8 N sulfuric acid [7].

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* Original Russian pagination. See C. B. Translation.