

ADSORPTION MECHANISM OF EXPANDER ACTION

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It was shown earlier [1] that "expanders" contained in the active material of the negative plate of the lead storage battery, which increase the discharge time, i.e., the utilization of the active material, may act by two different mechanisms. One mechanism of action of organic expanders is by adsorption on growing PbSO_4 crystals; this results in a less compact structure in the layer of PbSO_4 crystals, hinders anodic passivation of lead, and thereby assists oxidation of lead to a greater depth during discharge; i.e., it results in a higher "capacity" of the plate. In this case BaSO_4 crystals act as a "depot" for the surface-active expander during the charge period, when PbSO_4 crystals disappear. This "depot" is necessary for expanders which are adsorbed to only a small extent on metallic lead at potentials close to equilibrium, i.e., when the metal surface is positively charged.*

The second mechanism postulated for the action of organic expanders is one of adsorption of their components on the faces of the metallic lead crystals; this should influence the geometrical structure of the spongy active material formed electrolytically during each charge.

We have investigated the influence of surface-active substances on caking and swelling of the active material of plates contained in a large volume of solution.

The experiments were performed with coated plates containing various organic expanders, and also with plates free from organic compounds of any kind. Before preparation of the paste, the lead oxide and BaSO_4 were calcined at about 400° for several hours in order to remove any surface-active substances accidentally present in the starting materials. The sulfuric acid solution was first purified by passage of current between smooth lead electrodes immersed in the acid for 24 h at 1 A/cm^2 .

The change of the true surface area of the charged active material in the plates during the charge-discharge cycles as the result of caking or swelling was estimated by determinations of the hydrogen overvoltage and of the capacity of the electric double layer; electrocapillary curves were plotted for determination of the absorption of expanders on the metal surface.

Hydrogen overvoltage was determined at current densities in the range from $6 \cdot 10^{-3}$ to $1.3 \cdot 10^{-1} \text{ A/cm}^2$, calculated for the two-sided apparent area of the coated plate. The auxiliary mercury-mercurous sulfate electrode contained sulfuric acid of the same concentration, 4.8 M, as the cell with the plate under investigation. The plate grids were made from pure S_v grade lead in order to exclude the influence of antimony and accidental impurities on the hydrogen overvoltage. The capacity of the double layer was determined from curves for the fall of potential after disconnection of the cathodic polarizing current.

"Cycling," i.e., alternate charging and discharging of plates made from calcined materials, leads to appreciable caking of the active material. Deep cracks appear on the plate surface along the ribs and within the cells, and the active material becomes hard. The discharge life of such plates under "starter" conditions (at a discharge current density of 0.15 A/cm^2) drops by about two thirds by the time the fifth cycle is reached, and remains at a low level during prolonged cycling.

The hydrogen overvoltage on plates made from calcined materials remains unchanged in the first three cycles (Fig. 1, curves 1 and 2), but by the 10th and then the 20th cycle (not shown in Fig. 1) it increases by 40 mV over the value for the 1st cycle (in this case the same results were obtained for plates with and without BaSO_4). This increase

*It is known that the standard potential of lead in sulfuric acid is on the positive side of its zero charge potential by 0.34 V.

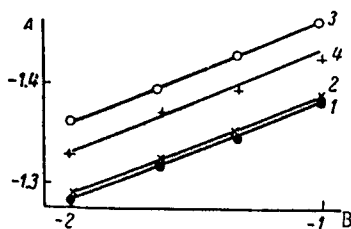


Fig. 1

Fig. 1. Effect of an organic expander on the potential of hydrogen discharge. A) Potential, φ (V); B) logarithm of the current density, $\log i$ (i in A/cm²). Hydrogen overvoltage in H₂SO₄ solution after: 1) 1st charge; 2) 2nd charge; 3) addition of SL to solution; 4) 5th charge, with SL; same in Fig. 2.

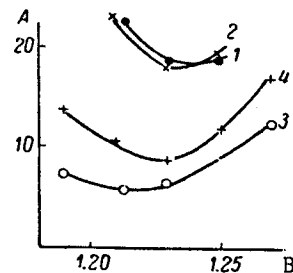


Fig. 2

Fig. 2. Effect of an organic expander on the capacity of the electric double layer. A) Capacity, $C \cdot 10^{-3}$ (μ F/cm²); B) potential, φ (V).

of hydrogen overvoltage in the course of cycling can be conclusively attributed to a decrease of the true plate area by a factor of 2.5 (by the time the 20th cycle has been reached), as any accidental organic impurities which might influence the hydrogen overvoltage had been removed by calcination of the materials used for preparation of the active paste. Measurements of the capacity of the double layer for these plates showed that by the 20th cycle the capacity had fallen by a factor of 2-3.5.

All this shows that by the 20th cycle the true surface area of these plates had decreased roughly two- to three-fold. Introduction of the organic expander SL into the pure electrolyte of a charged cell with plates made from calcined materials raised the hydrogen overvoltage by about 80 mV (Fig. 1, curve 3) and lowered the capacity of the double layer by a factor of 2.5 at the minimum point (Fig. 2, curve 3).

The presence of any of the organic expanders studied in the paste approximately halves the capacity of the double layer in comparison with the value for plates without organic substances.

They raise the hydrogen overvoltage by about 40-80 mV. All this indicates considerable adsorption of the organic expander components on lead. We used the electrocapillary method for obtaining semiquantitative data on adsorption of the following substances on mercury from saturated (with the exception of SL) solutions in sulfuric acid: hydrolyzed peat (P), humic acids (H), sodium lignosulfonate (SL), casting binder (CB), and tanning agent No. 4 (T4). Solutions containing CB and T4 produce the greatest lowering of surface tension in comparison with pure sulfuric acid in the region of positive surface charges, and solutions with P, the least (Fig. 3).

In the case of almost insoluble surface-active expanders these data on the variations of hydrogen overvoltage and capacity caused by introduction of expanders into the solution make it possible to estimate the change of true surface area during cycling from further changes of overvoltage and capacity.*

*This conclusion cannot be drawn with certainty for readily soluble organic substances (such as SL), because the organic substance can pass from the plate into the solution and then burn at the positive plate; this would also influence the capacity and overvoltage.

It must be pointed out that, as has been shown previously [1], adsorption of the expander, without cycling, itself lengthens the full starter discharge life of a lead battery plate approximately fourfold by decreasing passivation, without an increase of the true plate area.

The fact that hydrolyzed peat and humic acid used as expanders in storage batteries are relatively effective in lengthening the starter discharge life, whereas the adsorption of these substances on mercury has very low values at positive surface charges, indicates that adsorption on metallic lead has no significant effect on the increase of the starter capacity of the lead battery by these expanders.

At the same time, CB and T4, which are very effective expanders, lower the electrocapillary maximum sharply; this indicates considerable adsorption of these substances on the metal. Adsorption of acidic groups or molecules is characteristic in this case (Fig. 3); i.e., adsorption of groups or molecules which can be adsorbed on lead at potentials close to the equilibrium value for the system Pb/PbSO₄, H₂SO₄. Adsorption of basic groups also occurs in the case of CB.

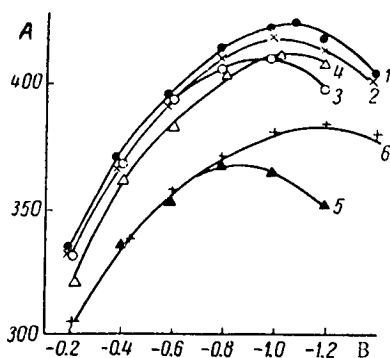


Fig. 3. Electrocapillary curves for solutions of expanders in sulfuric acid. A) Surface tension, φ , (dynes/cm²); B) potential against the mercurous oxide electrode (V). 1) Pure 4.8 M H₂SO₄ solution; 2) hydrolyzed peat; 3) humic acid; 4) SL treated with activated carbon in solution; 5) casting binder; 6) tanning agent No. 4.

Expanders which ensure a long discharge life of the negative plate under starter conditions do not cause excessive swelling during prolonged cycling. Conversely, certain organic expanders which cause strong swelling of the negative plate with subsequent shedding of the active material do not ensure adequate starter capacity of the plate. This is illustrated by the results of experiments with plates containing cotton waste treated with sulfuric acid, or acid-hydrolyzed peat (both together with BaSO₄), as expanders. Figure 4 shows that plates with cotton-barium sulfate expander were already strongly swollen by the 4th cycle (plate 1), while at the 11th cycle the swelling amounted to 12 mm of the plate thickness (plate 2), whereas plates with peat-barium sulfate expander were almost unchanged in appearance even at the 11th cycle (plate 4). It is known that swelling does not lead to increased capacity of the plates. The full discharge life of plates with cotton-barium sulfate expander, which swell strongly, fell by more than a half at the 5th cycle, whereas the discharge life of plates containing peat-barium sulfate expander, which were unchanged in appearance remained at a high level during prolonged cycling. These and other experiments showed that expanders of high solubility in sulfuric acid tend to cause greater swelling and that plate swelling due to expanders is not directly related to the effectiveness of their influence on the total discharge life of the plate.

The fact that the same organic expander can have different effects on plate swelling and on the total discharge life suggests that most of the expanders studied are not single substances in the adsorption sense, but consist of different groups of organic substances. One group of organic substances may lengthen the total discharge life, another may cause swelling of the active material, and this same group (or possibly a third) may raise the hydrogen overvoltage, i.e., the charge voltage.

The hydrogen overvoltage of a plate containing peat-barium sulfate expander remains almost without change during four cycles, and falls by about 40 mV only by the 20th cycle. Slight swelling of the plates occurs at this stage. The decrease of hydrogen overvoltage and the increase of the capacity of the double layer with progressive cycling

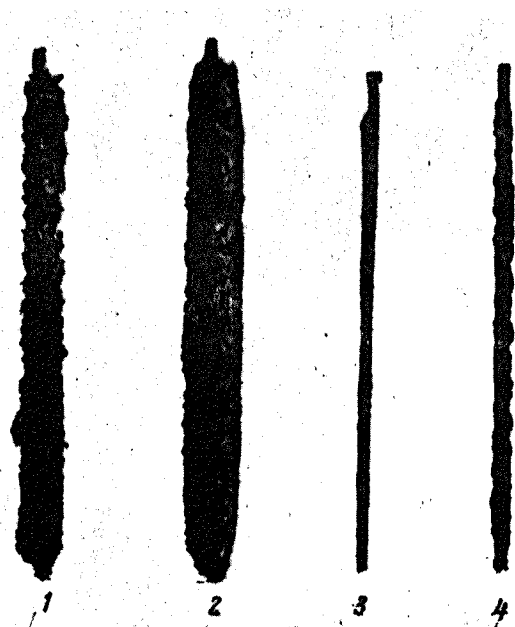


Fig. 4. Plates with expanders (end view). Expanders: 1,2) Cotton-barium sulfate; 3,4) peat-barium sulfate. Number of cycles: 1,3) 4; 2,4) 11.

of plates containing organic expanders indicates an increase of the true surface area of these plates and is associated with swelling of the plates; in the case of a soluble expander (Figs. 1 and 2, curve 4) it also indicates that the organic substances are oxidized at the positive plate. The oxidation is accompanied by a decrease of the total discharge life of the plate and shows, in confirmation of the theory [1], that adsorption of the effective component of the expander is reversible.

LITERATURE CITED

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