

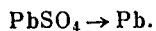
SULFATION MECHANISM OF LEAD STORAGE BATTERIES AND METHODS FOR ITS PREVENTION

T. I. Popova and B. N. Kabanov

There has been a considerable number of investigations dealing with the sulfation of negative plates of lead storage cells, as it is considered that many batteries become unserviceable owing to sulfation [1].

The term "sulfation" or "irreversible sulfation" is used in the literature to describe instances when discharged plates (i.e., plates covered with a layer of lead sulfate) do not become charged when the normal charging current is passed for the normal period of time.

Most authors attribute sulfation of negative storage-cell plates to growth of lead sulfate crystals or to formation of a "stable" form of these crystals, with a decrease of their solution rate [1-5]. It is assumed that dissolution of lead sulfate crystals is an intermediate stage in the charging process:



One of the authors of this paper [6] put forward an explanation of sulfation, which was attributed to adsorption of various surface-active organic substances on lead sulfate crystals, as the result of which the solution rate of the crystals is lowered. In that investigation the adsorption of various compounds on lead sulfate was determined indirectly from the increase of the cathodic polarization of the discharged plate caused by retardation of dissolution of the lead sulfate crystals by the adsorbed layer, and from the thickness increase of the protective lead sulfate layer, indicative of hindered crystallization.

The possibility of dissolution and crystallization of lead sulfate being retarded by organic substances follows from the work of Kolthoff and his associates [7] on the behavior of crystalline precipitates. They showed, in particular, that recrystallization of lead sulfate is retarded in presence of a number of organic substances. They determined the true surface of the crystals by adsorption of Methyl violet. In their opinion, the lead sulfate surface is covered by a continuous monomolecular layer of dye anions, which displace SO_4^{--} ions from the surface layer of the lead sulfate lattice. Therefore, the observed adsorption of Methyl violet is of specific (chemical) and not of electrostatic character. They showed that in a neutral solution of the dye the specific surface of a lead sulfate precipitate is only roughly halved in 8 days; this shows that the recrystallization rate is lower than in absence of dye. The adsorbed dye completely stops recrystallization of lead sulfate in 0.01 N nitric acid solution, as adsorption of the dye increases with increase of solution acidity.

These results suggested that in presence of surface-active substances in a storage cell the dissolution of lead sulfate crystals may be retarded, and this hinders the charging process. This is consistent with the result, reported by a number of authors, that increase of the expander concentration above a certain limit results in cell sulfation. This was reported by Ritchie [8] in tests of the action of various expanders, and by Rose [9] in a paper on sulfation test methods. Certain separator materials may also lead to sulfation.

The literature contains a large number of methods for sulfation prevention. However, the effectiveness and suitability of these methods are not known with accuracy.

EXPERIMENTAL

In our studies of the sulfation mechanism of negative storage-cell plates we investigated recrystallization of lead sulfate in pure solutions of sulfuric acid, and also studied the influence of adsorption of surface-active substances on the cathodic polarization of an electrode consisting of lead and lead sulfate, and therefore on the solution rate of lead sulfate crystals.

The law governing diffusion of lead sulfate to the surface of a lead electrode is complicated by the fact that the source of the substance may be partially within the diffusion layer. Therefore, the steady diffusion rate and the magnitude of the limiting current are determined not only by the solubility of the given salt but also by the solution rate of the crystals, especially those which are contained within the diffusion layer. For the same reason the rate at which the solution is stirred has almost no effect on the limiting current in surface-coated plates (agitation is negligible within the deep pores of pasted battery plates). The solution rate of lead sulfate crystals in cathodic polarization directly influences the lead sulfate concentration at the surface of the electrode being charged, and therefore the magnitude of the electrode potential.

The following methods were used in the investigation: 1) determination of the limiting current in the reduction of lead sulfate, from cathodic current strength—potential curves [10], 2) x-ray structural and microscopic analysis of samples of discharged lead electrodes, 3) determinations of the capacity of the double layer, 4) determinations of discharge capacity under intermittent (starter) discharge conditions.

The test electrodes were negative lead storage-cell plates of the pasted type (3 mm thick) of 5, 10, and 50 cm² apparent surface area, made from litharge (without expander). These plates were formed and conditioned in 6 N sulfuric acid. The electrodes were charged by a cathodic current of density 4–5 ma/cm² calculated on the apparent surface. The forming and conditioning of the plates was taken to be complete when the potential reached –0.6 v on the standard hydrogen scale. After the forming, the negative lead plates were conditioned by 8-fold charging and discharging. Discharge conditions: 10–13 ma/cm² (1–1.5 hours) to a potential of –0.2 v on the standard hydrogen scale. Charge conditions: 8–10 ma/cm² (2–3 hours) to –0.6 v.

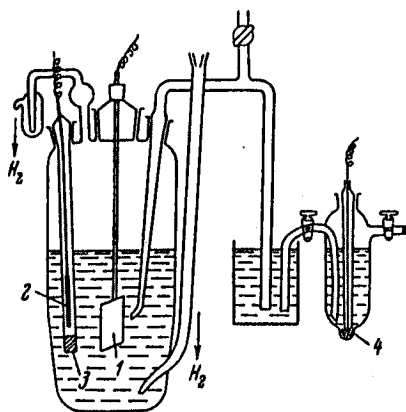


Fig. 1. Diagram of apparatus; explanation in text.

Discharged lead plates were used for the experiments, the discharge being of the short-term type at current density 65 ma/cm² down to –0.2 v. The discharge capacity of the plate was determined from its discharge time.

The polarization determinations were performed in an airtight vessel (Fig. 1) at room temperature. The lead electrode 1 was placed in the middle of the main vessel. The second (platinum) electrode 2 was contained in a tube separated from the main solution by the glass filter 3. The potential of the lead electrode was determined by the compensation method against a mercury—mercurous sulfate electrode 4, with the same acid concentration as in the main solution. The experiments were conducted in a hydrogen atmosphere.

The determinations of the cathodic polarization curves were started at low current densities, in the $2 \cdot 10^{-4}$ to $2 \cdot 10^{-1}$ amp/cm² range. A sharp rise of the electrode potential indicated that the limiting current for discharge of lead ions had been reached, and hydrogen liberation started. The polarization curves were determined after the electrode had been kept in the discharged state for 10 minutes, and 24, 48, and 120 hours (it was assumed that if an uncharged storage cell was kept for several days under the corresponding conditions the negative plates would undergo appreciable sulfation). In investigations of surface-active substances each negative lead plate was used in several experiments (being cleaned between the experiments) and was subjected to repeated discharging and charging (about 20–30 cycles).

After experiments with organic substances the electrode was washed in 8 N sulfuric acid to remove them, and then subjected to cathodic polarization in pure 8 N sulfuric acid for 1–2 hours at current density 80–100 ma/cm², and discharged at current density 65 ma/cm² down to –0.2 v to check the capacity.

The cleanness of the cleaned electrode was checked by the cathodic limiting current in 8 N sulfuric acid. Freshly prepared lead electrodes were used immediately after the discharge-charge cycles for experiments with pure sulfuric acid solutions.

The sulfuric acid solutions were purified by polarization with smooth lead anodes for 10-15 hours with a current of 100-200 ma. The organic substances present in traces were thereby oxidized at the anode, while metallic impurities in the acid were liberated at the cathode. For determination of adsorption of various organic substances the capacity of the double layer was determined at smooth lead electrodes (SV grade) by the usual alternating-current method in the frequency range from 1000 to 50,000 cycles/second with small cathodic polarization (the electrode potential was -0.4 v on the standard hydrogen scale) in pure sulfuric acid and in presence of various surface-active substances.

The x-ray structural analyses of discharged lead electrodes were performed in N. A. Shishakov's laboratory.* For the x-ray determinations discharged electrodes were used; they were previously kept for various intervals in the appropriate solutions, washed with redistilled water to remove traces of acid, dried, and powdered.

The behavior of negative lead electrodes subjected to the action of surface-active substances was checked by determinations of their discharge capacity. In practice, the discharge capacity was taken to be the quantity of electricity required to discharge a plate at the rapid rate (at constant current density of 65 ma/cm^2) down to a potential of -0.2 v.

After determination of the polarization curves the plates were charged, before determination of the discharge capacity, at current density $5-10 \text{ ma/cm}^2$ for 2-4 hours to a potential of -0.6 v. The discharge capacity of the plates used under starter conditions (at 65 ma/cm^2) was then determined.

Thus, the electrodes received the normal charge only, and if the charge process was hindered the electrode remained undercharged, and the discharge capacity was largely a measure of the completeness of the charge.

RESULTS

Cathodic polarization curves (Fig. 2) determined in pure sulfuric acid solutions showed that at all the concentrations tested (6, 7, 8, and 11 N) the limiting current for discharge of lead ions is almost the same, and is approximately $2 \cdot 10^{-1} \text{ amp/cm}^2$.

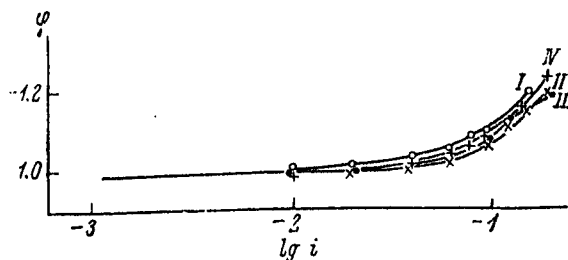


Fig. 2. Cathodic polarization curves determined after exposure of a lead electrode to H_2SO_4 solutions for 10 minutes and 15 days. H_2SO_4 concentrations: I) 11 N, II) 7 N, III) 6 N, IV) 8 N.

acid, and in 8 N sulfuric acid solutions containing extracts of unwashed Miplast (used as separator material in the storage cells), unleached pine wood, cedar and alder sawdust, etc. The results of x-ray analysis revealed the presence of numerous large crystals of lead sulfate (from 5 to 10μ in size) on all the specimens.

Microscopic examination at 680 and 1500 magnification showed a mass of fine lead sulfate crystals, the largest being approximately 1μ , on a discharged plate removed from the electrolyte immediately after discharge, washed, and dried. In addition to the fine crystals, crystals up to 2μ in size were found on plates kept in the discharged state in pure electrolyte for 3 days. Increase of the exposure time of the discharged electrode to

The limiting current does not vary with time, and it is the same for discharged electrodes kept in 8 or 11 N sulfuric acid solutions for 10 minutes and for 10 or 15 days. The discharge capacity was also virtually constant. Therefore, the growth of lead sulfate crystals, which undoubtedly occurs when the discharged electrodes are left in sulfuric acid solutions, does not reduce the solution rate of the sulfate.

We studied the effect of storage of the discharged plates under different conditions on the recrystallization of lead sulfate. Different specimens of the negative plates were subjected to x-ray and microscopic analysis after exposure in the discharged state for various periods from 3 days to 5 months in 8 N solution of pure sulfuric

* We take this opportunity to express our deep gratitude to N. A. Shishakov, and also to V. P. Moiseev for the determinations and calculations.

8 days caused some lead sulfate crystals to grow to $5\ \mu$. Finally, when discharged electrodes were kept for up to 5 months in pure acid solution or in a solution containing surface-active agents, some of the lead sulfate crystals grew to $10\ \mu$.

These determinations show that the surface-active substances tested do not retard recrystallization of lead sulfate significantly.

To determine the influence of surface-active substances on the solution rate of lead sulfate, polarization curves were determined for pure sulfuric acid solution and solutions of the following organic substances in 8 N sulfuric acid: 0.001 to 0.1 M resorcinol, 0.01 M mannitol, 0.001 M Methylene blue, 0.01 M Complexon, 0.04 M sodium lignosulfonate, and extracts of humic acid, peat, wood, Miplast,* saponin, etc.

All the substances tested lowered the limiting current for the reduction of lead ions 2 to 15-fold, according to the nature of the substance and the time of exposure of the discharged electrodes to solutions of these substances in 8 N sulfuric acid, and they all lowered the discharge capacity of the plates under starter discharge conditions. If Complexon was present in the electrolyte, the hydrogen overvoltage at the lead electrode was very much decreased, and the polarization curve assumed the form of a hydrogen-overvoltage curve without any inflection indicative of a limiting current. Because of the decreased hydrogen overvoltage the negative plate did not become charged, so that the discharge capacity of the electrode fell almost to zero.

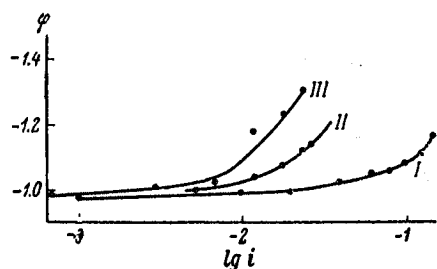


Fig. 3. Cathodic polarization curves determined for different solutions. I) 8 N H_2SO_4 , II) 8 N H_2SO_4 + 0.01 M mannitol (after 10 minutes), III) the same (after 24 hours).

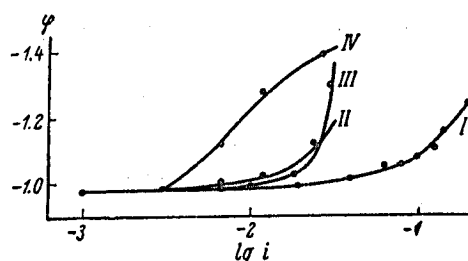


Fig. 4. Cathodic polarization curves determined for different solutions. I) 8 N H_2SO_4 , II) 8 N H_2SO_4 + saturated solution of sodium lignosulfonate concentrate (after 10 minutes), III) the same (after 14 hours), IV) the same (after 48 hours).

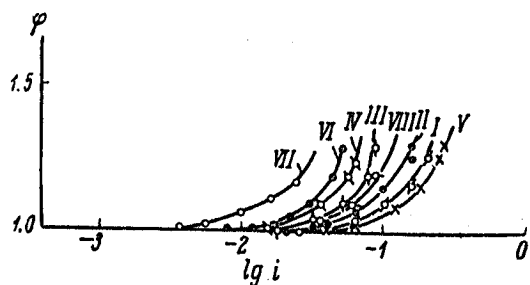


Fig. 5. Cathodic polarization curves determined for different solutions. I) 8 N H_2SO_4 , II) with added extract of unleached pine (after 15 minutes), III) the same (after 24 hours), IV) the same (after 48 hours), V) the same (after correction of electrode), VI) with added extracts of unleached pine and alder sawdust (after 10 minutes), VII) with added extracts of unleached pine and alder sawdust and 0.1 M resorcinol (after 1 hour), VIII) with added extracts of unleached pine and alder sawdust (after correction of electrode).

The results are illustrated by Figs. 3, 4, and 5, which give cathodic polarization curves determined after discharged electrodes had been kept for 10 minutes and 24 or 48 hours in 0.01 M mannitol solution, in saturated solution of sodium lignosulfonate concentrate, in extracts of pine wood and alder sawdust, and in 0.1 M resorcinol, all in 8 N sulfuric acid. The polarization curves show that after only 10 minutes of exposure of the discharged plates in these solutions the limiting current for the solution (the solution rate) of lead sulfate decreases. Increase of the exposure time to 1-2 days produces a 5 to 15-fold decrease of the limiting current. The discharge capacity, under brief discharge conditions, falls from 10-15 minutes to 1 minute and even to 20 seconds, which means that the electrodes are considerably sulfated.

For experimental convenience, resorcinol was used in detailed studies of the effects of surface-active substances on the charging of lead negative electrodes. According to [8], it is a model expander for negative

* It is interesting to note that extract of unwashed Miplast had a lowering effect on the limiting current and discharge capacity, whereas extract of washed Miplast had no influence on them.

lead plates on the one hand, and a substance with small molecules and good solubility in sulfuric acid on the other. Three different resorcinol concentrations, 0.001, 0.01, and 0.1 M, in 5, 6, 7, 8, 9.8, and 11 N sulfuric acid were used in studies of their effect on the limiting current of lead ion discharge and the discharge capacity of lead electrodes.

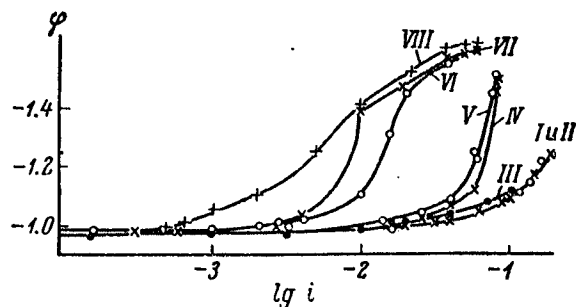


Fig. 6. Cathodic polarization curves determined for different solutions. I and II) 8 N H_2SO_4 (after 10 minutes and after 24 hours), III) 8 N H_2SO_4 + 0.001 M resorcinol (after 10 minutes), IV) the same (after 24 hours), V) 8 N H_2SO_4 + 0.01 M resorcinol (after 10 minutes), VI) the same (after 24 hours), VII) 8 N H_2SO_4 + 0.1 M resorcinol (after 10 minutes), VIII) the same (after 24 hours).

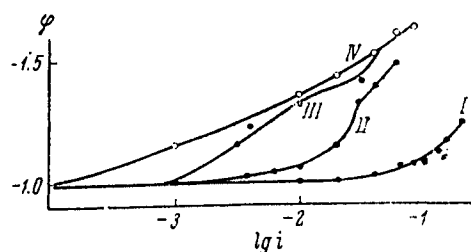


Fig. 7. Cathodic polarization curves determined for different solutions. I) 11 N H_2SO_4 (after 10 minutes and after 24 hours), II) 11 N H_2SO_4 + extract of untreated wood (after 1 hour), III) the same (after 24 hours), IV) the same (after 48 hours).

polarization curves. In some cases the curves become so flat that it is difficult to determine the limiting current, and the curves become straight lines in semilogarithmic coordinates (Fig. 7, Curves III and IV). In this case, the discharge capacity falls almost to zero after 48 hours of exposure. The probable cause of this change in the form of the curve is that the overvoltage for the reduction of lead ions increases under the influence of surface-active substances.

For determination of the mechanism of action of surface-active substances on the charging of a negative lead electrode in such cases it was of interest to determine whether the action of surface-active substances is the same when charged or discharged electrodes are exposed to their solutions, i.e., with predominant adsorption on the metal or on lead sulfate, respectively.

Figure 8 shows polarization curves determined for discharged and charged lead electrodes in pure sulfuric acid solution (after "correction" of the electrode) and in a 0.001 M solution of Methylene blue in 8 N sulfuric

acid. Figure 6 shows polarization curves determined in 8 N sulfuric acid in presence of different concentrations of resorcinol. It follows from the curves that the limiting current for solution of lead sulfate crystals depends on the resorcinol concentration in the electrolyte. With 0.001 M resorcinol the limiting current is decreased appreciably only after prolonged exposure of the electrode to the solution. The greatest decrease of limiting current (from $2 \cdot 10^{-1}$ amp/cm² to $6 \cdot 10^{-3}$ amp/cm²) is found in presence of 0.1 M resorcinol. Figure 6 shows that the retarding effect of resorcinol on dissolution of PbSO_4 increases with the time of exposure.

A small addition of resorcinol (0.001 M) increases the discharge capacity by about 50% on exposure of the discharged electrode in the electrolyte for 10 minutes and 24 hours. When the resorcinol concentration in the electrolyte was raised to 0.01-0.1 M, the discharge capacity fell from 8 to 1-2 minutes. In agreement with [8], our experiments with resorcinol showed that for each soluble expander there is an optimum concentration at which it improves the discharge characteristics of the electrode. At high concentrations the expander has the opposite effect.

With low resorcinol concentrations (0.001 M) the decrease of the limiting current of lead sulfate dissolution depends little on the sulfuric acid concentration. The sulfuric acid concentration has an effect in presence of 0.01-0.1 M resorcinol. In 5, 6, and 7 N sulfuric acid solutions addition of 0.1 M resorcinol lowers the limiting current 2 to 5-fold in comparison with the limiting current for discharge of lead ions in pure acid, while in 8, 9.8, and 11 N sulfuric acid the decrease is 20 to 40-fold. The maximum retarding effect was found in 9.8 sulfuric acid.

Certain organic substances, especially in high concentrations and with long exposure times of the discharged electrodes in the solutions, influence the form of the

acid. After exposure of a well-charged electrode for 24 hours in Methylene blue solution (Curve III, Fig. 8), the curve does not show an inflection characterizing the limiting current, and the electrode potential, starting from current density $2 \cdot 10^{-2}$ amp/cm², increases linearly with the logarithm of the current density; this is a sign of a high overvoltage for lead ion discharge. After the same length of exposure of a completely discharged electrode in the same solution of Methylene blue (Curve V, Fig. 8), on the contrary, the curve obtained has a distinct inflection, characterizing a limiting current and not an increase of overvoltage.

These experiments indicate that Methylene blue may be adsorbed both on lead sulfate crystals and on spongy lead, retarding the process in different ways.

Fig. 8. Cathodic polarization curves determined for different solutions. I) 8 N H₂SO₄ (on sulfated electrode), II) the same (after correction of the electrode), III) 8 N H₂SO₄ + 0.001 M Methylene blue (after 24 hours of exposure of charged electrode), IV) the same (after correction of the electrode), V) 8 N H₂SO₄ + 0.001 M Methylene blue (after 24 hours of exposure of discharged electrode), VI) the same (after correction).

minutes and 24 hours. It is clear from the configuration and shape of the curves that brief action of a mixture of powerful surface-active agents merely raises the reduction overvoltage for lead ions (Curve II), whereas prolonged adsorption results in the appearance of a distinct limiting current (Curve III). The decrease of the limiting current may be attributed to formation of a dense adsorption film on the metallic lead.

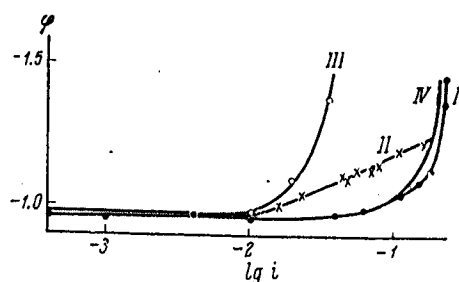


Fig. 9. Cathodic polarization curves determined for different solutions. I) 8 N H₂SO₄ solution, II) 8 N H₂SO₄ solution + saturated solution of a mixture of β-naphthol, thymol, and diphenylamine (after 1 hour of exposure of a charged electrode), III) the same after 24 hours of exposure of a charged electrode), IV) the same (after correction).

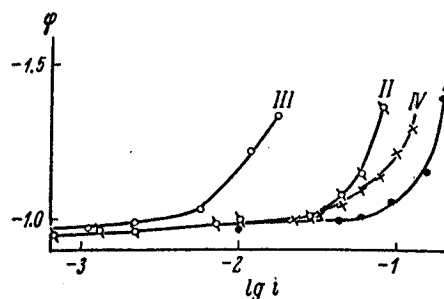


Fig. 10. Cathodic polarization curves determined for different solutions. I) 8 N H₂SO₄ solution, II) 8 N H₂SO₄ + saturated solution of a mixture of β-naphthol, thymol, and diphenylamine (after 1 hour of exposure of a discharged electrode), III) the same (after 24 hours of exposure), IV) the same (after correction of the electrode).

Figure 10 leads to the conclusion that these surface-active substances may also retard the dissolution of lead sulfate. The cathodic polarization curves in this figure were determined for an electrode exposed in the discharged state.

* Before the determination of the polarization curve the electrode was partially discharged in a solution of this mixture.

state for 1 and 24 hours in a saturated solution of a mixture of β -naphthol, diphenylamine, and thymol in 8 N sulfuric acid. The polarization curves show that the limiting current decreases with increase of the exposure time of a discharged electrode in this solution.

To verify the adsorbability of the substances tested on the surface of a negative lead plate, we determined the capacity of the double layer on a smooth lead electrode in pure 8 N sulfuric acid and in presence of these surface-active substances. The results of these experiments showed that addition of a mixture of β -naphthol, thymol, and diphenylamine to the electrolyte decreases the capacity of the double layer by nearly one-half at a potential of -0.4 v. Surface-active substances used in storage cells, such as humic acid extracts, wood extracts, or resorcinol, have almost no effect on the capacity of the double layer on a lead electrode. Addition of 0.01 M Methylene blue to 8 N sulfuric acid increased the capacity of the double layer at 20,000 cycles per second from $28 \mu\text{F}/\text{cm}^2$ to $39 \mu\text{F}/\text{cm}^2$. The increase of capacity may be tentatively attributed to a shift of the zero-charge potential in the negative direction owing to adsorption of Methylene blue anions. At the potential of -0.4 v at which the capacity was determined, increase of the positive surface charge could lead to increased deformation of the anions (as is known, the zero-charge potential on pure lead is -0.7 v).

In a number of cases the cell plates subjected to prolonged action of surface-active substances could not be corrected by the methods generally recommended for prevention of sulfation. For example, plates kept for 10-30 days in a solution of wood extract in 8 N H_2SO_4 did not regain their initial capacity after 6-8 hours of charging in dilute sulfuric acid. We therefore had to develop a more effective method for prevention of sulfation.

Negative lead battery plates subjected to prolonged action of surface-active substances were corrected by charging at a high current density ($100 \text{ ma}/\text{cm}^2$) for 1-2 hours in 8 N sulfuric acid. Correction of the plates may be performed even if various surface-active substances are present in solution. Examples of electrode correction are given in Figs. 5, 8, and 9, which show polarization curves for electrodes after exposure to surface-active substances, and after correction in the same electrolytes. It must be pointed out that after treatment with surface-active substances these plates could not be charged under the normal conditions (at $5 \text{ ma}/\text{cm}^2$), and the discharge capacity under starter conditions fell to zero. As the result of correction, the discharge capacity of the plates returned to the initial values, obtained in pure sulfuric acid solution. The following experimental results provide another example. Large plates were kept in the discharged state for 1-2 months in unleached pinewood extract in 11 N sulfuric acid, to which 0.1 mole of resorcinol per liter had been added. As the result of this treatment the plates could not be charged by the ordinary method, i.e., they were artificially sulfated. After being charged for 2 hours by a cathodic current at density $100 \text{ ma}/\text{cm}^2$, the plate was no longer sulfated, and the discharge capacity under starter conditions reached the initial value of $0.02 \text{ amp-hr}/\text{cm}^2$.

The correction method was also tested with a small storage cell with two negative plates, of 1 dm^2 total area. The negative plates were first artificially sulfated by exposure in a separate vessel for 2 months in an extract of unleached wood and 0.1 M resorcinol in 11 N sulfuric acid, after which the plates were left without electrolyte for one month. These plates were found to be sulfated, and could not be charged under the normal conditions (at $5-10 \text{ ma}/\text{cm}^2$). After correction at high current density (current strength 8-9 amps) for 1 hour, the capacity under starter conditions reached the initial value ($0.03 \text{ amp-hr}/\text{cm}^2$).

DISCUSSION OF RESULTS

It follows from literature data and our results that lead sulfate crystals grow in size as the result of recrystallization, which means that the rate of solution should decrease. Our experiments with different concentrations of pure sulfuric acid showed that the limiting current of lead ion discharge is independent of crystal size. From this it may be concluded that in absence of surface-active substances the limiting current is determined not by the solution rate of lead sulfate crystals but by the rate of diffusion of lead ions from the dissolving surface to the electrode. In fact, at limiting charging current density $i_n = \frac{2 \cdot 10^{-1}}{2000} = 10^{-4} \text{ amp}/\text{cm}^2$, calculated on the true surface (according to our data, the true surface of a charged lead electrode is 2000 times the apparent surface),* with the solubility of $\text{PbSO}_4 = 3.5 \cdot 10^{-9} \text{ mole/cc}$ and diffusion coefficient $D = 2 \cdot 10^{-5} \text{ cm}^2/\text{second}$, the effective thickness δ of the diffusion layer should be:

* The electrode surface, determined from the amount of adsorbed dye, was found to be $0.3 \text{ m}^2/\text{g}$.

$$\delta = \frac{n \cdot F \cdot D \cdot \Delta C}{i_n} = \frac{2 \cdot 10^5 \cdot 2 \cdot 10^{-5} \cdot 3.5 \cdot 10^{-9}}{10^{-4}} = 1.4 \cdot 10^{-1} \text{ cm}, \quad (1)$$

i.e., approximately $\frac{1}{100}$ of the thickness of the diffusion layer in a virtually unstirred liquid in absence of sources of the substance in the liquid itself. This effective thickness is roughly equal to the average distance between the surface of the lead sulfate crystals and the surface of the growing lead crystals. It is of the same order of magnitude as, or even greater than, the linear dimensions of the smallest crystals of lead sulfate which are the sources of the substance in the liquid. The certain increase in the size of these crystals which results from recrystallization of the salt in a discharged plate evidently does not cause any significant change in the distance between the growing lead crystals and the dissolving lead sulfate crystals. This distance (of the order of 1μ) is probably determined by the condition of maximum electrical conductivity and diffusion at the electrode surface, which results in directed growth of the lead dendrites toward the PbSO_4 crystals. The decrease in the solubility of the salt with increase of the acid concentration, which should decrease the limiting current [Eq. (1)] is evidently balanced by a decrease in the thickness of the diffusion layer due to increased packing density of the lead sulfate crystals on the lead. This last effect results in a decrease in the thickness of the passivating layer of lead sulfate.

Our experiments conclusively refute the usual explanation of the sulfation effect, which is based on the assumption that growth of lead sulfate crystals (due to recrystallization) retards solution of the salt so much that charging of the negative electrode becomes impossible. Our investigation confirmed the theory according to which a sharp retardation of the solution of lead sulfate (at least by a factor of some tens or hundreds) is caused by adsorption of various substances (poisons) on the lead sulfate crystals. When the limiting charging current becomes considerably less than the normal charging current as the result of poisoning, hydrogen is evolved during charging and the negative electrode remains virtually uncharged. This effect is facilitated by increase of the overvoltage of lead ion discharge, decrease of the hydrogen overvoltage (for example, by antimony, and by Complexon in our experiments), and possibly by increase of crystal size, which decreases the amount of surface-active substances required to cover the surface of all the crystals.

The fact described in the literature that after prolonged operation of a storage battery the lead sulfate crystals are larger on the positive than on the negative plate is explained, in our view, on the assumption that in the conditions prevailing on the positive plate surface-active substances are generally oxidized to water and carbon dioxide, and therefore they cannot prevent either recrystallization of lead sulfate in the discharged state or rapid solution of lead sulfate crystals during charging.

Negative plates kept for a fairly long time in solutions of surface-active substances are found to be sulfated, the limiting cathodic current on them falls sharply, reaching in many cases the value of 10^{-3} amp/cm², which corresponds to the normal thickness of the diffusion layer in absence of sources of the substance within it. This last result is possible in practice during retarded and simultaneous dissolution of the whole mass of lead sulfate crystals. The discharge capacity of such plates is low, for example, it may be 0.003 amp-hr/cm², because such plates cannot be fully charged under the usual charging conditions.

Surface-active substances cause sulfation when present in sufficient quantity in solution; for example, resorcinol in 0.01-0.1 M concentrations. At lower concentrations, such as 0.001 M, resorcinol is not a poison, as evidently it does not completely block the lead sulfate surface on adsorption, but merely retards solution somewhat and therefore acts as an expander. This accounts for the practical fact that soluble expanders have optimum effectiveness (in ensuring maximum capacity of the negative electrodes at high current densities) at a definite concentration.

In some cases an expander can be simultaneously a poison because of impurities present in it. These harmful impurities in expanders can be detected by our method for determination of the solution rate of lead sulfate from the limiting discharge current of lead ions.

Certain substances, which according to our experiments favor sulfation of negative storage-cell plates, are readily adsorbed on the surface of metallic lead (for example, a mixture of β -naphthol, thymol, and diphenylamine, and Methylene blue). This suggests that difficulties in charging negative plates after exposure to solutions of such surface-active substances may also be associated with hindered discharge of lead ions on metallic lead owing to formation of a dense adsorption layer (in accordance with M. A. Loshkarev's theory), penetration of which requires a high activation energy. In the electrodeposition of bivalent metals in presence of a mixture of diphenylamine, thymol, and β -naphthol, there is an apparent limiting current [11].

Thus, we may assume that sulfation of negative plates may be caused by adsorption of surface-active substances both on lead sulfate crystals and, in certain instances, on the surface of metallic lead. To determine the mechanism in the case of substances which are easily adsorbed both on the metal and on salt crystals, it is necessary to know how these substances are capable of spreading over solution-metal and solution-salt interfaces. In absence of surface volatility, previous adsorption of the substance on the surface of one of the phases conclusively determines the role of the retardation at this surface in the total rate balance. Apart from retardation of dissolution of lead sulfate and retarded reduction of lead ions, difficulties in charging of the negative electrode may also be caused by a decrease of the hydrogen overvoltage. This decrease is usually caused by antimony, and also by other substances such as the above-mentioned Complexon.

Our method for correction of sulfated plates by the use of high charging current densities (of the order of 100 ma/cm^2) is based on the concept that sulfation proceeds by an adsorption mechanism. At these current densities the electrode potential reaches high negative values (1.2-1.4 v on the negative side of the standard hydrogen electrode, and 0.5-0.7 v on the negative side of the zero-charge potential of lead) at which surface-active substances (especially of the anionic type) are desorbed from the spongy lead surface, partially reduced, and possibly removed by flotation from the surface of the lead sulfate crystals by the liberated hydrogen. With the exception of Complexon, all the substances tested increase hydrogen overvoltage when adsorbed on the electrode surface. This is observed during reduction of sulfated electrodes: desorption of resorcinol, various extracts of humic acid, and wood during reduction of lead at constant current density is accompanied by a gradual shift of the electrode potential in the positive direction, reaching 0.2-0.4 v during the charge time (1-2 hours).

SUMMARY

1. A polarization method for determination of the solution rate of lead sulfate has been developed and used for studying the sulfation mechanism of negative plates in lead storage cells.
2. The sulfation mechanism postulated earlier by one of the authors is confirmed; according to this mechanism, the sulfation effect is due to adsorption of surface-active substances on the surface of lead sulfate crystals, hindering dissolution of the crystals.
3. It is shown that in presence of substances which are easily adsorbed on lead difficulties arise in the charging of negative plates because of shielding of the spongy lead surface.
4. It is shown that if the negative electrode remains for a long time in the discharged state in absence of surface-active substances (when the lead sulfate crystals increase in size by recrystallization), no difficulties (sulfation) arise in charging of the electrode.
5. Our method for determination of the solution rate of lead sulfate from the polarization curves and from determinations of discharge capacity can be used for analysis of organic substances used as expanders, separators, etc., for impurities which are harmful to the negative electrode.
6. A new method has been developed for correction of sulfated plates by removal of adsorbed substances by means of very strong cathodic polarization.

LITERATURE CITED

- [1] G. W. Vinal, *Storage Batteries* (New York and London, 1955).
- [2] C. S. Barrett, *Ind. Eng. Chem.* 25, 297 (1933).
- [3] N. N. Lamtev, *Electric Storage Batteries* (ONTI, 1935) [In Russian].
- [4] C. Drotschmann, *Bleiakkumulatoren* (Weinheim, 1951).
- [5] M. Belov, *Elektrotechnik* 10, 3, 83 (1955).
- [6] B. N. Kabanov, *Dissertation* [In Russian] (1942); *Proc. Acad. Sci. USSR* 31, 582 (1941).
- [7] I. M. Kolthoff, *J. Amer. Chem. Soc.* 55, 2664 (1933); 56, 832 (1934).
- [8] E. J. Ritchie, *Trans. Electroch. Soc.* 92, 29 (1947); *J. Electroch. Soc.* 100, 53 (1953).

- [9] C. C. Rose, J. Electroch. Soc. 102, 157c (1955).
- [10] B. N. Kabanov, Proc. Second Conference on Metal Corrosion, 2 [In Russian] (1943), p. 82.
- [11] M. A. Loshkarev and A. A. Kryukova, J. Phys. Chem. 23, 209, 221, 1457 (1949).

Received April 29, 1957