

INFLUENCE OF THE TEMPERATURE ON THE CHARGING OF A LEAD ELECTRODE COATED
WITH A DEPOSIT OF LEAD SULFATE IN SULFURIC ACID SOLUTIONS

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As is well known, in order to improve the discharge characteristics of the negative electrode of a lead storage battery, special organic substances — expanders — are introduced to the active mass of the negative plate. At the same time, as has been shown previously [1], some surface-active agents and, in particular, those that are included in the expanders used in storage battery practice, are adsorbed on the crystals of lead sulfate and lower the rate of their dissolution, which, in limiting cases, leads to the irreversible sulfation of the negative plate of a lead storage battery.

At temperatures of -30 to -40°C , storage batteries scarcely accept a charge [2]. As had been shown in the literature [3], the charging current passing through the negative plate of a lead storage battery at constant overvoltage at -40°C is approximately proportional to the amount of lead sulfate in the plate. This fact, and also the dependence that this author [3] found of the capacity of the negative plate for accepting charge at a low temperature on the size of the particles of lead sulfate permitted him to conclude that the inhibition of the charging process at a low temperature is due to the slowness of the processes taking place on the surface of the crystals of lead sulfate, namely, to the slowness of the dissolution of the crystals of lead sulfate because of the adsorption on their surface of certain surface-active agents present in the expander. Purification of the expander led to a considerable improvement in the charging characteristics of the negative plate of a lead storage battery under low-temperature conditions [3].

However, even in the absence of an expander and of other surface-active agents the dissolution of PbSO_4 does not take place instantaneously. It has been shown by the impedance method that even in the absence of surface-active agents in pure 5.2 M sulfuric acid at all temperatures from $+40^{\circ}\text{C}$ to -40°C the dissolution and precipitation of lead sulfate on the surface of an electrode at the equilibrium potential is inhibited to an immeasurably greater extent than the stage of passage of the charge and, together with the diffusion of the lead compounds through the solution, determines the behavior of the electrode in an alternating current. If the comparison is made at the same current frequencies, with a fall in the temperature of the solution the precipitation of the salts is retarded to a greater extent than its diffusion.

In the presence of expanders, the role of the charge-transfer stage also becomes appreciable: the tanning agent BNF* retards this stage by approximately 2-3 orders of magnitude†, and the dissolution stage by a factor of only 2.5, but, nevertheless, the latter has a considerably greater effect on the overall rate of the process than charge transfer: thus, in the presence of BNF at 20°C the transfer resistance $R_f = 70$ and dissolution resistance $R_t = 440 \Omega \cdot \text{cm}^2$ at a capacity of the double layer of $10 \mu\text{F}/\text{cm}^2$.

In order to determine how they affect the rates of diffusion and dissolution of lead sulfate under the conditions of the passage of a direct current and to what limits of low temperatures the chargeability of the negative electrodes of a storage battery could remain adequate under the conditions of the absence of inhibition of the dissolution of PbSO_4 by sur-

*BNF is the product of the condensation of crystalline phenol and β -naphtholsulfonic acid with formaldehyde.

†These figures cannot be applied directly to the paste plate since in the experiments mentioned the BNF was introduced into the solution to saturation, and in the case of paste plates the expander is added to the active mass in an amount of 4 g/kg of lead powder.

face-active agents, in the present work we have studied over a wide range of temperatures the behavior of the process of cathodic reduction of a precipitate of lead sulfate formed on the surface of a lead electrode in the anodic polarization of lead in sulfuric acid. All the measurements were performed at a smooth lead electrode in 9.6 N sulfuric acid solution. Before an experiment the electrode (a lead wire 2 mm in diameter and 12-15 mm long fixed in a Teflon holder) was defatted, etched in nitric acid, and subjected to anodic polishing, as described previously. Then, after cathodic reduction for 1.5-2 h in the working solution in an atmosphere of hydrogen, the electrode was subjected to anodic polarization with a current of $3.3 \cdot 10^{-5}$ A for 55 min; under these conditions a precipitate of lead sulfate formed on the surface of the lead in an amount corresponding to approximately 50% of the amount of lead sulfate necessary for the complete passivation of the electrode. Before the experiment, the solution was saturated with lead sulfate. As the comparison electrode we used a mercury sulfate electrode filled with the working solution and separated from the working volume of the cell by a cock.

The polarization of the electrode was carried out with the aid of a P-5848 potentiostat. The dependence of the current on the time was recorded on the paper strip of a KSP-4 recording potentiometer. For thermostating the cell we used a thermostat of the U-3 type with a cold accumulator and a valve relay.

Figure 1a shows the dependence of the charging current on the time in the potentiostatic reduction of the precipitate of lead sulfate on the electrode in sulfuric acid solution containing no added surface-active agents. The potential of the electrode was fixed at 50 mV more negative than the working value, which corresponds approximately to that value of the shift in potential that is observed on the negative plate of a lead storage battery when a charging voltage of 2.4 V is applied to the cell (the Fiat method of controlling minimum charging current). Similar relationships obtained in solutions of sulfuric acid saturated with the expander BNF are shown in Fig. 1b. To ensure that the structure of the precipitate of lead sulfate on the surface of the electrode was the same in both cases, the preliminary anodic formation of a deposit of lead sulfate on the electrode was carried out in sulfuric acid solution containing no BNF.

A comparison of the results given in Fig. 1a and b shows that the freeing of the solution from surface-active agents leads to a marked increase in both the initial and the steady charging current at all the temperatures studied.

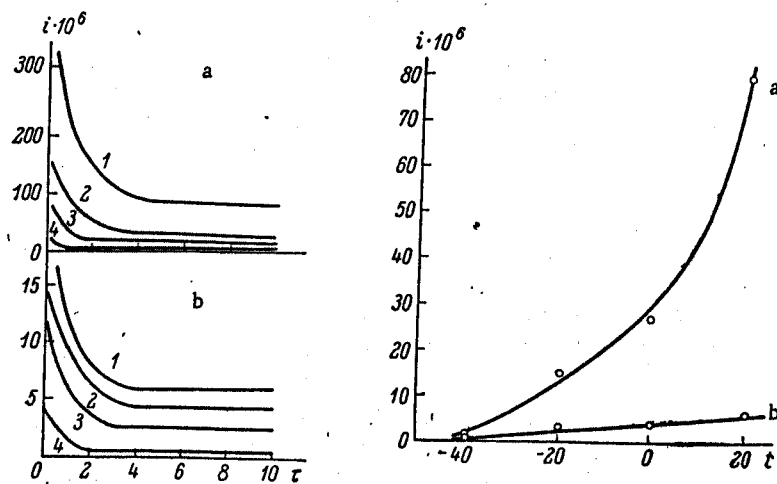
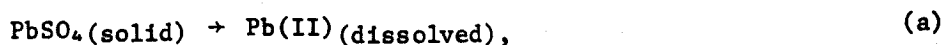


Fig. 1. Dependence of the current i (A/cm^2) on the time τ (min) in pure H_2SO_4 solution (a) and in H_2SO_4 solution saturated with BNF (b). Overvoltage - 50 mV. Temperature ($^{\circ}\text{C}$): 1) 20; 2) 0; 3) -20; 4) -40.

Fig. 2. Dependence of the steady charging current i (A/cm^2) on the temperature t ($^{\circ}\text{C}$) for pure H_2SO_4 solution (a) and for an H_2SO_4 solution saturated with BNF (b).

Figure 2 shows the dependence of the steady charging current (results of Fig. 1) on the temperature. It follows from Fig. 2 that a decrease in the temperature leads to a marked fall in the steady current which is almost linear at below-zero temperatures. In the electrolyte containing no surface-active agents, the fall in the current takes place more sharply than in their presence; down to a temperature of -40°C the charging current is higher in the absence of surface-active agents.

The process of the cathodic reduction of lead sulfate to lead in sulfuric acid solution takes place through the stages:



The rate of this process, equivalent to the charging of the negative electrode of a storage battery, may be determined as a function of the conditions of stage (a), (b), or (c). The rate of stage (b) depends on the rate of stage (a), since crystals of the salt, if they are within the diffusion layer at various distances from the surface of the metal, are a source of diffusing substance; the rate of their dissolution depends on the concentration at a given point of the layer of solution adjacent to the electrode. In one limiting case, when the rate of dissolution is very small, it is possible to assume approximately that the steady process takes place in accordance with the equation of linear diffusion

$$i_{\text{lim}} = n \cdot F \cdot D \cdot c / \delta, \quad (1)$$

when n is the number of electrons taken up, F is Faraday's number, and c is the concentration of Pb(II) .

At 20°C , the diffusion coefficient D , in our case for $4.8 \text{ M H}_2\text{SO}_4$, can be taken as $7 \cdot 10^{-6} \text{ cm}^2/\text{sec}$; the concentration of Pb(II) in the form of a mixture of Pb^{2+} , PbSO_4 , and $\text{Pb(SO}_4)_2^{2-}$ is $4.5 \cdot 10^{-6} \text{ mole/cm}^2$ [5]; with "natural" convection corresponding to a disk electrode [6] at a rate of stirring $\omega = 0.5 \text{ rps}$ or less [7],

$$\delta = 1.62 \omega^{-1/2} D^{1/2} \nu^{1/2} \approx 8 \cdot 10^{-3} \text{ cm} \quad (2)$$

(the kinematic viscosity ν is taken as 10^{-2}).

Then $i_{\text{lim}} = 0.6 \cdot 10^{-6} \text{ A/cm}^2$. In actual fact, at 20°C the density of the cathodic current on smooth lead, equivalent to the density of the charging current at a half-charged paste plate at the usual overvoltage of 50 mV but in the absence of an expander is, according to our results, $80 \cdot 10^{-6} \text{ A/cm}^2$ (Fig. 1a), i.e., two orders of magnitude higher than (even the limiting) current without sources of substance in the diffusion layer. This shows that within a layer having a thickness $\delta = 8 \cdot 10^{-3} \text{ cm}$, in that part of it which is adjacent of the surface of the metal, there are rapidly dissolving crystallites of lead sulfate. The same conclusion has been obtained by the impedance method for more concentrated solutions of sulfuric acid [8]. It is known [9] that the mean thickness of the layer of lead sulfate corresponding to half the amount of lead sulfate necessary for the preparation of the electrode at a current density for a 10-hour charge of a storage battery is approximately 10^{-4} cm ,* i.e., it actually forms only a small part of the layer with $\delta = 8 \cdot 10^{-3} \text{ cm}$.

At another limiting condition when the rate of dissolution of the PbSO_4 crystals was high, the current density at the first moment when the crystals were still in contact with the surface of the metal would exceed the exchange current and would be limited only by the rate of charge transfer [stage (c)]. This could continue only until the layer of crystals of the salt adjacent to the surface of the metal had dissolved and the dissolution of the crystals to the metal had begun to be limited by the rate of the whole process.† The exchange

*At greater current densities the thickness of the layer will, of course, be still less.

†The specific density of the lead formed is several times greater than the effective density of the salt consumed. The diffusional limitations will be somewhat smaller if the lead crystallized not in a smooth layer but in dendrites.

current i_0 of the Pb/Pb(II) 4.8 M H_2SO_4 system has not been accurately measured; however, from the known results [4] for a 5.2 M H_2SO_4 solution containing $PbSO_4$ in an amount close to saturation it may be concluded that $i_0 > 3 \text{ mA/cm}^2$, and for $1.5 \cdot 10^{-3} \text{ M Pb(NO}_3)_2$ it has been found [10] that $i_0 > 0.5 \text{ mA/cm}^2$, from which an approximate calculation for 5 M H_2SO_4 gives $i_0 > 10 \text{ mA/cm}^2$. consequently, only at cathodic current densities greater than $3\text{--}10 \text{ mA/cm}^2$ could the process be limited by stage (c). In our measurements (Fig. 1a) beginning from 15 sec, such high current densities were not recorded and, apparently, the limitation by stage (c) could not last more than a few seconds under these conditions.* During this time the distance between the surface of the metal and the layer of $PbSO_4$ crystals could not exceed 10^{-6} cm ; the limiting diffusion current through such a layer of solution would be of the order of 5 mA/cm^2 ; in actual fact, the current was less and continued to fall with time. This permits the conclusion that the rate of dissolution of $PbSO_4$ crystals even in pure 4.8 M H_2SO_4 solution at 20°C under the given conditions limits the rate of the process. In the presence of expanders (surface-active agents) and at low temperatures the retardation of dissolution is even greater.

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*The charging of the double layer was complete in less than 1 sec.