EFFECT OF TEMPERATURE ON THE ANODIC DISSOLUTION OF LEAD IN SULFURIC ACID

L. V. Kasparova, K. V. Rybalka, and B. N. Kabanov

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The discharge capacity of negative electrodes in lead storage batteries is known to depend substantially on temperature. A particularly drastic decrease in the discharge capacity with decreasing temperature is observed in the ignition discharge mode, i.e., at high current densities. The effect of temperature on the discharge characteristics of lead electrodes has not received due attention until recently, despite the fact that the number of papers dealing with the processes occurring in lead storage batteries is extremely large.

In the present work, investigations were performed both with smooth lead electrodes and with paste electrodes in an excess of sulfuric acid with specific gravity 1.32. The smooth electrodes were fabricated from S-000 lead, and had the shape of cylinders of 2 mm diameter and 15 mm height. They were pressed into teflon holders. Prior to the experiment, the smooth electrodes either were subjected to anodic polishing, followed by prolonged cathodic reduction in the working solution, as described in [1], or they were etched in nitric acid having a concentration of 1:3, and then, too, subjected to cathodic reduction. The paste electrodes had a size of 15 × 6 × 1.8 mm, the grid was fabricated from lead–antimony alloy containing 6% antimony. The paste used for these electrodes contained expander BNF (0.5%) and barium sulfate (0.4% of the weight of lead powder). In the work, potential–time curves were obtained under galvanostatic discharge conditions using a P-5848 potentiostat. The potential was read against a mercury–mercurous sulfate reference electrode, which was filled with working solution. A cathode-tube voltmeter was used for measuring the potential, and the values measured were recorded on paper with a KSP-4 recording potentiometer.

Values for the relative quantity $Q_t/Q_{20°C}$ for the discharge capacities of negative paste electrodes are reported in Fig. 1 as functions of temperature. Here the discharge capacity, Q, of an electrode is defined as the amount of charge which must be passed through the electrode at a given current density* for the electrode potential to shift by + 1 V away from the equilibrium value. It follows from Fig. 1 that the temperature variation of relative capacity depends substantially on the anodic current density; in the ignition discharge mode (curve 4), the negative electrode gives off practically no charge at −40°C.

The connection between discharge current density i and discharge time τ of negative plates at room temperature is known to be described satisfactorily by Peukert's empirical equation, which originally had been suggested for the lead storage battery as a whole [2]:

$$\tau = k \cdot i^{-n},$$

where k and n are constants which depend on sulfuric acid concentration and temperature.

The experimental data obtained by us for different temperatures are reported in Fig. 2 as plots of log τ against log i. One can see from Fig. 2 that a rather good linear dependence exists over a narrow range of current densities, for temperatures not below −20°C, between the logarithm of current density and the logarithm of the time required for complete passivation of the lead electrode. The values of n determined from these data for + 20, 0, and −20°C are 1.07, 1.15, and 1.4, respectively.

Peukert's equation nicely describes the decrease in discharge capacity of lead storage batteries which occurs with increasing current density and is a well-known effect in storage-battery practice. At lower temperatures, the dependence of discharge capacity on current density becomes more pronounced, as indicated by the higher values of n found at lower temperatures.

The paste electrode represents a complicated object of research, since the diffusion of electrolyte and reaction products in the pores of the active mass and the properties of the crystals of lead sulfate and of lead

* All current densities are reported per unit area of apparent surface.

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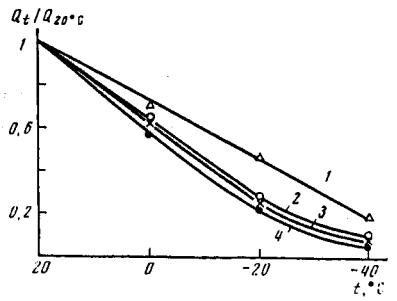

Fig. 1

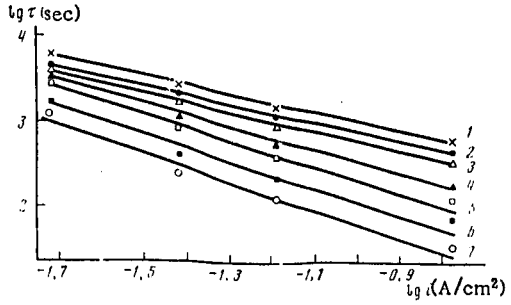

Fig. 2

Fig. 1. The relative capacity of lead paste electrodes as a function of temperature (t) at discharge current densities of 0.056 (1), 0.113 (2), 0.226 (3), and 0.452 A/cm² (4).

Fig. 2. The logarithm of passivation time as function of the logarithm of discharge current density of paste electrodes at 20 (1), 10 (2), 0 (3), −10 (4), −20 (5), −30 (6), and −40°C (7).

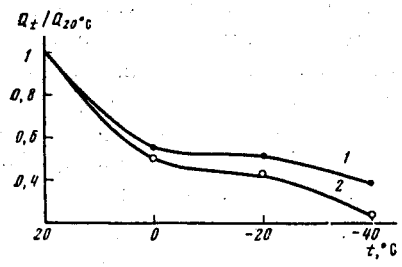

Fig. 3

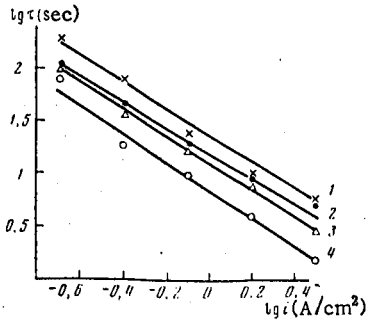

Fig. 4

Fig. 3. The relative capacity of smooth electrodes as a function of temperature in 10.4 N H_2SO_4 at 0.2 mA/cm² without (1) and with (2) expander BNF in the solution.

Fig. 4. The logarithm of passivation time of smooth electrodes as function of the logarithm of current density at 20 (1), 0 (2), −20 (3), and −40°C (4).

produced during the cycling of batteries are important in addition to the electrochemical processes occurring directly at the lead. It was desirable, therefore, to compare the results reported above for paste electrodes with measurements conducted at smooth electrodes. Figure 3 shows the relative discharge capacity of a smooth lead electrode as a function of temperature while the electrode was polarized with a current of 0.2 mA/cm², which is close to the discharge current during ignition (at this current density, passivation of the smooth lead electrode occurs within 5 min at 25°C when expander BNF is present in the solution). We see that the difference between the behavior of smooth lead electrodes and paste electrodes is in the significantly lower temperature dependence of the relative discharge capacity of smooth electrodes. It follows from Fig. 3 (curve 2) that the discharge capacity of smooth electrodes in the presence of expander BNF in the solution at −40°C is 23% of the discharge capacity found at room temperature, while for the paste electrode (Fig. 1, curve 4) it is only 5%. In addition, it follows from a comparison of curves 1 and 2 in Fig. 3 that in the absence of expander BNF, i.e., during discharge in pure sulfuric acid solution (curve 1), the temperature dependence of the discharge capacity is less pronounced than it is in the presence of expander. Of course, the absolute values of the discharge capacity are higher in the presence of expander, both at room temperature and at low temperature. Figure 4 presents plots of the logarithm of passivation time against the logarithm of current density for smooth lead electrodes at different discharge temperatures. In this case the values of n in Peukert's equation are 1.2, 1.26, 1.3, and 1.4 at temperatures of + 20, 0, −20, and −40°C, respectively, i.e., coefficient n increases with decreasing temperature, just as found in the case of paste electrodes, but this change is less pronounced for smooth electrodes. This appears to be due to the fact that diffusion of sulfuric acid in the pores of the active mass also influences the discharge capacity in the case of paste electrodes.

It is seen when comparing the data concerning the effect of temperature on the discharge capacity of paste and smooth electrodes, that the electrochemical processes occurring at the lead/sulfuric acid solution interface even at a temperature of −40°C will yield up to 23% of the discharge capacity obtained at 20°C, and hence cannot be the chief cause for poor efficiency of lead ignition batteries at low temperature. In addition, this comparison shows that it is possible in principle to improve the discharge characteristics of the negative electrode in low-temperature service.

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ADSORPTION WAVES DURING THE REDUCTION OF ANTHRAQUINONE-1,5-DISULFONIC ACID

E. M. Savenko, D. S. Leibman, and G. A. Tedoradze

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Prewaves are developed quite often in reversible systems [1], but subsequent waves (postwaves) are an appreciably rarer effect during the cathodic polarization of Hg in solutions of organic compounds. An analysis of data available in the literature led Tedoradze [2] to conclude that in all the cases described, one has to do with false waves usually caused by a deblocking of the electrode surface. In a research project on adsorption waves, we examined the electrochemical behavior of anthraquinone-1,5-disulfonic acid (ADA); chronopotentiometry and polarography (the DME) as well as methods involving the measurement of differential capacity (C vs E curves) and the rotating disk electrode (RDE) were used in the work.

According to [3], ADA yields a well-defined postwave. We have found, however, that at $c \leq 10^{-4}$, this wave is due to a polarographic maximum, and that the beginning ascent of the postwave corresponds to the potential of the desorption peak of reaction product. This wave is not due to impurities in the ADA, since it is not detected at the RDE. At the DME, the principal wave of ADA reduction is preceded by a wave which has all the properties of adsorption prewaves. This observation removes the possibility that a postwave exists in the system being examined.

Appreciably more complicated is the behavior of above material at concentrations above 10^{-4} M. Under these conditions the prewave disappears completely, and so does the polarographic maximum on top of the limiting diffusion current. A distinct wave appears in its place, which is not seen at the RDE. Investigations aimed at elucidating the nature of this wave are in progress.

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