

TRANSFER OF LEAD IN THE POSITIVE ELECTRODE OF A LEAD BATTERY

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One of the reasons for the limited life of contemporary lead batteries is the slipping of the active material of the positive electrode. One of the authors has developed a theory [1] according to which the slipping is caused by the decrease in strength of the layers of lead dioxide agglomerate formed from crystals of lead sulfate at the surface of the spongy active mass during charging. From this it was suggested that as a result of cycling the positive plates there should be a transfer of lead from within the active mass to the outside which should lead to swelling of the active mass and the decrease in its strength. Thus movement of lead in the mass of the positive electrode could be one reason for slipping of the mass. Several possibilities for the transfer of lead in the plate may be discussed. There is firstly diffusion in the solid phase but this occurs extremely slowly. It is known from a number of papers [2-6] that both the self-diffusion of lead and its diffusion in solid salts only occurs at a rate of 10^{-9} to 10^{-12} cm²/day even at high temperatures. For example the coefficient of diffusion $D_{Pb/Pb} = 10^{-9}$ cm²/day at 165°, $D_{Pb^{2+}/PbCl_2} = 1.47 \cdot 10^{-12}$ cm²/day at 166°, $D_{Pb^{2+}/PbI_2} = 6.31 \cdot 10^{-13}$ cm²/day at 114°, and $D_{Pb^{2+}/PbS} = 9.7 \cdot 10^{-11}$ cm²/day at 7.33°. Hence it can be assumed that the diffusion of lead in the solid phase of the battery plates consisting of lead, lead dioxide, and lead sulfate should be so small at comparatively low temperatures that it can be ignored. Secondly, because of the solubility of PbO₂ in sulfuric acid solutions [7], particles of lead dioxide will be dissolved in the pores of the active mass and these may move under the influence of diffusion in the direction of the negative pole. Thirdly, it is possible to have diffusion and migration of ions of lead at the lead surface and at the surface of the PbSO₄ crystals. For the case which interests us this has not been described and is probably very small. Finally during discharging a saturated solution of PbSO₄ is formed [1] from which PbSO₄ recrystallizes at the sides of the pores. Subsequently during charging it is dissolved and redeposited on the electrode as lead dioxide. It is evident that during discharge of the battery there is a transfer of lead ions in the pores, which are full of electrolyte, from the inside outwards to where the concentration of lead ions does not exceed saturation.

In examining the literature data on the transfer of material in the lead battery it is necessary to stop at a paper by Seith [8] in which was studied the exchange between the positive (and also the negative) plates of a battery and the solution. Seith succeeded in demonstrating that exchange occurred between each electrode and the solution. Exchange was the greater at the negative plates where it had a kinetic character and occurred without application of the current not only at the surface but also in the pores of the plate. The results of this work were not confirmed in later work [9] in which transfer from the negative to the positive plate was not observed nor was the transfer of a noticeable amount of lead into solution. The authors also did not observe migration of lead along the surface of the plates. Some authors have used labelled atoms [8, 9], but in one of these papers the method of measuring the radio-activity of the plates was unsuitable for the observation of lead transfer, which brings the results obtained into doubt [9].

We have studied the transfer of lead within the positive plates of a lead battery, while it was working at room temperature, by the radioactive tracer technique. The lead isotope Pb²¹⁰ (RaD) was chosen as the tracer. It was introduced into the paste used for preparing the positive plates of a lead battery. The paste was thoroughly mixed. The specific radioactivity was 73 counts/min/mg. Three coated plates were made which were placed so that a plate with radiolead was placed between two inactive plates. All three plates were hermetically sealed at the edges with lead. Thus three-layered electrodes weighing 8.7 g were prepared. Their radioactivity was measured on both sides with a Geiger-Müller counter. The plates were cast and cycled in sulfuric acid solution (s.g. 1.2). Each cycle consisted of a 15 h charge at 20-30 mamp and a 3-4 h discharge at 100-120 mamp. The radioactivity of the plate was measured after the charge or discharge and then the plate was subjected to cycling again. The

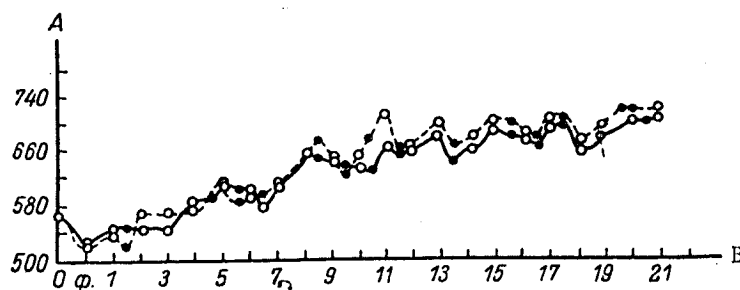


Fig. 1. Radioactivity of the outer sides of a three-layered electrode during cycling. A) Radioactivity (counts/min); B) number of cycles.

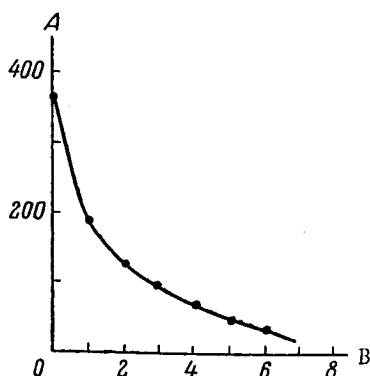


Fig. 2. Course of transfer of lead into the central inactive plate of a three layer electrode. A) Radioactivity (counts/min); B) number of section.

radioactivity was also measured after the plate had stood in the solution in the charged and discharged states. Since the transfer of lead occurred so slowly, the tests were carried out for 30-40 days. During this time 13 to 25 cycles were carried out. From the measurements of the radioactivity of the plate the rate and extent of movement from inside the plate to the outside was calculated. To determine the depth of the shift of lead into the inactive outer layers of the three-layered electrode the latter was separated into its constituents after the last cycle. Thin layers of the active mass were taken from the inner part of each of the outer inactive plates and the radioactivity of the plates were measured after removing each layer.

The results of the measuring the radioactivity of both outer sides of the three-layered electrode during cycling are shown in Fig. 1 (two curves). It is seen from the graph that the size of the radioactivity of the plate after formation is somewhat reduced which can be explained by the increase in the mass of the plate during conversion of PbO to PbO_2 . As a result of the increase in mass the absorption of the radiation of RaD in it increases and the measured radioactivity of the plate becomes smaller. The curves of Fig. 1 show that the radioactivity of the plates increases with the number of cycles. This indicates the movement of labeled lead from the inside to the outside of the plates. After 21 cycles the radioactivity of the plate rose to 220 counts in comparison with the activity of the plate before formation.

This is equivalent to the transfer of 0.1% of the lead from the active mass of the radioactive plate to the surface of the nonradioactive plate.

The activity of the plates did not change when they were kept in 8 N H_2SO_4 in the charged or discharged state for several days without current. These results show that the detectable diffusion of lead did not occur over several days without polarization. A definite transfer from within the active mass to the outside was observed during cycling.

The results of removing successive thin layers which show the course of the movement of the lead into the inactive outer layers of the three-layered electrode are given in Fig. 2. The average thickness of the slices was 0.17 mm. It is seen from Fig. 2 that the greatest quantity of radioactive lead is found in the first slice which is directly in contact with the radioactive layer. The rate of penetration is rather high since in 21 cycles the radioactive lead had penetrated to a depth of about 1 mm with an inactive thickness of about 2 mm. The outer side of the originally inactive plate appeared inactive after the removal of slices from the inner side which indicated that the radioactive lead had practically not left the plate. These experiments showed that the direction of transfer of the radioactive lead was from the center of the plate to the outside. This can be explained by movement of ions of lead (II) in the pores during cyclization as a result of diffusion consequent upon saturation of the solution during discharge. It is possible that somehow part of the lead simultaneously moves inwards. However there is no doubt that, because of the saturation of the solutions with lead sulfate at the surface of the active mass, the

movement of lead in the outer layer of the active mass during discharge is in an outward direction. After charging the solution outside is practically free from PbSO_4 . During charge of the plates the PbSO_4 outside the pores diffuses partially along the electrode and thus dendrites of PbO_2 can grow along the lines of force and lines of diffusion.

SUMMARY

1. It has been shown by the radioactive tracer method that a slow movement of lead occurs through the pores of the active mass of the positive plates of a lead battery during cycling. The movement only occurs during charge and discharge.

2. The occurrence of lead transfer provides a basis for the suggestion that the reason for slipping of the active mass is transfer of PbSO_4 in the electrolyte solution.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.