Some Preliminary Studies of Positive Grid Corrosion in the Lead-Acid Cell[1]

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ABSTRACT

Preliminary experiments in connection with positive grid corrosion in the lead-acid cell show: (a) PbO_2 and Pb undergo the solid phase reaction: $PbO_2 + Pb \rightarrow 2PbO$; (b) an intermediate film of PbO_2 is formed at the positive plate which does not cycle to $PbSO_4$; (c) the existence of an experimental relationship between grid growth and film formation; and (d) electrolyte concentration and time of cycle are important factors in corrosion under cycling conditions in constant-concentration acid. Explanations for these effects and the discharge and self-discharge reactions at the positive plate are offered.

Certain problems concerning the negative plate in connection with the concentration effect are briefly reviewed.

INTRODUCTION

This paper is an account of some preliminary experiments on positive grid corrosion. The experiments were not a complete study of any of the phenomena encountered; however, the results and discussion included may be of value in stimulating further thought and research on the problem.

The Solid Phase Reaction: $PbO_2 + Pb \rightarrow 2PbO$

During the course of work on the determination of the conductivity of PbO_2, it was observed that Pb-PbO_2 contacts gave poor and erratic conductivity. Because of this the following experiment was performed: powdered Baker's Analyzed PbO_2 was sandwiched between two freshly abraded, weighed lead sheets with proper contacts made to the lead so that the resistance of the combination could be determined. During the time necessary for making a measurement of the potential drop only, currents of about 15 ma/cm² (100 ma/in.²) were passed. The resistance was found to increase with time in a fashion shown in Fig. 1. After about 400 hours, the lead sheets were boiled in ammonium acetate solution and were found to have lost 8 and 19 mg/5.15 cm² (0.8 in.²). The experiment was repeated several times and although the reproducibility of the results was poor, resistance was always found to increase with time and the lead sheets always gave a weight loss of the same order of magnitude. It was considered that these results might be due to a solid phase reaction. In another experiment, granulated lead, freshly made by filing a lead block, was sealed in a glass bottle with the powdered PbO_2 and glass beads and rotated several days in a ball mill. The amount of lead used was in about two to one weight excess over the PbO_2 based on the above reaction. A sample of the starting material was subjected to x-ray analysis. The patterns of both components were easily identified. After six days the bottle was opened and the contents again subjected to x-ray analysis. The PbO_2 pattern was almost completely gone from the trace, while a very strong pattern for tetragonal PbO was present along with the Pb pattern somewhat reduced in intensity. It is concluded that PbO_2 undergoes a solid phase reaction with Pb, whereby the PbO_2 is reduced to tetragonal PbO while the Pb is oxidized to the same product.

A possible mechanism for this reaction based on the Volta effect is offered. Since PbO_2 has a conductivity approaching that of metals a contact potential may exist between the phases which is set up by migration of electrons from Pb to PbO_2. These electrons satisfy some of the Pb^{++} valence, releasing O^{--} for reaction. Reaction of Pb^{++} and O^{--} takes place at the interface and the PbO film continues to build up until its resistance becomes too high for passage of Pb^{++}, O^{--}, or electrons. This reaction offers a possibility for the corrosion mechanism at the positive grid in a lead-acid cell and could account for some of the self-discharge at the positive plate.

The process also offers a mechanism for the discharge reaction at the positive plate. During the discharge electrons are available from the negative plate as well as from the positive grid. They cross the Pb-PbO_2 interface and are distributed throughout the mass of the PbO_2 since it is a good conductor. At the solution interface O^{--} is released for the reaction with H^+ ions in the solution to form water, while the PbO formed at the surface of the particles reacts chemically with the H_2SO_4 of the electrolyte.

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At the negative plate Pb^{++} ions are released for reaction with the electrolyte.

Such a PbO$_2$-Pb contact potential could be an important part of the total cell potential.

Grid Growth

As a part of another investigation, corrosion studies were made on certain alloys by cycling samples in sulfuric acid solution about the positive plate potential. It was always observed, whenever the corrosion film had been built up for a week or so, that even after long discharge periods there existed a black, shiny, hard, brittle, adherent film underneath the outer PbSO$_4$ film. This film is a good electrical conductor and was shown by x-ray analysis to be PbO$_2$ containing small amounts of PbO. Evidently

better corrosion resistance than either the antimony alloy (6% by weight) or pure lead. Assuming that the mechanism given is responsible for growth, short-term tests were run in an effort to determine if there is a relation between corrosion and growth. These alloys were selected because the tin alloy corrodes at somewhat more than one half the rate for the antimony alloy and it has a tensile strength which is about one half that of the antimony alloy.

Samples of each alloy were cold-rolled to different thicknesses and cut into strips of two different widths. These strips were weighed and shorted to a positive plate and immersed to a depth of 17 cm (6.69 in.) in sulfuric acid (30 and 40% by weight). The system was cycled automatically twice daily for 20 days and the growth was measured from time to
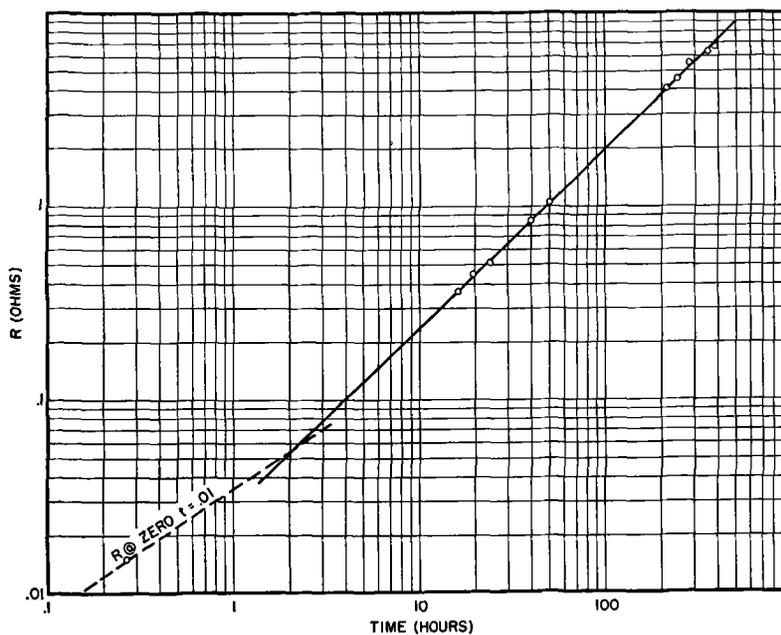

FIG. 1. Increase in resistance of a Pb-PbO$_2$ contact with time

this intermediate film was not being completely converted to PbSO$_4$ during the cycling process.

It has been suggested (1) that, since the PbO$_2$ film has a higher specific volume than the underlying metal, it may be subjecting the grid members to a tensile stress which might result in growth if the grid metal did not have enough strength or creep resistance. The hardness and adherence of the film is additionally indicative of the operation of such a mechanism which would be expected to be especially effective on soft alloys or pure lead[2].

The corrosion tests referred to above had been run on binary alloys of lead with tin and antimony. They showed that under the experimental conditions used a 4.5 per cent by weight tin alloy exhibited

[2] See, for example, the results of tests made on pure lead grids (W. H. Power, *et al.*, Naval Research Laboratory Report No. P-2908, January 9, 1947, Unclassified).

time. The percentage elongation is plotted against time in Fig. 2. At the end of the period the films were stripped and their weight losses determined. Assuming uniform corrosion over the whole length, the depth of corrosion of the samples was calculated. This figure was divided by the cross-sectional area of the sample and the result plotted against the per cent final elongation as shown in Fig. 3. This plot resulted in a straight line for the 4.5 per cent Sn alloy and may be roughly linear for the Sb alloy. A more careful study should establish the nature of these curves.

For purposes of discussion let it be assumed that the relationship is linear. Then by extrapolating the curves to zero per cent elongation it is found that the lines do not pass through the origin but have an intercept on the depth of corrosion per unit cross-sectional area axis. This is quite reasonable because
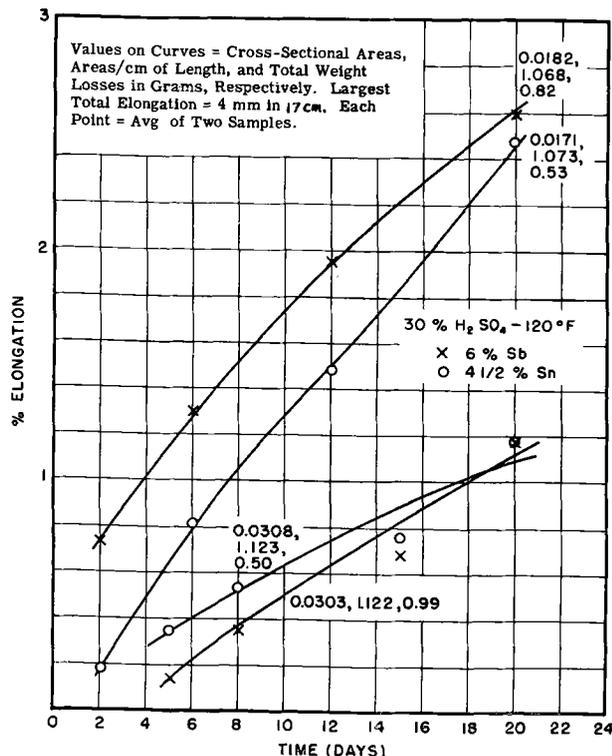
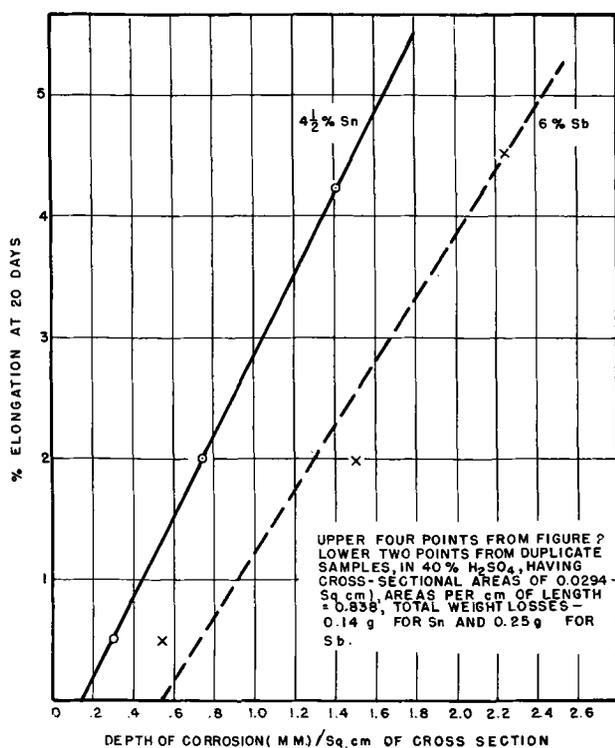FIG. 2. Rate of growth of 4.5% Sn alloy and 6% Sb alloy

FIG. 3. Relation between growth and film thickness and cross-sectional area.

there is a minimum tensile strength for elongation of metals and also a minimum load to induce creep. Furthermore, the slope of the Sn alloy line is greater than that drawn for the Sb alloy, which is again reasonable because these slopes should be related

to the tensile strength or the creep resistance of the alloys.

The growth factor should also be considered in conjunction with film thickening. Experimental cells sometimes fail in spite of the fact that corrosion of the positive grid has progressed to a relatively small extent. This could be due to lack of contact between the grid and the active material caused by grid growth and lack of film formation. Antimonial grids not only grow at a slower rate but form the grid film faster so that contact is maintained between the active material and the grid. Thus a grid of the 4.5 per cent Sn alloy should have its grid members spaced about twice as close as one made of the antimony alloy, because while it grows at about the same rate, the film thickens at about one half the rate. It should be pointed out that telephone batteries which had been on float for nine years exhibited appreciable looseness of the pellets in the positive grid structure, but actually gave satisfactory discharge characteristics (1), so that there may be other important factors involved. Nevertheless, further studies along these lines might be of considerable value in grid design.

The Effect of Electrolyte Concentration and Time of Cycle

The previous paper (2) has shown the importance of electrolyte concentration in the rate of PbO formation at lead anodes under constant potential conditions. To determine whether the effect also obtains under conditions of cycling potential, and to see if corrosion rates depend on potential conditions on charge and discharge, and time of cycle, the following work was done. An apparatus was constructed by means of which samples could be maintained, during cycling, at various constant charge potentials and various constant discharge potentials relative to a positive plate immersed in the electrolyte. The positive plates employed had sufficient capacity so that they were not polarized by currents of the magnitude drawn by the samples. The duration of the cycle could be varied between three minutes and forty-eight hours, and the ratio of charge to discharge time could be set at any desired value. The results of these tests will not be covered in detail. It is sufficient to state that considerable variation in corrosion rates was obtained under different conditions. In general, a combination of high charge and high discharge potentials and shorter cycling times favored more rapid corrosion.

Fig. 4 shows the results at various total times for different time cycles as a function of concentration for 4.5 per cent Sn alloy, Pb, and 6 per cent Sb alloy, all cold-rolled. This test was conducted at room temperature with charge potential at +0.25 and

discharge potential at −0.10 and 55 per cent of the time on the charge part of the cycle. These potentials are referred to the potential of the positive plate in the solutions concerned.

The tin alloy is shown to be more corrosion resistant than either Pb or Sn alloy under the conditions of the experiment. However, the most significant feature of these results is the effect of acid concentration on the corrosion rate. Increasing acid concentration from 10 per cent to 40 per cent results in decreased corrosion by a factor from 3 to 7 times. Thus it is shown, under certain cycling conditions
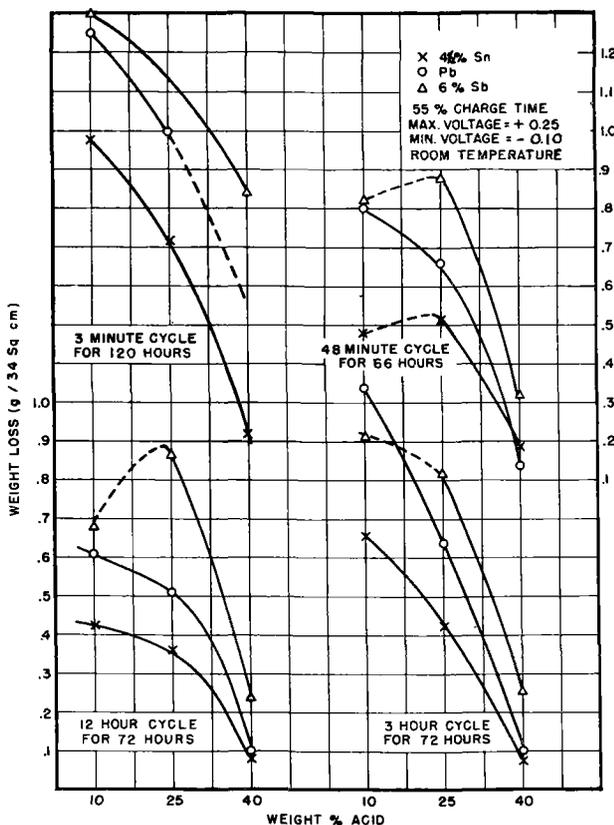

Fig. 4. The effect of acid concentration on corrosion of Pb and two alloys under various cycling conditions.

at least, that increasing concentration results in a decreased corrosion rate, just as it does under constant potential conditions.

Further examination of these data[3] shows that an increase in corrosion rate occurs as time of cycle is decreased. This is quite understandable when considered in connection with the previous data (2) where it is shown that the protective PbO_2 film is not established for one to eight hours or so, depending

[3] Log-log plots of weight loss vs. water activity show slopes ranging between about two and four. From this and the previous rate-activity data (2), it might be predicted that a study of corrosion during early PbO_2 formation will show a rate dependency as the fourth power of the water activity.

to a considerable extent on concentration and temperature. Therefore it should be expected that this factor will operate to a small or negligible extent for very short time cycles and to an increasingly large extent as time duration of cycle increases beyond one to eight hours, depending on conditions.

GENERAL DISCUSSION

As a result of this and the previous work (2) the following combination of mechanisms for corrosion at the positive lead grid is proposed. During charge, provided the potential does not become too high, a protective film of PbO_2 is built up more or less gradually at the lead surface. When the charge is stopped, or during discharge, electrons may move from the grid to the PbO_2 film, releasing O^{--} ions for formation of PbO at the Pb-PbO_2 interface. Furthermore, the PbO film becomes porous by fracture or recrystallization, whereupon the metal grid becomes available for reaction with the water of the electrolyte to form more PbO. Thus, on stand or discharge, corrosion of the grid may proceed by the two mechanisms more or less at the same time. At a pure lead grid corrosion during the charge part of the cycle should be slow, except during the initial period necessary to establish the protective film. Corrosion by the solid phase reaction would seem to be of considerably less importance in terms of rate than corrosion by action of the electrolyte through pores in the film, on the basis of the magnitude of the concentration effect.

Application of the concentration effect may prove to be of importance in extending battery life. However, these tests were all run at constant concentration, while in a battery concentration cycles over a considerable range. Thus, during discharge when potentials are shown to be most corrosive (2), water is being produced in the pores of the active material. Furthermore, during the first part of the charge the protective film may not be established and concentration of water in the pores is still at a comparatively high value, so that combination of these several factors may lead to a considerably smaller dependence of life on acid concentration in a cycling cell than might be indicated by the data obtained under constant concentration conditions.

Temperature cycling may also affect the corrosion rate, not only because higher temperatures speed up the rate of reaction, but also because such a cycle may promote cracking of the film thus contributing to its porosity.

On raising acid concentration, it is to be expected that self-discharge at the negative plate will be increased (3, 4), even for pure lead negative grids (5). However, it is indicated (5) that self-discharge is less at negatives with pure lead grids at high gravi-

ties, than at antimonial grids with lower gravities. Charging efficiency would also be expected to be decreased at the negative plate, leading to sulfation or hardening of the negative plate material. This is not necessarily a serious objection because it is expected that sulfated negative plates can be brought back (6, 7), especially if antimony can be excluded from the cell. The foregoing discussion is based on the assumption that the tests conform in a general way at least to conditions in a cycling cell. It also should be considered that even the longest of these tests was of short duration compared to normal battery life.

SUMMARY

PbO_2 undergoes a solid phase reaction with Pb to form tetragonal PbO. A mechanism involving the Volta effect is proposed. A contact potential between Pb and PbO_2 may be an important part of the cell potential and explain self-discharge and the discharge reaction at the positive plate.

An intermediate film of PbO_2 is formed by the corrosion process which does not cycle completely to $PbSO_4$. Because of this it retains its compact nature and may in large measure be responsible for slowing down grid corrosion.

Grid growth appears to be proportional to the depth of corrosion after an initial period. The initial period and the rate of growth are probably characteristic of the tensile strength or creep resistance of the metal.

Electrolyte concentration and cycle time are shown to be important factors in the corrosion process under constant-concentration conditions. These effects are discussed in terms of a cycling cell.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1951 issue of the JOURNAL.

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