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The Lead Calcium Battery

Part 4 - Comparison of Lead Calcium and Lead Antimony Cells in Float

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Previous Reports in this Series

"Part 1—Introduction and Background," J. Burbank and C. P. Wales, NRL Report 5693, Nov. 22, 1961

"Part 2—Small Portable Cells," J. Burbank and C. P. Wales, NRL Report 5770, May 2, 1962

"Part 3—Submarine Cells," J. Burbank and C. P. Wales, NRL Report 5773, May 29, 1962

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Four small portable lead acid cells were tested in a float cycle routine. Three of these cells had lead calcium alloy and one had lead antimony alloy in the positive grids. Otherwise the cells were identical. They were all pasted by the same manufacturer under the same conditions and with the same paste formulation. All cells had lead calcium negatives. Cells with the lead calcium alloy positive grids failed early in the test accompanied by excessive softening of the positive active material, as they invariably did in the earlier tests in this series of investigations.

The presence of antimony in the positive grid caused depolarization of the positive plate in the floating cell, as well as the usual depolarization of the negative on overcharge. The active material of the antimonial cell remained firm for the duration of the tests, and this cell had not failed at the conclusion of the investigation. X-ray diffraction showed that the antimonial cell's positive plate contained more α PbO_2 than the calcium cells, both before and after testing.

Electron microscopic examination of the positive active material showed that the antimonial cell contained much prismatic material with many intricate clusters of complex crystals. The failed calcium cells, although pasted with the same formulation, showed only nondescript nodular PbO_2 particles. The stability of the paste is believed to be related to the morphology of these particles.

It is concluded that the presence of antimony in the positive grid caused the prismatic crystallization of the active material and promoted formation of α PbO_2 because this was the only known difference in the two kinds of cell. The mechanism of the action of antimony is probably the preferential adsorption of one or both of the antimony ions SbO_2^+ or SbO_3^- on the growing surface of the PbO_2 crystal causing a development of holohedral faces; branching, twinning, and dendritic habits; and formation of α PbO_2.

INTRODUCTION

The lead calcium battery has been installed in recent years aboard submarines in float service. The cells failed early in life when they were maintained in a true float system, and it has been necessary to modify the method of use of these cells in order to obtain satisfactory performance. The failure in float resulted from an excessive softening of the positive active material and electron microscopy of the failing positive paste showed that it was essentially nondescript globular masses of PbO_2. These had no cohesion between individual particles, and the paste became progressively softer and washed from the grid (1-3).

Certain specific small size calcium cells were successful in a float test at this Laboratory but these were not made by the manufacturer of the submarine size cells. The particle morphology of the positive active material in these successful cells was found to be prismatic and there were many complex crystals that tended to interlock to form a mechanically stable positive active mass (3-5).

It is generally accepted among battery users that cells in float installations have a prolonged life expectancy because a float system just compensates for internal spontaneous losses in the cells (self-discharge), the active materials are kept in the fully charged condition, and the positive grid metal is maintained at a potential where it is anodically passivated. Tests at this Laboratory on thin plate lead antimony cells have shown that float extends the life compared to cycle and stand routines (6). The lead calcium cell was developed especially for float operation (7-9), and it was therefore most unexpected to have this kind of cell fail when installed on the sumbarines in float circuitry. The manufacturer of the failing cells was well experienced in supplying submarine storage batteries with lead antimony grids, and the failure cannot be attributed to any lack of technological "know-how." The common submarine fleet installation is not a float situation,

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and it was of interest to test an ordinary fleet-type antimonial cell from the same manufacturer under the same conditions that produced failure in the lead calcium cells. This report describes the results of this study with an antimonial cell.

EXPERIMENTAL

The cells used in this investigation were fabricated by cutting standard full-sized submarine cell plates from a single manufacturer, and the only difference between them was that one positive grid was a standard antimonial lead alloy, whereas the other grids were lead calcium alloy. The pasting and forming were carried out by the manufacturer under reputedly identical conditions. Portions of lead calcium alloy negative plates were used in all cells.

Four small cells were assembled, each having one positive and two negative plates, with standard submarine cell glass mat retainers and separators cut to size. Two sets of two cells each were run in series. The power supply, controller, and auxiliary electrode circuit of the battery analyzer of Work and Wales (10) were used to test the cells. A mercury, mercurous sulfate reference electrode in each cell was used to measure plate potentials with the plate and cell voltage and the current monitored continuously.

The cells were assembled in plastic cell cases and filled with 1.200 sp gr H_2SO_4. Charging was carried out according to the manufacturer's standard instructions, and following the initial charge, the specific gravity was adjusted to 1.250-1.260.

The cells, which were all positive plate limited, were given several cycles to develop capacity and then placed on the float cycle routine known to produce rapid failure in the lead calcium submarine cells (2,3). These tests are summarized in Table 1.

During the tests, the positive plates were inspected visually at intervals, and at the conclusion of the tests, the positive active material was examined by electron microscopy.

For the electron microscopic examination, samples of the paste were extracted with saturated ammonium acetate solution to remove any divalent lead compounds present. Drops of the slurry of extracted material were gently touched to the surface of distilled water in a 10 in. crystallizing dish. The particles floated out across the surface and were picked up on parlodion-covered specimen screens of the electron microscope. After drying, the particles were replicated with evaporated carbon (11).

Following replication, the parlodion supporting films were removed by solution in acetone. The The PbO_2 was dissolved in dilute HNO_3 containing H_2O_2, and the carbon replica was rinsed by floating on water. After air drying, the replicas were photographed in the electron microscope, model RCA EMU-2B.

The active materials from both kinds of positive plate were examined by x-ray diffraction using a General Electric XRD-5 X-Ray unit and copper radiation. The pastes were examined before and after the float cycle tests.

RESULTS AND DISCUSSION

Table 1 shows the capacities obtained from the cells, and also indicates that the cells with lead calcium alloy grids failed after a relatively very short test duration. The 90% fall in cell capacities, Curve B, Fig. 1, illustrates a typical failure of calcium cells in float installation. Failure was due to the positive plate in every case.

The capacity of the antimonial cell, Curve A, Fig. 1, changed hardly at all despite the fact that it did not receive the overcharge normally used to maintain antimonial cells and, this behavior was not unexpected in light of earlier work (6).

It had not been known with certainty whether the identical paste would stand up in an antimonial cell in float use but the results of the tests reported here show that the same paste in an

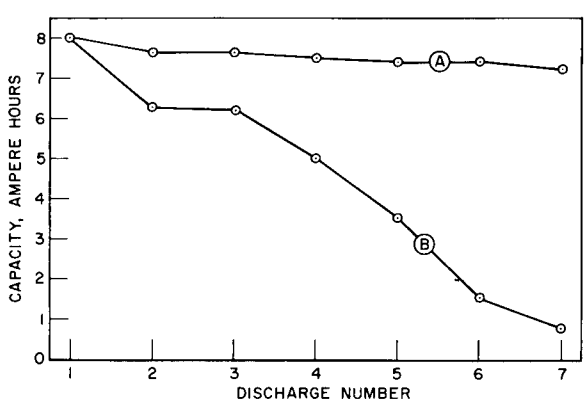


Fig. 1 - Change in cell capacity in shallow cycle test. Curve A - antimonial cell; curve B - lead calcium cell.

TABLE 1
Summary of Tests and Results

No.	Capacity Discharge (amp-hr)		Charge (amp-hr)	Float Cycles (No.)	Remarks
	Calcium Cells 1 and 2				
	1	2			
1	> 8.47	8.47	10.57	10*	Constant voltage charge with constant current overcharge
2	> 8.37	8.37	8.05	7	Float charge at 2.24 v/cell
3	> 7.65	7.65	7.53	9	Float charge at 2.24 v/cell
4	> 7.15	7.15	7.25	5	Float charge at 2.24 v/cell
5	> 7.13	7.13	7.25	7	Float charge at 2.24 v/cell
6	4.73	6.23	7.22	–	Positive active material was soft and mushy
	Calcium Cell 3				
1	8.00		8.40	8†	Float charge at 2.24 v/cell
2	6.30		7.36	9	Float charge at 2.24 v/cell
3	6.27		7.92	14	Float charge at 2.24 v/cell
4	5.03		8.37	12	Float charge at 2.24 v/cell with constant current overcharge
5	3.56		3.69	9	Float charge at 2.24 v/cell
6	1.53		4.53	9	Float charge at 2.24 v/cell with constant current overcharge
7	0.80		–	–	Test discontinued. Positive plate was soft and mushy.
	Antimonial Cell				
1	8.00		8.40	8	Float charge‡
2	7.60		9.17	9	Float charge
3	7.60		7.92	14	Float charge
4	7.50		8.37	12	Float charge
5	7.40		7.36	9	Float charge
6	7.40		7.70	9	Float charge
7	7.30		–	–	Test discontinued. Positive plate was firm and in good condition.

*One float cycle in the tests of calcium cells 1 and 2 comprised a discharge of 0.58 amp-hr at 1.16 amps, recharge by float with interim float. One cycle was given each work day until the next succeeding capacity discharge.

†One float cycle in the tests of calcium cell 3 and the antimonial cell comprised a discharge of 1 amp-hr at 2 amps, recharge by float with interim float. One cycle was given each work day until the next succeeding capacity discharge.

‡Calcium cell 3 and the antimonial cell were in series for these tests, and cell 3 was used as control for float and constant voltage charges. The effect of antimony on the cell and plate voltage could be followed in direct comparison to the antimony-free calcium cell. When required, the two cells were separated and handled individually.

antimonial cell did not fail as rapidly as in the calcium cells and gave no indication of incipient failure at the time the calcium cells failed and the tests were terminated.

When the cells were opened for inspection, the calcium positives were messy to handle; PbO_2 smeared readily over glass mats, paper towels, and glass rods used as probes; and enough washed off to heavily discolor the electrolyte. In contrast, the antimonial positives were cleaner, the glass mats were white and clear, and some PbO_2 wiped off on paper towels used to handle the wet

plates and the glass probes but not enough floated away to cause even a noticeable discoloration of the electrolyte. To be sure, the wet working positive plate of any lead cell is softer than the same plate dried, and PbO_2 can usually be smeared from the surface; however, the totally mushy condition of the failing calcium positive is much more pronounced and the softening proceeds through the thickness of the plate until the entire active mass may be washed out with a stream of water (2,3).

As far as is known, the sole difference between the positives in these cells was the presence of antimony in the grid metal. It is concluded that this antimony inhibits or prevents the softening of the paste.

The role of antimony in the lead acid cell has been appreciated by the battery industry for many years but it also gives rise to deleterious side effects in the cell. These have been tolerated because of the following beneficial effects: antimony hardens the grid alloy and improves castability of the melt; antimony minimizes grid growth by distributing corrosion across the body of the grains, relieving attack at the grain boundaries (12-16); and this present work shows that antimony aids in retention of the positive paste, hence preserving cell capacity.

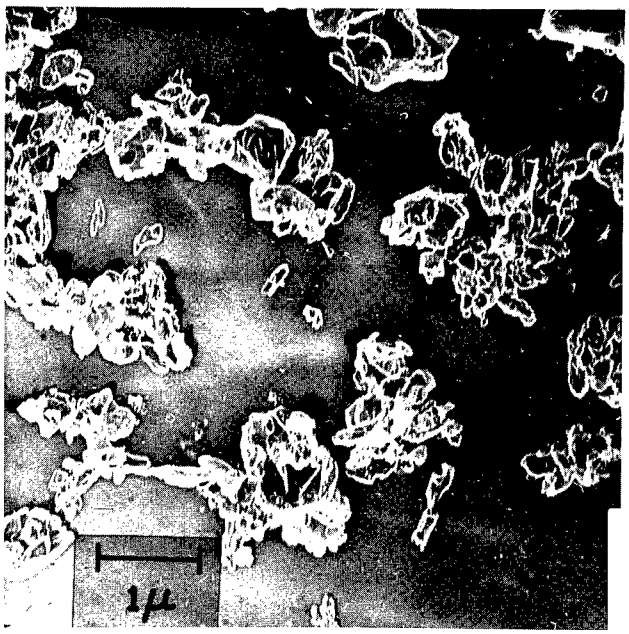
Antimony has a low hydrogen overvoltage which causes self-discharge of the negative plate. If sufficient antimony accumulates on this plate, it may not charge at all because all the current will go to generating hydrogen and little or none to converting $PbSO_4$ to Pb. This is the major disadvantage to having antimony in the cell. However, it has also been shown that antimony causes self-discharge of the positive plate, and its effect on polarization of grid metals has been previously pointed out (7-13). In addition, the evolution of the poisonous stibine is a decided drawback to the antimonial cell when it must be charged in confined spaces such as aboard submarines (17).

In this work with the antimonial and calcium cells, the calcium cell was used for voltage control (Table 1) in order to determine the electrochemical effects of the antimony. The migration of antimony in the lead acid cell was studied by means of radioactive isotopes and it was shown that the antimony accumulated to a significant extent in the positive active material (14,15). In this prepresent study, the presence of antimony in the positive grid caused 20-70 mv depolarization of the positive during the float periods (Table 1). A similar depolarization was observed in overcharge at constant current. However the positive plate voltages relative to the mercury, mercurous sulfate reference electrode of both the antimonial and calcium cells were identical during charge and discharge, and no electrochemical effect of the antimony was observed when the cells were under these conditions.

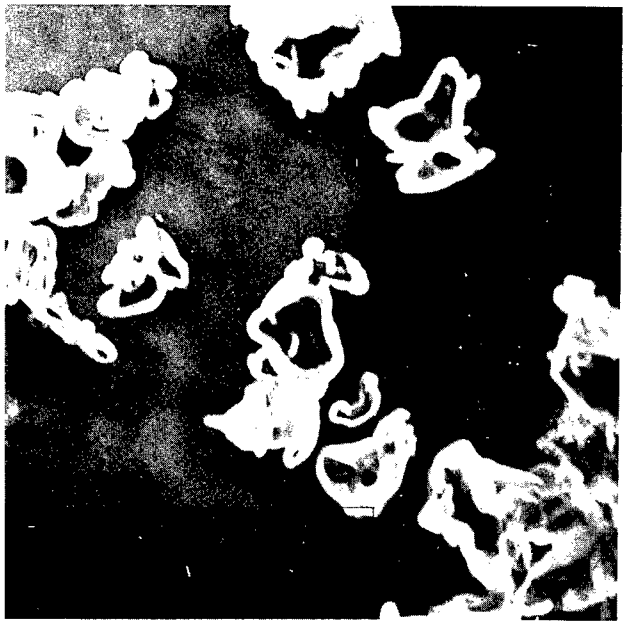
Electron micrographs of the positive active material showed that in the failing lead calcium cells, the individual particles were nondescript globules both before and after failure (2-5). Typical examples are shown in Fig. 2. In other related studies at this Laboratory of satisfactory antimony-free cells, the positive paste was shown to be made up of prismatic crystals and the stability of this paste was attributed to this morphology (3-5).

The positive paste from the antimonial cell used in this work was found to contain large amounts of prismatic material, typical examples of which are shown in Fig. 3. It should be emphasized that this material was stated by the manufacturer to be identical with the paste used in the calcium cells that has little or no prismatic form (Fig. 2). It is therefore concluded that the presence of antimony in the grid has dramatically affected the morphology of the PbO_2 particles formed in the paste. The electron micrographs indicate that the prismatic material forms extensive complex clusters that appear to be examples of multiple twinning or parallel growth. These imparted mechanical stability to the positive active material. The prismatic morphology observed by electron microscopy is believed to be necessary to maintain the firm texture of the positive plates in the lead cell. In other cells, this morphology observed by electron microscopy was accompanied by a sponge-like network of harder material, visible in the magnification range of the optical microscope (18); however, when the new, as-received antimonial positive plate used in this work was examined by the same techniques, no such network was visible (19). The intricate form of the crystals (Fig. 3) does suggest, however, that it may be possible for them to form a submicroscopic interlocking network. This would, of course, not be visible in the optical microscope.

The x-ray diffraction examination of the positive active materials showed that the paste

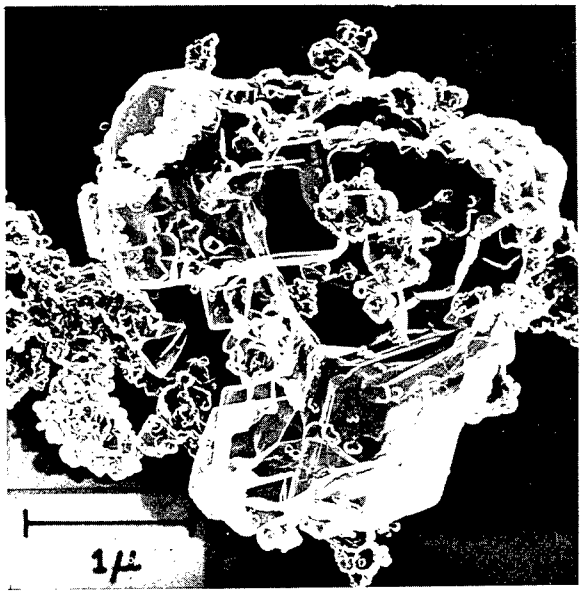


(a)



(b)

Fig. 2 - Typical examples of nondescript nodular PbO_2 particles. These particles were taken from lead calcium cells that consistently failed in float installations. (Reduction in printing approximately 40%.)

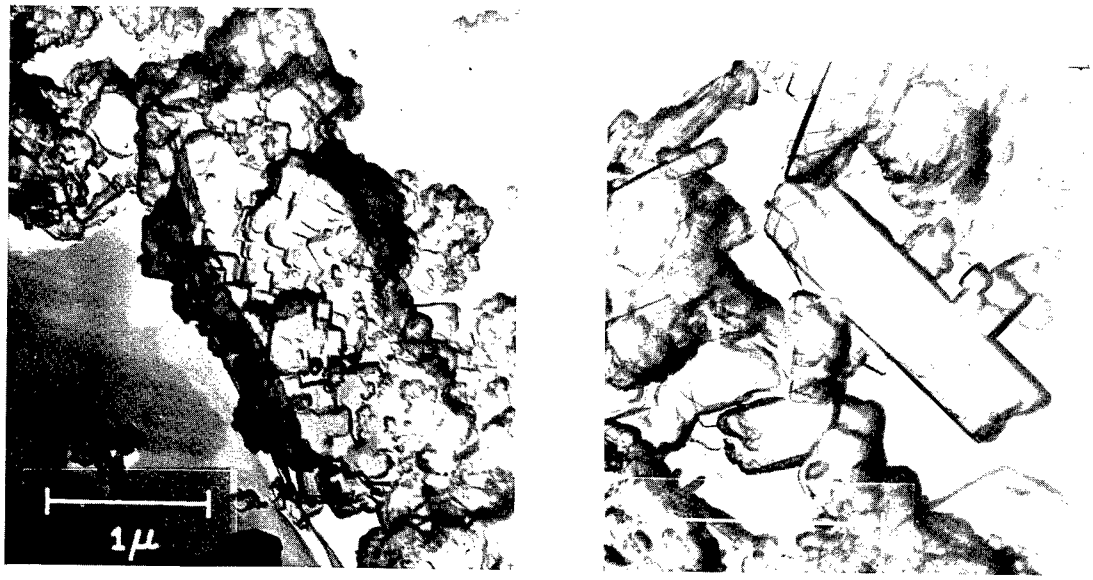


(a)

(b)

(c)

Fig. 3 - Typical examples of prismatic PbO_2 particles from lead antimony positive plates. The positive plate containing particles such as shown here was successful in the shallow cycle test and maintained its firm texture and capacity. (Reduction in printing approximately 50%.)



(d) (e)

Fig. 3 (Continued) — Typical examples of prismatic PbO_2 particles from lead antimony positive plates. The positive plate containing particles such as shown here was successful in the shallow cycle test and maintained its firm texture and capacity. (Reduction in printing approximately 50%.)

from the antimonial cell contained appreciable amounts of both α and β PbO_2, whereas the paste from the lead calcium cell contained a very large preponderance of β PbO_2 and only a very small amount of α PbO_2. At the conclusion of the tests, the amount of α PbO_2 in both types of plate had decreased, but a considerable amount of α PbO_2 was still present in the antimonial positive. Simultaneously, the amount of β PbO_2 had increased in both plates.

It has been suggested that there is a relation between α PbO_2 and positive paste retention in the lead acid cell (18). The presence of a large amount of α PbO_2 in the antimonial active material and the performance of the antimonial cell in the tests reported here lend further credence to this speculation. It is concluded from this study that antimony in the grid metal acts to promote the deposition of α PbO_2 in the active material during plate formation, possibly by the same mechanism as cobalt ion (20). The presence of α PbO_2 was accompanied by a firmer texture of the paste, by prismatic crystal habit, and by retention of cell capacity in the shallow cycle tests reported here. In the antimony-free calcium cells only a small amount of α PbO_2 was present, the paste softened and lost capacity in the shallow cycle tests, and the paste contained few, if any, prismatic crystals.

On the basis of these observations, it is concluded that the antimony exerts the direct and beneficial influence of causing prismatic PbO_2 formations in the positive active material. The mechanism of this action remains to be studied. However, it is likely that preferential adsorption of a soluble antimony species on the growing surface of the PbO_2 crystal may control the morphology. Antimony forms the ions SbO_2^+ and SbO_3^- at positive plate potentials (21). Metallic antimony itself becomes passivated by a heavy layer of Sb_2O_5* at this potential when current is flowing, but this oxide is rather soluble. The determinative influence of soluble species on electrodeposits is well known (20). This work indicates that the presence of antimony in the grid metal influences the morphological development of electrochemically formed PbO_2 in the positive plate of the lead acid cell, but the precise mechanism of this action remains to be clarified.

*Identified by x-ray diffraction of the anodic coating formed on antimony metal in H_2SO_4.

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