

**LEAD-CALCIUM ALLOY FOR LEAD-ACID BATTERY —EFFECT OF ADDITIVES ON CYCLING***R JANAKIRAMAN, P G BALAKRISHNAN, M DEVASAHAYAM and S PALANICHAMY*

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Two volts, three plates lead-acid cells with lead-calcium alloys were studied. Pure lead, lead-silver and antimonial lead grids were also included for the purpose of comparison. Except the latter alloy, all others showed poor life cycle performance. Hence to improve the cycle life of lead-calcium alloy cells, additives like antimony sulphate to the positive active material and phosphoric acid to the electrolyte were added separately and in combination. The performance with the additives was equivalent to that of the lead- antimony alloy cells.

**Key words:** Lead-calcium cells, additives, improved cycle life

**INTRODUCTION**

The conventional lead-acid battery has its grids composed of an alloy of lead and antimony. The addition of antimony to lead improves the fluidity of the metal and the tensile strength of the grid. The antimonial cell has a long cycle life. However, during overcharge the grid is anodically attacked and the antimony passes into solution. This is reduced at the negative plate and also it is deposited on the surface because of the difference in the electrode potentials of lead and antimony [ 1 ]. The hydrogen overpotential of antimony being lower than that of lead, this causes self-discharge of the spongy lead with the evolution of hydrogen [ 2 ]. This is the reason for the necessity for the proper maintenance of the battery.

The efforts to develop a maintenance-free battery led to the replacement of antimony by several metals such as lead-calcium [ 3 ], lead-calcium-tin [ 4 ], lead-antimony-cadmium [ 5 ], lead-arsenic [ 6 ], selenium and sulphur [ 7 ], lead-silver, lead-calcium-silver [ 8,9 ], cobalt [ 10 ] and other alloys. The addition of arsenic has been claimed to improve oxidation resistance and castability. Selenium and sulphur are supposed to improve castability. The lead-calcium alloy has been the most widely used alloy in many antimony-free grid batteries [ 11,12,13 ]. But there have been two major problems with the lead-calcium cells. Shedding of the active material has often led to a premature failure. Formation of high resistance films at the grid-active material interface has retarded normal charge acceptance [ 1 ]. Many researchers have confirmed that the failure of antimony-free cells results from the loss of adhesion of the positive active material to the grids [ 14,15 ]. The material in these cells became softer and the capacity began to fall away, but the material in the antimonial cell remained firm throughout the tests and it maintained its capacity. Intrinsic examination showed that the active material in the antimony-free cell had assumed a nodular crystalline structure, whereas in the cell with antimony, the lead dioxide took the form of massive prismatic conglomerates with clusters of interlocking crystals, which appeared to impart mechanical strength giving good cycling lifetimes. It was also recorded that the active material in the antimonial cell contains a higher ratio of alpha to beta lead dioxide [ 15,16 ].

In many of the lead-calcium cells the negative plates were found to be intact and there was no sign of corrosion of the grid. The positive active material had however softened. The alpha lead dioxide is known to contribute towards the life of the battery and the beta lead dioxide to its capacity [17]. The presence of antimony as cited above increased the alpha lead dioxide content in the plate.

Several additives such as phosphoric acid [18], antimony trioxide [19], strontium sulphate [20] etc. have been incorporated to improve the performance of lead calcium cells. It is proposed that the addition of phosphoric acid leads to the absorption of phosphate on the lead dioxide, modifying its crystal growth. The lead dioxide formed in the presence of phosphate is not easily reduced to lead sulphate and therefore the positive grid does not become insulated from the active material. These additives are supposed to bring about the beneficial effect of antimony. We have presented here our work on the performance of some antimony-free cells and the effect of antimony sulphate and phosphoric acid on their performance, separately and in combination.

**EXPERIMENTAL**

Lead-calcium alloy (0.08% Ca) and lead-silver (0.1% Ag) alloys were prepared thermally in an electric furnace with proper precautions to prevent oxidation of metal. Lead-antimony (5.5%) alloy was prepared by the usual method. Pure lead ingots (99.99%) were used for alloy preparations. Cells were fabricated with one positive plate and two negative plates. About 40 ml of 1.280 sulphuric acid was used as electrolyte in each cell. Microporous PVC separators were used. Grey oxide, of lead was used for paste preparation. 0.1% w/w of oxide, antimony sulphate was added to the concerned positive paste mix. All negative pastes contained 0.15% w/w carbon black and 0.3% w/w BaSO<sub>4</sub>. 1 ml of phosphoric acid (AR) was added to the electrolyte of the cells which were to be studied in its presence, at the time of initial charging. The capacity of these cells were taken as the average of the first three cycles at 20 hr rate. The cells were discharged at 5 hr rate (70 percent of 20 hr rate capacity) and charged for 18 hours at a current of one third of the discharge current.

Capacity test at 5 hr rate was carried out after every 5 cycles. Discharge was stopped when the cells reached 1.75V. Cycling test was stopped when the cell reached 75% of its initial capacity. The capacity of the cells were around 2 Ah depending on the active material content.

## RESULTS AND DISCUSSION

The life cycle tests on the cells with pure lead, lead-antimony, lead-calcium and lead-silver cells are shown in Fig. 1. The figure shows that lead and lead-calcium grid cells have comparable cycle life. But the antimonial cells have more than twice the number of cycles than the others. The active material in the antimonial cell was hard and firm. But in the lead-calcium cells, it was soft and these cells had lot of sediments. For the study with additives, only the lead-calcium cell was selected. One batch of cells was studied with antimony sulphate in the positive active material. The second batch had phosphoric acid added to the electrolyte and the third batch had antimony sulphate in the positive plate and phosphoric acid in the electrolyte. These results are shown in Fig. 2.

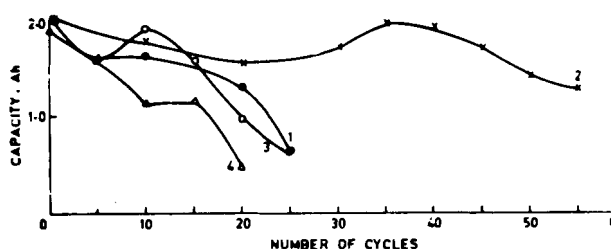


Fig. 1: Life cycle test results of lead-acid cells with different grid alloys: 1. ● --- ● Pure lead 2. × --- × Lead-antimony 3. ○ --- ○ Lead-calcium 4. △ --- △ Lead-silver

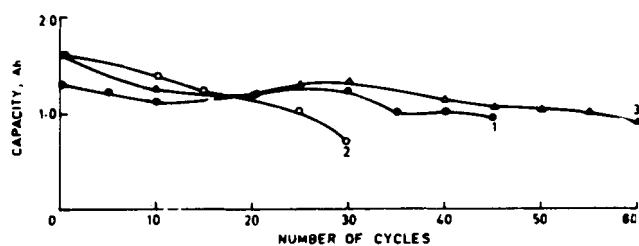


Fig. 2: Life cycle test results of lead-calcium cells with additives 1. ● --- ● Cell with phosphoric acid in electrolyte 2. ○ --- ○ Cell with antimony sulphate in positive plate 3. △ --- △ Cell with phosphoric acid in the electrolyte and antimony sulphate in the positive plate

In all cells with additives, the capacity reduction occurred upto the 5th cycle and then it remained stable. Here also the cell with antimony sulphate alone in the positive plate showed a poor

performance. But the effect of phosphoric acid alone is somewhat better ( curve 1 of Fig.2). The performance of the cell with both additives is much better as the life cycle compares well with that of the antimonial cell. As we have seen earlier, the addition of phosphoric acid prevents the hard resistant film formation between the grid and the active material. The lead-calcium grid has a tensile strength equivalent to that of antimonial cell [8]. Now the cycle life also is equivalent to that of antimonial cell. The active material in the cell with additives was firm and it had negligible shedding. The plates were very strong and absence of buckling was also observed. The shelf life of these cells is also expected to be good as it inhibits the rate of self-discharge reaction [21] and hence this could be a very good step towards the attainment of a maintenance-free battery.

## CONCLUSIONS

It is concluded that lead-calcium alloy cells with phosphoric acid in the electrolyte and antimony sulphate in the positive active material not only give good performance with regard to life cycle but also eliminate the problem of self-discharge caused by antimony.

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