

EFFECT OF VARIOUS GRID ALLOYS ON THE PERFORMANCE OF FLOODED LEAD ACID CELLS

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The conventional lead-acid batteries contain antimony as the alloying element that poisons the negative plate thereby facilitating premature evolution of hydrogen gas from the surface of the negative plate requiring periodical maintenance by way of adding distilled H₂O. In order to eliminate these effects, either low antimony - low cadmium or antimony free alloys are employed resulting in low maintenance or maintenance-free batteries that are presently in use in large quantities for various applications. In this paper, the authors compare the performance of flooded lead - acid cells with grid substrates containing Pb- low Sb -low Cd, Pb-Ca and a combination of both for positive and negative plates by subjecting the assembled cells at 5 hr discharge rates at different temperatures.

Keywords: Grid alloy and lead-acid cell.

INTRODUCTION

The conventional lead - acid batteries employ lead - antimony grid substrates for holding the active mass and also for current collection. Though antimony has favourable effects when alloyed with lead, it exerts undesirable influences on the negative plates of a lead - acid battery by migration from positive grid substrate during cycle service of the battery. Due to the poisoning of the negative plates by the migrated antimony, the negative plates are more prone to self-discharge because of the formation of local galvanic cells. This results in the loss of capacity of the negative plates. Moreover, the migrated antimony lowers the hydrogen over - voltage on lead thereby giving rise to the premature evolution of hydrogen gas. As a consequence of this, water that is present in the electrolyte is lost especially during overcharge. Because of this, it becomes always necessary to maintain the level of the electrolyte by way of "TOPPING UP" procedures [1]. This way of maintaining the level of the electrolyte is very difficult in various situations. The above facts necessitated the development of newer alloys that contain lesser amount of antimony or completely antimony free alloys so that the unfavourable effects of antimony as described above can be overcome to a greater extent. The newer alloys are lead - low antimony - low cadmium and lead-calcium-tin alloys. The batteries employing such alloys are classified as either low

maintenance lead-acid batteries or completely sealed maintenance free batteries. The working principle of completely sealed maintenance - free lead-acid batteries is described elsewhere [2]. In the case of sealed MF batteries the electrolyte is immobilized either by gelling it or getting it absorbed in absorbent glassmat (AGM) separators. Factors such as composition of the grid alloy, charging regime, overcharge factor etc. all exert well documented effects on the battery performance [3]. Though many studies have reported the effect of grid alloy composition on the performance of the cells, few have considered the role of Cd in the alloy. The literature available in this area is generally incomplete and this invites a detailed investigation on its effects on the performance of the cells. In the present investigations attempts have been made to study the influences of these alloys containing suitable composition for the conventional lead-acid cells wherein the electrolyte is in the flooded form. The performance of the cells with different substrates is very well compared in terms of the cell capacity at 5 hr rate discharge at different temperature.

EXPERIMENTAL

Table I provides a summary of the composition of the alloys that were employed in the production of the grids for the plates. Alloys of suitable compositions were prepared using lead, antimony, cadmium and calcium of 99.99% purity and grids were cast out of these alloys by gravity casting process.

TABLE I: Alloys employed in the production of grids

Cell No	Grid Constituents	
	Positive	Negative
1.	Pb-Ca 0.07% Wt - Sn 0.35% Wt	Pb-Ca 0.07% Wt
2.	Pb-Sb 1.50% Wt - Cd 1.50% Wt	Pb-Sb 1.50% Wt - Cd 1.50% Wt
3.	Pb-Ca 0.07% Wt - Sn 0.35% Wt	Pb-Sb 1.50% Wt - Cd 1.50% Wt
4.	Pb-Sb 1.50% Wt - Cd 1.50% Wt	Pb-Ca 0.07% Wt - Sn 0.35% Wt

The grids of both the plates measured 6.35 x 4.3 x 0.3 cm in dimension. Plates of both the polarities were prepared by pasting a mixture containing grey oxide, carbon black and sulphuric acid for the positive plate and the negative paste mix contained expander materials in addition to the above stated materials. The entire pasting process was followed by curing and electrochemical formation resulting in fully formed plates. Cells were then assembled, each cell consisting of one positive plate and two negative plates and insulated by PVC separators. When fully assembled and initial charged each cell contained a substantial excess of 1.280 sp gr sulphuric acid and in all the cells the weight of the active materials was found to be almost equal. Cells were then subjected to discharge/charge cycles at 5 hr rate discharge and 20 hr rate charge and the cells were then assessed for their performance at 303 K, 292 K, 283 K and 273 K as shown in Figs. 1 to 4 respectively.

RESULTS

Cells containing substrates with Pb-Ca-Sn alloy exhibit higher capacity than all the other cells at 5hr rate discharge performance at 303 K, 293 K and 283 K. As the temperature is decreased it is observed that the capacity of the cell with Pb-Ca-Sn alloy substrate falls rapidly and as the temperature reaches zero it is observed that the capacity of the cell with Pb-Ca-Sn alloys shows a lower capacity than all the other cells. From the curves drawn, a regular trend is noticed in the behaviour of the cells at 303 K, 293 K and 283 K. At these temperatures, the capacity of their cells with Pb-low Sb-low Cd is equal to the cell with a hybrid combination in which Pb-Ca-Sn alloy serves as the positive grid substrate whereas the hybrid cell with Pb-low Sb-low Cd alloy as the positive grid substrate shows the least capacity. At 272 K cells with hybrid combinations exhibit higher capacity than the other cells. Of the two hybrid combinations, cell with Pb-low Sb-low Cd as positive grid has a higher capacity than the other one.

DISCUSSION

The nucleation and growth mechanism for the discharge reaction with different alloys are very similar namely a two dimensional multilayer growth with progressive nucleation [4]. The higher capacity exhibited by the cell with Pb-Ca-Sn grid substrates for both the grids at 303 K, 293 K and 283 K is supported by the fact that the paste of these grid substrates is found to contain a larger proportion of β -PbO₂ with very small amount of α -PbO₂ [5] whereas the paste from antimonial cells contains appreciable amounts of both α & β PbO₂. The observed behaviour of Pb-Ca-Sn cell is in contrary to the results observed by Hans Tuphorn [6]. The experimental result is further supported by the fact that Pb-0.1% Wt Ca alloy exhibits conductivity 20% higher than that of Pb-Sb alloy [7]. This results in the higher utilization of the electrode active mass on account of an improvement in the current distribution within in the electrodes [8]. Moreover, Pb-Ca batteries exhibit a higher counter voltage when compared with conventional batteries. This provides Pb-Ca batteries very desirable properties [9].

Generally positive grids of Pb-Ca alloys are unsatisfactory for cycling operations. In the absence of tin they exhibit increased corrosion giving rise to shedding of active mass [10-12] due to the poor adherence to the grid and changes in the morphology of positive active material [13]. The above facts are in very good agreement with the observed behaviour of Pb-Ca cell. In case of cells containing Sb, it acts as form of glue for the PAM, thereby preventing the early shedding of active mass [14]. Unlike in the conventional cells, the presence of equal quantities of Sb-Cd in the experimental cell, though does not have a strong effect on the development of capacity during service life, the decline in capacity is not that much large as observed in the case of Pb-Ca cell. Genell and Lea [15] have reported the resistivity values for pure porous Pb as 18.3×10^{-5} ohms - cm at 298 K and for that of PbO₂ as 74×10^{-4} ohms-cm at 298K as reported by Thomas [16]. At -255 K their corresponding values would be about 14.8×10^{-5} ohms-cm and 60×10^{-4} ohms-cm. At 255 K and below the rate of diffusion and electrolyte circulation into the pores of active mass are very much hindered due to an increase in viscosity and resistance of the electrolyte [17]. The above facts clearly indicate that the porosity of the active mass plays a key role in deciding the performance of the cell at 273 K. In the present study, cells with hybrid systems are found to have more capacity than the remaining cells. This suggests the role of active mass is deciding the performance of the cells at 273 K and below.

CONCLUSION

From the available experimental data, it is concluded that Pb-Ca- Sn alloy grid substrates exhibit higher capacity than the other grid substrates at 303 K, 293 K and 283 K. But at

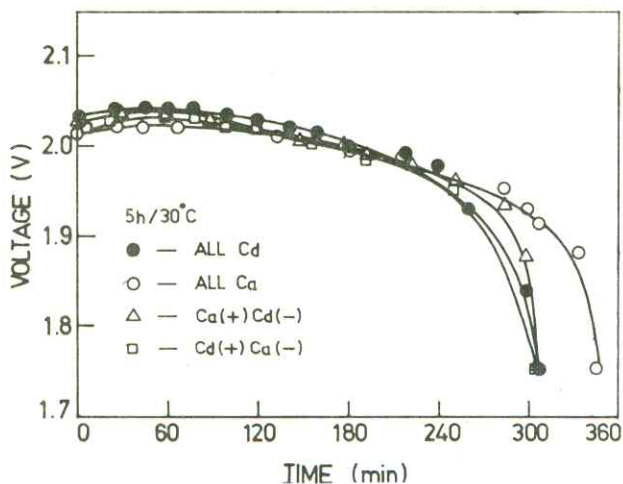


Fig. 1

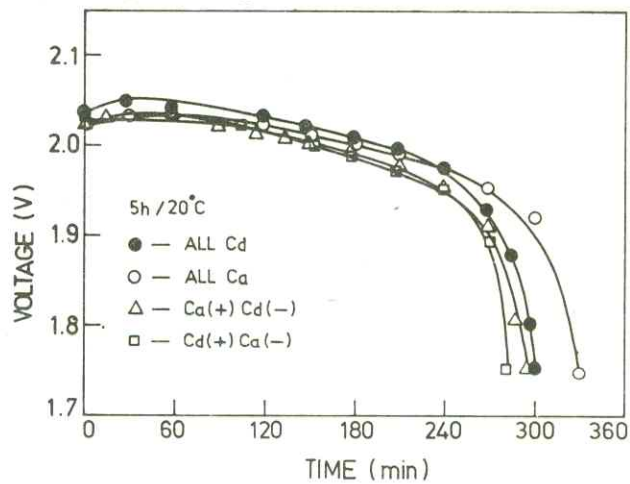


Fig. 2

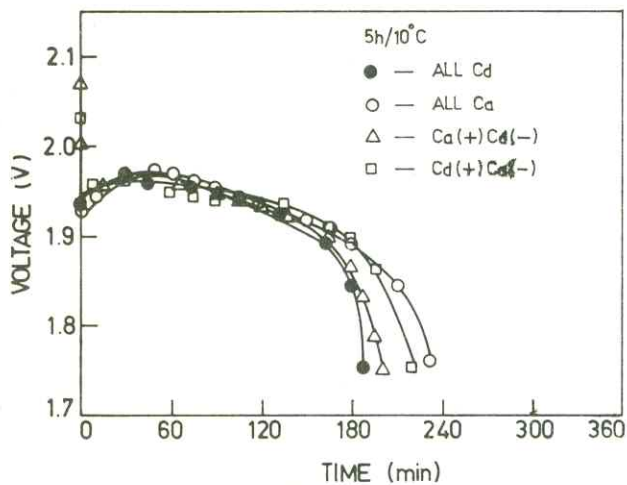


Fig. 3

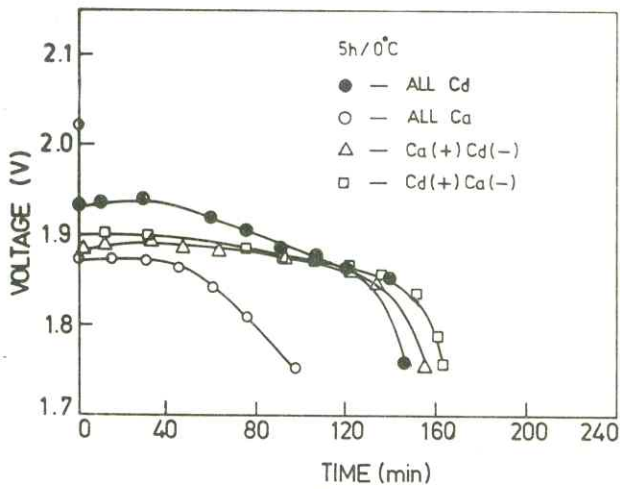


Fig. 4

Performance characteristics of flooded 2V, 2Ah cells at 5 h rate
 Fig. 1 at 303 K Fig. 2 at 293 K Fig. 3 at 283 K Fig. 4 at 273 K

273 K the hybrid grid substrate with Pb-low Sb-low Cd positive perform well over the other grid substrates.

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