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Development of maintenance-free dry calcium (MFDC) lead-acid battery for automotive use

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Abstract

A maintenance-free, dry calcium (MFDC) developed by the Panasonic Battery (Thailand) Co. Ltd. The battery is designed for automotive applications and is ready for use upon injection of the electrolyte. The MFDC battery employs grids made from a lead–calcium-based alloy. This feature suppresses undesirable loss of electrolyte and enables good recovery of capacity after a long time of storage or a long cycle-life. Moreover, the batteries is a dry-charged type and requires only a low frequency of recharging due to its suppressed self-discharge during storage. Transportation costs are reduced as the battery contains only a small amount of electrolyte during storage.

Keywords: Dry-charged battery; Maintenance-free; Lead-acid; Expanded grid; Lead–calcium–tin alloy; Grid

1. Introduction

The classical lead-acid automotive battery employed grids made from lead–antimony alloys, and required water addition at regular intervals. This is due to dissoluteai of antimony from the positive grid and subsequent deposition on the active material of the negative electrode to causes a lowering of the hydrogen overpotential and, thereby, a large loss of the electrolyte during battery use. Accordingly, there is a market demand for a maintenance-free battery that does not call for water addition. Efforts to lower the antimony content of the alloy and, eventually, to employ a substantially antimony-free lead–calcium–tin alloy have resulted in the maintenance-free battery. This design realizes an outstanding reduction in the frequency of water addition is now a principal automotive battery.

Initially positive electrodes made from lead–calcium–tin alloys gave unsatisfactory durability at high temperatures. This problem was overcome by using a positive plate made by expanding a cold-rolled sheet of a lead–calcium–tin alloy that had a surface treated with a lead–antimony–tin alloy [1].

The abundant presence of a dilute sulfuric acid electrolyte in a battery causes loss of capacity by self-discharge during storage for long periods of time, or at a high temperature. For example, batteries with grids of a lead–antimony alloy undergo self-discharge to the extent of 0.5–1.0% of capacity per day. Even a maintenance-free batteries with grids of a lead–calcium–tin alloy can suffer a self-discharge of about 0.1% of capacity per day. Accordingly, a dry-charged battery with a removable electrolyte is suitable when long periods of, storage are required, particularly at a high ambient temperature, or when it is shipped for export.

In order to satisfy the market requirements as stated above, a maintenance-free, dry calcium (MFDC) lead-acid battery has been developed. It has the salient features of both a dry-charged battery with a removable electrolyte that allows a long time of storage, particularly at a high temperature, and a maintenance-free operation that requires only a very low frequency of water addition.

A cast electrode plate is usually used for a dry-charged battery and after tank formation and drying, it is incorporated into a battery. By contrast, an expanded plate is used for the MFDC battery to provide maintenance-free operation and improved durability at high temperature. The formation of an expanded plate is, however, very difficult from a productivity standpoint. The MFDC battery is subjected to box formation and then part of its elec-

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trolyte is removed. The battery is therefore, stored as a drained charged battery.

2. Construction of MFDC battery

The components of the MFDC battery are shown schematically in Fig. 1. The positive and negative grids are both made from a lead–calcium–tin alloy and are fabricated by means of an method in which an alloy sheet is cold-rolled to an appropriate thickness, cut with slits, and then expanded.

A thin lead–antimony–tin alloy layer is formed on the surface of the positive grid in order to prevent: (i) degradation of the chargeability caused by formation of a passive layer between the positive grid and its active material as a result of, for example, storage is an over-discharged state; (ii) shortening of life caused by a lowering of the bonding strength between the grid and its active material [2].

A polyethylene sheet was used for the separator and took the form of an envelope for housing the negative plate.

The battery was subjected to box formation and 70% of the prescribed amount of the electrolyte was then discarded from the cell. The openings in the cells are seated tightly with an adhesive tape to complete the MFDC battery.

2.1. Composition and manufacture of positive grid alloy

The positive grid alloy of the MFDC battery was a lead–calcium–tin alloy as stated above. While there have been many reports on the proportions of calcium and tin, they are now selected so as to ensure battery durability at temperatures of 70 °C, or higher.

Batteries using positive grid alloys with different calcium and tin contents were examined for corrosion by oxidation of their grids after overcharge tests at 75 °C (840 h of charging at 4.5 A). The results are presented in Fig. 2.

The data show that a composition having a calcium content of 0.05–0.07 wt.% and an tin content of 1.2–1.8 wt.% gives good corrosion resistance. Accordingly, the positive grid alloy chosen for the MFDC battery contains 0.07 wt.% calcium and 1.3 wt.% tin.

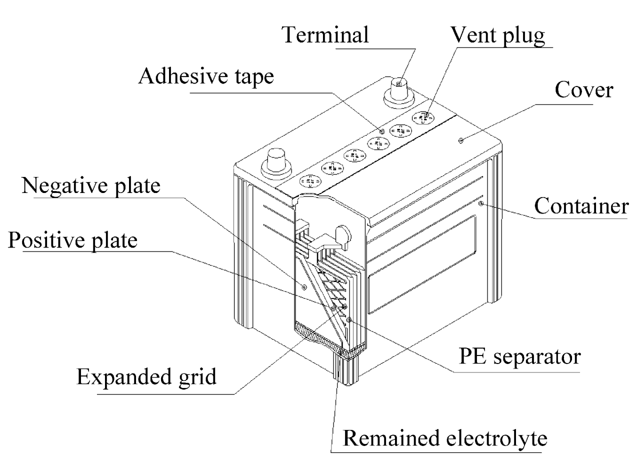

Fig. 1. Sectional view of MFDC battery.

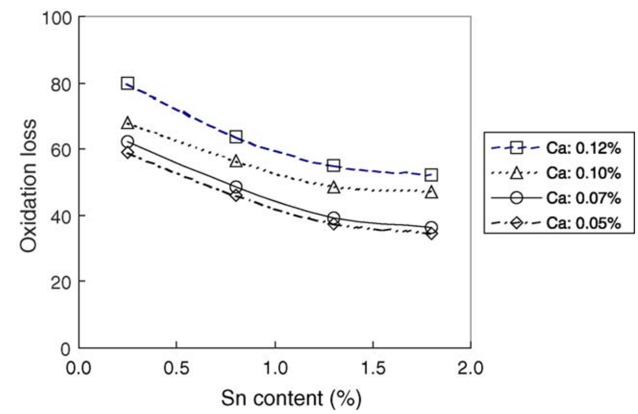

Fig. 2. Oxidation loss as a function of tin and calcium contents in positive grid alloys of MFDC batteries.

Both the cold-rolling conditions employed for manufacture of the lead alloy sheet and the alloy composition itself are important in producing a positive grid of improved corrosion resistance. A diagrammatic illustration of the process for rolling the lead alloy sheet is shown in Fig. 3. Careful study and selection of the cooling conditions make it possible to produce a lead alloy sheet with a finely-divided crystal structure that contributes greatly to improving the corrosion resistance.

In order to achieve improved chargeability after overdischarge and enhanced bonding strength between the grid and the active material, a lead–antimony–tin alloy foil was applied to the surface of the lead–calcium–tin alloy sheet and the two were rolled together as shown in Fig. 3. The rolled product was expanded to make a grid with a surface treated with a thin lead–antimony–tin alloy layer formed between the grid and the active substance as shown in Fig. 4.

2.2. Construction of ready-to-use MFDC battery

In order to make a reserve, or ready-to-use battery, it is usual practice to conduct tank formation on plates, remove the current-collector, etc., and then assemble them into cells. Cast grids are usually employed as the plates for tank formation. The MFDC battery, however, employs grids formed by expanding a rolled sheet, as described above, in order to exhibit the characteristics of a maintenance-free battery, and it is inappropriate from the standpoint of production efficiency to conduct tank formation. Thus, a study has been made of the possibility of conducting box formation in an electrolytic cell and then removing the electrolyte.

The amount of electrolyte remaining in the MFDC battery and the 5-h capacity after 1 or 3 months of storage at 60 °C are shown in Fig. 5. The residual capacity is shown as a percentage of the initial 5-h capacity. While a battery with a residual amount of electrolyte of 0% (i.e., a completely dry-charged battery) shows the best results of storage, even a battery with 30% electrolyte exhibits good results. Therefore, it was decided to take the productivity of the MFDC battery into account and leave 30% of the prescribed amount of electrolyte in the cells after box formation.

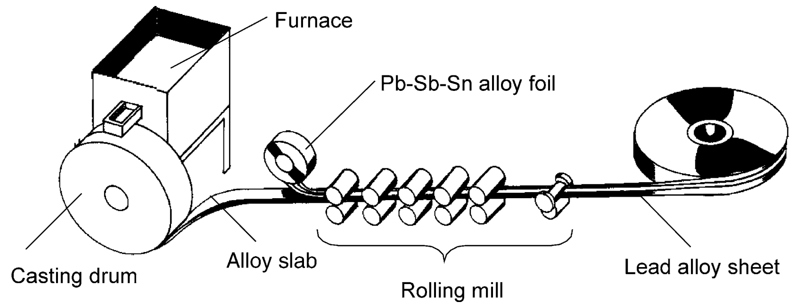

Fig. 3. Illustration of the rolling process for lead alloy sheet.

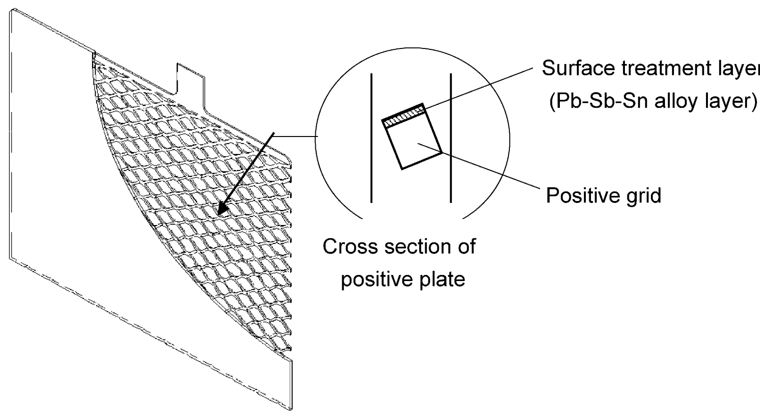

Fig. 4. Schematic of a grid with an attached foil.

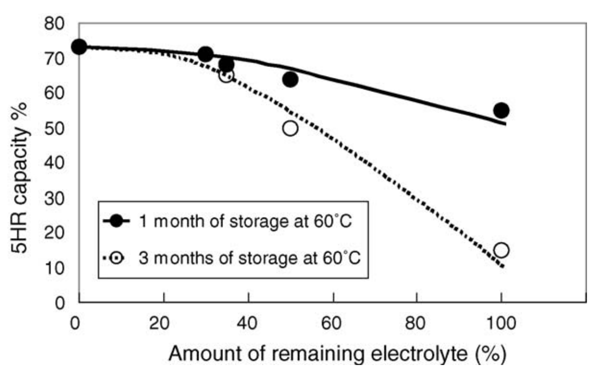

Fig. 5. Amount of residual electrolyte and capacity after 1 or 3 months storage at 60 °C.

3. Characteristics of MFDC battery

3.1. Storage

The 5-h capacity of each battery after storage at 60 °C is shown in Fig. 6. The MFDC battery and a comparative dry-charged battery (Pb–Sb alloy) were stored in the absence of electrolyte and, after storage, each battery was filled with the prescribed amount of electrolyte and its 5-h capacity was determined.

There is virtually no change in the capacity of the dry-charged battery, even after 3 months of storage. By contrast the MFDC battery suffers about 30% loss of capacity after 1-month of storage, but does not show any substantial reduction thereafter. On the other hand, a maintenance-free battery, which had been filled with electrolyte, experiences a capacity reduction of about 45% after 1-month and about 85% after 3 months.

The distribution of lead sulfate in the positive and negative plates of a MFDC battery and a filled-and-charged maintenance-free battery after 1-month of storage at 60 °C is shown in Fig. 7.

A negligible amount of lead sulfate is found in the plates of dry-charged battery, while a wide distribution of $PbSO_4$ is present in both the positive and the negative plates of the filled-and-charged maintenance-free battery. In the case of the MFDC battery, a high content of $PbSO_4$ is formed in less than 20% at the height of the positive and the negative plates, but only slight amounts are present in the remained of the plates.

The behaviour of the MFDC battery as stated above, is due to the fact that the bottom area of the plates that is contact with remaining electrolyte makes self-discharging the same as in a maintenance-free battery, whereas most of the area of the plates

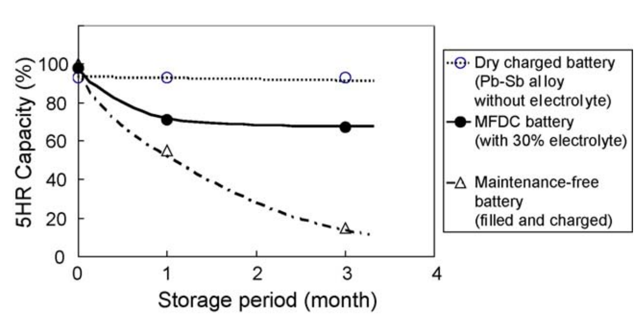

Fig. 6. Five-hour capacity after storage at 60 °C.

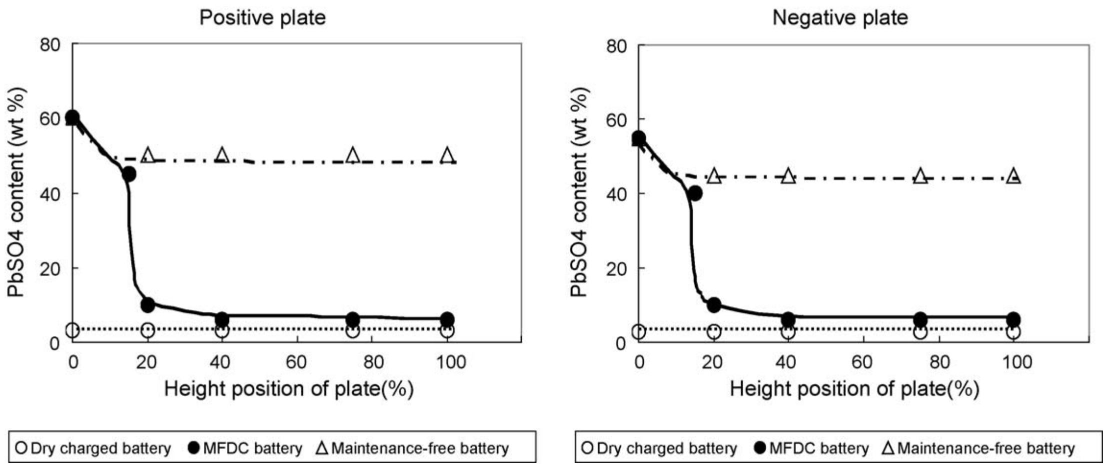

Fig. 7. Lead sulfate distribution in positive and negative plates after 1-month of storage at 60 °C.

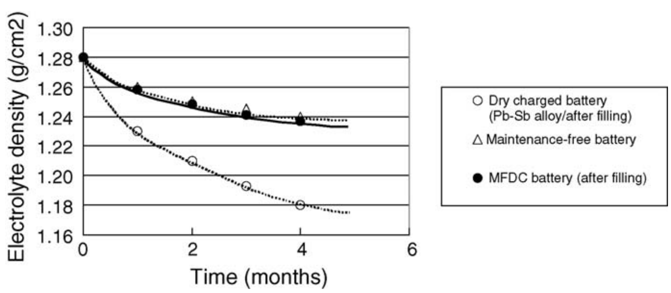

Fig. 8. Self-discharge characteristics at 40 °C.

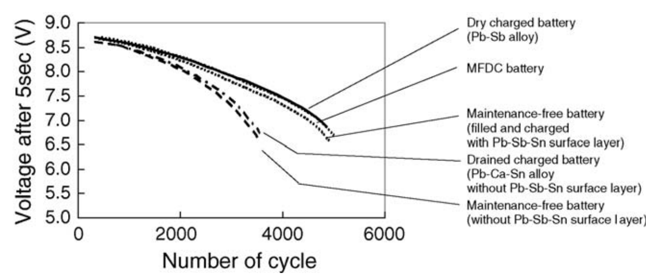

Fig. 9. Shallow cycle endurance at 75 °C after 1-month of storage at 60 °C.

that is exposed undergoes little self-discharge as in a dry charged battery.

3.2. Self-discharge

The MFDC battery and a comparative dry-charged battery (Pb–Sb alloy) were stored at 40 °C after injection of the prescribed amount of dilute sulfuric acid (1.280 rel. dens.). The self-discharge characteristics were determined by measurement of the decline in relative density of electrolyte. Both batteries display better storage than a typical dry-charged battery (Pb–Sb alloy), see Fig. 8. It is obvious that the low-antimony content of the MFDC battery, as well as that of the maintenance-free battery, makes it possible to suppress any deposition of antimony on the active material of the negative electrode and, thereby, any resulting reduction of hydrogen overpotential.

3.3. High-temperature cycle life

The results of a shallow cycle endurance test conducted at 75 °C, in accordance with the SAE J240 procedure after 1 and 3 months of storage at 60 °C are given in Figs. 9 and 10, respectively corresponding results obtained. The life tests of the MFDC battery and a typical dry-charged battery (Pb–Sb alloy) were conducted after the batteries had been stored in the absence of electrolyte and each had been filled with the prescribed amount of electrolyte.

The life test conducted at 75 °C after 1-month of storage at 60 °C gave good results for the dry-charged battery (Pb–Sb alloy), the MFDC battery, and a filled-and-charged maintenance-free battery with a Pb–Sb–Sn surface layer. On the other hand, poor performance was obtained from the drained charged battery (Pb–Ca–Sn alloy, without Pb–Sb–Sn surface layer) and the filled-and-charged maintenance-free battery without Pb–Sb–Sn surface layer.

It is obvious from the above information that the MFDC battery and the filled-and-charged battery have their corrosion resistance improved due to the positive plate being formed from a rolled sheet of a lead–calcium–tin alloy (0.07 wt.% calcium and 1.3 wt.% tin). The two batteries also have a high-temperature life comparable with that of the dry-charged battery (Pb–Sb alloy). This is because the lead–antimony–tin alloy surface layer gives an improved bonding strength between the grid and the active material and an improved charge-acceptance performance.

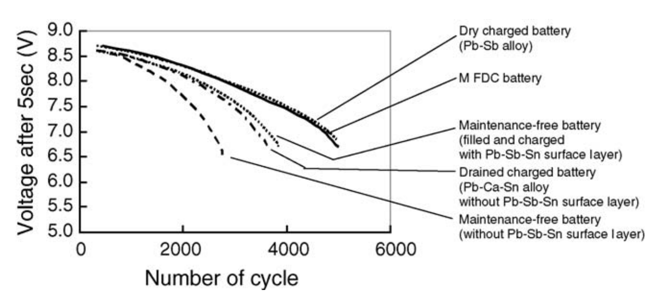

Fig. 10. Shallow cycle endurance at 75 °C after 3 months of storage at 60 °C.

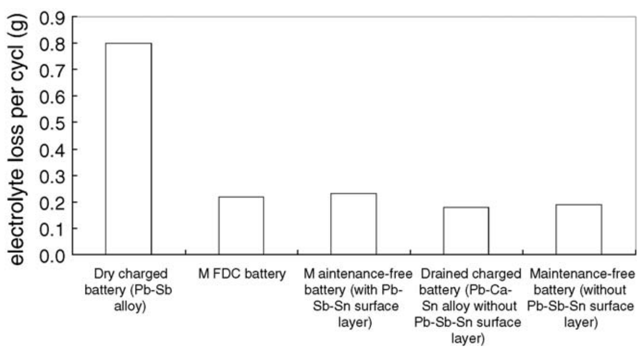

Fig. 11. Loss of electrolyte per cycle as determined by SAE J240a shallow cycle endurance test conducted at 75 °C.

The life test conducted at 75 °C after 3 months of storage at 60 °C show that the dry-charged battery (Pb–Sb alloy) and the MFDC battery yield results comparable with those obtained after 1-month of storage at 60 °C. By contrast, the filled-and-charged maintenance-free battery (with Pb–Sb–Sn surface layer) gives a shorter life. It is obvious that self-discharge has occurred in this battery during extended storage and has resulted in the formation of a passive layer of lead sulfate between the grid and the active material, and also within the active material itself.

3.4. Electrolyte loss

The loss of electrolyte per cycle as determined by the SAE J240a shallow cycle endurance test conducted at 75 °C is presented in Fig. 11. Both the MFDC battery and the filled-and-charged maintenance-free battery suffer only a small electrolyte loss, which is equal to about one-forth of that of the dry-charged battery (Pb–Sb alloy). Thus, both batteries are outstandingly maintenance-free.

4. Conclusions

The following conclusions can be drawn from this investigation on the MFDC battery:

(1) The battery can withstand a long time of storage like a dry-charged battery (Pb–Sb alloy). Upon injection of a prescribed amount of electrolyte at the time of its use, it exhibits the same characteristics as before storage.
(2) The battery can withstand storage after injection of electrolyte.
(3) The life of the battery at a high temperature is comparable with that of a traditional dry-charged battery (Pb–Sb alloy). This is a consequence of using a lead–calcium–tin alloy, rolling and a lead–antimony–tin alloy foil (expanding technology).
(4) Electrolyte loss from the battery is very small and as for a traditional filled-and-charged maintenance-free battery water addition is required less frequently.

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