PHENOMENA AT THE INTERFACE BETWEEN POSITIVE ACTIVE MATERIAL AND LEAD–CALCIUM–TIN GRIDS

K. TAKAHASHI, N. HOSHIHARA, H. YASUDA, T. ISHII and H. JIMBO

Matsushita Battery Ind. Co. Ltd., Storage Battery Div., 555, Sakaijuku, Kosai, Shizuoka 431-04 (Japan)

Introduction

Lead–calcium alloys were first used practically for lead/acid battery grids in 1935 [1]. Nevertheless, the grid alloy has only been widely used for maintenance-free automotive batteries during the past decade. The production of grids by the expansion process has been a key factor in the successful application of lead–calcium alloys. In addition, many quality problems associated with the introduction of expanded-metal grids have been gradually solved.

A comparison of antimonial and calcium alloys shows that the latter has significant advantages in maintenance-free applications. This is mainly due to a difference in hydrogen overvoltage, which results in a lower rate of water consumption and a smaller rate of self discharge in the case of calcium alloys. On the other hand, at the positive electrode, since grids are in direct contact with active material at a high potential, several interesting phenomena have been experienced during the process of battery grid improvement. These phenomena are mainly associated with the oxide product formed on the grid surface. This paper discusses studies on batteries using lead–calcium grids that are aimed at increasing the cycle life under deep-discharge conditions and recovering the performance after over-discharge.

Retardation of the early failure of batteries under deep-discharge service

When lead–calcium alloys are used to make grids, it is generally observed that the capacity of the battery rapidly decreases (early failure) under deep-discharge/charge cycling. This early failure is attributed to the development of an insulating barrier layer at the interface between the positive grid and the active material. This layer suppresses the diffusion of sulphuric acid to the interface [2]. In order to determine the phenomena that take place on the grid surface when access of acid is hindered, cyclic voltammetric studies have been carried out using pieces of Pb–Ca–Sn alloy of various compositions [3].

Figure 1 shows the voltammogram obtained in 1.25 sp. gr. sulphuric acid; this acid strength is generally used in automotive batteries. It can be
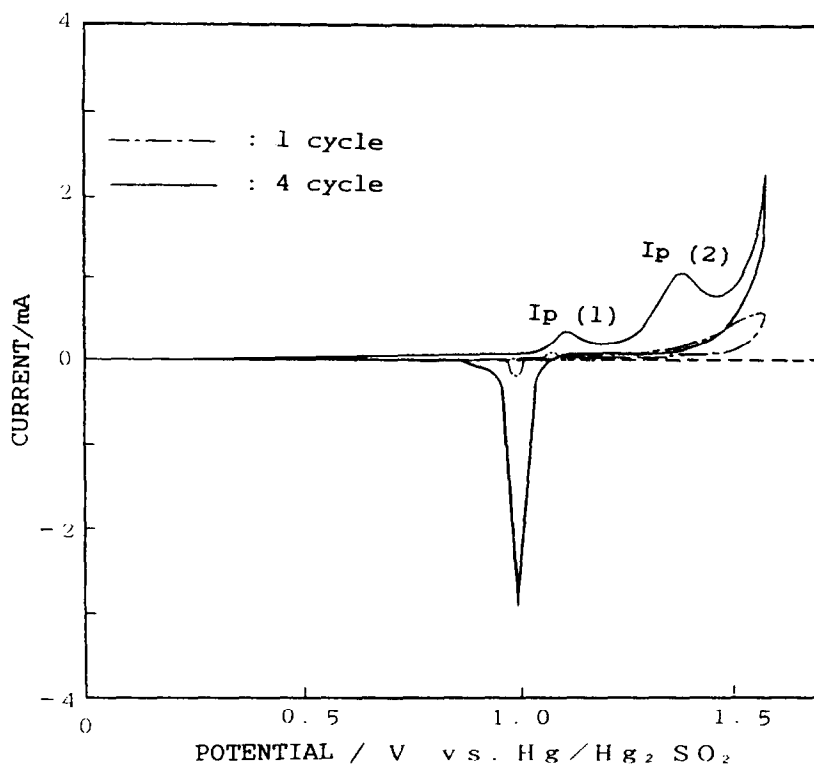
Fig. 1. Cyclic voltammograms for Pb–Ca–S.. alloy in 1.25 sp. gr. H_2SO_4; scan rate 125 mV s^{-1}.

seen that only a small current is generated during the first scan On further cycling, two oxide waves, Ip(1) and Ip(2), appear close to the voltage at which lead dioxide generally shows its characteristic current wave. In order to examine the properties of peaks Ip(1) and Ip(2) further, cyclic voltammetry has been performed in sulphuric acid solutions of various concentration. The resulting wave heights are shown in Figs. 2 and 3.

It is found that Ip(1), which appears at the lower voltage, is strongly dependent on acid concentration. For low concentrations, the height of this oxide wave increases rapidly with cycling and then reaches a limiting value [4]. The latter value is higher for acids of decreasing strength. The height of peak Ip(2), which appears at a higher voltage, also increases with cycling, but its height is influenced little by the electrolyte concentration (Fig. 3).

From the cycle-life testing of actual electrodes, it is found that failure is delayed when the concentration of sulphuric acid is decreased. It is therefore concluded that the oxide product formed on the surface corresponding to peak Ip(1) in the above voltammogram plays an important role in the early failure phenomena occurring between active material and the grid alloy.

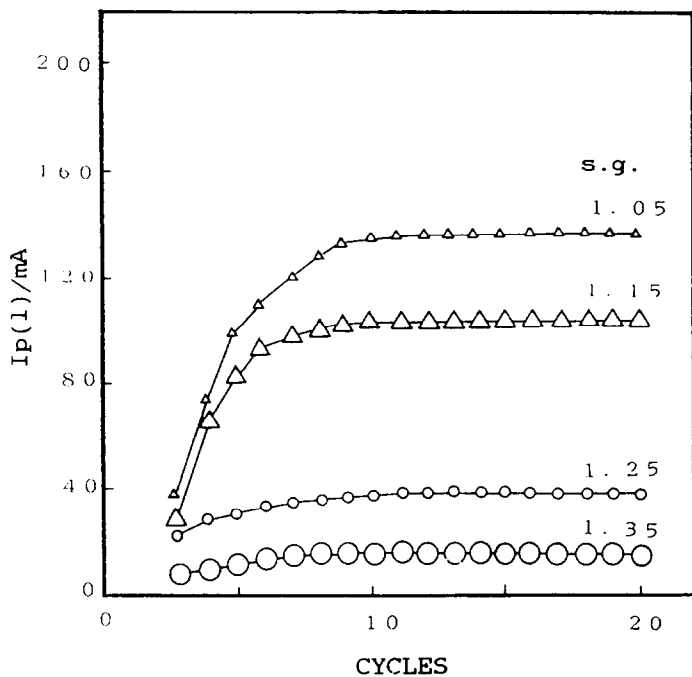The change in the height of wave Ip(1) was examined in the following three situations:

Fig. 2. Change in peak current Ip(1) (see Fig. 1) during voltammetric scans in various concentrations of H_2SO_4; electrode: Pb–Ca–Sn (Sn 0.3 wt.%).
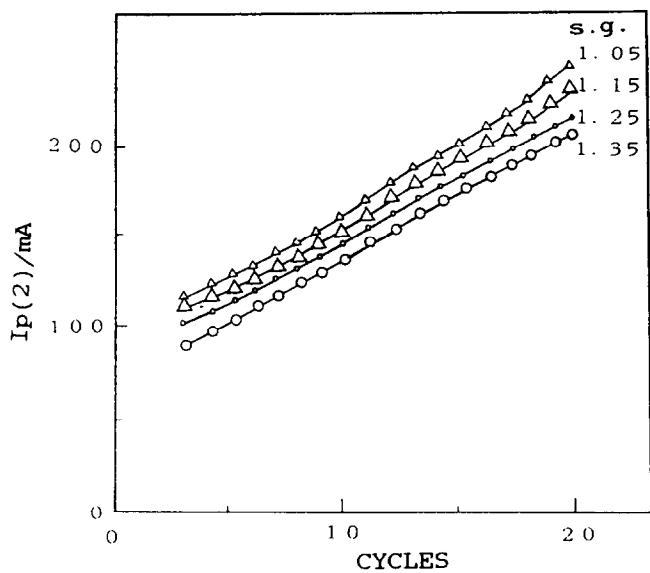

Fig. 3. Change in peak current Ip(2) (see Fig. 1) during voltammetric scans in various concentrations of H_2SO_4; electrode: Pb–Ca–Sn (Sn 0.3 wt.%).

(i) ten cycles were conducted in 1.05 sp. gr. H_2SO_4, the solution was then replaced by 1.35 sp. gr. H_2SO_4 and the cycling recommenced;

(ii) cycling was carried out in 1.05 sp. gr. H_2SO_4 and in 1.35 sp. gr. H_2SO_4;

(iii) ten cycles were conducted in 0.5 M Na_2SO_4 and then this solution was replaced by 1.25 sp. gr. H_2SO_4.

The results, presented in Fig. 4, show that the Ip(1) value, which increases during cycling in sulphuric acid of low concentration, remains at the same level when the solution is changed for one of higher concentration. However, the value then decreases on further cycling. On the other hand, in neutral solution, the rate of increase of the peak height is rather slow but, nevertheless, a relatively high value remains when the solution is replaced by sulphuric acid of high concentration. From these results it is concluded that the oxidation pre-treatment of the alloy in low-concentration sulphuric acid, or in neutral acid solution, should be effective in protecting plates from early-failure phenomena.

In the next study, tin was added to the alloy and the effect of this metal on the formation of oxide product corresponding to Ip(1) was examined. The results are shown in Fig. 5. As the number of cycles proceeds,
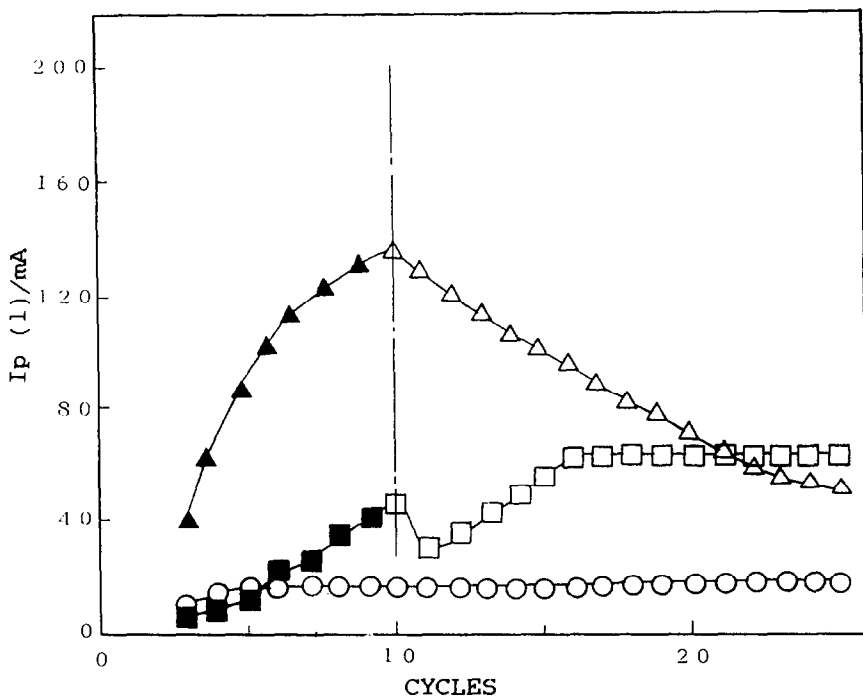

Fig. 4. Retaining effect of peak current Ip(1). ▲, in 1.05 sp. gr. H_2SO_4; ○, in 1.35 sp. gr. H_2SO_4; △, in 1.35 sp. gr. H_2SO_4 after 10 cycles in 1.05 sp. gr. H_2SO_4; ■, in 0.5 Na_2SO_4; □, in 1.25 sp. gr. H_2SO_4 after 10 cycles in 0.5 M Na_2SO_4.
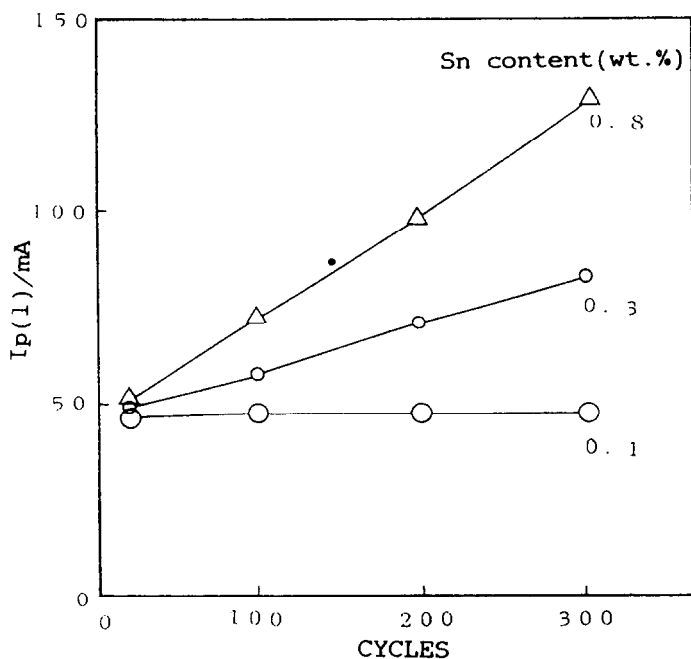
Fig. 5. Dependence of peak current Ip(1) on Sn content of Pb–Ca–Sn alloy during voltammetric scans; electrolyte: 1.25 sp. gr. H_2SO_4.

Ip(1) increases, even in suphuric acid of high concentration. Increasing tin content accelerated the rate of increase in the height of wave Ip(1).

   In summary, it is concluded from the above results that the oxide product corresponding to wave Ip(1) and the presence of tin both retard the early failure of batteries using lead–calcium grids. According to Panesar [5], the oxide product is thought to be α-PbO_2, but unequivocal experimental evidence in support of this view has yet to be obtained. Nevertheless, it is to be expected that a reliable automotive battery will be achieved when conditions are chosen under which the oxide material corresponding to wave Ip(1) is stable. At present, several of these conditions are already adopted in the design and production of automotive batteries with Pb–Ca–Sn alloy grids.

Recovery of battery performance after over-discharge

   A very small current sometimes continues to flow in automotive batteries, and the battery remains in a discharged state for a long period, e.g., when the car door is left half-open by mistake. Such situations result in the over-discharge of automotive batteries and, subsequently, to a marked increase in the internal impedance. Under these circumstances, the performance is very difficult to recover by recharging using a conventional constant-voltage method. This behaviour is shown in Fig. 6(A). In some cases,

the internal impedance reaches as much as 1 Ω, and a very solid resistance layer is formed that cannot be removed by constant-voltage charging at 14 - 15 V, which is the usual voltage setting of a car regulator. In such a situation, once the car engine is started with the help of a generator from a second car, the battery in the former car cannot be recharged in a short driving period and thus the car cannot be restarted should it stop again.

Figure 7(a) shows oxygen, sulphur, and tin profiles in a polished cross-section taken from near the grid of an over-discharged electrode. It is found that sulphur (from sulphuric acid in the electrolyte) is not present in the inner region of the surface where the amount of tin in the grid increases. It can also be seen that a diffusion layer of oxygen several μm thick is formed on the alloy surface. From these results, it can be reasonably concluded that the high resistance layer on the surface is not due to a so-called sulphation phenomena, but rather a diffusion layer is formed very close to the inside surface of the grid. According to Pavlov et al., assuming the formula of lead oxide to be PbO_x, a very high resistance layer is formed when $x <$ 1.7. It is also reported that when dry-charged (PbO_2) electrodes are washed and dried, the lead grid is oxidized from the surface in contact with PbO_2 towards the inside, and exhibits a very high impedance value due to a diffusion layer so produced. From these observations, it can be concluded that
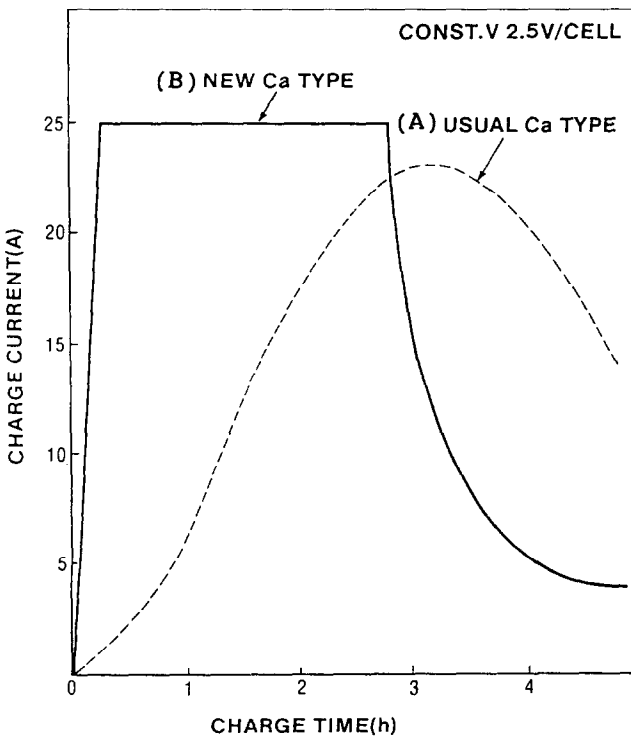

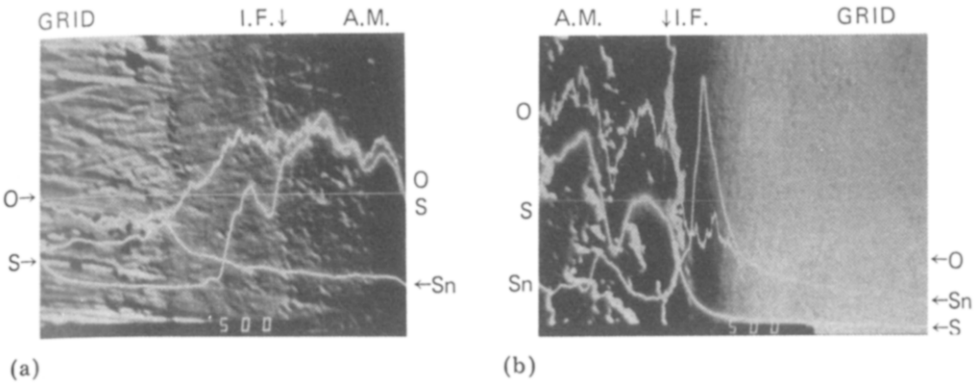Fig. 6. Rechargeability after over-discharge.

Fig. 7. Interface of grid and active material after over-discharge and a long stand period. (a) Usual Ca type; (b) new Ca type.

the passivation phenomena is due to a high impedance layer that is formed as a very thin surface layer on the grid, and that this layer prohibits charge acceptance.

It is also found that passivation phenomena do not always happen on over-discharge followed by a standing period. Figure 8 shows the design area in which these phenomena are observed. The parameter σ is the ratio of the weight of sulphuric acid in the battery to the weight of active material.

In the matrix shown in Fig. 8, the design areas where passivation phenomena are observed and not observed are classified. It is found that, regardless of battery size, the same passivation phenomena occur in high percentage in the region of $\sigma < 0.6$. The actual design areas that are employed for 50 A h batteries are shown in this matrix and it is seen that the σ value is sometimes over 0.6 and sometimes below 0.6. It is reasonable to conclude that this is the reason why passivation phenomena are observed in some cases, and not observed in other cases.

In order to examine the relation between the passivation phenomena and the formation of a diffusion layer at the grid surface in more detail, measurements were made of the open-circuit voltages of, first, batteries in which passivation phenomena were observed after over-discharge followed by a stand period and, second, batteries in which passivation phenomena were not observed. It was found that the voltages fell into two groups: one with values above 1.0 V, the other with values below 1.0 V. Passivation phenomena were not observed in batteries with voltages below 1.0 V. In batteries with voltages above 1.0 V, it is assumed that the amount of H_2SO_4 is smaller than that of the PbO_2 active material. Thus, unreacted PbO_2 remains with $PbSO_4$ when the battery is over-discharged and the electrolyte becomes very dilute. As a result, the grid is oxidized in an electrolyte that is close to water and a diffusion layer appears to be formed. On the other hand, in regions where σ is relatively high, *i.e.*, a higher amount of H_2SO_4 is present, acid still remains even after the voltage of PbO_2 has disappeared, and thus it is difficult for passivation to proceed. As discussed above, it has
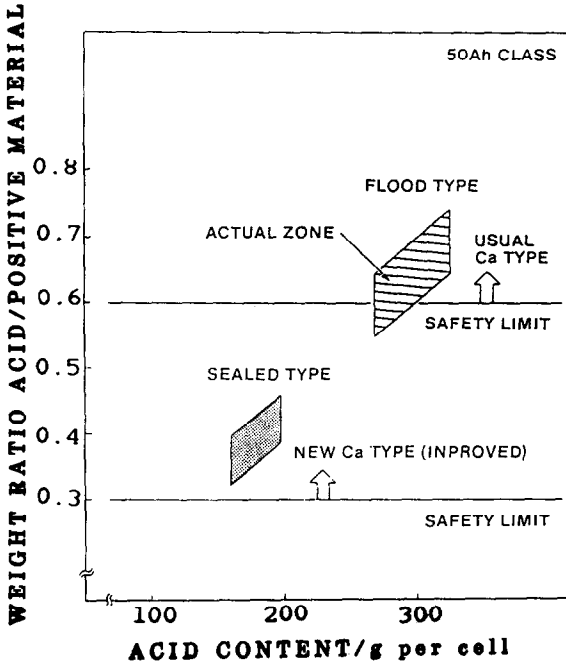
Fig. 8. Designs of rechargeable batteries.

become possible to avoid the formation of this high resistance layer by selecting proper design parameters. In the present designs, however, a large amount of active material is required for high performance and a small amount of H_2SO_4 is necessary to keep the battery weight low. These two limitations result in a desired low value for the σ parameter. Furthermore, in sealed batteries, the amount of electrolyte must be limited to a low value to enable gas transport and recombination. For these batteries, therefore, the σ value becomes considerably lower than the design limit at which passivation is avoided. This situation (shown in Fig. 8) requires approaches other than the selection of proper design parameters to avoid passivation phenomena and to improve over-discharge characteristics. To this end, an examination has been made of the effects of various additives.

It has been found that tin has a remarkable effect when present as 3 - 5 wt.% in the alloy. This level of tin, however, introduces serious alloy cost problems. Since the formation of the passivation layer is a phenomenon that occurs only on the surface of the grid, the authors' company has developed a unique grid expansion process in which a tin-rich layer is produced on the surface of rolled alloy sheet. This grid material is shown in cross-section in Fig. 9. Using the new alloy, batteries were fabricated with a low σ value. The behaviour of the charging current at constant voltage after the batteries were over-discharged and subjected to a stand period is represented by curve (B) in Fig. 6. It can be clearly seen that passivation phenomena are no longer
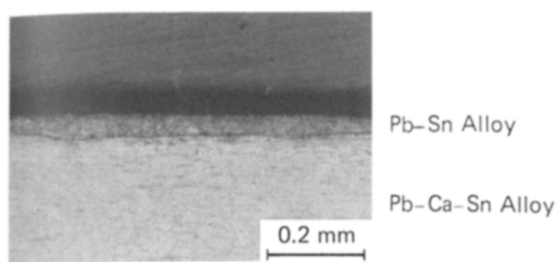
Fig. 9. Cross section of new Pb–Ca sheet coated with tin.

present and the current characteristics are almost the same as those of a normal battery. An elemental analysis of the grid/active material interface after over-discharge, followed by standing, is given in Fig. 7(b). Comparison of these data with that in Fig. 7(a) clearly indicates the presence of many tin peaks. These are due to the doped tin. Also, the oxygen diffusion layer which was observed on the conventional grid (Fig. 7(a)) has disappeared. In the new tin treatment process, only one surface out of four is covered by a tin-rich layer and, overall, the good protection against passivation phenomena is achieved. The technique has been applied to sealed type batteries in addition to conventional automotive units using lead–calcium grids and flooded electrolyte.

Conclusions

By studying the properties of the oxide product formed on the surface of grid alloys a search has been conducted for a successful means whereby lead–calcium alloys can be used in lead/acid batteries. Further detailed examination of the surface product is expected to advance the quality and performance of lead–calcium–tin alloys.

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