Analysis of the conditions that promote passivation on calcium–alloy grids in lead/acid batteries*

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Abstract

It is well known that calcium–alloy grids used in positive plates in lead/acid batteries often exhibit passivation phenomena Such phenomena do not always appear for a given set of conditions An investigation has been conducted of the conditions giving rise to grid passivation As a result, it has been concluded that high potential and low acid concentration are the major factors promoting an increase in impedance In addition, cell design variables such as the acid/active-material ratio and operational conditions such as over-discharge and squeeze discharge with a very low-rate current may also give rise to passivation It has been found that a new surface-treatment technology involving application of tin-rich and/or an antimony-rich, thin layer on the grid surface is very effective in overcoming this disadvantageous characteristic of calcium–alloy grids

Introduction

Recently, 'calcium-type' lead/acid batteries have been used widely for maintenance-free automotive batteries It has become well known that passivation phenomena can sometimes be experienced under certain operational conditions, e g during long standing after over-discharge, during very low-rate discharge under the influence of a leakage current in a car The passivation appears to develop as a result of interfacial reactions taking place at the calcium grids of the positive plates Nevertheless, the fact that, under the same conditions, the problem may, or may not, be encountered still remains a mystery Therefore, it is important to determine the nature and location of the effect, and to identify the key factors that promote its occurrence

In recent years, many authors have investigated and discussed passivation phenomena on calcium–alloy grids For example, Hein [1] presented passivation data for maintenance-free automotive batteries, and claimed that a high content of tin reduced, or eliminated, the resistance layer on lead–calcium grids In 1978, Pavlov [2] detected the presence of α-PbO_2 in the passivation layer Later, Pavlov *et al* [3] observed passivation during low-current discharge and showed that tin attacked the passivation layer and dramatically increased

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its conductivity under exposure to pulses of light Garche *et al* [4] suggested that a layer of $PbO_x (1 < x < 1\ 7)$ with a high impedance was produced on drying formed positive plates This was thought to develop via a solid-state reaction at the interface between the lead grid and the adjacent PbO_2 Workers from the same group later observed currentless passivation [5] This was explained in terms of the interfacial region in the $Pb/PbO_x/PbO_2$ system forming a n–p–n semiconductor junction [6]

Takahashi *et al* [7] identified two types of interfacial passivation phenomena One was early failure during deep-discharge cycling, while the other concerned difficulties in recovery after a long stand in a state of over-discharge Although such phenomena are related to problems in the interfacial region, it is likely that they occur at different locations within this region A schematic of the interfacial zone is given in Fig 1 The passivation phenomena appearing with cycling are considered to be associated with the characteristics of the inner active material or outer corrosion layer The problem can be ameliorated by the presence of tin and/or by decreasing the acid concentration (the latter promotes the formation of α-PbO_2) Passivation reactions taking place during long standing at low states of charge are likely to take place at the inner corrosion layer close to the grid surface Again, a tin-rich layer lessens the problem By contrast, however, the passivation is increased, rather than reduced, by decreasing the acid concentration
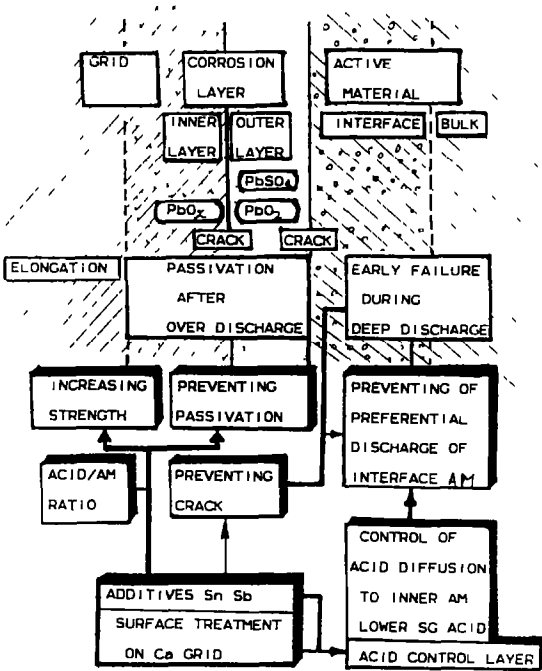

Fig 1 Schematic of passivation problems on lead–calcium battery grids

Analysis of passivated grids has revealed that passivation is due to the formation of a non-stoichiometric oxide $PbO_x(1 < x < 1 7)$

The above work was aimed at determining a 'safe' zone for cell/battery design using the weight ratio (σ) of sulfuric acid to active material as the control parameter Passivation after over-discharge and standing was observed for $\sigma < 0 6$ Treatment of the grid surface with a tin-rich layer using proprietary technology extended the safe zone to a lower value of σ This is necessary for sealed batteries that employ starved-electrolyte conditions Despite this success, there still remain many questions to be answered, see Table 1 The most curious aspect of passivation is that it does not always manifest itself under seemingly identical conditions Clearly, it is extremely important to determine the key parameters that encourage the onset of passivation

Experimental and results

Experiment 1

In order to search for parameters that promote passivation, studies were conducted under a matrix of open-circuit voltages (OCV) and acid specific gravities, as shown in Fig 2 This work was undertaken on many batteries having expanded, calcium type grids (0 07wt %Ca–0 5wt %Sn) The test schedule was as follows (i) $C/5$ discharge, (ii) closed-circuit stand for two weeks with 15 Ω resistor, (iii) open-circuit standing for two weeks After this procedure, both the open-circuit voltage and the rechargeability at a constant voltage of 14 8 V were tested

In Fig 2, the passivated (denoted by crosses) and unpassivated (denoted by circles) zones are mapped in matrix of OCV and acid specific gravity at the final stage of the stand period It can be seen that the passivated zone is distributed at higher OCV and lower specific gravity

Experiment 2

In this investigation, specimens were prepared from calcium alloy sheet that is used for expanded-type grids Some of these specimens were coated

TABLE 1

Passivation problems

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1	What are the electrochemical conditions that give rise to passivation?
2	Why is there no consistency in the appearance of passivation phenomena on overdischarged plates?
3	Does a tin-rich surface layer protect other parts of the (untreated) surface?
4	Must the grid be covered with active material for passivation to occur?
5	What is the extent of the protective effect of tin?
6	Is there an alternative to tin that does not also impair maintenance-free performance?
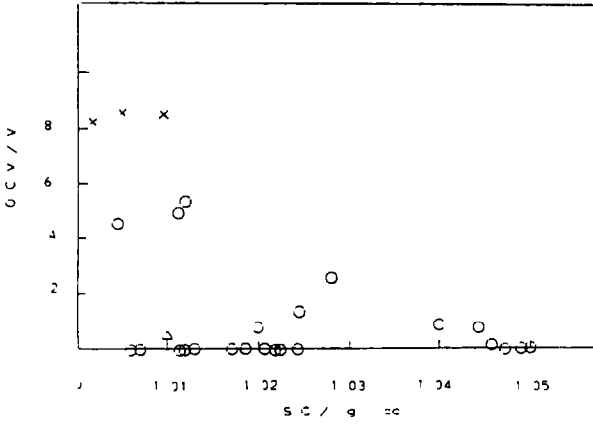
Fig 2 Passivation and *OCV* after over-discharge/long-standing of popular calcium-type battery Grid 0 07wt %Ca–0 5wt %Sn, over-discharge 2 weeks with 10 W lamp after *C*/5 discharge, standing 2 weeks at open circuit temperature 40 °C throughout the test
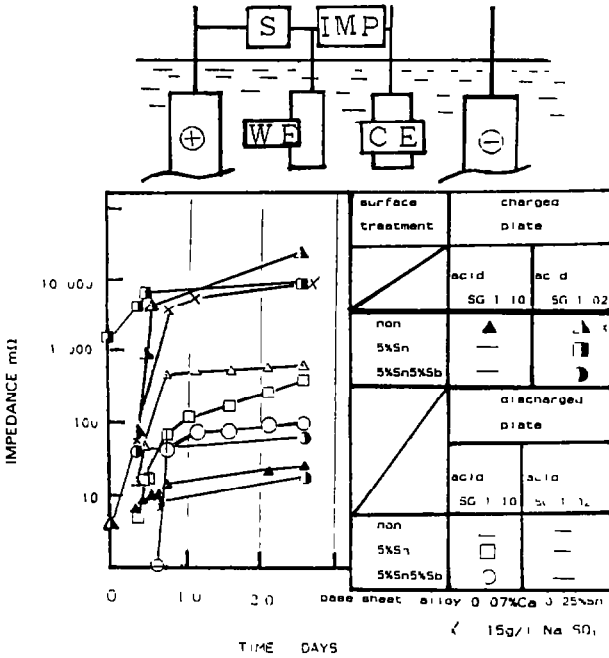

Fig 3 Impedance of various alloy grids in matrix of potential (high or low) and acid concentration

on one side with a thin (~10 μm) surface film applied by the technical method reported in ref 7

The test sequence of the base and treated alloys is listed in Fig 3 The base alloy contained 0 07 wt % Ca and 0 25 wt % Sn, while the surface film

consisted of 5 wt % Sn, or 5 wt % Sn and 5 wt % Sb The specimens were examined in acid of 1 10 or 1 02 sp gr , with/without Na_2SO_4, and were each connected to a charged positive plate that was either at a higher potential or was discharged to a lower potential (see Fig 3) During standing, the change in impedance was measured between the specimen (WE) and a fresh counter electrode (CE), with the switch (S) cut off Simultaneously, the *OCV* of the positive plate was measured against a reference electrode

The resulting impedance data are given in Fig 3 Specimens without the special surface layer exhibited a dramatic increase in impedance in acid of 1 02 sp gr and were easily passivated if connected to a charged plate having a higher potential When the sample was coated with a tin-rich surface layer, a similar increase in impedance was found in acid of 1 02 sp gr when it was connected to a charged plate having a higher potential By contrast, no increase in impedance under these heavy conditions was observed when 5 wt % Sb was incorporated in the surface film

None of the specimens displayed an impedance over 1000 mΩ when connected to a discharged plate Furthermore, Na_2SO_4 was found to exhibit no noticeable effects

A map of the plate *OCV* and acid specific gravity at the end of the stand test is presented in Fig 4 It appears that there are three zones (i) A is a heavily passivated zone, (ii) B is a weakly passivated zone, (iii) C is an
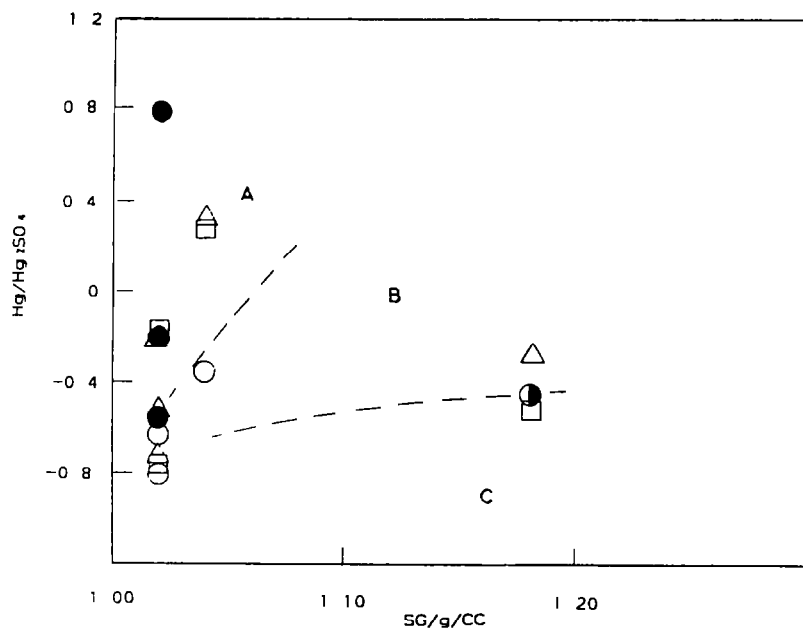

Fig 4 Passivation on various alloy grids in matrix of potential (high or low) and acid concentration (O) No surface treatment, (△) 5wt %Sn–5wt %Sb surface coating, (□) 5 wt % Sn coating Base sheet alloy Pb–0 07wt %Ca–0 25wt %Sn

unpassivated zone These data are similar to those obtained from Experiment 1 above

Experiment 3

In order to determine whether a coated alloy in an unpassivated condition could protect an untreated alloy surface, a base and a coated sample were mounted in the same cell within a high potential plate and a low acid specific gravity The resulting impedance data are given in Fig 5 The impedance of the uncoated alloy was found to increase to a very high value of over 10 000 Ω while that for the specimen with a tin-rich surface layer remained at a much lower level Thus, it can be concluded that treatment of localized parts of the alloy surface does not provide all of the surface with good protection Nevertheless, a partial coating is sufficient to yield practical improvement in battery performance

Experiment 4

In order to establish the level of tin required in the surface layer, two test schedules, using different combinations of potential and acid concentration, were applied to sealed batteries with calcium grids made from 0 07wt %Ca–0 25wt %Sn alloy and coated with 5 wt % Sn One set of batteries was discharged with a very low squeeze current of few mA (i e similar to the key-off current in a car) after $C/5$ discharge, while a second set was discharged immediately after charge The terminal voltage and rechargeability at a constant voltage of 14 0 V were measured periodically throughout the test After completion of each experimental run, the interfacial zone of the passivated grid was examined with scanning electron microscopy, electron probe microanalysis (EPMA) and X-ray diffraction techniques
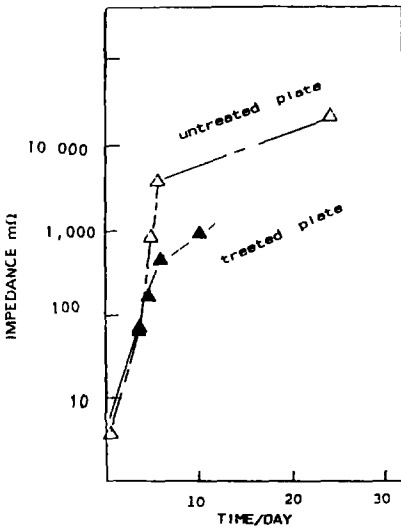

Fig 5 Passivation of bare lead–calcium alloy connected to treated plate

The change in terminal voltage, together with the recharge current curves at various stages, are presented in Fig 6 The terminal voltage of the unpre-discharged batteries remained at an initial high level for a long time By comparison, the voltage of the batteries not subjected to predischarge decreased sharply at an early stage The former batteries displayed poor rechargeability in the early stages despite the fact that the grids were covered with a tin-rich layer

Figure 7 shows an EPMA for tin superimposed on an electron micrograph for a passivated grid taken from the above tests It can be seen that the corrosion zone has passed through the tin-rich layer That is, passivation appears to be in the inner corrosion layer so that the tin layer cannot afford total protection Unfortunately, no new information on the corrosion product could be obtained from X-ray microdiffraction analysis of the inner corrosion layer
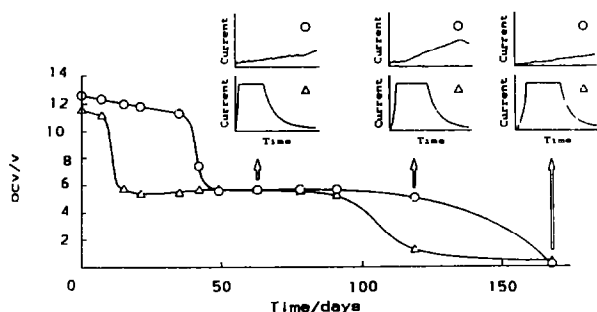

Fig 6 Rechargeability of a sealed battery at different over-discharge conditions generated by application of a squeeze current (△) Battery predischarged at $C/5$ rate, (○) battery not subjected to predischarge
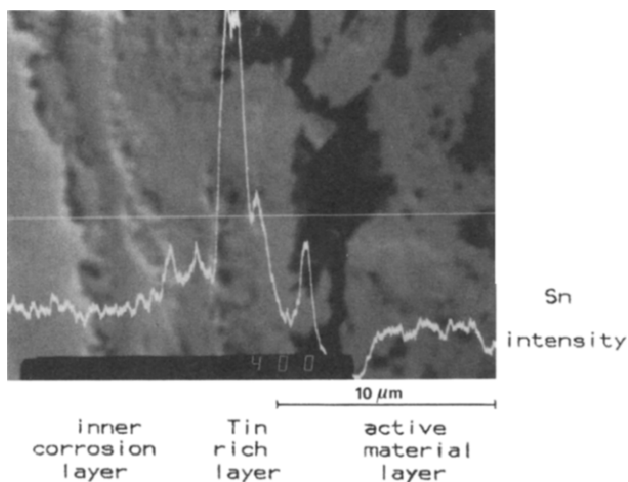

Fig 7 EPMA and SEM data for a passivated grid

Experiment 5

In order to discover how tin in the base alloy effects passivation phenomena in the inner side of the tin-rich surface layer under heavy corrosion conditions, the impedance of two types of sealed batteries with a base alloy of 0 25 or 0 5 wt % Sn was compared during application of a squeeze discharge without pre-discharge The results are given in Fig 8 Passivation was only observed on the grid with 0 25 wt % Sn alloy

Experiment 6

As mentioned above in Experiment 1, the incorporation of antimony in the surface layer is also effective On the other hand, it is well known that antimony impairs the maintenance-free characteristics of batteries To examine this point further, a battery with a grid protected by surface layer of 5 wt % Sn and 5 wt % Sb alloy was prepared and the water loss under SAE test conditions was measured

Figure 9 shows the water loss of several types of batteries during the test Batteries with grids having 5 wt % Sn and 5 wt % Sb on the surface display almost the same level of water loss as those without antimony In addition, the treated batteries exhibit good performance under heavy duty service
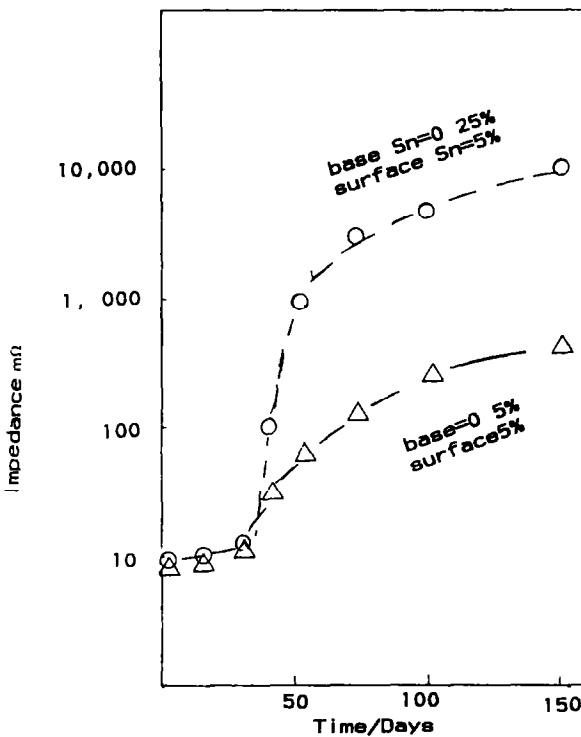

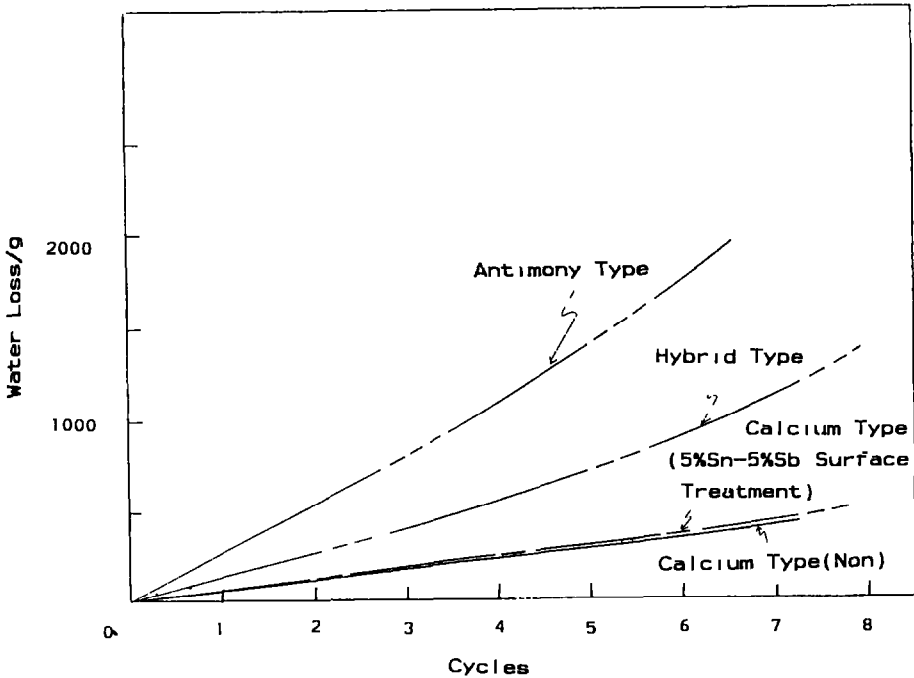Fig 8 Impedance of sealed battery during squeeze discharge without predischarge

Fig 9 Water loss during SAE test for batteries with 5wt %Sn–5wt %Sb surface-treated grid

Discussion and conclusions

(1) Passivation can be promoted by a combination of high potential and low acid concentration

(2) The 'safe' zone of battery design must take into account the matrix of sulfuric acid content and the weight ratio of acid to positive active material With such consideration, it is possible to avoid passivation phenomena On the other hand, a low ratio can result in a high potential and a low acid concentration

(3) The development of passivation depends upon the test schedule, i e , discharge current, pre-discharge before long stand, squeeze discharge These parameters create different combinations of acid specific gravity and potential

(4) A tin-rich surface layer can offer protection against passivation during long stand periods after over-discharge of flooded-electrolyte batteries Nevertheless, this protection may not extend to other parts of the grid surface that do not have this coating

(5) Squeeze discharge at a very low rate may promote severe passivation conditions in sealed batteries with starved electrolyte A thin tin-rich surface layer is insufficient to prevent such passivation

(6) A surface layer containing 5 wt % Sb and 5 wt % Sn is very effective in preventing passivation Furthermore, the antimony has no deleterious effect on the maintenance-free performance of batteries

Acknowledgements

References

1 D Hein, *Proc 87th Convention of Battery Council International, Hollywood, U S A*, 1975
2 D Pavlov, *Electrochim Acta, 23* (1987) 845
3 D Pavlov, B Monakhov, M Maja and N Penazzi, *J Electrochem Soc, 136* (1989) 27
4 J Garche, K Wiesener and N Anastasijevic, *J Power Sources, 10* (1983) 43
5 H Doering, J Garche, H Dietz and K Wiesener, *J Power Sources, 30* (1990) 41
6 J Garche, *J Power Sources, 30* (1990) 47
7 K Takahashi, N Hoshihara, H Yasuda, T Isu and H Jinbo, *J Power Sources, 30* (1990) 23