Aspects of lead/acid battery manufacture and performance

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Abstract

In keeping with previous Asian Battery Conferences, the meeting closed with an expert panel of battery scientists and technologists answering questions put by the delegates. The subjects under consideration were: *Leady oxide production:* choice of process; effect on paste mixing and plate curing. *Paste mixing:* temperature control; red-lead addition; paste degradation; expander addition. *Plate curing:* hydrocerussite formation; effect of oxide variety; tetrabasic lead sulfate. *Plate formation:* soaking time; acid sp. gr.; difficulties with negative plates. *Battery performance:* influence of depth-of-discharge; problems with perchloric acid; the memory effect; magic potions.

Leady oxide production

Question: Ball-mill oxide is reported to have finer particle size, a higher acid absorption value and similar output per hour, and to produce battery plates with higher capacity. Why, then, would a battery plant install a Barton-pot? Is there a drop-off in cycle life or some other adverse aspect of performance with ball-mill oxide?

D.A.J. RAND
　　　Three of the four features of ball-mill oxide as stated in the question are correct, namely:
　　　(i) the oxide particles of ball-mill oxide are much smaller than those produced by a Barton-pot, i.e., 2-3 versus 0.8-1.0 m^2 g^{-1};
　　　(ii) by virtue of (i), ball-mill oxide is the more reactive of the two varieties; typical acid absorption values for ball-mill and Barton-pot oxides are 220–240 and 140–180 mg H_2SO_4 per g oxide, respectively;
　　　(iii) a ball mill gives a lower output per unit space than a Barton pot (i.e., it has a larger footprint);
　　　(iv) ball-mill oxide enhances the initial discharge capacity of pasted plates.

The four major factors to be balanced when deciding to install a ball mill or a Barton pot are [1, 2]: cost, process and product control, environmental performance, and resulting battery characteristics, i.e.:

● cost: compared with a Barton-pot of equivalent output, a ball mill is about one-third more expensive to buy, consumes about one-third more power, and occupies one-third more space

● process/product control: a ball mill is easier to control — but has a slower response to change — than a Barton-pot; ball-mill oxide is more difficult to handle and store (the oxide is prone to aggregation and degradation); ball-mill oxide is less suitable for tubular plates (filling is more difficult, packing density is variable) but allows pasted plates to be processed faster

● environmental performance: ball mills emit more noise and have potentially higher dust emissions than Barton pots

● battery characteristics: pasted plates made from ball-mill oxide are mechanically stronger and give a higher initial capacity than those prepared from Barton-pot oxide

In the final analysis, the choice of process for flat plates will depend upon the pasting, curing and formation strategies that are in practice at the plant, as well as upon the target specifications that are set for the resulting battery product.

Question: Given its higher acid absorption value, does ball-mill oxide produce more heat during the paste-mixing process? If so, is the process more difficult to control using ball-mill oxide and will the mixture require a longer period to cool before pasting can commence?

D.A.J. RAND

Heat can be generated during the paste-mixing process from four possible sources: (1) the wetting of the oxide during the initial addition of water; (ii) the dilution of the sulfuric acid by the wet paste; (iii) the reaction between the acid and the lead oxide; (iv) the mixing operation itself (frictional effects).

By virtue of its higher surface area and greater degree of mechanical strain, ball-mill oxide generates more heat of wetting than its Barton-pot counterpart, but the effect is small for both varieties of oxide. If the same initial amount of water is added, the heat of acid dilution will be the same for both oxides. The heat of reaction of ball-mill product with sulfuric acid is higher because of the greater surface area of this oxide compared with the Barton-pot material. The heat added to the system by the mechanical work expended during mixing is greater for ball-mill paste because the greater reactivity of this oxide drives off water and gives rise to a stiffer paste. The finer particles of the ball-mill oxide pack more densely than those of Barton-pot oxide. Therefore, to achieve the same paste density with each variety of oxide, further water has to be added to the ball-mill paste towards the end of the mixing. This acts as a coolant so that, overall, there is very little difference in the final temperature of the two types of paste. As a consequence, ball-mill pastes do not require a cooling period before subsequent application to the plate grids.

Paste mixing

Question: What type of temperature control is required in paste mixing? Is there a maximum temperature above which paste is ruined? What is the maximum period of time that a mix can be held prior to pasting before it 'goes off'?

I.G. MAWSTON

Temperature control of paste mixing is usually achieved by means of water jackets that are fitted to the sides and the base of the mixer. It is also common to have air

extraction that causes cooling by forced evaporation of water from the surface of the paste. The upper limit of paste temperature is usually taken as 65 °C. There is no particular fixed time for holding paste mixes as the 'going off' phenomenon is a function of both the temperature and the composition when mixed. A reasonable practice is to cool the paste below 40 °C as soon as possible and to complete plate pasting within 1 h of release.

Question: For what battery applications is it desirable to add red lead to the positive-paste mix?

D. PAVLOV

It is useful to add red lead to the positive-paste mix in the following two situations:

(i) In cases of low-initial battery capacity (determined by the positive half-block). When it is not possible to make other changes in the production technology, an addition of red lead will increase the capacity.

(ii) When the time of plate formation has to be shortened. As is well known for automotive batteries, negative plates are formed in 10 to 12 h, while positive plates require over 18 h. The addition of 20 to 25 wt.% red lead will reduce appreciably the formation time for positive plates.

It should be noted that red lead is more expensive than leady oxide. Thus, the addition of red lead should be adjusted so that the resulting advantages will outweigh the increased costs of positive-plate production.

Question: What modification (if any) to the active material is achieved with red lead?

D. PAVLOV

Red lead (Pb_3O_4) results in the formation of β-PbO_2. Red lead reacts with H_2SO_4 during paste preparation, soaking and formation via the following reaction:

$$Pb_3O_4 + H_2SO_4 \longrightarrow \beta\text{-}PbO_2 + PbSO_4(PbO \cdot PbSO_4) \tag{1}$$
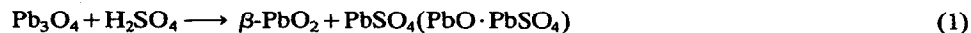
During formation, $PbSO_4$ is also oxidized to β-PbO_2.

Question: What are the optimum levels of red-lead addition?

D. PAVLOV

For automotive positive plates, the optimum level of red lead is 25 wt.%. For traction batteries, especially with tubular electrodes, the content of red lead may reach 60 wt.%.

Question: All battery manufacturers have experienced paste that has 'gone off' or 'set' prior to pasting. The further processing of such plates is usually troublesome. What actually happens to the paste?

I.G. MAWSTON

Improperly treated paste will prematurely undergo the hydro-set reaction. That is, the free lead will oxidize, the moisture content will fall and, perhaps most importantly of all, large crystals of basic lead sulfates will start to form. These crystals cause the paste to become very stiff and, sometimes, it becomes almost impossible to apply properly to the grids. In simple terms, such paste is in a half-way state between being

'fresh' and 'fully cured'. Plates prepared with badly overaged paste are of inferior quality!

Question: It appears that manufacturers of traction batteries use less expander in the paste formulation for traction batteries than for automotive batteries. What is a recommended level of addition of expander for both battery types? Is there a danger in using excess expander for deep-cycling batteries?

I.G. MAWSTON

Dealing purely with lignosulfonate types of expanders (low-temperature additives), it is common to use 0.2 to 0.35 wt.% for automotive batteries, and 0.1 to 0.2 wt.% for traction batteries. (Note, these percentages are based on the weight of oxide.) Unless the deep-cycle battery is being used at low-temperature regularly, there is a danger of getting ballooning negatives in service. Some expanders are appreciably soluble in weak acid and their use in deep-cycle batteries should be avoided. Automotive batteries can be regularly called upon to deliver high currents at low temperatures. Hence, they normally have more expander and generally have a more 'active' type. Excessive amounts can, however, give rise to problems in formation and can impair recharge efficiency, because of the lowered hydrogen overvoltage. The interaction of expanders with the carbon-black/barium-sulfate content is a very complex subject and requires a series of careful trials to match the individual oxide/paste formulations and battery types with the intended end-use of the battery.

Plate curing

Question: X-ray diffraction phase analysis of cured active material regularly shows 5–10 wt.% hydrocerussite. What is hydrocerussite? How and when is it formed? Is hydrocerussite responsible for the white crystals that are seen on cured plates after storage in ambient atmosphere? What effect does hydrocerussite have on active-material formation and battery performance?

L.T. LAM

The species of hydrocerussite (HC) that is usually observed in battery plates has the chemical formula: $2PbCO_3 \cdot Pb(OH)_2$.

The following data demonstrate how and when hydrocerussite is formed in battery plates. Figure 1 shows the change in phase composition during curing and drying of pasted plates in the curing oven of a battery factory. About 35 wt.% of tribasic lead sulfate ($3PbO \cdot PbSO_4 \cdot H_2O = 3BS$) was formed after paste-mixing. This value increased to about 40 wt.% during the initial stages of curing and then stayed approximately constant for the remainder of the process. There was, however, a marked decline in 3BS content during the drying period. At the same time, hydrocerussite and monobasic lead sulfate ($PbO \cdot PbSO_4 = 1BS$) were produced. It should be noted that the drying mechanism of the curing oven involved direct circulation of air through a gas burner.

Figure 2 shows the change in phase composition of ball-mill and Barton-pot oxides during storage under elevated temperature and a moist, CO_2-containing atmosphere. For ball-mill oxide, there was a marked decrease in both the free-lead and α-PbO contents with storage time. This behaviour was associated with the formation of hydrocerussite. The changes in the composition of the Barton-pot oxide were less dramatic. During degradation, both the oxides became gritty and changed colour.
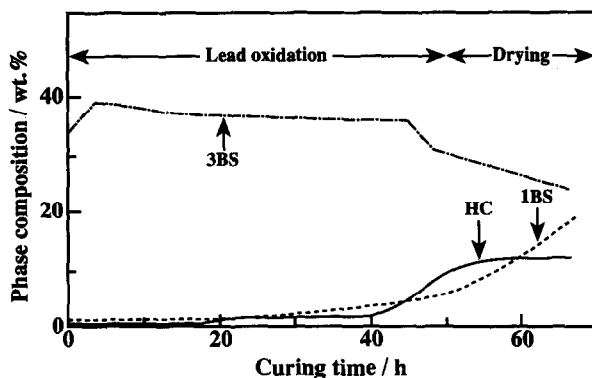
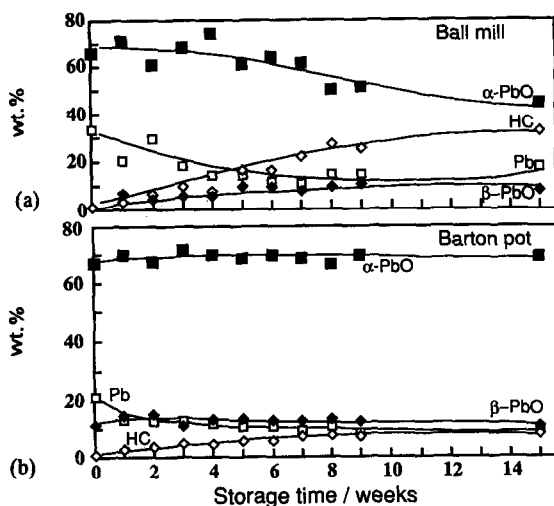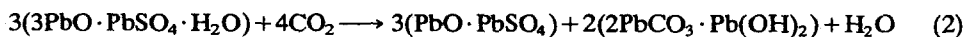Fig. 1. Decomposition of tribasic lead sulfate during curing.

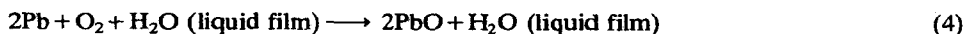Fig. 2. Degradation of leady oxides during storage: (a) ball-mill oxide; (b) Barton-pot oxide.

From these two examples, it is concluded that hydrocerussite can be generated from the following two sources:
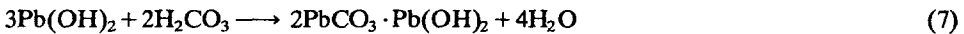
(i) Degradation of 3BS in the presence of carbon dioxide, i.e.:

$$3(3PbO \cdot PbSO_4 \cdot H_2O) + 4CO_2 \longrightarrow 3(PbO \cdot PbSO_4) + 2(2PbCO_3 \cdot Pb(OH)_2) + H_2O \qquad (2)$$

This is the situation observed in Fig. 1 where the carbon dioxide produced by the gas burner was brought into the curing oven. To avoid this problem, it is recommended that curing ovens should be fitted with indirect heating systems.

(ii) Degradation of PbO and oxidation of free lead in the presence of moisture and carbon dioxide, i.e.:

$$H_2O \text{ (vapour)} \longrightarrow H_2O \text{ (liquid film)} \qquad (3)$$

$$2Pb + O_2 + H_2O \text{ (liquid film)} \longrightarrow 2PbO + H_2O \text{ (liquid film)} \qquad (4)$$

$$PbO + H_2O \text{ (liquid film)} \longrightarrow Pb(OH)_2 \qquad (5)$$

$$H_2O \text{ (liquid film)} + CO_2 \text{ (gas)} \longrightarrow H_2CO_3 \tag{6}$$

$$3Pb(OH)_2 + 2H_2CO_3 \longrightarrow 2PbCO_3 \cdot Pb(OH)_2 + 4H_2O \tag{7}$$

This is the situation shown in Fig. 2. It is easier to produce hydrocerussite from ball-mill oxide than from the Barton-pot variety because of the higher reactivity of the former oxide (see comment by D.A.J. Rand, above).

Obviously, when cured plates are stored under elevated temperature (e.g., 35 °C) and a moist, CO_2-containing atmosphere, hydrocerussite can be formed through both processes (i) and (ii). (Note, cured plates contain residual amounts of PbO and free-lead.) Process (i) also gives rise to the production of 1BS. Unfortunately, both HC and 1BS are white in colour, so it is difficult to say that the white crystals seen on cured plates are exclusively hydrocerussite. It is necessary to determine their identity by the use of an X-ray diffraction phase-analysis technique, e.g., PEAKS [3].

If the hydrocerussite content in the cured plates is higher than 15 wt.%, it will cause shedding of plate material during the subsequent formation process. This is because reaction with sulfuric acid will give rise to CO_2 evolution that, in turn, will weaken and disintegrate the active-material structure.

There are no published data to show the effect of hydrocerussite on the cycle-life performance of batteries. It should be noted, however, that the formation of this material is accompanied by the development of 1BS. In this respect, Pavlov and Bashtavelova [4] have shown that cured plates with high levels of 1BS exhibit shorter cycle lives than conventional 3BS counterparts. Thus, the formation of excessive amounts of hydrocerussite must be avoided.

Question: The free-lead content of ball-mill oxide is usually much higher than that of Barton-pot oxide. If the requirement after curing is to have a maximum free-lead level of 2 wt.%, does this mean that plates pasted with ball-mill oxide will take longer to cure?

D.A.J. RAND

During the curing process, the oxidation of free-lead particles proceeds via an electrochemical mechanism. With correct processing conditions, each particle is surrounded by a sheath of water and develops anodic and cathodic sites. Lead is corroded at the anodes, and oxygen is reduced at the cathodes. Overall, the lead is converted to lead hydroxide that, in turn, probably loses some water and becomes hydrated lead monoxide. Fragments of the cathodic ends of the particles inevitably remain at the conclusion of curing and, collectively, these make up the target $\leqslant 2$ wt.% level of residual lead.

Although ball-mill oxide usually has a higher free-lead content than its Barton-pot counterpart, pastes made from ball-mill product will, in fact, cure faster. This is due to the marked difference in geometry of the free-lead particles in the two varieties of oxide. The particles are elongated (or flake-like) in ball-mill oxide, but spherical in Barton-pot oxide. The extended dimension of the free-lead particles in ball-mill oxide assists the oxidation process by allowing a better physical separation of the anodic and cathodic sites. Thus, the answer to this question is 'no'!

Question: Why are tetrabasic lead sulfate cured plates preferred for industrial batteries?

L.T. LAM

Industrial batteries generally use thick positive plates that are produced from high density paste. These batteries give long cycle life, but low active-material utilization.
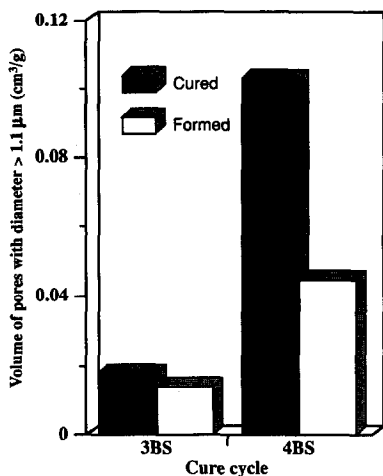
Fig. 3. Macropore volumes of cured and formed plates prepared by either the 3BS or the 4BS processing route.

In broad terms, there are two types of pores in formed plates, namely, micropores and macropores [5, 6]. Micropores provide the surface area upon which electrochemical reactions take place during battery charge and discharge. Macropores contribute mainly to the pore volume and provide pathways for the transport of reactant species between the bulk of the solution and the reactive sites in the interior of the plates. Thus, the macropores are a determinant of active-material utilization, especially in the case of thick plates. An increase in paste density will decrease the number of macropores. By contrast, a decrease in paste density will increase the proportion of macropores, but will reduce the mechanical strength of the plate. This is contrary to the requirement of industrial batteries, namely, long cycle life.

It has been confirmed that tetrabasic lead sulfate ($4PbO \cdot PbSO_4 = 4BS$) cured/formed plates produce more macropores than their tribasic lead sulfate ($3PbO \cdot PbSO_4 \cdot H_2O = 3BS$) counterparts (see Fig. 3). Furthermore, the robust crystalline network of 4BS is retained after plate formation. These two features — large numbers of macropores and a robust structure — are very important in the case of industrial positive plates. The former feature allows greater penetration of acid and, thereby, improves the active-material utilization, while the latter increases the mechanical strength of the plate.

Plate formation

Question: Is there an optimum soaking time for formation before applying the charging current?

D. PAVLOV

There is but scanty information in the literature on the processes that occur during soaking of the plates in H_2SO_4 solution prior to formation. These processes are related to sulfation of the paste and conversion of part of the 3BS, 4BS and PbO

into 1BS and PbSO$_4$. The changes in phase composition of the cured paste produce corresponding changes in its microstructure. The latter, in their turn, affect the processes of formation, on the one hand, and the structure of the active mass, on the other hand. That is why it is important to regard the period of soaking of the plates in H$_2$SO$_4$ solution as a separate technological procedure in the processing of positive and negative plates. Lam *et al.* [7] have studied the process of sulfation of 4BS pastes on continuous (25 to 30 h) soaking of the plates in H$_2$SO$_4$ and have found that such plates are faster to form. The results from an investigation conducted in my laboratories on the processes that occur during soaking of 3BS automotive plates in H$_2$SO$_4$ solutions of three different concentrations (sp. gr. 1.05, 1.15 and 1.25) will be reported in this Journal [8]. In general terms, when formation of automotive plates prepared with 3BS pastes is conducted in H$_2$SO$_4$ of sp. gr. 1.15, a soaking period of 2 to 4 h should ensure good battery performance.

Question: Is there an optimum specific gravity of formation acid?

D. PAVLOV

There is an optimum specific gravity of formation acid that ensures maximum battery performance. The value of this specific gravity depends on the type of battery (automotive, industrial, VRLA cells, etc.), on the type of grid alloy used (low-antimony, lead–calcium, pure lead, etc.), and on the phase composition of the paste (4BS, 3BS). Equally important is the type of formation cyclogram that is applied (i.e., the current changes and the duration of the rest periods during the different stages of formation). Thus, for example, automotive batteries with low-antimony grids and prepared with 3BS pastes exhibit optimum battery performance when formation is carried out in H$_2$SO$_4$ with a sp. gr. of 1.15.

Question: Occasionally, the surface of negative plates is very difficult to clear during formation and the accompanying positives are prone to overformation. (i) What is the cause of this problem? (ii) Does it occur in box formation where plates cannot be inspected? (iii) Are there any processing measures that can be taken to guard against this?

I.G. MAWSTON

I shall answer these questions in the order in which they are set.

(i) The cause is either overdrying (skin drying) or incorrectly conditioned plates. The plates do not 'clear' of lead sulfate because the surface, in the affected areas, is in poor mechanical contact (and, therefore, poor electrical contact) with the rest of the plate. No effective formation current can flow in these areas. Hence, no conversion to metallic lead can take place. Sometimes, the cause can be traced to detergents or to the use of old, unsuitable, or excessive amounts of organic expanders in the paste mix.

(ii) The problem can occur in box formation, particularly if the process is being performed in dilute acid, e.g., 1.100 sp. gr.

(iii) The following procedures should be adopted to minimize, or remove, the problem. Revise/reformulate paste mix expanders with respect to type, age, quantity. Use 0.2 to 0.3 wt.% of good quality expanders that have been stored dry for less than a year. Aim at 8 to 10% moisture content in paste, ex-skin drying. Check free lead and moisture after conditioning to verify that the process is correct. Consider lowering the ratio of acid-to-oxide in the paste mix if it is in excess of 7 ml (1.40 sp. gr.)/kg oxide.

Question: Box formation often results in the deposit of a black sooty substance on the underside of the battery lid and vent plug. What is this substance and does the extent of its presence cause any complications as far as battery performance is concerned?

I.G. MAWSTON

We have found that this material is usually carbon black that originates from the surface of the negative plate during formation. Carbon black is universally used as an additive in the negative paste. The deposit causes no problems with battery performance. Sometimes, however, this deposit can become 'excessive', or brown, or oily. If this is observed, it can indicate that other types of organic contamination are present. The source should be investigated, as it may prove to be deleterious.

Battery performance

Question: To what extent does the depth-of-discharge influence battery cycle life?

D. PAVLOV

We have DIN-tested low-antimony, automotive batteries with 3BS plates at 38% utilization of the positive active mass. It has been found that the depth-of-discharge should not exceed 50% for the batteries to meet DIN cycle-life requirements. Only with batteries produced by the advanced technologies that have been developed lately (e.g., high-temperature curing, 4BS pastes, optimum $Pb:PbO_2:H_2SO_4$ ratio in the cells, etc.) may the coefficient of positive active-mass utilization reach values that are higher than 50% under the same conditions of testing.

Question: To what extent does the depth-of-discharge affect the irreversible processes that determine the life of a battery?

D. PAVLOV

This is a fundamental question and I will try to answer it in general terms. During production of the plates (both negative and positive), the structure of the active masses consists in general of: (i) a skeleton (microstructure) that holds mechanically the active mass and conducts the current to each point in the plate; (ii) an energetic structure, i.e., that part of the active mass which takes part in the current-generating process during the charge and discharge reactions. The energetic part of the active mass is converted into $PbSO_4$ crystals during charge, and back into the active materials, Pb and PbO_2, during charge. As a result of these processes, the structure built during plate production is changed. Probably, the electric resistance of a number of zones in the active-mass skeleton is increased and, consequently, these zones participate, but less actively, in the current-generation process during the next discharge.

The same effect is observed in the pore system. Macropores (the basic transport highways along which the flows of ions and water move to reach every point in the active mass) undergo changes in cross section. In some regions, their cross section increases significantly and in others it is strongly reduced. This results in non-homogeneous participation of the different active-mass zones in the current-generation process and, hence, in capacity decline.

The non-homogeneous participation of the different plate regions in the current-generation process is a consequence of plate pulsation during charge and discharge. During discharge, the plates expand. During charge, they shrink. This is due to the

marked differences in molar volume between Pb and PbO_2, on the one hand, and $PbSO_4$ on the other hand. The greater the depth-of-discharge, the greater the amount of $PbSO_4$ that is formed and, hence, the greater the amplitude of plate pulsation. This leads to greater changes in the active-mass density, especially in the regions near the grid; these are the most critical sites in the plate. If pulsation of the plates is confined in volume (tightened active-block pack), their life is prolonged.

The active mass of positive plates contains both crystal and gel zones. Gel zones play the role of 'hinges' that prevent the skeleton structure from disintegrating on cycling. The structure and conductivity of gel zones depend on the content of dopants such as antimony, tin, etc. These dopants are linked to the polymer chains of gel zones and improve their conductivity and density. Consequently, the presence of certain dopants in certain amounts allows an increase in the depth-of-discharge without affecting the life of the battery. These effects are more pronounced in positive plates where the phenomena that give rise to PCL occur.

In most general terms, to keep the battery life unchanged, the depth-of-discharge (i.e., the coefficient of active-mass utilization) may be increased provided: pulsation of the plates is restricted; the positive active mass contains certain dopants; and the negative active mass contains chemically stable expanders.

Question: There are reports of battery failures due to impurities. One of these is perchloric acid. How does this impurity enter the battery? What is the effect on battery performance?

D.A.J. RAND

The appearance of perchloric acid in batteries is usually the result of contamination by chloride ions. Such poisoning can arise through bad housekeeping, the use of impure makeup water, the intrusion of sea spray (when batteries are located in coastal regions), and/or the degradation of cell components (e.g., poly(vinyl chloride) separators).

During charging of lead/acid batteries, the oxidative power of the positive plates is sufficient to convert any intrusive chloride ions to perchlorate ions. It is well known that perchlorate ions can enhance the corrosion of the lead (or lead-alloy) positive grids. Indeed, this feature is exploited in the formation of Planté plates. Uncontrolled attack by perchlorate results in destructive pitting corrosion of the grids. The extent of this corrosion depends on: (i) the composition and surface treatment of the grid; (ii) casting defects or surface irregularities in the metal or alloy; (iii) the concentration and supply of sulfuric acid at and to the corrosion sites: (iv) the imposed current density; (v) the temperature, and, obviously, (vi) the exposure time.

Despite the widely held view that the presence of chloride species in the electrolyte is harmful to battery performance, it would appear that very little effort has been made to determine precisely the 'safe' concentrations for these species. To my knowledge, no direct corrosion trials on the influence of added perchlorate have been reported for practical batteries. In the consequent absence of data, battery producers have been obliged to 'minimize' chloride contamination through the implementation of in-house, best-practice procedures. Upper limits for chloride concentrations are also set in standard specifications for the quality of both the sulfuric acid and the makeup water. For example, the Australian Standards fix the maximum permissible chloride level at 30 ppm for acid (1.840 sp. gr.) and 20 ppm for makeup water. In the USA, the corresponding values are 10 ppm (1.835 sp. gr. acid) and 5 ppm!

A distinctive and acute form of corrosion — discrete blisters or nodules — has been witnessed [9] on the positive pillars of stand-by power cells that were accidentally

contaminated with varying levels of chloride (up to 300 ppm). Although it was established that perchlorate was the driving force for the blister corrosion, no clear correlation could be found between the incidence/severity of the phenomenon and the measured level of perchlorate in the cell electrolyte. Under a certain set of conditions, an enrichment of perchlorate ions can occur in the meniscus region of positive pillars and, thereby, can give rise to intense and localized pitting corrosion.

Question: Is there a 'memory' effect in lead/acid batteries?

I.G. MAWSTON

The memory effect can be most pronounced in Ni/Cd batteries. If the battery is regularly discharged to, say, 20% of its capacity, it can 'remember' the depth-of-discharge. Over a period of time, if a greater capacity is demanded (say, 60%), it can be difficult to obtain it to a satisfactory end voltage. The 'cure' that is usually recommended is to exhaust the battery completely (e.g., leave a short across it for 24 h) and then apply an extended recharge. Lead/acid batteries can have a type of memory effect. This shows up as a lowered value of the slow-rate (i.e., 20-h) capacity if the battery has just previously been given a high-rate (i.e., 5-min) discharge to exhaustion, notwithstanding an intervening recharge.

D. PAVLOV

There is indeed a memory effect in lead/acid batteries. The memory carriers are the structures of the active masses or certain phases in the corrosion layer of the positive plate. In a series of studies [4, 6, 10], we showed that the memory carrier, for both the positive and the negative plate, is the skeleton structure of the active mass. The memory is created during the process of plate production and is relatively long lived. It has been established recently that the battery capacity during a given cycle is determined by the conditions of the previous charging cycle. These conditions determine the formation of a definite active-mass structure that creates a relatively short-lived memory (one to several cycles).

Question: From time to time, a 'magic' potion for improving battery performance appears on the market. The suppliers claim many wonderful effects on both good and failed batteries. The solution is usually pink or blue in colour and of low pH. Can you provide information on the possible composition of the products that many battery manufacturers encounter. Are there any possible beneficial or damaging effects with using such additives?

D.A.J. RAND

Many attempts have been made to develop an additive that will improve the performance of lead/acid batteries and, in particular, will extend charge/discharge service life. In most cases, the additive is directed towards automotive types of batteries. One or more of the following beneficial effects are claimed: (i) advantageous change in electrolyte sp. gr.; (ii) reduction, or elimination of troublesome sulfation; (iii) improved charge retention; (iv) reduced operating temperature; (v) reduced water consumption; (vi) prevention of electrolyte freezing; (vii) improved high-rate capacity; (viii) increased cycle life; (ix) rejuvenation of fading or dead batteries. It is of historical interest to note that by 1950, more than one hundred battery elixirs had been proposed.

It would appear that the majority of the additives target sulfated batteries and seek to restore the sulfate ion concentration in the electrolyte to the initial value for

a healthy battery. Magnesium sulfate and sodium sulfate, in mixtures of various composition, are the most common compounds chosen for this purpose. From analyses conducted in the CSIRO laboratories, however, other additives that have recently entered the market have been found to contain cadmium sulfate, aluminium sulfate or cobalt sulfate in addition to magnesium sulfate and/or sodium sulfate. The presence of aluminium sulfate results in a low pH, typically at a value of ~ 3. The colouring of the solution is usually artificial and, presumably, is added for cosmetic reasons or to add a touch of mystique to the product.

Over the years, exhaustive studies in the CSIRO laboratories on a wide variety of commercial 'panaceas' for lead/acid batteries have failed to confirm any of the benefits claimed by their suppliers. Moreover, in some instances, potentially hazardous features have been identified.

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