EFFECTS OF PHOSPHORIC ACID ADDITIONS ON THE BEHAVIOUR OF THE LEAD–ACID CELL. A REVIEW

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Summary

The electrochemical behaviour of a lead–acid cell changes significantly after the addition of small amounts of phosphoric acid (H_3PO_4) The observed phenomena have been studied for about 60 years In this historical review emphasis is placed upon the early work of Kugel and Rabl, for although much of this has remained unpublished, the findings have been applied successfully to the operation of practical batteries The work of Kugel and Rabl is therefore a remarkable example of early research in the battery industry. Subsequently, considerable additional knowledge has been collected, but there is still no clear understanding of the principal mechanism of the action of H_3PO_4 in lead–acid cells.

Introduction

The addition of phosphoric acid (H_3PO_4) either to the electrolyte or to the positive active material of a lead–acid cell has been practised since the turn of the century, and the resultant effect on cell behaviour has been studied extensively. Although a plethora of empirical data has been collected subsequently, the influence of small amounts of H_3PO_4 on reactions occurring at the positive electrode is by no means fully understood.

Around 1930, the German-based battery company Accumulatoren-Fabrik Aktiengesellschaft (AFA), which changed its name to VARTA Batterie AG in 1962, and in particular its Austrian subsidiary in Vienna (now ÖFA-Akkumulatoren GmbH), commenced the manufacture and marketing of lead–acid batteries with phosphoric acid additions under the DUROS trade name The production continued until the 1970s and some of the batteries remained in use in electric delivery vans of the Austrian Post Administration up to 1980. Over the years, it was considered necessary to support the DUROS system by detailed experimental research and, as a consequence, AFA/VARTA/OFA accumulated considerable knowledge on the effects of phosphoric acid additions In spite of the ravages of World War II, there survived a small file of reports and letters on various aspects of

phosphoric acid additions Most of the work was performed between 1926 and 1935 by Dr Moritz Kugel, who during that period was Director of Research at the Vienna factory, and his colleague Ing Max Rabl In 1926, a patent was granted to Kugel on the application of phosphoric acid in lead–acid cells [1] In retrospect, the first serious investigation on one of the most interesting topics of the lead–acid cell can be attributed to these two scientists

VARTA Batterie AG is celebrating its centenary in 1988 It is therefore timely to consider in this review the merits of the work of Kugel and Rabl, for not only is the work an excellent example of early research in the battery industry, but also most of the results have not been published In addition, attention is paid to the studies of other investigators on phosphoric acid additives that have been reported in the literature

The work of Kugel and Rabl

The addition of phosphoric acid (H_3PO_4), or phosphates mostly of the alkali metal and alkaline earth metal groups, either to the sulphuric acid electrolyte or to the positive active material of a lead–acid cell can be traced back to the 1890s An early patent by Boese [2] described the use of H_3PO_4 and red lead (Pb_3O_4) for the preparation of a paste that, after a short time, reacted to form a firm and hard active material of high porosity The latter material could be converted easily to either PbO_2 or metallic lead Brault [3] mixed lead oxide with alkali or alkaline earth phosphates (which were explicitly named among a number of other salts) and used the product, after addition of water and a complicated pretreatment with ammonia, for plate manufacture Again, it was claimed that a very stable active material was formed Finally, Cheney [4] asserted that a battery containing a sulphuric acid electrolyte with an addition of about 58 g of sodium phosphate per litre could be charged "more speedily" In all of these patents, no reference was made to any specific effects of the phosphoric acid/phosphate addition on the electrochemical behaviour of the lead–acid cell

In his first patent (filed 7 November, 1926), Kugel claimed that 10 - 20 g H_3PO_4 per litre of electrolyte prevented sulphation of the active material during open-circuit stand after deep discharge [1] The same was found to be true if meta- or pyro-phosphoric acid, or alkaline phosphate, was added instead In the first extension of this patent, Kugel reported changes in the H_3PO_4 concentration during charge/discharge cycling of the cell H_3PO_4 was absorbed by PbO_2 during cell charging and was released to the electrolyte on discharging In other words, H_3PO_4 behaved conversely to H_2SO_4 [5] Kugel also noticed that the H_3PO_4 concentration in the electrolyte gradually decreased on cycling and proposed that this loss should be made up by periodically adding further amounts of H_3PO_4 to the electrolyte In second and third extensions of the original patent [6, 7], Kugel and Rabl recommended the formation of pellets from metal oxides and H_3PO_4 mixes so that

the additive could be introduced into the electrolyte both conveniently and in the correct proportions. Needless to say, oxides harmless to the cell, such as those of Mg, Ca, Al, Zn, Cd, and Pb, were proposed as pellet-forming materials.

The foregoing, in essence, was the knowledge on H_3PO_4 additives published by Kugel and Rabl in 1926 Both researchers immediately became aware of the fact that H_3PO_4 actively influenced the electrochemistry of the $PbO_2/PbSO_4$ electrode In the following years, they devoted a considerable amount of work towards gaining a better understanding of various phenomena observed with H_3PO_4, as is attested by a file of internal (unpublished) AFA/VARTA/ÖFA reports and letters compiled between 1927 and 1935

In September 1927, a comprehensive investigation was initiated in order to study systematically the effect of H_3PO_4 additives on the formation (i e, anodic corrosion) of soft lead sheet electrodes, as well as on the capacity, active material shedding, and voltage increase of such plates Concentrations of H_3PO_4 were varied from 0 to 16 g l^{-1}. As recorded in an intermediate report dated 20 October, 1927 [8.1], the findings were most confusing. In one instance, a steady decrease in the corrosion rate with increasing amounts of H_3PO_4 was observed. This, however, could not be clearly reproduced in a second experiment. In addition, no conclusive results were obtained on capacity, shedding rate, and electrode potential On the other hand, it was found that H_3PO_4 reduced self discharge This report, although preliminary, demonstrates some of the difficulties a researcher has to face when experimenting with H_3PO_4 additives. Unfortunately, no final report on the project has survived

In a letter dated 10 May, 1928 and addressed to the AFA headquarters in Berlin [8 2], Kugel reported that a soluble Pb(IV)-species was formed in an H_3PO_4-containing electrolyte during charging of the positive electrode Concentrations up to 4 g Pb(IV) per litre electrolyte were determined analytically It was discussed in detail how the Pb(IV) content in the electrolyte depended on the H_3PO_4 content and how the highly oxidizing agent might interfere with the normal operational behaviour of a lead–acid cell The Pb(IV)-compound, which sometimes deposited as a bulky gel-like solid, oxidized organic materials such as wood separators or organic expanders. This resulted in densification of the lead in the negative electrode and, consequently, in early failure of that electrode. The soluble Pb(IV)-species was reduced to lead at the negative electrode where it formed a moss-like structure that occasionally resulted in a short-circuit of the cell Therefore, the formation of Pb(IV)-species was highly undesirable and preventive measures were developed Rabl proposed the addition of a small quantity of Fe^{2+} ions to the electrolyte (about 0 2 g Fe l^{-1}) in order to reduce the Pb(IV)-species.

Following the above letter, Kugel prepared a detailed report which represented the state-of-the art on phosphoric acid additives in mid-1928 [8.3]. The following points were highlighted in that report

(1) finely dispersed $PbSO_4$ crystals were formed on discharge,

(ii) the corrosion rate of lead was very low, which resulted in a reduced shedding rate for Planté electrodes,

(iii) the formation of soluble and solid gel-like Pb(IV)-species was associated with changes in the H_3PO_4 concentration during charge and discharge, and during cycling,

(iv) the amount of Pb(IV)-species formed during cell operation depended on the amount of H_3PO_4 added,

(v) Pb(IV)-species were also prepared chemically by the reaction of red lead (Pb_3O_4) with a mixture of H_2SO_4 and H_3PO_4 — a yellow solution was obtained which within a few hours, formed a white, solid gel that hydrolyzed to PbO_2 upon water addition

Various life tests were carried out on both stationary (Planté type) and automobile (Faure type) cells It was found that after a period of cycling the content of H_3PO_4 in the electrolyte (originally 7 g l^{-1}) was determined by both the rate of discharge and the state of charge

The rate of shedding of material in Planté-type cells (114 A h) when discharged at the 1 h rate is given in Table 1 It can be seen that an H_3PO_4 concentration of about 8 - 10 g l^{-1} results in a minimum amount of shedding Similar data were obtained from discharge tests at the 3 h rate

TABLE 1

Shedding of positive active material in Planté cells (114 A h) as a function of H_3PO_4 addition after 565 cycles
(Density of H_2SO_4 1 18 g cm^{-3})

H_3PO_4 (g l^{-1})	Shedded material (g/cell)
0	4053
4 (initially), 11 (later)	1240
8 (initially), 11 (later)	1106
12 (initially)	1769

Larger amounts of H_3PO_4 can be tolerated when sulphuric acid of greater strength is used, as shown by the data summarized in Table 2 The Pb(IV) content is more rapidly reduced by precipitation as the electrolyte concentration is increased For this reason, an H_3PO_4 concentration as high as 14 g l^{-1} has a beneficial effect

From above results, it is clear that the optimum dosage of H_3PO_4 depends on a number of parameters, such as electrolyte concentration, method of H_3PO_4 addition, etc As will be shown later, the PbO_2/H_2SO_4 electrolyte ratio and electrode type (Planté, Faure) are also important Kugel and Rabl were well aware of these important points Evidently, the mere notation of phosphoric acid dosage in terms of g H_3PO_4 l^{-1} is insufficient, this is understandable in view of the PbO_2/H_3PO_4 reaction(s) occurring in the cell (*vide infra*)

TABLE 2

Shedding of positive active material in Planté cells (70 A h) after 123 cycles, and capacity after 172 cycles as a function of H_3PO_4 content
(Density of H_2SO_4 1 28 g cm^{-3})

H_3PO_4 (g l^{-1})	Shedded material after 123 cycles (g/cell)	Capacity after 172 cycles (% of nominal)
0	612	86
8	344	86
11	196	98
14	108	108

In the final paragraphs of his report, Kugel briefly reported that when H_3PO_4 was added in optimum amounts, there was no deleterious effect on cell capacity. Indeed, Planté cells displayed an increase in capacity after a given period of operation due to a reduction in the rate of material shed. Further, it was stated that the cell voltage was higher during both discharge (i e , 50 - 100 mV) and charge (but to a lesser extent) Finally, the effect of Fe^{2+} ions on the Pb(IV) concentration was discussed in the sense mentioned above

The addition of Fe^{2+} ions to control the Pb(IV) concentration was obviously of vital interest during the following years In 1930, Kugel reported the effect of Fe^{2+} ion concentration on both the capacity and the shedding rate of Planté electrodes in electrolytes doped with 8 g H_3PO_4 l^{-1} [8.4]. Possible causes of active material shedding e.g, mechanical forces (gassing), reduction of Pb(IV)-compounds at the negative electrode, hydrolysis of Pb(IV)-compounds were discussed in detail As a result, it was stated that whereas $FeSO_4$ in quantities up to 0.05 g l^{-1} did not affect capacity, shedding or cell voltage, complete prevention of Pb(IV) formation did not occur before 0.2 g l^{-1} $FeSO_4$ had been added to the electrolyte This concentration, however, was too high since the electrode capacity decreased by 5% and material shed was increased by 80%. At that time, specifications for sulphuric acid allowed a maximum of only 30 mg Fe l^{-1}. In consequence, it was proposed to reduce the H_3PO_4 dosage

The effect of Fe^{2+} and Fe^{3+} ion additives was also tested in cells using Faure electrodes (pasted plates) [8 5] It was again found that the shedding rate increased with an increasing amount of Fe, regardless of valency state.

As mentioned above, the H_3PO_4 concentration in the electrolyte depended on the state-of-charge and, when compared in the fully charged state, it decreased gradually during the first cycles. If, however, H_3PO_4 was added to the active material during paste mixing, the H_3PO_4 concentration in the electrolyte increased during cycling and finally reached a constant value This trend can be seen in the data presented in Table 3 which have been taken from a report by Kugel [8.6]. It is also clear that the H_3PO_4

TABLE 3

H_3PO_4 contents in electrolyte and charged, positive active material of Faure plates during the first cycles

Charge no	1		2		3		4		5		6
Discharge no		1		2		3		4		5	
H_3PO_4 in electrolyte											
charged state (g l^{-1})	3 6		3 9		4 3		4 7		5 1		5 3
discharged state (g l^{-1})		4 7		5 3		6 0		6 5		6 8	
H_3PO_4 in positive material											
charged state (%)	2 5		2 4		2 1		1 9		1 7		1 6

content in the electrolyte was generally higher in the discharged state than in the charged state

Obviously, the H_3PO_4 distribution between electrolyte and active material approaches a state of equilibrium which probably depends on a number of different parameters, such as current density during charge and discharge, acid concentration, and temperature So far, there is no detailed information about these relationships

Whereas the experiments on Faure plates were performed at the ÖFA laboratory at Vienna-Liesing, another series of experiments was conducted at the AFA laboratory at Hagen/Westphalia [8.7] Again, the plates were prepared by using a paste containing probably about 2 - 3% H_3PO_4. The cycle life of these electrodes was tested in standard cells containing 9 electrodes (4 positives, 5 negatives), and compared with that of identical cells having no H_3PO_4 additive The results obtained after 300 - 327 cycles are shown in Table 4 It can be seen that the capacity of cells with the H_3PO_4 additive is 13 - 18% lower than the capacity of cells without H_3PO_4 additives, the difference depends on the discharge rate In the presence of H_3PO_4, the cell voltage at the beginning of discharge is generally increased by 10 - 20 mV It was further noted that the positive active material in H_3PO_4-containing cells adhered more firmly to the grid than in cells without H_3PO_4

TABLE 4

Cycle life data of 4 Ky 225 elements with/without H_3PO_4 addition

Cycle	Discharge rate (h)	Nominal $C/5$ capacity (%)		Voltage at start of discharge (V/cell)	
		With H_3PO_4	Without H_3PO_4	With H_3PO_4	Without H_3PO_4
300	5	60	68	2 04	2 02
325	5	58	66	2 03	2 02
326	10	58	67	2 04	2 03
327	1	50	59	2 03	2 02

TABLE 5

Effect of H_3PO_4 dosage on cycle life of Ky type cells (Faure)
(End of life taken as 60% $C/5$)

H_3PO_4 in positive paste (g kg^{-1} lead oxide)	Cycle life
9	220
20	330
29	490
40	720

As a consequence, the corresponding shedding of material was lower This latter observation was investigated in more detail with Faure-plate cells The results were summarized in an anonymous report many years later [8 8] confirming the data of Table 4. In addition, the effect of H_3PO_4 dosage on the cycling behaviour of electrodes was studied. The findings are presented in Table 5

It was further pointed out that the amount of material shed was reduced by about 50% if H_3PO_4 was added to the positive active material At an H_3PO_4 concentration of about 60 g kg^{-1} lead oxide an excessive mossing rate, $i e$, the formation and reduction of Pb(IV) material, resulted in early cell failure due to short circuits.

At this point, it might be of advantage to summarize briefly the results obtained by the Kugel/Rabl group up to about 1935 No original documents on research activities during the subsequent years have survived Nevertheless, it can be assumed that there was no abrupt stop to the work because the so-called DUROS cells continued to be manufactured and marketed. In brief during the Kugel/Rabl era, the following conclusions were reached for the effect of phosphoric acid in lead–acid cells

(i) retards sulphation on stand after deep discharge,

(ii) promotes the formation of Pb(IV)-species on charge (a yellow, soluble type and a solid, white compound), these may cause increased mossing and may oxidize organic materials ($i e$, separators, expanders);

(iii) reduces lead corrosion;

(iv) reduces self discharge;

(v) affects the cell voltage, more specifically the potential of the PbO_2 electrode;

(vi) reduces the shedding rate of positive active material;

(vii) increases the cycle life of lead–acid cells, more specifically the life of positive electrodes;

(viii) reduces the capacity of positive Faure plates by about 15%,

(ix) may increase the capacity of Planté electrodes due to lower shedding rates,

(x) behaves with regard to its concentration in the electrolyte in a manner opposite to the sulphate ion.

AFA/VARTA work around 1960

A new interest in gaining a more detailed knowledge of the various effects of H_3PO_4 additives on the behaviour of lead–acid cells arose within the AFA/VARTA organization in 1959 At that time, no member of the old generation of researchers and engineers was still active in the company In order to facilitate the knowledge transfer, Mr Norbert Rabl (who started his career at the OFA laboratory in Vienna-Liesing in 1926 under his father, Max Rabl, and Dr Kugel) was invited to participate in a colloquium on H_3PO_4 topics which was held at Hagen The results of this colloquium were documented in a very detailed report [8 9]. The following is a discussion of only those results that have not been mentioned in the above paragraphs

In his contribution to the colloquium, N Rabl reported on the reduced shedding rate of positive active material and attributed this phenomenon to the formation of the white, gel-like Pb(IV) compound which acted as a 'glue' for the PbO_2 particles It was suggested that the composition of this compound was $Pb(HPO_4)(SO_4)$ Due to the proposed glueing effect, it appeared that the positive active material showed an increased hardness when H_3PO_4 was present in the cell For this reason, the brand name DUROS was coined for cells and batteries that contained H_3PO_4

The question of correct H_3PO_4 dosage can only be answered empirically The equilibrium distribution of H_3PO_4 between positive active material and electrolyte can be calculated by using the following empirical equations

$$K_c = K_p + K_A \tag{1}$$

$$K_p = bK_A^{1/2} \tag{2}$$

where K_c = amount of H_3PO_4 in cell, K_p = amount of H_3PO_4 in positive active material, K_A = amount of H_3PO_4 in acid electrolyte, b = factor that depends on type of electrode and cell, acid density, etc

As was experienced in the AFA laboratory at Hagen [8 10], the gel-like Pb(IV)-compound could be electrochemically prepared in larger quantities in diaphragm cells by electrolyzing a diluted phosphoric acid solution (~2 5 M) between lead electrodes In the anode compartment, a yellow solution was formed initially After about 2 h, the electrolyte was gellified completely, the yellow colour disappeared within a further 3 - 4 h It was found that the gel acts as a strong oxidant The same yellow solution and the gel were also obtained by the reaction of red lead with an H_2SO_4/H_3PO_4 mixture, as mentioned above Again, the high mechanical stability of the positive active material was attributed to gel formation In parallel with these activities in Hagen, the AFA Central Laboratory at Frankfurt (since 1966 in Kelkheim) commenced a programme to identify the chemical nature of the Pb(IV)-species The results of this work have been published and are summarized below

Nature of Pb(IV)-species

From the above discussions, it follows that studies of the composition and other properties of the two Pb(IV)-species may assist the interpretation of the various phenomena observed in DUROS cells Using the electrochemical and chemical methods described above, substantial amounts of both Pb(IV)-compounds have been prepared and analyzed [9] The yellow, soluble compound was determined to be $2PbO_2 \cdot P_2O_5 \cdot xH_2O$ ($x \sim 2\,5$ - 3.0). No sulphate species were found in the material In solution, the yellow compound behaved as an anion and hydrolyzed to PbO_2 even in sulphuric acid solutions at concentrations typically used in lead–acid cells. With further addition of H_3PO_4, the yellow solution readily transformed to a white gel of composition $PbO_2 \cdot P_2O_5 \cdot xH_2O$. Again, no sulphate was detected. According to a later investigation of Huber and El-Meligy [10], however, it appears that the compound may have the composition $PbO_2 \cdot P_2O_5 \cdot SO_3$, and the structures $H_2[Pb(HPO_4)_2SO_4] \cdot xH_2O$ or $H[Pb(HPO_4)_2HSO_4] \cdot xH_2O$ have been tentatively proposed. In addition, Huber and El-Meligy identified white gel materials of the composition $H_2[Pb(H_2PO_4)_6]$ and $H_2[Pb(H_2PO_4)_2\text{-}(HPO_4)_2] \cdot 2H_2O$ which might form high molecular complexes. A survey on Pb(IV)-phosphates has been published by Frydrych and Lohoff [11].

Since it is evident that the formation of the soluble, anionic yellow compound is the primary reaction on anodization of a $PbO_2/PbSO_4$ electrode that may be followed by a precipitation and transformation to the gel compound in the pores of the positive active material, the observed decrease of the H_3PO_4 concentration in the electrolyte on charge appears to be plausible Equally, the higher potential of the positive electrode on charge and at the beginning of discharge, as well as the reduced relaxation in potential after termination of charge, by comparison with an electrode without H_3PO_4 addition, may also be attributed to the Pb(IV)-compounds. At the present time, this point cannot be substantiated because no thermodynamic data on the Pb(IV)-phosphates are available. On discharge, the Pb(IV)-compounds are reduced to $PbSO_4$, and phosphate is returned to the electrolyte. The variation of the phosphate content in positive active material has also been confirmed by the autoradiographical studies of Tudor *et al* [12]. These authors also recorded the specific behaviour of the H_3PO_4-containing electrode on the electrode potential mentioned above [13].

Whether the glue hypothesis developed for the explanation of the DUROS effect is correct remains a matter of debate. As shown by Mateescu [14], the film formed on a lead electrode in a H_3PO_4/H_2SO_4 electrolyte becomes adherent and compact after some cycling In this connection, an interesting result of Visscher [15] seems to be of importance. From cyclic voltammetric studies, Visscher found that the formation of α-PbO_2, which is considered to improve cycle life, is favoured after the addition of H_3PO_4 whereas the formation of β-PbO_2 is inhibited On the other hand, Sternberg *et al* [16] showed that the anodic formation of PbO_2 is greatly impeded by the presence of H_3PO_4. This appears to contradict the results of

Rasına *et al* [17] who stated that H_3PO_4 additions 'lower the overvoltage of the charging process $(PbSO_4 \rightarrow PbO_2)$'

Anodic corrosion of lead and self-discharge

The earliest evidence of H_3PO_4 addition causing a reduced anodic corrosion and self-discharge rate was presented by Kugel [8 1] Constant-potential corrosion studies on lead-sheet electrodes in H_3PO_4/H_2SO_4 electrolytes showed [18] that the electrolyte composition had no effect on the corrosion rate at the potential of minimum corrosion On the other hand, the results of Kugel have been confirmed repeatedly within the AFA/VARTA/ÖFA group and, more recently, by work in the U S A [19, 20] Therefore, the effect of H_3PO_4 on corrosion and self-discharge of a PbO_2 electrode can be accepted as fact It is, however, still unclear how the higher oxygen overvoltage observed by Rasına *et al* [17] fits this statement The morphology of the corrosion film is greatly affected by H_3PO_4, and it has also been shown [20, 21] that a lower self-discharge rate can only be observed when the corrosion film has been generated in the presence of H_3PO_4 The change in PbO_2 morphology due to H_3PO_4 has been confirmed recently [22]

Sulphation of active material

According to Kugel's first patent [1], H_3PO_4 was originally added to reduce the sulphation of active material, particularly in the deep-discharge state It was found that $PbSO_4$ in the presence of small amounts of H_3PO_4 was precipitated as very small crystals that were more finely divided than those precipitated in the absence of H_3PO_4 [8 3] The effect of H_3PO_4 additives on the $PbSO_4$ precipitation during discharge of positive Faure-type plates using Pb–Ca grids was confirmed by Tudor *et al* [12, 13, 23] Those authors found that (i) the formation of a $PbSO_4$ barrier layer around the grid wires, which promotes a premature loss of capacity, is largely prevented by adding H_3PO_4 to the electrolyte, (ii) a stable $PbSO_4$ distribution pattern is produced across the active material pellets which improves the cycling behaviour and reduces shedding. The addition of H_3PO_4 to a lead–acid cell appears, therefore, to act as a remedy for the early degradation of capacity that is observed on cycling of cells that do not contain any antimony in the grid [24]. The same effect is observed in Pb–Ca cells that employ an electrolyte with H_3PO_4 dosage immobilized by silica gel [25, 26] From impedance measurements on PbO_2 electrodes in phosphate electrolytes, Carr and Hampson [40] concluded that phosphate ions are adsorbed at the electrode. This phosphate may be responsible for the results obtained by Tudor *et al* [12, 13, 23] showing that an insulating $PbSO_4$ film did not develop on discharge in the presence of H_3PO_4 This was also confirmed by Sternberg *et al* [16]

Solubility-pH and potential-pH diagrams

During both plate manufacture (ιe, paste preparation and application, curing, and formation) and cell operation, the pH prevailing in the different process stages may vary between about 10 and -1 As a quick and comprehensive reference to the various compounds that may possibly be involved in the chemistry and electrochemistry of a galvanic system, it is common practice to calculate the relevant solubility-pH and the potential-pH (Pourbaix) diagrams from available thermodynamic data. Such diagrams have been constructed for the lead−acid system [27 - 30], as well as a solubility-pH diagram in the pH range 0 - 14 for the compounds PbO, $Pb_3(PO_4)_2$, and $PbHPO_4$ in H_3PO_4 solution [18] Bullock [21] was the first to calculate the solubility-pH diagram for the mixed-acid system $PbO−H_2SO_4−H_3PO_4−H_2O$ Most surprisingly, Bullock found $Pb_3(PO_4)_2$ to be stable over a wide range of conditions predominating in the corrosion film. From this point of view, it is possible that $Pb_3(PO_4)_2$ affects the PbO_2 morphology ($v s$) as well as the composition of the film at the grid/active material interface. There is still some uncertainty, however, about the value of the free enthalpy of formation (ΔG) of $Pb_3(PO_4)_2$. The value used by both Voss [18] and Bullock [21] has been taken from Latimer [31] Although the value differs from that given by Nriagu [32], it is identical with that of the U.S NBS [33] The latter, however, disappeared in a later NBS publication [34]. Consequently, the ΔG value given by Nriagu appears to be the most reliable Since the value differs by about 16 kcal mol^{-1} from that quoted by Latimer, a recalculation should be conducted Nriagu has also calculated the ΔG values of the basic lead phosphates $Pb_5(PO_4)_3OH$ (hydroxypyromorphite) and $Pb_4O(PbO_4)_2$, the latter having a "wide stability field" This indicates, again, the need for a recalculation of the solubility-pH diagram.

It is reasonable to assume that in an operating lead/acid cell the activity of the sulphuric acid solution is $a_{HSO_4^-} = a_{SO_4^{2-}} = 1$ and the activity of the H_3PO_4 added to this electrolyte is $a_{H_3PO_4} = a_{H_2PO_4^-} = a_{HPO_4^{2-}} = 0.1$ Under these conditions, $PbSO_4$ is stable over a wide pH range up to about pH = 5. Therefore, $PbSO_4$ is formed at the positive electrode on discharge and the difference in voltages due to the H_3PO_4 addition may be attributed to electrochemical couples such as $PbO_2 \cdot P_2O_5 \cdot xH_2O/PbSO_4$ (cf ref. 35) This is pure speculation, however, since ΔG values are not available for any of the Pb(IV)-compounds. A study of the thermodynamics of these compounds is essential

H_3PO_4-related aspects of practical battery operation

As pointed out in the introduction to this paper, lead−acid cells and batteries dosed with H_3PO_4 have been produced and marketed since about 1930. They have been used mainly in applications where regular and fre-

quent cycling is required, such as vehicle traction, battery-powered trains, and special stationary equipment In these cases, the reduced shedding rate of the positive active material and the longer cycle life are both extremely beneficial. On the other hand, the H_3PO_4-containing cells require special operational specifications and additional maintenance. It has been mandatory to operate the cells above 15 °C because the stability of the Pb(IV)-compounds increases with decreasing temperature and, consequently, at low temperatures there is a tendency to form lead dendrites (*i e*, mossing, see above) and, subsequently, short circuits Another troublesome requirement has been the close control of the H_3PO_4 concentration in the electrolyte, which has been considered to be particularly necessary during early service life. Occasionally, extra amounts of H_3PO_4 have to be added to the cell

Uncertainty over the correct H_3PO_4 dosage is one of the main reasons for the catastrophic cell behaviour that is occasionally observed In the literature, the addition of H_3PO_4 is given usually in grams per litre, although Kugel and Rabl have suggested that addition in terms of grams H_3PO_4 per gram (or cm^3) of PbO_2 is more meaningful This point has been discussed recently by Sternberg *et al* [16] It is probably even more significant to relate the amount of H_3PO_4 to the amount of PbO_2 as well as to the amount and concentration of H_2SO_4 because, as mentioned previously, the state of equilibrium clearly depends on all of these parameters In many investigations, this important aspect has not been fully taken into account

Phosphoric acid-containing cells have been almost exclusively equipped with Planté- or Faure-type electrodes. Tubular plates have never been used in combination with H_3PO_4 additives, despite the patent by Evers *et al.* [36] This is probably because tubular electrodes themselves exhibit an extraordinarily long cycle life Obviously, as the penetration of tubular-plate cells into the market grew and maintenance operations during cell operation became an economic problem of increasing importance, the benefits due to the H_3PO_4 additive were gradually devalued Nevertheless, a remarkable interest in H_3PO_4, has persisted, especially as Tudor *et al* [13] have shown that it may help to stabilize the capacity of cells using lead–calcium grids under cycling conditions For example, in sealed lead–acid cells utilizing lead–calcium grid alloys and immobilized electrolytes, a small amount of H_3PO_4 is sometimes used to improve the cycling performance [25]

Phosphoric acid is also present in lead–acid cells of the reserve type that can be activated by addition of water For this purpose, the required amount of concentrated sulphuric acid is immobilized by a boron phosphate gel which is spontaneously soluble in water [37 - 39] From the performance data reported for water-activated batteries with an electrolyte of H_3PO_4/H_2SO_4 in a molar ratio of about 1 100, it can be concluded that a number of the above mentioned phenomena relevant to H_3PO_4 have proved effective [39]

Final remarks

Phosphoric acid significantly influences the basic electrochemistry of a lead–acid cell. When added either to the electrolyte or to the positive active material, various phenomena can be observed which, in turn, are associated with the H_3PO_4 action in the cell. Reduced shedding of positive active material, decreased anodic corrosion of lead, lower self discharge, mitigation of the sulphation problems, and formation of Pb(IV)-compounds during charge are the most salient manifestations of the beneficial action of H_3PO_4. All of these phenomena were first recognized by Kugel and Rabl in the years around 1930 Both workers also demonstrated the practical application of their results and laboratory observations. Although the importance of H_3PO_4-related phenomena in battery operation has decreased somewhat since then, an interest in H_3PO_4 effects has continued to exist to the present day. In spite of an increasing fund of knowledge, however, the mechanism of H_3PO_4 interaction has still to be elucidated This situation clearly explains why the benefits of H_3PO_4 additions are not exploited universally in modern lead–acid batteries

Acknowledgements

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