

BEHAVIOUR OF THE $\text{PbO}_2/\text{PbSO}_4$ ELECTRODE WITH REGARD TO CHARGING REGIME AND SMALL ADDITIONS OF PHOSPHORIC ACID TO THE SULPHURIC ACID ELECTROLYTE

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Introduction

It has been well known for over 80 years that the capacity of a lead/acid cell depends greatly on the previous charge/discharge history [1 - 4]. For example, in 1907, Jumau [1] was able to relate this 'memory effect' to the positive electrode. As a consequence, it became a prerequisite in the battery industry to apply so-called 'equilibration charges and discharges' prior to a precise capacity determination in order to obtain stable and reliable data.

Only recently have investigations been directed towards determining the extent to which the various parameters of a cycle regime influence the capacity changes [5]. The charge current density, as well as the amount of charge and overcharge, have all been found to be of high significance. These findings have resulted in specifications that allow cycling at a capacity close to optimum without any premature degradation. In daily battery operation, however, practical conditions, such as adequate chargers or power requirements, are often far from optimum. It is still an important and possibly profitable goal, therefore, to search for means that may at the very least mitigate, if not completely sever, the relation between capacity and previous charge/discharge history.

From the work of Kugel and Rabl (reviewed in ref. 6), it is known that the addition of small amounts of phosphoric acid (H_3PO_4) to the sulphuric acid electrolyte results in a considerable increase in the cycle life of a $\text{PbO}_2/\text{PbSO}_4$ electrode. Moreover, Tudor *et al.* [7] have demonstrated the ability of H_3PO_4 additions to improve the capacity stability of a $\text{PbO}_2/\text{PbSO}_4$ electrode under a shallow cycle regime. Therefore, it may be surmised that a small amount of H_3PO_4 in the electrolyte decreases the sensitivity of the electrode to variations in the cycling parameters. It is now necessary to determine if, and how, H_3PO_4 additions influence the 'memory effect'.

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Experimental

Experiments were performed on Planté electrodes. Details of dimensions, electrolyte concentration, and equipment have been reported previously [5].

Phosphoric acid (as a solution in sulphuric acid of the same concentration as the electrolyte) was added in small quantities namely 1 - 4 g, during the charging period of a continuous cycling experiment. The addition was repeated at intervals of a few cycles until, finally, no change in capacity was observed. At this point, 16 g of H_3PO_4 in total had been added to the cell, which was equivalent to a molar ratio of $[H_3PO_4]/[H_2SO_4] = 0.9 \times 10^{-2}$.

Results

In a recent study [5], it was shown that a Planté electrode maintains its capacity on cycling at a stable and high level when most of the charge (about 70%) is returned at a high current density (about $C/1$ to $C/2$ rate) and at a limited amount of overcharge (about 15%, maximum 20%). This high-rate/low-rate charge method is designated 'regime A'. A rapid capacity decay is

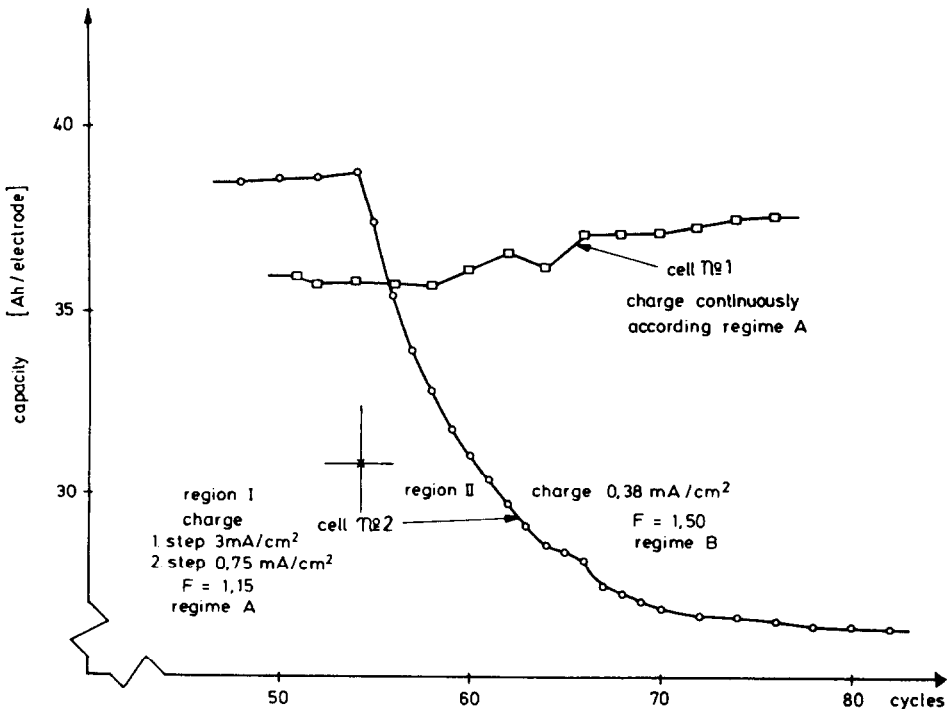


Fig. 1. Effect of charge regime on capacity of a Planté electrode (discharge current: 0.75 mA cm^{-2}).

observed when the recharges are performed at a low current density (about $C/10$ rate) and at high overcharges (about 50%); this procedure is referred to as 'regime B'. Typical capacity behaviour is illustrated in Fig. 1. It can be seen that a capacity decay of $\sim 25\%$ (depending on the discharge current density) can be generated by charge regime B. By contrast, charge regime A stabilizes the capacity at its highest level. The reason for the difference in behaviour of the PbO_2 electrode has been discussed elsewhere [5].

Effect of H_3PO_4 additions on capacity stability

In order to study the effect of H_3PO_4 additions on the capacity, electrodes were treated according to the procedures indicated in Fig. 1, but in the presence of 16 g H_3PO_4 per cell. When using charge regime A, the capacity decreased by $\sim 8\%$ within 15 cycles (Fig. 2, cell No 2). If the charge was switched to regime B, however (Fig. 2, cycle 240), the H_3PO_4 -containing cell was much more resistant to capacity decay than the cell without H_3PO_4 (*i.e.*, 5% loss *versus* 33% for cell No 2). Furthermore, most of the capacity losses occurred during the first 10 cycles after the electrode has been subjected to charge regime B. In total, the capacity decay produced by the H_3PO_4 addition was about 13%, whereas that for the cell without H_3PO_4 amounted to 33%. In summary, it can be said that H_3PO_4 addition to the electrolyte decreases the sensitivity of the capacity of Planté type $\text{PbO}_2/\text{PbSO}_4$ electrodes to variations in charge regime.

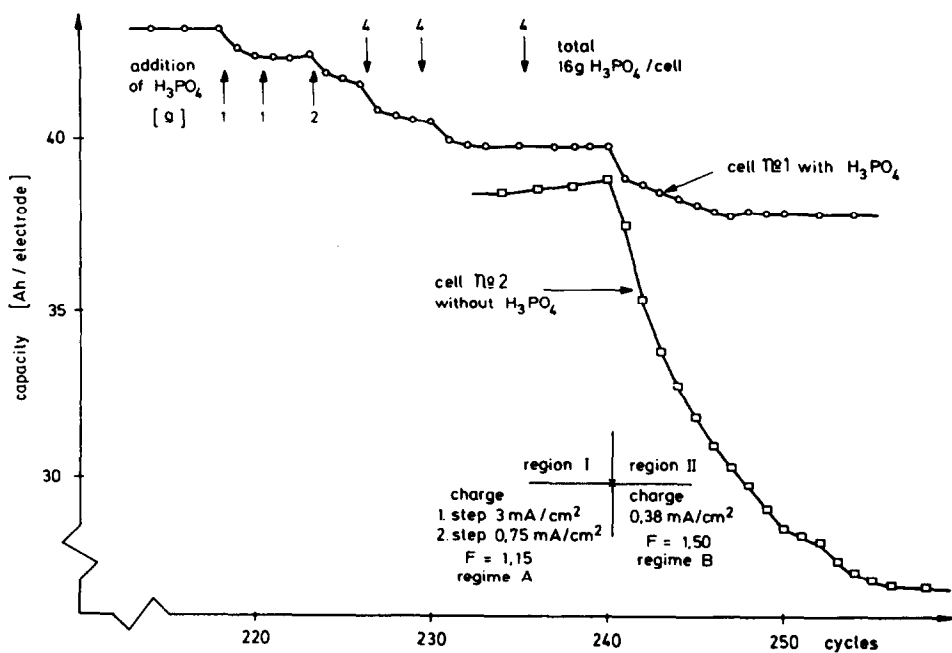


Fig. 2. Effect of H_3PO_4 addition on capacity of a Planté electrode in relation to charge regime.

Effect of H₃PO₄ additions as a function of discharge current density

It appears that there is no information available concerning the effect of discharge current density on the capacity of a PbO₂/PbSO₄ electrode in the presence of H₃PO₄ in the electrolyte. This is particularly true for electrodes that have been transferred to a low capacity state by applying charge regime B. For this reason, the performance of electrodes with both a high, and a low, capacity level was examined in the presence and absence of H₃PO₄ in the electrolyte. It should be pointed out that before a capacity measurement was taken, the electrode was returned to its original C/10 capacity state (by appropriate cycles) in order to exclude failure due to the 'memory effect'. The results of the experiments are collated in Table 1. The following conclusions may be drawn from these data:

● The capacity as a function of discharge current density decreases at a lower rate in the presence of H₃PO₄ than in its absence, regardless of the

TABLE 1

Capacity data of Planté PbO₂/PbSO₄ electrodes as a function of discharge current density, H₃PO₄ addition and capacity level

Discharge current density (mA cm ⁻²)	Rate (h)	EDV* (V/cell)	Capacity	
			Ah electrode	% C ₁₀
1. Electrode on high capacity level, without H ₃ PO ₄				
0.75	10	1.80	38.7	100
1.50	5	1.65	34.5	89
3.00	2	1.50	30.7	79
2. Electrode on high capacity level, with 16 g H ₃ PO ₄ /cell				
0.75	10	1.80	38.7	100
1.50	5	1.65	36.7	94
3.00	2	1.50	33.1	86
3. Electrode on low capacity level, without H ₃ PO ₄				
0.038	200	1.80	44.2	169
0.188	40	1.80	36.0	138
0.375	20	1.80	30.0	115
0.75	10	1.80	26.1	100
1.50	5	1.65	22.3	85
3.00	2	1.50	18.4	70
6.00	0.8	1.35	14.3	55
12.00	0.2	1.20	11.5	44
4. Electrode on low capacity level, with 16 g H ₃ PO ₄ /cell				
0.038	200	1.80	54.0	165
0.188	40	1.80	43.4	132
0.375	20	1.80	37.3	114
0.75	10	1.80	32.9	100
1.50	5	1.65	30.8	94
3.00	2	1.50	28.1	85
6.00	0.8	1.35	24.2	74
12.00	0.2	1.20	19.8	60

*EDV = end of discharge voltage.

capacity level; this is particularly evident in the current density range $0.375 - 6 \text{ mA cm}^{-2}$.

- In the presence of H_3PO_4 , the rate dependency of electrodes with a low-level capacity is similar to that of electrodes with a high-level capacity.

- In the absence of H_3PO_4 , the rate dependency of electrodes with a low-level capacity is higher than that of electrodes with a high-level capacity.

These results again indicate that H_3PO_4 additions decrease the sensitivity of the Planté electrode to the charge regime. Moreover, it can be stated that H_3PO_4 additions desensitize the Planté electrode in respect of the discharge rate.

Effect of H_3PO_4 additions on float charge behaviour

Planté-type cells are mostly used in standby applications. The float charge behaviour of the cell, and particularly that of the $\text{PbO}_2/\text{PbSO}_4$ Planté electrode, in the presence of H_3PO_4 is therefore of practical interest. The results of float tests performed at 2.23 V/cell are given in Table 2 and compared with those obtained on a cell without any H_3PO_4 addition. It can be seen that the potential of the PbO_2 electrode is increased by about 20 mV , while the stationary current decreases by 20% .

Effect of H_3PO_4 additions on electrode potential

It has been found both by Kugel and Rabl [6] and by Tudor *et al.* [7] that the potential of the PbO_2 electrode on discharge is changed significantly after H_3PO_4 has been added to the electrolyte. Typical potential-time curves, obtained on PbO_2 electrodes under discharge in the presence, and absence, of H_3PO_4 , are shown in Fig. 3. It is clear that the open-circuit potential relaxation after the end of charge is retarded, and the initial potential on discharge is higher, but declining more rapidly, when the electrolyte contains H_3PO_4 .

Discussion

From the results presented in Fig. 2, it can be concluded that an addition of 12 g of H_3PO_4 per cell (having a capacity of 43 A h at 0.75 mA cm^{-2}) is sufficient to stabilize the electrode's capacity. The addition of a further 4 g of H_3PO_4 produces no effect on the capacity. From the work of Kugel and Rabl, it is known that in the charged state about 25% of the total H_3PO_4 in the cell is retained in the active material, probably in the form of a Pb(IV) compound. As this is also found to hold for the Planté cell used here, it follows that about 3 g of H_3PO_4 are bound to the PbO_2 active material by an, as yet, unknown mechanism. If it is assumed that an insoluble $\text{Pb}(\text{HPO}_4)_2$ species is formed in the pores of the active material, and if it is further assumed that the mole volume of this species is $\sim 80 \text{ cm}^3 \text{ mole}^{-1}$, it can be calculated that 1.2 cm^3 of $\text{Pb}(\text{HPO}_4)_2$ is formed in the active material. The Planté electrode used in these

TABLE 2

Float charge of Planté cells at 2.23 V/cell

H_3PO_4 addition (g/cell) (mol l ⁻¹)		Stationary current (mA/electrode)	PbO_2 potential (V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$)
0	0	30	1.164
16	0.034	24	1.183

experiments contains 24 cm³ of PbO_2 [8] and, since it has a porosity of 50%, the electrode exhibits a total pore volume of 24 cm³. The following conclusions can be drawn from this calculation:

(i) The $\text{Pb}(\text{HPO}_4)_2$ occupies space in the pore volume and, consequently, fills about 5% of the total pore volume. This may explain the higher electrolyte flow resistance which is observed in Eloflux experiments with Fauré electrodes after H_3PO_4 addition.

(ii) The high electrode potential during discharge can be correlated to the $\text{Pb}(\text{HPO}_4)_2$ species. The calculated amount of $\text{Pb}(\text{HPO}_4)_2$ species in the pores, however, accounts for a capacity of only 0.8 A h. This small value cannot explain the high initial potential of the electrode over ~50% of the discharge time.

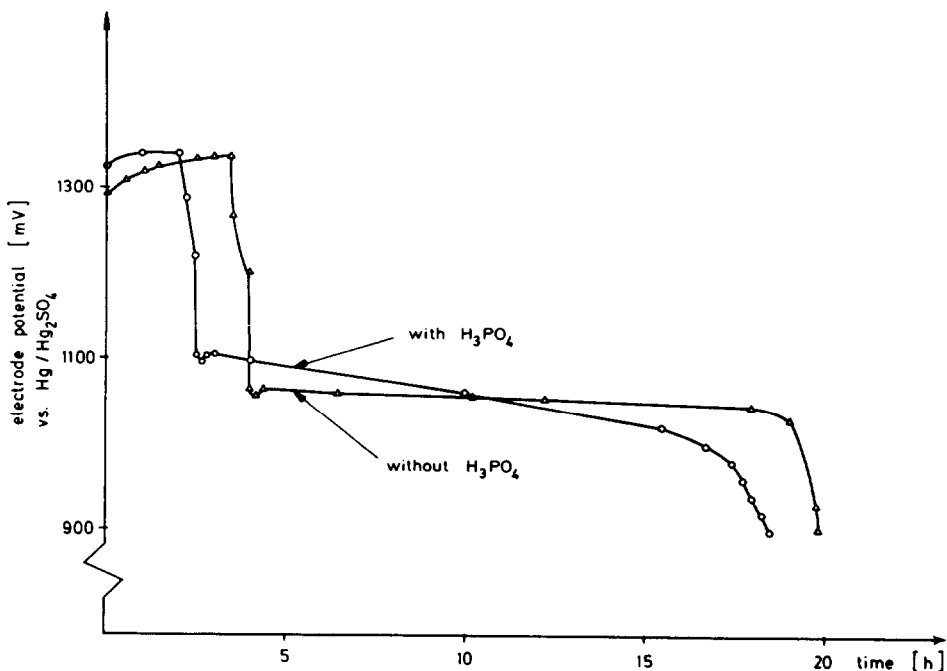


Fig. 3. Effect of H_3PO_4 on potential of a Planté electrode during discharge at 0.75 mA cm⁻².

(iii) In terms of the 'Kugelhaufen' electrode concept, the volume of the $\text{Pb}(\text{HPO}_4)_2$ species formed and retained in the electrode is 30 times the PbO_2 volume located in the neck zones [8].

Further, it can be calculated that the volume of $\text{Pb}(\text{HPO}_4)_2$ species, namely, 1.2 cm^3 , is equivalent to 0.4 cm^3 of PbO_2 . Since only $\sim 0.04 \text{ cm}^3$ of PbO_2 is located in the neck zones, it follows that these sensitive zones may very well be affected by the addition of H_3PO_4 .

Kugel has reported that the shedding of positive active material is largely reduced in the presence of H_3PO_4 (see ref. 6). Since it is very likely that the shedding depends on the corrosion of neck zones, it can be concluded that H_3PO_4 addition intervenes favourably in the neck zone reactions in a way that cannot, as yet, be explained in detail. It is expected, however, that these processes are also responsible for the improved load capability and the low sensitivity of the electrode to variations in charge parameters.

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