

## EFFECT OF PREVIOUS CHARGE/DISCHARGE HISTORY ON THE CAPACITY OF THE $\text{PbO}_2/\text{PbSO}_4$ ELECTRODE: THE HYSTERESIS OR MEMORY EFFECT

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### Summary

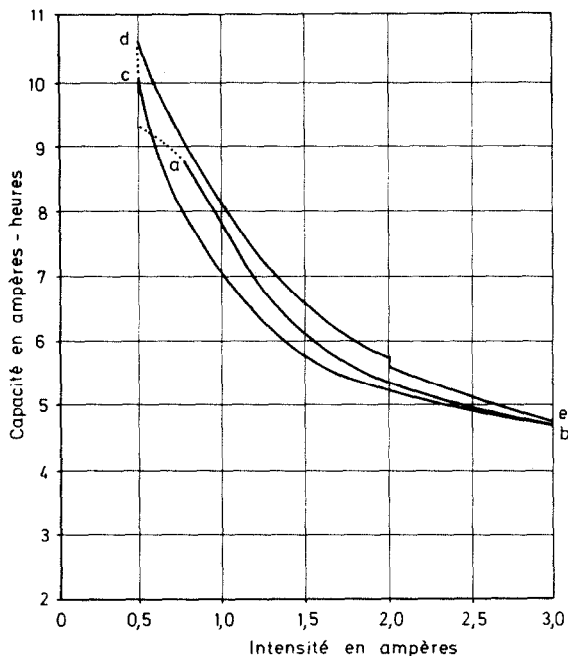
The effect of previous charge and discharge history on the capacity of Planté electrodes has been investigated. It is shown that the capacity level attained in cycling experiments depends on charge current density, overcharge and discharge current density of the preceding discharges, as well as on the relaxation after charge. As will become evident, the different effects observed for changes in charge and discharge parameters are closely related to the solid-state properties of  $\text{PbO}_{2-\delta}$ . An aggregate-of-spheres model has been developed to explain the various phenomena.

### Introduction

In 1898, Jumau [1] observed that the capacity of a  $\text{PbO}_2$  electrode depends on the current density applied during the preceding discharge. The capacity obtained at a given rate is decreased if the immediately preceding discharge is performed at a higher rate, and the converse holds true if the preceding discharge is carried out at a lower rate. Jumau used  $\text{PbO}_2$  electrodes of the Faure type with a thickness of 0.7 cm. The dependence of the capacity of these electrodes on the discharge current was determined by a stepwise increase and then decrease of the current density. The results revealed a hysteresis effect (Fig. 1). This hysteresis (or so-called "memory effect") was confirmed later by the U.S. National Bureau of Standards [2], particularly for "thin"  $\text{PbO}_2$  electrodes used in aircraft batteries (note, the thickness was not specified but may have been  $\sim 0.2$  cm). In his book *Lead-Acid Batteries*, Bode [3] states that the capacity "... is dependent on the history of discharge — at least of the last charge and discharge...". In other words, the capacity of a  $\text{PbO}_2$  electrode is determined not only by the preceding discharge but also by the charge regime. No claim has been made, however, as to which of the various charge and discharge parameters are the

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Courbe des capacités en fonction de l'intensité.

Fig. 1. The hysteresis effect of  $\text{PbO}_2$  electrodes (from Jumau's original paper 1898 [1]).

most important. Finally, in the book *Bleiakkumulatoren* published by VARTA [4], the memory effect is related to changes in the internal parameters of the  $\text{PbO}_2$  electrode (such as surface area and pore-size distribution) that are generated by variations in the charge/discharge conditions. Again, no experimental data were presented to show how these factors are related.

Jumau attributed the observed hysteresis to the amount of sulphuric acid available in the pore volume of the positive active material after recharge. This amount is determined by the quantity of  $\text{PbSO}_4$  formed during the preceding discharge and, since the latter is dependent on the discharge rate, the availability of acid in the pores after recharge will be a direct function of the previous discharge rate. As a consequence, the electrode capacity obtained on the subsequent discharge also depends on the rate of the previous discharge, provided that equilibration of the electrolyte concentration by diffusion is slow. If this assumption is correct, the memory effect will depend on the electrode thickness, the relaxation time between end-of-charge and start-of-discharge and, of course, the electrolyte concentration and temperature. Regrettably, neither Jumau nor the National Bureau of Standards specified the charge regimes that were used in their experiments. Jumau only stated that the discharge followed immediately after the charge.

In this paper, it will be shown that the memory effect is maintained even if the pore and bulk electrolyte concentrations have been equilibrated

either by long relaxation periods or by forced flow of bulk electrolyte through the pore system of the electrode. The effect of charge parameters on the capacity has been examined in another series of experiments.

## Experimental

The investigations were performed on Planté electrodes with dimensions: 12.7 cm × 21.1 cm × 0.8 cm. The electrode design is given in Fig. 2. The lamellar structure is produced from high purity, soft lead by a casting procedure. The lamella spacing is 0.07 cm. After anodic oxidation (formation) in diluted sulphuric acid, the lamellae are covered by a layer of PbO<sub>2</sub> with a thickness of 0.01 - 0.02 cm.

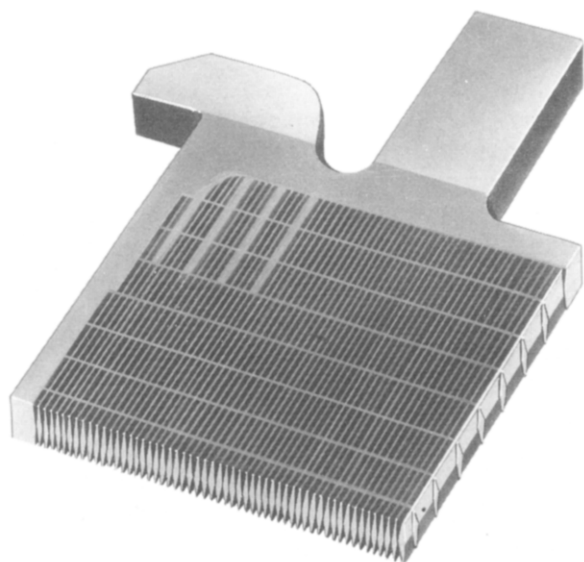


Fig. 2. Section of a Planté electrode.

Each Planté electrode was placed in a plastic container (dimensions: 15.3 cm × 18.2 cm × 36.4 cm) between two negative counter electrodes, each at a distance of 3.8 cm. Separators were slightly pressed onto the negative electrodes in order to avoid over-expansion of the active material. The experimental cell was filled with 4.7 l of 3.8 M H<sub>2</sub>SO<sub>4</sub> (density,  $\rho = 1.220 \text{ g cm}^{-3}$ ). Both the negative active material and the acid were present in excess, and thus did not determine the cell capacity. Charging and discharging were usually performed at constant current ( $\pm 0.5\%$ ) and at a temperature of 30 °C. The potential of the working electrode was measured against an Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode. Unless otherwise stated, all potentials are reported with respect to this electrode.

In a further series of experiments, Faure (pasted) electrodes were used. These were investigated under forced flow of electrolyte through the porous positive active material. Cell design and experimental conditions have been described in detail previously [5, 6].

## Results and discussion

### *The Jumau experiment (effect of previous discharge rate on electrode capacity)*

The Jumau experiment was repeated. The capacities of the Planté electrodes were determined at various rates by increasing and decreasing the discharge current in the following sequence: 2.5 A  $\rightarrow$  15.3 A  $\rightarrow$  30.0 A (or 40.0 A)  $\rightarrow$  15.3 A  $\rightarrow$  2.5 A. The end-of-discharge voltage (EDV) was 0.5 V. The recharge was performed using a two-step, constant-current procedure which, in principle, was a rough approximation to a constant-voltage charge. During the first step (performed at high rate, 15.3 A), about 65% of the discharged capacity was regained, while during the second step (performed at low rate, 2.5 A) charging was continued until 120% of the total discharged capacity was returned (*i.e.*, charge factor,  $F = 1.20$ ). This method maintained a high level of active material utilization during continuous cycling, as will be shown later. In order to re-examine Jumau's hypothesis, the relaxation time, *i.e.*, the rest period between the end-of-charge and the start-of-discharge, was varied in three steps: 0 h (*i.e.*, zero time), 2 h and 21 h.

Data obtained for a relaxation time of 21 h are presented in Table 1. Comparison of the 1st and 5th discharges, and the 2nd and 4th discharges, shows that there is a significant reduction in the electrode capacity. In other words, the memory effect is maintained even after a relaxation time of 21 h; a period that is more than sufficient to equilibrate the acid concentration by diffusion.

TABLE 1

Capacity of a Planté electrode at different rates  
(Relaxation time = 21 h.)

Discharge no.	Discharge current (A)	Capacity (A h)
1	2.5	39.7
2	15.3	24.8
3	40.0	16.1
4	15.3	22.4
5	2.5	37.6
6	2.5	38.3

TABLE 2

Memory effect (capacity difference) as a function of relaxation time (h) and previous discharge rate (A)

Relaxation time (h)	Capacity difference			
	1st/5th cycle (2.5 A)		2nd/4th cycle (15.3 A)	
	(A h)	(%)	(A h)	(%)
0	-0.8	-2.0	-3.5	-11.9
2	-0.6	-1.7	-2.1	-9.2
21	-2.1	-5.3	-2.3	-9.3

The data obtained for relaxation times of 0 h (*i.e.*, the conditions of Jumau's original experiment) and 2 h are of the same order of magnitude as those shown in Table 1 for 21 h of relaxation. To demonstrate this point, the capacity differences of the 1st/5th and the 2nd/4th discharges after different relaxation times are given in Table 2. The results clearly indicate that there is only a small, if, indeed, any, influence of the relaxation time on the memory effect. Further, it would appear that the effect does not disappear with increasing relaxation time, as would be expected if Jumau's acid diffusion hypothesis was correct.

Interesting capacity behaviour is observed when high-rate discharges are performed repeatedly. Results show (Table 3) that a series of three cycles at a discharge rate of 15.3 A causes a marked decrease in electrode capacity. For example, the decrease amounted to 5.2 A h (or 18% of the initial capacity) for discharges Nos. 2 - 6. In addition, the original capacity (No. 1) could not be completely restored, even after two discharges (Nos. 7, 8) at the original rate (2.5 A). Thus, the data of Table 3 confirm the long-established experience that intermediate low-rate discharges to 100% depth-

TABLE 3

Effect on capacity of repeated high-rate discharges

Discharge no.	Discharge current (A)	Capacity	
		(A h)	(%)
1	2.5	40.5	100
2	15.3	28.2	70
3	30.0	18.0	44
4	15.3	24.9	61
5	15.3	24.5	60
6	15.3	23.0	57
7	2.5	38.5	95
8	2.5	39.7	98

of-discharge are essential in order to obtain accurate data on the capacity/discharge-rate dependence of a lead-acid cell.

The memory effect has also been investigated by the so-called Eloflux method. In this method, a rapid equilibration of pore and bulk electrolyte is achieved by forcing the electrolyte through the porous active material of a Faure (pasted) positive electrode. A 3.39 M solution of  $\text{H}_2\text{SO}_4$  ( $\rho = 1.20 \text{ g cm}^{-3}$ ), in large excess compared with the electrode capacity, was used and a constant-potential charge at 2.35 V was applied. The discharges were performed under a continuous forced flow of electrolyte. By contrast, the charges were carried out in two steps, without forced flow, that were separated by a short period (10 min) of forced flow. This procedure is essential to achieve a stable capacity during cycling [6]. After termination of charge, the electrolyte was pumped through the electrode for a rest period of 5 h in order to ensure that the pore and bulk electrolyte concentrations were equilibrated.

The results obtained from the above experiments are summarized in Table 4. It can be seen that the electrode capacity at the 4 A rate decreases as the rate of the previous discharge is increased (*cf.* discharges Nos. 2, 4, 6 and 8). Comparison of discharges Nos. 1 and 10 indicates that the capacity at the 4 A rate is increased when the previous discharge is conducted at only 2 A. This improvement is (at least partially) lost by repeated 4 A discharges (*cf.* Nos. 11, 12). Evidently these results, as well as those described above, are in complete agreement with the findings of Jumau. It can be concluded, however, that the memory effect cannot be attributed to impeded electrolyte diffusion. Rather, the memory effect is more likely to be associated with the properties of the solid  $\text{PbO}_{2-\delta}$  itself ( $\delta$  denoting the deviation from stoichiometry of the compound,  $\text{PbO}_2$ ). These properties

TABLE 4

Capacity of an Eloflux electrode (Faure type) as a function of the rate of previous discharge [7]

Discharge no.	Discharge current (A)	Capacity		
		(A h)	(A h kg <sup>-1</sup> )	(%)
1	4	9.8	117	100
2	4	9.8	117	100
3	8	8.8	104	89
4	4	9.5	114	97
5	16	7.8	93	79
6	4	9.3	112	96
7	32	6.8	82	70
8	4	9.1	109	93
9	2	10.6	127	109
10	4	10.0	120	103
11	4	9.95	119	102
12	4	9.95	119	102

are strongly dependent upon the previous discharge rate, and also upon the previous charge history, as will be shown below.

*Effect of charge current density on the capacity of a Planté electrode*

As shown earlier [6], the acid concentration in the pores of the positive active material and, consequently, the level and the duration of the charge current density, all determine the electrode capacity on subsequent discharges. In order to investigate this relation more precisely, it is essential to study the dependence of the electrode capacity on both the charge current density and the amount of charge that is applied during the first step of recharge. It is self-evident that the upper limit of both parameters is related to the limiting current of the transformation of  $\text{PbSO}_4$  to  $\text{PbO}_2$ , *i.e.*, parasitic  $\text{O}_2$  evolution has to be avoided. The lower limit is determined by practical requirements, *i.e.*, mainly by the time necessary for the total recharge (this should not exceed 20 h). In a second step, the charge is completed and a constant percentage of overcharge is added, both at a low rate. Experience has shown that capacity changes resulting from parameter variations during the first step of charge do not appear on the first discharge. Rather, a number of charges and discharges is required for the electrode capacity to arrive at a level that is representative of the charge parameters employed.

The effect of charge current density on the capacity of a Planté electrode was studied first. The current was varied between 0.38 and 4.6  $\text{mA cm}^{-2}$ . All other parameters, in particular the amount of charge passed on the first step and the overcharge factor, were kept constant. All discharges were conducted at a constant rate of 0.75  $\text{mA cm}^{-2}$ . The results of these experiments are presented in Table 5. As expected, the capacity was found to decrease with decrease in the current density.

TABLE 5

Effect of charge current density on capacity of a Planté electrode  
(Charge on first step = 6.8  $\text{mA h cm}^{-2}$ ; overcharge = 20% of previous discharge capacity.)

Charge regime no.	Charge current density ( $\text{mA cm}^{-2}$ )		Capacity (% of highest value)
	1st step	2nd step	
1	4.6	0.75	100
2	3.0	0.75	96
3	1.5	0.75	90
4*	0.75	0.75	80

\*Constant-current charge.

The transition from one capacity level to another is shown in Fig. 3. In region I, a constant level of 96% is attained when cycling is performed with charge regime No. 2 (*cf.* Table 5). The charging regime No. 3 was used between cycles Nos. 105 and 123 (region II). It can be seen that the capacity

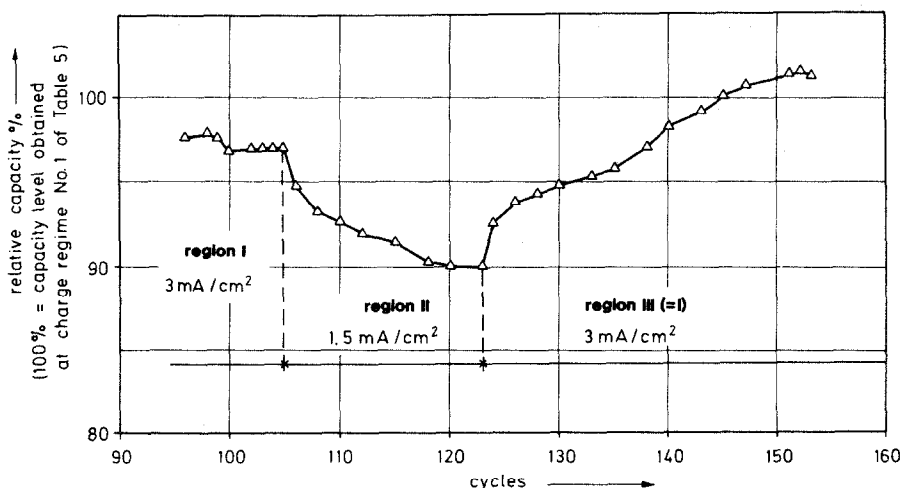


Fig. 3. Effect of charge current density on electrode capacity during cycling.

decreases continuously to a level of 90%. After cycle No. 123, charging was returned to regime No. 2. This resulted in a steady increase of capacity to a level greater than 100%. At first sight, this observation appears surprising. The excess capacity is due to the generation of additional active material by corrosion of the base lead during overcharge on each cycle. This phenomenon is discussed below.

An investigation was made of the effect of the amount of charge applied during the first step on the discharge capacity of the electrode. This was achieved experimentally by keeping the current density constant and varying the time of its application. Again, all discharges were carried out at  $0.75 \text{ mA cm}^{-2}$ . The results are presented in Table 6. Although only two experiments were performed, the findings again indicate the importance of the charge parameters of the first step on the subsequent discharge capacity.

TABLE 6

Effect of amount of charge on capacity of a Planté electrode  
(Current density on first step =  $4.6 \text{ mA cm}^{-2}$ ; overcharge = 20% of previous discharge capacity.)

Charge regime no.	Charge current density ( $\text{mA cm}^{-2}$ )		Charge of 1st step ( $\text{mA h cm}^{-2}$ )	Capacity (% of highest level)
	1st step	2nd step		
1	4.6	0.75	6.8	100
2	4.6	0.75	3.4	95



### Effect of overcharge on the capacity of a Planté electrode

In earlier literature on lead-acid cells, it has sometimes been stated that excessive overcharge of Planté electrodes results in a capacity decay (cf. ref. 8). This observation has been attributed to increase in the shedding of active material due to gassing. In the context of the present study, it is clearly important to re-examine this effect.

A series of experiments was conducted in which a Planté electrode was subjected to continuous cycling. All parameters, except the amount of overcharge, were kept constant. The results are shown in Fig. 4 and Table 7. Discharge capacities were determined at  $0.75 \text{ mA cm}^{-2}$ . Two conclusions can be drawn from these results:

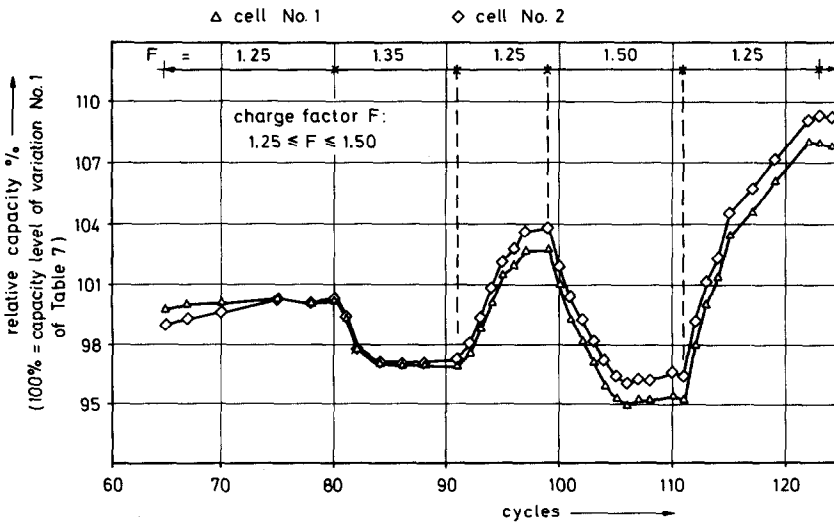


Fig. 4. Effect of overcharge on electrode capacity during cycling.

TABLE 7

Effect of overcharge on capacity of a Planté electrode  
 (1st step charge at  $3 \text{ mA cm}^{-2}$  and  $6.8 \text{ mA h cm}^{-2}$ ; 2nd step charge and overcharge at  $0.75 \text{ mA cm}^{-2}$ .)

Experimental sequence	Overcharge (% of previous capacity)	Capacity (% initial value)
1	25	100
2	35	97
3	25	103
4	50	95
5	25	108

(i) the capacity decreases as the amount of overcharge is increased (sequences 1, 2 and 4);

(ii) the capacity obtained at a constant amount of overcharge is greater than the initial value after the electrode has been subjected to periods of cycling with larger amounts of overcharge (*cf.* sequences 1, 3 and 5). This capacity increase can be attributed to the formation of additional active material during (excessive) overcharge through corrosion of the base lead. Thus, any increase in the shedding of active material is, apparently, more than compensated by the formation of corrosion material. The reason for the capacity decrease observed in the sequence 1, 2 and 4 is discussed below.

Since it can be expected that the effect of overcharge on capacity depends upon the potential (and, therefore, the current density), the influence of current density on the capacity level was investigated. The experiments were performed under conditions of continuous charge until a constant amount of overcharge, amounting to 300% of the previous capacity, had been applied. The results are given in Table 8. As is obvious, the capacity was found to decrease as the potential (current density) was increased.

TABLE 8

Effect of overcharge current density and potential on capacity of a Planté electrode at 300% overcharge

Current density (mA cm <sup>-2</sup> )	Potential (mV)	Change of capacity (% of initial level)
0.006	1156 - 1165	0
0.06	1223 - 1230	-1.7
0.6	1313 - 1322	-5.8

*Charge current density and overcharge synergism and its effect on the capacity of a Planté electrode*

It has been shown above that the charge current density, in particular when applied at low rates during the first step of charge, as well as the amount of overcharge, especially when applied at elevated PbO<sub>2</sub> potentials, both exert an adverse effect on the capacity of the Planté electrode during continuous cycling. Obviously, it is also important to study the interdependence and the possibility of a synergism between these two parameters. A Planté electrode was therefore cycled according to the following regime: charge at a constant current density of 0.38 mA cm<sup>-2</sup>, discharge at 0.75 mA cm<sup>-2</sup>, 30 min relaxation between charge and discharge. During cycling, the amount of overcharge was increased from 25% to 35% and then to 50% of the previous capacity. The result of this experiment is shown in Fig. 5. It clearly demonstrates that the capacity decreases continuously and

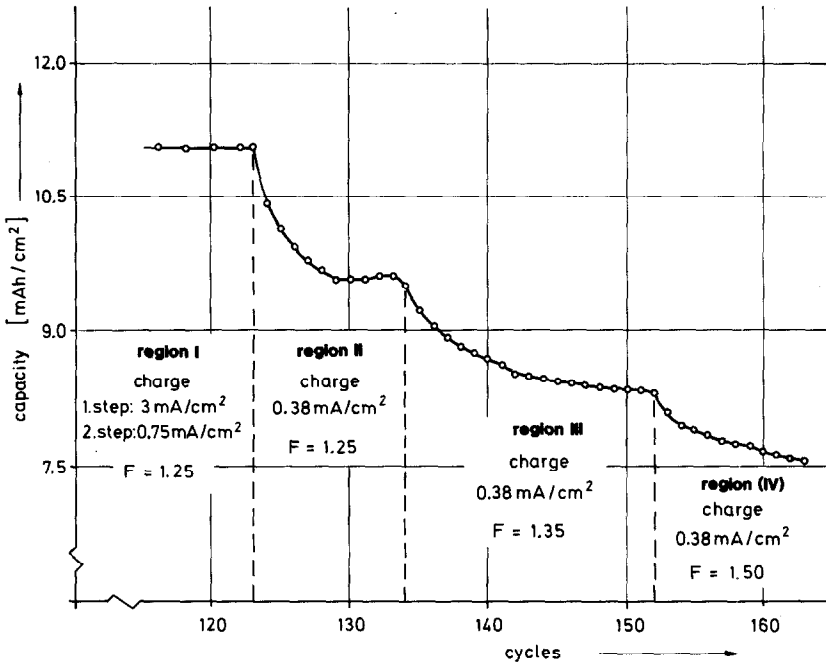


Fig. 5. Effect of charge current density/overcharge synergism on electrode capacity during cycling.

reaches different levels in accordance with the respective amount of overcharge. Overall, the capacity was reduced to about 68% of the initial value.

In a further experiment (see Fig. 6), cycling was performed first at a constant charge rate of  $0.37 \text{ mA cm}^{-2}$  (region II) and then at  $0.28 \text{ mA cm}^{-2}$  (region III), both with a charge factor,  $F$ , of 1.50 and a discharge rate of  $0.75 \text{ mA cm}^{-2}$ . Within 20 cycles at the latter charge rate, the capacity fell to 72% of the initial value. At this stage, a single discharge at the very low rate of  $0.023 \text{ mA cm}^{-2}$  immediately restored the initial capacity level (region IV). Thus, even a relatively small change in the charge rate from  $0.37 \text{ mA cm}^{-2}$  to  $0.28 \text{ mA cm}^{-2}$  is sufficient to cause an inflection of the capacity/cycle-number curve. This observation again confirms the influence of charge current density on capacity. As is evident from Fig. 6, the capacity obtained at the low rate of  $0.023 \text{ mA cm}^{-2}$  (point A) exceeds the initial, as well as the final, level by about 118%. It is still an important goal to activate in a cycling regime at least part of this "excess capacity" so that it can be also utilized at high rates. In summary, it is concluded that a capacity decay generated by the application of low charge current densities and high amounts of overcharge during cycling can be spontaneously compensated by one low-rate discharge, a fact that confirms conclusively the memory effect first demonstrated by Jumau.

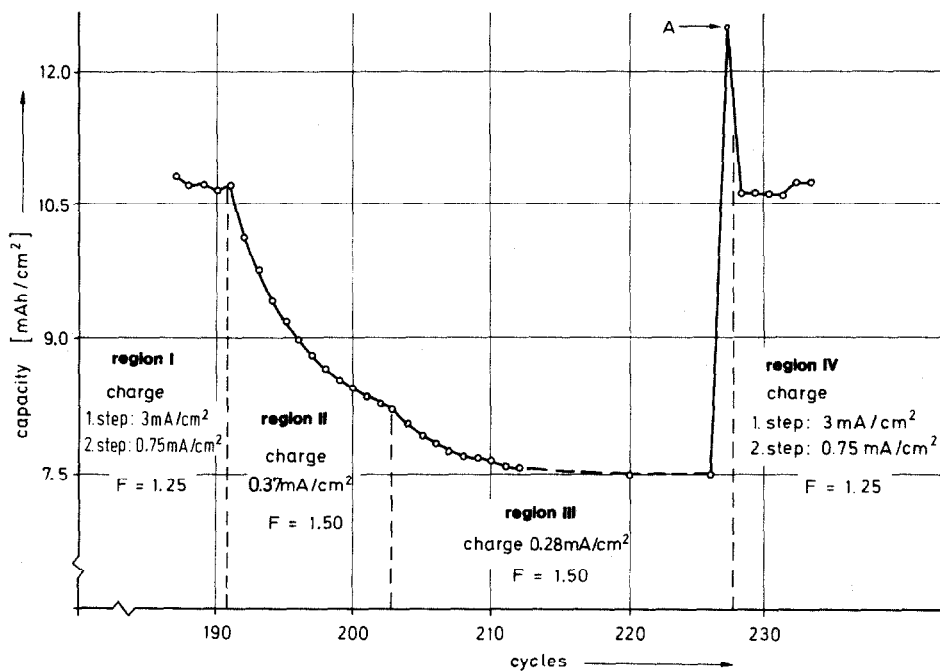


Fig. 6. Effect of low-rate charges and an intermediate low-rate discharge on electrode capacity.

#### *Effect of open-circuit relaxation on the capacity of a Planté electrode*

The relaxation of PbO<sub>2</sub> electrodes of the Faure type has been investigated previously under open-circuit conditions and in relation to temperature and time [6]. It has been found that, starting from a low level of active material utilization of 25 - 50 A h kg<sup>-1</sup>, an increase of 20 - 50 A h kg<sup>-1</sup> can be achieved after open-circuit stand for 20 - 70 h at 40 °C. Similar results have been obtained for Planté electrodes under the same conditions, but the capacity increase is smaller, namely, ~5%.

A more effective procedure for restoring capacity is as follows. The fully charged positive electrode is withdrawn from the cell, washed free from acid overnight, dried for 24 h at 60 °C, returned to the cell and immediately discharged without any intermediate application of charge. Interesting results are obtained when electrodes, yielding either a high level or a low level of capacity by application of the appropriate charge regime (*vide supra*), are subjected to this procedure (see Table 9). As can be seen from the data, the washing/drying relaxation method improves the active material utilization of low-capacity electrodes by 30 - 36%. Unfortunately, no method has yet been devised to maintain this advantage. From the data listed in the third column of Table 9, it is evident that there is a considerable loss of capacity on the next discharge.

TABLE 9

Capacity relaxation of Planté electrodes by intermediate washing and drying  
(Discharge rate  $0.75 \text{ mA cm}^{-2}$ .)

Initial capacity ( $\text{mA h cm}^{-2}$ )	Capacity increase after relaxation		Capacity loss on next discharge	
	( $\text{mA h cm}^{-2}$ )	(%)	( $\text{mA h cm}^{-2}$ )	(%)
<i>Low level</i>				
6.7	2.0	+30	-1.2	-60
7.6	2.7	+36	-1.2	-44
<i>High level</i>				
13.5	1.5	+11	-1.5	-100
13.0	1.4	+11	-1.4	-100

Somewhat surprisingly, electrodes operating at a high level of capacity also show an increase in utilization. Again, the "excess capacity" cannot be utilized permanently under the applied conditions. In the next discharge, the benefit is lost completely. On further cycling, the electrode remains at the original capacity level.

### The $\text{PbO}_2$ electrode as an aggregate of spheres

The phenomena described in the previous sections cannot be attributed to the specific lamellar design of the Planté electrode; they are more representative of a general feature of any  $\text{PbO}_2$  electrode regardless of its structure. Both Faure (pasted) and tubular plates also respond to similar variations in the charge and the discharge parameters. In order to understand the behaviour, recognition must be made of the following facts. The electrical resistance of a porous  $\text{PbO}_2$  mass formed in a battery electrode depends on the previous charge and discharge history. Recently, it has been demonstrated [9] that there is a linear relationship between the resistance and the utilization of active material. This, again, emphasizes the significance of the role played by the solid-state properties of  $\text{PbO}_{2-\delta}$ . On the other hand, the importance of the geometrical morphology of the porous  $\text{PbO}_{2-\delta}$  body on both the life and capacity of electrodes has been stressed repeatedly [10, 11]. In general, it can be stated that the structure of the positive active material is a porous aggregate of individual  $\text{PbO}_2$  crystals that are firmly welded together [10]. As has been shown by Kordes [12], the shape factor of  $\text{PbO}_2$  crystals taken from Faure plates is close to that of a spherical particle. Therefore, it is justified to consider the porous  $\text{PbO}_2$  mass as an aggregate of individual spheroids (or even spheres) that form an electrically conducting structure via narrow passages or necks at their contact zones. Such a configuration is very similar to that of a porous sintered body and, for this reason, it can be treated analogously by using the mathematical model developed by Winsel *et al.* [13] for a sintered specimen.

*Resistance of PbO<sub>2</sub> aggregates*

A unit volume of PbO<sub>2</sub> active material may contain  $n^3$  spheres of uniform radius,  $R$ . The volume,  $V_K$ , of each sphere is given by

$$V_K = \frac{4}{3} \pi R^3 \quad (1)$$

For a porosity,  $P$ :

$$n^3 V_K = 1 - P \quad (2)$$

Substituting eqn. (1) in eqn. (2) gives:

$$n = \frac{1}{R} \left( \frac{3(1-P)}{4\pi} \right)^{1/3} \quad (3)$$

In an aggregate, there may be  $n^2$  conducting rows of spheres in parallel per unit volume, each line having  $n$  spheres in series and, subsequently,  $n$  necks on both sides, at which the neck resistance,  $w_H$ , is observed. The resistance of one single line,  $\Omega$  is given by:

$$\Omega = 2nw_H \quad (4)$$

and, consequently, the specific resistance of the total aggregate,  $\bar{\omega}$ , is:

$$\bar{\omega} = \frac{2nw_H}{n^2} = \frac{2w_H}{n} \quad (5)$$

The neck resistance,  $w_H$ , at a circular constriction of radius,  $h$  (radius of the narrow passage or neck between two spheres), and a specific resistance,  $\omega$ , of the PbO<sub>2</sub> solid material is given by:

$$w_H = \frac{\omega}{4h} \quad (6)$$

Using this expression in combination with eqns. (3) and (5) yields:

$$\bar{\omega} = \omega \frac{R}{h} \left( \frac{\pi}{6} (1-P) \right)^{1/3} \quad (7)$$

Since the term  $(\pi(1-P)/6)^{1/3}$  at  $P = 0.5$  is close to 1, the specific resistance of the aggregated spheres is approximately determined by:

$$\bar{\omega} \cong \omega \frac{R}{h} \quad (8)$$

i.e., the value of  $\bar{\omega}$  is determined by the ratio of sphere radius to neck radius.

*Mechanics of PbO<sub>2</sub> aggregates*

The basic model for the following calculation is schematically illustrated in Fig. 7. This depicts two spheres of equal radius,  $R$ , connected via

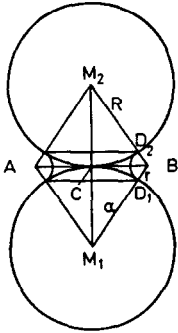


Fig. 7. Geometric relationships in an arrangement of two spheres connected by a neck.

a neck of radius,  $h$ . By virtue of the coherent surface of this configuration, a negative radius of curvature,  $r$ , is formed in the neck zone which, at a surface tension  $\sigma_0$ , gives rise to a Laplace pressure,  $P_h$ , in that zone, *i.e.*,

$$P_h = \sigma_0 \left( \frac{1}{h} - \frac{1}{r} \right) \quad (9)$$

The value of  $r$  can be expressed by other geometric parameters as shown earlier [13], *i.e.*,

$$r = h^2 / 2(R - h) \quad (10)$$

Thus, the Laplace pressure in the neck zone can be written as:

$$P_h = - \frac{2R\sigma_0}{h^2} \left( 1 - \frac{3h}{2R} \right) \quad (11)$$

The Laplace pressure,  $P_K$ , at the surface of the sphere is given by:

$$P_K = \frac{2\sigma_0}{R} \quad (12)$$

If the term  $3h/2R$  in eqn. (11) is neglected, which will create an error of about 15%, then:

$$\frac{P_h}{P_K} = - \left( \frac{R}{h} \right)^2 \quad (13)$$

The negative Laplace pressure,  $P_h$ , exerts a tension in the neck zone that causes an increase of this zone up to a limiting value of linear creepage,  $\sigma^*$ . At this point, it is assumed that:

$$P_h = \sigma^* \quad (14)$$

From eqns. (12) - (14):

$$-\frac{2R}{h^2} = \frac{\sigma^*}{\sigma_0} \quad (15)$$

By elimination of  $h$  and using eqn. (8), it follows:

$$\bar{\omega} = \omega \left( \frac{R\sigma^*}{2\sigma_0} \right)^{1/2} \quad (16)$$

Equation (16) indicates that on formation, or recharge, a  $\text{PbO}_{2-\delta}$  particle of globular structure is formed under the influence of the local parameters  $\sigma^*$  and  $\sigma_0$ . The surface tension,  $\sigma_0$ , of  $\text{PbO}_2$  in diluted sulphuric acid depends on temperature, acid concentration, and the potential at the electrochemical double layer. The value of  $\sigma_0$  exhibits a maximum at 1.7 V (*versus* SHE) in 4 M  $\text{H}_2\text{SO}_4$  [14] and its variation over a range close to this maximum is small. Since  $\text{PbO}_{2-\delta}$  formation occurs at about 1.7 V, it follows from eqn. (16) that the effect of the surface tension on the material resistance,  $\bar{\omega}$ , is not large. Evidently other factors determine the value of  $\bar{\omega}$  which, as has been pointed out above, depends very strongly on the charge and the discharge parameters. The quotient:

$$\Gamma = \frac{2\sigma_0}{\sigma^*} [\text{cm}] \quad (17)$$

can be regarded as a specific quantity that describes the equilibrium of the mechanical tension in the material. The value of  $\Gamma$  increases only when the  $\sigma^*$  value is decreased by increasing the temperature, or when  $\sigma_0$  is increased by diluting the acid.

#### *Thermodynamics of aggregates*

It is an irrevocable requirement that the  $\text{PbO}_{2-\delta}$  material in the neck zone has a lower potential than that of the sphere. If the reverse were true, then the  $\text{PbO}_{2-\delta}$  in the neck would be transformed to  $\text{PbSO}_4$  on discharge. Thus, the electrical contact would be interrupted before any of the  $\text{PbO}_{2-\delta}$  in the spheres could be discharged and, as a consequence, large amounts of active material would remain inactive. Under normal conditions, such a situation is not observed experimentally. However, as the above results clearly indicate, attack of the neck zones with its detrimental consequences on electrode performance may well occur when certain charge and discharge parameters are applied.

In formulating the thermodynamic differences between the  $\text{PbO}_{2-\delta}$  in the spheres and in the neck zones, we take into account the Laplace pressure terms only. Assuming a constant molar volume,  $V_0$ , the chemical potential is

$$\Delta\mu = V_0(P_h - P_K) \quad (18)$$

Substituting eqns. (11) and (12) in eqn. (18) yields:



$$\Delta\mu = \frac{2V_0\sigma_0}{R} \left( 1 + \frac{R^2}{h^2} - \frac{3R}{2h} \right) \quad (19)$$

and, consequently, the potential difference,  $\Delta\varphi$ , is given by:

$$\Delta\varphi = \frac{-\Delta\mu}{2F} = \frac{-V_0\sigma_0}{FR} \left( 1 + \frac{R^2}{h^2} - \frac{3R}{2h} \right) \quad (20)$$

Due to the limited phase range of the  $\text{PbO}_{2-\delta}$  system, the potential difference produces a disorder of the  $\text{PbO}_{2-\delta}$  in the sphere material that is different from that in the neck material. Pohl and Rickert [15], have derived the following relationship between the potential,  $\varphi$ , and the degree of disorder,  $\delta$ :

$$\varphi = 0.991 - 0.124 \log \delta - 0.0592 \text{ pH} \quad (21)$$

Using this relationship, the difference in potential between the spheres and the necks is calculated to be:

$$\Delta\varphi = -0.124 \log \frac{\delta_h}{\delta_R} \quad (22)$$

where  $\delta_h$  and  $\delta_R$  represent the disorder in the neck and the spheres, respectively. Combining eqn. (22) with eqn. (20), and neglecting the term  $3R/2h$ , produces:

$$\log \frac{\delta_h}{\delta_R} = 8.04 \frac{V_0\sigma_0}{FR} \left( 1 + \frac{R^2}{h^2} \right) \quad (23)$$

According to Pohl and Rickert [15], the lower limit of the phase range of  $\text{PbO}_{2-\delta}$  is characterized by:  $\delta_{\max} = 1.6 \times 10^{-2}$ . Since  $\text{PbO}_{2-\delta}$  has a finite phase range, it follows that the ratio  $h/R$  has a lower limit. This minimal "neck area" can be regarded as a two dimensional nucleus for the growth of the next  $\text{PbO}_2$  sphere. The latter, however, can only develop as long as  $\text{PbSO}_4$  is present in the electrode. On further charging, *i.e.*, beyond the limiting current of the transformation reaction, the value of  $\delta$  decreases and finally  $\text{O}_2$  is evolved as soon as the minimum value,  $\delta_{\min}$ , is exceeded. Since the active material utilization is decreased after an overcharge (see above), which is equivalent to an increase of the resistance  $\bar{\omega}$ , it follows from eqn. (8) that the ratio  $R/h$  is increased. Using eqn. (23), it can be concluded that the ratio  $\delta_h/\delta_R$  is at the lower limit due to overcharge ( $\text{O}_2$  evolution). In order to fully exploit eqn. (23), the disorder value  $\delta_R$  for  $R \rightarrow \infty$  is required. Furthermore, the surface tension is unknown. Nevertheless, useful information can be derived from the following estimates. The sphere radius is assumed to be  $R = 10^{-5}$  cm and the surface tension,  $\sigma_0$ , of  $\text{PbO}_2$  in diluted  $\text{H}_2\text{SO}_4$  to be  $10^{-4}$  Joule  $\text{cm}^{-2}$ . Since the molar volume,  $V_0$ , of  $\text{PbO}_2$  is  $24.6 \text{ cm}^3 \text{ mol}^{-1}$  and the Faraday constant is  $96500 \text{ A s mol}^{-1}$ , the first factor on the right-hand side of eqn. (23) is:

$$8.04 \frac{V_0 \sigma_0}{FR} = 0.0205[V] \quad (24)$$

Using the extreme  $\delta$  values given by Rickert and Pohl (*cf.* Fig. 3 in ref. 15):

$$3 \times 10^{-3} \leq \delta \leq 1.6 \times 10^{-2}$$

it can be shown that:

$$\log \frac{\delta_h}{\delta_R} \leq \log \frac{\delta_{\max}}{\delta_{\min}} = \log \frac{1.6 \times 10^{-2}}{3 \times 10^{-3}} = 0.727 \quad (25)$$

Thus, eqn. (23) becomes:

$$0.727 \geq 0.0205 \left( 1 + \frac{R^2}{h^2} \right)$$

and, consequently,

$$\frac{R}{h} \leq 5.9 \quad (26)$$

Since  $R$  is assumed to be  $10^{-5}$  cm, a minimum value of  $0.17 \times 10^{-5}$  is found for  $h$ . Substituting these values in eqn. (8) yields:

$$\frac{\bar{\omega}}{\omega} \leq 5.9 \quad (27)$$

This gives the maximum possible difference between the specific resistances of the aggregate and the solid  $\text{PbO}_2$ .

## Comparison of experimental results with the aggregate model

### *Jumau experiment*

The principal result of Jumau's experiment is that the capacity of a positive electrode obtained at a given rate is (i) high when the preceding discharge is performed at a lower rate and (ii) low when the preceding discharge is performed at a higher rate. This can be explained as follows. The neck zones in the aggregate, although normally protected against corrosion by virtue of their lower potential, are prone to attack at higher discharge rates (*i.e.*, at a higher polarization). The original structure, and in particular the neck zones, is not restored during the next recharge. Therefore, a lower capacity is observed. On the other hand, at low discharge rates the electrode potential remains above the neck potential. On account of the abundantly available  $\text{Pb}^{2+}$ , the neck zones may grow during discharge. Therefore, the conductivity of the aggregates is increased and after recharge (which may even add to the neck growth) a higher capacity is observed on the subsequent discharge.

### *Effect of charge current density on capacity*

It has been shown that the electrode capacity increases with increase in both the current density and the amount of charge passed during the first step of charging. This can be explained by reference to eqn. (8). At high rates and because of well-known kinetic reasons, small  $\text{PbO}_2$  particles are produced during charge, *i.e.*, the sphere radius  $R$  is small. In addition, due to a higher energy dissipation and, as a consequence, a lower limiting value for  $\sigma^*$ , the neck radius,  $h$ , may become larger. Taken together, the two effects cause the ratio  $R/h$  to decrease with increasing charge current density. Therefore, an increase is observed in both the conductivity of the aggregate and the capacity. The reverse holds true for small current densities and small amounts of charge during the first step of charge.

### *Effect of overcharge on capacity*

The capacity of an electrode decreases with increase in both the overcharge (*i.e.*, the time at which the electrode is exposed to the overpotential) and the overpotential. Equation (8) can be used again to explain this phenomenon. On applying a high overvoltage, the value of  $\delta$  is minimized. As a consequence, lead ions ( $\text{Pb}^{4+}$ ) are forced to migrate from the neck zones into the spheres, since no  $\text{Pb}^{2+}$  ions are available in the electrolyte. Thus, the volume of the neck zone decreases, *i.e.*,  $h$  decreases. Overall, the ratio  $R/h$  increases. As a result, the conductivity and, simultaneously, the capacity both decrease. In the extreme case, the value of  $\delta$  in the  $\text{PbO}_{2-\delta}$  contained in the neck zone becomes so large (due to the  $\text{Pb}^{4+}$  migration) that the material is below the lower limit of the phase range (*vide supra*) and spontaneously disintegrates. This process may explain the common problem of shedding of active material during overcharge. The shedding phenomenon is usually attributed to mechanical forces exerted by  $\text{O}_2$ -development. However, according to the aggregate model, oxygen is only a vehicle for transporting particles that have already disintegrated.

### *Effect of relaxation on capacity*

The capacity of an electrode with a low level of active material utilization is increased after open-circuit stand in the electrolyte. The capacity growth appears to be dependent on both time and temperature. This can be explained as follows. Due to self discharge,  $\text{Pb}^{2+}$  is formed at the surface, and in the neck zone is oxidized back to  $\text{PbO}_{2-\delta}$ . Thus, the neck zone and, simultaneously, the conductivity and the capacity all increase.

While the capacity recuperation on open-circuit appears to be rather slow, a more rapid effect occurs when the electrode is washed, dried, and then tested for capacity. In this case, the electrolyte is diluted down to pure water. During this procedure, the surface tension,  $\sigma_0$ , of  $\text{PbO}_2$  in the electrolyte increases as the electrolyte concentration decreases. According to eqn. (16), an increase in  $\sigma_0$  is equivalent to a decrease in the aggregate resistance,  $\bar{\omega}$ , and it can therefore be expected that the described relaxation procedure must bring about a capacity increase.

## Percolation and passivation

In a practical lead-acid cell, the discharge capacity obtained on constant-current discharge is usually limited by the availability of electrolyte in the pores of the positive electrode. As a consequence, discharge at the same current density may be continued after a sufficient period of rest. In the case of Eloflux electrodes, or in the case of Planté electrodes in an excess of electrolyte, passivation by sulphate formation and/or interruption of electronic conduction (lack of percolation) determine the end of discharge. In other words, the discharge cannot be continued after a rest period. If passivation is the dominating factor, it can be further expected that the conductivity of the  $\text{PbO}_2$  agglomerate is subsequently decreased because the neck zones are attacked due to the higher polarization. This process will occur uniformly throughout the active material. In an electrode of low conductance (small neck radii  $h$ ), however, attack ("thinning") of the necks will occur preferentially in the region of the current collector. Under this condition, parts of the active material may remain unpassivated. Overall, the local resistance will control the current distribution. Further investigations of these phenomena are being conducted.

## Conclusion

For many decades, it has been known that the charge/discharge history has a significant effect on the capacity and, equally important, on the cycle life of a  $\text{PbO}_2$  electrode. A detailed understanding of the influence of charge and discharge parameters has been lacking. The work reported here has shown that the Planté type of electrode is an excellent tool for examining such phenomena. It has also been found that other electrode configurations provide analogous behaviour.

The results demonstrate the significance of the solid-state behaviour of  $\text{PbO}_{2-\delta}$ . An initial attempt has been made to associate the experimental outcome with behaviour predicted by a recently developed aggregate-of-spheres model. It is considered that this model will not only stimulate further research on  $\text{PbO}_2$  electrodes but will also prove applicable to other electrode systems.

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