Journal of Power Sources, *33* (1991) 231-244

Reversible capacity decay of positive electrodes in lead/acid cells

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Abstract

It is well known that the capacity of the positive electrodes of a lead/acid cell is affected greatly by various processes occurring during battery operation. Some of them result in an irreversible electrode degradation, while others are reversible. This paper discusses the reversible capacity decay (which is closely related to the 'memory effect') for various types of electrodes and batteries. Qualitatively, the same effects have been found with Planté, Faure and tubular electrodes. *In situ* measurements of the resistance of the active material using the Eloflux technique indicate that the effects are related to changes in the PbO_2 structure. The experimental results are qualitatively explained by a recently developed model for the active-material structure.

Introduction

Many operational regimes may shorten the cycle-life of lead/acid batteries. Apart from those regimes that are definitely known to give irreversible capacity deterioration on cycling, there are some that promote a capacity decay that can be reversed after the operational regime has been changed adequately.

The reversible capacity decay has been a matter of concern since about the turn of the century. Cahen and Donaldson [1] have shown that the capacity level (and, therefore, *per definitionem*; the cycle-life) very much depends on the charge regime. Jumau [2] demonstrated that the capacity is a function of the previous discharge rate. In addition, he could attribute this specific cell behaviour to the positive electrode. From the literature, phenomena that can be described as an influence of the charge/discharge history on the capacity of a positive electrode under a cycling regime are known as the 'memory effect'.

A few years ago, it became evident from experiments performed on Planté-type electrodes [3] that the following operational cycling regimes result in a progressive decay in capacity:

- constant current charges at low rates (*C*/10 and smaller)
- high-rate overcharges and large overcharge quantities (as long as water loss does not interfere)
- successive high-rate discharges

0378-7753/91/$3.50

This capacity decay (more precisely: the decrease of active-material utilization) can be reversed again by a high-rate/low-rate charge and minimizing overcharge. Thus, the original capacity can be restored. Altogether it can be stated that the capacity level (utilization level) of a positive Planté electrode is controlled in wide limits by the proper selection of the charge/discharge parameters, provided that the active material maintains its shape and rigidity and the capacity is not acid-limited. This specific behaviour is not a property of the Planté electrode alone. As will be shown in this paper, it is a general feature of the PbO_2 active material and is independent of the electrode design.

Experimental and results

Most of the work has been performed on Planté electrodes in single electrode experiments and with excess of electrolyte [3]. In the case of Faure-type electrodes, the phenomena have been studied mainly under forced flow of electrolyte through the porous active material; the results have been compared with those obtained under stationary electrolyte conditions. As far as tubular plates are concerned, single electrode experiments have been carried out. In addition, cells of commerically available batteries of 400 A h nominal capacity have been tested.

Planté electrodes

In order to demonstrate the analogous behaviour of various electrode designs with respect to reversible capacity decay, it appears to be of advantage to review briefly the basic results that have been obtained earlier [3] during the investigation of the capacity of Planté electrodes as a function of charge current density, quantity of charge, and overcharge. Charging has been performed using a two-step regime with a high-rate/low-rate current profile.

In a first experiment, a study was made of the effect on the electrode capacity of the current density (or charge rate) applied during the first step (i.e., the high-rate charge period). The quantity of high-rate charge as well as the total quantity of charge were kept constant. The results of this experiment are presented in Table 1. As can be seen, the capacity decreases as the current density applied during the first part of the charging period is decreased.

In a second experiment, the effect on the electrode capacity of the quantity of charge applied at a constant rate during the high-rate charging period was investigated, while the total quantity of charge was always 120% of the previous discharged capacity. The results of this experiment are summarized in Table 2. Although tested at two different steps only, it is obvious that the capacity declines with decreasing quantity of charge.

In a third experiment, the effect on the electrode capacity of the quantity of overcharge applied at low rate ($\sim C/10$) during the second step of

TABLE 1

Effect of charge current density of first step on capacity of Planté electrode[a]

First step charge (A)	First step charge rate (h)	Capacity (% of highest value)
15.0	1	100
10.0	2	96
5.0	5	90
2.5	10	80

[a] Charge in second step: 2.5 A/electrode (~ $C/10$); total charge: 120% of previous discharge capacity; first step charge with 2.5 A is equivalent to constant-current charge rate at ~ $C/10$.

TABLE 2

Effect of quantity of charge applied during first step (high-rate) on capacity of Planté electrode[a]

Quantity of charge, first step (A h)	Capacity (% of highest value)
23	100
12	95

[a] First step charge rate ~ $C/1$; second step charge rate ~ $C/10$; total quantity of charge = 120% of previous discharge capacity.

TABLE 3

Effect of quantity of overcharge on capacity of Planté electrode[a]

Quantity of overcharge (% of previous capacity)	Capacity (% of initial value)
25	100
37	97
50	95

[a] First step charge rate ~ $C/2$; second step charge and overcharge rate ~ $C/10$.

the charging regime was studied keeping constant the parameters during the high-rate charge period. The results obtained are given in Table 3. The data show that the electrode capacity decreases as the quantity of overcharge is increased.

Finally it is of practical interest to study the effect of a charge/overcharge synergism on the capacity level of an electrode. From the previous results, in particular those presented in Tables 1 and 3, it might be concluded that the influence of charge current density and overcharge effects is additive. In order to prove this hypothesis, an electrode was initially cycled by application of a two-step high-rate/low-rate charging regime with a fixed quantity of overcharge to consolidate an optimum and constant capacity level. After this, a low-rate (*C*/20) charge was applied and the quantity of overcharge successively increased. The results of these experiments are shown in Fig. 1. Evidently, the electrode capacity attains specific levels within 10–20 cycles. As expected, these decrease with increasing quantity of overcharge. More specifically, if compared with the data of Table 3, the results collected in Table 4 show that the overcharge effect becomes stronger as the charge rate is lowered.

These changes in the actual capacity cannot be attributed to insufficient recharge of the electrode. In any case, the active material consists of nearly 100% PbO_2 after recharge. The dischargeability of this PbO_2 at a

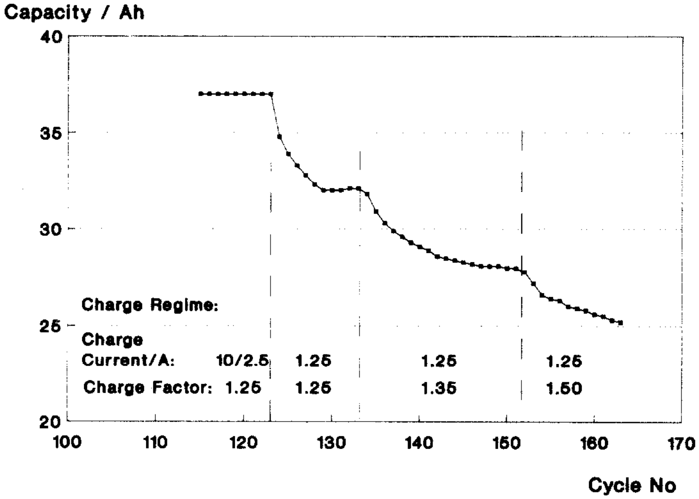

Fig. 1. Planté type electrode in excess of electrolyte. Decreasing charge current and increasing charge factor reduce capacity.

TABLE 4

Effect of charge/overcharge synergism on capacity level of Planté electrode during cycling

Charge regime (A)	Overcharge factor	Capacity level (A h)	Relative capacity (%)	
2 steps 10/2.5	1.25	37	100	
1 step 1.25	1.25	32	87	100
1 step 1.25	1.35	28	76	88
1 step 1.25	1.50	25	68	78

given discharge rate definitely depends, however, on the charge regime applied in a cycling experiment. In addition, the capacity decay can be reversed and the capacity itself can be restored to its maximum value within a few cycles as soon as a favourable charge regime is applied.

The capacity level of a positive electrode is also determined by the preceding discharge conditions, as known since 1898 from Jumau's definitive experiment [2]. High-rate discharges decrease the capacity obtained on the subsequent cycle. Jumau attributed this phenomenon to the amount of acid available in the pore volume of the electrode. High-rate discharge produces small quantities of $PbSO_4$ in the pores because of the low depth-of-discharge and, consequently, during the next charge also small quantities of acid are produced. If this hypothesis of 'impeded' acid diffusion were correct, Jumau's effect (memory effect) should be a function of the duration of the rest period between end of charge and begin of next discharge. The memory effect should disappear if the length of this interval is sufficient for acid equalization by diffusion.

It has been found, however, that even after a period of 22 h the memory effect of a Planté electrode (whose active material thickness is less than 0.2 mm) is fully observed. Consequently, the memory effect reflects a specific status of the $PbO_{2-\delta}$ solid-state properties rather than an 'impeded' electrolyte diffusion. This is confirmed by Eloflux experiments on Faure type electrodes.

Faure electrodes

The reversible capacity decay has been clearly and reproducibly demonstrated for the first time in experiments with a forced flow of electrolyte through the porous active material of positive Faure electrodes, the so-called Eloflux experiments. The advantages of the Eloflux method have been described elsewhere [4].

The following results have been obtained.

(i) The charge regime applied during cycling affects considerably the capacity determined at a given rate. In general, it can be stated that, during the charge period, the Pb^{2+} concentration in the pore electrolyte should be maintained at its lowest possible value for about 70% of the recharge. This can be achieved by a constant voltage or an adequate two-step (high-rate/low-rate) constant current recharge, both of which produce high acid concentration in the pore electrolyte and, consequently, a low Pb^{2+} concentration. Forced electrolyte flux during the first recharge period at high rates is found to be detrimental to the capacity level, since it decreases quickly the acid concentration in the pore electrolyte down to the bulk electrolyte concentration (and increases the Pb^{2+} concentration) [5].

(ii) The charging conditions described under (i) to achieve an optimum capacity level produce an electrode status that is not affected by the application of forced electrolyte flux during long rest periods at open circuit. In other words, the actual capacity level is a function of the $PbO_{2-\delta}$ solid–state properties, not of concentration differences between pore and bulk electrolytes [5].

(iii) Borger *et al.* [6] have shown that there exists a linear relationship between the electronic resistance of PbO_2 and its capacity level.

(iv) Hullmeine and Borger [3, 7] investigated Jumau's memory effect in Eloflux experiments. By this method, a rapid equalization of pore and bulk electrolyte is achieved in a rest period between the end of charge and the beginning of the subsequent discharge, which they extended up to 5 h. Apart from this special treatment, they conducted their experiment similar to Jumau's original experiment. The results are presented in Table 5. Evidently, they are in close agreement with those of Jumau. The memory effect cannot, however, be explained by an impeded acid diffusion mechanism, because of the Eloflux treatment placed between charge and discharge. Obviously, the memory effect must be attributed to the solid-state properties of $PbO_{2-\delta}$.

Apart from these investigations, Hullmeine and Borger [8] have demonstrated the effect of the previous charge history on the capacity in an experiment performed with standard automotive type electrodes. The experimental conditions were as follows:

Electrode no.	Charge regime
1	$C/10$ rate, constant current
2	Three-step regime (i) $C/1$ rate (ii) $C/5$ rate (iii) $C/10$ rate

TABLE 5

Capacity of Eloflux electrode (Faure type) as a function of previous discharge rate (cf. refs. 3 and 6)

Cycle no.	Discharge current (A)	Capacity (A h)	(%)
1	4	9.8	100
2	4	9.8	100
3	8	8.8	89
4	4	9.5	97 (< cycle 1)
5	16	7.8	79
6	4	9.3	96 (< cycles 1, 4)
7	32	6.8	70
8	4	9.1	93 (< cycles 1, 4, 6)
9	2	10.6	109
10	4	10.0	103 (> cycle 1)
11	4	9.95	102 } ~ cycle 1
12	4	9.95	102

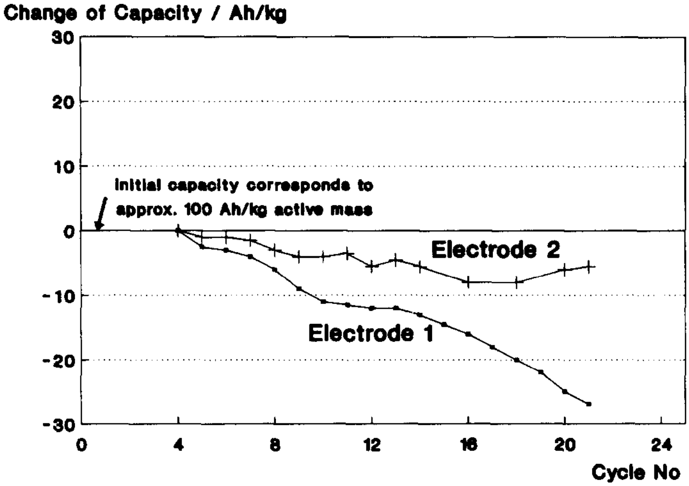

Fig. 2. Automotive-type electrodes (d = 1.8 mm) in excess of electrolyte, discharged at $C/5$ rate. When charged at $C/10$ rate, capacity decreases much faster than for three-step regime of $C/1 \rightarrow C/5 \rightarrow C/10$.

The results are shown in Fig. 2. Accordingly, electrode no. 1, which is cycled under the $C/10$ (low) rate charge, exhibits a gradually decreasing capacity. Electrode no. 2, however, which is charged by a three-step regime with a high-rate ($C/1$) charge at the beginning, maintains its capacity. This behaviour is in complete agreement with that of Planté electrodes discussed in the previous section.

Tubular electrodes

The effect of the previous charge history on the capacity level of tubular electrodes was studied in single-electrode experiments with excess of electrolyte. Segments of positive tubular plates from traction batteries cut to a size suitable for laboratory handling were used. In order to investigate the effect of grid alloy constituents on the capacity behaviour, electrodes with spines cast from Pb–10wt.%Sb, Pb–1wt.%Sb and Pb–Ca–0.3wt.%Sn alloys have been tested. Two antimony-free pasted electrodes were used as counter electrodes [9].

Discharges were performed at a current of 2 A. Under these conditions, the active-material utilization was found to be more than 150 A h kg^{-1} under an optimum charge regime. A two-step charging procedure with different current densities was applied. The current during the first step was varied, while the current during the second step was always 1 A. The overall quantity of charge was usually 120% of the previous discharge capacity. The potential of the positive electrode, which always limited the capacity of the cell, was observed with respect to a reference electrode.

Figure 3 depicts results for two electrodes with a Pb–Ca–0.3wt.%Sn spine (without any antimony). Their capacities reached a constant level of about 31 A h after 10 cycles, when the charge current during the first step

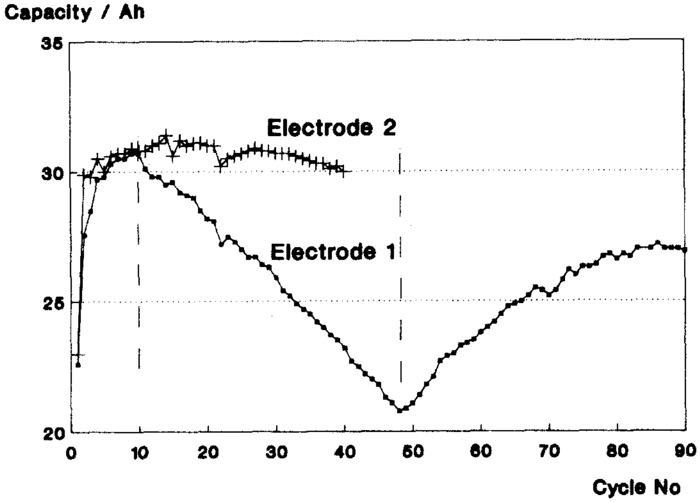

Fig. 3. Tubular-plate electrodes in excess of electrolyte, discharged with 2 A and charged with two-step regime. If 4 A is applied during first step (electrode 1, cycles 1–10; electrode 2 continuously), capacity is kept constant. Capacity decreases if 1 A is applied (electrode 1, cycles 11–48), but increases again after switching back to 4 A (electrode 1, cycles 49–90). Second-step charge current always 1 A.

was 4 A. While charging was continued in this manner, the capacity of electrode no. 1 stabilized at this level. If, however, the charge current was changed to 1 A for electrode 1, after the first step, the capacity immediately decreased steadily by about 1% per cycle. When, after about 45 cycles, the 4 A/1 A charge regime was re-introduced, the capacity of electrode 1 increased again. About 60% of the capacity loss was recovered in this experiment.

Similar investigations have been carried out on electrodes with grid alloys containing 1 or 10 wt.% Sb. All electrodes showed an initial active-material utilization of 150 A h kg^{-1}, or more, in cells with excess of liquid electrolyte. Under deep-cycling conditions applying the 1 A/1 A charge regime, the steepest decline was observed on the electrodes with antimony-free grids (Fig. 3). In the case of the 10 wt.% Sb grids, it was about half as steep, while the 1 wt.% Sb grid electrodes exhibited intermediate behaviour. It appears that in presence of antimony the capacity decay is retarded.

When the active-material utilization was limited (e.g., by immobilizing the electrolyte), the relative capacity decrease was significantly lower. In cells with gelled electrolyte, the electrodes showed an initial utilization of about 125 A h kg^{-1} when cycled on the 4 A/1 A regime. After switching over to the 1 A/1 A regime, the relative capacity decrease per cycle amounted to only about 60–80% of that in the case of liquid electrolyte, independent of the grid alloy. This influence of electrolyte immobilization on the capacity may be related to:

(i) the lower active-material utilization

(ii) a different acid concentration profile within the electrode pore system during charge and discharge due to the absence of convection and, consequently, a significantly different solubility of Pb^{2+} ions, which appears to be one of the key parameters of the effect (cf. refs. 3 and 6).

The reversible capacity decay was observed on all electrode types, independent of spine alloy or immobilization of the electrolyte. In any case, the capacity decrease is a problem of dischargeability. Neither shedding of the active material nor stratification of the acid were observed in any instance. The electrodes were fully charged during cycling, as verified either by chemical analysis or by following a non-electric treatment described previously [3, 6] for other electrode types (Fig. 4). The electrode with poor dischargeability was removed from the cell at the end of the charging procedure, washed free of acid for three days, and dried at 60 °C. When placed back to the cell and immediately discharged (without any intermediate charge), there was a pronounced increase of capacity with respect to the capacity before this treatment: about 80% of the capacity loss was recovered. Sometimes the original high capacity level or even more (see also ref. 11) was attained.

The effect of overcharge (see ref. 3) was also found to be of importance for tubular electrodes. The capacity of the electrode decreases as the quantity of overcharge is increased, regardless of the applied charging regime.

The results on single tubular-plate electrodes in an excess of electrolyte are confirmed by experiments on commerical cells with this electrode type.

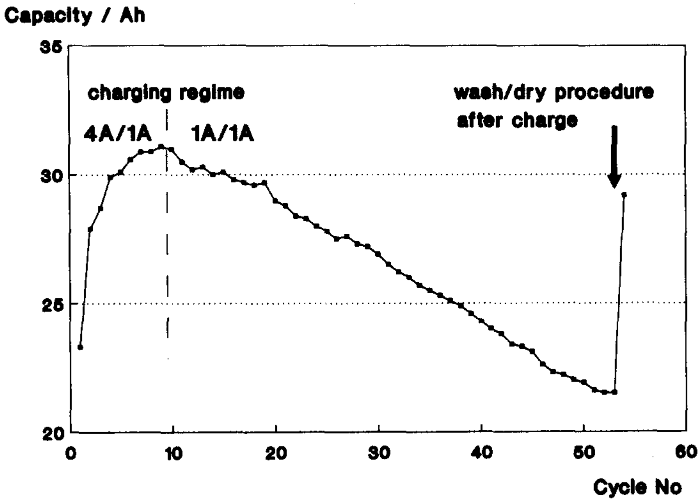

Fig. 4. Tubular-plate electrode in excess of electrolyte, discharged with 2 A and charged with two-step regime. If 4 A is applied during first step (cycles 1–10), capacity is kept constant. Capacity decreases if 1 A is applied (cycles 11–53). Second-step charge current always 1 A. After charge at cycle 53 washing/drying procedure applied and 80% of capacity loss is restored.

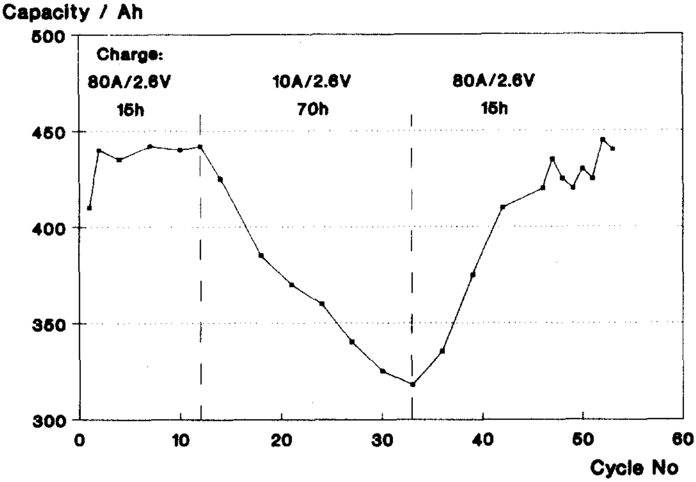

Fig. 5. Traction cell with positive tubular-plate electrodes. If charged using 10 A, the capacity decreases. If the maximum current is 80 A, capacity recovers.

Figure 5 shows the capacity of a cell with liquid electrolyte running on deep cycles. When discharged at the $C/5$ rate, its capacity remained stable when the charging current was limited to 80 A. But when the charging current was limited to 10 A, the capacity decreased continuously (about 27% within 20 cycles), until the initial charging regime was re-used. Then, the capacity increased until the level was re-attained. With both charging regimes, the positive electrode always became fully charged. To prevent acid stratification, the electrolyte was stirred and its concentration observed.

A similar cell with gelled electrolyte (acid stratification can be excluded) showed qualitatively the same results. The capacity decrease was evident (about 22% within 50 cycles), but not as steep as for the cell with liquid electrolyte. The possible reasons have been discussed already for the single-electrode experiments. The full initial capacity of this cell could be recovered after the initial charging regime was re-applied.

These results clearly demonstrate that tubular electrodes exhibit equivalent behaviour to Planté or Faure electrodes when subjected to charge parameter variations.

Discussion

Reversible capacity decay: type of electrode and mass utilization

The experimental results obtained clearly demonstrate that a reversible capacity decay of the positive active material is observed under certain operational cycling conditions on all types of electrodes (Planté, Faure and tubular plates). It has been demonstrated further that the capacity can be recovered by changing to other operational conditions or by several special treatments (e.g., rest times, washing/drying the charged electrode).

The extent of the deterioration depends very much on the operational conditions. If the utilization of the positive active material is reduced by time-limited discharge or by acid depletion in the porous system (thick electrodes, immobilized electrolyte, etc.), the capacity decay is also diminished. Even if the average material utilization of the electrode is not high (as may occur during high-rate discharges), a locally high mass-utilization may cause a capacity decay.

The fastest degradation has been found with Planté electrodes in an excess of electrolyte [3], and with Faure electrodes under forced flow-through of electrolyte [6]. For these two electrode types, the access of electrolyte to the porous system is not diffusion controlled. With thick tubular electrodes (where the access of electrolyte is impeded) the capacity decrease is less pronounced, even in an excess of electrolyte, where a material utilization about twice as high as in commerical cells can be achieved. The mechanical strengthening by the gauntlet may also have a beneficial effect on the active-material structure of tubular plates.

The capacity decay occurring after high-rate discharges in accordance with the Jumau experiment can also be reversed by introducing low-rate discharges. For this reason, battery engineers are accustomed to perform low-rate discharges before the determination of reproducible battery capacity data.

Many of the parameters of the laboratory experiments presented here have been different from those in commerical batteries. When tested in an excess of electrolyte, the active-material utilization was much higher than that in electrolyte-limited commerical cells. But under extreme conditions, the effects are more pronounced and can be studied clearly and individually from other non-reversible deterioration processes, which in technical cells may often outweigh the effects under study.

The difficulties of reproducing the reversible capacity decay in technical cells may be the reason for the very different statements and speculations that are connected with this effect. Nevertheless, all the features that have been reported can be understood qualitatively when a simple aggregate of spheres model is applied.

Porous PbO_2 active mass — an aggregate of spheres

Recently, it has been proposed that the porous PbO_2 electrode can be regarded as an aggregate of spheres ('Kugelhaufen') that are connected by necks with each other [3, 10]. The 'Kugelhaufen' is based on a mathematical model that has been developed to understand the mechanical, electrical and thermodynamic properties of pressed and sintered metal powders [11]. The electrical resistance of such a morphological structure is mainly determined by the resistance of the contact areas between the spheres. Current distribution and penetration depth of the electrochemical reaction into the electrode during discharge and charge are determined by the ratio of the electronic conductivity of the active material and the ionic conductivity of the electrolyte. Thereby, the reaction distribution and the capacity of the electrode depends very sensitively on the properties of the necks, although these neck zones amount to only 0.2% of the total PbO_2 volume. Small changes in the necks may cause considerable changes in electrode behaviour.

In such an aggregate of spheres, the contact areas consist of $PbO_{2-\delta}$ as does the bulk material, but both zones differ in potential (and, consequently, in their δ values, e.g., ref. 12) due to different Laplace pressures (convex PbO_2 particles, 'spheres', and concave contact zones, 'necks'). The potential of the necks is always negative with respect to that of the spheres. Otherwise, the neck zones would be preferably discharged, and the discharge would be prematurely terminated by the quickly growing resistance of these neck zones.

This 'Kugelhaufen' model allows a phenomenological description of the capacity behaviour of the $PbO_{2-\delta}$ electrode as a function of different charge and discharge regimes (for details see refs. 3, 6 and 10). The overall conductivity of the active material is determined by the neck zones and their restrictive resistance. *In situ* measurements with the Eloflux method have shown a strict relationship between the active-material utilization and the active-material resistance [6] when changes were caused by application of different charging regimes.

Beyond this, the 'Kugelhaufen' model may explain some of the effects of additives to the active material or to the electrolyte. A hypothesis for the effect of redox couples having a potential lower than that of the $PbO_2/PbSO_4$ electrode has been given in ref. 13. By this, the influence of small amounts of additives, like tin, to the electrolyte on the performance of the PbO_2 electrode can be explained. If phosphoric acid is reacting in these sensitive neck zones, the overall performance will also be changed [14, 15]. The details of the reaction mechanisms have still to be investigated.

Conclusions

Under certain operational conditions a reversible capacity decay of PbO_2 electrodes is observed. Although fully charged, the material utilization is reduced when successive cycles are performed with:

- low charging current densities
- large quantities of overcharge
- high-rate discharges

The capacity can be reversed to its original value by changing to appropriate operational conditions. It has been show that these capacity phenomena are independent of electrode design (Planté, Faure and tubular plate). It is claimed that the phenomena can be attributed to the specific solid–state properties of $PbO_{2-\delta}$. Very strong proof for this theory is the recovery of the capacity of a charged electrode by the washing/drying procedure, i.e., without any electrical treatment.

But there are differences in the extent of the effect: the decay has been found to be less pronounced (or even suppressed)

- when the positive mass is less utilized (due to time-limited discharge, thick electrodes, immobilization of the electrolyte)
- in the case of the presence of special additives (tin, antimony, phosphoric acid)

Effects similar to acid depletion (which Jumau [2] supposed to be relevant according to the previous discharge and charge) can be excluded as has been shown by equalization of the pore and bulk electrolyte by Eloflux experiments and rest times between two cycles of Planté electrodes. Nevertheless, the acid density effects the solubility of Pb^{2+} and, therefore, is an important parameter that must be taken into account.

In situ measurements of the resistance of the positive mass and of the interface between mass and grid using the Eloflux method [6] show that:

- the active-mass resistance markedly increases during discharge
- the active-mass resistance in the fully-charged state may increase under certain operational regimes
- an increase in the active-mass resistance in the fully-charged state correlates to a decrease of capacity
- the increase in the active-mass resistance in the fully-charged state as well as the capacity decay can be reversed by special treatments mentioned above
- the interface between mass and grid appears not to be involved in this process

Phenomenologically, the behaviour can be described using the 'Kugelhaufen' model. As only about 0.2% by volume of the PbO_2 is situated in the neck zones, very little structural changes at these sites may cause large overall changes in the electrode behaviour. Due to different Laplace pressures, the potential of the necks is always negative with respect to that of the spheres. As a consequence, the necks are protected from being discharged under normal conditions. Debilitating structural changes may happen, e.g., in the case of locally high material utilization. These changes may accumulate when detrimental operational conditions are applied repeatedly.

Relaxational and capacity recovering processes may take place via the liquid phase, e.g., during rest times or the washing/drying process; the latter appear to be sufficient to restore the original morphology. Small amounts of additives, such as tin (a hypothesis for the mechanism of tin redox couples is given in ref. 12) and antimony ions or phosphoric acid [13, 14], may produce large overall changes, if they react primarily with the PbO_2 neck zones.

Acknowledgements

The authors express their thanks to their colleagues W. Borger, G. Ely, U. Hullmeine, H. Laig-Hörstebrock and A. Winsel for experimental assistance, offering of unpublished results, and many fruitful discussions.

References

1 A. A. Cahen and I. H. Donaldson, *The Electrician XLI*, 1898, p. 674.

2 L. Jumau, Sur la rôle de la diffusion dans le fonctionnement de plaques positives de l'accumulateur au plomb, *Rev. d'Electricité, L'Eclairage Electrique XVI*, No. 36, 1898, p. 413.

3 U. Hullmeine, A. Winsel and E. Voss, *J. Power Sources, 25* (1989) 27.

4 U. Hullmeine and W. Kappus, *Electrochim. Acta, 27* (1982) 1677.

5 J. Bohmann, U. Hullmeine, E. Voss and A. Winsel, Active material structure related to cycle life and capacity, *ILZRO Project LE-277, Final Rep.*, Dec. 1982.

6 W. Borger, U. Hullmeine, H. Laig-Hörstebrock and E. Meissner, in T. Keily and B. W. Baxter (eds.), *Power Sources 12*, Int. Power Sources Symp. Committee, Leatherhead, U.K., 1989, pp. 131–144.

7 U. Hullmeine and W. Borger, unpublished results, VARTA, 1984.

8 W. Borger and U. Hullmeine, unpublished results, VARTA, 1986.

9 G. Ely and E. Meissner, unpublished results, VARTA, 1988.

10 A Winsel, E. Voss and U. Hullmeine, *J. Power Sources, 30* (1990) 209.

11 V. E. Rückborn, B. Willer and A. Winsel, in D. Behrens (ed.), *DECHEMA Monographien*, Vol. 102, VCH, Weinheim, 1986, pp. 513–541.

12 J. P. Pohl and S. Atlung, *Electrochim. Acta. 31* (1986) 391; S. Atlung and J. P. Pohl, *Electrochim. Acta, 31* (1986) 873.

13 E. Voss, U. Hullmeine and A. Winsel, *J. Power Sources, 30* (1990) 33.

14 U. Hullmeine, E. Voss and A. Winsel, *J. Power Sources, 30* (1990) 99.

15 E. Voss, *J. Power Sources, 24* (1988) 171.