

Reversible capacity decay of PbO₂ electrodes Influence of high rate discharges and rest times

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Abstract

A capacity decay of PbO₂ electrodes on cycling can be induced and reverted again under certain operating conditions. This is a general property of the PbO₂ material, not of special electrodes. While application of low initial recharge current and overcharge of the already fully-charged PbO₂ electrode had already been shown to induce capacity decay, continuous cycling with high discharge currents has been found to be detrimental, too. On the other hand, cycling with rest times seems to be favourable to recover capacity, besides other treatments, e.g., cycling with high initial recharge current, full discharges at very low rate, and washing/drying of the charged PbO₂ electrode. The results are discussed in view of the 'Kugelhaufen' model, which phenomenologically describes the features of the reversible capacity decay.

Introduction

Some of the phenomena, which are subsumed under the topic 'reversible capacity decay' of the lead dioxide electrode, are already known since the beginning of this century [1–3]. The amount of capacity, which can be drawn from the electrode under cycling operation, depends on its history, i.e., on the former treatment of the electrode, on the conditions of the former cycles, discharge and recharge currents, etc. Therefore, the designation 'memory effect' has been used.

When lead/acid batteries with antimony-free positive grids came up, the delicate influence of antimony on the behaviour of the lead dioxide electrode became obvious. This was denoted as the 'antimony-free effect'. Many scientific and technical works have been done during the last decades to understand and overcome this problem. Several theories have been developed. Initially, changes of morphology, structure, crystallite size and loss of mechanical strength of the active material were detected and supposed to be the origin of the effect. Later on, the 'hydrogen loss model', which seems to be disproved today [4], was developed. Recently, the historical work and the actual knowledge on the capacity decay has been reviewed by Hollenkamp [5], who called the phenomenon 'premature capacity loss' (PCL). Nowadays, two mayor notions seem to exist, the 'barrier layer' model and the 'Kugelhaufen' model.

The 'barrier layer' model assumes the development of a barrier between active PbO₂ material and current collector (grid). This could be a nonconductive layer formed from corrosion material at this interface, or even unfavourable oriented cracks in the corrosion layer, which would reduce electrical and mechanical connection between active material and grid [6]. Indeed, an interface layer between mass and grid of failed positive plates has been reported by several authors. Basic compounds like α -PbO

may exist under a thin PbSO_4 diaphragm [7, 8]. However, these compounds have been found even with cycled electrodes showing no capacity loss [9], i.e., their existence is not a special feature of degraded plates.

On the other hand, the 'Kugelhaufen' model ('aggregate of spheres' model) [10, 11] supposes a successive deterioration of the connections ('necks') between the single PbO_2 crystallites on cycling under certain conditions. By this, the active mass' resistivity is increased, leading to a successive concentration of the discharge reaction in the regions near to the current collector. There the current density is increased compared to its average value, and in consequence the available capacity is reduced. The successive increase of active material resistivity in the charged state, strictly correlated to the available capacity, was demonstrated by *in situ* experiments [12], while no analogous changes of the active mass/grid resistance was found at the same time.

Obviously the capacity can be recovered again, when (by any means) the active mass conductivity is increased again, and in consequence the discharge reaction is homogenized. Many experiments show that the capacity loss is not an accidental process, but can be intentionally induced and intentionally reverted again just by changing the conditions of cycling or by other treatments.

Status of experience

Especially under view of the 'Kugelhaufen' model the 'reversible capacity decay' is called 'reversible insufficient mass utilization' (RIMU) [10]. To portray this effect, and to avoid any confusion or mixture with other phenomena, the main characteristic features are summarized:

- it is a property of the positive electrode
- there is no principal failure of the current collector (corroded grids, etc.)
- shedding of the material is not a primary characteristic
- discharge at medium and high rates, although the active PbO_2 material is fully charged, leads to reduced medium/high-rate capacity
- discharge at (very) low rates is possible as usual, i.e., the full low-rate capacity is available

This means, that the RIMU is not a consequence of:

- lack of recharge: on the contrary, overcharging of the already fully-charged electrode aggravates the situation [11, 13]
- stratification of the electrolyte (as the effect has been found with electrolyte immobilized with gel or glass microfibre mat as well as with free electrolyte and forced flow-through of electrolyte [12, 13])
- thermopassivation (which is a solitary phenomenon observed on activation of dry charged positive electrodes, which suffered a high-temperature treatment during manufacture [14])
- storage passivation (which is solitary phenomenon after extended storage [15]; on the contrary, open-circuit voltage (OCV) storage has beneficial influence on the RIMU)
- passivation after overdischarge (which seems to be an inhibition of recharge [16])
- pauperization of electrolyte (idea of Jumeau, 1898 [1]); the effect takes place even when the concentration of the electrolyte is kept constant by forced flow-through of electrolyte [12].

The RIMU is qualitatively independent of:

- the type of electrode and the thickness of the positive active material layer: it has been found with Planté, pasted and tubular electrodes [13]

- the state of electrolyte: immobilized, liquid, or forced flow-through [13]
- the grid alloy: it has been found with grid alloys containing 10%, 2.4% and 1 wt.% of Sb, with Sb-free grids made of Pb–Ca or Pb–Ca–Sn, and with pure lead grids (Planté electrodes) [11–13]

but it depends quantitatively on these parameters: thin active material layer (thin pasted plates and Planté electrodes), high mobility and high excess of electrolyte (forced flow-through), and low content of Sb seem to promote RIMU, while thick (tubular) electrodes, immobilized electrolyte, high content of Sb in the grid alloy, tin ions [17] and phosphoric acid [18] in the electrolyte seem to reduce the sensibility with respect to unfavourable cycling conditions.

The ‘reversible capacity decay’ is induced:

- only by cycling, not by floating (except of excessive float currents, which do not only compensate self-discharge, but lead to major overcharge)
- by cycling with low initial recharge current density [11–13]
- by overcharge of already fully-charged PbO₂ electrode [11, 13]. The reversible capacity decay is promoted
- by deep discharges (high active material utilization)
- by good electrolyte support (e.g., forced flow-through [12], excess of electrolyte, thin electrodes [13])
- by absence of Sb, Sn, phosphoric acid, etc.

The most surprising and fascinating property of the effect is its reversibility:

- by cycling with high initial recharge current density [11–13]
- by (one or two) discharges at very low rate [11, 13]
- by washing and drying of the electrode without any additional electrical treatment [11–13]
- by OCV rest times of the charged electrode (especially at elevated temperature) [8, 12, 19]
- by addition of tin ions to the electrolyte [17]

The process of decay and restoration of capacity can be performed several times in the same way [11, 13], when series of cycles with detrimental and favourable conditions are performed alternately.

The decay of the active material utilization is due to a successive change from cycle to cycle of the solid state properties of PbO₂, which can be experimentally observed via the reduction of the active PbO₂ material conductivity correlating strictly with the capacity [12]. Dependent on discharge/recharge conditions, the active material utilization finally arrives at a stable utilization level (niveau) [11, 17, 18]. In view of the ‘Kugelhaufen’ model, the connecting edges of PbO₂ crystallites are bottle necks for the current. Their thickness and conductivity determines the specific conductivity of the active mass, and thereby the current distribution. The more the conductivity is reduced, the more inhomogeneous is the current density and the local active material utilization in the electrode. This leads to reduced electrode capacity (average mass utilization) compared to the case of more homogeneous current distribution. Nevertheless, the local mass utilization nearby the grid may be so high, that a dense, nonconductive layer of discharged mass may have been formed at end-of-discharge. But this layer would be the consequence of the increasing inhomogeneity of discharge reaction, and not the primary reason of the capacity decay [20].

Furthermore, when the connections between the crystallites are totally disrupted, in the very end, softening and even shedding of the active material is to be expected [21].

On the other hand, restoration of the connection sites is assumed to be the reason for restoration of the original electrical performance. The conditions of cycling determine the destruction or reconstruction of the crystallite network. Furthermore, especially the currentless procedure of washing and drying of the electrode [11–13] is able to restore structure and capacity without any electrical treatment. As most types of *ex situ* analyses (scanning electron microscopy, X-ray analysis, etc.) have to be done for instrumental reasons with washed and dried samples, these samples do not represent the original status, but their properties may be changed during preparation. This aggravates investigations on the ‘reversible capacity decay’ and emphasizes the importance of *in situ* experiments [22].

This work deals with high-rate discharges and rest times during cycling as two other examples of detrimental and favourable cycling conditions. Old experimental findings [1] are confirmed and discussed in view of the ‘Kugelhaufen’ model.

Experimental

The experiments have been carried out with laboratory cells, which have been specially designed for high discharge rates. Their capacity is about 10 A h at discharge with 2 A (5 h rate), and about 4 A h at 80 A (3 min rate). They have thin, tubular shaped electrodes with an active material layer of about 0.6 mm effective thickness. This enables quick recharge; 1000 and more continuous cycles at 75% depth-of-discharge (DOD) (5 h rate) can be performed without any loss of capacity with an *IU*-charging regime applied for only 6 h. All current collectors are made of pure lead, i.e., the cells are totally free of Sb, Sn, etc. The electrolyte is immobilized. With these cells, cycling under different conditions has been performed.

Cycling regime A: continuous high-current partial cycles. Discharge with 80 A, time limited for 2 min, i.e., 2.67 A h (cycles 1–6: 3 min, i.e., 4 A h); after capacity decay, discharge was stopped when cell voltage reached 1.0 V. Recharge according to different *IU*-schemes: 10 A/2.35 V for 4 h (cycles 1–7), 10 A/2.45 V for 4 h (cycles 9–98) and 10 A/2.35 V for 6 h (cycles 99–550). There were no OCV rest times (permanent cycling). 2 A discharge have been performed until the cell voltage reached 1.0 V to test the actual capacity, and to recover capacity when capacity decay has occurred.

Cycling regime B: continuous high-current full cycles. Discharge with 90 A until cell voltage reached 1.0 V. Recharge according to *IU*-scheme: 10 A/2.35 V for 17 h, OCV rest times of 6 h after every discharge before recharge.

Cycling regime C: continuous high-current partial cycles. Discharge with 80 A, time limited for 2 min, i.e., 2.67 A h. Recharge according to *IU*-scheme: 10 A/2.35 V for 6 h, OCV rest times of 6 h after every discharge before recharge.

Cycling regime D: continuous high-current partial cycles. Discharge with 80 A, time limited for 2 min, i.e., 2.67 A h. Recharge according to *IU*-scheme: 10 A/2.35 V for 16 h; there were no OCV rest times (permanent cycling).

Results

The results obtained with the cell cycled according to regimes A, B, C, and D are given in Figs. 1, 2, 3 and 4, respectively. In part (a) of the Figs., the capacity

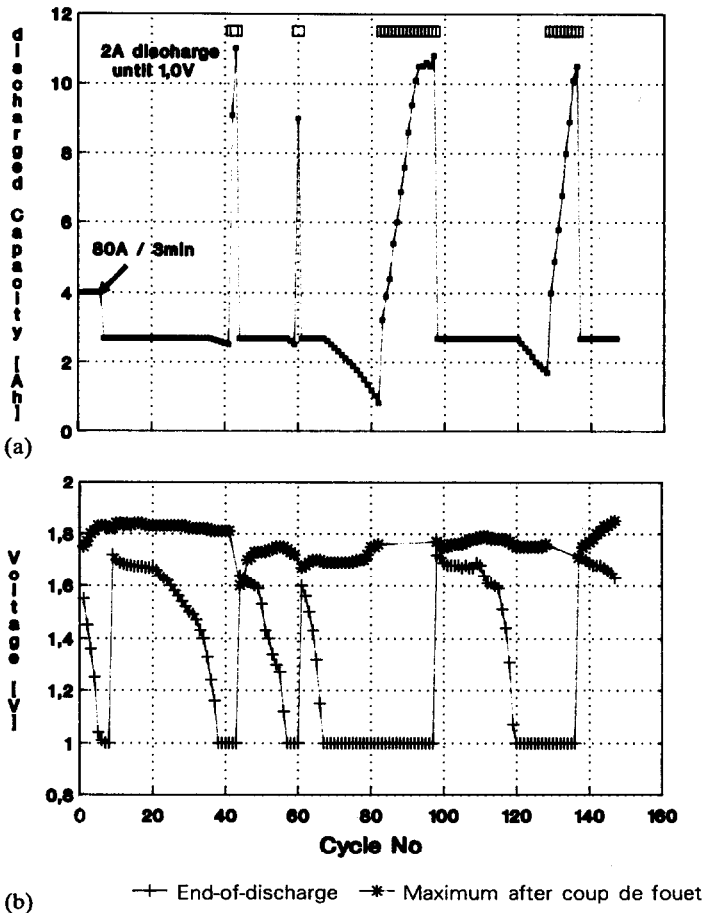


Fig. 1. Cycling according to regime A: continuous high-current partial cycles (80 A/3 min and 80 A/2 min), no rest periods, recharge 4–6 h; (a) discharge capacity, (b) EOD voltage and voltage after 'coup de fouet'.

drawn from the cell is shown. In part (b), the end-of-discharge (EOD) voltage is presented. This is a constant value in case of the full cycles of regime B. Its decline in case of the time-limited discharges of regime A indicates capacity loss (Fig. 1(b)). In parts (b) of the Figs., the maximum voltage during discharge, i.e., the maximum after the minimum of the 'coup de fouet' (Spannungssack) [23] in the beginning of discharge, is also given.

Figures 1(a) and 1(b) show, that a high-current discharge promotes a capacity decay from initially about 4 A h to less than 2.5 A h in cycles 1 to 41. This can be seen from the EOD voltages of the partial cycles, which decreased from cycle to cycle until in cycle 38, the definite EOD voltage of 1.0 V was reached. Then the capacity, which could be drawn from the cell, fell below 2.67 A h. Even more extreme is the result after about cycle 70, when in the same situation as in cycle 41, cycling was continued until in cycle 82, the 80 A capacity had decreased below 1 A h, i.e., less than 25% of the initial value.

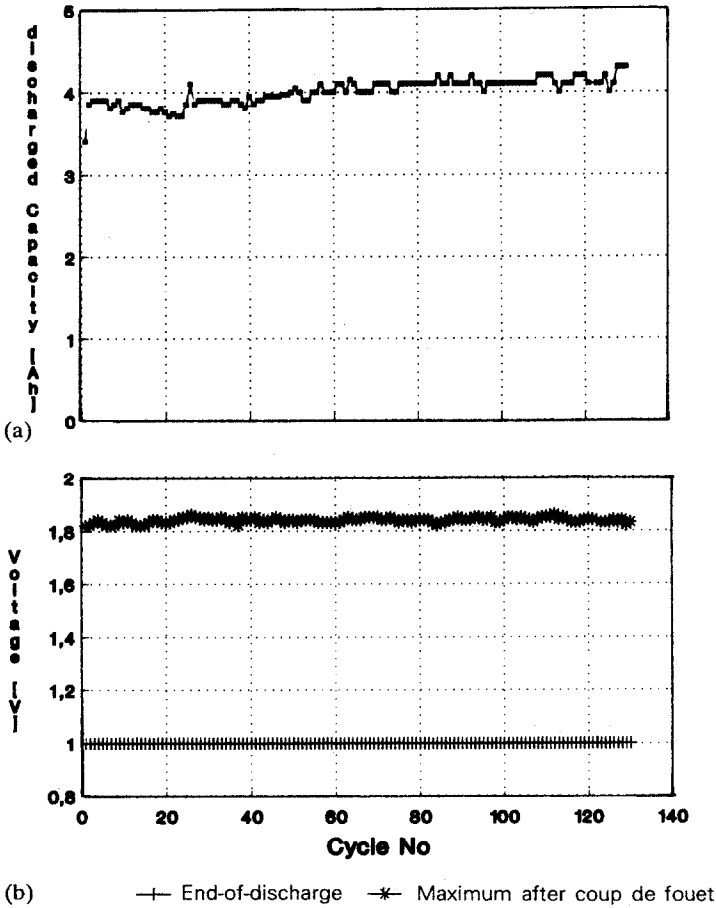


Fig. 2. Cycling according to regime B: high-current full cycles (90 A to 1.0 V), 6 h OCV rest period before recharge of 17 h; (a) discharge capacity, (b) EOD voltage and voltage after 'coup de fouet'.

However, not only the 80 A capacity was dramatically reduced, but even the 2 A capacity, as can be seen in cycle 42 and much more pronounced in cycles 83 ff., where the 2 A capacity was very poor (3.2 A h) with respect to cycle 43 (10.7 A h). The effect is shown once again, when the 2 A capacity in cycle 128 is compared to cycle 97. This is obviously not a matter of deficiency of recharge, as the voltage at the beginning of discharge seems not to be reduced when the 80 A capacity decreases (Fig. 1(b)), which would be expected in the case of insufficient recharge. Also the application of an increased recharge voltage of 2.45 V instead of 2.35 V (from cycle 8 to 98), or the extension of the time of recharge from 4 to 6 h (from cycle 99 onward), did not change the situation.

In any case, the capacity was restored again with the same charging regime, when full discharges with 2 A were performed: the 2 A capacity increased again, e.g., in cycles 83 ff. from about 3.2 A h to more than 10 A h. This demonstrates that despite the much higher average DOD (>10 A h) than during the high rate cycles

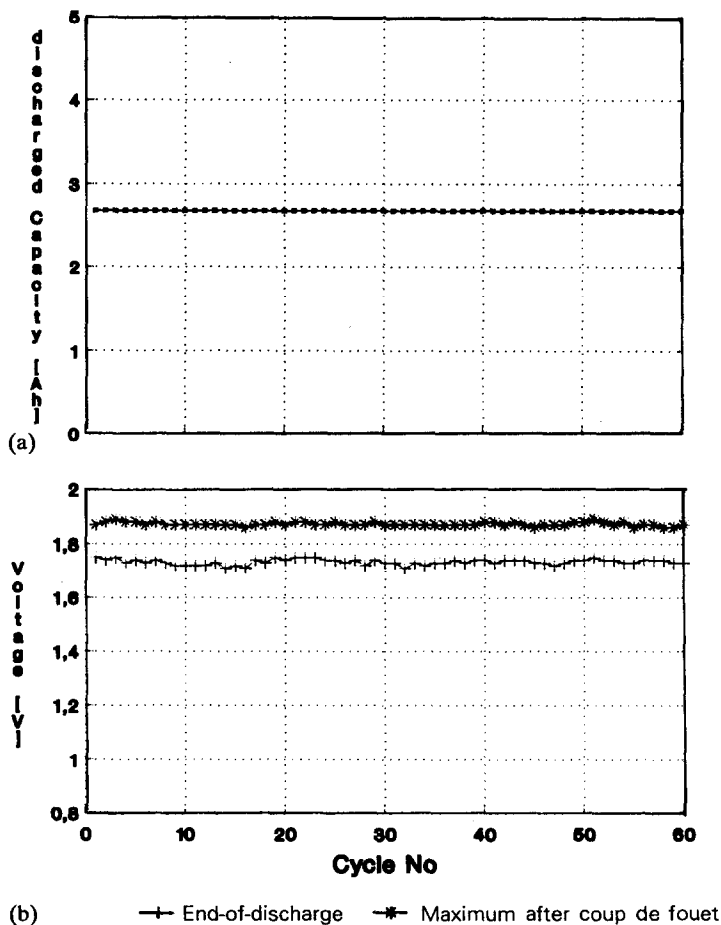


Fig. 3. Cycling according to regime C: high-current partial cycles (80 A/2 min), 6 h OCV rest period before recharge of 6 h; (a) discharge capacity, (b) EOD voltage and voltage after 'coup de fouet'.

(4 A h... <1 A h), the *IU*-scheme was sufficient to recharge the cell. There is no reason, why a charging regime should leave the cell in a state-of-charge of only 30%, while it is otherwise suitable to restore the state-of-charge (cycle 83, and ff.).

These procedures have been repeated several times: during high-rate discharge cycles, the capacity decreased (as well the 80 A as the 2 A capacity). When full cycles with the same charging regime but 2 A discharge were performed, the capacity increased again until the full 2 A capacity of about 10 A h was restored again. The 80 A capacity was restored again, too. But when the cycling scheme was switched back to high-rate discharge, a rapid capacity decay came up again. Altogether, this procedure was repeated for 550 cycles in the same manner. Only the first 150 cycles are shown in the Figs.

Successive high-rate discharge do not necessarily deteriorate the mass utilisation. Figure 2 shows the results, which were obtained with another cell examined according to cycling regime B, i.e., with full high-rate cycles and a rest time before recharge.

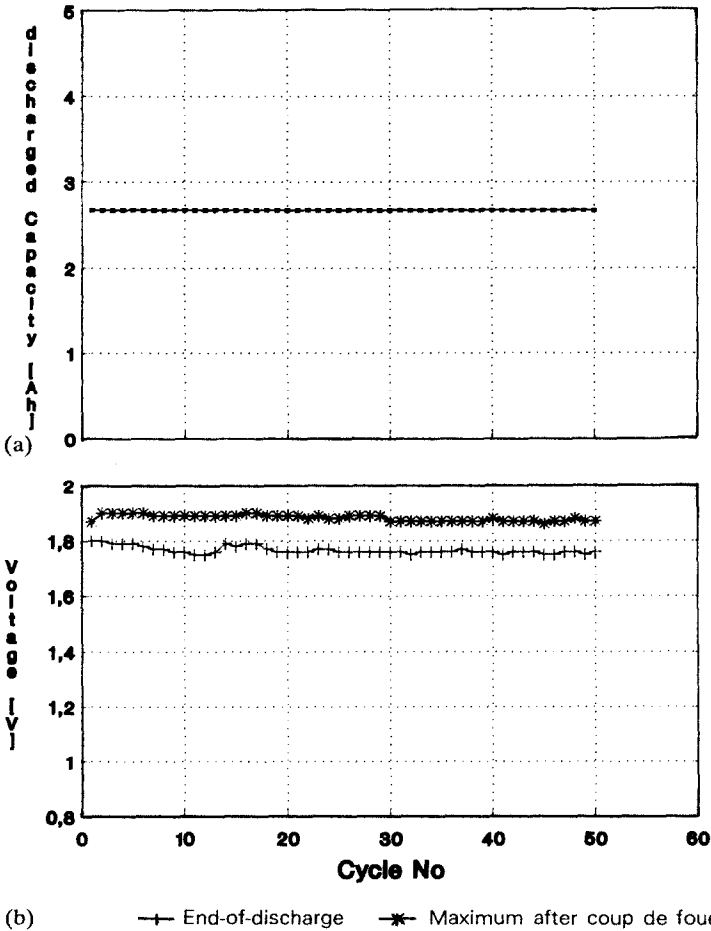


Fig. 4. Cycling according to regime D: continuous high-current partial cycles (80 A/2 min), no rest periods, recharge 16 h; (a) discharge capacity (a), (b) EOD voltage and voltage after 'coup de fouet'.

Obviously, the rest time of some hours, after high-rate discharge and before begin of recharge, prevents capacity decay persistently, although full cycles are believed to be more critical for capacity degradation than partial cycles. The extended period of recharge of regime B with respect to regime A was an unintended consequence of the cycling equipment used. However, it does not provide a 'better charged' cell: as shown above, the short period of recharge of regime A is sufficient to recharge the cell, even when more than 10 A h had been discharged (see above), much more than during high-rate discharge. During the last 10 h of recharge of the cell cycled according to regime B, a (over)charging current of ≤ 30 mA was measured.

On the other hand, the period of recharge with nearly no charging current could have a similar effect like a rest period at OCV. Such an OCV rest period of the charged electrode has been reported to be favourable to recover the capacity [19]. On the other hand, excessive overcharge at high-positive potential is known to reduce capacity [11, 13]. But in the present case of overcharging at low charging voltage (i.e.,

low charging potential of the positive electrode), the period might be more prosperous than destructive.

This interpretation is supported by the results obtained with cells which were cycled according to regimes C and D, respectively. Figure 3 shows, that recharge with 2.35 V for 6 h is sufficient, when it is preceded by a rest period of 6 h (regime C). Some relaxation seems to take place during this period at OCV. If this rest period is omitted – like in Fig. 1 – capacity decreases, when this short charging regime is applied.

On the other hand, the extended charging time of 17 h with the same charging voltage of 2.35 V (regime D) is prosperous, too, although the charging regime does not include any OCV period.

Discussion

In view of the 'Kugelhaufen' model, the following scenario is assumed within the PbO_2 active mass at high-rate discharges (for simplicity a one-dimensional geometry, as in tubular shaped electrodes, is assumed, see below):

Initially, with the intact electrode, the discharge reaction at high rates preferentially takes place in the outer portions of the positive mass, in vicinity to the electrolyte, to minimize voltage drop. On the other hand, in case of low discharge rates, ohmic losses are of minor importance with respect to the charge-transfer overvoltage, which tends to homogenize the discharge reaction over all of the active material.

When the discharge proceeds, the maximum of the current density distribution will move away from the vicinity of the electrolyte to the region near to the current collector. But there electrolyte supply is worse than in the vicinity of the separator. Therefore, when discharge is finished by pauperization of electrolyte, a maximum of material utilization near to the electrolyte is to be assumed, i.e., this region contributes more than in average to capacity.

In view of the 'Kugelhaufen' model, the (concave shaped) connection sites of the PbO_2 crystallites ('necks') have an equilibrium potential well below that of the (convex shaped) crystallite surfaces [10, 11], which dominate the electrode potential. Therefore, these sites are protected from discharge at OCV and moderate discharge rates. But, on high discharge rates, the electrode may be polarized well below this potential, the connection sites themselves may be discharged, and the electrical connections between adjacent PbO_2 crystallites become thinner and may (at least partially) disrupt.

It may be that the PbO_2 structure in the region near to the electrolyte is progressively prejudiced by the high local mass utilization in the consecutive high-rate discharges. An indication for the critical influence of high mass utilization are the results of cycles 1 to 6: the decrease of EOD voltage is much faster at the discharge period of 3 min compared to the later cycles with only 2 min discharge (Fig. 1(b)). When the recharge takes place immediately after the EOD, the electrode is going to be recharged with its porous system filled with still pauperized acid. This means that, during the initial part of the recharge time, the acid density in the porous system is relatively low. Recharge started under this condition seems to produce an unfavourable PbO_2 structure with reduced active material conductivity, i.e., the partially-disrupted connections of the crystallites are not restored again. This has already been seen in Eloflux electrodes, when forced flow-through of electrolyte was performed in the beginning of recharge, and the acid concentration was artificially kept low [12]. The survived connections are sufficient to recharge the active material again to PbO_2 , as the charging current is

one to three orders of magnitude lower than the discharging current; however, they fail to carry the high current during discharge more and more.

After several cycles under these conditions, the situation becomes aggravated: the regions in some distance from the current collector are electronically badly connected. These regions (with high contribution to capacity in the intact electrode, as the electrolyte support is best here) scarcely take part in the discharge reaction, although fully charged. Concentration of the discharge reaction near to the current collector means extremely inhomogeneous active material utilization, and as a consequence the capacity is reduced.

However, with a rest period inserted prior to recharge, internal equilibration currents have time to flow. The solubility of Pb^{2+} ions is increased in diluted acid (cf. beneficial effect of the washing/drying procedure [11–13]!). Deposition of PbO_2 at the connection sites (which have a lower equilibrium potential than the average electrode) and structural relaxation may take place. Before the start of recharge, acid from the separator has time to diffuse into the electrode's porous system. Due to this, recharge takes place in regions of electrolyte with higher concentration, which seems to restore a more favourable PbO_2 structure. This is in good agreement with experiments with forced flow-through electrodes: the capacity could kept high when the electrolyte was not forced through the electrodes during the initial part of recharge [12]. Mass conductivity is improved again. The regions far away from the current collector are electronically connected again. As they can take part in the discharge reaction again, active material utilization is more homogeneous, and capacity is recovered.

The capacity recovery by moderate-rate discharges (here about 5 h rate) is working via a different mechanism: as the electronic mass conductivity is not so important at this rate, even the mass regions weakly connected to the current collector are discharged, at least in part. Discharge at moderate rate, i.e., low discharge polarisation, is preserving the connection sites. Weakened and destroyed sites are recovered, as PbO_2 can be deposited there even during discharge, since the electrode potential is still above the (low) connection site equilibrium potential. All this improves capacity step by step during successive cycles under those conditions.

In extreme case, i.e., when discharge is performed with extreme low currents (about 100 h rate), the capacity is already recovered within one or two cycles, as has been shown already with different electrode types [11, 13].

The interpretation of the disintegration and reconstruction of the connecting network of PbO_2 crystallites is simplified by the cylindrical geometry of the thin tubular electrodes of the cells used in these experiments. They can be treated as an electrode with only one (radial) dimension like the Planté electrode, with regions near to the current collector and far from the electrolyte on the one hand, and regions far from the current collector, in proximity to the electrolyte on the other hand. In the case of pasted electrodes with grid-shaped current collectors, the effects of vicinity and distance to current collector and electrolyte will superimpose each other in a more complicated way.

Conclusion

The experiments show, that the 'reversible capacity decay' or 'reversible insufficient mass utilization'(RIMU) can be induced not only by unfavourable conditions of recharge (low-initial recharge current density, extensive overcharge) of the positive electrode, but also by certain conditions of discharge. Discharge at high rates may prejudice or

even disintegrate the connection sites of the PbO_2 crystallites and, consequently, locally reduce the intrinsic electronic conductivity of the positive active mass. Therefore regions far from the current collector are less and less involved in the discharge reaction, despite the fact that they are fully charged, and capacity decreases.

The RIMU at consecutive high-rate cycles is avoided by OCV rest periods before the start of recharge. It is recovered by full cycles at moderate discharge rates. Periods at low charging voltages, after recharge has been completed, seem to be favourable, too.

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