

Phosphoric acid as an electrolyte additive for lead/acid batteries in electric-vehicle applications

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Abstract

The influence of the addition of phosphoric acid to the electrolyte on the performance of gelled lead/acid electric-vehicle batteries is investigated. This additive reduces the reversible capacity decay of the positive electrode significantly which is observed upon extended cycling when recharge of the battery is performed at low initial rate. This is important when low-rate on-board chargers are used. Pulsed discharge, typical for electric-vehicle application, induces reversible capacity decay more than constant-current discharge at a same depth-of-discharge, as well with as without the addition of phosphoric acid. By contrast, hindrance in presence of H_3PO_4 for both the recharge and the discharge reaction helps to homogenize the state of many individual cells during cycling in long battery strings. Reversible capacity loss, which occurs after extended cycling and when pulsed discharge is applied, can be recovered by a single discharge at very low rate with batteries with and without the addition of phosphoric acid. The discharge-rate dependency of the capacity is significantly reduced when phosphoric acid is added. The pulse discharge behaviour may be better, even if the nominal capacity is reduced. The experimental findings of the influence of phosphoric acid addition is discussed in terms of the aggregate-of-spheres model of reversible capacity decay. © 1997 Published by Elsevier Science S.A.

Keywords: Lead/acid batteries; Phosphoric acid addition; Electric vehicles; Reversible capacity decay; Capacity recovery; Premature capacity loss; Antimony-free effect

1. Introduction

Changes in the structure of the positive active material (PbO_2) of lead/acid batteries on cycling induce changes in the performance of the positive electrode, and may limit cycle life. This is one of the main problems with the application of lead/acid batteries in electric road vehicles (EVs). The type and degree of these changes in the PbO_2 material depend, besides cell-design parameters such as electrode thickness, mass porosity, electrolyte concentration, grid alloy, etc., on the operating conditions of the battery. High-rate discharge, which is typical for EV duty, and low recharge rates, which are typical for on-board chargers with low power, have been shown to reduce capacity, and are rather unfavourable with respect to cycle life; on the other hand, rest times may be favourable [1–8]. Modern EV batteries have design properties that are expected to make them prone to the influence of the recharge

current: thin plates for good high-rate properties, high active material utilization for good specific energy, and low-antimony or antimony-free positive grids for low water loss. By contrast, immobilized and starved electrolyte designs may reduce the problem [3].

Several changes within a battery may induce performance losses during extended duty. In this paper, only changes in the positive electrode active material are discussed. Other degradation mechanisms, i.e., water loss, changes in negative active material structure, corrosion of current collectors, shorting, etc., are not considered.

Attention has focused on two critical sites of the positive electrode where processes that induce capacity decay on cycling may be located and which may limit cycle life. These sites are the following:

(i) Chemical or structural changes at the grid/active material interface are believed to be the origin of capacity loss phenomena, leading to increased ohmic drop in that zone ('barrier-layer' theory). The poor electronic conductivity of this region may lead to a poor accessibility of the active material within the pellet. Conductivity and struc-

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tural properties may be influenced by dopants such as Sn, Sb, Ag, As, etc., or by the ratio of grid/mass interface area to active material, see Refs. [9–20] for details.

(ii) Different cycling conditions may modify the properties of the positive active material. It has been found that cycling under ‘unfavourable’ operating conditions, i.e., low initial recharge current, overcharge of already fully charged cells, high discharge-current rates, etc., may result in capacity decay [1–5]. This capacity decay can be prevented or even reversed, however, by switching over to cycling with higher initial recharge current. The term ‘reversible insufficient mass utilization’ (RIMU) [1,21,22] is used to describe these experimental findings; it is a characteristic feature of the positive PbO_2 electrode, and depends only slightly on electrode design [3].

The presence of antimony reduces capacity fading significantly, and influences both the grid/mass interface and the active material properties [23–26]. This behaviour became known as the ‘antimony-free effect’ (AFE).

The ‘barrier-layer’ theory argues that healthy active material areas, or even whole pellets, become more and more poorly connected to the current-collecting grid, and, hence, induce capacity loss. Cracks due to mechanical stress in the corrosion zone of the grid, as well as poorly conductive lead(II) oxide phases, have been suggested as possible reasons for separating the active material from the grid. Changes in the active material structure itself, apart from that in the grid/mass interface region are believed to be of minor importance. It should be noted, however, that the compounds which are believed to impede current flow have been found to be present already just after formation [27], which does not allow the loss of capacity to be explained in terms of the generation of these compounds. Furthermore, it has been shown that it is the resistance of the active material rather than that of the grid/mass interface which correlates with capacity loss [2,28]. If the grid/active material interface is indeed the limiting site for mass utilization and cycle life, increasing the area of this interface is a promising strategy to reduce this adverse behaviour [29,30]. No explanation has been given, however, for the capacity recovery effects in terms of the barrier-layer theory.

The RIMU concept, on the other hand, regards such localized changes in the grid/mass-interface zone not as the cause but rather the effect of preceding changes in the active mass structure of the whole pellet [31]. These changes of the active mass depend on the operating conditions, and can be reversed. The main experimental findings of the RIMU effect of the PbO_2 electrode are as follows:

1. There is no lack of recharge; chemical analysis shows a full state-of-charge of PbO_2 .
2. Extra overcharge does not improve, but may aggravate the situation [1,3]. Increasing capacity loss with increasing overcharge is reported also from another laboratory [32].
3. Recharge with low initial current density may induce

successive capacity loss, while there is less or even no capacity decay, when recharge is performed at higher initial recharge rate [1,3,5].

4. An existing capacity decay due to the recharge effect in (3) can be reversed by switching to a recharge regime with higher initial recharge current [1,3,25,33].
5. Discharge at high rates promotes capacity loss, which may be recovered again when cycling is continued with low-rate, deep-discharges [4].
6. Recovery of lost capacity is possible by switching to cycling under more favourable conditions (which provide permanent operation at high capacity level [1,2,4,21]), i.e., by deep-discharge at very low rates [1,3], by special treatments of the electrode (e.g., washing free of acid and drying [1–3,25], especially at elevated temperature), or currentless rest times [4,25].

Further experimental findings and details are given in Refs. [1–5,21,33–38] and summarized in an Appendix to Ref. [29].

The ‘Kugelhaufen’ (aggregate-of-spheres, AOS) model, based on the behaviour of sintered bodies [39], describes semi-quantitatively the phenomena at the connecting sites of the particles of the PbO_2 active material, and, thereby, explains the experimental findings of RIMU [1,21,22,40,41]. Unfavourable cycling conditions may successively induce a porous PbO_2 structure with poor mechanical and electrical connection between the particles that comprise the porous electrode. Increasing active material resistance of this skeleton will induce a more and more inhomogeneous current distribution over the active mass, with successive constriction of the discharge/recharge processes to the active material area near to the grid, as has been found in electrodes [42]. This means excessive mass utilization in the region, which aggravates the situation from cycle to cycle and leads to premature ageing of the mass in the vicinity of the grid. Unusual chemical compounds and/or structures with poor conductivity may be formed. The best known phenomenon is active material softening.

The dependency of the actual capacity of a lead/acid battery positive electrode on its cycling history was first described in the last century [43,44]. Some information about previous operation seems to be stored in the ‘memory’ of the positive electrode (i.e., a ‘memory effect’, see literature cited in Ref. [34]). The Kugelhaufen model attributes these findings to structural changes of the active material. These changes can be (at least partially) reversed again, i.e., a ‘re-set’ is given to the electrode ‘memory’. While other models of PCL phenomena are still on an intuitive level, the Kugelhaufen model is a semi-quantitative approach that describes all known effects including capacity recovery.

Some other concepts have been advanced to explain the successive capacity loss of the PbO_2 electrode. The ‘hydrogen loss’ model is no longer under discussion [45]. More recently, the ‘gel model’ has been developed; it

proposes the co-existence of crystal and amorphous (hydrated gel-like) areas of PbO_2 , the ratio of which is influenced by chemical additives (alloy compounds) [15,46–51]. Very recently, the influence of external pressure on the PbO_2 active material, which has been demonstrated formerly under different conditions [42,52–56], has attracted attention again [57]. Different experimental findings of capacity decay are usually summarized by the term ‘premature capacity loss’ (PCL) [20] and reviewed in Ref. [58]. It should be noted, however, that the experimental fact of capacity recovery, identified by the term RIMU, is not covered by the term PCL.

In battery duty, the discharge depends on the application and can hardly be adapted to the requirements of the battery. It is important to determine, however, the impact of different discharge conditions on the overall behaviour of the battery. In EV application, discharge is not performed with constant current or power, but it depends on the actual traffic condition and on the driver. Several standardized pulse discharge tests have been introduced to simulate these operating conditions.

The recharge regime is much more open to optimization, and allows some opportunities to extend cycle life. Goals have been to investigate the impact of different recharge and discharge conditions on both the active material utilization and the cycle life of the PbO_2 positive plate, to study improvements that may be achieved by the addition of phosphoric acid to the electrolyte, and to achieve some insight into the mechanism of phosphoric acid addition. Furthermore, recovery of lost discharge capacity as one of the major features of reversible capacity loss by special ‘treatments’ within limited time periods gives additional perspectives.

2. Phosphoric acid

The addition of phosphoric acid to the electrolyte of lead/acid batteries has been practised since the 1920s [59]. The main motivations were reduction of sulfation (especially in the deep-discharge state) and extension of cycle life by reduced shedding of positive active material. For these benefits, some reduction in capacity was accepted.

The influence of phosphoric acid in the electrolyte is found to be manifold. The most important effects are as follows:

- phosphate is incorporated in the PbO_2 structure [60–63] and released during discharge to become incorporated in the corrosion layer [24,61]
- reduction of sulfation on stand after deep-discharge
- reduction of lead corrosion [64,65], but not at the potential of minimum corrosion [66]
- reduction of self-discharge kinetics [61,64,65], but only when H_3PO_4 is present at PbO_2 formation [61]
- increase of the positive electrode equilibrium potential [61,62]
- reduction of the positive electrode shedding rate [20,62]
- increase of the cycle life of the positive electrodes, e.g., [20,62,63]
- reduction of the capacity of the positive electrodes, e.g., [67]
- promotion of formation of $\alpha\text{-PbO}_2$ [68,69]
- impedance of the anodic PbO_2 formation [60,62,67,70,71]
- impedance of the discharge reaction [70], but only when H_3PO_4 is present at PbO_2 formation [65]
- precipitation of PbSO_4 in finer crystals [72]
- prevention of the formation of the PbSO_4 ‘barrier’ layers on Pb–Ca grids [20,62,63]
- more homogeneous formation of PbSO_4 over the PbO_2 material pellet, improving cycling behaviour and reducing shedding [20,62,63]
- remedy for early capacity degradation of cells with Sb-free positive grid alloy [23]
- change of PbO_2 morphology [61,64]
- application of phosphoric acid in gelled-electrolyte cells is successful [73]
- increase of the hydrogen overvoltage [74]
- increase of the oxygen overvoltage [70,75]
- increase of the solubility of Pb(IV) ions [60], which may increase mousing and induce some risk of short circuits due to dendrite formation, especially at lower temperatures
- possible oxidation of organic materials such as separators and expanders by Pb(IV) species, some described in Refs. [66,76]

The most critical parameter of H_3PO_4 application is its dosage. Improper distribution, etc., may be the origin of disastrous performance which has been occasionally found, but scarcely published. As one of the major perspectives of phosphoric acid addition is cycle life, it is valuable to quantify its effects under EV operation conditions. The influence of H_3PO_4 on the RIMU effect with Planté electrodes has already been described [33].

3. Experimental

3.1. Test specimen and equipment

Investigations on the influence on cycling performance of different operating regimes were performed with EV monoblock batteries and with single cells of the same cell design. A comparison was made of batteries and cells, with and without phosphoric acid addition to the electrolyte. The cell design comprised pasted plates with a positive-grid alloy of Pb–0.07wt.%Ca–0.3wt.%Sn and a negative-grid alloy of Pb–0.1wt.%Ca. The positive-plate material was produced from Barton pot oxide and cured via the tribasic lead sulfate route. After curing, the plates were tank-formed. One variant of the gelled electrolyte contained about 30 g l^{-1} of phosphoric acid as an addi-

Table 1
Constant-current (CC) recharge schemes

	4 I 95	4 I 36	4 I 25	4 I 15	Termination criterion
Step 1: constant current (A)	95	36	25	15	until 2.40 V per cell
Step 2: constant current (A)	18	18	12	8	until 2.40 V per cell
Step 3: constant current (A)	4	4	4	4	until 2.40 V per cell
Step 4: constant current (A)	4	4	4	4	no voltage limit, 1 h
Total duration of recharge (h)	7	8–9	9	11	

tive. The cells showed a nominal capacity of about 160 Ah at the 5 h rate.

3.2. Full cycling with different recharge regimes

Battery strings, with and without H_3PO_4 additive, that each consisted of 12 cells, performed continuous full cycle tests (100% depth-of-discharge, DOD) with discharge always at the 1 h rate (120 A) down to 1.69 V/cell. Several different constant-current (CC) and constant-current/constant-voltage (CC/CV) schemes were compared. CC recharge was performed according to a regime developed in the author's laboratory [77]. The applied recharge regime comprises four CC steps, the first three are voltage limited. When the voltage limit is reached, the following step with reduced current is started immediately. The fourth step is time-limited without voltage limitation. The CC recharge schemes are listed in Table 1. In addition to simple CV recharge schemes, some modified schemes comprising a third CV step were tested. Table 2 gives the CV recharge schemes tested.

3.3. Pulsed-discharge test according to the RWE scheme

High-rate discharges appear to stress the battery much more than discharges with moderate discharge currents [6–8] (for an extreme example for the adverse effect of high-rate discharge, see Ref. [4]). EV duty consists of a complex mixture of discharge pulses at different rates. For comparison under laboratory conditions, duty cycles are simulated by schemes that consist of repeating phases with a special pulse pattern. These include: the 'Simplified Federal Urban Driving Schedule' (SFUDS) developed in the USA, the ECE-15 scheme used in Europe, and the 24 h test of the German public power utility company, RWE.

The RWE test scheme simulates an operating day with

three driving (discharge) periods. During each of these 34 min driving periods (each incorporating two different discharge rates, regenerative braking, and a short rest period), 50 Ah is discharged at an average discharge current of ~ 88 A. The first driving period is followed by a rest period of 30 min, and another identical driving period. Then a recharge period of 5 h is applied to simulate an opportunity charge during the day-time. As the recharge current in the standard version of the RWE test is limited to only 15 A (similar to a simple on-board charger), 75 Ah are recharged without reaching the voltage limit of 2.40 V/cell. After this opportunity charge, a third pulse discharge period is performed. The rest of the day and the night is used for complete recharge ('I 15 U').

The RWE pulse-discharge cycle scheme is summarized in Table 3. Each pulse discharge period consists of 34 equal pulse periods of 1 min each as shown in Table 4; 1.472 Ah are discharged during one of this 1 min pulse periods. During the whole discharge period, 34×1.472 Ah = ~ 50.0 Ah are discharged.

3.4. Full cycles with half-cell potential investigations

For each of the variants, with and without phosphoric acid addition, a battery of 6 single cells in series was tested completely and independently. The single cells were free standing and well separated in a temperature-controlled water bath (26 °C). To avoid expansion of the cell containers, the cells were fixed in a clamp holder. All cells were equipped with Hg/Hg₂SO₄ reference electrodes.

For the investigation of the influence of different recharge schemes, the batteries performed full cycles with 100 A discharge current (end-of-discharge voltage 1.69 V/cell in average), i.e., about the 1.5 h rate. For recharge, schemes with different initial recharge currents were compared, and also CC and CV schemes with the

Table 2
Constant-current/constant-voltage (CC/CV) recharge schemes

	I 36 U	I 36 UU	I 36 UU'	I 25 U	I 25 UU'	I 15 U	I 15 U*	Termination criterion
Step 1: constant current (A)	36	36	36	25	25	15	15	to voltage limit
Step 2: constant voltage (V)	2.37	2.40	2.37	2.40	2.37	2.40	2.43	duration: see below
Step 3: constant voltage (V)		2.52	3.6 A/2.49 V		3.6A/2.49V			for 1 h
Total duration of recharge (h)	10	12	11	11	11	17	12/17	

Table 3
RWE pulsed-discharge cycle scheme (for $C_5 = 160$ Ah battery)

Period of pulse cycling test	Ah balance
(a) Series of 34 pulse cycles of 1 min duration each; see below, Table 4	-50
(b) Rest time ($I = 0$) of 30 min	0
(c) Series of 34 pulse cycles of 1 min duration each; same as (a)	-50
(d) Recharge with 15 A for 5 h (upper voltage limit not reached)	+75
(e) Series of 34 pulse cycles of 1 min duration each; same as (a)	-50
(f) Recharge with 15 A/voltage limit 2.40 V/17 h = 'I 15 U'	> +75

same initial recharge current were applied, to study separately the influence of initial recharge current as well as to compare CC and CV recharge.

3.5. Recovery of capacity lost due to reversible capacity decay

These experiments were performed with the batteries with phosphoric acid addition. The batteries were continuously operated with discharge with 100 A to 1.67 V/cell and recharge according the '4 I 26' scheme.

4. Results

4.1. Full cycling with different recharge regimes

The capacities of the two battery variants performing this full cycle test are shown in Figs. 1 and 2, respectively. The types of charging regime that were applied are indicated. Obviously, changes of the recharge schemes induced immediate changes of the capacity in the case of the battery without H_3PO_4 additive. After some cycles at the same regime, a (more or less stable) capacity level was reached and appears to be representative of the actual charging regime.

Also with cells containing phosphoric acid, changes in the recharge schemes induced immediate (but minor) changes in the capacity (Fig. 2). During the first 50 cycles, however, a marked capacity increase is superimposed on these recharge influences. Therefore, a (more or less sta-

ble) capacity level, representative of the actual charging regime, cannot be seen in this part of the experiment, as was the case for cells free of phosphoric acid.

The relative change in capacity due to changes of the recharge schemes is only some per cent at maximum, i.e., much less than in the case of the H_3PO_4 -free cells. This is also true when CV and CC recharge schemes with the same initial recharge current are compared, and when schemes with different initial recharge currents are compared. Even if there is some indication that the capacity level is generally poorer with a CC/CV recharge scheme than with a CC regime, this is not (as) significant as it is in case of batteries free of H_3PO_4 .

4.2. Pulsed-discharge test according to the RWE scheme

The RWE pulsed-discharge endurance test was performed with two 6 V monoblocks in series. Fig. 3 shows the capacity of the batteries without H_3PO_4 on discharge at 120 A (to 1.69 V) during initial full cycles and at periodic capacity tests under these conditions after groups of pulsed-discharge cycles.

Prior to pulse testing, full cycling (100% DOD) at the 1 h discharge rate (120 A to 1.69 V) was performed. In the beginning the '4 I 36' recharge scheme was applied, but was changed later to the RWE standard recharge scheme 'I 15 U'. This change induced a continuous capacity reduction, which is in accordance with the previous experience (reduced recharge current plus CV instead of CC). After about 110 full cycles at 120 A, the operation was changed, and several series of pulsed-discharge cycles according to RWE were performed.

Table 4
Pulsed discharge period according to RWE (for $C_5 = 160$ Ah battery)

Period	Current ('-' indicates discharge) (A)	Duration(s)	Ah Balance
Discharge	-280	10	-0.778
Discharge	-100	30	-0.833
Recharge	+100	5	+0.139
Rest time		15	0
Total		60	-1.472

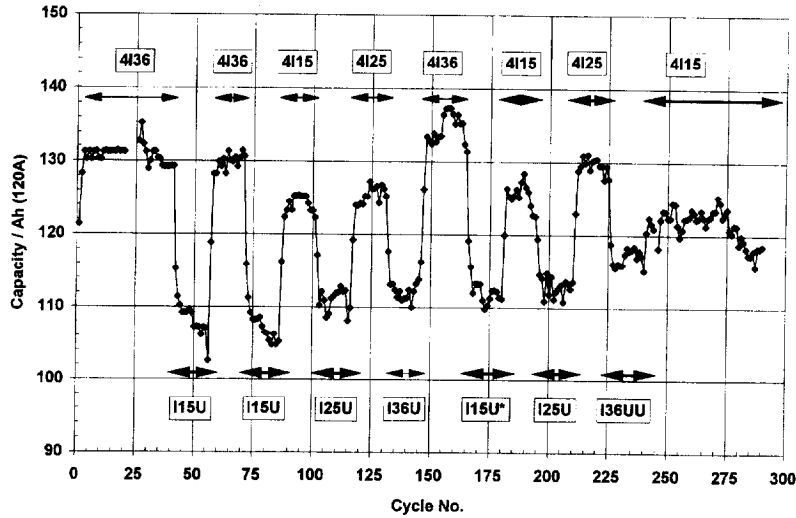


Fig. 1. Capacity during full cycling test, different recharge schemes, cells without H_3PO_4 .

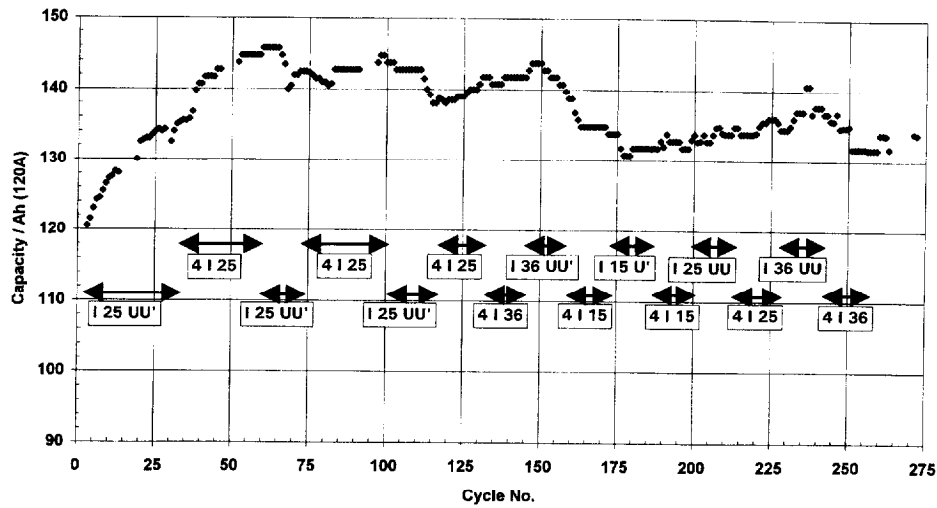


Fig. 2. Capacity during full cycling test, different recharge schemes, cells with H_3PO_4 .

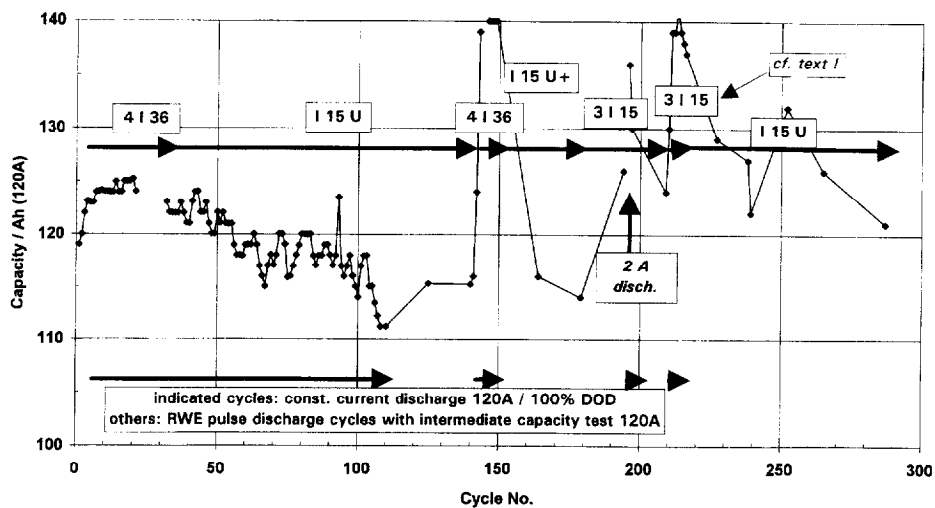


Fig. 3. Pulse cycling test according to RWE, different recharge schemes, cells without H_3PO_4 .

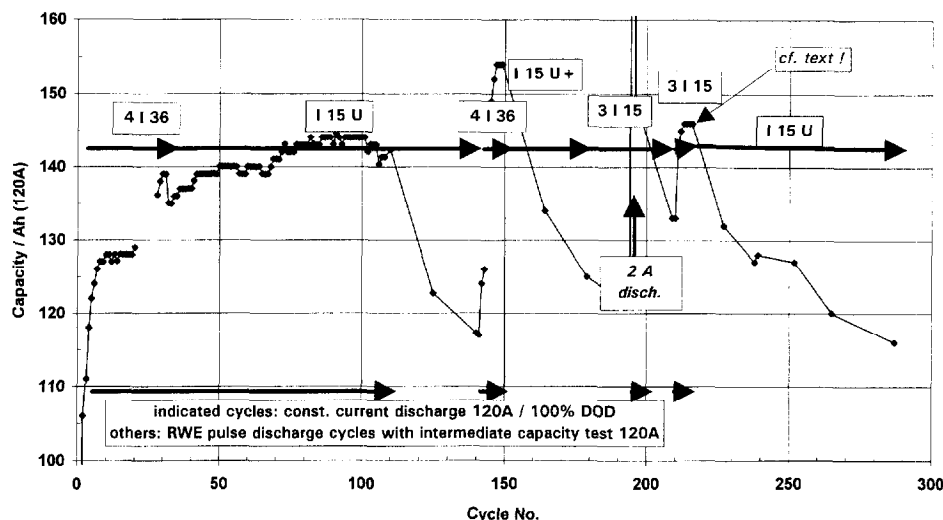


Fig. 4. Pulse cycling test according to RWE, different recharge schemes, cells with H_3PO_4 .

A capacity test after about 30 pulse cycles (cycle no. 140) showed about 115 Ah. This capacity level, similar to that at the end of the full cycle test at cycle no. 110, seems to be representative for the standard RWE testing scheme (including recharge 'I 15 U'). This does not show the capacity that the battery is principally able to give. In cycles nos. 141 to 148, full cycles instead of pulsed discharges were performed. The recharge scheme was switched to '4 I 36' and this resulted in a marked increase in capacity to a level of about 140 Ah. This level could not be maintained when the test was switched back to pulsed discharges, despite the fact that the recharge scheme 'I 15 U' with higher voltage was applied.

Change of recharge scheme to '3 I 15'¹ at cycle no. 179 improved the capacity to about 126 Ah after 15 pulsed-discharge cycles, which is significantly better than with 'I 15 U' and 'I 15 U*', but still less than the level obtained during full cycles at 120 A discharge (nos. 141 to 148).

This indicates that the reduced capacity level after several pulsed-discharge cycles is a reversible capacity decay phenomenon. To prove this, a 100% DOD discharge was performed with a very low current (2 A) in cycle no. 195, yielding 213 Ah. This procedure of discharge with a very low discharge rate has been found to recover a capacity loss due to the RIMU [1,3]. Indeed, a high capacity of ~136 Ah was obtained on subsequent discharge at 120 A. This high capacity level was lost again on the following series of pulsed-discharge cycles; ~125 Ah were obtained again in cycle no. 209.

A capacity level of about 125 Ah appears to be characteristic for the pulsed discharges, when the recharge scheme '3 I 15' is applied, and is approached when cycling is

started at another capacity level: it increases when the capacity was lower before (e.g., in cycle no. 178), and it decreases when the capacity is higher before (cycle no. 197). The capacity level at '3 I 15' recharge is significantly higher than the 115 Ah level achieved with the standard RWE recharge scheme 'I 15 U' (cycles nos. 110 to 140).

In cycles nos. 208 to 215, full cycles (120 A) were performed with recharge according to '4 I 15', but with increased duration (2 h instead of 1 h) of the last step. This procedure induces a rapid rise in capacity. Nevertheless, the high capacity level is lost again on subsequent pulsed discharges.

The batteries containing H_3PO_4 were cycled in the same manner as the untreated samples. The capacity on discharge at 120 A (to 1.69 V) during initial full cycles and at periodic capacity tests under these conditions after groups of pulse cycles are shown in Fig. 4. After some 20 full cycles with the '4 I 36' recharge scheme, several discharges at different rates were performed (not shown in Fig. 4). A significant capacity increase was observed (similar to that in Fig. 2), which was not found with the batteries that contain no H_3PO_4 (cf., Fig. 3). At cycle no. 31, recharge was changed to the 'I 15 U' scheme. While this change of the recharge scheme had induced a successive capacity reduction with batteries without H_3PO_4 (cf., Fig. 3), the capacity continued to increase very slowly with batteries with the additive, probably due to a successive increase in the positive-material porosity during cycling. There is no indication of lack of recharge with the 'I 15 U' regime — a completely different behaviour compared with the H_3PO_4 -free batteries.

Pulsed-discharge tests with the 'I 15 U' scheme were started after some 110 cycles, as with the cells containing no H_3PO_4 . The capacity level of ~145 Ah, reached at the end of the full cycle test at cycle no. 110, seems to be typical for the standard RWE testing scheme (which includes 'I 15 U' recharge) in the case of batteries that contain H_3PO_4 . This is much better 20–25% than with

¹ Recharge scheme '3 I 15' is identical to '4 I 15', but recharge step 2 is skipped. This simplified scheme was used here due to equipment restrictions.

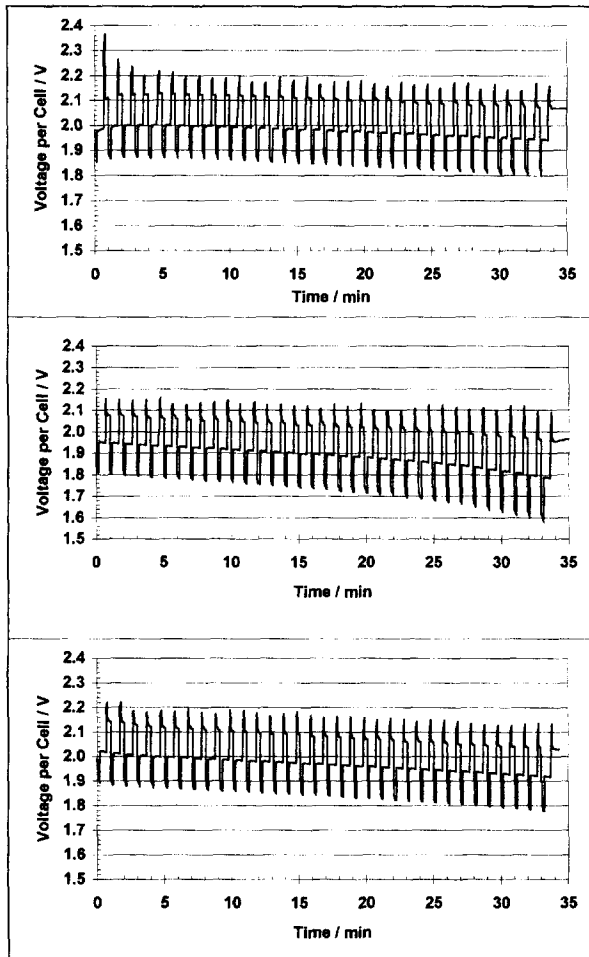


Fig. 5. Pulsed-discharge test according to RWE, cycle no. 120, cells without H_3PO_4 . Voltage per cell during 1st, 2nd, and 3rd pulsed-discharge period.

batteries that contain no additive under the same operating conditions (cf. Fig. 3). This capacity level was immediately lost when the discharge regime was switched to pulses instead of constant currents, i.e., when capacity tests were performed in cycles nos. 125 and 140, a much lower capacity was found. At cycle no. 140, i.e., after 30 pulsed-discharge cycles according to RWE, the capacity was very similar to that of the battery containing no H_3PO_4 (~ 115 Ah). Again, this does not show the capacity that the battery is principally able to deliver. As in the case of the batteries containing no H_3PO_4 , some full cycle tests instead of pulsed discharges were performed during cycles nos. 141 to 148. The recharge scheme was switched to '4 I 36', and, in the same manner as with the battery containing no H_3PO_4 , a marked and continuous increase in capacity was observed to a level of over 150 Ah (cf., Fig. 4). From the better behaviour of batteries with H_3PO_4 in the electrolyte during the initial 110 full cycles with recharge scheme 'I 15 U' (cf., Figs. 1 and 3), and from the minor influence of the initial recharge current density on capacity when H_3PO_4 is present (v.s.), it is concluded that

this capacity recovery would also have taken place if during the full cycles nos. 140 to 148 the 'I 15 U' recharge scheme had been applied instead of the '4 I 36' schedule.

Again, as for batteries without H_3PO_4 , this capacity level of ~ 150 Ah, reached after some cycles with CC discharge, could not be maintained when cycling was switched back to pulsed discharge, despite the fact that the recharge scheme 'I 15 U*' with higher voltage was applied. Moreover, a change of recharge scheme to '3 I 15' at cycle no. 179 did not influence capacity markedly as was the case with H_3PO_4 -free batteries (Fig. 3): there is no significant superior behaviour with CC schemes with cells with this additive.

In cycle no. 195, a 100% DOD discharge was performed with a very low current (2 A), yielding 228 Ah, and recovered the capacity loss due to the RIMU as with the H_3PO_4 -free battery. Indeed, again a high capacity of ~ 147 Ah was obtained on subsequent discharge at 120 A. This level was lost again, however, on the following set of pulsed-discharge cycles; again ~ 133 Ah were obtained in cycle no. 209. This is only little better than with the

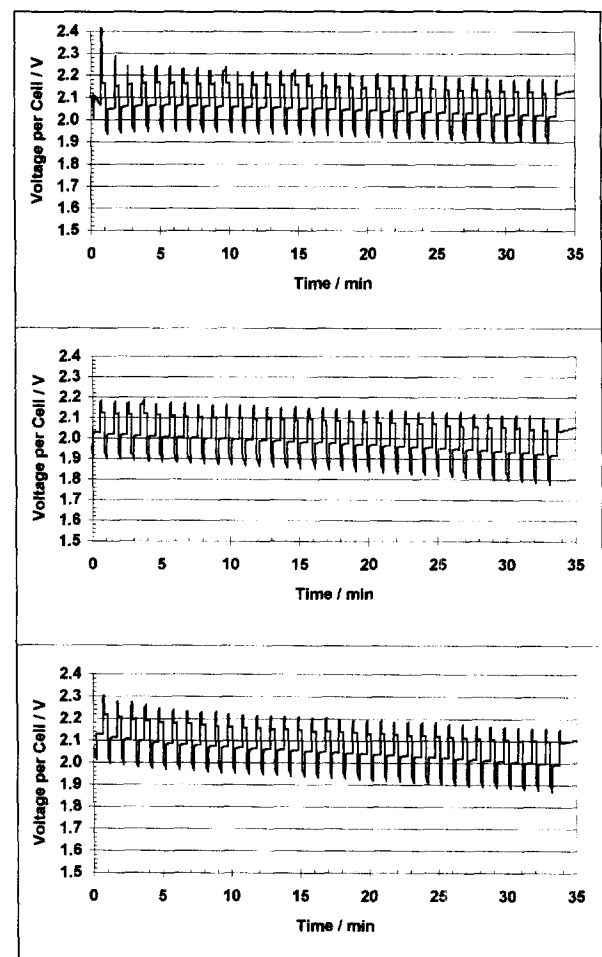


Fig. 6. Pulsed-discharge test according to RWE, cycle no. 120, cells with H_3PO_4 . Voltage per cell during 1st, 2nd, and 3rd pulsed-discharge period.

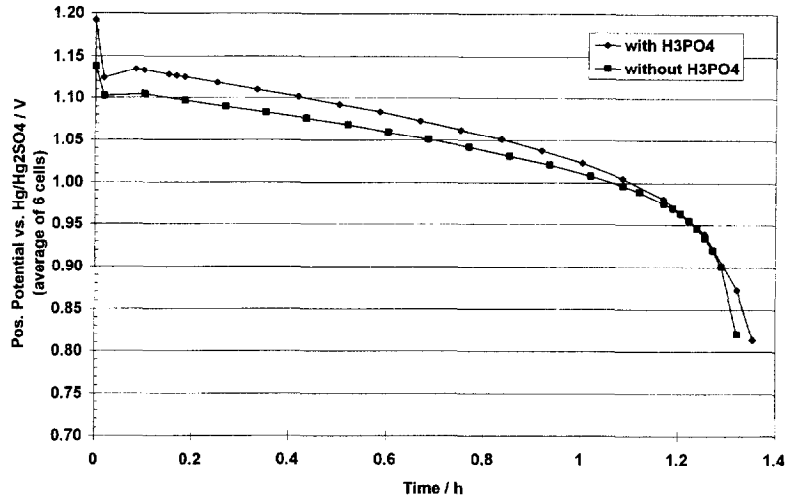


Fig. 7. Average positive potential of six single cells with and without H_3PO_4 , during discharge at 100 A on cycle no. 56.

battery without phosphoric acid. A capacity level of about 125 Ah appears to be characteristic for pulsed discharges of batteries with phosphoric acid additive, i.e., when the recharge schemes '1 15 U' or '3 I 15' are applied. This capacity level is similar to that achieved with batteries without phosphoric acid additive with the more effective '3 I 15' scheme. In cycles nos. 208 to 215, full cycles (120 A) were performed with recharge according to '4 I 15' with increased duration (2 h instead of 1 h) of the last step. The latter induced a rapid rise in capacity. The high capacity level is lost once again, however, on subsequent pulsed discharges.

The voltages during the three pulsed-discharge periods of cycle no. 120 are shown as an example for the two sets of batteries in Figs. 5 and 6. At end of the second pulsed-discharge period, 100 Ah are discharged from the battery (state-of-charge = $\sim 17\%$ of 1 h rate capacity). This is the most critical stage of the whole test, as the battery has to provide a discharge pulse of 280 A at this

low state-of-charge. When the data in Figs. 5 and 6 are compared, it is obvious that the cell voltage under pulse load is higher and the voltage drop at the beginning of a pulse is less with the batteries containing H_3PO_4 .

4.3. Influence of phosphoric acid additive on positive half-cell potentials

On permanent full cycling with recharge schemes '4 I 15', '1 15 U', '4 I 36', '1 36 U', '4 I 95', '1 95 U', a behaviour similar to that for the monoblock batteries (Figs. 1 and 2) was obtained with groups of single cells (for details see Ref. [38]). Monitoring of half-cell potentials during cycling of the single cells provides considerable insight into the different behaviour of cells with and without phosphoric acid electrolyte.

The differences of the positive potentials of the two cell variants during discharge and recharge ('4 I 36') on cycle no. 56 are given as examples in Figs. 7 and 8. In both

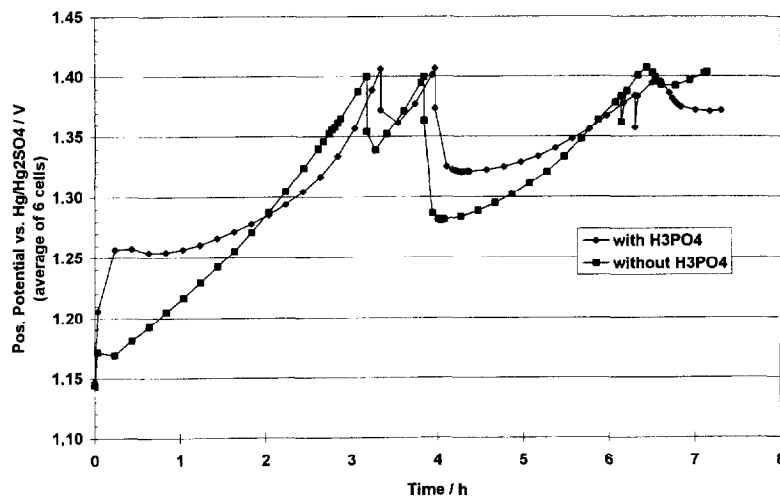


Fig. 8. Average positive potential of six single cells with and without H_3PO_4 , during recharge according to scheme '4 I 36' on cycle no. 56.

cases, average data for six cells of the same type are shown. On discharge, the positive potential of the cells with H_3PO_4 additive is initially about 30 mV higher than that of the undoped cells. This corresponds to the well-known, higher positive open-circuit potential with this additive [61,62]. As there is little influence of H_3PO_4 on the negative half-cell potential on discharge, addition of phosphoric acid gives a higher cell voltage during a long period of recharge. During the course of discharge, however, the positive-potential curve is more steep with H_3PO_4 such that the difference is reduced more and more, and after 1.3 h of discharge, the two curves come together. At the very end-of-discharge, the characteristics of the two types of battery differ significantly. The curvature of the positive potential of the cells without H_3PO_4 is much more pronounced, and the potential falls more rapidly. For the cells with phosphoric acid, this decrease in potential is much more gradual, despite the fact that the curve had initially been steeper.

On recharge, the situation of the two batteries also differs significantly. Just after the start of recharge, the positive potential of the cells containing phosphoric acid polarizes by about 80 mV more than that of the cells free of H_3PO_4 . There is then a period of little further increase in positive potential, while the H_3PO_4 -free cells show a continuous increase. When the cell voltage reaches 2.40 V/cell on average, and the first recharge step (36 A) is switched to the second step at 18 A, the positive potential is about 1.40 V in both cases. During the second and most time of the third recharge step, the positive potential is higher with the cells containing H_3PO_4 when the same recharge current is applied. By contrast, at the end of the third current step at 4 A, and during the last step without voltage limitation at 4 A, the positive potential is lower for the battery with H_3PO_4 .

These two examples show that phosphoric acid inhibits both the discharge and the recharge reactions. In the case of recharge, this inhibition seems to be limited to the period when the positive potential is dominated by the recharge reaction. At the very end-of-recharge, the potential is largely determined by the oxygen-evolution reaction.

4.4. Changes in PbO_2 morphology induced by phosphoric acid

According to reports in the literature, cycling of the PbO_2 electrode in electrolyte containing phosphoric acid

leads to a finer pore structure with a smaller average pore diameter, and to an increased internal (BET) surface of the electrode [59,69,71,72]. In other words, after cycling in phosphoric acid electrolyte, the porous PbO_2 structure is composed of smaller PbO_2 crystal units. A change from a three-dimensional growth of PbO_2 with progressive nucleation to a two-dimensional growth with instantaneous nucleation is indicated [69]. This was confirmed by experiments with positive electrodes of the same type that were used above for the cycling experiments. For three different conditions (in the fully-charged state), namely:

1. after formation in electrolyte free of phosphoric acid, before any further cycling;
2. after 150 full cycles (5 h rate) in electrolyte without phosphoric acid, and
3. after 150 full cycles (5 h rate) in electrolyte with 35 g l^{-1} phosphoric acid,

the internal BET surface area and the porosity (mercury intrusion method) of the positive electrode were measured, and the apparent density, the average and the most frequent pore radius were determined. The results are summarized in Table 5.

A comparison of the electrode parameters obtained after cycling without and with phosphoric acid additive showed that:

1. the porosity/pore volume increases with both variants in the same manner; the apparent density is accordingly reduced;
2. the average pore radius is not changed after 150 cycles without phosphoric acid, but is reduced markedly with the additive;
3. the most frequent pore radius is reduced only slightly after cycling without phosphoric acid, but by more than a factor of five after 150 cycles with the additive, and
4. the BET surface area is increased by about 50% after 150 cycles without H_3PO_4 , but by a remarkable 700% when the additive is present in the electrolyte. (Note, this high value is not an artefact caused by SiO_2 of a gelled electrolyte, as this experiment was performed in liquid electrolyte.)

These data clearly demonstrate that significant changes occur in the positive material upon cycling in electrolyte containing phosphoric acid additive. These changes in the internal parameters of the PbO_2 electrode help to understand the reduced influence of initial recharge current density with batteries containing this electrolyte additive: the phosphoric acid induces a finer structure which is

Table 5
Physical data of pristine formed plates (without H_3PO_4) and after 150 cycles

Sample	Porosity (%)	Average pore radius (μm)	Most frequent pore radius (μm)	BET surface ($\text{m}^2 \text{g}^{-1}$)
After formation	49	0.4	0.5	3.5
150 cycles without H_3PO_4	61	0.4	0.4	5.1
150 cycles with H_3PO_4	61	0.15	0.09	25

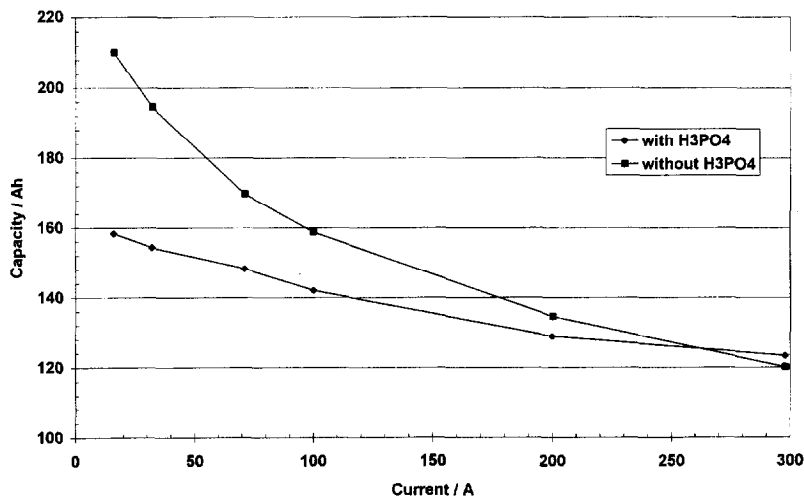


Fig. 9. Discharge capacity vs. discharge rate for single cells without and with H₃PO₄ additive.

known [40] to be beneficial for permanent cycling at a high level of active material utilization. If this additive is not present, a high initial recharge current density may act in a similar manner, i.e., by enhancing nucleation over crystal growth.

4.5. Changes of discharge-rate capability induced by phosphoric acid

Addition of phosphoric acid is claimed in the literature (e.g., [67]) to reduce discharge capacity. It should be noted, however, that all data reported were obtained at rather low discharge rates ($C/5$ and lower). When cycling capacities of identical batteries, but without and with phosphoric acid additive are compared, a somewhat higher capacity is found with the doped battery at about the 1 h rate (cf., Figs. 1 and 2). These results, although contradic-

tory at the first glance, can be explained if the addition of phosphoric acid to the electrolyte influences the rate capability, i.e., has a different influence on capacity at high and low discharge rate. To investigate this, the rate capabilities of the single cells used for the half-cell potential investigations were tested after they had performed some 200 cycles. The results are given in Fig. 9. It is obvious that the addition of phosphoric acid reduces the discharge-rate dependency of the capacity markedly. While at low rates the capacity is significantly reduced (confirming the 'experience' reported in literature), there is a cross-over at higher rates, and at very high rates, the battery with H₃PO₄ additive yields the higher capacity. The relatively better high-rate performance of cells with phosphoric acid is plausible due to the higher internal (BET) surface (v.s.). This agrees also with the superior behaviour that is observed with pulsed discharge (Figs. 5 and 6).

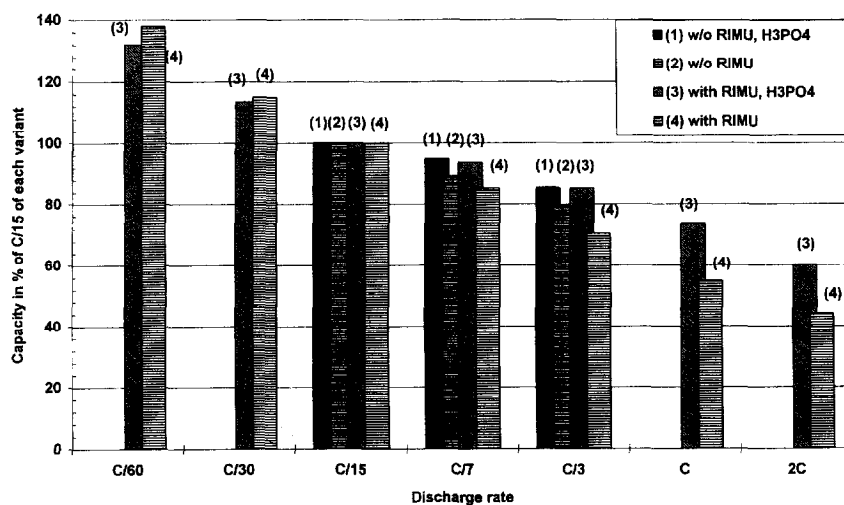


Fig. 10. Rate dependency of capacity, normalised to $C/15$, of four variants, data from Ref. [33].

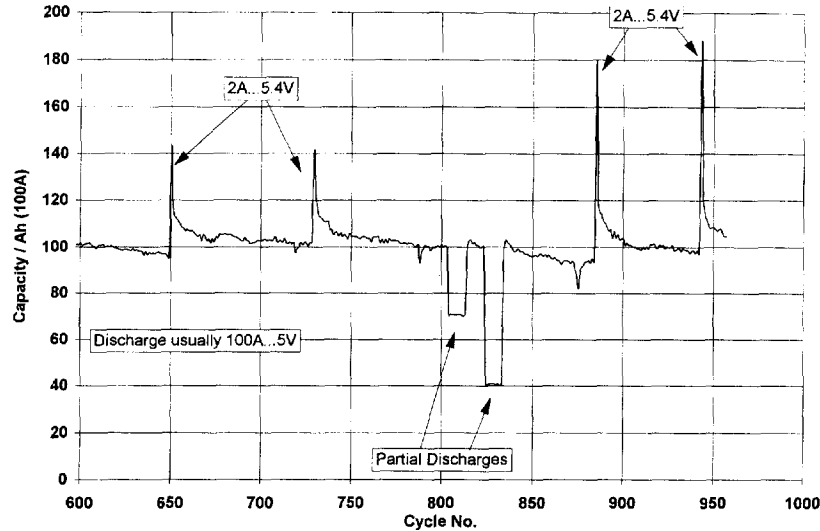


Fig. 11. Recovery of capacity lost on continuous cycling (RIMU) with low-rate discharge.

These results from EV traction batteries with pasted positive plates are supported by previous findings on the influence of phosphoric acid additive on the rate capability of Planté-type positive electrodes [33]. Furthermore, these data provide some conclusions on the sensitivity of the rate dependency on the presence of phosphoric acid in both the 'healthy' state of the electrode and when it suffers from 'RIMU'. Data for four batteries (with/without H_3PO_4 , and healthy/suffering from RIMU) are compared in Fig. 10. It can be deduced that the addition of phosphoric acid to the electrolyte reduces the rate dependency of capacity not only in the healthy state, but also when the electrode suffers from RIMU.

4.6. Recovery of capacity lost due to RIMU

When batteries had been continuously operated for 620 cycles with discharge at 100 A and recharge according to '4 I 26', the capacity had dropped just below 100 Ah. At cycle no. 650, a low-rate discharge at 2 A to 1.8 V/cell was performed. This treatment was tested already successfully when EV batteries suffered from RIMU due to pulsed-discharge cycling (Figs. 3 and 4). After this treatment, the capacity at 100 A increased by 27% from 95 to 121 Ah in the next cycle. When cycling with 100 A discharge was continued, the capacity decreased again successively, but was above the 100 Ah limit for about a further 75 cycles. The results are given in Fig. 11. At cycle no. 729, the low-rate discharge procedure was repeated, with the same beneficial result. Later, after an extended period of cycles with only partial discharge, the procedure was applied twice more. The increase in capacity (at

100 A) was always about 25% or more, but the durability of this recovery appears to be shortened more and more.

5. Discussion and summary

The actual capacity of gelled EV batteries depends very much on the history of operation, especially on the discharge and recharge rates. On permanent cycling, the capacity levels off at a value that is characteristic for the given cycling regime.

The results on the influence of the initial recharge current on actual capacity of EV batteries confirm qualitatively the previous findings. The degree of sensitiveness on the recharge scheme depends much on the other cycling conditions, e.g., pulsed-discharge versus CC discharge, CC versus CV recharge, and especially on the presence or absence of H_3PO_4 additive in the electrolyte.

5.1. Effect of initial recharge current density

When no phosphoric acid additive is used, the full cycle test (100% DOD, 1 h rate) indicates a dependency of the capacity level on the initial recharge current: the capacity is about 5% lower when the initial recharge current is at the 10 h rate than at the 4 h rate, the capacity at the 6 h rate lies in between. This tendency holds for different CC and CC/CV recharge schemes. The capacity seems to stabilize at a level that is representative of the actual cycling conditions. Superimposed on this effect of the initial recharge current rate, CV recharge generally seems to induce an additional effect of some lack of recharge with H_3PO_4 -free batteries, despite the fact that the recharge factor is higher with CV than with CC recharge [29]. This may be due to the rather low final electrode polarization as a consequence of limited cell voltage in the case of CV

recharge. With CC recharges, an end-of-charge voltage of more than 2.6 V/cell was obtained. This lack of recharge was gradually improved — but not overcome — by increasing the voltage during the CV period, or by the introduction of a second CV period of 1 h duration at markedly elevated voltage. It is doubtful whether these are desirable strategies, as the factor of recharge is increased even more and, hereby, will induce heat evolution and, presumably, water loss.

Investigations on the influence of DOD conditions show that in addition to full cycling (100% DOD) partial cycling may lead to a capacity decay, when low initial recharge currents are applied [29].

The investigation on cells containing phosphoric acid as an additive to the electrolyte showed similar influences of the recharge scheme, but to a much smaller extent. This is true for CC and CV schemes with the same initial recharge current, as for different initial recharge currents. The factor of recharge is much less susceptible on switching from CC to CV recharge than that for cells free of phosphoric acid [29].

5.2. Pulsed-discharge experiments

The main conclusions from the pulsed-discharge cycling tests are as follows:

1. Pulsed discharge (according to the RWE testing scheme) degrades the capacity level more than does CC discharge to 100% DOD, when a similar degree of average active material utilization is obtained. This is in accordance with previous findings that have demonstrated capacity loss with cycling at high discharge rates, both with actual EV operation, and with simulated EV operation.

2. This harmful effect of pulsed discharge is efficient for cells containing H_3PO_4 in the same manner, and to similar extent, as it is for cells free of H_3PO_4 .

3. This reduction of capacity has been shown to be a RIMU phenomenon: the degradation of the positive electrode can be reversed provided it has not proceeded too far. Capacity recovery by a discharge at very low rate is efficient also with batteries containing phosphoric acid additive. The effect is the same as with losses due to extended cycling with CC discharge. This recovered capacity is lost again when pulsed-discharge cycling is continued. Such recovery treatment can be applied several times when necessary. This phenomenon corresponds to the author's previous findings on capacity loss upon cycling with CC discharge.

4. Capacity loss upon pulsed discharge is not a special feature of the RWE discharge scheme; it is a general phenomenon that high-rate discharges, such as pulsed discharges, reduce the capacity level. Different pulsed-discharge regimes differ in the extent of this effect, as do different positive-plate features (e.g., thickness, active material structure). Therefore, experiments with other pulsed-discharge schemes, such ECE-15 or SFUDS, may be helpful to evaluate different battery designs, or to

compare quantitatively the adverse effects of the given test regimes, but are not expected to give more information on the general RIMU phenomena.

5. The cell voltage under pulsed load is higher, and the voltage drop at the beginning of a pulse is less, with the batteries containing H_3PO_4 . In particular, the latter show superior behaviour under pulsed-discharge duty.

6. CV recharge schemes (e.g., 'I 15 U') may be not optimally suited for a test as the RWE standard test. A marked capacity reduction was found (~ 10 Ah) when the recharge scheme was changed from '4 I 36' to 'I 15 U' with batteries without phosphoric acid additive. No such capacity reduction is induced by this recharge scheme with cells that contain H_3PO_4 . An explanation for this is given below.

7. The superior capacity level with CC recharge schemes, compared with CV schemes, (note, comparison of schemes with the same initial recharge current density only) which was found already on CC discharge testing, was found also on pulsed-discharge testing. This is true, despite the fact that the factor of recharge was even lower with CC recharge. This difference cannot be overcome by additional overcharge.

5.3. Influence of phosphoric acid additive

Phosphoric acid addition reduces the sensitivity of the actual battery capacity on the recharge scheme. This is especially true for the influence of the initial recharge current, which is a 'memory effect' phenomenon. Within the view of the 'Kugelhaufen' model, this behaviour is a straight-forward consequence of a change in the morphology of the PbO_2 structure that is induced by the presence of phosphoric acid.

Phosphoric acid appears to inhibit both the discharge and the recharge reaction of the PbO_2 electrode. It induces distinct shifts in the positive half-cell potential, both on discharge and on recharge. Cycling in electrolyte containing phosphoric acid at an overvoltage increased by H_3PO_4 reduces the PbO_2 crystallite size, and increases the internal BET surface. A skeleton consisting of many small particles with numerous connecting sites has a lower resistivity [40]. Such a structure of many small (instead of less and larger) particles connected to each other is, in the view of the 'Kugelhaufen' model, less prone to RIMU and helps to keep the cycling capacity both stable and high. Explanation of the experimental finding in terms of the 'Kugelhaufen' model [8] is as follows. The apparent resistance of an aggregate of crystals is determined by the resistance of the 'neck zones', i.e., the sites connecting the individual crystallites, while the bulk resistivity of the crystallites is of much less significance. As the shape of the 'neck zones' is more or less a specific property of the active material, it is the number of such 'neck zones' connected in series and in parallel that determines the apparent resistivity of an aggregate of crystals. When the diameter, d , of the crystallites in an imaginary cube-shaped volume of active mass

including $n \times n \times n$ crystallites is reduced to $d/2$, the number of crystallites is increased to $2n \times 2n \times 2n$. When a current is fed through such a cube-shaped volume, it has to pass $2n \times 2n$ chains of crystallites with $2n$ 'neck zones' in series each. The resistance of such a structure is twice as low as that of the previous structure of $n \times n$ chains with n 'neck zones' each, because there are four times more chains in parallel each with double the resistance. This lower apparent conductivity of the PbO_2 structure is beneficial, as high active material resistance leads to inhomogeneous discharge, which is the origin of capacity loss in view of the 'Kugelhaufen' model. A review of the 'Kugelhaufen' model view of the experimental results, can be found in the Appendix of Ref. [29].

Such a fine PbO_2 particle structure is set up by high overvoltage during recharge, which favours nucleation over crystal growth. A high overvoltage may be created either by a high recharge current (which has been found to stabilize capacity with batteries free of H_3PO_4) or by the addition of phosphoric acid (Fig. 8).

The correlation between high cycling capacity and high BET surface of the positive active material (i.e., fine PbO_2 particles) is also shown by the results from batteries containing no phosphoric acid additive given in Ref. [78]: cycling with high-rate recharge induced higher BET surface ($4.5\text{--}5.8 \text{ m}^2 \text{ g}^{-1}$) and a higher capacity level than those obtained with medium recharge rate ($3 \text{ m}^2 \text{ g}^{-1}$).

Phosphoric acid also inhibits the discharge reaction, (Fig. 7). This should lead to a homogenization of the charge-transfer reaction within the active material pellet, which is indeed indicated by the less pronounced curvature of the positive potential at the very end-of-discharge. This effect reduces scattering of the end-of-discharge positive potentials of the single cells, when they are connected in a battery string. This means reduced probability of reversal of a single cell at the end-of-discharge; an effect that is advantageous for the life of long-string batteries.

5.4. Rate capability

The increased internal electrode surface and the increased overvoltages on discharge due to the addition of phosphoric acid reduces significantly the discharge-rate dependency of the capacity. The additive promotes a lower capacity at a low rate, but a higher capacity at very high rates. Therefore, the pulsed-discharge behaviour of such batteries may be improved, even if their (nominal) capacity at the $C/5$ rate is reduced. This reduction of the discharge-rate dependency of the capacity by phosphoric acid additive is true for both healthy electrodes and those suffering from RIMU.

5.5. Recovery of capacity lost due to reversible capacity decay

Earlier investigations in the author's laboratory on reversible capacity loss have shown recovery of lost dis-

charge capacity not only subsequently on continuous cycling under 'beneficial' operating conditions (cf., Figs. 1 to 6), but also by special 'treatment' within limited time periods [1–4,21,25].

RIMU induced by CC discharge and by pulsed discharge can also be recovered to a great extent by a single cycle that consists of a CC discharge at a very low (e.g., 100 h) rate followed by standard recharge. This treatment has been shown to be effective with gelled, flooded [1,3] and AGM [38] batteries, both with and without phosphoric acid additive. It is helpful when RIMU has arisen due to high-rate discharge, as well as to extended standard cycling.

Technical EV batteries which have suffered from RIMU due to permanent full cycling showed a capacity increase of about 25% or more. It took about 75 full cycles until the previous (poor) capacity level was reached again. This treatment can be applied several times, when RIMU has occurred again.

Such a special 'treatment' of the battery, which does not need any supervision by staff, etc., and which could take place at a week-end or during a regular technical check in the workshop, would be a promising approach to extending cycle life. Nevertheless, this technique cannot turn an old worn-out battery into a new one. Capacity recovery lasts only for a limited number of cycles (here, about 75), and the effect seems to become weaker the more it is applied. When a battery has reached its end-of-life criterion, however, it can be brought several times over this criterion again. The total number of cycles the battery can be used in an EV might be increased by an appreciable amount. This may contribute to the improvement of battery durability more than many other approaches. Occasional recovery of capacity may be an alternative or at least a supplement to compensate for the capacity decay which has to be expected to be left also after all these approaches have been made effective.

6. Conclusions

From all these results, it is obvious that the influence of initial recharge current density on the cycling capacity is also present with state-of-the-art EV traction batteries. Having been widely ignored in the past, the superposition of the 'initial recharge current' effect and some lack of recharge with CV recharge schemes may be one of the problems of comparing the properties of EV batteries of different design. When batteries with and without phosphoric acid additive are compared, this different behaviour with respect to recharge schemes has to be carefully considered to avoid misinterpretation. Batteries without phosphoric acid additive may be poorly evaluated only due to an inadequate recharge regime with low initial recharge rate, which may induce reversible capacity decay. In addition, recharge according to CV schemes is not sufficient to

give a multi-cell string of cells without phosphoric acid additive a complete recharge within practical periods of time.

The addition of phosphoric acid to the electrolyte may be helpful for EV batteries due to several reasons:

1. The cells are more tolerant with respect to (low) initial recharge rates (memory effect). As the phenomena of RIMU cannot simply be 'switched off', H_3PO_4 may be helpful to reduce the capacity decay when only low recharge currents are available (on-board charger) and/or the simple and gentle CV recharge scheme is applied.
2. The sensitivity with respect to CV recharge schemes is reduced (lack of recharge).
3. The discharge-rate dependency of the capacity is significantly reduced. The pulsed-discharge behaviour may be better, even if the (nominal) capacity at the 5 h rate is reduced.

Pulsed discharges with high-rate discharge periods are much more harmful to the actual battery capacity than discharging the battery with the average current density at constant rate to the same DOD. This effect has been proven to be a RIMU phenomenon. With respect to capacity loss induced by high-rate pulse discharges, cells with phosphoric acid additive do not show a significant reduced sensitivity.

RIMU, induced by CC discharge or by pulsed discharge, can be efficiently recovered by a deep-discharge at very low rate, followed by an appropriate recharge. This treatment is effective for cells both with and without phosphoric acid additive, and can be repeated successfully several times.

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