

# How to understand the reversible capacity decay of the lead dioxide electrode <sup>1</sup>

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## Abstract

Unfavourable cycling conditions may successively lead to a porous PbO<sub>2</sub> structure with poor mechanical and electrical connection between the particles of which the porous electrode is built. Increasing active material resistance of this skeleton will induce a more and more inhomogeneous current distribution over the active mass, with successive restriction of the discharge/recharge processes to the active material area near to the grid. This leads to excessive mass utilisation in this very region, which aggravates the situation from cycle to cycle. The results are active material softening and shedding. This change of PbO<sub>2</sub> structure can be reverted, when cycling is continued with modified regimes. By this and by other means, lost capacity may be recovered. This effect is called reversible capacity decay or reversible insufficient mass utilization (RIMU). The Aggregate-of-Spheres Model (AOS), based on the behaviour of sintered bodies, describes semi-quantitatively the phenomena at the connecting sites of the particles of the PbO<sub>2</sub> active material, explaining the experimental findings of reversible capacity decay. The main features of reversible capacity loss are discussed in terms of AOS explanations, in order to work out strategies and limits for the improvement of lead/acid battery performance. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Lead/acid battery; Positive electrode; Lead dioxide (PbO<sub>2</sub>); Cycling application; Premature capacity loss (PCL); Antimony-free effect (AFE); Reversible capacity decay (RIMU); Capacity recovery; Aggregate-of-Spheres (AOS) model; Kugelhaufen Model

## 1. Background

It is now 100 years since, for the first time, the dependence of the actual capacity of a lead/acid battery on its previous operating conditions was reported: Jumeau [1] demonstrated that the capacity depends on the discharge rate of the preceding cycle. Cahan and Donaldson [2] showed the influence of the recharge regimes applied in previous cycles on the actual capacity.

These experiments were repeated and the authors' interpretations for these hysteresis effects were shown to be misleading (cf. Refs. [3,4]). But these early publications are milestones in the history of the lead/acid battery, as this type of 'memory effect' and the related phenomena became more obvious and more important, the more other shortcomings of the lead/acid battery system were overcome during the last century.

Unfortunately, even today it is not common knowledge that capacity may depend on the history of the electrical use of the battery, and that capacity losses due to this may be recovered in many cases, although 'memory effect' has been reported in many handbooks [5–8].

Various failure modes are known to occur during storage, trickle-charge, and cycling of lead/acid batteries, and these may limit life or at least reduce capacity and power performance. The type of failure mode depends both on battery design and on the history of its use [8,9], and may be completely different for cycling and float batteries [10]. Positive grid corrosion and mechanisms involving water loss and electrolyte stratification like sulphation and shedding [8,11] were the main phenomena limiting battery life in former times. However, after introduction of low-antimony and antimony-free grids with high corrosion resistance, degradation of the positive electrode performance became one of the major weak links with cycling batteries and attracted great interest. This became even more obvious with immobilized electrolyte cell designs suppressing both water loss and stratification, especially when high acid concentrations are used.

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<sup>1</sup> Dedicated to: Prof. August Winsel, the father of the Agglomerate-of-Spheres Model, on the occasion of his 70th birthday in August 1998.

The term ‘premature capacity loss’ (PCL) has been introduced [12] to summarise phenomena at the positive electrode, which may result in an early, unexpected capacity reduction of a lead/acid battery (significantly before its end of design life), well below its designed capacity. The term PCL is used for ‘mysterious’ phenomena related to the positive electrode, which are not standard knowledge of the battery manufacturing community. More precisely the term is used for unexpected and interfering effects located within the positive active material and/or at the grid/active material interface. With this interpretation of the term PCL, a comprehensive review of the open literature until about 1990 has been given [13].

However, poor definition of what is really meant by ‘PCL’ has caused a lot of confusion in recent years, culminating in discussion at the LABAT’93 Conference, when even acid stratification was identified as one form of PCL. Fortunately, at the same place, Voss [14] proposed a hierarchy scheme (Fig. 1) of all the premature electrode failure (PEF) modes which are presently known (Fig. 11 in Ref. [14]). This was soon approved at the PCL Study Group of ALABC [15].

This classification by Voss is of great help for clear understanding of different phenomena. Especially the term ‘passivation’ is now protected from being misused as euphemism for ‘I really do not know why this has happened...’.

Following Giess, it is now common practice to distinguish at least two different limiting processes at the positive  $\text{PbO}_2$  electrode, one related to ohmic losses at the mass/grid interface (PCL 1), and the other related to the bulk active material (PCL 2) (p. 83 in Ref. [15]) [16]. It is difficult to justify a clear borderline between the active material and the corrosion layer zone of a battery after prolonged duty, but for the time being, this two-fold classification is acceptable and useful.

In the 1960s, the term ‘antimony-free effect’ (AFE) was created because very early and unexpected capacity loss had been found with positive plates comprising lead-

calcium (antimony-free) grid alloys. Intensive investigations (cf. citations in Refs. [4,13]) did not yield a full understanding of the effect. Some authors initially believed in a destructive effect of the calcium (‘calcium-effect’), but later the lack of antimony was claimed to be decisive (‘antimony-free effect’). Extensive work has been done to get insight into the beneficial action of antimony [17–19] and other additives like tin (‘tin-free effect’) [18,20–24] to the positive electrode. The influence of the addition of phosphoric acid to the electrolyte on the capacity loss phenomena was also intensively investigated [25,26]. Recent experimental results and interpretations of the increased robustness of capacity in the presence of  $\text{H}_3\text{PO}_4$  and an overview of the more recent literature are given in Ref. [27].

However, at least since about 1980, it has been clear that similar unexpected early capacity decay may also come up with electrodes based on grids comprising 3.8% of antimony [28] (even as much as 10% Sb in tubular plates [29]), and the term ‘antimony-free effect’ is not suitable any more. One of these reports [28] provided an early indication of the reversibility of this capacity loss.

## 2. Introduction

### 2.1. Historical overview of approaches to explain positive electrode capacity loss phenomena

Many publications dealt with the grid/active material interface (PCL 1), searching for poorly conducting Pb(II)-compounds like  $\text{PbSO}_4$ ,  $\alpha\text{-PbO}$ , mixed oxides, poorly conducting  $\text{PbO}_2$ -species, or simply cracking of corrosion material perpendicular to the current path (cf., e.g., Refs. [12,30–35]). Such layers and/or structures could cause an ohmic voltage drop in this zone, limiting discharge prematurely at a technically relevant electrode potential similar to that for thermopassivation effect [22–24,36–38]. But, as Pb(II)-compounds can be found even in healthy plates with full capacity (e.g., Ref. [39]), the presence of such compounds at the grid/mass interface is no unambiguous proof for the existence of a high resistive layer.

The ‘Gel Model’ proposes the co-existence of amorphous (gel-like) and crystalline areas of  $\text{PbO}_2$ , which determine the conductivity of the structure, and the ratio of which is influenced by chemical additives (e.g., grid alloy components). Ageing is explained as conversion of amorphous material into the poorly conductive crystalline structure [40–49].

Today the qualitative ‘barrier layer’ hypothesis still lacks quantification and model predictions which could be proved or disproved by experiments. However, already 10 years ago, in situ experiments strongly indicated [50] that it is not the grid/mass interface resistance but rather the active material resistance (cf. Refs. [51–53]) which corre-

### Premature Electrode Failure Hierarchy

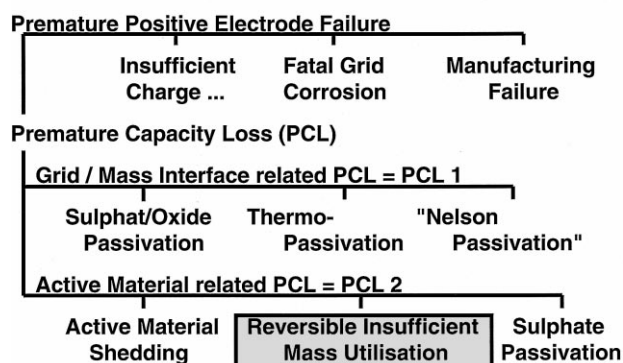


Fig. 1. Classification of positive electrode capacity loss phenomena according to Voss (cited after Refs. [14,15]).

lates with capacity loss. Such in situ measurements are very helpful to identify the limiting processes, and with another experimental set-up, those findings were recently confirmed [54–56].

These findings convinced many of those researchers who previously favoured the ‘Barrier Layer Model’ to look more into the active material properties (e.g., Ref. [57]).

Previously, the mass related PCL phenomenon (PCL 2) had attracted less interest, although already in the 1960s and 1970s, structural changes of the  $\text{PbO}_2$  active material, as well as changes of crystalline disorder, had been presumed to be the origin of the so-called ‘antimony-free effect’. Many qualitative approaches searched for the successive development of an inactive  $\text{PbO}_2$  compound, which—by some unexplained reason—would not contribute to the discharge/recharge reaction.

The ‘Hydrogen-Loss Model’ [58–65] presumed the reduction of structural disorder, due to decreasing hydrogen content in the  $\text{PbO}_2$  lattice, to be the origin of the capacity loss, but this has shown to have little practical validity for the PCL effect [66]. There is a deviation  $\delta$  from the exact stoichiometry  $\text{PbO}_2$  in the  $\text{PbO}_{2-\delta}$  structure, possibly due to incorporation of hydrogen or hydrogen species into the lead dioxide lattice, which depends on potential and acid concentration [67–69].

The ‘Corraloid Model’ (e.g., Refs. [70–76]) was based on the experimental finding that, upon cycling, the original homogeneous  $\text{PbO}_2$  pore structure tends to change into a corraloid-like structure with coarse voids.

However, no ‘inactive’  $\text{PbO}_2$  species could be identified in any case, and no attempt at quantification of these phenomenological approaches is known.

Among the models which have been proposed to describe successive capacity loss of the  $\text{PbO}_2$  electrode, the ‘Agglomerate-of-Spheres’ (AOS) model [77] is, up to now, the only semi-quantitative approach to the PCL puzzle

- which describes the consequences of structural properties and their changes on a mathematical basis,
- which uses parameters based on physical properties of the positive porous electrode structure and of  $\text{PbO}_2$ ,
- which is able to explain the experimental findings, also the recovery of lost capacity, and
- which makes predictions, which can be (and have been) checked by experiments.

A short review covering the literature and knowledge until about 1990 has been published by Voss and Winsel [4]. Unfortunately, this approach is often misinterpreted or simply ignored.

## 2.2. Capacity reduction due to poor electronic conductivity of the active material

While the theoretical capacity of the active  $\text{PbO}_2$  material in the positive electrode of the lead/acid battery is about  $224 \text{ A h kg}^{-1}$ , only about  $160\text{--}170 \text{ A h kg}^{-1}$

( $\approx 70\%$ ) can be discharged in practice even at a low rate in an excess of electrolyte [78]. This ultimate limit is caused by the lack of electronic conductivity of the discharge product  $\text{PbSO}_4$ , which is an insulator, while  $\text{PbO}_2$  is a semiconductor [7]. Therefore, electronic pathways from the sites of the charge transfer reaction to the current collecting grid may be successively cut during discharge, until the voltage drop at this ohmic resistance terminates discharge even at very low discharge rates. This successive loss of conductivity leads to a progressive inhomogeneity of the current distribution: the discharge reaction is restricted more and more to the areas near to the current collector [79].

Extensive work on the limiting role of the electronic conductivity of battery active masses has been performed by Metzendorf [78] and Euler et al. [80]. Percolation theory is a helpful means to understand and quantify these mechanisms ([81,82], and literatures cited in Ref. [81]).

Recently, the influence of external pressure on the  $\text{PbO}_2$  active material, which had been demonstrated under different conditions many times [11,51,83–88], has attracted attention again [57,89–93]. The goal is to overcome the tendency of  $\text{PbO}_2$  to expand during cycling, to keep the active mass volume constant, and so to avoid the development of a highly porous, low density,  $\text{PbO}_2$  structure with poor mechanical and electrical interconnection between the individual mass particles.

However, compression can be no more than a means to keep the  $\text{PbO}_2$  electrode structure in shape, as is done with tubular-type electrodes. The avoidance of electrode expansion is a precondition to keep the electrode healthy, i.e., it is *essential* in order to avoid capacity loss, mass softening and even mass shedding [11]. However, compression alone is *not sufficient*: reversible capacity decay, including mass softening, may occur even with tubular plates [27,29,41]. Electrode compression has been shown to reduce neither active material resistance nor grid/mass interface resistance [94,95].

Furthermore, compression on the overall cell stack may harm the structure of the separator and/or the negative electrode and may induce problems there [96]—a side-problem, which is avoided with tubular design.

Sometimes compression is applied in order to compensate for potential shrinkage of the separator and the negative electrode, which should not be confused with the PCL issue of the  $\text{PbO}_2$  structure.

Practical batteries, however, are usually intentionally designed for limitation of the depths of discharge even at low discharge rates by the amount of acid, because high active material utilisation is believed to reduce cycle life. Therefore, and especially with thicker plates at technical relevant discharge rates, it is the depletion of acid in the porous system during discharge which leads to increasing polarisation and limits capacity.  $\text{Pb}^{2+}$  ion concentration is increased on discharge by diaphragms of the discharge product  $\text{PbSO}_4$ , covering  $\text{PbO}_2$  sites and inhibiting  $\text{Pb}^{2+}$

ions from diffusing away from the  $\text{PbO}_2$  surface. Diffusion hindrance on a macro-scale is caused by pore plugging by  $\text{PbSO}_4$ , which needs a larger volume than the parent  $\text{PbO}_2$ . All this increases electrode polarisation.

From this it is clear that details of the internal structure of the  $\text{PbO}_2$ , i.e., porosity and pore size distribution as well as the inner (BET) surface, are important parameters determining the positive active material utilisation, and any change of these internal parameters will influence the electrode capacity.

### 2.3. Changes of the $\text{PbO}_2$ structure

The most significant changes of the internal structure are caused by cycling of the electrode. However, recharge is not the plain reversal of charge, because different mechanisms are involved.

For discharge, the dissolution/precipitation mechanism is widely accepted.  $\text{PbSO}_4$  is deposited by chemical precipitation, i.e., some super-saturation is possible.

On recharge,  $\text{PbO}_2$  is deposited by electro-crystallisation, i.e., the  $\text{Pb}^{2+}$  concentration can never exceed the saturation concentration of  $\text{PbSO}_4$  [28]. Therefore, the maximum possible charging rates are less than the corresponding discharge rates. Furthermore, electro-crystallisation of  $\text{PbO}_2$  does not take place at exactly the same position where  $\text{PbO}_2$  was dissolved during discharge.

From this principle difference of discharge and recharge reactions, it is evident that the active material structure of the porous electrode is changed during cycling. Such changes of the structure, and of internal parameters (pore size distribution, BET surface) are described in many publications, e.g., Refs. [10,28,70,79,83,97–99].

Already in 1971, Simon and Caulder [70] came to the conclusion that “... the structure developed in the plate is evidently a function of the mode of operation and of such factors as gas formation, current density, and rate and habit of crystal growth” (p. 665). They believed the development of the ‘coralloid structure’ and the increase of the amount of ‘inactive’  $\text{PbO}_2$  to act like a ‘memory’ remaining from cycle to cycle and giving rise to capacity loss [100].

This is the basis of the ‘memory effect’, a term which has been used for decades [4]: information about the operating history is stored in the structure of the active material. The most recent processes are dominating, but also former cycles may influence the actual properties, especially if extreme conditions (e.g., deep discharge) had taken place.

In consequence, recovery of previous capacity loss is possible, if the active material structure can be reconverted to a more prosperous one. This is what is meant by ‘reversible capacity decay’ or ‘reversible insufficient mass utilisation’ (RIMU) [77].

Previously, it was unclear what type of changes of the internal structure take place, and which of the discharge

limiting processes summarised above is influenced by such changes.

### 2.4. Experimental findings on reversible capacity decay

In several handbooks on lead acid batteries, the influence of the discharge history is mentioned. Bode [7] states that the capacity “... is dependent on the history of discharge-at least of the last charge and discharge”. In the VARTA handbook [6] the effect is related to changes in the internal parameters of the electrode (surface area and pore-size distribution), which might be influenced by the charge/discharge conditions. Also Vinal [5] and Burbank et al. [101] mention this effect.

Despite being referred to also in more recent reviews [9,13], the following experimental findings are frequently not taken into account in the course of discussions on PCL: (1) that capacity decay does not come randomly like an unforeseeable calamity in many cases. It is a phenomenon caused by the operating conditions such as discharge, recharge, rest times, temperature, and which can either be intentionally brought about or avoided/reduced by appropriate operating conditions (within the limitations of the construction details of the battery); (2) that capacity decay may be reversible in many cases, i.e., lost capacity can be (partially or even completely) recovered by changes of operating conditions or special treatments; and (3) that these phenomena have not been found only under ‘artificial’ laboratory conditions, with special set-ups, but are relevant also for technical batteries under common practical operating conditions.

In fact many experiments on phenomena related to RIMU [77] have been well documented and published within the last two decades.

The main experimental findings of the RIMU effect of the  $\text{PbO}_2$  electrode are: (1) there is no lack of recharge: chemical analysis shows a full state of charge of  $\text{PbO}_2$ , and (2) extra overcharge does not improve, but may aggravate the situation [3,29,102]; (3) recharge with low initial current density may induce progressive capacity decay, while there is less or even no loss, when recharge is performed at higher recharge rate [3,27,29,103]; (4) an existing capacity decay due to this recharge effect can be recovered successfully by switching to a recharge regime with higher initial recharge current [3,26–29]; (5) discharge at high rates promotes capacity loss, which may be recovered when cycling is continued with low/medium-rate deep discharges [104]; (6) recovery of lost capacity is possible by switching to cycling under more favourable conditions (which provide permanent operation at high capacity level [3,27,50,77,104], by deep discharge at very low rates [3,27,29], or by special treatments of the electrode, e.g., washing free of acid and drying [3,28,29,50], especially at elevated temperature, or by currentless rest times [28,104].

Further experimental findings and details are given in Refs. [3,4,20,26–29,77,103–108] and summarized in Refs. [4,109,110].

All these results show clearly, that the reversible capacity decay is a general feature of the  $\text{PbO}_2$  electrode. Neither the capacity loss nor its recovery is limited to certain grid alloys (e.g., Sb-free, PbCa), certain electrode designs (Planté, pasted, tubular), or certain experimental set-ups (e.g., immobilized electrolyte or forced electrolyte flow).

The basic ideas of the AOS model and references to the original literature are given in Section 3.

Experimental findings on the different RIMU phenomena [109,110] are interpreted in terms of the AOS model in Section 4, and ordered according to the different battery operating parameters which can be used to induce or to avoid and recover this capacity decay.

### 3. Basic ideas and approximations of the AOS model

The reversible capacity decay is a phenomenon, where the capacity of an electrode is reduced, but the chemical composition and the overall amount of active material are still unchanged. Therefore, a change of the current distribution and/or of the potential distribution must take place.

The central question is: where is the information about the state of the electrode stored, i.e., *where is the 'memory' located?*

Based on in situ experiments [50] which clearly showed, that the apparent conductivity of the porous  $\text{PbO}_2$  structure of a fully charged electrode is well correlated to the capacity which can be drawn from that electrode, while the conductivity of the grid/mass interface does not show such a correlation (recently confirmed by Calabek et al. [54–56]), the following approach was set up: the 'memory', where information of previous operating conditions is stored, is the porous structure of the  $\text{PbO}_2$  active material, which is disintegrated and rebuilt again during cycling in a manner which depends on the very cycling conditions, but

may be modified also without any discharge/recharge process.

The structure of the electrode, which determines the discharge behaviour, i.e., the discharge capacity, is established to some extent by the previous recharge or even the formation [76]. And this recharge depends to some extent on the conditions of the previous discharge, etc.

The apparent conductivity of the  $\text{PbO}_2$  structure in the fully charged (and healthy) state is so high, that no significant inhomogeneity of current distribution is induced even at very high discharge rates [81,82,107]. Only at the very end of discharge, when a significant portion of active material is converted to insulating  $\text{PbSO}_4$ , does the decreasing conductivity of the structure induce an inhomogeneous current distribution: the discharge current is restricted to the regions near to the current collector [50,83,107]. However, when the conductivity of the  $\text{PbO}_2$  structure is already poor in the fully charged state, an inhomogeneous current distribution will occur much earlier in discharge, which means reduced active material utilisation in the regions far away from the current collector, and lower capacity.

Thus, a favourable active material structure, giving high capacity, may be obtained if the charge (and discharge) conditions are chosen appropriately. And, vice versa, an 'unfavourable' cycling history may induce capacity decay. As float batteries are usually only rarely cycled, their active material structure differs significantly from that of cycling batteries after extended service [10].

#### 3.1. The AOS model structure

In general, it is accepted that the structure of the positive active material is a porous aggregate of individual  $\text{PbO}_2$  crystals which are firmly welded together [97,98,111] (Fig. 2). From the field of sintered bodies it is well known, that the apparent conductivity of an aggregate of particles is mainly determined by the 'constriction resistance' at the connecting zones of the particles, i.e., by the number and

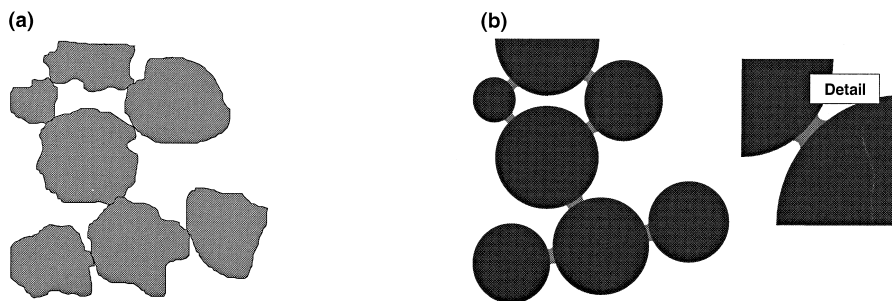
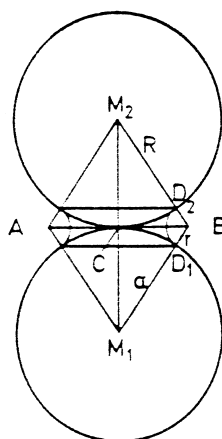


Fig. 2. The lead dioxide electrode consists of individual  $\text{PbO}_2$  particles with mainly outward curvature (convex) of their surface. They are mechanically and electrically interconnected to each other by tiny connection zones which have an inward oriented (concave) curvature (a). (a) Schematic view of  $\text{PbO}_2$  particle agglomeration. For simplification and mathematical treatment, the AOS model approximates the  $\text{PbO}_2$  particles by balls and the connection zones (necks) by an rotational hyperboloid (b). (b) Approximation for better understanding and easy mathematical treatment.

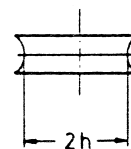
### Geometry of AOS Structure

any open porous system has both concave and convex inner surfaces

approximated as  
**Agglomerate Of Spheres**



from: Winsel, Voss,  
Hullmeine,  
JPS, 25 (1989) 27



**geometry of ball (convex) & neck (concave)**

Fig. 3. Geometrical situation at a neck, the connecting site of two spheres (after Ref. [3]).

the geometry of the (small width) connecting zones, and much less by the bulk conductivity of the particles [105,112,113].

Based on a mathematical model to describe mechanical and thermodynamic properties of a pressed and sintered metal powder body [112], the AOS model of the  $\text{PbO}_2$  structure has been developed [3,77,105,114–118] employing the main features of this electrode. These papers give the mathematical derivations in detail.

Special aspects of the model are critically discussed and more formulas derived in Refs. [119,120].

The approximation of the  $\text{PbO}_2$  structure as an 'aggregate of spheres' (i.e., in German language 'Kugelhaufen') is straightforward. The convex surface of uniform curvature is justified by X-ray measurements [121], from where it can be deduced that the shape factor of  $\text{PbO}_2$  is close to that of a spherical particle. SEM pictures (e.g., Refs. [71,116]) and recent work applying scanning tunnelling microscopy [122] support this view. If a structure consisting of ball-shaped particles of equal size is assumed, the typical  $\text{PbO}_2$  BET surface of  $5 \text{ m}^2 \text{ g}^{-1}$  means a particle diameter of 120 nm.

The estimation of ball-shaped particles of equal diameter is the simplest approximation to calculate the geometry of the small width connecting zones, the 'necks' of the sintered body, and to estimate their conductivity. This does not mean that uniform and perfectly ball-shaped  $\text{PbO}_2$  crystallites are claimed to be the unit particles of a  $\text{PbO}_2$  electrode: it is just a simplification. Recently, the mathematical treatment was extended for a distribution of particle sizes [116].

Fig. 3 shows the geometry at a neck, the connecting site of two spheres. Due to the different sign of the surface curvature, the sign of the energy from the surface tension of the solid  $\text{PbO}_2$  phase is different for the 'ball' and the 'neck' sites. This difference in Gibbs' free energy  $\Delta G$  is equivalent to different equilibrium potentials  $\phi_{\text{eq}}$  of the

$\text{PbO}_2/\text{PbSO}_4$  electrode at the  $\text{PbO}_2$ /electrolyte interface of 'ball' and 'neck' surfaces.

The dependence of the equilibrium voltage of an electrochemical couple on the surface curvature of the electrode is well known: particles of different size (with different convex surface curvature) differ in potential, as the tendency of components to go into solution is higher at highly outward-curved surfaces than at flat or even inward-curved surfaces. This effect is similar to the higher solubility of finely dispersed material compared to coarse particles, which show lower dissolution energy, and to the higher vapour pressure of fine liquid droplets compared to a flat liquid surface.

The dependence of equilibrium potential on surface curvature is sketched in Fig. 4. The sign of the potential difference depends on the particular electrochemical couple.

With the  $\text{PbO}_2/\text{PbSO}_4$  electrode, there is a higher tendency for  $\text{PbO}_2$  to leave the lattice at the convex spheres than at the concave necks.  $\text{PbO}_2$  goes into solution as  $\text{Pb}^{2+}$  and two  $\text{O}^{2-}$  ions, leaving behind two positive charge units, which give a more positive local equilibrium potential at the sphere sites. On average,  $\text{Pb}^{2+}$  leaving the spheres has an increased probability to be electro-deposited at the neck sites. A more negative potential at the

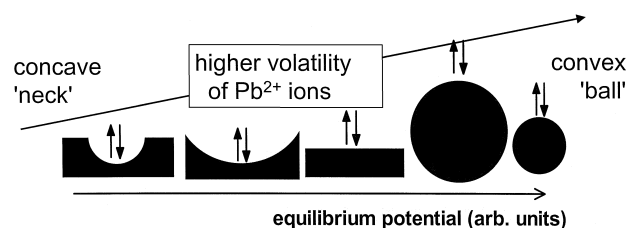


Fig. 4. Sketch of potential difference at electrode surfaces of different curvature (potential value and sign in arbitrary units).

particle interconnection sites allows for underpotential deposition of  $\text{PbO}_2$ , which stabilizes the neck areas against discharge. Obviously the necks are more noble than the spheres. Otherwise, the lead/acid battery would never be a technical product.

The consequences of the AOS approach are as follows (references are given for more details).

### 3.2. Conductivity of an AOS structure

Simple calculations according to the ‘ball and neck’ geometry (Fig. 3) show [3,77,105] that the specific resistance  $\rho$  of such an agglomerate of balls differs from the specific resistance of the bulk  $\text{PbO}_2$  material  $\rho_0$  by the ratio  $R/h$  of sphere radius  $R$  to neck radius  $h$ ,

$$\rho = \rho_0 R/h \quad (1)$$

### 3.3. Mechanics of an AOS structure

When particles (approximated by ‘balls’) are mechanically and electrically connected to each other via ‘neck’-shaped sites, they have convex curved surfaces, while the necks have a concave surface curvature (Fig. 3). Therefore, the surface tension  $\sigma_0$  of  $\text{PbO}_2$  creates a Laplace pressure, which has different signs for these two types of surfaces of the sintered body.

The Laplace pressure is [3,77,105,116]

$$P_R = 2\sigma_0/R \quad \text{on the ball surface (radius } R), \text{ and} \quad (2)$$

$$P_h = -2\sigma_0 R(1 - 3h/2R)/h^2 \quad (3)$$

on the neck zone surface (radius  $h$ ).

The surface tension  $\sigma_0$  of  $\text{PbO}_2$  is a driving force for enlargement of the neck region (i.e., an increase of neck radius  $h$ ). This will take place as long as the Laplace pressure exceeds the yield stress  $\varepsilon_0$  of the  $\text{PbO}_2$  material [3,77,105], i.e., until  $P_h = \varepsilon_0$ . Therefore, the equilibrium value of  $P_h$  is determined by the yield stress  $\varepsilon_0$ . The yield stress decreases with increasing temperature, which leads to increasing neck radius  $h$  with higher temperatures. This explains the accelerated recovery of lost capacity after storage of the charged electrode at elevated temperatures.

With some approximations, the relation [3,77,105]

$$2R/h^2 = \varepsilon_0(T)/\sigma_0(T) \quad (4)$$

is obtained, i.e., the equilibrium value of the ball-to-neck ratio  $R/h$  is given by mechanical properties  $\varepsilon_0$  and  $\sigma_0$  of the material, and only one of the two parameters  $R$  and  $h$  is really free.

The apparent resistance  $\rho$ , which is proportional to  $R/h$ , increases when  $R$  increases [3]:

$$\rho = \rho_0 \sqrt{\{R\varepsilon_0(T)/2\sigma_0(T)\}} \quad (5)$$

In other words: it is beneficial to have an aggregate consisting of small particles, as such a finer structure has higher apparent conductivity, if all the other parameters are the same.

More considerations on the mechanical properties of an AOS structure and comparisons with data from dilatation and rupture experiments of  $\text{PbO}_2$  material are given in Refs. [106,107,115,116,123].

### 3.4. Potentials at the surface of the AOS structure

Different Laplace pressure means different free energy of molecules at these surfaces, and—in electrochemical terms—a different equilibrium potential of the  $\text{PbO}_2$  electrode at the convex and concave inner surfaces. This potential difference has been calculated [3,77,105] to depend on sphere radius  $R$ , neck radius  $h$ , surface tension  $\sigma_0$ , the molar volume  $V_0$  of  $\text{PbO}_2$  ( $= 24.6 \text{ cm}^3 \text{ mol}^{-1}$ ), and Faraday’s constant  $F$

$$\Delta\Phi \approx -(V_0\sigma_0/FR)(1 + R^2/h^2) \quad (6)$$

if  $h \ll R$  is assumed.

From the experimental fact that  $\text{PbO}_2$  electrodes can be discharged with a high active mass utilisation, it can be concluded that the  $\text{PbO}_2/\text{PbSO}_4$  equilibrium potential at the neck zones is lower than at the convex zones (Fig. 5). Otherwise, on discharge the neck zones would be preferably discharged and converted to  $\text{PbSO}_4$  first, and the conductive contact between the crystallites would be interrupted immediately: the  $\text{PbO}_2$  electrode could not be technically used at all.

The difference in equilibrium potential between convex ‘balls’ and concave ‘necks’ has been estimated [3,77,105]. The deviation from stoichiometry  $\delta$  of  $\text{PbO}_{2-\delta}$  decreases with increasing  $\text{PbO}_{2-\delta}$  electrode potential  $\Phi$  [67] (an alternate representation of the deviation of the Pb:O ratio from the ideal value 2 is the incorporation of hydrogen species [68,69] into an lead oxygen lattice, e.g.,  $\text{PbO}_2\text{H}_{2x}$ )

$$\Phi = 0.991 - 0.124 \log(\delta) - 0.0592 \text{ pH} \quad (7)$$

Therefore, the value of  $\delta$  in the balls ( $\delta_R$ ) is lower than in the neck zones ( $\delta_h$ ), and the potential difference (if the same pH is estimated at the ball and the neck surfaces) is given by

$$\Delta\Phi = -0.124 \log(\delta_h/\delta_R). \quad (8)$$

On the other hand, according to thermodynamics, the difference in potential  $\Delta\Phi$  is determined by the model parameters (Eq. (6)), which provides a relation between the  $\delta_h/\delta_R$  ratio and the model parameters:

$$\log(\delta_h/\delta_R) = 8.04(V_0\sigma_0/FR)(1 + R^2/h^2) \quad (9)$$

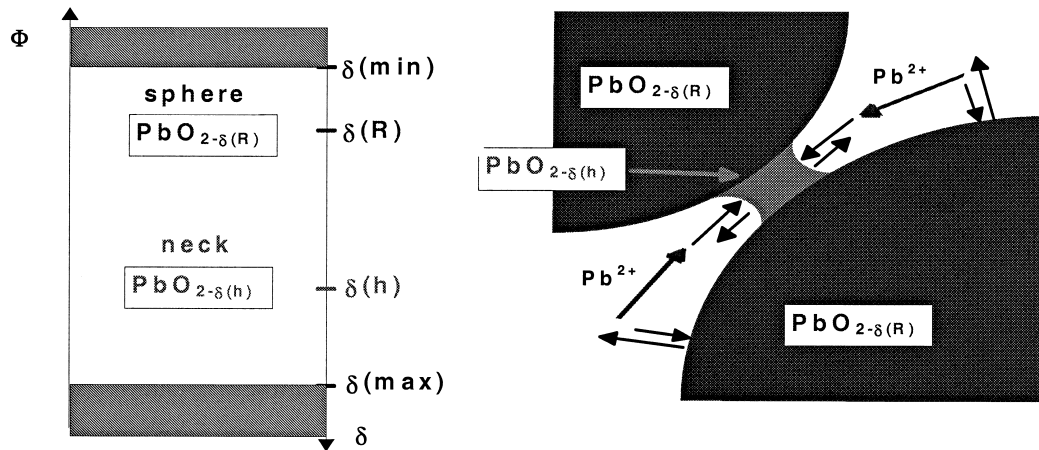


Fig. 5. Potential difference at the neck and the sphere surface, when the electrode is at OCV. The various potentials  $\Phi$  and stoichiometry deviations  $\delta$  at the neck and the sphere surface have to be within the phase range  $\delta_{\max} > \delta(h) > \delta(R) > \delta_{\min}$ . The migration of  $\text{Pb}^{2+}$  from the sphere via the electrolyte to the neck is indicated.

The lower and upper limits of the phase range of  $\text{PbO}_{2-\delta}$  are marked by the stoichiometry deviations  $\delta_{\max} = 0.016$  and  $\delta_{\min} = 0.003$  [67], which limit the ratio  $R/h$ . (N.B.: there are different values of the phase range given in the literature, e.g.,  $0 \leq \delta \leq 0.05$  for  $\beta\text{-PbO}_2$  [124], inducing other limitations for the  $R/h$  ratio and the potential difference).

Assuming a ball radius  $R = 10^{-7}$  m, which is in good agreement with SEM and BET surface data, and a surface tension of  $\sigma_0 = 1 \text{ J m}^{-2}$  (taken from solid state data in Ref. [125,126]), only structures with  $R/h$  ratios fulfilling the relation

$$R/h \leq 6 \quad (10)$$

should be stable under equilibrium conditions.

For the extreme case of  $R/h = 6$ , there is  $\delta = \delta_{\max}$  at the neck and  $\delta = \delta_{\min}$  at the sphere surface [3,77,105], and a potential difference  $\Delta\Phi$  between neck and sphere surfaces of  $\approx 90 \text{ mV}$  ‘protects’ the necks from being discharged. Without such a potential difference,  $\text{Pb}^{2+}$  would go into dissolution during discharge at the tiny necks as well as at the bulky spheres: the  $\text{PbO}_2$  structure would disintegrate very soon, and the lead/acid battery would never have been a technical product. Fig. 5 shows the potentials and the stoichiometry deviation  $\delta$  at the sphere and neck sites.

All this is true in the equilibrium state of the fully charged electrode. The AOS model does not give any predictions for the dimensions of crystallites of the discharged material, their location and connection with each other and with the remaining  $\text{PbO}_2$  particles.

### 3.5. The neck area as a nucleus for the growth of a new crystallite

Following the ideas of the model [106], the minimum ‘neck area’ can be regarded as a two dimensional nucleus

for the growth of the next  $\text{PbO}_2$  sphere, at least as long as  $\text{PbSO}_4$  is present and  $\text{Pb}^{2+}$  is available in the electrolyte. Such a new nucleus is formed on the surface of a growing  $\text{PbO}_2$  particle when the Laplace pressure  $P_R = 2\sigma_0/R$  caused by the surface tension  $\sigma_0$  (which decreases with particle size  $R$ ) is not sufficient to overcome the yield stress  $\varepsilon_0$  of  $\text{PbO}_2$  any more [116–118]. See Fig. 6 for a sketch of the nucleation and development of an AOS structure.

### 3.6. Volume of the neck zones

Assuming the maximum ratio of sphere radius  $R$  to neck radius  $h$  of  $R/h \approx 6$  [3,77,105], and the simple ball/neck geometry, the  $V_h: V_R$  ratio of the active  $\text{PbO}_2$  material volume in the neck zones  $V_h$  to the volume in the spheres  $V_R$  can be calculated to be in the order of  $2\text{--}3 \times 10^{-3}$ , if the ratio  $R/h$  approaches its maximum value. In other words: less than 1% of the total  $\text{PbO}_2$  volume is located in the neck zones [3,20,77,105,112,116].

In Ref. [106], the neck radius was estimated from mechanical measurements to be about  $0.15 \mu\text{m}$ , and the ratio  $R/h$  to be about 3.2. This fits well to the limiting value calculated above.

### 3.7. Experimental proof for the AOS predictions

The crucial experimental proof for the AOS approach is the dependency of the active material resistance and also of the mechanical rigidity on the operating conditions, i.e., rates of recharge and discharge, etc.; cf. especially Refs. [50,52–56,106,107,117,118,123]. In many cases, both the active material resistance and the grid/mass interface resistance were measured, and it was clearly demonstrated that the latter does not correlate with the actual capacity.



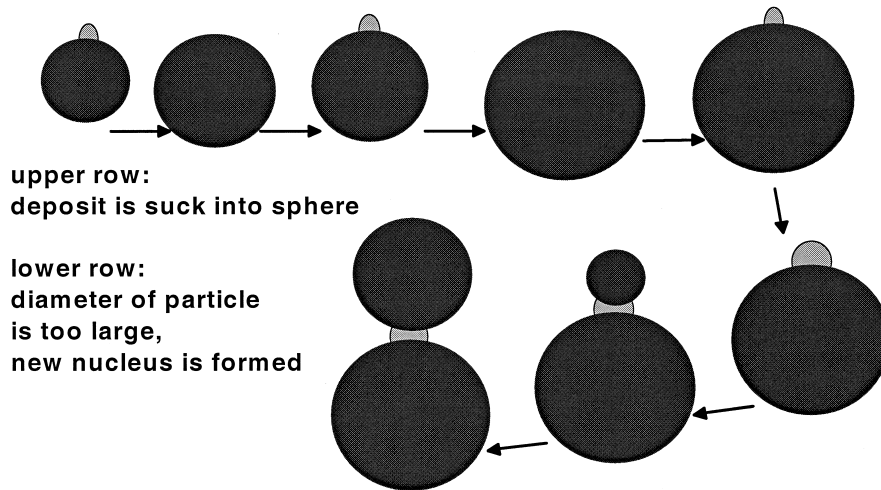


Fig. 6. Sketch of nucleation on the surface of a growing  $\text{PbO}_2$  particle of radius  $R$ , when the Laplace pressure  $P_R = 2\sigma_0/R$  caused by the surface tension  $\sigma_0$  (which decreases with particle size  $R$ ) is not sufficient to overcome the yield stress  $\varepsilon_0$  of  $\text{PbO}_2$  any more.

Also mechanical pressure on the active material does not reduce the active material resistance [94,95].

#### 4. Interpretation of premature capacity loss and reversible capacity decay phenomena in terms of the Agglomerate-of-Spheres Model

The main effects characterising the reversible capacity decay have been summarized in Section 2.4. They are discussed individually and the original literature is provided for reference in the paragraphs below (cf. Refs. [109,110] for a more detailed review of the experimental findings).

##### 4.1. Effect of recharge current rate on capacity decay

*Summary:* To keep the electrode capacity high, it is important to have the recharge reaction to be performed with current of sufficient rate, i.e., at high (over)potential [3,29,41,55,103,127]. It is extremely important to have, at least in the very beginning of recharge, a sufficiently high recharge rate [50,103].

The superiority of recharge with high-rate pulses rather than with constant current applying the average current rate of pulse- and off-periods to extend cycle life has been well known for many years (e.g., Refs. [128,129]). Obviously, it is the actual current density upon electro-deposition of  $\text{PbO}_2$ , (which is higher with pulse charge) rather than its average value which is decisive.

The recent development of quick switching electronics provides the chance to make use of this strategy without harming the battery [96,130–133], and this may really improve cycle life.

Electrodes are more sensitive to the recharge rate, the thinner are the plates and the higher is the positive active

material utilisation [134,135] (unfortunately, the type of recharge scheme is not specified in that paper).

Generally, the sensitivity to low-rate recharge is reduced as the thickness of the active material layers on the current collector increases, as the amount of antimony in the grid alloys increases, as the electrolyte is immobilised [29], and as phosphoric acid is added to the electrolyte [27].

*AOS view:* At high rates of recharge, i.e., high recharge polarisation, the formation of nuclei is favoured for kinetic reasons with respect to growth of crystallites which are already there.  $\text{PbO}_2$  crystallites are produced with an average radius  $R$  smaller than at lower recharge rates [116], which can be seen from a higher BET surface [131,132] (cf. Ref. [27]). A  $\text{PbO}_2$  structure consisting of smaller crystallites shows a higher conductivity and therefore a higher capacity on discharge [27,108,114]—which is clearly shown by experiments [131,132].

In addition, local temperature at the  $\text{PbO}_2$  nuclei may increase due to the high overpotential present at high recharge rates. This may reduce the limiting value of yield stress  $\varepsilon_0$ , leading to increased neck radius  $h$  [77,105]. Therefore, the  $R/h$  ratio may be smaller after high rate recharge, and again the apparent aggregate resistance  $\rho$  is reduced and therefore the discharge capacity increased [27,108,114].

If the thickness of the electrode layer on the current collector is increased, this usually reduces the specific active material utilization, which is beneficial for cycle life. Furthermore, a thick active material layer will induce more increase of acid concentration during recharge in the interior layers due to limited rate of concentration equilibration. Recharge in acid of increased concentration is helpful following the arguments given in Section 4.9. This explains, why thick traction battery plates suffer much less from early wearing out than thin pasted and Planté-type plates [29].

The influence of antimony and phosphoric acid on the recharge-rate effects are discussed in Sections 4.7 and 4.8, respectively.

#### 4.2. Effect of overcharge on capacity decay

*Summary:* After complete recharge of the positive electrode, any further overcharge should be avoided in order to keep the electrode capacity high [3,29]. The avoidance of shedding is related to this (cf. references in Ref. [136], where shedding is believed to be the reason of the effect).

Similar results are reported in Refs. [102,137,138], but there were both shedding and stratification involved.

Especially, overcharges at high voltages (i.e., high positive potentials, e.g., on pulse overcharge) have been shown to harm capacity [129]. Also recharge schemes with high overpotentials well before the achievement of the fully charged state are detrimental.

*AOS view:* On overcharge, the potential at the sphere surfaces (the high sphere surfaces dominate the overall potential of the electrode, while the neck surfaces contribute little to the mixed potential) is much higher than the  $\text{PbO}_2/\text{PbSO}_4$  equilibrium potential. Therefore, the  $\text{PbO}_{2-\delta}$  stoichiometry deviation  $\delta$  at the convex sphere surface is reduced and approaches  $\delta_{\min}$ .

The following explanation is given in Refs. [77,105]: As the electrolyte is depleted from lead ions under such conditions, lead from the neck region passes into solution and is forced to migrate to the spheres, where there is surplus oxygen. This means a material loss at the neck zones, i.e.,  $h$  decreases. The neck zone stoichiometry value  $\delta$  of  $\text{PbO}_{2-\delta}$  increases to its limit  $\delta = \delta_{\min}$ . The  $R/h$  ratio increases when  $h$  is decreased, and the increase of the apparent aggregate resistance  $\rho$  [54,55] induces reduction of capacity.

If dissolution of lead continues, the neck radius  $h$  reaches its boundary value, the neck phase becomes unstable, disintegrates, and the connection is lost, leaving electrically and mechanically separated particles; this softening is the beginning of shedding [11].

This explanation assumes a mechanism, which suspends the potential protection for the neck region, which is not obvious. The following explanation seems to be more appropriate: upon extensive overcharge, the stoichiometry approaches its limit  $\delta = \delta_{\min}$  not only at the sphere, but also at the neck surface. At the oxygen-rich phase border, i.e., with maximum O:Pb ratio, the lattice stability is much lower than in the middle of the range of existence. This means a mechanical weakening of the neck areas, which makes them prone to disintegration.

Weakening of the particle interconnection means softening, which is the origin of the shedding phenomenon [11], usually attributed to mechanical forces, exerted by bubbles of evolved oxygen. According to the AOS model, oxygen bubbles are not the reason to break particle connections, but only the vehicle for transportation of particles, whose

neck interconnections has been disintegrated. Duration of overcharge as well as the value of overcharge polarisation decide the extent of the effect. The chemical composition of the sludge is mostly  $\text{PbO}_2$  [11].

#### 4.3. Effect of previous discharge current rate and depth of discharge on capacity decay

*Summary:* Cycling with discharge at high rates, either with constant current or with pulse discharge, shows more tendency for capacity loss than discharge at lower rates (when the other cycling parameters are kept constant), e.g., Refs. [48,72,103,139–144].

The reversibility of this effect is shown in Refs. [1,3,5,26,29,41,50,104,129]: the  $\text{PbO}_2$  electrode shows a memory effect with respect to the previous discharge rate: its capacity at a certain rate (in  $\text{A kg}^{-1}$ ) is higher, the lower the rate of the preceding discharge. Furthermore, when several cycles at the same discharge rate were followed by cycles at another rate, a couple of cycles had to be performed until a stable equilibrium value of the capacity was obtained. The new level is representative of the actual cycling conditions.

This is true for all types of electrode and grid alloy [29]. See Section 4.5 for capacity recovery by low rate deep discharge.

*AOS view:* Thanks to their lower equilibrium potential with respect to the sphere surfaces (v.s.), the neck zones are usually protected from being reduced even when the electrode is discharged.

But, at high negative polarisation of the electrode, as in case of high discharge rates and/or deep discharge, the  $\text{PbO}_2$  is reduced and converted to  $\text{PbSO}_4$  in the neck areas too (but still at lower specific rate than at the sphere surface). The electronic conductivity of the whole  $\text{PbO}_2$  agglomerate structure is impoverished [52,56], when more and more neck areas become thinner or are even completely disrupted.

When the conductive neck connection between adjacent crystallites has been disrupted, a special driving force is needed to restore the original structure at the neck zones during the subsequent recharge (cf. Section 4.1). Otherwise, the conductivity of the structure is reduced and the electrode capacity is diminished permanently.

On the other hand, during low rate discharge with low polarisation, the electrode potential is always above the local  $\text{PbO}_2/\text{PbSO}_4$  equilibrium potential of the neck zones. Therefore, no discharge reaction takes place in this area, and the electronic connections are not harmed.

Furthermore, the conductive neck zones may even grow during low rate discharge: there is an abundance of  $\text{Pb}^{2+}$  ions in the electrolyte, when discharge takes place on the convex sphere surfaces in the neighbourhood of the concave-shaped necks. These  $\text{Pb}^{2+}$  ions are oxidised and accumulated at the neck surface, since at that location the potential is still a little bit above the  $\text{PbO}_2/\text{PbSO}_4$  equilib-

rium. This may explain, why low rate discharge is not only without any harm, but even beneficial for the electrode capacity, as the aggregate conductivity is increased, and a higher capacity is obtained on the subsequent discharge.

#### 4.4. Recovery of capacity decay during open-current rest periods

*Summary:* Capacity decay can be reverted by rest periods in the fully charged state [3,28,50,129,137,145,146]; this effect is accelerated and enhanced by storage at elevated temperature. Time scale for this process is hours to weeks. However, even after extended rest periods, lost capacity is only partially recovered.

Rest periods in the (partially) discharged state prior to recharge helped to avoid or reduce capacity loss [104].

*AOS view:* During rest periods of the electrode at OCV, which is mainly determined by the OCV potential of the high surface of spheres, the neck surfaces are positively polarised well above their local OCV. Due to self discharge of  $\text{PbO}_2$  during OCV standing,  $\text{Pb}^{2+}$  is formed at the sphere surfaces and released to the electrolyte.  $\text{Pb}^{2+}$  ions preferentially migrate in the liquid phase to the neck zones, where they are oxidised and electroplated as  $\text{PbO}_2$  again, because the local potential at the necks is higher than the local OCV. The growth of the neck zone improves the aggregate conductivity and capacity, as  $R/h$  is decreased.

This process takes place on OCV rest times at any state of charge. It is the reverse process of the deterioration of necks on overcharge (cf. Section 4.2).

In addition, a solid state phase process may take place at elevated temperature. The limiting value of yield stress  $\varepsilon_0$  is reduced at higher temperature, which leads to increased neck radius  $h$ . Therefore, the  $R/h$  ratio may be smaller after storage, and accordingly the aggregate resistance  $\rho$  is reduced. This improves the discharge capacity in the subsequent discharge.

A capacity recovery by 15% after 2 months of open circuit stand given in Refs. [145,146] was interpreted as a consequence of increased electrode stack pressure, without giving proof or explanation why this should have happened. The AOS interpretation for this finding is, however, straightforward.

Rest periods in the (partially) discharged state prior to recharge will allow for equilibration of acid concentration between the electrode pore system and the separator by diffusion. If a high-rate discharge directly preceded the recharge (as was the case with Ref. [104]), this equilibration leads to an increase of acid concentration which will help to avoid or reduce capacity loss (cf. Section 4.9).

#### 4.5. Recovery of capacity decay by low rate deep discharge

*Summary:* Deep discharge at a (very) low rate results in recovery of previously lost capacity. In many cases, one

single discharge brings back a great portion of lost capacity [3,27,29,108,129,147,148]. Deep discharge at low rate has been applied by battery engineers for decades, when precise and reliable capacity data have been required [149].

*AOS view:* The processes inducing capacity recovery during OCV rest times have been discussed already in Section 4.4. Upon discharge, the electrode potential is below the OCV of the spheres surface, which dominates electrode potential, and  $\text{Pb}^{2+}$  is released to the electrolyte. However, at very low rates, discharge polarisation is rather low, and the electrode potential may still be above the neck surface OCV (cf. Section 4.3). Therefore,  $\text{Pb}^{2+}$  from the electrolyte can be electroplated at the necks, increasing the neck strength, which of course is much quicker when there is a surplus of  $\text{Pb}^{2+}$  present in the electrolyte. Therefore, a low-rate discharge is much more efficient than simple rest time, but is based on the same process.

#### 4.6. Recovery of capacity by ‘non-electric treatments’

*Summary:* The ‘memory’ of the  $\text{PbO}_2$  electrode can be ‘cleared’ by dismounting the fully charged electrode, washing with water and drying. This acts like a ‘reset command’: any previous capacity loss is recovered to a great extent when the electrode is placed back into the electrolyte [3,29,50]. A similar phenomena was found when switching the electrode to an electrolyte with lower concentration [18,19].

If this procedure is performed in a healthy electrode, the next discharge gives ‘extra’ capacity, exceeding the normal capacity. However, this is soon lost [3].

*AOS view:* The processes inducing capacity recovery during OCV rest times have been discussed already in Section 4.4. Extended OCV periods, especially at increased temperature will lead to an increase of capacity recovery, which is rather slow, i.e., needs many hours, days, or even weeks.

When the electrode is washed free of acid, the same result is obtained nearly instantaneously. In water (or low-concentration electrolyte),  $\text{Pb}^{2+}$  solubility is much higher than in technical sulphuric acid. Therefore, the  $\text{Pb}^{2+}$  migration in the electrolyte to the necks, which is stabilizing these zones (cf. Section 4.4), is significantly enhanced. The effect of washing and drying is based on the same process as rest times.

When the electrolyte concentration is decreased, the surface tension  $\sigma_0$  of  $\text{PbO}_2$  in the electrode is increased, which decreases the apparent aggregate resistance  $\rho$  according to Eq. (5), and this recovers lost capacity.

#### 4.7. Influence of tin and antimony on capacity decay

*Summary:* The addition of tin ions to the electrolyte reduces the sensitivity of the electrode capacity to recharge parameter variations [20,21]. Tin from the grid alloy has a stabilizing effect, too [18,20–24,34].

The beneficial effect of antimony as a grid alloy component [17–19,28,29,35,42–47,49] has been known even

since electrodes with low-antimony or antimony-free grid alloys were introduced, because these initially showed poorer life performance.

*AOS view:* Redox couples like  $\text{Sn}^{2+}/\text{Sn}^{4+}$ , which have a potential lower than that of the  $\text{PbO}_2/\text{PbSO}_4$  electrode, are expected to stabilise the electrode capacity of a high level, independent of the discharge and recharge conditions [20,21].

A possible explanation is that  $\text{Pb}^{2+}$  ions are set free from the particle surfaces when  $\text{Sn}^{2+}$  from the electrolyte are oxidized to  $\text{Sn}^{4+}$ . These  $\text{Pb}^{2+}$  ions primarily migrate to the anodically polarised neck zones, and are oxidised there, increasing the neck zone thickness. This reduces the apparent aggregate resistance, which recovers lost capacity.  $\text{Sn}^{4+}$  ions stay in the electrolyte and may be reduced at the negative electrode to  $\text{Sn}^{2+}$  (i.e.,  $\text{Sn}^{2+}$  could run a catalytic process) or even to  $\text{Sn}^0$ .

Another explanation may be the formation of mixed Pb/Sn oxides with high stoichiometry deviation  $\delta$  in the neck region, which would have a very low equilibrium potential. Such a compound would be even more stable with respect to discharge than is  $\text{PbO}_{2-\delta}$ , when  $\delta = \delta_{\max}$  [20]. Unfortunately, there is little knowledge about such mixed Pb/Sn oxides.

The same argument holds with the antimony redox couple  $\text{Sb}^3/\text{Sb}^{5+}$ . Mixed Pb/Sb oxides have been found to be discharged at lower potentials compared to pure  $\text{PbO}_2$  [35,150,151].

#### 4.8. Influence of phosphoric acid on capacity decay

*Summary:* The addition of phosphoric acid to the electrolyte reduces sensitivity of cycling capacity to recharge and discharge conditions (cf. Sections 4.1 and 4.2) [26,27,41,108,148]. This is a more precise wording for the well-known ‘stabilisation of capacity’ effected by this additive [12,25,30,31].

*AOS view:* When phosphoric acid is added to the electrolyte, the recharge reaction is hindered, which can be seen from the increase of the positive overvoltage on recharge. Nucleation is enhanced compared to crystal growth, which leads to a finer crystal structure with many neck interconnections. According to literature data, cycling of the  $\text{PbO}_2$  electrode in electrolyte containing phosphoric acid leads to a finer pore structure with smaller average pore diameter, and to an increased internal (BET) surface of the electrode ([25,27,108] and references therein). In other words: after cycling in phosphoric acid electrolyte, the porous  $\text{PbO}_2$  structure is composed of smaller crystal units.

A finer crystal structure has a lower apparent resistance of the crystalline agglomerate, which explains the stabilisation of capacity [27,108,114].

Calculation of the amount of lead/phosphoric acid compounds, which are formed in the positive electrode, shows that this is much more than the amount of material

which builds up the neck zones of the structure (cf. Section 3.6). Therefore, direct influence of phosphoric acid on the neck zones cannot be excluded [26]. As phosphoric acid is known to reduce shedding of active material [25], which in terms of the AOS model is caused by weakening of the neck zones, a (mechanical and electrical) stabilisation of the neck zones by phosphoric acid compounds has to be assumed [26].

#### 4.9. Influence of acid concentration on capacity decay

*Summary:* Capacity is stabilized (or even improved) when recharge is performed under conditions, when  $\text{Pb}^{2+}$  concentration is low [28]. One of the means to provide this is high acid concentration in the pore system, which can be achieved by high filling acid [103] and by high-rate recharge [28,50,103].

*AOS view:* The beneficial influence on capacity of high acid concentration during recharge has similar origins to the effect of high rate recharge rates (high overpotential, cf. Section 4.1):  $\text{Pb}^{2+}$  solubility is low, and, for kinetic reasons, formation of nuclei is favoured with respect to growth of crystallites.  $\text{PbO}_2$  crystallites are formed of with smaller radius  $R$  than at lower recharge rates. A  $\text{PbO}_2$  structure consisting of smaller crystallites shows a higher conductivity and a higher capacity on discharge [27,108,114].

#### 4.10. Dilatation and shrinkage (‘breathing’) of the $\text{PbO}_2$ structure during cycling

*Summary:* On recharge (and formation), there is an outward-oriented mechanical force acting from the  $\text{PbO}_2$  agglomerate on its environment; on discharge, this force is oriented inwards (shrinkage). As a consequence, the porous  $\text{PbO}_2$  body expands on recharge (and formation), and contracts on discharge [52,106,107,115,123].

The experimental findings seem to be contradictory at first sight to the fact, that the molar volume of the charged material  $\text{PbO}_2$  is higher than that of the discharged material  $\text{PbSO}_4$ . However, one cannot draw conclusions from this fact about the apparent volume of a porous structure with about 50% porosity: there is enough void volume left to compensate for the molar volume increase on discharge. The molar volume increase takes place via a dissolution/precipitation process, which will give little force on the crystallites (at least at low and medium depths of discharge [106]).

*AOS view:* Due to the higher equilibrium there, discharge takes place mainly at the convex regions and conserves the necks. Therefore, the model ‘spheres’ are deformed like a rugby ball [117,118]. Due to the action of the surface tension, the particle shape of minimal energy, i.e., a spherical shape, is approached again, but with lower radius  $R$ . As long as all particles are interconnected, i.e., the neck zones are conserved, the whole aggregate structure will shrink [106,107,114,115,123].

Only at very high depth of discharge the high amount of precipitated  $\text{PbSO}_4$  will disrupt some necks, and then the shrinking tendency is stopped or even reverted [106].

Recharge is the reverse process: electro-crystallisation takes place mainly at the equator of the balls (becoming lenticular), and again surface tension has the tendency to minimise the particle surface. Therefore, a ‘ball’ with greater radius  $R$  is formed, and the distance between the necks increases: the apparent volume of the agglomerate structure increases, which can be measured macroscopically [106,107,115,123].

## 5. Conclusion

When lead/acid batteries are cycled, the active materials of both the positive and the negative electrode undergo a reversible dissolution/precipitation process, which successively changes the structure of these porous electrodes: initial structure information is lost, and the actual structure is mainly determined by the previous operating conditions. Especially with the  $\text{PbO}_2$  electrode, this may induce an increase of apparent electrode volume, changes of particle and pore size distribution, material softening and even shedding, establishment of the so-called coralloid structure or of structural and chemical inhomogeneity near to the current collector—and capacity loss.

The phenomenological term ‘premature capacity loss’ (PCL) has been introduced to summarise phenomena, which may result in an early, unexpected capacity reduction of a battery (significantly before end of its design life), well below its designed capacity. Various technical means have been discussed to retard or even to prevent such capacity losses.

The influence of discharge and recharge conditions ‘history’ on the battery capacity has been known for over 100 years (‘memory effect’), and structural modifications of the  $\text{PbO}_2$  electrode have been investigated for more than 30 years. The increasing interest in low-antimony and antimony-free positive grids alloys have especially encouraged this research work (‘antimony-free effect’).

In the 1980s, the reversibility of many capacity degradation effects of the  $\text{PbO}_2$  electrode was experimentally proven, and these findings have been confirmed in the meantime by various research groups. When extended cycling is performed at low recharge rates and/or at high discharge rates (especially with pulse discharge), or when extended overcharge is applied (especially at a high overcharge potential), a successive capacity decrease can be observed. However, this capacity loss can be successfully reverted when cycling is continued under more beneficial operating conditions, with medium or low discharge rates and (initially) high rate recharge, avoiding any overcharge after the cell has achieved its full SOC. Besides this stepwise capacity recovery over many cycles, a ‘reset’ can

be given to the ‘memory’ within the  $\text{PbO}_2$  electrode either by extended rest times in the fully charged state (especially at elevated temperatures) or by a single full discharge at a very low rate. Capacity is significantly increased again after such a treatment, often up to the previous level. However, when operation is continued under disadvantageous conditions, capacity decay occurs.

Positive electrodes with grid alloys rich in antimony or tin have been found to be less prone to reversible capacity decay effects, and also the addition of phosphoric acid to the electrolyte makes the  $\text{PbO}_2$  electrode much more tolerant with respect to recharge and discharge conditions.

The AOS model is a semi-quantitative theoretical approach to explain these Reversible Capacity Decay effects. Considering the energy of the surface tension of the porous percolating  $\text{PbO}_2$  structure, consisting of particles with mainly convex surfaces, interconnected by tiny bottle-neck like areas with concave surface, this model deduces different local equilibrium potentials  $\phi_{\text{eq}}$  at the  $\text{PbO}_2$ /electrolyte interface, depending on the curvature of the surface. This mixed-potential situation is dominated by the large convex particle surfaces (> 99% of the overall internal electrode surface) which define the overall electrode potential, while  $\phi_{\text{eq}}$  is significantly lower at the neck zones, which are therefore protected from being discharged in most cases. This protection of the interconnection sites from discharge is the precondition for any technical application of the lead/acid battery, because otherwise the individual  $\text{PbO}_2$  particles would lose their mechanical and electrical interconnection during the very first discharge. Dissolution and electro-crystallisation of lead dioxide in these neck zones and its exact stoichiometry  $\text{PbO}_{2-\delta}$ , (with  $\delta > 0$  depending on local potential, acid concentration, and temperature) depend on the cycling condition history control the decrease or increase of the width of the necks, which in turn determines the mechanical and electrical connection between the individual particles and hence the electrical performance of the electrode.

The AOS model provides an interpretation for most of the findings of the capacity decay of  $\text{PbO}_2$  electrodes, and the tendencies which show up when different electrode and cell designs or additives are compared. The influence of operating history on the actual performance is explained, and this cannot be simply overcome by technical means like cell stack compression or other cell designs alone, as it is the active material structure itself which is demolished and rebuilt with every discharge and recharge cycle. The AOS model explains the improvement of cycle life when high-rate (pulse) recharge is applied and the harm which may arise from pulse discharge, and it recommends the avoidance of overcharge. A poor structure leads to an inhomogeneous distribution of current and mass utilization, and it is the origin of capacity loss. Furthermore, the mechanical rigidity is weakened, which leads to mass softening and may lead to mass shedding. However, until this deterioration has proceeded too far, the more benefi-

cial PbO<sub>2</sub> material structure can be reformed, and capacity may be recovered.

The AOS model was proposed in 1988, but it is still under development. It provides a helpful tool to understand phenomena with dissolution/precipitation electrodes like PbO<sub>2</sub>, and to develop strategies to improve the performance and life of those electrodes in batteries.

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