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The lead dioxide electrode

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The recent literature dealing with the redox mechanism of the lead–acid cell positive electrode is reviewed. The basic electrochemistry of lead dioxide in its various polymorphic modifications and states of subdivision is considered in relation to the important aspects of electrode technology of which the major industrial application of the material is the conventional lead–acid cell. The proposed mechanism of the reduction (discharge) of lead dioxide in various acidic solutions are considered in relation to the present state of electrode kinetic theory. The reverse reaction by which lead dioxide is formed and the parasitic intrusion of the self discharge are dealt with as a precursor to the total cyclic process. It is concluded that in a number of respects the mechanisms proposed do not adequately represent the totality of the experimental observations. Such shortcomings are emphasized and extensions to present research are proposed.

1. Introduction

The lead dioxide electrode, especially as the positive electrode (cathode) in the lead–acid battery, has always been of considerable scientific interest. This stems, in the first place, from the central role which the lead–acid cell has played in the development of electrical power sources, and in the second, to the complex chemistry and electrochemistry of lead dioxide itself.

There have been many reviews in this general area, namely those by Vinal [1], Ness [2], Morehouse *et al.* [3], Hoare [4], Burbank *et al.* [5], Ruetschi [6], Voss [7] and Weissman [8], while Pohl and Rickert [9] and Carr and Hampson [10] have concentrated on the lead dioxide electrode. Hill [11] has reviewed the application of diffraction techniques in studies of battery performance.

Over the last fifteen years a number of interesting ideas and theories have been developed which, to a greater or lesser extent, have received scientific approval. The picture is somewhat confusing with regard to a number of important aspects, particularly the polymorph identity and interconversion and, more importantly, the mechanism for the reduction of the dioxide. With the lead battery industry making great changes in the grid alloy constitution, paste compositions and separator materials, together with the introduction of the fully-sealed (recombination) concept, battery effects have resulted which require an explanation not uniquely forthcoming. It was considered that a critical review of the relevant published material would be a positive and necessary contribution to the advancing front of contemporary lead cell electrotechnology. We have reviewed publications (excluding patents) on the positive electrode up to February 1985.

2. Non-stoichiometry of 'PbO_2'

The deviation from exact stoichiometry has been confirmed by several investigators [12–19] and can be represented [20] either by

$$PbO_{2-\delta}(xH_2O)$$

or

$$PbO_{2-y}H_z$$

This deviation, δ, has been determined [21] as a function of the partial pressure of oxygen (P_{O_2}) in the oxide

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$$\delta\alpha[P_{\mathrm{O}_2}(\mathrm{PbO}_2)]^{-1/8.4}$$

and $\delta_{\max}$ (approximately 1.6×10^{-2}) is in agreement with a disorder model containing interstitial protons ($\delta = 2K^{1/4}P_{\mathrm{O}_2}^{-1/8}$, where K represents the equilibrium constant for the hydrogen incorporation reaction).

Possible disorder models of PbO_2 have been proposed [21] involving:

i. Oxygen vacancies.
ii. Interstitial protons.
iii. Quasi-free electrons.

The presence of free electrons (Hall effect measurements give an electron density of $10^{21}\,\mathrm{cm}^{-3}$) [22] in the oxide can be explained by non-stoichiometry or incorporation of hydrogen. Reutschi and Cahan [14] consider that the free electrons are produced by an oxygen deficiency which is possibly caused, in part, by replacement of O by OH. They also report, however, that further removal of oxygen produces a non-conducting oxide with a decreased concentration of free electrons. The conductivity of the oxide (battery material resistivity $= 7.4 \times 10^{-3}\,\Omega\,\mathrm{cm}$) [23] can be increased [24] by approximately 30% by increasing the pH from -1 to $+5$. This corresponds to a change in δ of three orders of magnitude.

Rickert and co-workers believe that oxygen vacancies may be assumed because of the oxygen deficiency [9] (work by Kabanov *et al.* [25] and Schendler [26] is cited as support for this assumption). They propose a model [21, 27, 28], for the oxide, where the presence of interstitial lead is excluded (this is based on work by Bone *et al.* [29]). However, ellipsometry and reflection spectroscopy have been used [30] to show the presence of Pb(II) in the lattice of electrodeposited β-PbO_2 on gold, thus contradicting the earlier work. Further evidence for the involvement of lead in the disorder model has been supplied by neutron powder diffraction studies [31] of PbO_2 taken from positive battery plates. These show a severe cation disorder in α-PbO_2 and near stoichiometry for β-PbO_2. Similar studies by Santoro *et al.* [32] were consistent with the presence of hydrogen in β-PbO_2 (observations indicated the possibility of OH groups); however, these workers were unable to establish unambiguously lead or oxygen deficiencies.

Moseley *et al.* [33] used high resolution transition electron microscopy (TEM) to study the defect structure of PbO_2 and suggested full stoichiometry with respect to oxygen and a small lead deficiency. In a later paper [34] they reported the use of TEM and inelastic neutron scattering to study the relationship between the amount of hydrogen present in the oxide and the difference in analysis figures for total lead and lead (IV). These figures suggest the presence of a proportion of reduced lead, i.e. other than Pb(IV) (probably Pb(II)) and charge balance by a component of the hydrogen. The following formula for the oxide was suggested:

$$\mathrm{Pb}^{4+}_{(1-x/2)}\mathrm{Pb}^{2+}_{(x/2)}\mathrm{H}^{+}_{x}\mathrm{O}_2$$

The results of an investigation of free electron concentration, as a function of the chemical potential of oxygen (in PbO_2), are in agreement with a disorder model having interstitial protons as the dominating disorder (there is evidence that this is common in a large class of metal oxides [35]).

Jorgensen *et al.* [36] obtained neutron diffraction data for β-PbO_2 from plates cycled in D_2SO_4 and H_2SO_4 and concluded that the hydrogen content was 0.21 hydrogen atoms per PbO_2 unit. Their results suggest that at least part of the hydrogen is incorporated in the lead dioxide lattice, and non-stoichiometry is due to a lead deficiency of 3–5%.

Quasi-elastic neutron scattering and X-ray diffraction (XRD) studies [37] of chemical and electrochemical samples of α-PbO_2 and β-PbO_2 (at temperatures ranging from 77 to 550 K) indicate the presence of $\mathrm{O{-}H\cdots O}$ groups which twist the lattice. The authors propose that electrochemically formed PbO_2 is more capable of playing an active role in the electrochemical process due to a more even distribution of protons (favouring conductivity). The question of the situation and form of hydrogen in the oxide also led to the use of X-ray photoelectron spectroscopy [38]. Two kinds of 'adsorbed water' were observed: surface adsorbed and a water or hydroxyl species occupying lattice vacancies.

Simon and coworkers [39–41] used differential thermal analysis (DTA), NMR and mass spectroscopy to follow structural changes in PbO_2 with cycling. They found that the electrochemically inactive PbO_2 obtained from plates cycled to failure was similar to chemically prepared PbO_2, and suggested that the loss of a hydrogen species was connected to the loss of activity and, consequently, capacity. This led them to suggest that the hydrogen species must be involved in the reduction process ($PbO_2 \rightarrow PbSO_4$). However, nuclear diffraction studies [32, 36, 42] and XRD [42] do not support this theory as the observed amount of coupled $O^{2-}/(OH^-)$ and Pb^{4+}/Pb^{2+} substitution is low (0.01 hydrogen atoms per formula unit).

Dawson *et al.* [43], using scanning electron microscopy (SEM), X-ray and thermal analysis, state that the PbO_2 becomes more stoichiometric and less reactive with cycling and the suggestion is made that this is due to the solid state discharge/charge cycle.

Several papers [44–47] have been published by Ricket, Pohl and co-workers in which the PbO_2 electrode is treated as a non-stoichiometric electrode. They state that the following partial currents must be considered:

i. $Pb(\text{in } PbO_2) = Pb^{2+}(aq) + 2e(\text{in } PbO_2)$
ii. $H_2O = O(\text{in } PbO_2) + 2H^+(aq) + 2e(\text{in } PbO_2)$
iii. $H(\text{in } PbO_2) = H^+(aq) + e(\text{in } PbO_2)$

Anodic and cathodic pulse experiments and rotating ring disc electrodes were used to show that on anodic polarization the initial reactions are lead dissolution and oxygen deposition (for cathodic polarization lead deposition and oxygen dissolution) which leads to a change in the stoichiometry of the dioxide. It is only this change that makes it possible for lead and oxygen to be deposited or dissolved (i.e. the Pb^{2+} current is in the opposite direction to that on initial polarization) in the absolute ratio 1:2 under stationary state conditions. They also concluded that the exchange current for oxygen is much greater than that for lead. When a potential is applied to the electrode, a 'stoichiometry changing current' flows (this current can account for up to 1% of total positive capacity) [48] which may be a hundred times the stationary current. Because of the rapid diffusion in the lead dioxide volume during this change it is assumed that hydrogen, in the form of electrons and protons, is the diffusing species and that the stoichiometric changing current is therefore due to incorporation of hydrogen (earlier work by Pohl and Rickert [49, 50] showed that hydrogen can easily diffuse through and 'dissolve' in electrochemically deposited lead dioxide).

On the basis of their work on the concentration, mobility and thermodynamic behaviour of free electrons in PbO_2, Pohl and Schlechtriemen [51] confirm a disorder model of PbO_2 where protons on interstitial sites and quasi-free electrons are the dominating disorder centres. They suggest that hydrogen incorporation occurs by the following equilibrium reaction:

$$Pb^{2+}(aq) + 2H_2O = PbO_2 + 2H(\text{in } PbO_2) + 2H^+(aq)$$

3. Discharge in H_2SO_4

The overall reaction on discharge can be represented by

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e = PbSO_4 + 2H_2O$$

or allowing for the nonstoichiometry:

$$PbO_n + (2n - 1)H^+ + HSO_4^- + 2(n - 1)e = PbSO_4 + nH_2O \text{ [52]}$$

Beck *et al.* [53, 54] state that, as reversibility of the above reaction requires that the total free-energy change is equivalent to the electrochemical work, spontaneous non-electrochemical steps can be excluded in the mechanism. On this basis the following are excluded:

$$H_2O \longrightarrow (OH) + H^+ + e$$

(Electrochemical)

$$PbSO_4 + 2(OH) \longrightarrow PbO_2 + H_2SO_4$$

(Non-electrochemical)

$$PbO_2 + 2e \longrightarrow PbO + O^{2-}$$

(Electrochemical)

$$PbO + H_2SO_4 \longrightarrow PbSO_4 + H_2O$$

(Non-electrochemical)

A great deal of work has been done, using several techniques, to study the physical changes in the active material during discharge or cycling. The initial ratio of α-PbO_2 : β-PbO_2 in a sample of the active material is affected by its method of preparation [55]. Although the difference in reduction potentials (α-PbO_2 = 1.7085 ± 0.0005 V versus SHE and β-PbO_2 = 1.7015 ± 0.0005 V versus SHE in 4.4 M H_2SO_4) [14] means that, at this pH, α-PbO_2 is thermodynamically more reactive [56], the formation of a more finely dispersed $PbSO_4$ film on α-PbO_2 hinders acid penetration [57] and it is therefore β-PbO_2 which contributes most capacity.

The discharge of α-PbO_2 and β-PbO_2 [58] in 0.1 M H_2SO_4 has been examined and a difference and dissolution–precipitation for β-PbO_2. Further support for the dissolution–precipitation is given by:

i. The high electric field required to force Pb^{2+} or SO_4^{2-} across the $PbSO_4$ layer would limit the thickness of the surface layer participating in the reaction to a few ångstrøms, whereas the observed plate capacity demands a thicker reaction layer [59].
ii. Dawson *et al.* [43] conclude that the discharge of β-PbO_2 follows a dissolution–precipitation mechanism at the electrode surface when the overpotential (η) is low, while at high overpotential they conclude that the solid-state reduction of the interior also occurs.
iii. SEM [60] was used to elucidate the processes occurring during the reduction of PbO_2 and it confirmed a solution–precipitation mechanism.

Hampson and co-workers [61, 62] have examined the reduction of β-PbO_2 using stationary and rotating disc electrodes for potential step and linear sweep experiments. They have concluded that the reduction process is terminated by a blocking film of $PbSO_4$, and no evidence of diffusion control via the electrolyte was found whilst using a large excess of H_2SO_4 (at low acid concentrations the discharge reaction is controlled by diffusion in solution, while in stronger acid control changes to the solid phase mechanism [63, 64]. Broad reduction peaks for porous electrodes were interpreted in terms of the reaction being driven more deeply into the pore structure as the front of the electrode becomes more resistive. Work on the reduction of PbO_2 [65] in various concentrations of H_2SO_4 showed that the capacity decreased with increasing H_2SO_4 concentration. It was concluded that the $PbSO_4$ film is mechanically sounder and becomes passivating at smaller thicknesses in concentrated H_2SO_4. The optimum concentration appears to be 1.0 M H_2SO_4 [66]. SEM [67] was used to study microstructural changes at various depths in the porous electrode (during reduction) and the conclusion reached was that the front surface is almost fully utilized early in the reduction sweep (1250 mV to 700 mV in 5 M H_2SO_4).

A microscopic examination [68] of PbO_2 during discharge substantiates the theory of crystallization polarization, i.e. an overpotential required to initiate lead sulphate nucleation, while later work [69] on the reduction of PbO_2 (formed by cycling a pure lead electrode in H_2SO_4) concluded that the electrocrystallization of $PbSO_4$ occurs via progressive nucleation and two-dimensional growth.

By plotting $[PbO(OH)^+]$ versus $[H^+]$, Vanyukova *et al.* [70] have shown that PbO_2 dissolution occurs via the following mechanism:

$$PbO_2 + H_2O = PbO(OH)_2$$

$$PbO(OH)_2 + H^+ = PbO(OH)^+ + H_2O$$

Confirmation of the presence of a soluble Pb^{4+} species during discharge/charge of the positive electrode in H_2SO_4 has been provided by work using a rotating ring-disc electrode [71, 72].

4. Discharge in other electrolytes

In order to overcome the problem of formation of an insulating layer, several workers have investigated the discharge mechanism in acidic lead perchlorate solutions. In a series of papers, Hampson *et al.* [73–76] report investigations of electrochemical reactions at α-PbO_2 and β-PbO_2 in $HClO_4$. Passivation of β-PbO_2 occurs when the capacity for Pb (II) has been exceeded in the electrolyte near the electrode. The mean value of the double layer capacity, C_L, is 79 $\mu F\,cm^{-2}$ (indicating a roughness factor of about 3–4) and the exchange current is 0.17 mA cm^{-2} in 1 M Pb^{2+}, 3 M H^+, 6.85 M total ionic concentration at 25° C. A galvanostatic technique was used [75] to investigate the discharge mechanism of β-PbO_2. As the potential increases, the mechanism changes from a single two-electron step to two successive single-electron transfer steps. It is suggested that the mechanism at high overpotential is:

$$PbO_2 + 2H^+ = PbO_2(H^+)_2ads$$
$$PbO_2(H^+)_2ads + e = [HO \cdot Pb \cdot OH]^+$$
$$[HO \cdot Pb \cdot OH]^+ + e = Pb(OH)_2$$
$$Pb(OH)_2 + 2H^+ = Pb^{2+} + 2H_2O$$

Explanations given for the low reaction order of Pb^{2+} ($\simeq 1$ to $\simeq 0.3$) observed at low [Pb^{2+}] are: adsorption of Pb^{2+} at the electrode, or self-discharge.

The discharge of α-PbO_2 in acid perchlorate solutions [76] is closely similar to that of β-PbO_2 and any differences are explained in terms of an equilibrium process,

$$\alpha\text{-}PbO_2 \rightleftharpoons \left\{\begin{matrix} Pb^{2+} \\ H^+ \end{matrix}\right\} \rightleftharpoons \beta\text{-}PbO_2$$

Carr and Hampson [77] have studied the reduction of α-PbO_2 in aqueous NaOH. The reaction involves the mass transport of OH^- ions by diffusion in solution and the suggested mechanism is:

$$Pb + 2OH^- = Pb(OH)_2 + 2e$$
$$Pb(OH)_2 + OH^- = Pb(OH)_3^-$$
$$Pb(OH)_3^- = PbO + OH^- + H_2O$$

Interest has been shown [78–80] in the effect of phosphoric acid on the positive electrode. Phosphate is reversibly adsorbed on PbO_2 during charge and this modifies the crystal growth on the grid producing a structure which is more difficult to reduce to $PbSO_4$. Failure due to formation of a resistive film at the grid/active material interface is, therefore, forestalled. These effects occur with additions of H_3PO_4 as low as 0.2 wt% and involve the formation of $Pb_3(PO_4)_2$ as an intermediate in the corrosion of Pb to PbO_2.

5. Self-discharge

Self-discharge of the positive electrode can occur via the following reactions:

$$Pb + PbO_2 + 2H_2SO_4$$
$$= 2PbSO_4 + 2H_2O$$
$$PbO_2 + 2H^+ + SO_4^{2-}$$
$$= PbSO_4 + H_2O + \tfrac{1}{2}O_2$$

with pure materials having a slower rate of self-discharge [81].

Bullock and Laird [82] conclude that self-discharge is first order with respect to H_2SO_4 and that there is a change in the predominant reaction, possibly due to formation of tetragonal PbO on the positive grid. Self-discharge, due to short circuit through the separators, is reported by Iliev and Pavlov [83]. $PbSO_4$ crystals form in the separators and are then oxidized or reduced during charging.

6. Charging

Two overvoltage-dependent rate constants control the oxidation of $PbSO_4$ to PbO_2:

i. Rate of formation of nuclei.
ii. Rate of growth.

The overvoltage required to initiate oxidation (nucleation overvoltage) varies from 0.1 V at 45° C to 0.15 V at 15° C [84]. At constant temperature and overvoltage the second rate constant is dependent upon the potential at which the $PbSO_4$ was formed (this controls crystal size). The nature of the solution affects both the rate of formation of nuclei and the rate of growth and, hence, these processes must occur at an interface in contact with the solution.

As there is no interference from diffusion effects, the concentrations of all reacting species at the surface must be constant during oxidation of the deposit. The results of Fleischmann and Thirsk [84] are consistent with an independent acceleration of the reaction by a reduction in the concentrations of SO_4^{2-} and H^+. This supports the following mechanism:

$$Pb^{2+} + 2H_2O = PbO_2^{2-} + 4H^+$$
$$PbO_2^{2-} \longrightarrow PbO_2 + 2e$$

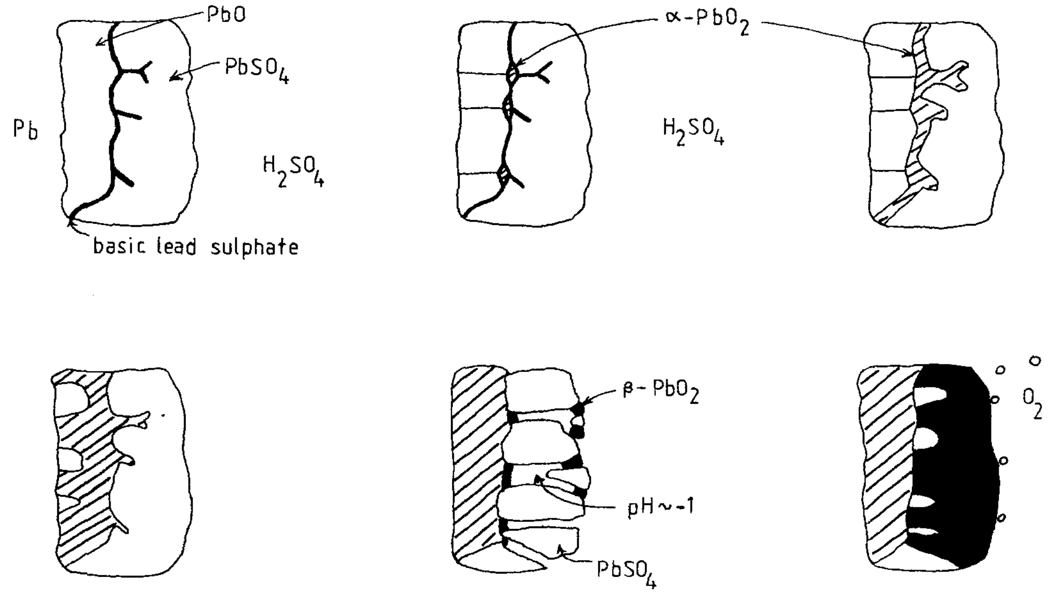

Fig. 1. Schematic model illustrating the formation of PbO_2.

The kinetics of the $PbSO_4/PbO_2$ electrode have been studied by Valeriote and Gallop [85, 86], at temperatures ranging from $-50°C$ to room temperature. They reported 2D nucleation and growth with either progressive or instantaneous nucleation. Linear sweeps between 0.4 and 1.7 V versus Hg/Hg_2SO_4 show a current plateau rather than a peak at temperatures $\geqslant 0°C$, and two peaks $-10°C$ to $-20°C$ (except at fast scan rates). As the temperature is lowered, the first process is inhibited or the second enhanced. The formation of PbO_2 is illustrated by schematic model (Fig. 1) [86]. Formation occurs via the following steps:

i. $PbO \rightarrow PbOH^+ \leftarrow Pb(OH)_2$
ii. $PbOH^+$ diffuses to the lead surface where it is oxidized (local pH $\approx$ 8).
iii. α-PbO_2 grows as filaments into the basic lead sulphate region.
iv. Formation of α-PbO_2 occurs at the expense of PbO. When the PbO has been consumed, the pH rapidly decreases.
v. This leads to β-PbO_2 formation in the pores through $PbSO_4$, and
vi. Consumption of the $PbSO_4$.

At constant potential, the current is controlled sequentially by three diffusion processes ($PbOH^+$, H^+ or OH^-, $PbOH^+$), followed by at least two electrocrystallization stages (α-PbO_2, β-PbO_2) and further intervals of diffusion control. Pavlov and Dinev [87] suggest the following mechanism

$$\text{Pbo} \xrightarrow[\text{Phase}]{\text{Solid}} PbO_n \longrightarrow \alpha\text{-}PbO_2$$

in the pores of a $PbSO_4$ membrane. When this reaches the $H_2SO_4(aq)$, the oxidation of $PbSO_4$ to β-PbO_2 occurs via a dissolution–precipitation mechanism.

In a study [88] of the oxidation of $PbSO_4$ produced by discharge of β-PbO_2, the current–time plot (after a potentiostatic pulse into the oxidation region) showed a simple falling transient indicating that sufficient centres were initially present for growth of PbO_2. This view is supported by Simon *et al.* [89] who believe that the PbO_2 remaining at the end of discharge is surrounded by $PbSO_4$, thus providing a conductive path through the $PbSO_4$ for initial formation of PbO_2 within the $PbSO_4$. Under the conditions used (5 M H_2SO_4) the oxidation was independent of rotation speed, indicating that ionic lead species do not leave the electrode during this process. However, evidence [72] (from rotating ring-disc experiments) has been reported for the existence of soluble Pb(IV) species during charging of the $PbSO_4/PbO_2$

electrode, thus supporting the dissolution–precipitation mechanism.

Pohl and Schendler [90] have investigated the kinetics of growth of PbO_2 on Pb and find that, during an initial period, a closed PbO_2 layer is formed anodically on the lead surface. Subsequent growth follows a parabolic rate law with a 'parabolic tarnishing constant' ($K_{PbO_2} \simeq 10^{-11}\,cm^2\,s^{-1}$). The rate determining step is the diffusion of O^{2-} and electrons through the oxide layer. The growth and nucleation of PbO_2 is, furthermore, dependent on the alloying agent [91], i.e. 3D growth with progressive nucleation on Pb and Pb–Ca–Sn, instantaneous nucleation and intermediate 2-3D growth for Pb–Sb.

7. Effects of cycling

The density of the active material decreases substantially [92] and progressively on deep or shallow cycling, and cycle life can be improved by compression of the active mass [93]. This is due to suppression of the decrease in cohesion between the PbO_2 particles.

Addition of antimony to the positive grid enhances cycle life [94]. The antimony appears to act as a nucleating catalyst for PbO_2 while inhibiting crystal growth. The $PbSO_4/PbO_2$ layer formed on cycling (between 600 and 1250 mV versus Hg/Hg_2SO_4 in H_2SO_4) [91] is thicker on a Pb–Sb or Pb–Ca–Sn electrode than it is on pure lead. Results indicate that the layer on the Pb–Sb electrode has high porosity. The service life is also increased by raising the operating temperature [42] (at low temperatures the discharge is terminated by a voltage drop in the pores of the active material [67]).

Simon and Caulder [95] find that the mode of deposition and the crystal form of $PbSO_4$ changes with increasing cycle life. These workers also state that an 'electrochemically inactive' form of PbO_2 is present and that its concentration increases with cycling. This probably leads to the development of a reticulate structure and might be necessary for the formation of the coralloid structure.

Another possible mechanism for the formation of the reticulate structure is a solid-state reduction process in the interior of the electrode [43]. It is suggested that this process would also reduce the deviation from stoichiometry. The formation of this coralloid structure, with cycling, has been studied by Chang [96]. The structure is initiated at the surface and proceeds into the plate causing the production of larger pores (after 50 cycles pores with diameter $> 25\,\mu m$ were found in the outer electrode).

A correlation has been observed [42, 97] between the initial α-PbO_2:β-PbO_2 ratio and battery cycle life. As the ratio falls early in cycle life (to about 0.16) and then levels off, it is suggested that it is the plate curing/formation conditions, rather than the initial α-PbO_2:β-PbO_2 ratio, that determines the performance. XRD data provide strong evidence that grid passivation by a sulphate layer is a key factor in plate failure along with breakdown in α-PbO_2 and β-PbO_2 electrochemical activity and β-PbO_2 microstructure. In the later paper [42] these workers report that the decline in capacity at all operating temperatures is due to failure on discharge (β-$PbO_2 \rightarrow PbSO_4$), not charge. This suggests that electrical isolation is responsible (grid corrosion becomes more important at higher temperatures).

Matthews *et al.* [64] conclude that the initial increase in the discharge capacity with cycling can be explained in terms of an increase in porosity rather than an increase in the ratio of β-PbO_2 to α-PbO_2 [98–100]. The relative amounts of α-PbO_2 and β-PbO_2 change with cycling: firstly, due to the acid in the environment

$$\alpha\text{-}PbO_2 \longrightarrow PbSO_4 \longrightarrow \beta\text{-}PbO_2 \; [58]$$

and secondly, by a disproportionate reaction

$$\beta\text{-}PbO_2 \longrightarrow PbO_x \text{ (lower oxides } 1 < x < 2)$$

$$PbO_x \xrightarrow{\text{disp.}} Pb^{2+} + \alpha\text{-}PbO_2 \; [101]$$

The concentration of amorphous material (< 100 Å) increases slightly with cycling, while its utilization declines more rapidly than that of crystalline material [102].

Lead dioxide, formed on lead sheet in H_2SO_4, is initially prismatic but it loses its prismatic character with cycling [103]. Restricted cycling (of these positive planté electrodes) in a low state of charge ($< 25\%$) is to be avoided as it makes complete recharging difficult [104] (pasted Pb–Sn–Ca and Pb–Sb electrodes [105] also recharge slowly when fully discharged) and results in deterioration of the electrode structure.

Two limiting structures have been proposed [106] for the active material:

i. 'Agglomerate type' which determines properties and cycle life of the plate.
ii. 'Crystalline type' – this microstructure determines the energy performance and stability of the plate. The conclusion is that during cycling irreversible processes occur along the lines: type i. → type ii. → individual crystallites → softening and shredding → cell failure.

8. Concluding remarks

Deviation from stoichiometry in lead dioxide is dependent upon pH of the surrounding environment or P_{O_2} in PbO_2. The status of the hydrogen species present in the oxide is still undecided. Possible explanations are: formation of OH groups in the lattice (balancing for Pb(II)), or adsorbed water.

Discharge of β-PbO_2 occurs via a dissolution–precipitation process, while that of α-PbO_2 may occur via α-$PbO_2 \rightleftharpoons \beta$-$PbO_2 \rightarrow$, or surface reaction.

A more detailed study is required to determine to what extent Pb^{4+}(aq) is involved.

Cycle life can be increased by:

i. Compression of the active material.
ii. Addition of antimony to the positive grid.
iii. Higher operating temperatures.
iv. Improved plate preparation (correlation of cycle life with initial $\alpha:\beta$ ratio).

Failure occurs by:

(a) Isolation of the active material.
(b) Increase in the ratio of macropores to micropores.
(c) Grid corrosion.

Control of pore size and distribution in positive pastes may well lead to an increase in cycle life. However, further work is required in this area to ascertain the ratio of macropores to micropores which is necessary to maintain reasonable electrolyte flow while decreasing failure due to loss of active material.

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