Journal of Power Sources, *27* (1989) 91 - 117

OXYGEN CYCLE IN SEALED LEAD–ACID BATTERIES

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(Received December 20, 1988)

Summary

This review is concerned with problems associated with the evolution of hydrogen and oxygen and their ionization in sealed lead–acid batteries. The roles of the separator and of admixtures in the battery constituents are discussed in detail, and the possible applications of the batteries are briefly evaluated.

1. Introduction

Several types of sealed lead–acid batteries are now available on the world market. These are distinguished by the condition of the electrolyte, which is either immobilized by the addition of colloidal silicic acid (thixotropic gel electrolyte), or absorbed in a non-woven fabric made mostly from glass microfibers. A lesser number of batteries of this kind contain an excess of immobilized electrolyte and auxiliary electrodes placed in the gas space for the ionization of hydrogen and oxygen [1, 2].

The sealed lead accumulators differ from the classical ones by their construction; they are distinguished by the following main features [3 - 6]:

(a) use of non-antimonial lead alloys (low Sb content: 1 - 2% is a compromise; the presence of Sb in truly maintenance-free batteries is excluded);

(b) immobilization of the electrolyte (gelled electrolyte or electrolyte absorbed in separators);

(c) mechanical strengthening of the constituents (gelled electrolyte or tight assembly of the separator with electrodes);

(d) transfer of ions as well as oxygen through the separator acting as an electrolyte support;

(e) reduction of the "dead" space for sludge and gases (favourable for the energy density, W h dm^{-3});

(f) use of a pressure release valve combined with a moisture separator;

(g) use of controlled charging (initial galvanostatic charging combined with subsequent constant-voltage charging).

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0378-7753/89/$3.50

These new technological features result in improved functional properties:

(a) functioning in any position;
(b) no water addition ("topping up") necessary;
(c) problem-free installation (no explosion hazard);
(d) comparable, or even lower, internal resistance;
(e) lower self-discharge rate;
(f) increased cycle life.

These properties provide new fields of application for lead–acid batteries, *e.g.*, domestic electronic equipment (portable video recorders, portable television sets, electronic flash lights, etc.) where they begin to compete with sealed Ni–Cd batteries and primary cells. The above advantages are accompanied by some disadvantages when compared with classical accumulators, *e.g.*, hitherto low automation of the manufacturing process, limited short-time, high-rate discharges, and lower resistance to deep discharges.

Since the addition of water represents a substantial part of battery maintenance, the term "maintenance-free" normally means that addition of water during the normal service life of a battery is not necessary [5, 7]. According to DIN 43 539, Part 2, the maximum permissible rate of water decomposition for a 12 V automotive battery is 6 g per A h after charging for 21 days at 14.4 V and 40 °C.

Strictly, the term "maintenance" of an accumulator means [8]: periodic addition of water, periodic recharging after an extended storage time because of self discharge, charging immediately after discharge, avoidance of overcharging to prevent antimony poisoning, avoidance of deep discharge and, eventually, purification of the contacts.

In Europe, automotive batteries do not contain non-antimonial grids, reportedly because the demand for maintenance-free batteries is not great enough. Only a few manufacturers use lead–calcium grids, while most producers use grids of low-antimony alloys (1.5 - 2.7% Sb). By using modern glass microfiber separators, which do not contaminate the electrolyte with organic impurities, it should be possible to lower the antimony content in the grids to 1.2%.

According to United Kingdom law, the term "maintenance-free" cannot be used in connection with batteries — even if only cleaning of the contacts is required. Therefore, the term "non-spillable", or the like, is proposed, specifying that no water addition is necessary. At present, British manufacturers use alloys with about 2% Sb and materials free from Fe, Cl, etc.

The term "sealed accumulator" is likewise inaccurate. A lead–acid battery of this sort must, in contrast to sealed Ni–Cd cells, be provided with a pressure release valve permitting the excess hydrogen evolved at full charge or during over-charge to be removed. (Only Ni–Cd cells of higher capacity require a similar valve preventing damage resulting from unskilled charging.) Thus, the term "sealed lead–acid cells" must be understood to mean "valve-regulated, sealed, lead–acid cells" [9].

The so-called gelled electrolyte displays a somewhat complicated behaviour in respect of the transport of ions, and particularly oxygen; the latter is conditioned by the formation of microscopic cracks during partial drying out and solidification of the electrolyte [8, 10 - 14]. From the point of view of an efficient oxygen cycle, absorption of the electrolyte in microfibrous separators seems to be preferable [6], and, moreover, it simplifies production. This is in accord with contemporary production trends. Therefore, in the present review emphasis is placed on systems in which the electrolyte is absorbed in the separators.

2. Basic considerations

A thermodynamic evaluation of the reactions proceeding in a lead–acid battery during charging and overcharging shows that both hydrogen oxidation (on the positive lead dioxide electrode) and oxygen reduction (on the negative electrode) is possible [14]:

$$Pb + HSO_4^- = PbSO_4 + H^+ + 2e^- \qquad E_r = -0.35\ V \tag{1}$$

$$PbO_2 + HSO_4^- + 3H^+ + 2e^- = PbSO_4 + 2H_2O \qquad E_r = 1.69\ V \tag{2}$$

$$H_2 = 2H^+ + 2e^- \qquad E_r = 0.05\ V \tag{3}$$

$$O_2 + 4H^+ + 4e^- = 2H_2O \qquad E_r = 1.28\ V \quad \text{(in 5 M } H_2SO_4 \text{ vs. NHE)} \tag{4}$$

A complicating factor is that the overpotential for hydrogen ionization on the positive electrode is higher than 1.7 V and the overpotential for oxygen reduction on the negative electrode exceeds 1.6 V [14].

The SO_4^{2-} ions are considered by some authors to be the reacting species. The second-stage dissociation constant for H_2SO_4, however, is K_2 = 0.01. Hence, in the region of practical concentrations (1 - 5 M), the dissociation to the second stage can be neglected [15].

The principle of the so-called oxygen cycle (*i.e.*, formation of oxygen at the positive electrode and its reduction at the negative electrode) was studied in detail, after the second world war, in connection with sealed Ni–Cd batteries, and the work carried out in the J. Heyrovský Institute during research on plastic-bonded, non-lamellar electrodes for Ni–Cd cells has contributed to the understanding of its mechanism [16 - 19].

The main conditions for the functioning of the oxygen cycle in sealed Ni–Cd batteries are as follows:

(a) higher negative electrode capacity compared with the positive electrode;

(b) absence of free electrolyte and presence of electrolyte absorbed in the pores of the electrodes and in the separator;

(c) easy transfer of gaseous oxygen from the positive electrode to the negative electrode, which is covered with an electrolyte film (*i.e.*, the presence of gas pores in the separator and a gas space besides the electrode system).

Hence, the oxygen cycle in sealed Ni–Cd batteries proceeds as follows: gaseous oxygen, evolved at the positive electrode during the advanced stage of charging, is transported by convection to the electrolyte film covering the negative electrode where it dissolves and diffuses to the surface of the Cd electrode. It then reacts in one of two possible ways:

(a) the "chemical" mechanism, based on interaction between cadmium and oxygen, *i.e.*, on the corrosion reaction

$$Cd + \tfrac{1}{2}O_2 + H_2O \longrightarrow Cd(OH)_2 \qquad (5)$$

(b) the electrochemical mechanism involving direct electron transfer

$$\tfrac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^- \qquad (6)$$

In addition, the reduction of cadmium hydroxide takes place during charging or overcharging

$$Cd(OH)_2 + 2e^- \longrightarrow Cd + 2OH^- \qquad (7)$$

With increasing oxygen pressure, the role of reaction (6) compared with reaction (7) increases until it becomes, during overcharging, the only cathodic reaction at the Cd electrode.

Under open circuit or during initial discharge, the oxygen cycle continues according to the corrosion mechanism [5]. This can be interpreted as a short-circuited Cd–O_2 cell involving cathodic reduction of oxygen, eqn. (6), and anodic oxidation of cadmium

$$Cd + 2OH^- \longrightarrow Cd(OH)_2 + 2e^- \qquad (8)$$

Thus, the resulting cell reaction is the sum of reactions (6) and (8), *i.e.*, reaction (5).

The oxygen cycle can easily be realized at the negative electrode since the potential for hydrogen evolution on cadmium is at least 100 mV more negative than that for reaction (7), and the excess capacity of the Cd electrode permits the reduction of oxygen before it is fully charged, *i.e.*, before the evolution of hydrogen commences. Therefore, especially with smaller types of sealed Ni–Cd batteries, pressure-release valves are not necessary and the batteries can normally be charged and overcharged for up to several weeks without apparent damage.

With sealed lead–acid batteries, the evolution of hydrogen presents some problems. Oxidation of hydrogen at the PbO_2 electrode proceeds very slowly at a high overpotential, so that it is negligible for practical purposes [14, 20 - 22].

A two stage corrosion mechanism is given in the literature for the oxygen cycle in sealed lead–acid batteries [23, 24]:

$$\mathrm{Pb} + \tfrac{1}{2}\mathrm{O_2} \longrightarrow \mathrm{PbO} \qquad (9)$$

$$\mathrm{PbO} + \mathrm{H_2SO_4} \longrightarrow \mathrm{PbSO_4} + \mathrm{H_2O} \qquad (10)$$

although these probably consist of two partial electrochemical reactions (1) and (4). The resulting reaction, in any case, is:

$$\mathrm{Pb} + \tfrac{1}{2}\mathrm{O_2} + \mathrm{H_2SO_4} \longrightarrow \mathrm{PbSO_4} + \mathrm{H_2O} \qquad (11)$$

The electrochemical mechanism proceeds during charging according to reaction (4) [23]. Reaction (9), which is considered as controlling, is relatively rapid and it is normally controlled by the rate of diffusion of oxygen in the electrolyte [24, 25].

Accordingly, there is a similarity between the oxygen cycles in both systems; they both have different courses during charging or overcharging and during idling or discharging [26].

In the case of sealed lead accumulators, the conditions for the realization of the oxygen cycle are theoretically more favourable than with sealed Ni–Cd batteries; the solubility, C_{O_2}, and diffusion coefficient, D_{O_2}, of oxygen are greater in 5 M H_2SO_4 (lead accumulator electrolyte) than in 7 M KOH (Ni–Cd accumulator electrolyte) [27 - 30a], as is shown in Table 1.

One obstacle to functioning of the oxygen cycle at the lead electrode is the existence of a passivating film (*cf.* Section 5) and the evolution of hydrogen. The first step towards its suppression is to increase the hydrogen overpotential, *i.e.*, to use very pure raw materials (active materials, grids, electrolyte, separators, etc.); in particular the use of antimony as the alloying element is not recommended. A further step involves controlled charging (see Section 6).

The evolution of hydrogen at the lead electrode is undesirable for the oxygen cycle since it represents a competitive reaction (a sort of parasitic current), and, moreover, hydrogen at the electrode surface lowers the partial pressure of oxygen, thus suppressing the reduction kinetics. This problem will be dealt with in more detail in Section 6 together with the inhibition of hydrogen evolution.

On the other hand, the oxygen cycle reduces hydrogen evolution at the lead electrode. The latter is depolarized by oxygen, hence its potential decreases during prolonged overcharging of the sealed lead accumulator [14]. A similar effect is observed if oxygen is introduced into a laboratory sealed

TABLE 1

Solubility and diffusion coefficient of oxygen

Electrolyte	C_{O_2} (mmol l^{-1})	D_{O_2} 10^{-5} ($cm^2\ s^{-1}$)
5 M H_2SO_4	0.65 [27, 28]	0.8 [29]
7 M KOH	0.1 [27, 28, 30]	0.6 [27, 28]

lead–acid cell [26, 30b] during overcharging (at 2.35 V per cell): the oxygen depolarization of the negative electrode causes doubling of the current and a simultaneous shift of the potential of both electrodes to more anodic values [31].

The currents corresponding to oxygen reduction, I_{OR}, and hydrogen evolution, I_H, constitute the total current, I, during overcharge of a sealed lead accumulator, and this is equal to the oxygen evolution current

$$I = I_{OR} + I_H \tag{12}$$

The currents due to evolution of hydrogen and oxygen obey the Tafel dependence on the electrode potential. A deviation from the linear Tafel dependence was observed in the case of oxygen reduction [14].

The efficiency, η, of suppresion of the hydrogen evolution by the oxygen cycle can be calculated as follows [22]:

$$\eta = \left(1 - \frac{I_H}{I}\right) \times 100\% \tag{13}$$

where the value of I_H is found from the hydrogen content of the accumulator's gas space (from the composition and gas evolution rates), and I denotes the mean charging (or overcharging) current. The efficiency η is proportional to the efficiency of the oxygen cycle during cycling of the accumulator [22].

Perhaps the only advantage in the construction of sealed lead accumulators operating on the oxygen cycle is that the capacity of the negative electrode does not have to exceed that of the positive electrode [4] (in contrast to sealed Ni–Cd cells). This is because the evolution of oxygen commences at the positive electrode if it is charged to about 70%, whereas the evolution of hydrogen starts at the negative electrode if it is charged to more than 90%. Thus, excess negative electrode capacity is not used in modern commercial sealed lead accumulators, but rather an excess positive capacity is sometimes used to prolong the life expectancy of the battery [32 - 34].

The removal of evolved heat from a sealed accumulator (mainly the Joule heat) must be considered. During overcharging, the accumulator functions as an electrolyser for the decomposition of water.

First consider a vented cell, where the gases escape into the atmosphere carrying both water vapour and heat. The heat evolution, Q, (in J s^{-1}) in such an electrolyser cell is given by the equation [35]

$$Q = -I\frac{\Delta H}{nF} + IU \tag{14}$$

where I denotes the current flowing through the cell, U is the terminal voltage, ΔH the free enthalpy change for the decomposition of water, equal to 285.8 kJ mol^{-1}, and $n = 2$ is the number of electrons for an H_2O molecule. After setting $U = 2.35$ V we obtain

$Q = 0.87I$ (J s^{-1})

The cumulative evolution rate of $H_2 + O_2$ (in mol s^{-1}) is $3I/4F$ and the heat capacity of the gases (at constant pressure) is 29 J mol^{-1} K^{-1}, hence the heat carried away by the gases at a temperature difference ΔT will be $(3I/4F)$-$29\Delta T$ or

$2.2 \times 10^{-4} I\Delta T$ (J s^{-1})

which is negligible compared with Q in view of the practical values of ΔT.

An analogous calculation shows that the heat carried away by water vapour contained in the gases is also negligible (mean heat of evaporation of water 2385 J g^{-1}, vapour tension above 5 M H_2SO_4 11 mmHg at 20 °C [36], 35 and 94 mmHg at 40 and 60 °C on the assumption of the same temperature dependence as with pure water). At temperatures from 40 to 60 °C the values are in the range 0.016 - 0.047 J s^{-1}.

In the case of an hermetically sealed lead–acid accumulator the overall chemical process during overcharging is zero, hence we set $\Delta H = 0$ in eqn. (14), and the heat evolved during current passage will be much larger:

$Q = 2.35I$ (J s^{-1})

In both cases, the overcharged battery must be cooled with air, and the smaller the battery the more efficient is the cooling (higher ratio of surface area to volume).

Our calculations show the untenability of the opinion that gases escaping from an overcharged battery significantly contribute to the removal of heat [37].

A temperature increase reduces the internal resistance; this leads, at a constant charging voltage, to an increased charging current with more heat generation. In an extreme case the battery may thus be damaged by an effect known as "thermal runaway".

3. Kinetics of oxygen reduction at lead electrodes

Several authors studied the reduction of oxygen on smooth lead electrodes in solutions of H_2SO_4. With a rotating disc electrode they found, in 0.1 - 10 M H_2SO_4, a limiting diffusion current for the cathodic reduction of oxygen in accord with the Levich equation [29, 38 - 40]; the reduction seems to be inhibited by adsorption of SO_4^{2-} ions in the region of lead dissolution [38]. At potentials more negative than −1.0 V against an Hg/Hg_2SO_4 electrode the oxygen reduction current adds to the current of hydrogen evolution, which is independent of the rotation rate of the electrode [29, 40].

Important experimental data are summarized in Table 2. The diffusion coefficient of oxygen, D_{O_2}, was calculated from the Levich equation assuming a four-electron reduction. Since its value in aqueous solution is known

TABLE 2

Data for experiments with the rotating disc electrode

H_2SO_4 conc. (mol l^{-1})	0.1	0.3	3.0
$10^6\ \nu$ ($m^2\ s^{-1}$) [36]	1.014	1.037	1.477
$10^3\ C_{O_2}$ (mol l^{-1}) [28]	1.14	1.06	0.72
$10^5\ D_{O_2}$ ($cm^2\ s^{-1}$) [38]	1.84	1.83	1.08

to be equal to 1.90×10^{-5} $cm^2\ s^{-1}$ [28], the values obtained are real and substantiate the four-electron reduction of oxygen.

From the temperature dependence of the limiting current the apparent activation energy for oxygen reduction was calculated as 13.8 kJ mol^{-1} — evidence for diffusion as a rate-controlling step [29]. The same conclusion follows from a study of the oxygen reduction on a stationary, half-immersed electrode from a lead wire covered with a 6 - 20 μm thick electrolyte film. Another important finding is that the cathodic evolution of hydrogen is enhanced by the presence of oxides on the electrode surface [41].

It is noteworthy that the kinetics of electrochemical dissolution of lead in sulphuric acid was found to be influenced by the presence of oxygen [39] but the mechanism of this effect is not clear.

In studying the electrochemical reduction of oxygen on lead and its alloys Pb–Sb and Pb–Ca–Sn, no influence of the electrode material was found [42, 43].

Since about 1975 studies of oxygen reduction on lead electrodes have been motivated by the realization of the oxygen cycle in sealed lead–acid batteries. It was found that the mechanism of the oxygen cycle was similar to that in Ni–Cd sealed batteries [44], although the evolution of hydrogen at the lead electrode makes a difference.

The current density for the reduction of oxygen at a stationary lead electrode is very low, of the order of 10^{-4} A cm^{-2}, and the thickness of the diffusion layer is of the order of 10^{-2} cm [14]. The current density for the reduction of oxygen on a rotating lead-disc electrode at angular velocities up to 324 s^{-1} is (in a saturated oxygen solution) substantially higher, about 2 mA cm^{-2} [29], and similar values were obtained with a half-immersed lead electrode (film thickness 6 - 20 μm), namely, 1 - 3 mA cm^{-2} [41]. On the other hand, the oxygen evolution rate at the PbO_2 electrode during overcharging is usually much higher (at least an order of magnitude higher charging currents are used). This is why some authors studied the forced transport of oxygen from the positive electrode through the separator into the pores of the negative electrode, as will be discussed in more detail in Section 8.

4. Catalysis of oxygen reduction at lead electrodes

The oxygen evolved in sealed lead–acid batteries is removed either by recombination (reaction with hydrogen to form water) or by the oxygen cycle.

To achieve recombination, the presence of both gases in a stoichiometric ratio, in so-called catalytic plugs containing metals of the platinum group, is necessary. Sometimes, however, other constructional means are used, *e.g.*, the catalyst is placed in the separator, or forms either a floating layer on, or is dispersed in, the electrolyte [14].

The reduction of oxygen in sealed accumulators is governed by a similar mechanism to that at positive electrodes in primary and secondary metal–oxygen cells or in fuel cells. It is natural, therefore, to consider its catalysis with the aim of both increasing the current load during charging and overcharging [18, 19, 46], and improving low temperature charging.

The means of catalysing oxygen reduction in sealed lead batteries, however, are limited as the catalysis must be selective, otherwise hydrogen is catalytically evolved simultaneously. Most of the economic catalysts for oxygen reduction, which are well proven in alkaline media, lower the hydrogen overpotential in acidic media.

The reduction of oxygen in sealed lead accumulators can be enhanced by using an auxiliary electrode or a so-called bifunctional negative lead electrode [2, 27]. Other authors use additives in the electrolyte [47 - 49].

For economic auxiliary electrodes, graphite (*e.g.*, in the form of woven fabric), active carbon, and hydrophobized lead have been verified [1, 2, 14]. The potential of these electrodes is usually controlled by connection to the main negative electrode through a non-linear resistance (diode). This also permits some inexpensive N-4 catalysts (phthalocyanine, tetraazaannulene, porphyrins, etc.), known from the studies of fuel cells, with acid electrolyte, to be used [50].

From the point of view of large-scale production, both the auxiliary electrodes and the bifunctional lead electrodes appear promising. The former may be hydrophobized lead shaped to ensure oxygen access and contact with the bulk of the electrolyte [2]. A bifunctional lead electrode functions both as the battery electrode and as an oxygen reduction electrode. There is an analogy with the cadmium electrode in sealed Ni–Cd batteries. The functioning of bifunctional negative electrodes is, in both cases, conditioned by the formation of a three-phase interface — electrode–electrolyte–gas. This depends on the quantity of electrolyte, the oxygen transfer through the separator, and the structural parameters of the negative electrode [27].

Practical tests of sealed accumulators provided with auxiliary hydrophobized lead electrodes, however, showed a gradual increase of hydrogen evolution at the auxiliary electrode, apparently caused by gradually decreasing hydrogen overpotential. Therefore, research is now more concerned with bifunctional lead electrodes utilizing the transfer of oxygen from the positive electrode through the separator to the negative electrode, as will be discussed in more detail in Section 8.

In recent years, some authors proposed to catalyse the oxygen reduction by doping the electrolyte [49]. They followed the time dependence of the pressure in an hermetically closed glass cell in which a negative lead electrode wetted with the electrolyte was placed. The initial pressure drop to negative values (consumption of the enclosed oxygen) proved the catalytic action of the additive. The pressure then gradually increased owing to hydrogen evolution at the lead electrode.

The time dependence of the pressure, P, was given by the following equation [48]*

$$P = P_O[\exp(-At) - 1] + B(t + t_O)^{1/2} \tag{15}$$

where A, B, P_O and t_O are parameters depending on the experimental conditions; the constant A characterizes the decrease of pressure (reduction of oxygen), B characterizes the increasing portion of the P–t dependence (evolution of hydrogen).

The reduction of oxygen can be accelerated by adding a depassivator to the electrolyte, whereby the evolution of hydrogen and the formation of a passivating layer on the surface of the lead electrode are also suppressed. Efficient organic depassivators are mainly 3,5-diaminobenzoic acid, 2-benzimidazolethiol, and nicotinic acid [48, 51]. Of the inorganic additives, 10^{-5} M Cd^{2+} ions [52, 53] or 100 p.p.m. Sn, As, Sb, or Te [47] all catalyse the reduction of oxygen, but they also lower the overpotential of hydrogen (except for Cd^{2+} ions).

Since the catalytic effect of these additives was studied at the equilibrium potential of the lead electrode (on open circuit) [47 - 49], it is not known how they function in a sealed lead–acid battery during cycling.

5. Passivating layers on lead electrodes

A passivating film is formed on the lead accumulator electrode either during discharge or during the oxygen cycle which may be inhibited by the film.

The formation of the passivating film during the oxygen cycle is given by eqns. (9) and (10). The initially formed oxide is converted to sulphate by contact with the electrolyte, which can react according to the equation [54]

$$(x + 1)PbO + H_2SO_4 + (y - 1)H_2O \longrightarrow PbSO_4{\cdot}xPbO{\cdot}yH_2O \tag{16}$$

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*See also ref. 47 where, however, the term D/P_Ot stands for At.

where the value of x characterizes how basic is the product and controls the equilibrium potential of the lead electrode ($E_r = -0.35$ V at $x = 0$ and $+0.30$ V at $x \rightarrow \infty$). The passivating film favours the evolution of hydrogen during charging [55]. Ellipsometric studies revealed that the rate of growth of the layer follows the stationary diffusion rate of oxygen ($i_d = 1.25 \times 10^{-4}$ A cm^{-2}) [56]. The layer was found to be selectively permeable to hydrogen ions, which are appreciably smaller than O_2 molecules. Therefore, the corrosion of the lead electrode with the evolution of hydrogen can proceed even in the presence of the passivating layer [57], whereas it adversely affects the oxygen cycle.

Similar results were obtained during the reduction of oxygen at a stationary lead wire electrode [41] (Section 5). The cathodic evolution of hydrogen was enhanced by the presence of the passivating layer, whereas the reduction of oxygen was slowed down.

In commercial lead–acid batteries, the problem of the passivating layer is solved by the addition of expanders to the lead electrode, but their influence on the oxygen cycle has not been studied. Some relevant facts are given below.

A list of 350 additives which may influence the mechanical and electrical properties of the negative plates in lead–acid batteries was given by Ritchie in 1947 [58]. These should improve the discharge ability at low temperatures and high current loads. The most popular are lignins, cellulose, and substances containing humic acids. In respect of the oxygen cycle, the expanders should maintain sufficient porosity of the passivating layer to ensure access of ions and oxygen to the lead surface [59].

The problem is that, while the expander prevents passivation of the lead electrode during discharge (during anodic oxidation), it hinders the reduction of $PbSO_4$ during charging [60 - 66]. For example, calcium ligninsulphonate is adsorbed onto the surface of the lead electrode, and free Pb^{2+} ions become more available during anodic oxidation leading to $PbSO_4$. Thus, the discharge properties of the negative electrode are improved. On the other hand, the surface sites for the deposition of lead are apparently blocked by the expander and charging is adversely affected [67]. This results in a cathodic overpotential.

Passivating layers on lead electrodes have also been studied by impedance and infrared (IR) spectroscopy methods. The two techniques were used recently to study the oxygen cycle in sealed lead accumulators [68]. Since the impedance method yields data about the presence and behaviour of product layers on the negative electrodes [69], valuable information concerning the oxygen cycle can be obtained. The rise in the impedance also permits the passivation layer on the lead dioxide electrode to be studied [70 - 72]. The impedance method was further used to investigate the effect of expanders on the anodic oxidation of the negative Pb electrode [73, 74]. Studies of the negative electrodes, using this technique [75 - 77] demonstrated a correlation between the porosity and the degree of passivation on the one hand and the impedance values on the other.

6. Inhibition of hydrogen evolution at the lead electrode

The evolution of hydrogen at the negative Pb electrode is undesirable from the point of view of both self discharge and the kinetics of oxygen reduction. The corrosion (self discharge) reaction involves both the evolution of hydrogen, accompanied by the oxidation of lead, and the oxidation of the positive lead grid [25]:

$$Pb + H_2SO_4 \longrightarrow PbSO_4 + H_2 \tag{17}$$

$$Pb + PbO_2 \longrightarrow 2PbO \tag{18}$$

The hydrogen evolved cannot be reoxidized at the positive electrode at an acceptable rate [14, 20 - 22], and its reaction with $PbSO_4$ [9] or PbO [2] present on the surface of the negative electrode appears doubtful. It is therefore desirable to suppress the evolution of hydrogen as far as possible.

The following provisions have been proposed to minimize the evolution of hydrogen:

(i) replace the Pb–Sb grid alloy with Pb–Ca or Pb–Sn–Ca alloys;
(ii) ensure the purity of all constituents of the sealed battery;
(iii) control the voltage during charging or overcharging;
(iv) make suitable additives to the electrolyte.

Non-antimonial grids with a Ca content in the range 0.06 - 0.1%, and 0.4% Sn, are prepared either by casting or by stretch metal technology [49]. Metals which lower the overpotential of hydrogen must be suppressed as far as possible. The addition of up to 0.05% Sn to Pb hinders the evolution of hydrogen, but at higher concentrations (up to 1.7%) it has a catalytic effect [79]. Conversely, the addition of Ca to Pb up to a concentration of 0.05% promotes the evolution of H_2, then hinders it [80]. The evolution of hydrogen by the corrosion reaction at a porous lead electrode with an alloy grid of 99.7% Pb + 0.2% Sn + 0.1% Ca is negligible at usual concentrations of the electrolyte, and becomes marked only in 52% H_2SO_4 [43].

Since about 1975, various authors began to investigate the inhibition of hydrogen evolution using organic or inorganic additives in the electrolyte. By comparing twenty-four elements it was found that as little as 10 p.p.m. Sb, As, Co, Mn, Ni, or Te enhanced hydrogen evolution at the negative Pb electrode during galvanostatic charging [47, 81, 82]. The underpotential deposition of Cd on lead, however, suppressed the evolution of hydrogen [52]. With bismuth, either no effect was observed [83] or it caused a moderate inhibition similar to Cr, Sn, and Se [47]. Of the organic compounds, a marked inhibition effect was caused by 3,5-diaminobenzoic acid, one of the so-called depassivators [48] (compare Section 4), and by oak sawdust and *o*- and *p*- substituted benzaldehydes, which are assumed to be preferentially adsorbed on the antimony-covered surface of the negative grid [84].

The inhibition of hydrogen evolution was observed under open-circuit conditions and the results must, hence, be judged with care. Hydrogen evolution in a sealed lead–acid battery takes place mainly during charging and overcharging, *i.e.*, at an appreciably more negative potential.

Another method of decreasing the evolution of hydrogen in sealed lead accumulators is by controlled charging. At the beginning of charge, charging proceeds galvanostatically and then at constant voltage. The limit recommended for sealed lead accumulators with gelled electrolyte is 2.30 - 2.35 V [8, 31, 53], which is 0.2 V lower than with the accumulators containing an excess of free electrolyte. This is made possible by the higher charging efficiency of accumulators with gelled electrolyte, in which the oxygen cycle relies on microscopic cracks in the electrolyte [53].

The choice of a suitable charging voltage depends on the potentials of both charging reactions as well as on the evolution of gases at the electrodes. The potentials of the electrodes should lie between the potential of the charging reaction and that of gas evolution. For sealed lead accumulators with electrolyte absorbed in the electrodes and separator, the recommended charging voltage is usually the same as that for the accumulators with gelled electrolyte, *i.e.*, 2.35 V.

For a sealed lead accumulator with grids containing no antimony and with gelled electrolyte, the voltage at which gassing of both electrodes occurs is 250 mV less than when the grids contain antimony. Under cycling conditions this difference rises to 400 mV; the hydrogen overpotential of the lead electrode is lowered by adsorption of antimony coming from the positive electrode. Thus, in a sealed accumulator, the difference between the charging voltage and that which will initiate gassing is larger than in an unsealed cell.

7. Influence of antimony on the oxygen cycle

Anodic corrosion of the positive grid made from a Pb–Sb alloy leads to the formation of SbO_3^- anions, which are transported by diffusion and migration to the negative electrode. Here, they are first reduced to SbO^+ and $SbOSO_4^-$ ions, which catalyse the evolution of hydrogen, and afterwards antimony is deposited on the lead electrode surface [85]. Recent voltammetric measurements have shown that during anodic polarization of the alloy 96% Pb + 4% Sb at -0.36 V against Hg/Hg_2SO_4 in 30% H_2SO_4, antimony passes into the solution in the form of Sb_2O_3 [86].

The current corresponding to hydrogen evolution, or self-discharge of the negative electrode, increases proportionally with the quantity of antimony deposited on the electrode [84, 87, 88] as well as with the content of Sb in the grid. If Sb_2O_3 is added to the electrolyte prior to formation, its effect is much weaker than if it is added afterwards [89].

Figure 1 is a plot of voltammetric curves obtained on a rotating lead disc electrode (6.4 mm dia.) in 5.3 M H_2SO_4 with, and without, the addition of 15 mg l^{-1} of Sb (in the form of $Sb_2(SO_4)_3$) [84]. It can be seen that the evolution of hydrogen, in the potential range shown, only takes place in the presence of antimony.

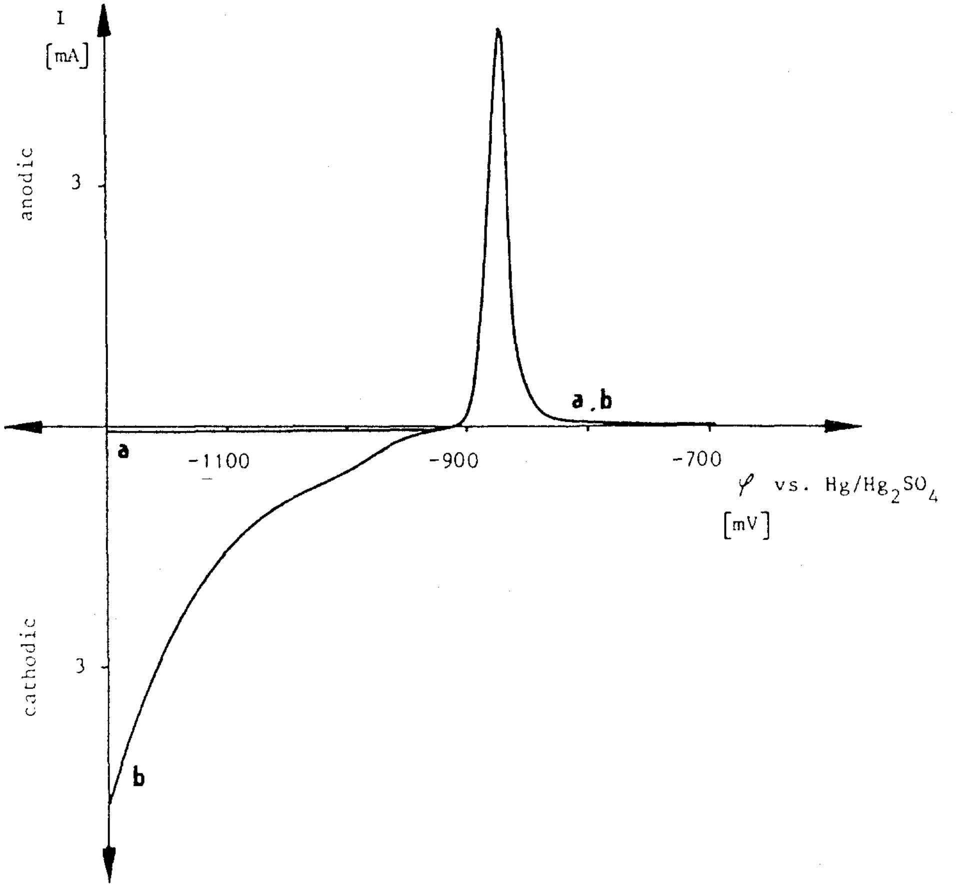

Fig. 1. Linear potential sweep of a lead-disc electrode in H_2SO_4. Curve a, 0 mg l^{-1} of Sb(III); b, 15 mg l^{-1} of Sb(III). (According to ref. 84.)

If, for example, the behaviour of sealed lead accumulators (Sonnenschein, FRG) with grids containing 4% antimony is compared, using the so-called Ford test (charging at 2.3 V per cell), with other containing no antimony, it can be seen that the gassing of cells with non-antimonial grids is ten times lower [8]. Replacing the Pb–Sb alloy (3.5% Sb) with a Pb–Ca alloy, however, markedly decreases the cycle life of the battery (due to the positive electrodes). Therefore, antimony continues to be used for the grids of traction and reserve batteries, which cannot be declared as maintenance-free.

In addition to the marked catalytic effect of antimony on the evolution of hydrogen, a strong catalytic effect on the reduction of oxygen was also observed [47]. It is assumed that pressure measurements could reliably distinguish the catalytic effects on the two reactions (details about the method are given in Section 4). A catalytic effect of antimony on the reduction of oxygen should be accompanied by a similar effect on its anodic evolution, which has been observed [90].

8. Transport of oxygen through the separator in sealed lead–acid batteries

The mechanism of oxygen transport from the positive electrode through the separator to the negative electrode, covered with an electrolyte film, can be described by combining the laws of Faraday (evolution of oxygen during charging or overcharging), Henry (dissolution of oxygen in the electrolyte film) and Fick (diffusion of oxygen to the electrode surface). The transport of oxygen through the separator proceeds by convection. The respective laws can be formulated as

$$m = \frac{IMt}{nF} \tag{19}$$

$$C = kP \tag{20}$$

$$\frac{m}{t} = \frac{DM}{\delta} CS \tag{21}$$

where m denotes the mass of oxygen evolved at time t, I is the current, M the molar mass of oxygen, n is 4, the number of electrons, F Faraday's constant, C is the concentration of oxygen at the film surface, k Henry's constant, P the partial pressure of oxygen, D its diffusion coefficient, δ the thickness of the electrolyte film, and S the effective surface area of the electrode.

On combining the three laws, we obtain

$$I = \frac{D}{\delta} kPSnF \tag{22}$$

It follows from this equation that the rate of oxygen transport is directly proportional to the effective surface area, S, of the lead electrode and inversely proportional to the thickness of the electrolyte film, δ. For a lead electrode saturated with electrolyte, the effective surface area is close to the geometric one. With regard to the real film thicknesses (Section 3), the current due to oxygen reduction is at least an order of magnitude lower than the current consumed in the evolution of oxygen at the positive electrode during charging or overcharging. Therefore, the aim is to increase the effective surface area covered by the electrolyte film, and thus we are led to the role of the separator in oxygen transport.

The role of the separator in sealed accumulators is manifold: in addition to ensuring the transport of ions and preventing the transport of electrons between the electrodes (*e.g.*, in Ni–Cd batteries), it must also permit the transport of oxygen bubbles from the positive electrode to the negative electrode and, eventually, act as an electrolyte reservoir.

The problem of transporting oxygen bubbles through the separator already existed in sealed Ni–Cd batteries, but, surprisingly, it was not dealt with in detail in the literature during the fifties and sixties. The first serious studies in this field were published toward the end of the seventies by workers at Saratov University (USSR) who were motivated by the need to increase the efficiency of the oxygen cycle in sealed Ni–Cd batteries [91, 92]. This can only be done by increasing the rate of oxygen ionization at the cadmium electrode to ensure a dynamic equilibrium with the rate of oxygen evolution at the positive electrode. To this end, the oxygen–electrolyte interface must be increased, since enhancing the kinetics of oxygen reduction by introducing auxiliary electrodes or catalysts brings problems due to their limited stability.

The interfacial area between oxygen and the electrolyte (adhering on the cadmium electrode) can be increased if the separator is provided with gas channels. The oxygen pressure in the gas channels increases during charging or overcharging, causing the electrolyte to be partially expelled from the pores of the cadmium electrode [44], which are then covered with an electrolyte film. Thereby the effective surface area increases and the diffusion path for oxygen in the electrolyte decreases, *i.e.*, the oxygen reduction kinetics are enhanced. This is the so-called internal diffusion regime [91].

The above mechanism of oxygen transport through the separator has been denoted as the filtration mechanism; its role in the overall transport (filtration and transport via the gas space besides the electrode system) is controlled by [91, 92]:

(i) the quality of the separator–electrode contact (adhesion);
(ii) the thickness of the separator;
(iii) the size and number of gas pores in it.

The first study of how a lead electrode–separator combination functions during oxygen reduction in a sealed lead accumulator was published at the end of the sixties [55] (prior to the above-mentioned studies of the filtration mechanism). The separator was made of microporous rubber and was applied to either one, or both, sides of the porous lead electrode. The results showed that the reduction of oxygen at the lead electrode in 1.7 - 9.1 M H_2SO_4 proceeded most effectively when the electrode was in contact with the gas space on one side. Accordingly, the separator function consisted solely of ensuring the transport of ions.

Further works were concerned with the filtration mechanism. With the separators under study, it was found that the fraction of pores filled with oxygen increased with the evolution of oxygen up to a maximum and then decreased [14]. This was apparently due to an increasing escape of oxygen along any flaws between the separator and the electrode, causing a drop in the efficiency of the oxygen cycle. Therefore, it is important for the separator to adhere well to both electrodes leaving only flaws smaller than the pore dimensions in the separator.

Of the different separators, the fraction of gas-filled pores was highest (up to 50%) with asbestos and glass microfibre fabric containing pores similar in diameter to those in the lead electrode. On the other hand, in porous PVC the highest content of gas-filled pores was much lower [14]. Other authors [54] used an electrode system which permitted the rate of oxygen evolution at the positive electrode, and the kinetics of its reduction at the negative electrode, to be controlled potentiostatically. The electrolyte was immobilized in structurally different separators (porous PVC, glass fabric, asbestos, cotton) and a gelled electrolyte was used for comparison. The efficiency of the oxygen cycle was determined by using a relation of the form, eqn. (25), in Section 9 below; its highest value was 32% (with a soft cotton separator), while somewhat lower values were obtained with a soft glass fabric. Porous PVC and hard glass fabric had low efficiencies. The results obtained with the gelled electrolyte were surprisingly good, lying between those of the soft cotton and of the soft glass fabric separators.

In spite of using a low current density for oxygen evolution (down to 1.5 mA cm^{-2}), however, no dynamic equilibrium between the evolution and ionization of oxygen was attained. This is evidence that the role of the internal diffusion regime in the system studied was too low. It was shown later that this was due to an imperfect arrangement of the electrodes and separator leading to escape of oxygen from the measured system.

The problem was dealt with in further work [93] in which the electrodes were tightly sealed at the boundaries in order to prevent oxygen loss. This provision led to an increased efficiency of the oxygen cycle, the results being comparable with sealed lead–acid batteries. The highest efficiency (about 90%) was obtained with separators containing small pores (1 - 2 μm) similar to those in the negative electrode (asbestos, glass microfibres). This permitted optimum filling of both the separator and the negative electrode with the gas (*cf.* ref. 14). Porous PVC was comparable with the free electrolyte having a measured efficiency of about 50%.

The importance of the quality of the separator is also evidenced by the work at Chloride [94] dealing with the wetting and transport properties of glass microfibre separators in connection with the oxygen cycle.

In a separator of this kind the diffusion coefficient of oxygen was measured as a function of the degree of saturation with the electrolyte. At a saturation of 90 - 100% the diffusion coefficient was about 10^{-5} cm^2 s^{-1}, corresponding to the values given in Table 2. In the saturation range 60 - 90%, the value of the diffusion coefficient rose by four orders of magnitude to 0.1 cm^2 s^{-1}, corresponding to the diffusion of oxygen in argon (from literature data 0.2 cm^2 s^{-1}). At saturations below 60%, therefore, the separator behaves as if the electrolyte were completely absent. A saturation between 60 and 90% is recommended for sealed lead–acid batteries with the proviso that the lower limit must be determined with regard to the desired electrochemical parameters (current-carrying capability, capacity, and cycle life).

The conductivity measurements showed [94] that the conductivity of the separator is inversely proportional to the degree of saturation (the dependence is linear in logarithmic coordinates).

The capillary elevation (wicking effect) of the electrolyte was studied in separators placed either vertically or horizontally and with variable compression. The elevation in the vertical position was governed by the Washburn equation (taking into account the counteracting force of gravity). Compression of the separator brings about a decrease of the effective pore radii so that the capillary elevation becomes slower. If the separator is placed horizontally, the wicking effect is governed by the Washburn equation without the gravitational term. Wicking is an important factor, as uniform distribution of the electrolyte over the separator area is essential for proper functioning of the accumulators.

The use of the glass microfibre fabric as separator and electrolyte support in sealed lead–acid batteries appears to be preferred. The material is highly resistant to the electrolyte and the random arrangement of glass fibres with an anisotropic distribution of pores permits the existence of two kinds of pores — those which are perpendicular to the separator plane are markedly larger than those parallel to it. The fibres are perfectly wetted with the acid electrolyte, which is distributed so as to attain the minimum surface energy. It is important for the transport of oxygen that at a low degree of saturation the fine pores are "drowned" first and the larger ones, perpendicular to the separator plane, remain free until the degree of saturation reaches 90% or higher [94].

The use of glass microfibre separators has greatly increased in recent years (since 1980) with a concurrent decrease in price. Separators from glass fibres of variable thickness are also produced (*e.g.*, 20% of 0.9 μm fibres, 70% of 2.9 μm, and 10% of 4.1 μm), containing systems of fine (electrolyte) and coarse (gas) pores [95].

Historically this glass microfibre fabric was originally developed for highly efficient glass filters in the field of nuclear research during the second world war. Later it was used for the purposes of filtration in a broader context, and still later as a light and efficient insulator material in cosmic research. Its use in maintenance-free lead accumulators was patented by the firm Gates Energy Products in 1970 [96].

9. Determination of the efficiency of the oxygen cycle

The efficiency of the oxygen cycle can be determined either gravimetrically or volumetrically.

The gravimetric method [11, 14, 24, 78, 97 - 100] consists of determining the loss of mass, Δm, of a sealed lead–acid battery (due to decomposition of water), which is compared with the maximum possible loss, $\Delta m_{\max}$, calculated from the overcharging current, assuming that the electrolysis of water is the only reaction taking place and that all of the evolved gases escape by the pressure-release valve. The efficiency of the oxygen cycle, η_{OC}, is then calculated as

$$\eta_{OC} = \left(1 - \frac{\Delta m}{\Delta m_{max}}\right) \times 100\% \qquad (23)$$

The method is suitable for cells of low capacity, with which the loss of mass can reliably be determined. The value of η_{OC} can reach values close to 100% [24, 98]. Accordingly, a battery that does not show any loss of mass is considered to be hermetically sealed.

The volumetric method [31, 54, 100 - 102] is more suited for cells of higher capacity and large mass, which cannot be weighed accurately enough. Since hydrogen prevails in the gas space of these batteries, eqn. (13) is used to calculate the efficiency of the oxygen cycle. The efficiency can also be calculated from the following equation based on the modified volumetric method [22]

$$\eta_{OC} = \left(1 - \frac{I_{O_2}}{I}\right) \times 100\% \qquad (24)$$

where I_{O_2} denotes the current calculated from the oxygen content in the gas space of the battery and I is the mean charging or overcharging current. At a controlled voltage of 2.35 V per cell, values of η_{OC} approaching 100% were obtained [22].

It can be shown that eqns. (13) and (24) must give identical results within experimental error. If I_H is eliminated from eqns. (12) and (13), the result is

$$\eta = (I_{OR}/I) \times 100\% \qquad (25)$$

The total current in eqn. (24) is obviously equal to the sum of the currents due to reduction of oxygen and to its increase in the gas space

$$I = I_{OR} + I_{O_2} \qquad (26)$$

On eliminating I_{O_2} from eqns. (24) and (26) we again obtain eqn. (25).

Accurate measurement confirmed that the reoxidation of hydrogen at the positive electrode is negligible. The CO_2 content formed by anodic oxidation of organic material (impurities) from the separator was measured as 0.7 - 0.8% and did not vary appreciably during cycling. The presence of nitrogen was between 2.5 and 6.9% and was due to imperfect sealing and air enclosed in the sealed system; the calculations were corrected for this quantity [22].

According to workers at Sonnenschein [11] the efficiency of the oxygen cycle in sealed lead batteries with gelled electrolyte increases linearly with the nominal capacity, C, between 5 and 20 A h according to the equation

$$\eta_{OC} = 1.66C + 60(\%) \qquad (27)$$

The efficiency of oxygen ionization in sealed lead accumulators during cycling depends strongly on the way in which the electrolyte is immobilized. In the case of the gelled electrolyte, the efficiency hardly varies on cycling and remains high. If the electrolyte is absorbed in the glass fabric, the efficiency is initially low and, during cycling, gradually approaches the same high value as with the gelled electrolyte [14]. This is probably related to the improved mechanical contact between the expanding lead electrode and the separator, which favourably influences the transport of oxygen from the positive electrode to the negative electrode (see Section 8).

10. Characteristics of commercial lead–acid batteries operating on the oxygen cycle

This section serves to illustrate, without giving a complete overview, the sealed, maintenance-free lead accumulators which have been produced.

Some 30 years ago, the West-German firm Sonnenschein introduced a maintenance-free lead accumulator with a thixotropic gelled electrolyte (Dryfit PC, 1 - 36 A h) [103]. It was found later that the oxygen cycle was realized in this battery type during careful charging owing to the formation of microscopic cracks in the electrolyte [8]. It was provided with a pressure-release valve and the electrode grids contained no antimony. During the seventies its production was increased and today it includes batteries of up to 1500 A h capacity either with plate (1 - 200 A h) or tubular (70 - 1500 A h) positive electrodes [104 - 106]. The production of maintenance-free lead accumulators based on the same principle started later at the firm Globe Union with capacity in the range 1 - 30 A h [31]. During the eighties, Globe Union (now the Battery Division of Johnson Controls) enlarged the range of these accumulators, *e.g.*, by 6 V/125 A h batteries for electromobiles with a controlled charging voltage of 2.32 - 2.35 V per cell.

The annual increase in the production of vented and sealed lead–acid batteries is now about 4.5 and 10%, respectively [14]. The latter will probably find more extended application in domestic electronic equipment. In West Germany only 1% of automotive batteries, and about 3% of stationary batteries, are of the maintenance-free type [107].

There is increasing production of sealed lead batteries with the electrolyte absorbed in a relatively thick separator (2 - 5 mm) with a volume porosity greater than 90% for domestic electronic equipment. These are produced in Europe by VARTA (FRG), SAFT (France), Chloride (Great Britain); in U.S.A. by Gates Energy Products, Eagle-Picher, and Gould; and in Japan by YUASA and Japan Storage Association [3]. The energy characteristics of these batteries are 23 - 34 W h kg^{-1} or 50 - 80 W h dm^{-3}.

Three types of maintenance-free battery have been introduced onto the contemporary market by VARTA. These, together with their basic characteristics, are given in Table 3. They are obviously intended for

TABLE 3

Maintenance-free lead–acid batteries (VARTA, FRG)

Designation	“accu Pb”	“accu Pb/R”	“Solid block”
Form	prismatic	cylindrical	prismatic
Main application	portable devices	reserve batteries	stationary batteries
Voltage/capacity[a]	2 - 12 V/1 - 9.5 A h	2, 6 or 12 V/2.7 or 5.2 A h	6 V/80 - 100 A h; 12 V/10 - 60 A h
Casing and lid	shock-proof Terluran[b]	polypropylene and metal envel.[c]	polypropylene
Safety valve	conical	rubber	not known
Grid material	Pb/Ca/Sn	soft Pb	Pb/Ca/Sn
Separator	corrugated plastic foil	glass microfibre web	polyester microfiber web
Electrolyte	thixotropic gel	H_2SO_4 solution (1.3 g cm^{-3})	H_2SO_4 solution
Charging[d] (20 °C)	90% max. $11I_{20}$ and 2.3 V	95% at max. $100I_{20}$ and 2.45 V	90% per 8 - 10 h and 2.27 V
Const. overcharging	I_{100}; 2.35 V (max. 1 week)	not specified	not specified
Self discharge (20 °C)	3% per month	6 - 8% per month	not specified

[a] Nominal capacity at 20 h discharge (I_{20}) to 1.75 V per cell.

[b] An “absorber” is placed between the electrodes and the lid to prevent penetration of the electrolyte into the valve. Electrodes provided with silver tabs soldered to lead contacts. Epoxy resin sealing.

[c] When used as a battery, the lid and bottom are made of plastic.

[d] At constant charging voltage, or a combination of a galvanostatic and a potentiostatic regime.

domestic electronic equipment (up to about 10 A h) and stationary applications (up to 100 A h). Powerful sealed lead accumulators (18 A h) for aircraft are produced by Gates Energy Products (U.K.) [108]. SLI (starting, lighting, ignition) batteries with capacities between 2.5 and 25 A h are produced by Johnson Controls (U.S.A.) [23]. The data show that the capacity of commercial sealed lead–acid batteries has markedly increased during recent years.

In 1986, the Japan Storage Association produced 19 different types of 6 - 12 V sealed batteries of capacity 1 - 24 A h. Whereas in 1973 their production was about two million units, in 1985 it increased to 53 million [109]. The YUASA Battery Company built a branch plant in South Wales during the eighties to supply the European market. Today, the production programme involves 22 types of cells and batteries of capacity 0.7 - 65 A h. The transport of oxygen from the positive electrode to the negative electrode takes place through glass microfibre separators [110]. The previous accumulators of 1 - 8 A h capacity, whose production started in the mid-sixties, employed a combination of porous synthetic resin with glass fibres, soaked with the electrolyte. There was also an intermediate type, whose production started in 1970, with negative electrodes which were extended into the gas space of the accumulator.

The possibility of using commercial sealed lead–acid batteries for photovoltaic systems, *i.e.*, for solar energy storage, was tested by Sandia National Laboratory [78]. Large, sealed batteries with a capacity up to 3000 A h for telecommunications have been developed in Japan [6]; the electrolyte contains relatively little colloidal silicic acid and is absorbed in glass microfiber separators, the charging voltage is only 2.23 V per cell and it is claimed that negligible maintenance is necessary.

A sealed lead accumulator of 2.6 A h capacity for domestic electronic equipment has been developed in the USSR; it contains pasted electrodes with a Pb–Ca grid and gelled electrolyte with 5% Aerosil.

All commercial sealed lead–acid batteries produced today can, in the advanced charging stage, only be charged (or overcharged) at controlled voltage. Their mechanically resistant casing is made of organic polymers, *e.g.*, styrene–acrylonitrile copolymer [107], polypropylene [107], polypropylene with a protective metal envelope [111], butadiene–styrene–acrylonitrile copolymer [6], or shock-resistant Terluran [111].

In all cases, the casing is provided with a pressure-release valve which is activated at overpressures between 3 and 350 kPa according to the battery type [3, 24, 78, 102, 112, 113]. These values are much lower than those of sealed Ni–Cd batteries.

The sealed lead–acid batteries bring some changes in the mass relations between the active materials and the electrolyte compared with the classical ones. Suppose that the combined contents of both active materials and electrolyte is 100 per cent.; the contents of the particular constituents in the main battery types are given in Table 4. The data were recalculated according to ref. 4.

TABLE 4

Mass relations for battery constituents

Electrolyte state	Free	Absorbed	Gelled
Pos. act. mater.	43.6	37.8	39.0
Neg. act. mater.	31.6	40.9	42.3
Electrolyte	24.8	21.3	18.7
Total	100	100	100

As mentioned in Section 2, no negative electrode capacity excess has been used during recent years, hence the data in Table 4 have changed somewhat in favour of the positive electrode. In any case, the capacities of sealed lead batteries, especially of those with gelled electrolyte, are limited by the quantity of electrolyte used.

11. Conclusions

A distinct trend toward increasing application of glass microfibre separators in sealed lead–acid batteries has been observed during the last several years. The grids are made mainly of the alloys Pb–Sn–Ca (for stationary batteries) and Pb–Sb with a low Sb content (for automotive batteries); pure lead is used exceptionally. Contemporary development suggests that sealed lead–acid batteries of relatively low capacity will be widely used, mainly in domestic electronic devices where the lower price of the active material compared with nickel and cadmium is a distinct advantage. The necessity of controlled charging voltage is not a major problem in portable equipment with a built-in current source.

The previous optimistic forecasts about the use of sealed lead–acid batteries as automotive batteries have not been met during recent years for economic reasons. Instead of the earlier "antimony-free" batteries, "low-antimony" batteries are now used. The prospects for the development and use of large stationary and reserve batteries of the sealed type, however, look optimistic.

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