# Methods to Restore the Water Decomposed During Charge and Overcharge of Lead—Acid Batteries. VRLA Batteries

After the introduction of lead-calcium-tin alloys in the manufacture of the grids for lead-acid batteries and the use of inhibitors to the hydrogen reaction on the negative plates, the wet-charged battery technology found wide application in the battery industry. The charging voltage was limited and these batteries were considered to be maintenance free. Their service life, however, depended very much on strictly observing the conditions of charging, especially the maximum charging voltage limit. Battery engineers and manufacturers began looking for methods to recombine the hydrogen and oxygen gases evolved during battery charge and overcharge into water again. Thus, the water loss problem would be resolved, too. Water loss of the cell leads to an increase of the  $H_2SO_4$  electrolyte concentration and hence to passivation of the positive plates. Three principal techniques have been developed for the recombination of hydrogen and oxygen to water, and these will be discussed further in this chapter.

# 14.1. Recombination of Hydrogen and Oxygen into Water Using Catalytic Plugs

The progress of power industry, telecommunication technology and military equipment during the past decades has increased the need for ample amounts of reserve (back up) energy and power. The cheapest source of reserve (back up) power is the lead—acid battery. Hence, production of stationary lead—acid cells with high capacity for use in multicell arrays for standby operation has increased significantly. However, the maintenance of these batteries, i.e. to monitor and sustain the necessary electrolyte level in the cells, requires highly skilled and trained personnel, and is fairly expensive. The first attempts to resolve this problem were aimed at recombining hydrogen and oxygen by the use of a catalytic plug. This technique found a wide application and was rapidly developed during the 1950s and through the 1970s.

It was based on the following chemical reaction:

$$2H_2 + O_2 \rightarrow 2H_2O_{vapour} + 114 \text{ kcal}$$
(14.1)

$$H_2O_{vapour} \rightarrow H_2O_{liquid} + 9 \text{ kcal}$$
 (14.2)

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Both the chemical reaction (14.1) and the phase transition (14.2) are exothermic processes and a considerable amount of heat is generated, which poses a serious problem to designers and engineers, namely how to evacuate the heat released within the small volume of the catalytic plug. If the rate of the reaction between hydrogen and oxygen increases abruptly, the temperature in the plug may reach values of up to 430 °C, i.e. the ignition point of the gas mixture, and an explosion may occur. In order to prevent this to happen, a number of various catalytic plug designs have been developed. Three of these are presented in Fig. 14.1 [1–4].

The basic principles taken into account in the design of catalytic plugs include the following:

- To provide high catalyst surface for the reaction between hydrogen and oxygen to proceed, and to rapidly return the recombined water back to the electrolyte so as to sustain high efficiency of the catalyst.
- To ensure intense heat exchange between the catalytic plug and the ambient atmosphere, so as to prevent overheating of the plug and ignition of the gas mixture.
- To restrict the catalytic reaction to proceed up to a definite temperature, lower than the ignition point of the H<sub>2</sub>/O<sub>2</sub> mixture, and if this temperature limit is exceeded to vent out the unreacted hydrogen and oxygen gases to the ambient atmosphere and thus prevent further temperature rise; when the maximum temperature limit is reached, an electric signal is sent to the charging device to reduce the charging current and thus it slows down the evolution of hydrogen and oxygen, or to stop charging altogether.

The efficiency of the catalytic plug depends mostly on the type of catalyst used. Generally, metals of the platinum group (platinum, palladium, ruthenium) are used for the purpose. Oxygen and hydrogen are adsorbed onto the catalyst surface and a series of chemical reactions proceed between them, with the formation of a number of intermediate products ( $H_2O_2$ ,  $OH^-$  and others), until water is formed at the end. For this recombination reaction to proceed at a high rate, the catalyst should have a high surface. It is therefore deposited onto a carrier with a high surface and resistance to high temperatures. The very first catalyst carrier used was asbestos, which was later substituted for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, vitreous silicate (SiO<sub>2</sub>), and lately some types of carbon have proved to be very efficient catalysts of this reaction.

The catalyst efficiency is measured by the ratio of the volume of restored (recombined) water in the plug vs. the volume of the decomposed water. Watanabe and Yonezu have determined the gas recombination efficiency of some catalyst materials as a function of the overcharge current [5]. Figure 14.2 shows the obtained results.

It is evident from the data in the figure that the highest efficiency in recombining hydrogen and oxygen to water is observed when palladium is used as a catalyst. The platinum—ruthenium catalyst exhibits the lowest catalytic activity.

For a full recombination of hydrogen and oxygen by the chemical reaction (14.1), the two gases should be evolved in a stoichiometric proportion in the cell (2:1). This ratio is sustained in the



Figure 14.1:

(a) Catalytic plug from VARTA [1]; (b) Catalytic plug from Japan storage battery [2]; (c) Aquagen catalytic plug from Hoppecke [3,4].

battery when fully charged and during the period of overcharge. This is not the case, however, when the battery has been cycled, discharged and is in the process of charge. Under these conditions, oxygen evolution starts on the positive plates when the battery reaches 70% state of charge (SOC). The evolved oxygen increases the pressure in the cells above the critical level and when it is vented out results in water loss. When the cell (battery) is charged to 92–95% SOC, a reaction of hydrogen evolution starts on the negative plates. The evolved hydrogen and oxygen



Figure 14.2:

Oxygen and hydrogen recombination efficiencies for different catalyst plugs as a function of overcharge current [5].

gases form a  $H_2/O_2$  mixture in the space above the active block. This gas mixture enters the catalytic plug where the recombination reaction proceeds. With increase of the hydrogen content in the mixture the rate of this reaction increases to reach a maximum value when a stoichiometric ratio between the amounts of the two gases is reached. This process leads to a increase of the generated heat and hence causes the temperature in the plug to rise. The heat exchange between the catalytic plug and the surrounding medium is intensified until a stationary rate of the recombination reaction, and hence a stationary plug temperature, is reached.

The reaction between hydrogen and oxygen produces water. The latter covers the surface of the catalyst and thus retards the reaction of water recombination. To avoid the formation of a water film on the catalyst surface, the catalyst carrier is treated with a hydrophobic substance, e.g. PTFE (polytetrafluoroethylene or teflon). The condensed water runs down draining paths back into the cell. The plug may be fitted with a stopper as well to prevent the  $H_2SO_4$  electrolyte to get into the plug and to deactivate the catalyst.

When the plate grids were cast from alloys containing above 6.0 wt% of Sb or above 0.2 wt% of As, at cell voltages higher than 2.40 V, stibine (SbH<sub>3</sub>) or arsine (AsH<sub>3</sub>) formed on the negative plates. These gases reacted with the catalyst and poisoned it. Various methods were proposed to remove SbH<sub>3</sub> and AsH<sub>3</sub> from the H<sub>2</sub>/O<sub>2</sub> gas mixture. The introduction of lead—calcium—tin alloys for the manufacture of the grids has proved to be the most effective solution to the above problem.

Sometimes, hydrogen sulfide ( $H_2S$ ) is generated on the negative plates by the reduction of sulfur-containing particles. The latter may be obtained under extreme conditions of charging. Hydrogen sulfide has a strong poisoning effect on the catalyst. Absorbents of  $H_2S$  may be introduced on the gas path to the catalyst if there is a probability of such processes to occur.

Catalytic plugs have undergone significant development and improvement in terms of both construction and functional efficiency, as well as with regard to reliability and safety of operation. At present, catalytic plugs are highly efficient and reliable, but fairly expensive, too. Their increased application in remote area and photovoltaic battery systems calls for further improvement of these devices.

# 14.2. Recombination of Hydrogen and Oxygen to Water on Auxiliary Catalytic Electrodes

This method is based on electrochemical reduction of oxygen in a closed oxygen cycle (COC) and electrochemical oxidation of hydrogen in a closed hydrogen cycle within the cell. The above electrochemical reactions proceed on auxiliary catalytic electrodes partially immersed in the electrolyte and connected by means of electronic devices (ED) to the negative electrode (for oxygen reduction) and to the positive electrode (for hydrogen oxidation), respectively. A schematic diagram of a lead—acid cell with auxiliary catalytic electrodes is presented in Fig. 14.3.



#### Figure 14.3:

Experimental lead—acid cell with auxiliary electrodes with tungsten carbide (WC) used as catalyst. ED1 and ED2 are electric devices [10].



Figure 14.4:

Volt-ampere characteristics of H<sub>2</sub> and O<sub>2</sub> reactions on partially immersed electrodes containing different catalysts: (•) WC (200 mg cm<sup>-2</sup>); (o) WC + C (200 mg cm<sup>-2</sup> + 10 mg cm<sup>-2</sup>); (x) C + Pt (100 mg cm<sup>-2</sup> + 6 mg cm<sup>-2</sup>). Temperature 30 °C; H<sub>2</sub>SO<sub>4</sub> with 1.28 rel.dens. [11].

The auxiliary electrodes intended to facilitate the reduction of oxygen comprise of, for example, carbon-teflon porous mass catalyzed with silver [6,7] or phthalocyanine [8]. Ruetschi and Ockermann have established that both hydrogen oxidation and oxygen reduction can proceed on the same auxiliary electrode [9]. In our institute, we developed auxiliary catalytic electrodes with tungsten carbide (WC) or a mixture of WC and active carbon as catalyst [10–12]. Figure 14.4 presents the volt-ampere curves of the hydrogen and oxygen reactions on partially immersed auxiliary electrodes with different catalysts: WC alone, or WC plus active carbon (WC+C), or platinum (Pt) [10–12].

The data in the figure indicate that the catalytic activity of the WC+C electrode towards oxygen reduction is commensurate with its activity towards hydrogen oxidation. Active carbon added to the WC enhances the electrode's catalytic activity with regard to both reactions. Electrodes catalyzed with Pt are twice more efficient than the WC and WC+C electrodes, but they are much more expensive as well. Hence, we focused our attention on the WC+C catalytic electrodes. Further in this chapter, we will discuss the behaviour of WC-based auxiliary catalytic electrodes during operation of 12 V/82 Ah cell.



**Figure 14.5:** Changes in cell voltage and oxygen and hydrogen currents during charge [12].

### 14.2.1. Cell Charge

Figure 14.5 illustrates the changes in cell voltage and in the current of the oxygen and hydrogen reactions during charge [12]. Following a partial discharge, the cell was charged with a current of 2 A and the cell voltage, as well as the currents on the WC1 and WC2 electrodes were measured. During cell charge, the current in the outer circuit is distributed as follows:

$$I = (I_{\rm Pb} + I_{\rm H_2})_{\rm Pbplate} + (i_{O_2})_{\rm WC1}$$
(14.3)

$$I = (I_{PbO_2} + I_{O_2})_{PbO_2plate} + (i_{H_2})_{WC2}$$
(14.4)

At the beginning of charge, no hydrogen nor oxygen is evolved:

$$I_{\rm H_2} = 0$$

and

 $I_{0_2} = 0$ 

Since the resistance of the electronic devices ED1 and ED2 is high, the entire current is utilized for charging the plates. When the positive plates reach 70% SOC, oxygen evolution starts, i.e.  $(I_{O_2})_{PbO_2plate} > 0$  and the total current *I* is distributed as follows:

$$I = (I_{\rm PbO_2} + I_{\rm O_2})_{\rm PbO_2 plate}$$
(14.5)

$$I = (I_{\rm Pb})_{\rm Pbplate} + (i_{\rm O_2})_{\rm WC1}$$
(14.6)

The current of the oxygen reaction  $(i_{O_2})_{WC1}$  increases (Fig. 14.5).

When the negative plates are charged to 95% SOC, hydrogen evolution starts and  $(I_{\text{H}_2})_{\text{Pbplate}} > 0$ . The total current of the negative plates is distributed as follows:

$$I = (I_{\rm Pb} + I_{\rm H_2})_{\rm Pbplate} + (i_{\rm O_2})_{\rm WC1}$$
(4.3)

The generated hydrogen recombines with part of the evolved oxygen on the WC1 and WC2 electrodes, whereby the current  $I_{0,2}$  decreases.

When the PbO<sub>2</sub> and Pb plates are fully charged, the charge currents become  $I_{Pb} = 0$  and  $I_{PbO_2} = 0$ . In this case:

$$I = (I_{\rm H_2})_{\rm Pbplate} + (i_{\rm O_2})_{\rm WC1}$$
(14.7)

$$I = (I_{O_2})_{PbO_2plate} + (i_{H_2})_{WC2}$$
(14.8)

Figure 14.5 shows that after reaching full charge, the currents  $(i_{O_2})_{WC1}$  and  $(i_{H_2})_{WC2}$  are very low, which indicates that the total amount of hydrogen and oxygen has recombined on the WC1 and WC2 electrodes.

The above equations are valid for the case when hydrogen and oxygen are produced in stoichiometric amounts. However, about 1-2% of the evolved oxygen diffuses through the corrosion layer on the positive grid and oxidizes the grid metal, thus the stoichiometric ratio between hydrogen and oxygen is disturbed. This leads to slow accumulation of hydrogen in the cell. To prevent increase of the gas pressure in the cell, the latter should be furnished with a valve which opens at a given pressure and lets the gases out of the cell.

As can be seen in Fig. 14.5, the maximum appears in the  $(i_{O_2})_{WC1}$  curve always at the end of charge. This peculiarity in the behaviour of the oxygen reaction current may find practical application, namely the WC1 electrode can be used as a sensor indicating the end of charge. The obtained electric signal can be transmitted to the control unit of the charging device for the latter to reduce or stop the charging current.



**Figure 14.6:** Changes in cell pressure during discharge [12].

# 14.2.2. Cell Discharge

During discharge, evolution of hydrogen and oxygen on the Pb and PbO<sub>2</sub> electrodes stops and the gases which are already released continue to recombine on the WC1 and WC2 electrodes, which leads to decrease in gas pressure in the cell and eventually to formation of vacuum. To avoid gas leakage into the cell, in our tests the cell was placed in a sealed chamber. The pressure in the chamber and the hydrogen and oxygen currents ( $i_{H_2}$  and  $i_{O_2}$ ) flowing through the WC1 and WC2 electrodes were measured. The changes in cell pressure during discharge are presented in Fig. 14.6.

It can be seen that after 6 h, a high vacuum is created (500 mm Hg), which is sustained throughout the subsequent discharge. No changes in the  $i_{H_2}$  and  $i_{O_2}$  currents are observed. It was established that, under the action of the vacuum formed during discharge, the pores of the WC1 and WC2 electrodes were filled with electrolyte, as a result of which the catalytic activity of the two electrodes declined. It is, therefore, essential that a safety valve is mounted in the cell lid that will let air into the cell when the vacuum reaches a value of 30 mm mercury.

# 14.2.3. Open Circuit

When, during overcharge, the current is switched off, hydrogen and oxygen evolution stops, but the processes of recombination on the catalytic electrodes continue. The pressure in the cell decreases, as during discharge. Moreover, due to the potential differences between the Pb and WC1 electrodes, respectively the PbO<sub>2</sub> and WC2 electrodes, self-discharge processes may

occur in the cell. The negative plates are most affected by the self-discharge processes as a result of which hydrogen is evolved.

Tests of high-capacity stationary cells with auxiliary catalytic electrodes were conducted at a number of battery plants, but on grounds of certain technical and economical considerations, this method of recombination of hydrogen and oxygen has not found wide practical application in the battery industry.

# 14.3. Valve-Regulated Lead—Acid Batteries (VRLAB)

# 14.3.1. General Principles of VRLAB Design and Operation

The general principle of operation of valve-regulated lead—acid batteries can be summarized as follows:

- Water decomposition at the positive plates results in evolution of  $O_2$  and formation of  $H^+$  ions.
- $O_2$  and  $H^+$  ions diffuse to the negative plates through gas and electrolyte channels in the separator.
- Reaching the negative plates, oxygen is reduced and reacts with hydrogen ions to form water.
- The thus produced water diffuses through the separator to the positive plates, thus restoring the water decomposed by electrolysis.

The above processes form the so-called closed oxygen cycle (COC). The latter reduces substantially the water loss during charge and overcharge of the battery, making it maintenance-free.

There are two basic technologies employed in VRLA batteries depending on the type of separator used and the electrolyte state:

(1) Batteries with absorptive glass mat (AGM), in which the electrolyte is absorbed by the AGM separator. Absorptive glass mat comprises up to 85% borosilicate glass microfibres with a length of 1-2 mm and 15% polymer fibres (polyethylene, polypropylene, etc.) used as reinforcement binders. The glass fibres are hydrophilic and absorb electrolyte, whereas polymer fibres provide mechanical strength to the separator as well as partial hyrophobicity, which facilitates the formation of gas channels.

At the beginning of operation of this type of VRLA battery, 95% of the AGM pores are filled with electrolyte and the remaining 5% form gas channels along which the oxygen flows between the two plates. With time of cycling, the battery loses water and the saturation of the AGM separator with electrolyte gradually decreases to 90%, then to 85%, etc. Consequently, the efficiency of the COC increases, which, however, is associated with thermal problems and leads eventually to capacity decline.

(2) Batteries with gelled electrolyte (gel batteries), in which the electrolyte is immobilized in the form of a tixotropic gel of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> particles, several nanometers in diameter. An additional polymer separator, like the ones used in flooded batteries, separates the positive from the negative plates. At the beginning of operation of gel batteries, they behave like flooded batteries (with liquid electrolyte) and lose water. As a result of this water loss, the gel shrinks and cracks are formed in it. These cracks provide open paths for the oxygen evolved at the positive plates to reach the negatives and thus the COC starts to operate, as a result of which the water loss stops. The mechanism of operation of the COC in VRLA batteries is the same, irrespective of the type of separator system used (AGM or gel/separator).

The cells in VRLA batteries have a pressure relief valve (instead of the gas vent in flooded batteries) which sustains a definite pressure in the gas space above the active block comprising plates and separators. The reaction of oxygen reduction at the negative plates significantly reduces the oxygen gas pressure in this part of the active block. A diffusion gradient forms in the active block, which directs the oxygen flow towards the negative plates. The pressure relief valve is, therefore, a mandatory component in the construction of valve-regulated lead—acid batteries.

In this chapter, we will focus our attention mostly on VRLAB with AGM separator. In the 1970s, McClelland and Devitt invented the first valve-regulated lead—acid cell with electrolyte immobilized in microporous glass mat with gas channels in the AGM and a safety valve mounted on the cell lid, and thus forced the COC to proceed within the active block [13]. Figure 14.7 presents a schematic diagram of the transport of oxygen,  $H^+$  ions and water between the two



Figure 14.7:

Schematic representation of the internal COC in a valve-regulated lead-acid cell [14].

plates of opposite polarity [14]. The oxygen flows move along two paths: (1) along the open gas channels through the AGM separator and (2) dissolved in the electrolyte, moves along electrolytic channels filling pores of a definite diameter. The diffusion coefficient of oxygen in the gas channels is six orders of magnitude higher than the oxygen diffusion coefficient in the electrolyte. Hence, the flow of oxygen dissolved in the electrolyte is ignored as being negligibly small.

Further, in this chapter we will discuss the processes that occur in a VRLA battery: (a) during charge between 70% and 95% SOC, when the battery is charged and the COC operates; and (b) during overcharge, when the reactions of the COC mostly proceed.

### 14.3.2. Reactions that Proceed in VRLA Cells During Charge and COC

Figure 14.8 presents schematically the electrochemical reactions involved in the charge process and in the COC in a VRLA cell between 70% and 95% SOC. The reactions are stoichiometric so as to preserve the electroneutrality of the cell. The total cell current *I* is distributed between the two types of reactions as follows: (1)  $(1-\theta)I$  is the current utilized for charging the cell and (2)  $\theta I$  is the current of the reactions involved in the COC. These are the basic processes that take place during cell charging with operating COC. Besides these reactions, the other processes occur as well, at a very low rate are as follows:

- *Positive grid corrosion.* The oxygen evolved on the positive plates penetrates through the interface grid/active material and oxidizes the lead alloy of the positive grid (see Chapter 2.11, p. 91). The rate of this process depends on grid alloy composition, cell temperature, positive plate potential and battery duty.
- *Corrosion of negative plate lugs and connecting strap.* In flooded batteries, these components of the negative active block are wet or partially immersed in electrolyte. This thin



#### Figure 14.8:

Schematic representation of the electrochemical reactions that proceed in a VRLA cell during charge and those involved in the COC.

electrolyte film is electroconductive, so the potential of these components is close to that of the negative plates, hence the plate lugs and the strap are cathodically protected [15]. In VRLA batteries, the electrolyte is absorbed in the AGM separator and the strap and lugs of the negative plates are exposed to oxygen containing atmosphere, conditions facilitating greatly the corrosion processes. The straps for lead—acid batteries are commonly cast from Pb-0.8/2.5 wt% Sn alloys. A description of the corrosion of VRLAB straps is provided in Chapter 4.6 (p. 199) of this book. The process of strap and plate lug corrosion consumes part of the oxygen that would otherwise take part in the COC, which leads to certain, though minimum, water loss.

- Oxidation of the organic expander component (lignosulfonate). When exposed to oxygen attack at temperatures higher than 40 °C, the rate of lignosulfonate disintegration is accelerated considerably, which leads to the formation of CO<sub>2</sub> and H<sub>2</sub>O. With time of polarization, the concentration of CO<sub>2</sub> in the gas mixture increases. Part of these gases are vented out to the atmosphere, which results in the loss of oxygen and water.
- Hydrogen evolution. Although, theoretically, no hydrogen evolution is expected to occur within the above SOC range (70–95%), and hence the balance of the reactions in Fig. 14.8 should remain unaffected, this is not always the case in practice. There are certain impurities in the grid alloys or in the electrolyte which deposit on the surface of the negative plates forming active centres of lower overpotential of hydrogen evolution. Hence, generation of hydrogen starts in these centres, though, at a low rate. Consequently, the balance of the reactions in Fig. 14.8 is disturbed, which results in (though small) water loss. This effect of hydrogen evolution on the negative plates can be alleviated by its oxidation, even at a low rate, on the positive plates, thus forming a hydrogen cycle [16–18].
- *Reduced electrolyte stratification.* In flooded batteries, gravitation causes the formation of vertical layers of different electrolyte concentration (i.e. electrolyte stratification). This creates potential differences between the top and bottom parts of vertical cells [19] and leads eventually to slow self-discharge processes. In VRLA batteries, the electrolyte is immobilized, which allows the cells to be positioned (mounted) horizontally as well. Thus, the degree of electrolyte stratification is reduced substantially and hence the service life of the cells is extended.

Having made this overview of the processes that occur in VRLA cells during charge, we can distinguish four groups of zonal processes that deserve to be discussed in more detail. These are (a) processes on the positive plates; (b) processes on the negative plates; (c) transport processes through the separator and (d) thermal processes in VRLAB.

# 14.3.3. Behaviour of the Positive Plates in VRLABs During Charge and Oxygen Cycle

Figure 14.8 presents a scheme of the basic reactions that proceed on the positive plates at between 70% and 95% SOC. It is interesting to disclose the mechanism of these two



Figure 14.9:

Changes in positive plate potential and in intensity of the diffraction lines for  $\beta$ -PbO<sub>2</sub> (3.50 Å) and for PbSO<sub>4</sub> (3.00 Å) during charge [20].

types of reactions (charge reactions and COC reactions) and to establish how they are interrelated.

Our research team investigated these processes employing X-ray diffraction analysis in combination with potential measurements of the positive plates vs.  $Hg|Hg_2SO_4$  reference electrode [20]. The changes in crystallinity of the lead dioxide active material (PAM) were followed during charge and discharge of cells with one positive and two negative plates. Samples were taken from the positive active material and X-rayed, as taken out of the cell with  $H_2SO_4$  solution on it, and then the solution was washed away with water. Figure 14.9 shows the

changes in positive plate potential and in intensity of the characteristic diffraction lines for  $\beta$ -PbO<sub>2</sub> (3.50 Å) and for PbSO<sub>4</sub> (3.00 Å) during cell charge. The abscissa represents both the real time in minutes and the SOC. The latter is expressed by the ratio between the quantity of electricity that has passed during charge vs. the quantity of electricity obtained during the previous discharge,  $C_{\rm ch}/C_{\rm disch}$ .

The following conclusions can be drawn from the data in the figure:

- The PbSO<sub>4</sub> diffraction line intensity decreases linearly with time, the slope being the same for the two types of measurements, up to the 240th minute of charge. This is a period that corresponds to full oxidation of the PbSO<sub>4</sub> formed during the preceding discharge.
- The intensity of the PbO<sub>2</sub> diffraction line changes following Faraday's law, until reaching 65–75% SOC. In this region, a visible evolution of oxygen takes place, and at 108% SOC, oxygen is released vigorously all over the plate surface in the form of 'boiling'. Peters *et al.* [21] have established that at above 70–80% SOC, the charge acceptance decreases in a rather complex manner. Oxygen evolution could be expected to reduce the slope of the curve PbO<sub>2</sub> diffraction line intensity vs. charge time, but this curve should keep rising as PbO<sub>2</sub> formation goes on. Figure 14.9 shows, however, that the intensity of the β-PbO<sub>2</sub> line stops growing. This may mean that, after reaching 65–75% SOC, further charging yields only amorphous PbO<sub>2</sub>. That is hardly the case. More probably, oxygen is sorbed both by the newly forming PbO<sub>2</sub> particles and by the already formed ones, and destroys parts of the β-PbO<sub>2</sub> crystal lattice. Oxygen sorption by PbO<sub>2</sub> particles was studied and demonstrated by Ruetschi *et al.* [22] and by Kabanov *et al.* [23].

In the samples with  $H_2SO_4$  solution, the crystal zones of the newly forming PbO<sub>2</sub> particles at 65–75% SOC cannot compensate for the increased amorphization caused by the incorporation of oxygen into the particles formed before the cell reaches 65–75% SOC. In the washed active mass, the two processes are compensated and hence the curve is parallel to the abscissa.

Influence of  $O_2$  on the crystallinity of  $PbO_2$  particles. The charged cell was left on open circuit for 1 h, then a charging current of 5 A was switched on for 40 min and the circuit was open again. Samples were taken all the time and X-rayed when taken out of the cell, still wet with H<sub>2</sub>SO<sub>4</sub>. The results from these analyses are presented in Fig. 14.10 [20].

When the circuit was open, the electrode (plate) potential decreased, while the intensity of the X-ray diffraction line for  $PbO_2$  increased. On closing the circuit, the intensity decreased again and the potential rose. Since the plate was fully charged, the current was utilized entirely for oxygen evolution. Consequently, the variations in the diffraction line intensities are due to release of oxygen from the  $PbO_2$  particles when the current was switched off and its re-entering the  $PbO_2$  particles, when the current was switched on again. With increase of the amount of oxygen incorporated in the particles, their amorphous zones grow, which leads to increase in electrode polarization, i.e. in active material specific resistance.



Behaviour of positive plate potential and intensity of the diffraction line for  $\beta$ -PbO<sub>2</sub> (3.50 Å) at open circuit and during overcharge [20].

A mechanism of the reactions of oxygen evolution was proposed in references [24] and [25], and is discussed in more detail in Chapter 2.10.3 (p. 89) of this book.

# 14.3.4. AGM Separator and Transport Processes Between the Positive and Negative Plates

#### Structure and functions of the AGM separator

In flooded batteries, the primary function of the microporous separator is to isolate the plates with opposite polarity and prevent electronic contact between them, while at the same time to ensure high ionic conductivity and thus allow ionic flows to move freely between the plates. The AGM separator used in VRLA batteries has a number of additional functions such as the following:

- It absorbs the electrolyte (the third active material in the battery) and thus immobilizes it.
- Provides gas transport channels of relatively large pores for the diffusion of oxygen and thus facilitates the operation of the COC.
- Provides ion transport channels along which ionic fluxes can pass between the two types of plates for the redox reactions to proceed, i.e. ensures high ionic conductivity.



**Figure 14.11:** Scanning electron micrograph (SEM) of AGM separator.

• Being under compression in the active block, the AGM separator minimizes the adverse effect of the pulsation of the positive active material on cycling [26], by constraining the expansion of PAM in volume.

Figure 14.11 shows a scanning electron micrograph (SEM) of an AGM separator sample. It comprises fibres of different thickness (fibre diameters from 0.1 to 10  $\mu$ m) with a length of between 1 and 2 mm, made of chemical grade borosilicate glass. The proportion between the different fibres determines the balance between the different functions of the separator and its price. The firbes are hydrophilic and absorb the electrolyte. Finer fibres (i.e. fibres with smaller diameters) have higher surface and form pores of smaller radii in the separator, but are more expensive. AGM separators contain also between 15 and 18% polymer fibres of polypropylene, polyethylene, etc., which are added to reinforce the mechanical strength of the separator, but also (due to their partial hydrophobicity) to facilitate the formation of gas channels and to reduce the separator price. The AGM separator has an anisotropic structure, which is a result of the technology of its manufacture, similar to the paper making technology. This structure is characterized by pore diameters of between 2 and 4  $\mu$ m in the x-y plane of the separator sheet and pore sizes of between 10 and 30 µm in the direction perpendicular to the separator x-y plane [27]. The small pores in the x-y plane have the function to distribute the electrolyte across the separator thickness and to sustain the wicking rate when the separator is partially saturated with electrolyte. The large pores form the open gas channels.

Table 14.1 summarizes the effects of fibre diameter on the technical characteristics of the AGM separator [27].

Fibre diametre (µm) Fibre length (m kg <sup>-1</sup> ) (m m <sup>-3</sup> ) Surface area (m <sup>2</sup> kg <sup>-1</sup> ) (m <sup>2</sup> m <sup>-3</sup> ) Pore size Tensile strength	$\begin{array}{c} 0.1 \\ 4.7 \times 10^{10} \\ 1.1 \times 10^{13} \\ 14800 \\ 3.5 \times 10^{6} \\ \rightarrow \\ \rightarrow \end{array}$	$\begin{array}{c} 0.5 \\ 1.9 \times 10^9 \\ 4.5 \times 10^{11} \\ 2960 \\ 7.1 \times 10^5 \end{array}$	1.0 4.7 × 10 <sup>8</sup> 1.1 × 10 <sup>11</sup> 1480 3.5 × 10 <sup>5</sup> Increasing Decreasing	$2.0$ $1.2 \times 10^{8}$ $2.8 \times 10^{10}$ $741$ $1.8 \times 10^{5}$ $\rightarrow$ $\rightarrow$	$5.0 \\ 1.9 \times 10^{7} \\ 4.5 \times 10^{9} \\ 296 \\ 7.1 \times 10^{4}$	$\begin{array}{c} 10.0 \\ 4.7 \times 10^6 \\ 1.1 \times 10^9 \\ 148 \\ 3.6 \times 10^4 \end{array}$
Tensile strength	$\rightarrow$		Decreasing	$\rightarrow$		
Cost	$\rightarrow$		Decreasing	$\rightarrow$		

Table 14.1: Influence of fibre diameter on separator characteristics.

#### Gas transport through the AGM separator

The transport of oxygen from the positive plates, where it is evolved, to the negative plates, where it is reduced, is realized through the following stages.

First, microbubbles of oxygen are formed in the pores of PAM filled with electrolyte. The microbubbles then coalesce into discrete gas bubbles which gradually displace the electrolyte from the plate pores towards the separator. The separator pores are filled with electrolyte. The gas bubbles reach the plate surface. Small amounts of the oxygen gas dissolve in the electrolyte, the major part of the gaseous oxygen phase remaining in the form of gas bubbles at the interface plate/separator. The AGM separator has a non-homogeneous structure, hence the oxygen gas accumulates at those sites on the AGM surface with lower fibre density (loose structure) or where there are some voids between the separator and the plate (tubular electrodes/AGM).

Percolation of the oxygen gas into the separator is facilitated by more intimate contact between the glass mat surface and the surface of the positive plate. This is achieved by applying compression to the active block. There are two possible mechanisms of this process:

- (1) At low compression of the active block, the gas accumulated at the interface plate/AGM separator will increase in volume. Under the action of gravitation, the gas flow will be directed vertically. The electrolyte has three times higher density than that of the gas, so it will push the gas upwards to the gas space above the active block. Thus, oxygen will leave the active block. The rate of this vertical gas flow depends on the current flowing through the cell, the electrolyte temperature and the service condition of the cell (i.e. new or after long service).
- (2) At high compression of the active block, the separator is pressed tightly against the plate and the gas bubbles enter the separator. They move in the horizontal direction trying to crease gas channels in the separator. The glass mat structure has a non-uniform density and the gas bubbles will penetrate into the zones of lower fibre density. Hence, the gas flow may occasionally move in the direction not only parallel to the separator surface, but also perpendicular to it. However, the primary gas flow direction is through the AGM separator towards the negative plate where the gas pressure is the lowest and

the pressure gradient pushes the oxygen gas flow in this direction. Under this pressure, the gas flow displaces the electrolyte from the separator pores and thus forms gas channels. When these uninterrupted gas channels are formed, the transport of oxygen between the positive and the negative plates is accelerated.

In the manufacture of AGM separator materials for VRLA batteries, the thickness is quoted (measured) under a controlled standard pressure of 10 kPa. To improve the separator contact with the plates, the plate groups (active blocks) are compressed so as to reduce the separator thickness by about 25%. In tall stationary batteries, this compression is sustained by fastening the active blocks (plate groups) with polymer tapes before inserting them into the battery container.

#### Pore system of the AGM separator

The performance characteristics of a VRLA cell depends greatly on the capillary properties of the AGM separator, i.e. its ability to keep all pores along the separator height filled with electrolyte and to prevent drainage of acid which would lead to electrolyte stratification. These properties of the AGM separator are related to its structure and especially to the pore size distribution. A comprehensive study of the structure of AGM separators was performed by Culpin [28]. He conducted wicking measurements of AGM separators made of a mixture of fine and coarse glass fibres. Strips of these separators were held vertically with their lower ends immersed in  $H_2SO_4$  solution of 1.28 rel. dens. and the time of electrolyte wicking to different heights was measured. The wicking rates (height/wicking time) for AGM separators containing 0%, 10%, 50% or 100% fine fibres are presented in Fig. 14.12.

A well-pronounced linear relationship is observed. By employing Washburn equation and subsequent theoretical processing, Culpin came to the Laplace equation:



**Figure 14.12:** Effect of fibre mix on wicking characteristics; percentage of fine fibres as shown [28].

$$P = \frac{2\gamma\cos\theta}{r} \tag{14.9}$$



**Figure 14.13:** Effect of fibre mix on capillary pressure [28].

where *P* is the capillary pressure, *r* is the pore radius,  $\gamma$  is the interfacial tension and  $\theta$  is the contact angle. Figure 14.13 shows the relationship between the reciprocal pore radius and the percent content of fine fibres (diameter < 1 µm) in the AGM mix. This dependence indicates that there is a linear relationship between capillary pressure and fibre size in a two-component AGM mix. Thus, by altering the proportion between fine and coarse fibres in the mix it is possible to produce AGM material of pre-defined pore size structure.

Figure 14.14a shows the pore size distribution by diameter for an AGM separator sample, as obtained by low-pressure intrusion methods [29].



Figure 14.14:

Pore size distribution in (a) glass microfibre separator; (b) (- - -) positive and (----) negative active materials [29].

As evident from Fig. 14.14a, about 90% of the pore volume consists of pores with diameters between 10 and 24  $\mu$ m. These are mainly pores in the *z* plane. About 5% of the large pores have diameters within the range from 30 to 100  $\mu$ m, and a small percentage of the pores are < 10  $\mu$ m in diameter. In the VRLA cell, the pore system of the AGM separator is in close contact with the pore systems of the two types of plates. The pore size distribution by diameter for positive and negative active materials is presented in Fig. 14.14b [29]. But there are small differences in pore size distribution between the two plates. For new, fully formed plates, 80% of the porosity of the active materials is due to pores with diameters smaller than 1  $\mu$ m. These are values considerably lower than the median pore diameter of the AGM separator. Within a compressed active block, the AGM separator is pressed against the plates, thus an intimate contact is ensured between the two surfaces. After the cell is evacuated, it is filled with electrolyte, the latter being absorbed first in the plate pores and then in the separator. The AGM separator should be 96% saturated with electrolyte according to the technological specification.

When the plates start gassing, the electrolyte is pushed out of the plate pores and is readily absorbed into the pores of the separator, thus the latter is fully saturated. On switching off the current, the gas leaves the plate pores and electrolyte is re-absorbed in these pores from the separator. Thus, only the largest diameter pores in the AGM separator remain empty, while the plate pores are again filled with electrolyte. So the parameter 'electrolyte saturation' holds mainly for the AGM separator.

Figure 14.15 shows the changes in volume porosity of an AGM sample with a basic weight of 225 g m<sup>-2</sup>, as a function of applied pressure (up to 138 kPa). Porosity is defined as the ratio (as a percentage) of void volume to total volume of AGM [30].

The AGM porosity changes insignificantly under the action of the above pressure. The battery container should have very thick walls to resist to such a high pressure. Hence, the volume porosity is affected but slightly by the pressure applied on the x-y separator plane [30].

Why does pressure exert such a small effect on separator porosity? The glass mat structure comprises fibres lying at random, but predominantly in the x-y plane of the AGM sheet, with



**Figure 14.15:** Separator porosity as a function of pressure [30].

the largest pores in the z-direction perpendicular to the x-y plane. Compression of the sheet would be expected to have weak effect on pore size in the z-direction. This was actually confirmed by Culpin in reference [28]. This is not the case, however, with the pore size in the x-y direction. These pores change significantly under pressure. Thus, a 15% compression yields a 50% reduction in pore diameter [31].

#### Critical gas pressure for electrolyte displacement from the AGM pores

In VRLA batteries, reduction of oxygen at the negative plates is a diffusion controlled process and depends on the degree of electrolyte saturation of the AGM separator. Because of the high gas/liquid interfacial tension, the contact area of the glass fibres with the gas phase should be very small. Hence, the pores with small diameter (i.e. with large surface) will be filled with electrolyte first at the expense of the larger pores. With increase of the AGM saturation, the larger pores are filled with electrolyte, too. At 90% saturation, the largest separator pores are full and the remaining 10% of gas form separate bubbles in the AGM which do not play a notable role in the transport of oxygen through the separator [29]. Consequently, oxygen diffusion proceeds through the liquid and the diffusion flow is small. At 60% saturation, oxygen diffuses through the gas phase and the oxygen cycle operates at a rate three orders of magnitude higher than that at 90% saturation. The situation is different in a compressed active block, where the evolved oxygen gas has a greater volume than that of the water which produced it and, hence, a gas pressure is created in the separator pores, which grows when electric current flows through the cell until a critical pressure is reached, which displaces the electrolyte from the larger pores and open gas channels form between the positive and the negative plates. If we assume that the pores in the separator are cylindrical, with a contact angle of the  $H_2SO_4$  electrolyte on glass equal to zero, then movement of the gas in the pores will start



**Figure 14.16:** Critical displacement pressure vs. mean pore diameter [29].



**Figure 14.17:** Cell internal resistance as a function of separator saturation ( $H_2SO_4$  density 1.28 g ml<sup>-1</sup>) [30].

when the pressure at the separator surface becomes greater than the capillary pressure (see Eq. 14.7). The critical pressure required to displace electrolyte for different pore diameters, at a surface tension of  $\gamma = 75$  dyne cm<sup>-1</sup>, is shown in Fig. 14.16 [29].

For AGM with high electrolyte saturation, a capillary pressure of 9 cm Hg (1.8 psi) is needed for the gas to flow through pores of 20  $\mu$ m diameter and a higher pressure is required to displace the electrolyte from the smaller pores.

It follows from all above said that the separator saturation with electrolyte exerts a very strong influence on the rate and efficiency of the COC in VRLA batteries.

#### AGM separator saturation and electrical resistance of the VRLA cell

It can be generally assumed that, during operation of the VRLA cell, electrolytic and gas channels form in the microporous AGM separator. The electric current is carried by ionic flows moving along the electrolytic channels. Therefore, the ratio between the two types of channels in the separator exerts a strong influence on the electrical resistance of the cell and hence on its discharge power. The proportion of electrolytic and gas channels in the AGM separator depends on its saturation with electrolyte. It is interesting to determine the saturation level below where the cell resistance increases. Figure 14.17 shows this relationship as obtained by Crouch and Reitz [3] with the help of a 1 kHz impedance bridge. A pressure of 10 kPa was applied to the active block.

The curve in the figure shows that down to 80% saturation of the AGM, the resistance remains constant and low. At saturations below 80%, it increases rapidly to reach a 40% higher value at 60% saturation than that at 80% saturation level.

The transition point to higher resistance depends on the diameter of the fibres in the AGM (which affects the median radius and the surface of the pores), on the pressure applied to the active block and on the separator thickness. It has been established that 1.5 mm thick AGM separator absorbed with  $H_2SO_4$  electrolyte of 1.28 rel. dens. has a specific resistance of 20 m $\Omega$ .cm<sup>2</sup> [30]. This is a relatively low resistance.



**Figure 14.18:** Effect of cell saturation on reserve capacity at 25 A [32].

Correlation between cell saturation with electrolyte and its capacity and electrical characteristics

Valve-regulated lead—acid batteries operate under conditions of slight deficiency of  $H_2SO_4$  electrolyte as a result of which, on deep discharge, the concentration of the  $H_2SO_4$  in the plate pores drops down to very low values and thus it may become the capacity limiting active material. In an attempt to compensate partially for the  $H_2SO_4$  shortage, many VRLA battery manufacturers use  $H_2SO_4$  solutions with concentrations higher than 1.28 rel. dens. Elevated  $H_2SO_4$  concentrations, however, cause passivation of the positive plates and capacity decline. It is therefore not recommended.

On the other hand, saturation affects the electrical resistance of the cell, i.e. the influence of discharge current on cell capacity increases.

Figure 14.18 illustrates the effect of cell saturation on its reserve capacity on discharge with a current of 25 A [32]. The reserve capacity is a linear function of saturation at low discharge currents.





Effect of saturation on high rate capacity. Notes: Results are for a 12 V battery. Conductivity ratio is the battery conductivity compared to the conductivity at 100% saturation. The 30 s voltage refers to the battery discharged at the rated cold cranking current at  $-18^{\circ}$ C. After 30 s on discharge the requirement is that the battery voltage be in excess of 7.2 V [32].



**Figure 14.20:** The steady state currents at 2.55 V,  $Ta = 22^{\circ}C$ , at different saturations [33].

Figure 14.19 shows the relationship between battery voltage at the 30th s of discharge with the rated cold cranking current at -18 °C [32]. The requirement is that the battery voltage should be in excess of 7.2 V. The obtained results show that this requirement is met down to 78% cell saturation. Another finding is that the dependence of the 30th s voltage on saturation is not a linear relationship for discharge at low temperatures and high currents. This behaviour of the battery may be related to its conductivity as a function of saturation. The conductivity is represented in Fig. 14.19 as a ratio between the battery conductivity at a given saturation to the conductivity at 100% saturation. The data in the figure indicate also that, above 78% saturation, the battery conductivity increases and so does its voltage.

Figure 14.20 presents the changes in cell current at 2.55 V as a function of saturation at 22  $^{\circ}$ C [33].

At this voltage and at saturations higher than 80%, the cell current increases by 3.5 A with 10% decrease in cell saturation. When the saturation drops below 80%, the current rises rapidly, probably, because new gas channels are opened between the positive and negative plates, facilitating oxygen diffusion to the negative plates where it is electrochemically reduced. In order to verify this conjecture, volt-ampere tests of model 4.5 Ah cells with saturations between 75% and 77% were conducted at 22 °C. The obtained results are presented in Fig. 14.21 [33].

Up to 2.45 V, a relatively low current flows through the cell. At 2.48 V, the current increases abruptly. This is obviously related to the onset of oxygen evolution at the positive plates and its diffusion to the negatives along available free gas channels in the AGM separator at 75–77% saturation. For this high current to flow through the cell, besides the rate of oxygen transport between the two plates, another important parameter is the transport of  $H^+$  ions along the electrolytic channels between the plates (Fig. 14.8).



Figure 14.21:

Cell current vs. applied voltage for 4.5 Ah cells with 75-77% saturation polarized at 22°C [33].

The experimental data in Fig. 14.21 indicate that the diffusion of hydrogen ions does not impede the operation of the oxygen cycle. Due to the high mobility of  $H^+$  ions, even the reduced number of electrolytic channels (75%) suffice to sustain high rate of the electrochemical reaction of oxygen reduction.

Having reviewed the transfer of oxygen and hydrogen ions between the positive and negative plates, let us now discuss the processes of reduction of oxygen at the negative plates.

#### 14.3.5. Charge Processes at the Negative Plates of VRLA Batteries and COC

#### General picture of the processes of charge, overcharge and COC at the negative plates of VRLABs

During charge of a VRLA battery, the only reaction that proceeds at the negative plates, up to 70% SOC of the battery, is the charge reaction (Fig. 14.8):

$$PbSO_4 + 2e^- + 2H^+ \rightarrow Pb + H_2SO_4 \qquad (14.10)$$

Within this SOC region, only one electrode system,  $Pb|PbSO_4|H_2SO_4$ , is operating. The behaviour of this electrode was discussed in Chapter 2.3 (p. 47) of this book.

When the SOC of the valve-regulated lead—acid battery exceeds 70%, a reaction of water decomposition with evolution of oxygen starts at the positive plates, parallel to the basic charge reaction:  $PbSO_4 \rightarrow PbO_2$ . The evolved oxygen passes through gas channels in the AGM separator reaching the negative plates where it is reduced via two reactions:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$
 (14.11)

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$
 (14.12)

Thus, a second electrochemical system,  $O_2|H_2O$ , forms at the negative plate (Fig. 14.8). This system will affect both the potential of the plates and the charge processes that take place there.

When the SOC of the negative plates reaches 92–95%, a reaction of hydrogen evolution starts on the lead surface, i.e. a third electrode system forms.

$$2\mathrm{H}^{+} + 2\mathrm{e}^{-} \rightarrow \mathrm{H}_{2} \tag{14.13}$$

The behaviour of the hydrogen electrode on polarization of the lead surface was discussed in Chapter 2.4 (p. 56) of this book.

When the plates are fully charged, operation of the first electrode system stops and the processes of oxygen reduction and hydrogen evolution start at different rates. So, during charge of a VRLA cell, from one to three electrode systems are operating, depending on the SOC of the cell.

Oxidation of hydrogen at the positive plates is a slow process. The evolved hydrogen remains in the cell and causes the gas pressure above the active block to increase, thus retarding the oxygen reaction. When the gas pressure exceeds a certain critical value, the cell valve opens and lets the gas mixture of hydrogen and oxygen out to the surrounding atmosphere. The cell loses water. The amount of vented out gas mixture depends on the voltage applied to the cell or on the charging current.

#### Thermal phenomena during operation of the COC

Let us examine the phenomena that occur during constant voltage polarization at 2.40 V of a partially charged VRLA cell [34]. Figure 14.22 presents a full picture of the changes in all six measured parameters (current, cell voltage, positive and negative plate potentials, temperature and gassing rate). After 1 h of polarization, the potential of the positive plates passes through a small maximum, while that of the negative plates passes through a small minimum.

During this A period, the cell is charged and when the positive plate potential,  $\varphi^+$ , reaches its maximum, a reaction of oxygen evolution starts. With increase of the quantity of electricity charged into the cell, the latter is fully charged and the rate of oxygen evolution increases. This leads first to the formation of gas bubbles in the positive active material and in the AGM separator, while at the negative plates, reactions of hydrogen evolution and of partial reduction of oxygen start.

After 2.5 h of polarization, open gas channels form between the positive and the negative plates, and the COC becomes the dominating process. The oxygen reaction is accelerated and hence the cell current starts to increase. The heat released by the reactions of oxygen reduction causes the cell temperature to rise. The potential of the positive plates decreases, while that of negatives increases. Besides the reduction of oxygen, hydrogen is also evolved at the negative plates. The reaction of oxygen reduction produces more heat and the temperature in the cell increases further.



Figure 14.22:

Polarization of a VRLA cell at 2.40 V. The thermal runaway (TRA) phenomenon is manifested by changes in (a) current and voltage; (b) positive and negative plate potentials; (c) cell temperature and gassing rate [34].

The oxygen evolved at the positive plates is not entirely reduced at the negatives and, together with the evolved hydrogen, it causes the gas pressure in the cell to rise until, after 3.5 h of polarization, the cell valve opens and lets the gases out, i.e. the cell starts gassing. Part of the heat generated by the reactions in the cell is carried away with the vented gas flow to the surrounding atmosphere. The elevated temperature in the cell creates a temperature gradient between the cell and the surrounding medium, and the heat dissipates out of the cell to the surroundings. When higher current flows through the cell more Joule heat is produced, which is the second source of increased heat generation in the cell. With increase of the temperature in the cell, the latter's heat exchange with the surroundings is intensified. At higher temperatures, the overpotential of oxygen evolution is reduced and hence the latter reaction is accelerated. However, the oxygen flow to the negative plates is limited by the capacity of the gas channels in the AGM separator to transfer this flow. Consequently, non-recombined hydrogen and oxygen gases leave the cell. The rate of oxygen reduction is retarded and the cell current reaches a maximum. The temperature rise continues for some more time due to the heat generated by the Joule effects and by the reactions at the negative plates, but it is accompanied by intense heat release from the cell. The accelerated reaction of water decomposition at the positive plates causes the concentration of the H<sub>2</sub>SO<sub>4</sub> electrolyte in and near these plates to increase, which leads to their partial passivation. The rate of the oxygen evolution reaction is retarded, the cell current decreases and so does the gassing rate, too. The cell temperature passes through a maximum and begins to decrease thereafter. This slows down the reduction of oxygen and hence less heat is generated by this reaction. The cell tends to reach a steady state at which the amount of heat generated in the cell becomes equal to the heat dissipated to the surroundings and thus the cell temperature and cell current remain constant.

Figure 14.22 indicates that there exists a correlation between cell current and temperature. The heat generated in the cell causes its temperature to rise, which lowers the overpotential of oxygen evolution and thus accelerates this reaction. The higher temperature increases the rate of the oxygen transport to the negative plates and consequently the rate of the oxygen reduction at the negatives, too. The latter reaction generates more heat, which causes the cell temperature to rise further. Thus, during the period between  $I_{CO_2O}$  and  $T_{max}$  (Fig. 14.22), there is a self-accelerating interrelation between the reactions of the oxygen cycle, as illustrated in Fig. 14.23 [35]. This phenomenon was called 'thermal runaway'.

A general picture of the thermal phenomena responsible for changes in cell temperature during operation of the COC is presented in Fig. 14.24. The figure shows the processes which cause temperature rise and those which reduce the temperature in the cell. These processes are in dynamic state. At the beginning of cell polarization, the phenomena causing the temperature to increase (i.e. exothermic reactions, Joule effects) are predominating, as a result of which the cell temperature rises rapidly. However, the elevated temperature and the high cell current intensify the heat exchange of the cell with the surrounding medium, the gassing rate increases



Figure 14.23:

Schematic representation of the processes at the two electrodes which are in positive (self-accelerating) interrelation.

and so does the rate of water evaporation, etc. Thus the thermal effects of the two types of processes begin to compensate each other and, after a certain period of time, the cell gets into a steady state.

The maximum temperature of normal operation of a lead—acid battery is 60 °C. Above this temperature, the rates of expander decomposition in the negative plates and of grid corrosion in the positives increase significantly. The evaporation of water from the cell is also accelerated. It is therefore essential that operation of the COC should not lead to thermal runaway with temperature rise above the upper limit value of 60 °C.



#### Figure 14.24:

A general scheme of the phenomena responsible for changes in cell temperature during operation of the COC.



Figure 14.25:

Cell temperature as a function of applied current at quasi-steady state conditions under free air convection [36].

A series of galvanostatic polarization experiments with stepwise increase of the current were performed aimed to determine the quasi-stationary characteristics of the system at each current step [36]. In order to evaluate the heat exchange between the cell and the surrounding medium, the latter was sustained constant. The *T* vs. *I* dependences were studied at three ambient temperatures: 19 °C, 30 °C and 45 °C. The obtained results are presented in Fig. 14.25 [36].

The experimental data in the figure show that the cell temperature is a linear function of applied current

$$T = T_0 + b I (14.14)$$

Where  $T_0$  is the temperature of the cell at I = 0 (for our experiments it corresponds to the ambient temperature,  $T_0 = T_a$ ) and *b* is the slope of the curve. The slopes of the three straight lines are almost the same:  $b = 15.2 \text{ KA}^{-1}$ , 16.1 KA<sup>-1</sup> and 15.3 KA<sup>-1</sup> at 19 °C, 30 °C and 45 °C, respectively. The very close values of *b* for the three experiments indicate that the mechanism of heat generation within the cell does not change and the temperature rise is a direct result of current increase.

The temperature rise with increase of the applied current within the period marked with B in Fig. 14.22 depends on (a) ambient temperature, (b) applied cell voltage, (c) AGM separator type (it determines the maximum oxygen flow that can be transferred between the plates) and (d) cell container design and material (they determine the heat transfer coefficient of the cell). By appropriate selection of the above parameters the temperature rise during operation of the COC can be limited to  $60 \,^{\circ}$ C.

#### Types of currents flowing between the positive and negative plate in a VRLA cell

The above described general picture of the processes that occur at the positive and negative plates of a VRLA cell would not be complete if the processes of positive grid corrosion are omitted.

During overcharge of a VRLA cell, the oxygen evolved by the electrochemical reaction at the positive plates is distributed as follows: the major part of this oxygen diffuses to the negative plates and is reduced there, another part oxidizes the grids of the positive plates and a third part is vented out of the cell. In each electrochemical system, the sum of the rates of the cathodic reactions should be equal to the sum of the anodic reaction rates, in order to preserve the electroneutrality of the cell. Under the above conditions, the following currents will flow through the VRLA cell:

$$\left[i_{O_2} - i_{gc} - i_{O_2out} + i_{H_2CHC} + i_{H_2out}\right]^+ = \left[i_{O_2R} + i_{H_2}\right]^-$$
(14.15)

where  $i_{gc}$  is the current generated by the grid corrosion reaction,  $i_{H_2CHC}$  is the current of hydrogen oxidation at the positive plates,  $i_{O_2R}$  is the current of oxygen reduction at the negative plates.

The conditions of cell polarization can be selected so that no oxygen nor hydrogen would leave the cell, i.e.  $i_{O_2out} = 0$  and  $i_{H_2out} = 0$ . In this case:

$$\left[i_{O_2} - i_{gc} + i_{H_2CHC}\right]^+ = \left[i_{O_2R} + i_{H_2}\right]^-$$
(14.16)

Evolution of hydrogen can be suppressed by addition of appropriate inhibitors to the negative active material. Then, the amount of water lost will be equal to the amount of oxygen involved in the corrosion reaction. Since the corrosion current is too low, VRLA batteries will need no maintenance for years of service.

#### Mechanism of the oxygen reduction at the negative plates

(a) Electrochemical mechanism of  $O_2$  reduction (Fig. 14.26)



#### Figure 14.26:

Schematic representation of the electrochemical reactions of oxygen reduction with formation of hydrogen peroxide as an intermediate product.

It has been established that reduction of oxygen on the lead electrode surface proceeds in two stages, whereby hydrogen peroxide is formed as an intermediate product. The reactions involved in this mechanism are electrochemical and can be represented by the following equations:

$$O_2 = 2H^+ + 2e^- \to H_2O_2 \tag{14.11}$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O + 383.9 \text{ kJ mol}^{-1}$$
 (14.17)

In this mechanism, the lead surface plays the role of a source of electrons. The reaction is exothermic and significant amount of heat is generated. The end product of the above two reactions is water, which diffuses to the positive plates.

(b) Reduction of oxygen with formation of PbO as an intermediate product (Fig. 14.27) Lead is readily oxidized (via a chemical reaction) by atmospheric oxygen in humid medium. The lead electrode surface is negatively charged and there are negligible concentrations of SO<sub>4</sub><sup>2-</sup> ions, or none at all, on this surface. Hence, a chemical reaction of Pb oxidation proceeds, involving one atom of the oxygen molecule, while the other atom participates in an electrochemical reaction of reduction.

$$Pb + O_2 + 2H^+ + 2e^- \rightarrow PbO + H_2O + 457.6 \text{ kJ mol}^{-1}$$
 (14.18)

Since the electrode surface on which the above reaction proceeds is highly cathodically polarized, the PbO formed is reduced to lead through an electrochemical reaction:

$$PbO + 2H^{+} + 2e^{-} \rightarrow Pb + H_2O \qquad (14.19)$$

Thus, PbO is an intermediate product formed by a chemical reaction of oxygen reduction, which is then reduced to Pb through an electrochemical reaction. If we sum up the two reactions, we will see that the water decomposed to evolve oxygen at the positive plates is restored at the negative plates via reactions of different nature.

#### **Figure 14.27:** Schematic representation of the reactions of oxygen reduction with oxidation of lead and formation of PbO as an intermediate product.



Figure 14.28:

Schematic representation of the reactions of oxygen reduction with formation of  $H_2O_2$  and PbO as intermediate products.

(c) Reduction of oxygen with formation of  $H_2O_2$  and PbO as intermediate products (Fig. 14.28) In this mechanism, the electrochemical reaction of  $H_2O_2$  formation (reaction 14.11) proceeds first on the lead surface. Hydrogen peroxide is a strong oxidant and oxidizes the lead surface via the following chemical reaction:

$$H_2O_2 + Pb \rightarrow PbO + H_2O + 317 \text{ kJ mol}^{-1}$$
 (14.20)

On the cathodically polarized surface, PbO is readily reduced to Pb via the electrochemical reaction (14.19) as a result of which water is formed, too.

(d) Reduction of oxygen with formation of H<sub>2</sub>O<sub>2</sub>, PbO and PbSO<sub>4</sub> as intermediate products (Fig. 14.29)

In this mechanism, the hydrogen peroxide formed by the electrochemical reaction oxidizes the lead surface first via the chemical reaction (14.20) yielding PbO. If, for

 $O_2 + 2H^* + 2e^- \rightarrow H_2O_2$   $H_2O_2 + Pb \rightarrow H_2O + PbO$   $PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O$   $PbSO_4 + 2H^* + 2e^- \rightarrow Pb + H_2SO_4$   $H_2SO_4$   $2H^*$ 



#### Figure 14.29:

Schematic representation of the reactions of oxygen reduction with formation of  $H_2O_2$ , PbO and PbSO<sub>4</sub> as intermediate products.

some reason, there is  $H_2SO_4$  on the lead surface, it reacts with PbO according to the reaction

$$PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O \tag{14.21}$$

The above reaction is in competition with the electrochemical reaction (14.19). The lead sulfate formed on the highly cathodically polarized surface will be reduced to Pb via the reaction

$$PbSO_4 + 2H^+ + 2e^- \rightarrow Pb + H_2O \qquad (14.22)$$

So, reduction of oxygen at the lead surface may proceed via four different mechanisms involving different chemical reactions. Which of these mechanisms will be the dominating one(s) depends on the local conditions in the pores of the negative active material: ion concentration, pH of the solution filling the pores, temperature and gas phase pressure.

All above mechanisms have one process in common, namely the oxygen molecules have to reach the lead surface. And the latter is covered by a thin liquid film. The processes that occur during the transport of oxygen molecules through the liquid film and the latter's behaviour have been studied by Kirchev *et al.* [37]. A schematic representation of a cross-section through a pore in the negative active material is presented in Fig. 14.30.

The surface of the lead particles surrounding the pore is covered by a thin liquid film in which the oxygen molecules have to dissolve and diffuse to the lead surface, where they are



#### Figure 14.30:

Micrograph of an open gas pore in NAM and a scheme of the cross-section through the NAM pore [37].



Figure 14.31:

Schematic representation of the electrochemical mechanism of oxygen reduction in active centres at the phase boundary metal/thin liquid film (see point (a) in Section "Mechanism of the oxygen reduction at the negative plates" chapter) [37].

reduced via one of the above discussed mechanisms. The diffusion coefficient of  $O_2$  in the solution is within the range  $1/2 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>, depending on the acid concentration. Figure 14.31 shows a scheme of the electrochemical mechanism of oxygen reduction at the interface metal/thin liquid film [37].

Reactions (14.11) and (14.12) are integrated in the scheme. h is the thickness of the thin liquid film. Khomskaya *et al.* have established that diffusion of oxygen through the liquid film wetting the surface of the lead crystals surrounding the pore is the slowest stage in the COC [38]. This conjecture has been supported by Maja *et al.* [39–41]. Oxygen transport to the negative plates and oxygen reduction at the surface of these plates have been studied, employing mathematical models and computer simulations, first by Bernardi and Carpenter [42], and later by Newman and Tiedemann [43] and Gu *et al.* [44].

# Summary

This chapter made an overview of the main techniques employed to suppress the effect of the side reactions of water decomposition through catalytic recombination of  $H_2$  and  $O_2$  to water (catalytic plugs) or through operation of a COC (VRLAB). These methods have reduced, or even eliminated, the need for battery maintenance, as a result of which maintenance-free batteries are gaining ever increasing share of the battery production nowadays.

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# PART 6

# Calculation of the Active Materials in a Lead–Acid Cell