

Energy balance of the closed oxygen cycle and processes causing thermal runaway in valve-regulated lead/acid batteries

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Abstract

A model for the reactions involved in the closed oxygen cycle in valve-regulated lead/acid batteries and the associated energy transformations is proposed. When electric current flows through the closed oxygen cycle, a certain amount of electric energy is converted via electrochemical processes into chemical energy, i.e. the products obtained may interact spontaneously as a result of which the system returns to its initial state. During these spontaneous reactions, the chemical energy is converted into heat. Depending on the type of the reactions involved in oxygen reduction on the negative plate, the closed oxygen cycle may proceed in two different electrochemical systems: (i) oxygen is reduced through electrochemical reactions yielding the electrochemical system $\text{PbO}_2/\text{H}_2\text{O}/\text{O}_2//\text{O}_2/\text{H}_2\text{O}/\text{Pb}$, and (ii) oxygen is reduced through chemical reactions forming the electrochemical system $\text{PbO}_2/\text{H}_2\text{O}/\text{O}_2//\text{PbSO}_4/\text{Pb}$. The energy introduced into the system for activation of the closed oxygen cycle is different for the two electrochemical systems. The quantity of this energy is calculated in the present work using thermodynamic data. During the closed oxygen cycle the electric energy is transformed into chemical energy which, in turn, is converted into heat. Part of this heat causes the cell temperature to increase and another part dissipates into the surrounding air. The amount of the former heat depends on the heat capacity of the battery and is influenced most strongly by the quantity of the electrolyte. It has been established that the rate of oxygen evolution on the positive plate depends strongly on the temperature. When the heat exchange between the battery and the surrounding medium is poor, the reactions of the closed oxygen cycle may enter (through the heat and oxygen flows between the positive and the negative plates) into self-accelerating interrelations, which may lead to thermal runaway. To avoid this, an adequate heat exchange should be maintained between the battery and the surrounding medium, the rate of the oxygen reaction should be kept down and a high heat capacity of the battery and small water loss on its operation should be ensured.

Keywords: Lead/acid batteries; Energy balance; Thermal runaway; Valve-regulated lead/acid batteries; Closed oxygen cycle

1. Introduction

Valve-regulated lead/acid batteries (VRLAB) operate under closed oxygen cycle (CO_2C). Oxygen is evolved at the end of charge and during overcharge of the lead dioxide plates in lead/acid batteries. It flows along the pores or channels of the immobilized electrolyte to the negative plate where it is reduced. Thus there is no water loss and the battery needs no maintenance [1–3].

For the CO_2C to be activated, a certain amount of electrical energy is introduced into the cell. This energy is needed for the electrochemical reactions to proceed. The latter result in the formation of active substances (oxygen and lead) which interact with each other thus bringing the cell back to its initial state. During these processes the electrical energy, introduced into the cell as chemical energy is converted into heat. The latter has to leave the system. Otherwise the temperature in the cell will increase. Hence, during the processes of the

closed oxygen cycle, a transformation of energy proceeds in the cell and the latter becomes a heat generator.

The heat released during operation of the CO_2C causes the temperature of the cell to rise (Fig. 1(a)). A difference is created between the temperatures of the cell and of the surrounding medium. Consequently, part of the heat from the lead/acid cell dissipates in the surrounding medium. With the time of cell operation, a moment is reached when the

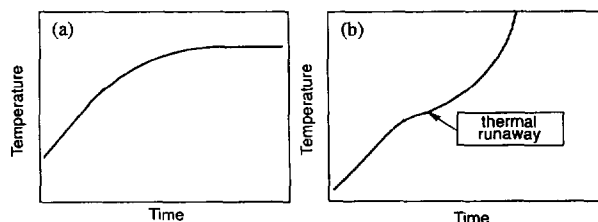


Fig. 1. Schematic representation of changes in temperature on activation of the CO_2C : (a) under adequate heat exchange, and (b) under poor heat exchange between the battery and the ambient air.

amount of heat released from the cell becomes equal to the amount of heat generated in the cell by the CO_2C . The cell temperature reaches a new and higher stationary level (Fig. 1(a)) which corresponds to the rates of the CO_2C and of the heat exchange.

Mass utilization of VRLABs has evidenced the following phenomenon. When the temperature in some of the cells increases substantially (e.g. over $50\text{--}60^\circ\text{C}$), certain phenomena proceed in one or more of the battery cells that cause a self-accelerating temperature rise (Fig. 1(b)). This phenomenon was called ‘thermal runaway’ [4,5]. The mechanism of the processes causing thermal runaway is not quite clear yet.

The present paper will focus mainly on the processes that occur during the CO_2C in VRLAB. In fact, parallel to the CO_2C other processes take also place in the VRLAB such as:

(i) *Corrosion of the positive plate grid.* Part of the oxygen evolved on the positive plate (about 2%) penetrates into the corrosion layer and oxidizes the plate grid. Hence, part of the oxygen is excluded from the CO_2C .

(ii) *Corrosion of the lugs and strap of the negative half-cell.* These are oxidized to PbO and PbSO_4 which are not reduced to Pb . Thus another part of the evolved oxygen is excluded from the CO_2C [6,7].

(iii) *Electrochemical evolution of hydrogen on the negative plate.* At high temperatures, sometimes this process proceeds at a higher rate than that of the CO_2C . During this process, part of the water is also excluded from the CO_2C [8,9]. This effect of the evolution of hydrogen diminishes as part of the hydrogen is reduced on the positive plates [10,11].

The influence of the above three types of processes on the CO_2C is manifested in water loss. The latter will not be discussed here.

The aims of the present paper are: (i) to elucidate the processes that occur during the CO_2C in VRLABs; (ii) to determine the associated energetic transformations, and (iii)

to establish the processes causing thermal runaway and the possible ways of preventing it.

2. Reactions of oxygen evolution on the lead dioxide plates and its reduction on the negative plates of lead/acid batteries

2.1. Oxygen evolution on the PbO_2 plate

The mechanism of the processes of oxygen evolution on the lead dioxide positive plates of lead/acid batteries is rather complex and there is no unanimous concept of this mechanism in the literature for the time being [12,13]. However, for the purposes of the present thermodynamic investigation it is sufficient to give the overall reaction with its initial and end products disregarding its kinetics



The oxygen electrode formed on the PbO_2 plate can be represented as $\text{PbO}_2/\text{H}_2\text{O}/\text{O}_2$.

2.2. Reduction of oxygen on the surface of the lead plate

There are two generally accepted mechanisms for this reaction leading to the formation of different electrochemical systems. These mechanisms are schematically presented in Fig. 2.

2.3. Reduction of oxygen through electrochemical processes

The oxygen evolved on the positive plate flows along the pores or channels of the immobilized electrolyte and reaches the lead surface of the negative plate where the following electrochemical reaction proceeds (see Section 2.1, Fig. 2)

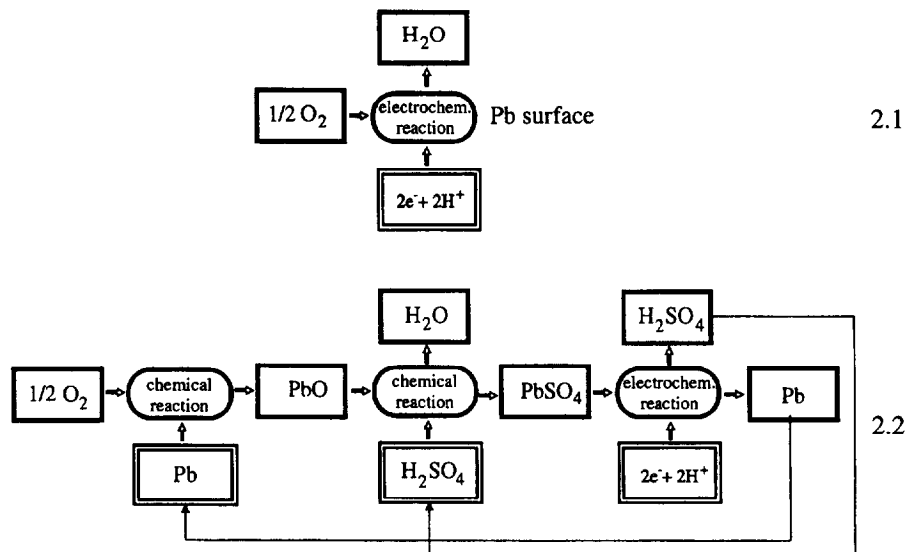
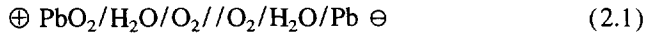


Fig. 2. The two types of reactions on reduction of oxygen on the negative plate: (2.1) electrochemical reduction of oxygen, and (2.2) chemical reduction of oxygen with subsequent electrochemical reaction.



It is known that the mechanism of the process of oxygen reduction on Pt and active carbon is a two-step process. First, oxygen is reduced to H_2O_2 and then the latter is reduced to H_2O [12]. The second reaction is most often rate determining as a result of which a certain concentration of H_2O_2 is formed in the solution. There are no data in the literature evidencing the presence of H_2O_2 in VRLABs.

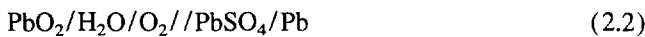
In this mechanism of the reduction of O_2 , the CO_2C comprises the electrochemical system



2.4. Reduction of oxygen through chemical reactions

The reactions that proceed according to this concept are presented schematically in Fig. 2 (see Section 2.2). When the oxygen flow reaches the lead surface it oxidizes it to PbO . The latter is unstable in H_2SO_4 solution. A chemical reaction proceeds between them resulting in the formation of H_2O and PbSO_4 . Through an electrochemical reaction, the latter is reduced to lead and H_2SO_4 is evolved [4,14]. The reduction of PbSO_4 to Pb proceeds at small polarization of the Pb/PbSO_4 electrode (100–150 mV). The oxygen flow and the chemical reactions of lead oxidation supply PbSO_4 for the subsequent electrochemical reaction (Fig. 2). It has been established that the potential of the Pb/PbSO_4 electrode remains unchanged within a wide range of currents. Therefore, the changes in cell voltage are transferred on the potential of the positive plate only.

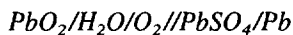
When reduction of O_2 proceeds according to this mechanism, the following electrochemical system is formed



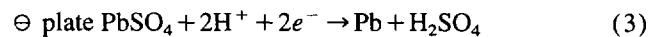
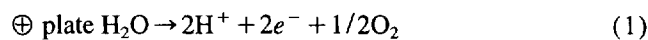
The electrochemical system (2.2) differs from that denoted with (2.1). Consequently, the two electrochemical systems will need different quantities of electric energy to be introduced into the lead/acid cell for the CO_2C to operate. The above energy transformations will be discussed below starting with the system (2.2).

3. Determination of the heat released by the reactions involved in the CO_2C

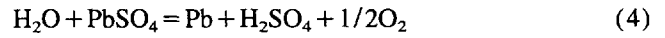
3.1. Electrochemical reactions in the system



The following reactions proceed in the above electrochemical systems:



The overall reaction taking place in the $\text{PbO}_2/\text{H}_2\text{O}/\text{O}_2//\text{PbSO}_4/\text{Pb}$ electrochemical system can be expressed by the equation



The changes in energy of the electrochemical system during reaction (4) can be calculated by the Gibbs–Helmholtz equation

$$W_e = \Delta H_4 - T\Delta S_4$$

where

(i) W_e is the energy consumed for doing useful work (Gibbs energy) during the reaction (4).

(ii) ΔH_4 is the change in enthalpy of the system during the reaction (4). It corresponds to the total amount of energy introduced into the electrochemical system, which is equal to the difference between the molar enthalpies of the end products and the initial substances

$$\begin{aligned} \Delta H_4 &= (\Delta H_{\text{Pb}} + \Delta H_{\text{H}_2\text{SO}_4} + 1/2\Delta H_{\text{O}_2}) \\ &\quad - (\Delta H_{\text{H}_2\text{O}} + \Delta H_{\text{PbSO}_4}) \\ &= [\text{O} + (-194.55) + \text{O}] \\ &\quad - [(-68.32) + (-219.82)] \text{ kcal/mol} \end{aligned}$$

$$\Delta H_4 = 93.64 \text{ kcal/mol}$$

The enthalpy values are taken from Ref. [15].

(iii) ΔS_4 is the change in entropy of the system during reaction (4). It is determined from the difference between the molar entropies of the end products and the initial substances of reaction (4) [15], and expressed in cal/(mol K).

$$\begin{aligned} \Delta S_4 &= (\Delta S_{\text{Pb}} + \Delta S_{\text{H}_2\text{SO}_4} + 1/2\Delta S_{\text{O}_2}) \\ &\quad - (\Delta S_{\text{H}_2\text{O}} + \Delta S_{\text{PbSO}_4}) \\ &= (15.49 + 37.50 + 0.549 \cdot 0) - (16.71 - 35.51) \\ &= 25.27 \times 10^{-3} \text{ kcal/(mol K)} \end{aligned}$$

(iv) T is the temperature in degree Kelvin. Let us assume that the electrochemical system operates at 25 °C, i.e. 298 K.

(v) $T\Delta S$ is the energy bound into the system and utilized for changing the structures of its components.

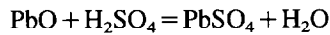
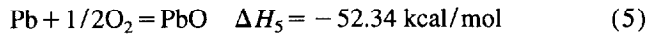
When we substitute the above numerical values in the Gibbs–Helmholtz equation we obtain

$$\begin{aligned} W_e &= 93.58 - 298 \times 25.27 \times 10^{-3} \\ &= 93.58 - 7.53 = 86.05 \text{ kcal/mol} \end{aligned}$$

When 93.58 kcal/mol of energy is introduced into the electrochemical system $\text{PbO}_2/\text{H}_2\text{O}/\text{O}_2//\text{PbSO}_4/\text{Pb}$, 86.05 kcal/mol will be consumed for doing useful work for production of O_2 and Pb (Gibbs energy), and 7.53 kcal/mol is the bound energy utilized for structural changes in the system's components.

3.2. Spontaneous chemical reactions in the electrochemical system $PbO_2/H_2O/O_2//PbSO_4/Pb$

As a result of the electrochemical reactions (1) and (3) Pb and O_2 are formed in the cell, which in the presence of H_2SO_4 react spontaneously when they get in contact with each other according to the following chemical reactions:



$$\Delta H_6 = -41.26 \text{ kcal/mol} \quad (6)$$

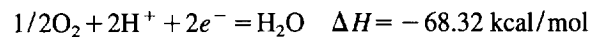
where ΔH_5 and ΔH_6 are the heat effects of reactions (5) and (6), respectively. A negative sign is used to denote the heat released by the system and a positive sign marks the heat introduced into the system. The rate of reaction (5) between O_2 and the lead surface is very high. This can be seen when lead battery plates, formed and washed with water, are dried in the air. After a certain period of time their temperature increases so rapidly that they 'burn'. The total heat released by reactions (5) and (6) is equal to

$$Q = -52.34 - 41.26 = -93.60 \text{ kcal/mol}$$

This heat corresponds to the energy introduced into the system (2.2) through the electrochemical reactions. As the chemical reactions bring the system back to its initial state, both the Gibbs energy and the bound energy $T\Delta S$ are released in the form of heat.

3.3. The $PbO_2/H_2O/O_2//O_2/H_2O/Pb$ electrochemical system

The reaction of O_2 reduction proceeding on the negative plate can be represented by the equation



The heat effect of this exothermic reaction is 68.32 kcal/mol. When the CO_2C proceeds in the $PbO_2/H_2O/O_2//O_2/H_2O/Pb$ electrochemical system, the heat released in the cell will be 27% less than that released in the $PbO_2/H_2O/O_2//PbSO_4/Pb$ system. This difference is due to the occurrence of a second closed cycle on the negative plate only, namely formation of $PbSO_4$ and its reduction to Pb (Fig. 2.2).

4. Heat capacity of the active block of one lead/acid cell

Electrochemical and chemical processes occur in the active block of the lead/acid cell as a result of which a certain amount of electricity is generated or accumulated and the CO_2C proceeds. The active block consists of positive and negative plates kept apart by separators and immersed in H_2SO_4 solution with a definite concentration.

In addition to its electric capacity the active block has also heat capacity. The latter is determined by the amount of heat yielding an increase in temperature of the active block by 1° .

The heat capacity K_{ab} of the active block of one lead/acid cell is equal to:

$$K_{ab} = (m_g C_g) + (m_{NAM} C_{NAM}) + (m_{PAM} C_{PAM}) \\ + (m_{H_2SO_4} C_{H_2SO_4}) + (m_{sep} C_{sep})$$

where m denotes the weights of the cell components: m_g of the grid, m_{NAM} of the negative active mass, m_{PAM} of the positive active mass, $m_{H_2SO_4}$ of the H_2SO_4 solution, and m_{sep} of the separators; C denotes the respective specific heat capacities in cal/(g K). To determine the heat capacity of the lead/acid cell, the heat capacities of the case, the lid and the vent of the cell should be added to the above equation.

Let us determine the heat capacity of the active block of one 54 Ah lead/acid cell and based on this example let us establish which components of the cell affect most strongly this heat capacity. Table 1 gives the weight of the individual components building up the active block of one such cell with absorptive glass mat (AGM). Table 2 presents the specific heat capacities of the components of the active block as taken from Ref. [15]. Let us assume that the specific capacity of the lead alloys and of NAM are equal to that of lead. The specific heat capacity of AGM is equal to that of glass (i.e. between 0.88 and 0.23 cal/(g K) [16]). Let us assume an average value.

Using the data from Tables 1 and 2 we can determine the heat capacity K_{ab} of the active block of a 54 Ah lead/acid cell as follows:

$$K_{ab} = (21)_g + (39)_{PAM} + (16)_{NAM} + (460)_{H_2SO_4} + (7.5)_{AGM}$$

$$K_{ab} = 543 \text{ cal/K}$$

On comparing the heat capacities of the individual cell components it can be seen that the H_2SO_4 solution is responsible for 85% of the active block heat capacity. Hence, small changes in electrolyte quantity in the active block change substantially the heat capacity of the latter. Thus a 10%

Table 1
Weights of active block components

	Unit weight m (g)	Number per cell	Total weight
Positive grid	80	5	400
Negative grid	50	6	300
PAM	120	5	600
NAM	85	6	510
H_2SO_4 , sp. gr. 1.28			680
AGM			50

Table 2
Specific heat capacities

	C (cal/(g K))		C (cal/(g K))
Pb	0.0305	H_2O	1
PbO_2	0.0646	H_2SO_4 (sp. gr. 1.28)	0.676
H_2SO_4	0.339	glass	0.15

decrease in electrolyte quantity results in 8.3% decrease in heat capacity of the active block.

Based on these data an assessment of the heat Q_τ released in the active block for one second of the operation of the CO₂C at a current of 1 A can be made. Let us assume that there is no heat exchange between the cell and the surrounding medium

$$Q_\tau = m_O \Delta H = \frac{It}{nF} \Delta H$$

where $I = 1$ A, m_O is the number of oxygen gram atoms obtained for $t = 1$ s when 1 A of current flows, F is the Faraday constant, $n = 2$ are the electrons released by one oxygen atom, ΔH is the heat effect of the exothermic reactions of O₂ reduction. When the CO₂C proceeds in the PbO₂/H₂O/O₂//PbSO₄/Pb electrochemical system, $\Delta H = 93.60$ kcal/mol. $Q_\tau = 0.4848$ cal of heat is released in the active block of the cell for 1 s, and for 1 min the heat released is 29.09 cal.

In the PbO₂/H₂O/O₂//O₂/H₂O/Pb electrochemical system, $Q_\tau = 0.354$ cal of heat will be released for 1 s, and 21.24 cal for 1 min.

The time τ for which the temperature of the active block increases by 1 K may be determined by dividing the heat capacity by $Q_\tau \times \tau = 18.67$ min for the PbO₂/H₂O/O₂//PbSO₄/Pb system. If the cell loses 30% of its water and the current becomes 2 A (this can happen during the second half of battery life), then $\tau = 7$ min.

5. Influence of temperature on the rate of oxygen evolution

The rates of the reactions in the CO₂C are determined by the rate of oxygen evolution. This rate depends on the potential of the oxygen electrode and on temperature. The Tafel dependences of the electrochemical reaction of oxygen evolution on the PbO₂ layer at different temperatures are presented in Fig. 3. Experimental data from Ref. [17] are used.

The effect of temperature on the rate of oxygen evolution can be determined by keeping the potential of the oxygen electrode constant (for example equal to 1.3 V versus a Hg/

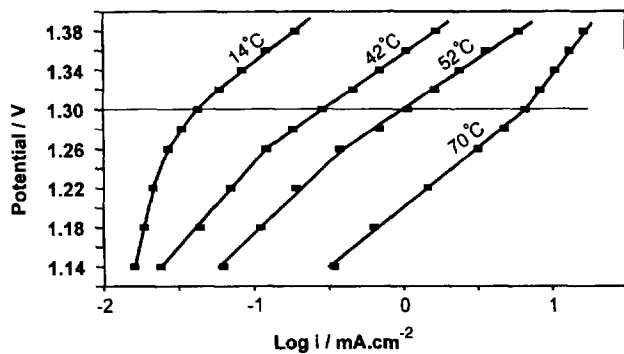


Fig. 3. Tafel dependences of the oxygen electrode at different temperatures. The potential of the oxygen electrode is measured versus a Hg/Hg₂SO₄ reference electrode.

Hg₂SO₄ electrode) and comparing the currents at two different temperatures. At 42 °C, the electric current flowing through the electrode is 0.263 A/cm² against 1.072 A/cm² at 52 °C. Hence, a 10 °C increase in temperature brings about a four-fold increase in the rate of oxygen evolution. This indicates that the oxygen reaction is very sensitive to the changes in temperatures.

6. Self-accelerating interrelations between the reactions of the CO₂C

The processes of the CO₂C are very strongly affected by the heat exchange between the battery (cell) and the surrounding medium. This influence can be assessed quantitatively only provided the following data are known:

- (i) what is the cell (battery) design;
- (ii) what are the thermal properties (heat transfer coefficients) of the materials from which the battery case and lid are made;
- (iii) what are the parameters of the surrounding medium (manufacturers of VRLA batteries have specific requirements with regard to the ambient temperature of battery operation).

In the Sections 6.1 and 6.2 we will discuss the phenomena that proceed in the active block in two extreme cases of heat exchange between the battery and the surrounding medium:

- (i) very intensive, (ii) and very weak.

6.1. Phenomena occurring in the active block during the CO₂C under conditions of intense heat exchange between the cell and the surrounding medium

As a result of the exothermic reactions of oxygen reduction on the negative plate the overall temperature of the cell increases. This causes an increase in the rate of oxygen evolution on the positive plate when the cell voltage is maintained constant (Fig. 4). The oxygen flow towards the negative plate increases, which in turn accelerates the reaction of oxygen reduction and hence the quantity of heat released per unit of time. Thus the reactions taking place on the two plates are interrelated through the heat and the oxygen flow (Fig. 4). The efficiency of these interrelations are affected by the heat exchange. The latter may break down these interrelations. On increase of temperature in the cell, the temperature difference

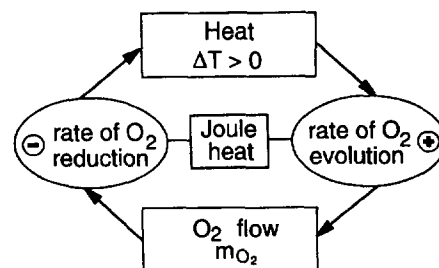


Fig. 4. Schematic representation of the self-accelerating interrelations between the reactions of the CO₂C in a lead/acid cell.

between the cell and the surrounding medium increases too. Consequently, the heat flow out of the cell into the surrounding air increases, as a result of which the temperature rise in the cell is slowed down. This in turn slows down the rate of oxygen evolution on the positive plate. When the rate of heat dissipation in the surrounding medium becomes equal to the rate of heat generation by the CO_2C , the cell temperature remains constant and the processes in the cell as well as the current of the CO_2C reach a steady-state., see Fig. 1 (a).

6.2. Phenomena occurring in the active block during the CO_2C under conditions of poor heat exchange between the cell and the surrounding medium

In this case the interrelations between the CO_2C processes on the negative and on the positive plates are stable under the influence of the heat and the oxygen flow (Fig. 4). The rate of the CO_2C increases with time due to the fact that the processes involved in the CO_2C are in self-accelerating interrelations leading to thermal runaway. The more intensive is the oxygen cycle the more intense is the heat generation and consequently the faster the temperature rise leading to higher rate of oxygen evolution (Fig. 1(b) and Fig. 4). Thermal runaway occurs in the lead/acid cell when the increase in the rate of oxygen evolution becomes directly dependent on the increase in the rate of oxygen reduction on the negative plate and vice versa. Thus a moment will be reached when the oxygen flow would not be completely reduced on the negative plate. Oxygen will accumulate in the cell. The gas pressure in the cell will rise and the vent will open to let the gas out into the air. Thus through release of the accumulated oxygen out of the cell the self-accelerating interrelations between the reactions are broken because of the decreased oxygen flow needed for the exothermic reactions on the negative plate. As a result of this the rate of temperature rise decreases, i.e. the phenomena causing thermal runaway are suppressed. This method of solving the thermal runaway problem is associated with water loss which in turn decreases the heat capacity of the cell (battery).

There are cases, however, when the battery operates at higher temperatures and stronger currents. In these cases, even when the vent is open, the self-accelerating interrelations between the processes of the CO_2C continue as a result of which the gas pressure in the cell continues to increase. A moment is reached when the case of the cell can no longer stand the high pressure and may crack or even explode.

We should add to the above description of the phenomena leading to thermal runaway also the Joule heat released when electric current flows through the cell. The released Joule heat increases with the square of the current passing through the cell. Thus the stronger is the current the greater the Joule heat released. Hence, the Joule heat facilitates further the self-accelerating interrelations between the processes of the CO_2C .

6.3. Methods for suppressing the phenomena creating self-accelerating interrelations between the processes of the CO_2C

The following measures may prevent the processes of the CO_2C from getting into self-accelerating interrelations:

(i) An intense heat exchange between the cell and the surrounding medium. This can be achieved by keeping the ambient temperature low and/or by ensuring a good air convection round the cells (batteries).

(ii) A low rate of the oxygen reaction which is controlled by the charger device. When as a result of temperature rise the current starts to increase, the cell voltage should be decreased (i.e. temperature correction of the cell voltage).

(iii) Reliable VRLA battery vents.

(iv) Higher and relatively stable heat capacity of the battery throughout its cycle life. Minimum water loss on battery operation.

All above considerations were made on the assumption that no other processes except the reactions of the CO_2C proceed in the cell. In fact, however, a number of other processes take place in the active block of the cells (as mentioned in the Introduction), e.g. positive grid corrosion, negative lug and strap corrosion, hydrogen evolution on the negative plate, etc. All these processes lead to water loss and to decrease in heat capacity of the cells which may limit the battery life. During the second half of the cycle life of the VRLA battery, a refill with water and restoration of the heat capacity and of the H_2SO_4 concentration may improve considerably the life of the battery.

VRLA batteries are finding ever increasing application in various spheres of human activity. If both the design of these batteries and the conditions of their operation comply with the above outlined recommendations, VRLA batteries may prove to be a very reliable power source of stable performance and long cycle life.

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