

Mechanism of the oxygen cycle reactions proceeding at the negative plates of VRLA batteries

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Abstract

The paper discloses the mechanism of the reactions of oxygen reduction at the negative plate involved in the oxygen cycle in VRLA batteries. Experimental methods have been developed for determining both the current of the electrochemical reduction of oxygen and the current of the oxygen cycle. Through these methods it has been established experimentally that the reduction of oxygen that results in the formation of water proceeds through an electrochemical mechanism of oxygen reactions and a chemical mechanism of reactions between the intermediate products of the oxygen and hydrogen reactions at the negative plate.

A general mechanism has been proposed which involves the elementary reactions of oxygen reduction and of hydrogen evolution. The first stage of the reduction of oxygen results in formation of hydrogen peroxide that reacts (through a chemical reaction) with the atomic hydrogen evolved by the decomposition of water (chemical mechanism of water formation). Hydrogen peroxide can be reduced to H₂O by an electrochemical reaction as well (electrochemical mechanism of water formation). Both mechanisms of water formation (chemical and electrochemical) are in competition as they use the same intermediate product (H₂O₂) of the oxygen reaction. At low temperatures, the electrochemical mechanism is the dominating one and at high temperatures, it is the chemical mechanism. A modified version of the general mechanism of oxygen reduction is proposed in which OH radicals and oxygen atoms are formed as intermediate products. Which of the above mechanisms will be activated, depends on the potential of the negative plate, the temperature and the catalytic properties of the lead surface (and of the alloying additives used) as well as on the saturation of the negative plate with electrolyte. The proposed mechanism indicates that the hydrogen reaction plays an important role in determining the efficiency of the oxygen cycle.

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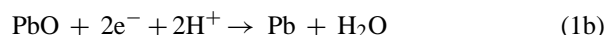
Keywords: State-of-charge; Valve-regulated lead–acid battery; Thin liquid film

1. Introduction

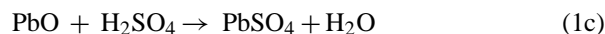
When the state-of-charge (SOC) of a valve-regulated lead–acid battery (VRLAB) exceeds 70% during battery charge, a reaction of oxygen evolution starts at the positive plates parallel to the basic charge reactions. If the degree of electrolyte saturation (S_{at}) of the active block (positive plus negative plates with AGM separator between them) is less than 96%, the evolved oxygen passes through gas channels in the AGM separator reaching the negative plates where it is reduced to water. H₂O moves back to the positive plates. Thus, an oxygen cycle is formed.

Various mechanisms for the reduction of oxygen at the negative plates have been proposed in the literature:

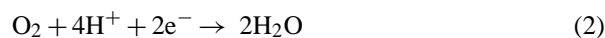
(a) chemical reactions mechanisms



or



(b) electrochemical reactions mechanism



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While the exact mechanism of the reactions of oxygen reduction on the lead surface is not yet elucidated, most of the researchers are unanimous regarding the slowest elementary process that limits the rate of the oxygen cycle. It has been assumed that the slowest elementary process involved in the reduction of oxygen is the diffusion of oxygen molecules through the thin liquid film (TLF) that covers the lead crystals of the negative active mass [1–7]. In a previous paper of ours we investigated the properties and the stability of the TLF [8]. Based on the DLVO theory the thickness of the TLF has been determined. It depends on the radius of the pores in the NAM and the surface tension at the gas/electrolyte interface. An equation has been derived giving the oxygen reduction current as a function of reaction surface, TLF thickness and polarization time.

The rates of oxygen evolution or reduction is influenced by the temperature of the cell, the potentials of the negative and positive plates, and S_p the electrolyte saturation of the active block [9–13].

The aim of the present work is to disclose the mechanism of the reactions involved in the oxygen cycle that proceed at the negative plates. In order to achieve this aim it is necessary:

- first, to create a method for determining the current of the electrochemical reduction of oxygen at the negative plate and the efficiency of this reaction;
- second, to create a method for determining the oxygen cycle current and efficiency, and
- third, to determine the efficiencies of the oxygen cycle and of the electrochemical reduction of oxygen as a function

of negative plate potential at constant temperature and saturation of the cell with electrolyte.

2. Experimental

2.1. Cell and experimental conditions

Experimental VRLA cells were assembled comprising two positive and one negative (1.5 Ah) plates separated by AGM separator (H&V, 440 g m^{-2} , BCI thickness 2.6 mm) and a Hg/Hg₂SO₄ reference electrode. Fig. 1 presents diagrammatically the experimental set up. The plates had dimensions $1.7 \text{ mm} \times 60 \text{ mm} \times 51 \text{ mm}$ and Pb–1% Sn–0.1% Ca grids. All plates were tank-formed and dry charged. 15% compression was applied to the AGM separators. The negative plate was the working electrode and the positive plates were simultaneously counter-electrodes and oxygen source. The rate of the gas flow leaving the cells was measured by a flowmeter of our own design [12].

The cells were flooded with sulfuric acid solution with s.g. 1.27 and left to soak for 30 min, after which the excess electrolyte was removed until the desired saturation level. These cells were connected to a potentiostat/galvanostat MSTAT4+ (ARBIN Instruments). First, the cells were conditioned by setting them to 10 charge–discharge cycles employing the following program: discharge at 300 mA until the potential of the negative plate reached $\varphi = -0.7 \text{ V}$ (versus Hg/Hg₂SO₄ ref. electrode), followed by charge at 300 mA until charge factor (FC) 105% and then further charge at 150 mA until

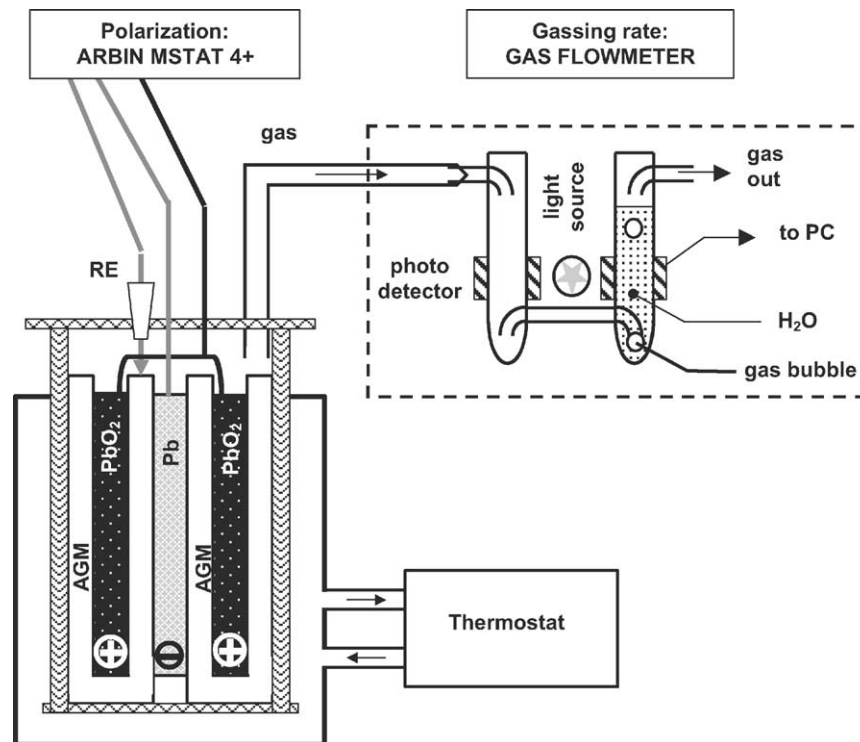


Fig. 1. Scheme of the experimental set up.

FC = 125%. The saturation of the active block with electrolyte had a constant value of 83 or 100%, which was controlled via the cell weight. The kinetics of the process of oxygen recombination was investigated through linear sweep voltammetry (LSV) from -1.05 to -1.30 V at potential scan rate 0.02 mV s^{-1} . All experiments were performed at constant temperature, 15 or $50 \text{ }^\circ\text{C}$ ($\pm 0.1 \text{ }^\circ\text{C}$). The rate of the gas leaving the cells was measured continuously and re-calculated in current units.

2.2. Oxygen cycle current at the negative plate determined by electrochemical and gas flow measurements

As the cells were fully charged, the main reactions that proceeded at the two types of plates were the reactions of water decomposition to H_2 and O_2 , and the reduction of O_2 and formation of water at the negative plates. Let us ignore the reactions of corrosion of the positive grids.

When the charged cells were set to overcharge, reactions of electrochemical reduction of oxygen and decomposition of water with evolution of hydrogen took place at the negative plates. The rates of these reactions can be represented by the respective currents.

The H_2 evolved on the negative plate is divided into two parts: one is oxidized inside the cell ($I_{\text{H}_2\text{oxi}}$) and the other one leaves the cell ($I_{\text{H}_2\text{out}}$)

$$I_{\text{H}_2} = I_{\text{H}_2\text{oxi}} + I_{\text{H}_2\text{out}} \quad (\text{M1})$$

The OxCy current (I_{OC}) is determined by the equation:

$$I_{\text{OC}} = I_{\text{np}} - I_{\text{H}_2\text{out}} \quad (\text{M2})$$

I_{np} is the current that flows through the negative plate

$$I_{\text{np}} = I_{\text{O}_2\text{red}} + I_{\text{H}_2\text{oxi}} + I_{\text{H}_2\text{out}} \quad (\text{M3})$$

If we substitute Eq. (M3) in Eq. (M2) we will obtain:

$$I_{\text{OC}} = I_{\text{O}_2\text{red}} + I_{\text{H}_2\text{oxi}} \quad (\text{M4})$$

The OxCy current is equal to the sum of the current of oxygen reduction plus the current of the chemical reaction of hydrogen oxidation inside the cell.

The current of oxygen reduction ($I_{\text{O}_2\text{red}}$) was determined experimentally through the following method. First, the electrode polarization curve was registered between -1.050 and -1.300 V at 83% electrolyte saturation. Under the above conditions, the reactions of O_2 reduction and of H_2 evolution proceed simultaneously. After that the cell was flooded with electrolyte ($S_{\text{at}} = 100\%$) and the polarization curve was registered again within the above potential region. The latter polarization curve is determined by the electrochemical reaction of hydrogen evolution alone. The difference between the currents of the two polarization curves gives the current of the electrochemical reduction of oxygen ($I_{\text{O}_2\text{red}}$).

The efficiency of the reaction of electrochemical oxygen reduction ($\eta_{\text{O}_2\text{red}}$) can be calculated by the following formula:

$$\eta_{\text{O}_2\text{red}} = \frac{I_{\text{O}_2\text{red}}}{I_{\text{np}}} \quad (\text{M5})$$

The efficiency of the oxygen cycle (η_{OC}) can be determined by the formula:

$$\eta_{\text{OC}} = \frac{I_{\text{O}_2\text{red}} + I_{\text{H}_2\text{oxi}}}{I_{\text{np}}} \quad (\text{M6})$$

3. Results and discussion

3.1. Dependence of the current of electrochemical reduction of oxygen on the potential of the negative plates

Fig. 2 presents the current I_{np} that flows through the cell at 100% state-of-charge of the negative plates as a function of negative plate potential at $S_{\text{at}} = 100$ and 83%. At 100% electrolyte saturation, the current of hydrogen evolution follows the Tafel dependence and is considerably lower than the current flowing through the cell at $S_{\text{at}} = 83\%$. The difference between the currents measured at $S_{\text{at}} = 83\%$ ($I_{83\%}$) and at 100% saturation ($I_{100\%}$) at the same potential of the negative plate gives the current of the electrochemical process of oxygen reduction ($I_{\text{O}_2\text{red}}$). The current versus potential curve obtained as a result of this calculation is presented in Fig. 2b.

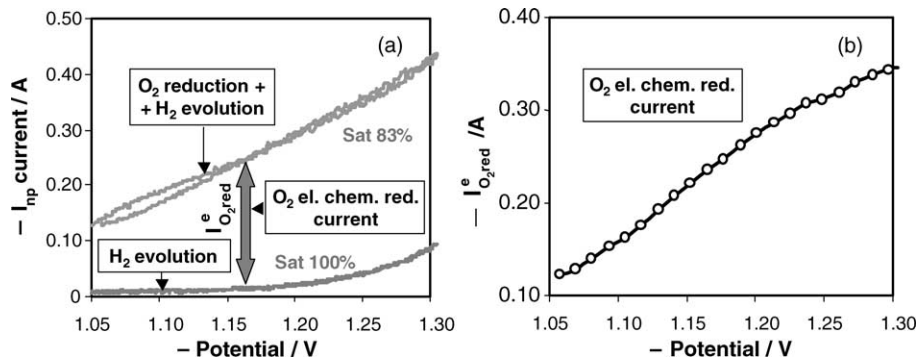


Fig. 2. (a) Negative plate current vs. potential at $15 \text{ }^\circ\text{C}$ and electrolyte saturations of 83 or 100%. (b) Dependence of the current of electrochemical reduction of oxygen vs. negative plate potential as determined from the polarization curves in (a).

On the basis of this experimentally established dependence, we can identify the slowest elementary process involved in the oxygen cycle, which limits the rate of the electrochemical reduction of oxygen at the negative plate.

The dominating concept in the literature is that the process of electrochemical reduction of oxygen is impeded by the diffusion of oxygen molecules through the thin liquid film that covers the surface of the negative active mass crystals [1–5]. The structure of the interface metal/TLF, through which electrons from Pb transfer to the O₂ molecules in the TLF for the electrochemical reaction to proceed, is rather complex. So we assumed that the charge transfer is also a slow process. In the electrochemical science, the correlation between current and potential of a process, limited by diffusion and charge transfer difficulties, can be represented by the following equation [14]:

$$\varphi^- = \frac{RT}{\alpha nF} \ln \frac{I_0}{I_d} + \frac{RT}{\alpha nF} \ln \left(\frac{I_d}{I} - 1 \right) \quad (\text{M7})$$

where φ^- is the potential of the negative plate, T the temperature, F the Faraday's constant, R the molar gas constant, α the transfer coefficient, I_0 the exchange current and I_d the diffusion current. Using this equation we determined the values for I_d , I_0 and α for which the equation fits well the experimental curve presented in Fig. 2b. These values are as follows: $I_0 = 7.16 \times 10^{-5} \text{ mA cm}^{-2}$, $I_d = 7.05 \text{ mA cm}^{-2}$ and $\alpha = 0.06$. The current densities were calculated versus the geometrical area of both surfaces of the negative plate. The value for α is very low, which is an indication of a strongly asymmetrical potential barrier for the electron transfer from the metal to the O₂ molecules in the double layer. The continuous line in Fig. 2b presents the dependence $I_{\text{O}_2\text{red}} = f(\varphi^-)$ as determined by equation (M7) for the above values for α , I_0 and I_d . The dots mark the experimentally obtained values. A fairly good fit is observed. This is an experimental support of the hypothesis for the limiting role of the diffusion of O₂ molecules through the TLF and of the charge transfer process.

3.2. Efficiency of the oxygen cycle determined by measuring the gas flow leaving the cell

The measurement was performed at 15 °C and $S_{\text{at}} = 83\%$. Fig. 3a shows the gas flow that leaves the cell (re-calculated as current) as a function of the potential of the negative plate. Gassing starts at potentials more negative than -1.20 V , which means that the oxygen cycle operates at 100% efficiency up to -1.20 V at the above temperature and saturation.

Fig. 3b presents the respective dependencies for the efficiency of the electrochemical reduction of oxygen and of the oxygen cycle. It can be seen that the OxCy efficiency is higher than the efficiency of the electrochemical reduction of oxygen at the negative plate. The difference between these two efficiencies is determined by the reaction of hydrogen oxidation inside the cell (Eqs. (M5) and (M6)). This reaction improves the OxCy efficiency. If there were no such reaction

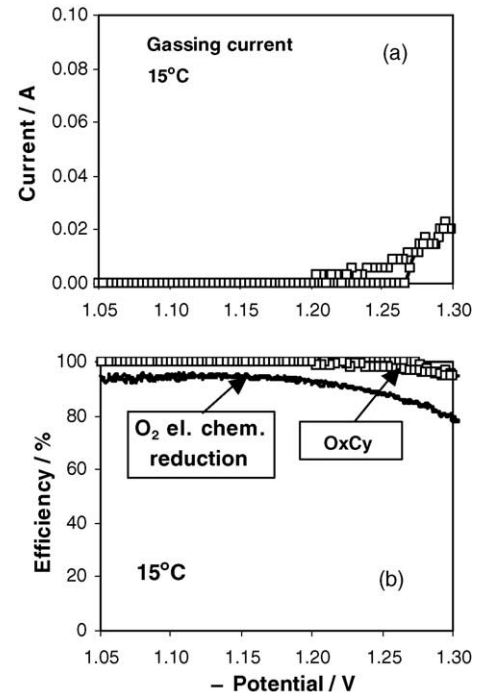


Fig. 3. (a) Gassing current (rate of gas leaving the cell) as a function of negative plate potential at 83% electrolyte saturation and 15 °C. (b) Efficiencies the oxygen cycle and of the electrochemical reduction of oxygen as a function of negative plate potential at an electrolyte saturation of 83% and $t^\circ = 15 \text{ °C}$.

of hydrogen oxidation inside the cell, then $I_{\text{H}_2\text{oxi}} = 0$. The difference ($\eta_{\text{OC}} - \eta_{\text{O}_2\text{red}}$) proves experimentally that part of the hydrogen is oxidized inside the cell.

Fig. 3b evidences also that the major part of the oxygen flow that reaches the negative plate is reduced through the electrochemical reaction.

3.3. Dependence of the currents of the negative plate (I_{np}), of hydrogen evolution (I_{H_2}) and of the hydrogen flow leaving the cell ($I_{\text{H}_2\text{out}}$) on negative plate potential at 50 °C

Fig. 4 presents the dependencies of the current flowing through the cell at the two saturation levels ($S_{\text{at}} = 83$ and 100%) as well as of the gas flow leaving the cell ($I_{\text{H}_2\text{out}}$) at $S_{\text{at}} = 83\%$ versus the negative plate potential. On comparing the data in Figs. 2a and 4 it can be seen that at $S_{\text{at}} = 83\%$ the I_{np} currents differ but very slightly at the two temperatures. This is not the case, however, for 100% electrolyte saturation. In the latter case, the overvoltage of hydrogen evolution decreases with temperature increase and the current rises, following the Tafel dependence, with increase of negative plate potential.

The gassing current versus potential curve shows that a gas flow leaves the cell at potentials more negative than -1.17 V and it is but a weak gas flow. The difference ($I_{\text{H}_2} - I_{\text{H}_2\text{out}}$) indicates that a great amount of H₂ is oxidized inside the cell.

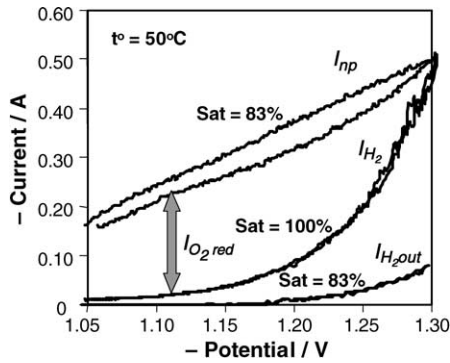


Fig. 4. Dependencies of the I_{np} current flowing through the negative plate at an electrolyte saturation of 83%, the I_{H_2} current of hydrogen evolution at an electrolyte saturation of 100% and the I_{H_2out} current of the gas leaving the cell at $S_{at} = 83\%$ as a function of negative plate potential at 50°C .

Fig. 5 shows the efficiencies of the electrochemical oxygen reduction and of the oxygen cycle as a function of potential at $S_{at} = 83\%$ and $t^\circ = 50^\circ\text{C}$. There is a substantial difference between these two efficiencies. η_{O_2red} declines very quickly with increase of φ and reaches 10% at -1.30 V . The efficiency of the oxygen cycle at the same potential (-1.30 V) is 85%. This substantial difference implies that the reduction of O_2 proceeds mainly by a chemical reaction between oxygen and hydrogen. Which is this chemical reaction?

3.4. Mechanism of the reactions involved in the oxygen cycle at the negative plate

We can assume that hydrogen is oxidized at the PbO_2 plates in the cell. Khomskaya et al. [15] and Maya and Penazzi [16] have established experimentally that this reaction proceeds at a very low rate. Hence, it will play no substantial role in the oxidation of H_2 inside the cell. Then the reaction of hydrogen oxidation must proceed at the negative plates.

According to Heyrovsky [17] and Vitek [18], in acidic medium reduction of oxygen proceeds in two stages. These

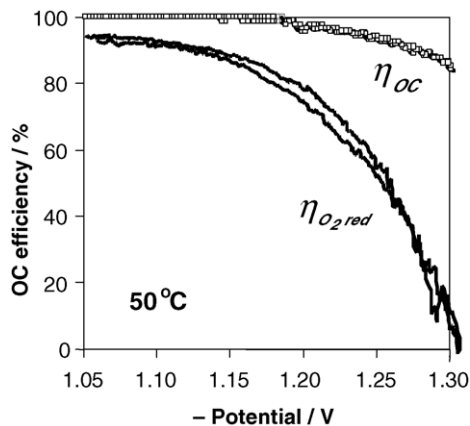
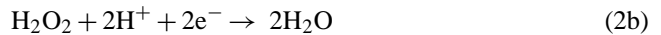


Fig. 5. Efficiencies of the oxygen cycle and of the electrochemical reduction of oxygen with formation of water as a function of negative plate potential at $t^\circ = 50^\circ\text{C}$ and an electrolyte saturation of 83%.

are in fact the stages of reaction (2):



Most often the mechanism of H_2O_2 formation in acidic medium is given by the following elementary reactions [19]:



Our attempts to detect H_2O_2 in the solution near the negative plate have failed, which gives us grounds to assume that H_2O_2 is consumed immediately after its formation at the very lead surface.

The reactions of hydrogen evolution in acidic medium include:



The latter reaction (3b) results in formation of a gas phase.

The potential of the negative plates is by 1.7 V more negative than the equilibrium potential of the H_2O/O_2 electrode on the PbO_2 surface. This means that reactions (2a) and (2b) will proceed at a high rate.

The potential region within which we polarized the negative plates was more negative than the potential of hydrogen evolution. Hence, reactions (3a) and (3b) will also proceed at a fairly high rate.

We assume that, at a certain potential, both reactions of oxygen reduction and of hydrogen evolution proceed simultaneously at the lead surface. We also assume that the intermediate products of these reactions interact. H_2O_2 is a very strong oxidant. And H_{ad} is a very strong reducer. Hence, they react with each other and the following chemical reaction proceeds:



Thus, the intermediate products of the two electrochemical reactions (2a) and (3a), react through the chemical reaction (4) to form water. This is a chemical mechanism of water formation. Beside the processes involved in this mechanism, reaction (2b) of electrochemical reduction of H_2O_2 to water also proceed at the lead surface. Let us call the latter mechanism electrochemical mechanism of water formation.

Part of the hydrogen atoms (H_{ad}) interconnect to form molecules, according to reaction (3b). These hydrogen molecules form a gas phase. This part of the hydrogen atoms is excluded from the mechanism of water formation, thus reducing the efficiency of the oxygen cycle.

The above reactions can be summarized in the scheme presented in Fig. 6. According to this mechanism, the reduction of oxygen at the negative plate proceeds through the formation of H_2O_2 first. Then, part of the H_2O_2 is electrochemically reduced to H_2O following reaction (2b). We determine that

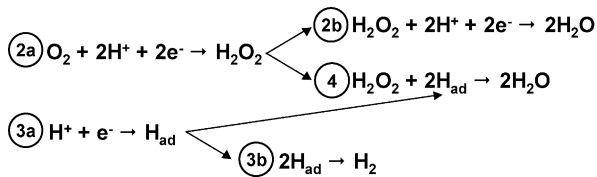


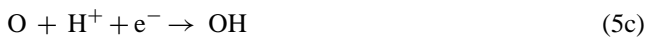
Fig. 6. Scheme of the oxygen cycle reactions involved in the reduction of oxygen and the evolution of hydrogen as well as in the chemical and electrochemical mechanisms of water formation at the negative plate.

part of the H_2O_2 from the polarization curves at $S_{\text{at}} = 83$ and 100% and this is the electrochemical mechanism of water formation. Another part of H_2O_2 reacts with hydrogen at the surface of the lead crystals forming water through a chemical reaction. This is the chemical mechanism of water formation. Since both mechanisms use one and the same initial substance, H_2O_2 , they are in competition. Which one will proceed at a higher rate would depend on the potential of the negative plate, the cell temperature and the saturation of the negative plate with electrolyte.

The above described mechanisms indicate that the hydrogen reaction plays an important role in the reduction of oxygen at the negative plate. And secondly, the oxygen and hydrogen reactions are interrelated by a common mechanism, which determines the efficiency of the oxygen cycle.

3.5. Modified mechanism of the reduction of oxygen in acidic medium

It has been established that the oxygen reduction in acidic medium may also proceed with no formation of H_2O_2 according to the following reactions [20]:



The above reactions, too, result in the formation of very strong oxidants, OH radicals and O atoms. These will react with H_{ad} to form water. This is a modified chemical mechanism of water formation.



Which of the reactions of oxygen reduction (involving formation of H_2O_2 or of OH radicals and O_{at}) will proceed will depend greatly on the catalytic action of the lead surface and the additives to the grid alloys. Probably, the polymer molecules of the expander, adsorbed onto the lead surface, will also exert some effect on the rate of the processes of formation of H_2O_2 , OH or O_{at} . The experimental methods employed by us do not allow to determine which of the intermediate products react with hydrogen at the lead

surface. But this is not the aim of the present work after all.

It has been established that on carbon, Ni, Fe and Co electrodes in KOH solution the mechanism of oxygen reduction passes through a stage of formation of hydrogen peroxide, whereas on Pt, Pd and Ag electrode in acidic and in alkaline medium mainly the mechanism involving formation of O_{at} and OH radicals holds, excluding the formation of hydrogen peroxide in the potential range where the charge transfer is the rate control process [20]. Peroxide formation in general occurs at high cathodic polarization, when the process is under diffusion controlled conditions [20]. This is the case with the reduction of O_2 at the negative plate.

4. Conclusions

Two methods have been developed for determining the current of electrochemical reduction of oxygen at the negative plate as well as the current and efficiency of the oxygen cycle.

It has been confirmed experimentally that oxygen diffusion through the thin liquid film wetting the surface of the lead particles in the negative active mass and charge transfer determine the rate of the electrochemical reduction of oxygen.

A mechanism of oxygen reduction at the negative plate is proposed, which involves hydrogen reactions, too. Parallel reactions of oxygen reduction and of hydrogen evolution proceed at the surface of the lead crystals of the negative active mass. The oxygen reaction proceeds with formation of H_2O_2 as an intermediate product or OH radicals, HO_2 and O atoms are formed through a modified mechanism. Irrespective of the particular mechanism of the first stages of oxygen reduction, strong oxidants are formed at the lead surface: H_2O_2 , OH, O_{at} . Simultaneously, a reaction of hydrogen evolution proceeds at this surface at the same potential, whereby hydrogen atoms are formed as an intermediate product. H_{at} are a strong reducer. They interact with the intermediate products of the oxygen reaction (H_2O_2 , OH, O_{at}) through a chemical reaction which results in formation of water (chemical mechanism). The above oxygen and hydrogen reactions are interrelated by a common mechanism.

Which of the initial reactions of oxygen reduction will proceed and at what rate will H_2O_2 , OH radicals and O atoms form, will depend on the potential of the negative plate, the temperature, the catalytic effect of the lead surface (and the alloying additives) as well as on the saturation of the negative plate with electrolyte.

Beside the chemical mechanism of water formation also electrochemical reactions of reduction of the intermediate products of the oxygen reaction proceed at the lead surface, which result in the formation of water, too. This electrochemical mechanism is in competition with the chemical mechanism of water formation. Our experiments have shown that at low temperatures the electrochemical mechanism of water

formation predominates, whereas at high temperatures the chemical mechanism is the predominating one. The latter is related to the influence of temperature on the overvoltage of hydrogen.

Both the chemical and the electrochemical mechanisms of water formation operate at high efficiency. Hence, there is but a small water loss in VRLAB. Parallel to the above two reaction mechanisms, a process of formation of hydrogen molecules and of a gas phase also occurs at the lead surface and in the electrolyte layer that is in contact with it. The rate of the above process determines the efficiency of the oxygen cycle. Most probably, the lead surface influences this process, too. The formation of H₂ molecules is also part of the general mechanism of the reactions of hydrogen evolution and oxygen reduction. This mechanism indicates that the hydrogen reactions at the negative plate play a very important role in improving the efficiency of the oxygen cycle and hence reducing the water loss in VRLAB.

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