

Effect of ratio of active masses on operation of VRLA batteries

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Abstract

The gravimetric and barodynamic methods were used to investigate the effect of ratio of active masses (RAM) on efficiency of internal oxygen cycle (IOC). © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Operation of the encapsulated storage battery to a greater extent differs from the operation of the conventional non-encapsulated battery. In the first case along with the necessity to secure in the optimum way, the course of the major current forming reactions, it also necessary to optimize the course of the secondary processes such as evolution and absorption of oxygen, evolution of hydrogen, corrosion of the positive current collector, self-discharge of the negative electrode. The main task of such optimization should be both retention of the high electrical characteristics and minimization of the gas evolution which leads to irrecoverable loss of water by the battery.

The balance of processes at charge could be described by the equation [1]

$$I_{EV,O} + I_{Ch}^+ = I_{Ch}^- + I_{RED,O} + I_{EV,H} \quad (1)$$

where: $I_{EV,O}$: current utilized for evolution of oxygen at the positive electrode; I_{Ch}^+ : current utilized for charge of positive active mass (PAM); I_{Ch}^- : current utilized for charge of negative active mass (NAM); $I_{RED,O}$: current utilized for recovery of oxygen at the negative electrode; $I_{EV,H}$: current utilized for evolution of hydrogen at the negative electrode.

At the end of charge I_{Ch}^+ and I_{Ch}^- are, respectively, charge currents utilized for compensation of the self-discharge of PAM and NAM.

It is evident that part of evolved oxygen will take part in the corrosion process at the positive electrode and thus:

$$I_{EV,O} = I_{EV,O(1)} + \frac{V_{corr}}{k} \quad (2)$$

where V_{corr} : rate of corrosion ($dm/d\tau$), k : electrochemical equivalent, $I_{EV,O}$: current utilized for evolution of oxygen transported to the negative electrode.

In general, all oxygen do not evolve at the positive electrode ($I_{EV,O}$) and those will be recovered at the negative electrode, and only at $\beta I_{EV,O}$. Then, while considering the low rate of self-discharge of the positive electrode, we will get:

$$I_{EV,O} = \beta \left(I_{EV,O} - \frac{V_{corr}}{k} \right) + I_{Ch}^- + I_{EV,H} \quad (3)$$

It is evident that β depends on the magnitude of the charge current. If the current is less than a certain critical value, then all evolved oxygen will have enough time to reach the negative electrode and will be recovered at it. In this case, $\beta = 1$ and

$$\frac{V_{corr}}{k} = I_{Ch}^- + I_{EV,H} \quad (4)$$

A conclusion follows from Eq. (4) which was made earlier in the paper [2], that at high rate of corrosion there will take place a drop in self-discharge of the negative electrode. At high rate of corrosion a significant part of oxygen evolved at the positive electrode will be tied by the corrosion process, which will diminish the magnitude of current $I_{RED,O}$ and will increase the fraction of charge current utilized for compensation of self-discharge of NAM (I_{Ch}^-). It is evident that the way of decrease in the loss of the capacity at expense of the high rate of corrosion is not acceptable. The similar effect could be achieved at expense of the drop in the rate of self-discharge of NAM in application of the super-purity materials free from the impurities capable of reducing overvoltage of oxygen evolution, or at expense of optimization of the magnitude of the charge current. However, compensation of

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the self-discharge at expense of increase in the charge current may lead to the negative effect connected with hydrogen evolution, the rate of oxidation of which at the positive electrode is extremely low and hence to the irrecoverable loss of water. The other way to mitigate the effect of self-discharge is related to increase of NAM content in the battery. It is known that the rate of recombination of oxygen depends on the discharge degree of NAM. The paper [3] shows that at the discharge degree below 70%, the rate of oxygen recovery is the lowest. It is clear that the higher the stock of NAM, the lower is its discharge degree with the same discharge capacity and the higher is efficiency of the oxygen recombination process. However, the increase in NAM content reduces specific characteristics of the batteries. In this work, the study is made of the effect of ratio of active masses (RAM) on efficiency of the internal oxygen cycle (IOC) with the aim to determine the optimum value of RAM.

2. Experimental

2.1. Gravimetric test

2.1.1. Test method

The gravimetric test was conducted on the VRLA battery with capacity of 13 Ah. Weight ratio of NAM to PAM (RAM) equaled 1, 1.05, 1.10, 1.15 and 1.20. The batteries were filled with acid 1.28 g/cm^3 and tested by the cycling method comprising the 2-stage charge with 20% overcharge and discharge with current $0.65C_{20}$. At the end of each charge, the batteries were weighed to the nearest $\pm 0.01 \text{ g}$. Control discharges were carried out every 20 cycles to determine the full capacity of the batteries.

2.1.2. Results and discussion

The dependence of the change of weight of the battery (ΔP) with different RAM on number of cycles performed (N) were obtained. Fig. 1 shows the typical curve $\Delta P = f(N)$ with three discernible sections. For approximately 15 cycles, the loss of weight of the batteries was increasing. In the

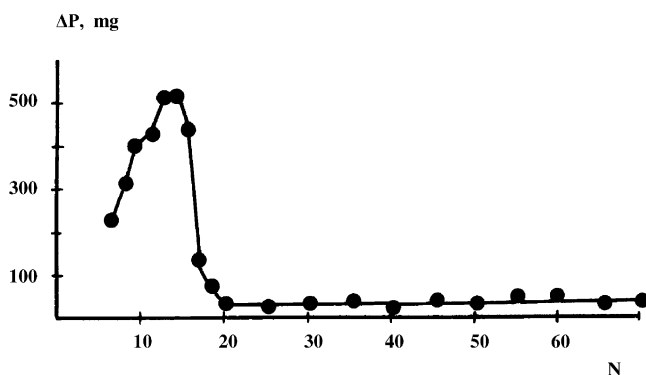


Fig. 1. Dependence of loss of weight of batteries on number of cycles performed.

range of 15–25 cycles, the loss of weight sharply dropped. And finally, starting approximately from 30th cycle, the loss of weight stabilizes at the low level. The first section characterizes the behavior of the battery with 100% filling of the separator with electrolyte. In this case, all oxygen evolving at charge is deported to the gas space of the battery due to extremely low efficiency of the oxygen recombination process. The increase in the loss of weight of the batteries is related to that at the first cycles, there is reforming of PAM and the increase in the fraction of the current utilized for oxygen evolution. At the second section, as a result of irrecoverable loss of water in the separator, the gas channels are formed and efficiency of IOC increases at expense of sharp increase in the rate of oxygen transport from the positive to the negative electrode as a result of replacement of molecular diffusion of oxygen via the liquid phase by gas one. At the third section, the electrolyte filling is optimized and efficiency of IOC is at its maximum.

Fig. 2 shows the dependence of the overall losses of weight of the batteries at each of three sections on magnitude of RAM. It is seen that at the first section, the loss of water does not depend on RAM, which follows from the low efficiency of the oxygen cycle. In this case, the losses of water depend mostly on current and duration of charge. At the second and third sections, the losses of weight depend on RAM and decrease with drop in NAM content. It is important to note that with increase of RAM above 1.15 the losses of weight of the batteries become independent of NAM content at a given test mode. Thus, increase in NAM content promotes higher efficiency of IOC.

Fig. 3 shows the dependence of the losses of weight of the battery per cycle (third section) on number of cycles. It is seen from Fig. 3, that with increase in number of cycles

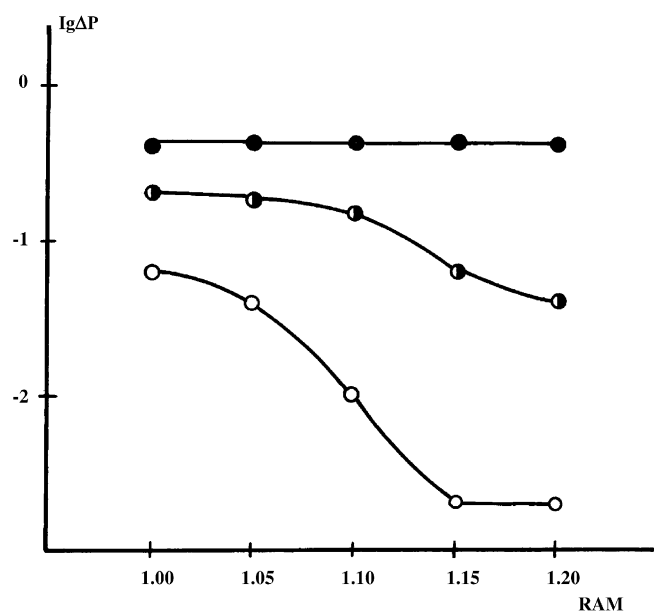


Fig. 2. Dependence of loss of weight of batteries on RAM at the first (●); second (◐); and third (○) sections.

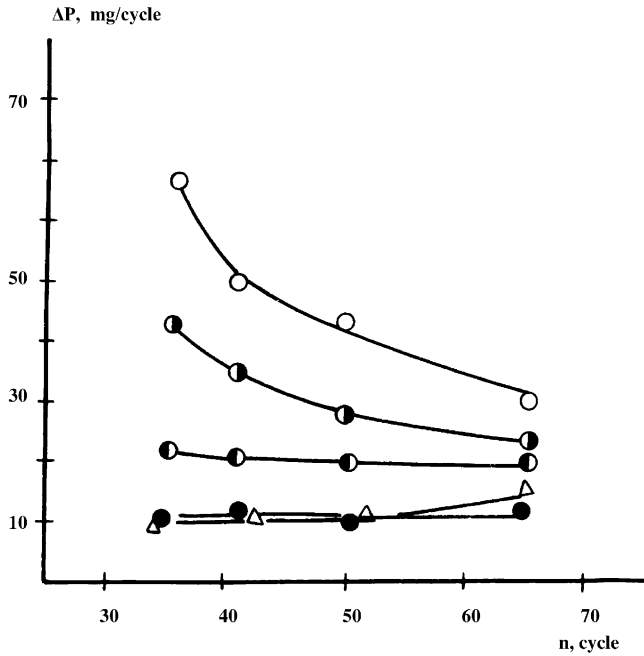


Fig. 3. Dependence of loss of weight of batteries per cycle on RAM and number of cycles performed (RAM: 1.0 (○); 1.05 (●); 1.10 (○); 1.15 (●); and 1.20 (△)).

performed the losses of weight of the battery depend to a lesser degree on RAM. Here, approximation of values ΔP occurs at expense of increase in efficiency IOC of the batteries with lower NAM content.

The resulting dependence could be explained on the basis of the following process model. It is known that the sulfate skin formed at discharge of lead is a barrier for diffusion of oxygen and prohibits its recombination. At charge, the reduction of lead propagates from the current-carrying elements to the surface of the electrode. On the other hand, at charge, oxygen starts to evolve at the positive electrode before the negative electrode is recovered completely and hence, the rate of its oxygen recovery will depend on the degree of oxidation of the surface of the negative electrode. It is evident that with the increase in NAM content this value, with the same discharge modes, will increase, which should help increase in the efficiency of the oxygen recombination process. This statement could be confirmed by evaluation of the losses of weight of the battery depending on the depth of discharge (DOD) (Fig. 4). It is seen from Fig. 4 that the higher the DOD, the bigger are the losses of weight of the battery at the next charge. However, with the increase in NAM content the losses of weight drop, which is related to decrease in the oxidation degree of NAM at the same discharge modes.

It was shown earlier that with cycling, there occurs the approximation of the magnitudes of losses of weight of the batteries with different RAM, mainly at expense of the IOC efficiency of the batteries with lower NAM content (Fig. 2). Assuming that the losses of electrolyte occur mainly from the separator with larger pores than the electrodes, one can

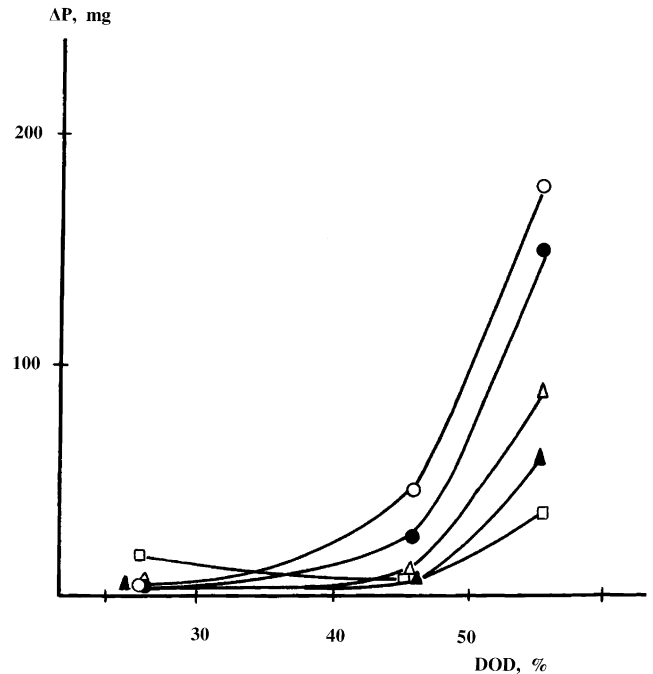


Fig. 4. Dependence of loss of weight of battery on DOD and RAM: 1.0 (○); 1.05 (●); 1.10 (△); 1.15 (▲); and 1.20 (□).

calculate the electrolyte filling of the separator (L_S) at any cycle by the equation:

$$L_S = \frac{V_{el}}{V_{SEP}} = \frac{fn\gamma_{SEP}V_{SEP} - \Delta P/d_{el}}{fnV_{SEP}} = \gamma_{SEP} - \frac{\Delta P}{fnV_{SEP}d_{el}} \quad (5)$$

where: V_{el} and V_{SEP} : volume of electrolyte and separator, respectively; d_{el} : density of electrolyte; γ_{SEP} : porosity of separator; f : degree of separator compression; n : the number of separators in the batteries.

Table 1 shows values of electrolyte filling of the separators in batteries with different RAM after 70 cycles.

It is seen from Table 1, that L_S strongly depends on RAM. Based on this findings, one can assume that the increase in oxygen recombination efficiency for the batteries with low excess of NAM at extended cycling is related to increase in the number of gas channels in the separator and respective enlargement of the surface of the negative electrode at which oxygen recombination takes place.

However, drop in electrolyte filling of the separator should result in lower capacity characteristics of the battery. Fig. 5 shows the dependence of the capacity of the battery on magnitude of RAM. Discharge was carried out with current of $0.05C_{20}$ to the terminal voltage of 1.8 V at the 21, 41 and 71st cycles. It is seen from Fig. 5, that at initial cycles, the capacity of the batteries drops with increase in NAM

Table 1
Electrolyte filling of separators

RAM	1.00	1.05	1.10	1.15	1.20
L_S (%)	80.0	82.5	86.2	89.5	93.0

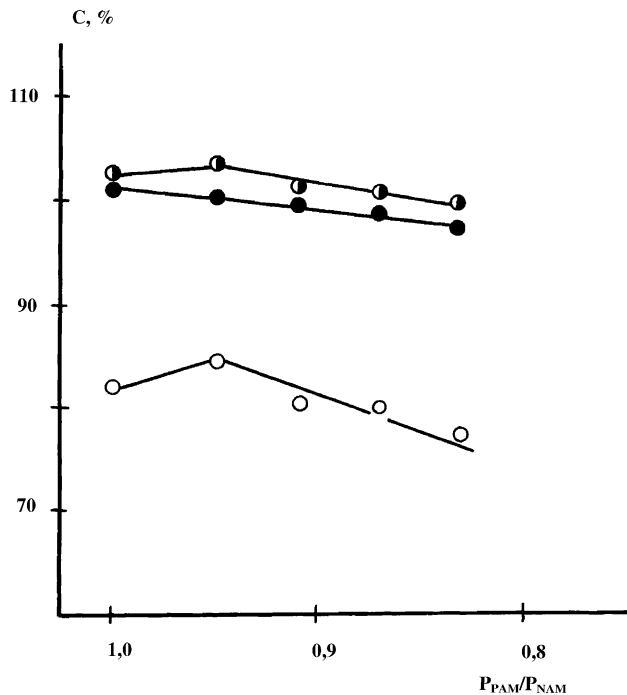


Fig. 5. Dependence of capacity of batteries on RAM and number of cycles performed. Cycle number: 21 (●); 41 (◐); and 71 (○).

content. However, already at the 71st cycle the batteries with RAM = 1.0 demonstrated a drop in capacity as contrasted to the batteries with higher NAM content, which could be attributed to increase of their internal resistance at expense of drop in electrolyte filling of the separator.

In Fig. 3, one can note a certain increase in loss of weight of the batteries with RAM = 1.20 after 70 cycles. Such drop in IOC efficiency is attributed to that the high rate of oxygen recovery at constant magnitude of the recharge current leads to development of the self-discharge of NAM, since the fraction of charge current utilized for its compensation is small.

2.2. Barodynamic tests

2.2.1. Test method

The cells allowing measurements of internal pressure of the tested models of the batteries were fabricated for conducting the barodynamic tests. The models consisted of two positive and three negative electrodes measuring 47 mm × 82 mm. The electrodes were separated by the glass fiber separator AXM300 with thickness of 2.03 mm (at 10 kPa), basis weight 300 g/cm², average pore size 3.2 μ. The cells were filled with acid 1.28 g/cm³ and subjected to the cycling process in the following mode: discharge with current of 0.25 C₂₀ for 1.5 h and charge with current of 0.06 C₂₀ to 15% overcharge. At the end of the charge, the pressure in the cell was recorded. Then the cells were held for 17 h, during which pressure measurements were also taken. The cells were fabricated with RAM 1.05 and 1.20.

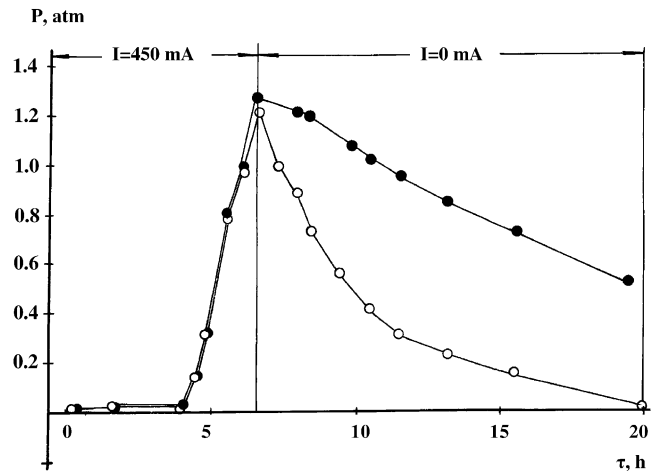


Fig. 6. Change in pressure inside battery with RAM 1.20 (○); and 1.05 (●) in the course of charge and retention without current.

2.2.2. Results and discussion

Fig. 6 shows the typical curves of change in pressure in the course of charge and retention without current of the models with RAM 1.05 and 1.20. It is seen from Fig. 6 that sharp increase in pressure related to the oxygen evolution process corresponds to the degree of charging approximately of 90% which is consistent with the findings of the paper [4]. The increase in pressure in the cell (ΔP) could be described by the equation:

$$\Delta P = RT \frac{(I_{\Sigma} - I_{\text{Ch}}^{+} - I_{\text{RED,O}}) \Delta \tau}{4FV_{\text{g}}}, \quad (6)$$

where: I_{Σ} : charge current; I_{Ch}^{+} : current utilized for PAM charging; V_{g} : gas volume of the cell; τ : time. At the end of charge, I_{Ch}^{+} is low and ΔP starts to increase, if $I_{\Sigma} > -I_{\text{RED,O}}$. With $\Delta P > 0$, the oxygen recovery current equals some critical value ($I_{\text{RED,O}} = I_{\text{CR}}$), whose value is determined by the rate of diffusion of oxygen into the zone of reaction and could be calculated by the Eq. (6).

At the end of charge and disconnection of current, there takes place a drop in pressure characterizing the efficiency of the oxygen recombination process. It is clear that with RAM = 1.20, the efficiency of the oxygen recovery process is significantly higher than for the batteries with RAM = 1.05.

Fig. 6 shows the dependence of the increase in the overall internal pressure of the batteries with RAM = 1.05–1.20 on cycling duration. It is seen from Fig. 6 that with increase in CAM, the internal pressure at cycling drops which indicates the increase in IOC efficiency.

Recovery of oxygen depolarizes the negative electrode and hence the increase in IOC efficiency (increase in NAM content) should promote the decrease in background pressure of hydrogen. The quantity of evolved oxygen could be evaluated by the magnitude of the internal pressure in the battery established after disconnection of the charge current [3], which is connected with a sufficiently high rate of

Table 2
The pressure in the models in 17 h after the charge (P)

Number of cycles	The DOD preceding the charge (%)	P (kPa) RAM	
		0.95	0.83
43	15.6	0.030	0.020
40	26.0	0.040	0.030
44	100	0.055	0.040

oxygen recovery and practically zero rate of oxidation of hydrogen. Table 2 shows the dependence of the residual pressure in the models (in 17 h after disconnection of the charge current) on RAM magnitude and the DOD preceding the charge. It is seen from Table 2 that the model with higher NAM content had a lower hydrogen pressure.

And finally, Fig. 7 shows the dependence of the increase in pressure in the models on RAM magnitude and the number of cycles performed. The resulting figures confirm the results of the gravimetric tests and indicate that with cycling the efficiencies of the oxygen recombination in the models with different RAM are getting closer at expense of

increase in rate of oxygen recovery in the models with lower NAM content.

Based on general considerations, one can assume that drop in efficiency of oxygen recovery with increase in the DOD could be attributed to the change in the electrolyte filling of the separator due to displacement of acid out of pore of the electrodes at discharge when drop in their porosity takes place. This may result in partial flooding of the gas pores of the separator and decrease in the oxygen transport rate. The precondition for this is the satisfaction of the following condition:

$$\Delta V_1 > \Delta V_2 \quad (7)$$

$$\Delta V_1 = (\gamma_{\text{Ch}}^+ - \gamma_{\text{D}}^+)V^+ - (\gamma_{\text{Ch}}^- - \gamma_{\text{D}}^-)V^-$$

$$\Delta V_2 = V_{\text{H}_2\text{SO}_4} - V_{\text{H}_2\text{O}} = 0.86k \frac{Q_{\text{P}}}{d_{\text{H}_2\text{SO}_4}}$$

where: ΔV_1 : overall decrease in volume of pores of the electrode; ΔV_2 : change in volume of electrolyte at discharge; γ_{Ch}^+ , γ_{D}^+ , γ_{Ch}^- , γ_{D}^- : porosities of the charged and discharged positive and negative electrodes, respectively; V^- and V^+ : volumes of negative and positive electrodes, respectively; k :

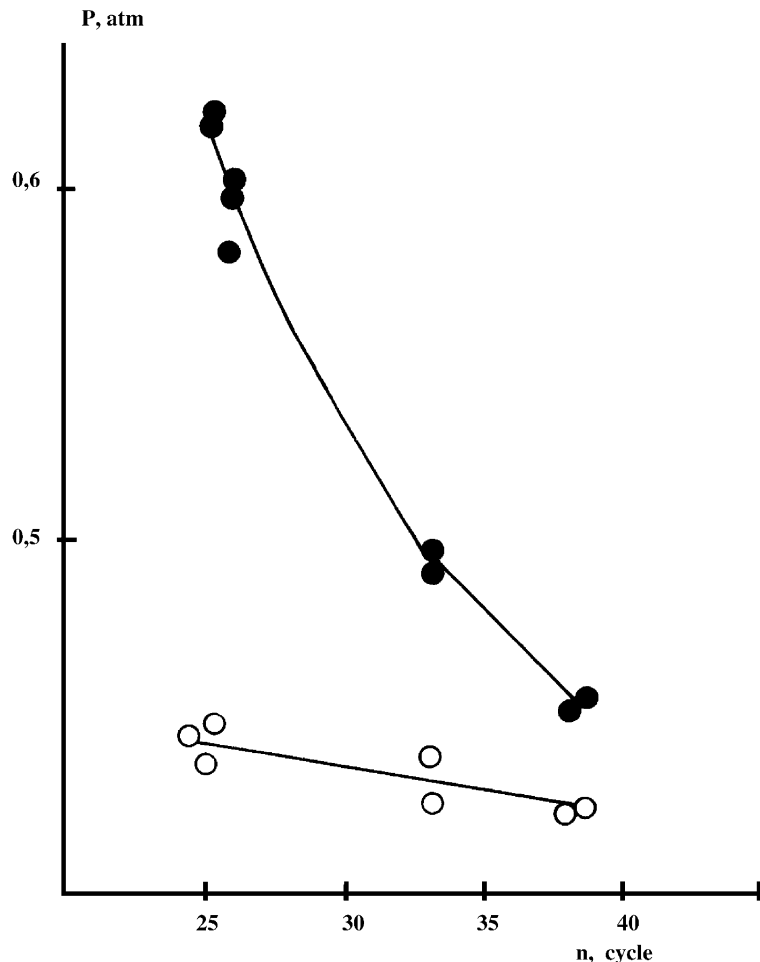


Fig. 7. Dependence of internal pressure of batteries with RAM 1.20 (○); and 1.05 (●) on number of cycles performed.

electrochemical equivalent of acid; Q_p : discharge capacity; $d_{\text{H}_2\text{SO}_4}$: density of acid. For the models tested in this work, one can derive that $\Delta V_1 = 6.8 \text{ cm}^3$, and $\Delta V_2 = 15.9 \text{ cm}^3$, that is $\Delta V_1 < \Delta V_2$ and the mechanism of drop in IOC efficiency at expense of separator flooding is not possible.

3. Conclusions

The effect of RAM on efficiency of the oxygen recombination by the gravimetric and barodynamic methods was investigated in this work. It was demonstrated that with the increase in NAM content in the battery, the IOC efficiency rises. A conclusion was drawn that the optimum value of RAM equals 1.15–1.20. With higher number of cycling the rate of oxygen recovery depends on RAM to a lesser degree,

which is attributed to the increase in IOC efficiency of the batteries with low value of RAM. However, here occurs the noticeable loss of electrolyte by the separator and capacity of such batteries drops. Increase in RAM also leads to lower build-up of background pressure of hydrogen in the battery. In subsequent works, the batteries with RAM <1 will be tested.

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